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Expanding the Hammett Correlations for the Vinylheptafulvene Ring-Closure Reaction

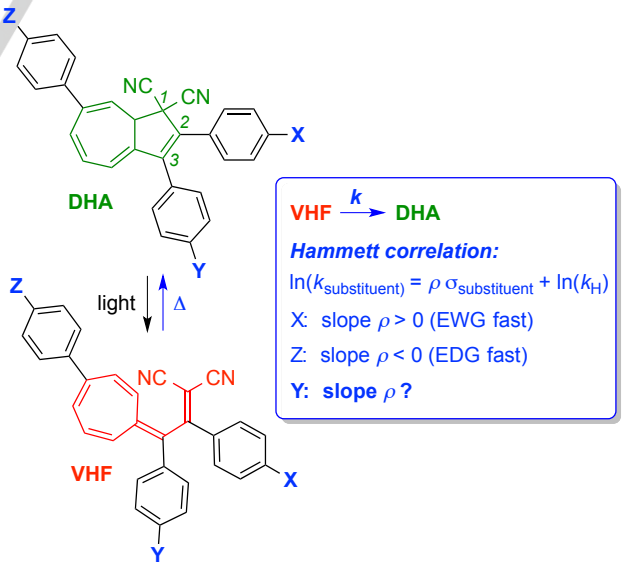
Martin Drøhse Kilde,[a] Mia Harring Hansen,[a] Søren Lindbæk Broman,[a] Kurt V. Mikkelsen,*[a] Mogens Brøndsted Nielsen*[a]

Abstract: A selection of 2,3-diarylated photochromic dihydroazulenes (DHAs) has been prepared using two different protocols. The first protocol relies on the synthesis of a 3-bromo-substituted dihydroazulene, which in a final step is subjected to a Suzuki cross-coupling reaction. In the second protocol the two aryl substituents are introduced early in the synthesis. The DHAs are photoactive and undergo light-induced ring-opening reactions to form vinylheptafulvene (VHF) isomers. These VHFs quickly return at room temperature to DHAs in thermal ring-closure reactions. The kinetics of these reactions was studied at -20 °C for two series for which the substituent at the C-2 position (DHA numbering) was kept constant, in both cases revealing a linear free-energy relationship (Hammett correlation). The relationships show that an electron-donating substituent at C-3 (the exocyclic VHF carbon) enhances the ring-closure reaction – in contrast to its influence when placed at C-2. In a computational study (density functional theory calculations), three different methods were benchmarked against the experimental results. In all, this work shows for the first time how the VHF to DHA switching is influenced by donor-acceptor substitution at the exocyclic heptafulvene carbon.

Introduction

Molecular switches that undergo isomerization reactions upon external stimuli have attracted attention in various fields within supramolecular chemistry, materials science, molecular electronics, biotechnology, and solar energy storage.[1] Some applications require fast conversions between isomers, while others require slow. Therefore, establishing how functionalization of the molecular switch influences the switching behavior has a prominent role for advancing the various fields.

We have in the past years focused attention on the dihydroazulene/vinylheptafulvene (DHA/VHF) photo/thermoswitch with two cyano groups at C-1 (Scheme 1).[2] The DHA to VHF conversion is photo-induced, while the back-reaction from VHF to DHA is thermally stimulated.[3] We have previously found that this thermal back-reaction (TBR) can be tuned to occur within seconds[4] to years[5]. Systematic studies have shown that the ring-closure reaction follows linear free-energy relationships, Hammett correlations,[6] for donor/acceptor substitution at either the vinyl position (Ar-X; C-2, based on DHA numbering) or at the seven-membered ring (Ar-Z; C-7).[7] Interestingly, the slope (ρ) has opposite signs for these substitution patterns; that is, an electron-withdrawing substituent enhances the ring-closure when placed at C-2, while it retards the ring-closure when placed in the seven-membered ring at C-7 which was also found in a calculational study by Shahzad *et al.*[8] Incorporation of a phenyl group at the exocyclic carbon of VHF (Y = H; C-3) is known to lead to a remarkable enhancement of the rate of the ring-closure reaction,[9] but the exact influence of donor/acceptor substitution has not yet been established at this position. We therefore decided to investigate the behavior of a series of compounds with various aryl groups at C-3 and fixed groups at C-2; *i.e.*, 2,3-disubstituted compounds. Synthetically, functionalization at C-3 was achieved via two different routes. The first route took advantage of our previously reported protocol for incorporating a bromo-substituent at C-3 of DHA with X = H and with no aryl substituent in the seven-membered ring.[10] In the other procedure, developed by Daub and co-workers,[9] the substituent at C-3 is incorporated in the beginning of the synthesis. From six 2,3-diarylated compounds, we could generate two series of Hammett correlations.



Scheme 1. Dihydroazulene/vinylheptafulvene (DHA/VHF) photo-/thermoswitch. The Hammett correlation has been verified for X and Y substituents. Notice that the slope ρ will differ by a factor of ln(10) if log is used instead of ln in the equation. EWG = electron-withdrawing group; EDG = electron-donating group.

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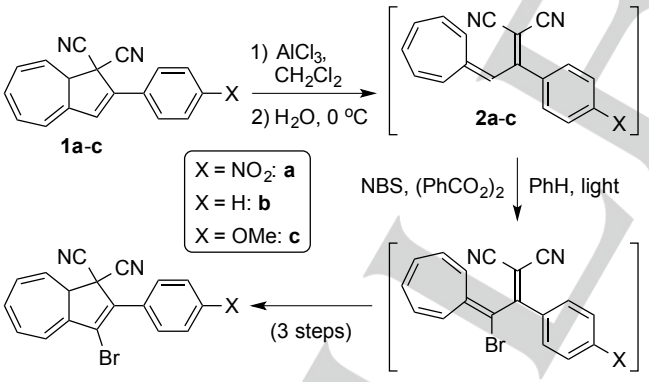
Results and Discussion

Synthesis

DHAs **1a**-**c** (X = NO_2, H, OMe; Scheme 2) were synthesized by our previously reported procedures.[11] These compounds were then subjected to a ring-opening-bromination-ring-closure procedure.[10] This procedure proved to be tolerant towards both an electron-withdrawing group (EWG), NO_2, and an electron-donating group (EDG), OMe, at position C-2. Thus, treatment of **1a**-**c** with $AlCl_3$ in CH_2Cl_2 at rt resulted in ring-opening, furnishing VHFs **2a**-**c** as intermediates after quenching with water. These were subsequently subjected to a radical bromination reaction with *N*-bromosuccinimide (NBS), benzoyl peroxide, and light in benzene as solvent. In a subsequent ring-closure reaction, the corresponding 3-bromo-substituted DHAs **3a**-**c** were achieved in excellent yields (Scheme 2). In the case of the formation of **3a** (X = NO_2) and **3b** (X = H), the reaction could be followed by the naked eye by a visible color change from red to yellow. DHAs **3a**-**c** were isolated as yellow solids of various stabilities. Compound **3c** had to be purified by flash column chromatography and decomposed within a couple of days on the shelf at rt in the dark. Therefore it had to be stored cold (-18 °C) or used shortly after purification. Nevertheless, it was possible to grow a crystal suitable for X-ray crystallography from CH_2Cl_2/heptane confirming the position of the bromine (Figure 1). Compound **3b** colorized upon standing on the shelf at rt in the dark, but was still usable without any observed impurities. On the other hand, compound **3a** could be purified by dry column vacuum chromatography and seemed bench stable when kept in the dark at rt for at least a period of one year.



3a (78%), **3b** (72%), **3c** (84%)

Scheme 2. Synthesis of 3-bromo-substituted DHAs. NBS = *N*-bromosuccinimide.

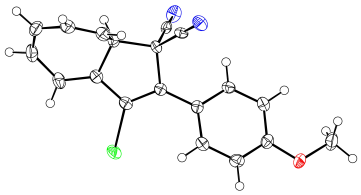
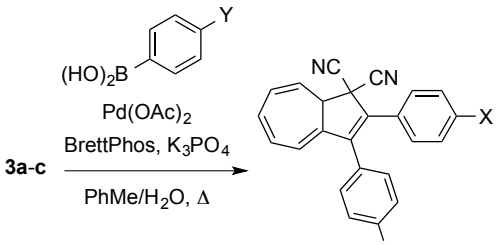


Figure 1. Molecular structure of **3c** (crystals grown from CH_2Cl_2/heptane) with displacement ellipsoids at 50% probability for non-H atoms (CCDC 1509120).

Isolation of the VHFs **2a**-**c** was possible by addition of ice-cold heptane to the cold solution of VHFs in CH_2Cl_2 followed by removal of the CH_2Cl_2 by rotary evaporation to give a precipitate in the cold heptane. This precipitate was filtered to yield the VHFs in yields of 66% (**2a**), 67% (**2b**), and 54% (**2c**).

Next, we wanted to investigate the possibility for using the two new bromides **3a** and **3c** and the known **3b** as precursors for incorporating aryl groups at C-3 of DHA. Previously, we found **3b** to be unreactive in Sonogashira and Suzuki cross-coupling reactions.[10] Nevertheless, using a catalytic system consisting of Brettphos/$Pd(OAc)_2$ and heating overnight, we managed partly to perform Suzuki cross-couplings between **3a**-**c** and phenylboronic acid or *p*-methoxyphenylboronic acid. The reactions gave in some cases the desired DHAs, albeit in low yields, while in others mainly azulene products. The product outcomes are summarized in Scheme 3, Figure 2, and Table 1. Isolation of the arylated DHAs required tedious purification by repeated chromatography due to incompletion of the reaction and significant amounts of different by-products, including the fully unsaturated azulenes shown in Figure 2. A coupling between **3c** and *p*-nitrophenylboronic acid was also attempted, but only azulene products were formed.



X =	NO_2	H	OMe
Y = H	**4a**	**4b**	**4c**
Y = OMe	**5a**	**5b**	**5c**

Scheme 3. Suzuki cross-couplings. BrettPhos = 2-(dicyclohexylphosphino)-3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-biphenyl. For yields, see Table 1.

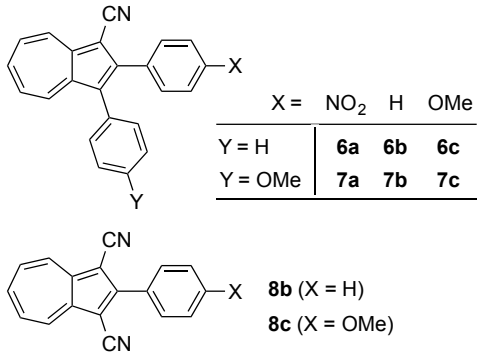


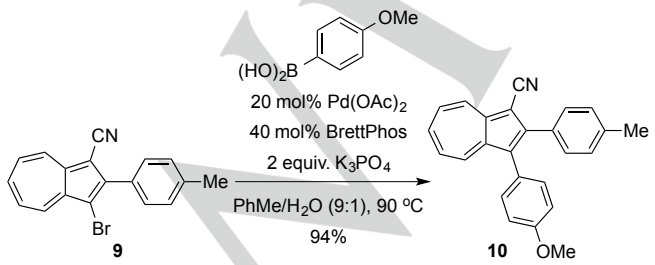
Figure 2. Azulene by-products; for yields, see Table 1.

Table 1. Product yields of Suzuki cross-couplings[a] (see Scheme 4 and Figure 2).

Entry	X	Y	Temp. [°C]	Products (Yields)
1	NO_2	H	75	**4a**[b], **6a** (traces)
2	NO_2	H	85[c]- 95	**6a** (17%)
3	NO_2	OMe	75	**5a** (4%), **7a**[b]
4	H	OMe	65	**5b** (4%), **7b**[b]
5	H	OMe	80	**7b** (27%), **8b** (traces)
6	OMe	H	65[c]	**4c** (3%), **6c** (13%), **8c** (6%)
7	OMe	OMe	65	**5c** (4%), **7c**[b]

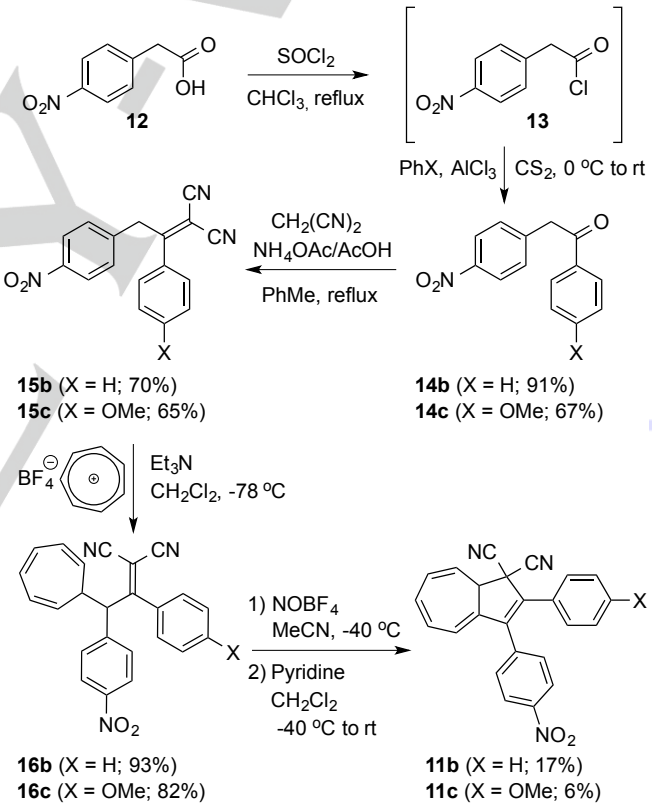
[a] In general, all reactions were performed overnight. [b] Not isolated, but judged present according to TLC analysis. [c] Reaction did not go to completion.

To put the reluctance of 3-bromo-substituted DHAs to undergo Suzuki cross-couplings, in combination with degradation, under the reaction conditions into perspective, we subjected the known[11] azulene derivative **9** to a coupling with *p*-methoxyphenylboronic acid, which furnished the azulene **10** in almost quantitative yield (Scheme 4). Thus, the Suzuki cross-coupling works very well for simple azulene substrates. The molecular structures of azulenes **6a**, **6c**, **8c**, and **10** were confirmed by X-ray crystallographic analysis (see SI).



Scheme 4. Suzuki cross-coupling of 3-bromo-substituted azulene derivative.

In order to obtain the two 3-(*p*-nitrophenyl)-substituted DHA derivatives **11b** (X = H) and **11c** (X = OMe), we turned to the original protocol developed for **4b**, where the substituent is included early in the synthesis.[9] The two DHAs were prepared in six steps starting from *p*-nitrophenylacetic acid **12** (Scheme 5), which was converted to the corresponding acid chloride **13** with $SOCl_2$ in refluxing chloroform. Friedel-Crafts acylations of this intermediate with benzene and anisole gave the ketones **14b** and **14c**, respectively. Next, Knoevenagel condensation between these products and malononitrile in refluxing toluene was performed to provide products **15b** and **15c**, respectively. From these compounds, the corresponding cycloheptatriene derivatives, **16b** and **16c**, were formed by treatment with tropylium tetrafluoroborate and triethylamine in CH_2Cl_2 at -78 °C. The products were then oxidized by treatment with nitrosonium tetrafluoroborate at -40 °C followed by pyridine to give the VHFs that when allowed to reach rt spontaneously underwent thermal cyclization to form the DHAs **11b** and **11c**. This last step went in rather poor yield for both compounds, while all the preceding steps went in good to high yields. The known[9] DHA **4b** was prepared according to the same method.



Scheme 5. Synthesis of 2,3-diarylated DHAs.

Optical Properties and Switching Studies

The DHAs were subjected to UV-Vis absorption studies in EtOH. Representative spectra are shown in Figure 3 and the longest-wavelength absorption maxima are listed in Table 2. For DHA **5a** (X = NO_2), photoisomerization did not occur with isosbestic points, and we have therefore limited detailed studies to the X = H and OMe derivatives (see Scheme 6). Thus, these DHAs were all photoactive, undergoing light-induced conversion to VHFs

upon irradiation at 365 nm. Yet, as the back-reaction was very fast for all of them at rt, the VHF to DHA first-order kinetics had to be studied at low temperature (-20 °C) in EtOH. The absorption maxima of the different VHFs and the rate constants (k) for the ring-closure reactions are listed in Table 2. All the conversions occurred with isosbestic points in the absorption spectra. The molecules can be categorized in two classes, each containing three compounds with either X = H or X = OMe. Figure 4 shows a plot of ln(k) against the Hammet σ_Y-values for each of these series (with Y = OMe, H, NO_2). A linear correlation is observed in each case with a negative slope. Thus, we see clearly that an EDG at C-3 enhances the ring-closure, while the opposite is true for an EWG.

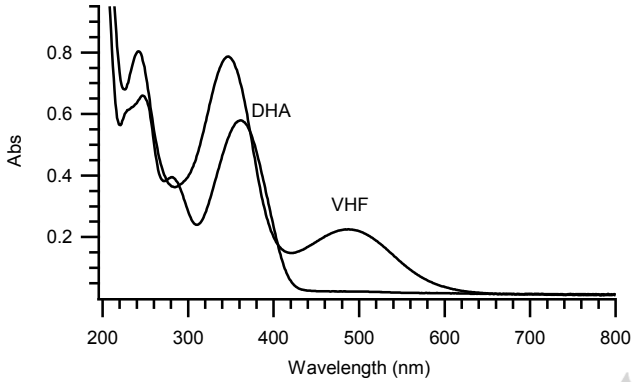
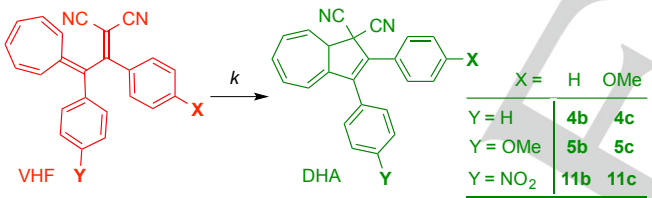


Figure 3. UV-Vis absorption spectra recorded in EtOH at -20 °C of **4c** and its corresponding VHF.



Scheme 6. The rate constants (k) for the TBRs were determined for the series X = H and X = OMe.

Table 2. Absorption maxima and VHF-to-DHA kinetics data (-20 °C) for the DHAs **4b**, **5b**, **11b**, **4c**, **5c** and **11c** and their corresponding VHFs in EtOH.

DHA label	X	Y	DHA λ_{max} (nm)	VHF λ_{max} (nm)	$k_{-20\,^{\circ}C}$ (s^{-1})	$t_{1/2}$ (min)
5a	NO_2	OMe	381			
4b	H	H	332	316, 493	47.0 x 10^{-5}	25
5b	H	OMe	349	314, 510	57.5 x 10^{-5}	20
11b	H	NO_2	327	415, 490	27.1 x 10^{-5}	43
4c	OMe	H	361	347, 488	14.7 x 10^{-5}	79
5c	OMe	OMe	360	340, 498	18.8 x 10^{-5}	61
11c	OMe	NO_2	346	365, 485	9.94 x 10^{-5}	116

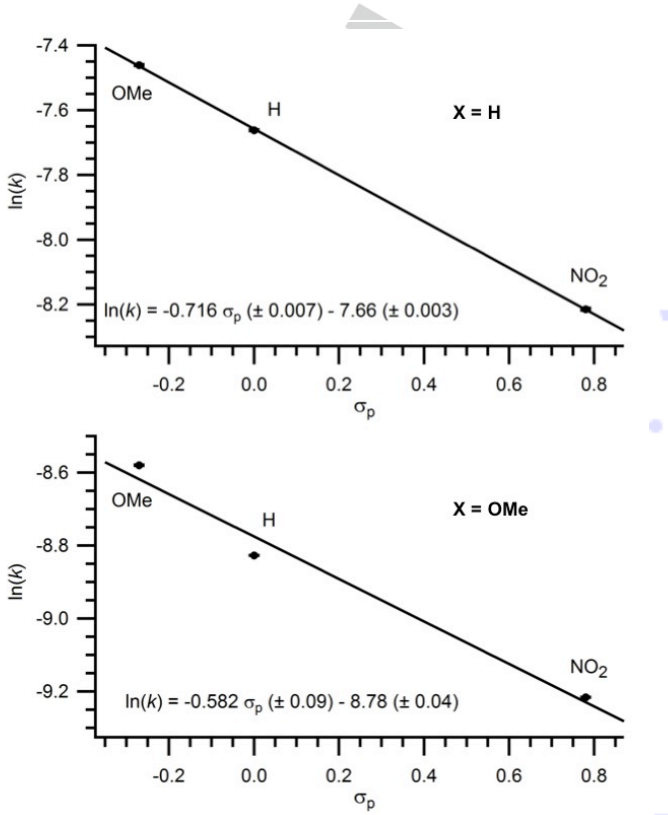


Figure 4. Hammett correlations for thermally induced ring-closure (VHF → DHA) substituted at C-3 at -20 °C in EtOH. Top) X = H; Correlation based on **4b**, **5b**, and **11b**. Bottom) X = OMe; Correlation based on **4c**, **5c**, and **11c**. Estimated error bars are included.

Computational Study

To add further support for the substituent dependency on the thermal back-reactions, we subjected the two series of compounds to a computational study. Calculations were performed using Density Functional Theory (DFT) and the Gaussian 09 program package.[12] Solvent effects were taken into account using a polarizable continuum model with the integral equation formalism variant (IEFPCM).[13] All calculations were done using EtOH as solvent. Three exchange-correlation functionals (CAM-B3LYP,[14] M06-2X,[15] and PBE0[16]) in conjunction with the 6-311+G(d) basis set were applied, since earlier studies[17] have shown adequate performance over a range of solvents for similar molecular structures. Only the *R* enantiomers of the DHAs were taken into account. The temperature was set to -20 °C (253.15 K) corresponding to the experimental conditions. All the calculated transition states (TSs) were confirmed as first order saddle points by one single imaginary frequency. All optimized structures (DHA, s-*cis*/s-*trans* VHF, and TS structures) and Gibbs free energies are included in the SI. The thermal back-reaction (TBR) barrier is determined as the energy difference between the s-*cis*-VHF and the TS structure. These Gibbs free energies of activation are shown in Figure 5 for the two series of compounds. First of all, we note that the barriers are significantly lower than that previously

obtained for the VHF of the parent system **1b** (ca. 100 kJ mol^{-1})[17], which is in line with the ultrafast TBRs observed experimentally. The differences in barriers are quite small between individual compounds in both series, but we do find the same trends as observed experimentally. Thus, for all methods (except for M06-2X with X = OMe), the barrier height increases when going from an EDG (OMe) to an EWG (NO_2) on position Y. Now, for a direct comparison to experiment, we need to consider also the s-*trans*/s-*cis* pre-equilibrium since its equilibrium constant *K* may differ for the various substitution patterns. These equilibrium constants are listed in Table 3. From the Eyring equation, the Gibbs free energies of activation were converted to rate constants, and these were then multiplied by *K* / (*K*+1). The ratios between these rate constants are plotted in Figure 6. Again, the CAM-B3LYP and PBE0 functionals give the same relative rates as observed experimentally, while the results from the M06-2X functional deviate from the experiments.

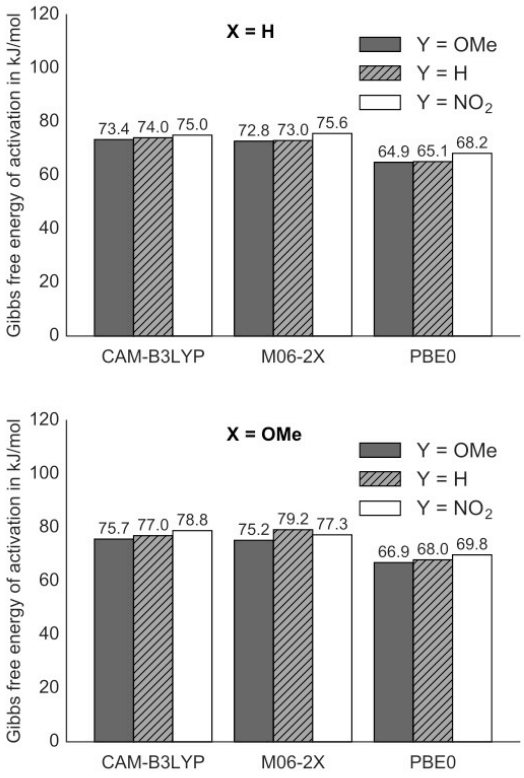


Figure 5. Calculated Gibbs free energies of activation for the s-*cis*-VHF → DHA conversion in EtOH at -20 °C. Top) X = H; compounds **4b**, **5b**, and **11b**. Bottom) X = OMe; Compounds **4c**, **5c**, and **11c**.

Table 3. Calculated equilibrium constants for the s-*trans*-VHF ⇔ s-*cis*-VHF equilibria at -20 °C (going from s-*trans*-VHF to s-*cis*-VHF) based on three different functionals.

X	Y	CAM-B3LYP	M06-2X	PBE0
H	H	6.61	0.82	1.18
H	OMe	8.71	0.40	1.11
H	NO_2	4.59	1.72	0.71
OMe	H	6.23	2.26	1.71
OMe	OMe	3.70	2.19	0.86
OMe	NO_2	4.52	1.64	0.85

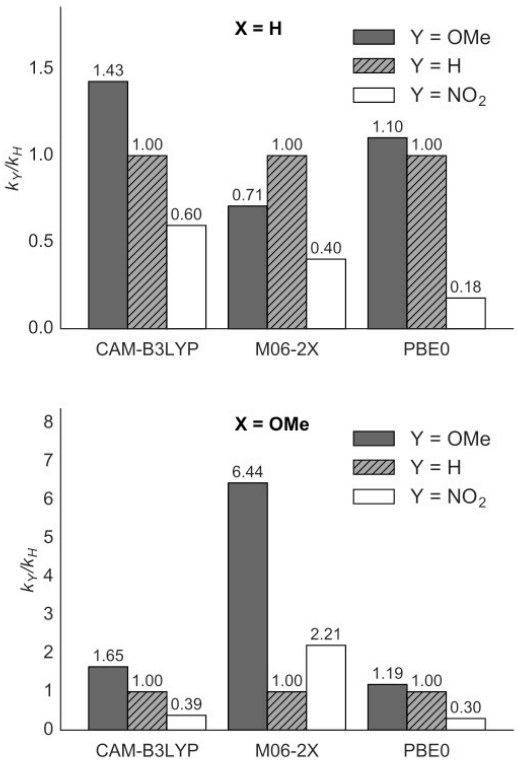


Figure 6. Calculated ratios between rate constants (k_Y/k_H) for the VHF → DHA conversion in EtOH at -20 °C taking the s-*trans*/s-*cis* pre-equilibrium constant *K* into account; each rate constant obtained from the Gibbs free energy difference between s-*cis*-VHF and the TS structure was multiplied by *K* / (*K*+1) Top) X = H; compounds **4b**, **5b**, and **11b**. Bottom) X = OMe; Compounds **4c**, **5c**, and **11c**.

Conclusions

We have employed two synthetic protocols for achieving a selection of 2,3-diarylated DHAs. The one protocol relied on ready access to 3-bromo-substituted DHAs, but suffered from rather poor yields from the subsequent Suzuki cross-couplings. In the other protocol both aryl groups were incorporated early in the synthesis. The individual steps here proceeded in high yields, except, however, for the final oxidation step to generate VHF/DHA. In total, we have managed to prepare six new 2,3-diarylated DHAs. The ring-closure kinetics of the corresponding VHFs of five of these compounds together with the VHF formed from the known 2,3-diphenyl-substituted DHA was studied at low

temperature. The compounds can be categorized in two classes where the substituent at the VHF vinyl position (C-2 of DHA) is the same, while the substituent at the exocyclic VHF carbon (C-3 of DHA) is varied. For each of these classes a Hammett correlation was obtained, characterized by a negative slope. This result implies that electron-donating groups at C-3 enhance the ring-closure reaction. The influence of a substituent at this position is hence opposite to that previously established for a substituent at C-2. The experimental results were supported by DFT calculations when using the CAM-B3LYP and PBE0 functionals, but only partly based on the M06-2X functional. In all, this is the first systematic study revealing how the VHF ring-closure reaction is influenced by donor-acceptor substitution at position C-3 of DHA, which is important in the design of fast or slow molecular switches for various applications.

Experimental Section

General Methods. All handling of photochromic compounds was done in the dark. All operations involving photochromic DHAs (evaporation of solvents, column chromatography, and reactions) were done in glassware wrapped in aluminum foil. All reactions were done under nitrogen (using a gas bubbler) or argon (balloon technique). All palladium-catalyzed Suzuki couplings were performed in solvents flushed with argon (on an ultrasound bath, letting argon flow through the solvent for at least 10 min). All chemicals and solvents were obtained from commercial suppliers and used as received unless otherwise stated. $CDCl_3$ was passed through activated Al_2O_3 before use. Thin-layer chromatography (TLC) was carried out in the dark on commercially available precoated plates (silica 60) with fluorescence indicator; color change from yellow to red upon irradiation with UV light (365 nm, *not* 254 nm) indicated the presence of a DHA. All melting points are uncorrected. All spectroscopic measurements were performed in a 1-cm path length cuvette using a cryostat, placed inside a UV-Vis spectrophotometer, which kept the temperature at -20 °C. UV−Vis absorption spectra were obtained by scanning the wavelengths from 800 to 200 nm. Absorption data for the VHF were obtained after light-induced ring opening of the corresponding DHA using a UV lamp (365 nm). The thermal back-reaction was followed by heating the sample (cuvette) by the cryostat unit in the UV-Vis spectrophotometer. NMR spectra were acquired on 300 MHz, 400 MHz, or 500 MHz instruments. 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). All processing of the NMR spectra, calculation of coupling constants, peak-picking, and so forth were done without exponential apodization (line broadening), but NMR spectra presented in the SI are shown with exponential apodization equal to 0.3 Hz for ^{1}H and 1.0 Hz for ^{13}C.

2-(2-(2,4,6-Cycloheptatriene-1-ylidene)-1-(4'-nitro-phenyl)ethylidene)malononitrile (2a). To a stirred solution of **1a** (204 mg, 0.677 mmol) in CH_2Cl_2 (30 mL) at rt, was added $AlCl_3$ (300 mg, 2.25 mmol). After continued stirring for approximately 20 min (complete ring-opening to the VHF were furnished as judged by TLC (Note 1)), the mixture was cooled using an ice-bath and quenched by addition of ice-cold water (100 mL) after which the phases were separated. The aqueous phase was extracted with ice-cold CH_2Cl_2 (3 x 50 mL) and the combined organic phases were dried with $MgSO_4$ and filtered. To the cold CH_2Cl_2 solution heptane (100 mL) was added, and then the CH_2Cl_2 was removed upon concentration *in vacuo*. The resulting precipitate was collected by suction filtration and washed with ice-cold heptane (50 mL) to afford the title compound (134 mg, 0.445 mmol, 66%) as a metallic blue powder (Note 2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 6.81–6.75 (m, 1H), 6.54–6.47 (m, 2H), 6.43–6.35 (m, 2H), 6.01 (dd, *J* = 12.1, 7.9 Hz, 1H), 5.82 (dd, *J* = 12.1, 2.3 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.87, 154.43, 149.23, 142.68, 141.64, 136.67, 135.71, 135.57, 135.09, 134.97, 129.66, 125.06, 118.29, 114.57, 114.01, 77.57 ppm. Elem. anal. calc. for $C_{18}H_{11}N_3O_2$ (301.09): C: 79.75%, H: 4.82%, N: 9.71%, found: C: 57.02%, H: 2.70%, N: 10.93%. Note 1) If further starting material was present, more $AlCl_3$ was added. Note 2) The compound turns back to **1a** in crystalline form within an hour at rt and was thus stored cold at -18 °C.

2-(2-(2,4,6-Cycloheptatriene-1-ylidene)-1-phenylethylidene)malononitrile (2b). To a stirred solution of **1b** (262 mg, 1.02 mmol) in CH_2Cl_2 (35 mL) at rt was added $AlCl_3$ (412 mg, 3.09 mmol). After continued stirring for approximately 20 min (complete ring-opening to the VHF was furnished as judged by TLC (Note 1)), the mixture was cooled using an ice-bath and quenched by addition of ice-cold water (100 mL) after which the phases were separated. The aqueous phase was extracted with ice-cold CH_2Cl_2 (3 x 50 mL) and the combined organic phases were dried with $MgSO_4$ and filtered. To the cold CH_2Cl_2 solution, heptane (100 mL) was added, and then the CH_2Cl_2 was removed upon concentration *in vacuo*. The resulting precipitate was collected by suction filtration and washed with ice-cold heptane (50 mL) to afford the title compound (175 mg, 0.682 mmol, 67%) as a metallic green powder (Note 2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 3H), 7.41 – 7.35 (m, 2H), 6.74 – 6.65 (m, 1H), 6.42 – 6.35 (m, 2H), 6.33 (s, 1H), 6.30 – 6.24 (m, 1H), 5.92 – 5.81 (m, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 169.10, 154.09, 142.53, 135.66, 135.30, 135.21, 135.18, 134.59, 133.71, 131.20, 129.87, 128.26, 119.16, 115.19, 114.71; one signal missing. Note 1) If further starting material is present, more $AlCl_3$ is added. Note 2) The compound turns back to **1b** in crystalline form within an hour at rt and was thus stored cold at -18 °C.

2-(2-(2,4,6-Cycloheptatriene-1-ylidene)-1-(4'-methoxy-phenyl)ethylidene)malononitrile (2c). To a stirred solution of **1c** (162 mg, 0.566 mml) in CH_2Cl_2 (30 mL) at rt was added $AlCl_3$ (220 mg, 1.65 mmol). After continued stirring for approximately 20 min (complete ring-opening to the VHF was furnished as judged by TLC (Note 1)), the mixture was cooled using an ice-bath and quenched by addition of ice-cold water (100 mL) after which the phases were separated. The aqueous phase was extracted with ice-cold CH_2Cl_2 (3 x 50 mL) and the combined organic phases were dried with $MgSO_4$ and filtered. To the cold CH_2Cl_2 solution, heptane (100 mL) was added and then the CH_2Cl_2 was removed upon concentration *in vacuo*. The resulting precipitate was collected by suction filtration and washed with ice-cold heptane (50 mL) to afford the title compound (136 mg, 0.475 mmol, 84%) as a metallic green powder (Note 2). Note 1) If further starting material is present, more $AlCl_3$ is added. Note 2) The compound turns back to **1c** in crystalline form within an hour at rt, and was thus stored cold at -18 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.69 – 6.63 (m, 1H), 6.35 (dd, *J* = 9.0, 3.5 Hz, 2H), 6.27 (s, 1H), 6.26–6.22 (m, 1H), 5.95–5.88 (m, 2H), 3.87 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.88, 162.32, 154.02, 142.26, 135.41, 135.33, 134.95, 134.18, 133.33, 130.47, 126.96, 119.38, 115.67, 115.17, 115.04, 75.69, 55.60 ppm.

3-Bromo-2-(4'-nitrophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (3a). To a stirred solution of DHA **1a** (507 mg, 1.68 mmol) in CH_2Cl_2 (50 mL) at rt was added $AlCl_3$ (670 mg, 5.03 mmol) (Note 1). After continued stirring for approximately 20 min (complete ring-opening to the VHF as judged by TLC; Note 2), the mixture was cooled using an ice-bath and quenched by addition of ice-cold water (100 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (4 x 50 mL).

The combined organic phases was dried with $MgSO_4$, filtered and concentrated *in vacuo*, while the flask was kept in an ice-bath. The resulting red residue (Note 3) was then dissolved in benzene (40 mL), and NBS (800 mg, 4.49 mmol) was added. The solution was stirred for 5 min after which benzoyl peroxide (30 mg, 0.12 mmol) was added. The solution was irradiated with a 500-W white-light halogen lamp kept at a distance of ca. 1.5 m from the reaction mixture. After 1.5 h, the solution had changed color from red to orange-yellow. The organic layer was quenched with water (100 mL) and washed with brine (100 mL), dried over Na_2SO_4, and finally filtered. The solvent was removed *in vacuo* and the crude residue was dissolved in CH_2Cl_2, Celite was added and the mixture was concentrated *in vacuo*. Purification by dry column vacuum chromatography (SiO_2, 15–40 µm 12.6 cm^2, 0–15% EtOAc/heptanes, 1% steps, 40 mL fractions) gave the title compound (500 mg, 1.32 mmol, 78%) as yellow crystals. TLC (25% EtOAc/heptanes), R_f = 0.49, (toluene): R_f = 0.62. M.p. 113–116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.6, 2H), 7.90 (d, *J* = 8.6, 2H), 6.75–6.68 (m, 1H), 6.66–6.59 (m, 2H), 6.42–6.36 (m, 1H), 5.81-5.75 (dd, *J* = 10.3, 3.7 Hz, 1H), 3.80 (br s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.75, 137.19, 135.13, 133.92, 132.89, 130.31, 130.23, 129.47, 128.51, 124.42, 123.75, 119.67, 113.95, 111.64, 48.90, 47.25 ppm. Elem. anal. calc. for $C_{18}H_{10}BrN_3O_2$ (320.20): C: 56.86%, H: 2.65%, N: 11.05%, found: C: 57.02%, H: 2.70%, N: 10.93%. HRMS (MALDI+ FT-ICR, ditranol) *m/z* 377.98796 (100%), 379.98595 (91.4%) [M-H$^-$], calcd. for ($C_{18}H_9BrN_3O_2^{+}$ $^{79/81}$Br) *m/z* 377.98727 (100.0%), 379.98522 (97.3%). Note 1) The solution turned immediately dark red. Note 2) Red spot is sign of VHF whereas the DHA is yellow. 3) The residue can instead of red have a metal green color.

3-Bromo-2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (3b). To a stirred solution of DHA **1b** (310 mg, 1.21 mmol) in CH_2Cl_2 (40 mL) at rt under an argon atmosphere was added $AlCl_3$ (440 mg, 3.30 mmol) (Note 1). After continued stirring for approximately 20 min (complete ring-opening to the VHF as judged by TLC; Note 2), the mixture was cooled using an ice-bath and quenched by addition of ice-cold water (100 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic phases was dried with $MgSO_4$, filtered and concentrated *in vacuo*, while the flask was kept in an ice-bath. The resulting red residue (Note 3) was then dissolved in benzene (40 mL), and NBS (430 mg, 2.42 mmol) was added. The solution was stirred for 5 min after which benzoyl peroxide (30 mg, 0.12 mmol) was added. The solution was irradiated with a 500-W white light halogen lamp kept at a distance of ca. 1.5 m from the reaction mixture. The reaction progress was monitored by TLC until no sign of VHF. Then, the suspension was filtered, CH_2Cl_2 (100 mL) was added and the organic layer was washed with water (100 mL), brine (100 mL), dried over $MgSO_4$, and finally filtered. Purification by flash column chromatography (SiO_2 40-63 µm, loading: CS_2, 10% EtOAc/heptane) gave the title compound (290 mg, 0.865 mmol, 72%) as yellow crystals. TLC (toluene): R_f = 0.72. M.p. 125–127 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72–7.68 (m, 2H), 7.54–7.50 (m, 3H), 6.68 (dd, *J* = 11.3, 6.4 Hz, 1H), 6.57 (dd, *J* = 11.3, 6.0 Hz, 1H), 6.54 (dd, *J* = 6.4, 1.2 Hz, 1H), 6.35 (ddd, *J* = 10.1, 6.0, 2.0 Hz, 1H), 5.77 (dd, *J* = 10.1, 3.9 Hz, 1H), 3.77 (dt, *J* = 3.9, 2.0 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.62, 135.94, 131.95, 130.91, 130.54, 130.42, 129.17, 128.91, 128.23, 127.08, 122.21, 119.75, 114.41, 112.04, 48.99, 47.56 ppm. HRMS (MALDI+ FT-ICR, ditranol) *m/z* 333.00251 (100%), 335.00046 (98.9%) [M$^+$], calcd. for ($C_{18}H_{11}BrN_2^{+}$ $^{79/81}$Br) *m/z* 333.00219 (100%), 335.00024 (97.3%). Note 1) The solution turned immediately dark red. Note 2) Red spot is sign of VHF whereas the DHA is yellow. Note 3) The residue can instead of red have a metal green color.

3-Bromo-2-(4'-methoxyphenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (3c). To a stirred solution of **1c** (323 mg, 1.13 mmol) in CH_2Cl_2 (40 mL) at rt was added $AlCl_3$ (500 mg, 3.79 mmol) (Note 1). After continued stirring for approximately 20 min (complete ring-opening to the VHF as judged by TLC; Note 2), the mixture was cooled using an ice-bath and quenched by addition of ice-cold water (100 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic phases was dried with $MgSO_4$, filtered and concentrated *in vacuo*, while the flask was kept in an ice-bath. The resulting red residue (Note 3) was then dissolved in benzene (45 mL), and NBS (620 mg, 3.48 mmol) was added. The solution was stirred for 5 min after which benzoyl peroxide (15 mg, 0.062 mmol) was added. The solution was irradiated with a 500-W white light halogen lamp kept at a distance of ca. 1.5 m from the reaction mixture. The reaction progress was followed by TLC until no sign of VHF (approximately 3 h). Then the suspension was filtered and the organic layer was washed with water (100 mL), brine (100 mL), dried over $MgSO_4$, and finally filtered. Purification by flash column chromatography (SiO_2 40–63 µm, loading: CS_2, 10% EtOAc/heptane) gave the title compound (346 mg, 0.947 mmol, 84%) as yellow crystals that in time change color to purple. TLC (toluene): R_f = 0.52. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.9 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.67 (dd, *J* = 11.3, 6.4 Hz, 1H), 6.54 (dd, *J* = 11.3, 6.1 Hz, 1H) 6.51 (dd, *J* = 6.4, 1.2 Hz, 1H), 6.34 (ddd, *J* = 10.1, 6.1, 2.0 Hz, 1H), 5.76 (dd, *J* = 10.1, 3.9 Hz, 1H), 3.88 (s, 3H), 3.75 (dt, *J* = 3.9, 2.0 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.21, 136.31, 136.20, 131.60, 130.50, 130.42, 128.21, 125.56, 123.04, 121.70, 119.65, 114.66, 114.61, 112.30, 55.55, 48.95, 47.33 ppm. HRMS (MALDI+ FT-ICR, ditranol) *m/z* 363.01340 (100%), 365.01136 (100%) [M-H$^-$ $^{79/81}$Br], calcd. for ($C_{19}H_{12}BrN_2O^{+}$ $^{79/81}$Br) *m/z* 363.01275 (100.0%), 365.01071 (97.3%). Crystals suitable for X-ray crystallography were grown from CH_2Cl_2/heptane.

1,8a-Dihydro-2-(4'-methoxyphenyl)-3-phenylazulene-1,1-dicarbonitrile (4c). To a stirred solution of **3c** (165 mg, 0.457 mmol) in a mixture of toluene (18 mL) and water (2 mL) were added phenylboronic acid (135 mg, 1.11 mmol), K_3PO_4 (165 mg, 0.810 mmol), BrettPhos (112 mg, 0. 24 mmol), and $Pd(OAc)_2$ (23 mg, 0.12 mmol). The reaction mixture was heated at 65 °C overnight, after which it was quenched with a saturated aqueous solution of NH_4Cl and diluted with CH_2Cl_2 (100 mL). The organic layer was washed with a saturated aqueous solution of NH_4Cl (3 × 50 mL), dried with $MgSO_4$, filtered, and the solvents were removed *in vacuo*. The residue was subjected to flash column chromatography (SiO_2 40-63 µm, loading: CS_2, gradient elution 80−100% toluene/heptane), which gave **6c** (20 mg, 0.060 mmol, 13%) as a blue bright solid and **8c** (8 mg, 0.03 mmol, 6%) as a red solid. Fractions containing **4c** were concentrated *in vacuo* to give a brown oil with major impurities. This brown oil of **4c** was subjected to flash column chromatography (SiO_2 40-63 µm, loading: CS_2, 13% EtOAc/heptane) which gave **4c** (5 mg, 0.01 mmol, 3%) as a yellow solid. **4c:** TLC (toluene): R_f = 0.42, (12.5% EtOAc/heptane): R_f = 0.48. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.34 (m, 3H), 7.30 (d, *J* = 8.9 Hz, 2H), 7.18 (ddd, *J* = 5.7, 3.0, 1.5 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.55 (dd, *J* = 11.2, 6.2 Hz, 1H), 6.49 (dd, *J* = 11.2, 5.9 Hz, 1H), 6.34 (ddd, *J* = 10.0, 5.9, 1.9 Hz, 1H), 6.03 (d, *J* = 6.2 Hz, 1H), 5.82 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.78 (s, 3H), 3.73 (dt, *J* = 4.0, 1.9 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.29, 144.09, 140.42, 136.02, 133.03, 131.31, 130.54, 130.43, 129.42, 129.04, 128.91, 127.64, 123.93, 120.40, 119.55, 116.02, 114.29, 113.32, 55.39, 50.23, 47.18 ppm. HRMS (ESP+, FT-ICR, TFA added) *m/z* 358.12023 [M$^{+\bullet}$], calcd. for ($C_{25}H_{18}N_2O^{+\bullet}$) *m/z* 358.12024. **6c**: TLC (toluene): R_f = 0.17 ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 9.8 Hz, 1H), 8.38 (d, *J* = 9.8 Hz, 1H), 7.78 (t, *J* = 9.8 Hz, 1H), 7.52 (t, *J* = 9.8 Hz, 1H), 7.50–7.46 (m, 2H), 7.41 (t, *J* = 9.8 Hz, 1H), 7.38–7.31 (m, 3H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.04, 151.07, 144.30, 140.37, 139.67, 137.63, 136.25, 134.27, 132.44, 130.52, 129.62, 128.60, 127.93, 127.50, 127.04, 117.94, 114.24, 96.22, 55.43 ppm; one signal missing due to overlap. HRMS (MALDI+ FT-ICR, ditranol) *m/z* 335.13076 [M$^{+\bullet}$], calcd. for ($C_{24}H_{17}NO^{+\bullet}$)

m/z 335.13101. Crystals suitable for X-ray crystallography were grown from CH_2Cl_2/heptane. **8c**: TLC (toluene): R_f = 0.07 ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 9.9 Hz, 2H), 8.08 (d, *J* = 8.9 Hz, 2H), 8.02 (t, *J* = 9.9 Hz, 1H), 7.83 (t, *J* = 9.9 Hz, 2H), 7.13 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.94, 155.24, 145.74, 140.95, 137.32, 131.65, 131.31, 124.29, 116.47, 115.12, 96.33, 55.66 ppm. HRMS (ESP+, FT-ICR, TFA added) *m/z* [M+H$^+$] 285.10261, calcd. for ($C_{19}H_{13}N_2O^+$) *m/z* 285.10224. Crystals suitable for X-ray crystallography were grown from CH_2Cl_2/heptane.

1,8a-Dihydro-3-(4'-methoxyphenyl)-2-(4'-nitrophenyl)azulene-1,1-dicarbonitrile (5a). To a stirred solution of **3a** (100 mg, 0.263 mmol) in a mixture of toluene (18 mL) and water (2 mL) were added *p*-methoxyphenylboronic acid (120 mg, 0.789 mmol), K_3PO_4 (112 mg, 0.526 mmol), BrettPhos (56 mg, 0.11 mmol), and $Pd(OAc)_2$ (12 mg, 0.053 mmol). The reaction mixture was heated at 75 °C overnight, after which it was diluted with CH_2Cl_2 (100 mL), washed with a saturated aqueous solution of NH_4Cl (3 × 50 mL), dried with $MgSO_4$, filtered, and the solvents were removed *in vacuo*. The residue was redissolved in CH_2Cl_2, Celite was added and the mixture was concentrated. Purification by dry column vacuum chromatography (SiO_2 15–40 µm, 12.6 cm^2, (1) toluene/heptane, 0−60% 10% steps, 60–75%, 5% steps, 75–85%, 2.5%, 40 mL fractions), (2) THF/heptane 0−20%, 5% steps, 20– 37.5%, 2.5% steps, 40 mL fractions) gave **5a** (4 mg, 0.01 mmol, 4%) as a dark yellow solid. TLC (75% CH_2Cl_2/heptanes): R_f = 0.64. M.p. 67–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.65–6.55 (m, 2H), 6.38 (ddd, *J* = 10.0, 4.6, 1.8 Hz, 1H), 6.21 (d, *J* = 5.0 Hz, 1H), 5.80 (dd, *J* = 10.0, 4.2 Hz, 1H), 3.82 (s, 3H), 3.73 (dt, *J* = 3.8, 1.7 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 160.74, 148.28, 147.65, 139.10, 138.63, 132.51, 131.90, 131.18, 130.75, 129.94, 127.85, 124.09, 123.51, 122.76, 119.64, 115.54, 114.81, 112.74, 55.48, 50.15, 46.72. HRMS (MALDI+ FT-ICR, ditranol) *m/z* 406.11940 [M-H$^-$], calcd. for ($C_{25}H_{16}N_3O_3^+$) *m/z* 406.11862.

1,8a-Dihydro-3-(4'-methoxyphenyl)-2-phenylazulene-1,1-dicarbonitrile (5b). To a stirred solution of **3b** (112 mg, 0.334 mmol) in a mixture of toluene (18 mL) and water (2 mL) were added *p*-methoxyphenylboronic acid (169 mg, 1.11 mmol), K_3PO_4 (155 mg, 0.730 mmol), BrettPhos (79 mg, 0.147 mmol), and $Pd(OAc)_2$ (17 mg, 0.076 mmol). The reaction mixture was heated at 65 °C overnight, after which it was quenched with a saturated aqueous solution of NH_4Cl and diluted with CH_2Cl_2 (100 mL). The organic layer was washed with a saturated aqueous solution of NH_4Cl (3 × 50 mL), dried with $MgSO_4$, filtered, and the solvents were removed *in vacuo*. The residue was subjected to flash column chromatography (1) (SiO_2 40–63 µm, loading: CS_2, gradient elution 80−100% toluene/heptane), (2) (SiO_2 40–63 µm, loading: CS_2, 13% EtOAc/heptane), which gave **5b** (5 mg, 0.014 mmol, 4%) as a yellow solid. TLC (toluene): R_f = 0.47, (15% EtOAc/heptanes): R_f = 0.31. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.36 (m, 2H), 7.32–7.28 (m, 3H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.58 (dd, *J* = 11.2, 6.2 Hz, 1H), 6.52 (dd, *J* = 11.1, 5.9 Hz, 1H), 6.35 (ddd, *J* = 9.9, 5.8, 2.0 Hz, 1H), 6.12 (d, *J* = 6.1 Hz, 1H), 5.81 (dd, *J* = 10.0, 4.2 Hz, 1H), 3.80 (s, 3H), 3.72–3.69 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.10, 145.20, 140.14, 135.47, 131.97, 131.27, 130.82, 130.79, 129.26, 129.04, 128.82, 127.56, 124.54, 120.87, 119.65, 115.94, 114.38, 113.15, 55.38, 50.16, 47.26 ppm. HRMS (MALDI+ FT-ICR, ditranol) *m/z* 362.14150 [M$^{+\cdot}$], calcd. for ($C_{25}H_{18}N_2O^{+\cdot}$) *m/z* 362.14136.

1,8a-Dihydro-2,3-bis(4'-methoxyphenyl)azulene-1,1-dicarbonitrile (5c). To a stirred solution of **3c** (150 mg, 0.410 mmol) in a mixture of toluene (18 mL) and water (2 mL) were added *p*-methoxyphenylboronic acid (207 mg, 1.36 mmol), K_3PO_4 (190 mg, 0.895 mmol), BrettPhos (105 mg, 0.196 mmol), and $Pd(OAc)_2$ (21 mg, 0.094 mmol). The reaction mixture was heated at 75 °C overnight, after which it was quenched with a saturated aqueous solution of NH_4Cl and diluted with CH_2Cl_2 (100 mL). The organic layer was washed with a saturated aqueous solution of NH_4Cl (3 × 50 mL), dried with $MgSO_4$, filtered, and the solvents were removed *in vacuo*. The residue was subjected to flash column chromatography (1) (SiO_2 40–63 µm, loading: CS_2, gradient elution 80−100% toluene/heptane), (2) (SiO_2 40–63 µm, loading: CS_2, 4% EtOAc/CS_2), which gave **5c** (6 mg, 0.02 mmol, 4%) as a yellow solid. TLC (toluene): R_f = 0.41. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.56 (dd, *J* = 11.1, 6.2 Hz, 1H), 6.49 (dd, *J* = 11.1, 5.9 Hz, 1H), 6.36–6.29 (m, 1H), 6.07 (d, *J* = 6.2 Hz, 1H), 5.79 (dd, *J* = 9.9, 4.1 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.70–3.67 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.18, 160.00, 143.72, 140.51, 135.39, 131.35, 130.80, 130.45, 130.42, 127.55, 124.97, 124.23, 120.24, 119.53, 116.12, 114.46, 114.30, 113.38, 55.40, 55.40, 50.17, 47.12 ppm. HRMS (ESP+, FT-ICR, TFA added) *m/z* 393.16150 [M+H$^+$], calcd. for ($C_{26}H_{20}N_2O_2^+$) *m/z* 393.15975.

2-(4'-Nitrophenyl)-3-phenylazulene-1-carbonitrile (6a). To a stirred solution of **3a** (92 mg, 0.242 mmol) in a mixture of toluene (18 mL) and water (2 mL) were added *p*-methoxyphenylboronic acid (94 mg, 0.77 mmol), K_3PO_4 (101 mg, 0.476 mmol), BrettPhos (78 mg, 0.14 mmol), and $Pd(OAc)_2$ (17 mg, 0.076 mmol). The reaction mixture was heated at 85 °C overnight and then allowed to reach rt. A substantial amount of starting material was left in the reaction mixture (judged by TLC) and it was then flushed with Ar for 15 min with the help of sonication, and additional *p*-methoxyphenylboronic acid (99 mg, 0.81 mmol), BrettPhos (81 mg, 0.15 mmol), and $Pd(OAc)_2$ (20 mg, 0.089 mmol) were added. The reaction mixture was heated at 95 °C for one additional day, after which it was diluted with CH_2Cl_2 (100 mL), washed with a saturated aqueous solution of NH_4Cl (3 × 50 mL), dried with $MgSO_4$, filtered, and the solvents were removed *in vacuo*. The residue was redissolved in CH_2Cl_2, Celite was added and the mixture was concentrated *in vacuo*. Purification by dry column vacuum chromatography (SiO_2 15–40 µm, 12.6 cm^2, toluene/heptane, 0−100%, 20% steps, 100% until the product was eluted from the column, 40 mL fractions) gave **6a** (15 mg, 0.043 mmol, 17%) as blue crystals. TLC (toluene): R_f = 0.26. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 9.8 Hz, 1H), 8.46 (d, *J* = 9.8 Hz, 1H), 8.20 (d, *J* = 8.9 Hz, 2H), 7.90 (t, *J* = 9.8 Hz, 1H), 7.65–7.59 (m, 3H), 7.51 (t, *J* = 9.8 Hz, 1H), 7.45–7.39 (m, 3H), 7.25–7.22 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.64, 147.61, 144.25, 141.12, 140.85, 140.28, 139.01, 137.67, 134.03, 131.34, 131.33, 130.40, 129.07, 128.74, 128.25, 127.99, 123.82, 117.26, 96.23 ppm. HRMS (ESP+, FT-ICR, TFA added) *m/z* 373.09518 [M+Na$^+$], calcd. for ($C_{23}H_{14}N_2O_2Na^+$) *m/z* 373.09475. Crystals suitable for X-ray crystallography were grown from CH_2Cl_2/heptane.

3-(4'-Methoxyphenyl)-2-phenylazulene-1-carbonitrile (7b). To a stirred solution of **3b** (90 mg, 0.27 mmol) in a mixture of toluene (18 mL) and water (2 mL) were added phenylboronic acid (140 mg, 0.921 mmol), K_3PO_4 (130 mg, 0.612 mmol), BrettPhos (89 mg, 0.081 mmol), and $Pd(OAc)_2$ (18 mg, 0.16 mmol). The reaction mixture was heated at 80 °C overnight, after which it was quenched with a saturated aqueous solution of NH_4Cl and diluted with CH_2Cl_2 (100 mL). The organic layer was washed with a saturated aqueous solution of NH_4Cl (3 × 50 mL), dried with $MgSO_4$, filtered, and the solvents were removed *in vacuo*. The residue was subjected to flash column chromatography (SiO_2 40–63 µm, loading: CS_2, gradient elution 20% EtOAc/heptane), which gave **7b** (24 mg, 0.072 mmol, 27%) as a blue solid and traces of **8b** as a pink solid both with minor impurities. Analytically pure samples were obtained by recrystallization from CH_2Cl_2/heptane. **7b**: TLC (toluene): R_f = 0.33. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 9.8 Hz, 1H), 8.33 (d, *J* = 9.8 Hz, 1H), 7.75 (t, *J* = 9.8 Hz, 1H), 7.52 (t, *J* = 9.8 Hz, 1H), 7.45–7.35 (m, 6H), 7.29–7.26 (m, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.09, 151.01, 144.53, 140.33, 139.19, 136.94,

135.72, 135.19, 131.98, 131.36, 129.41, 128.77, 128.10, 127.65, 127.40, 126.51, 118.17, 114.19, 95.85, 55.39 ppm. HRMS (MALDI+ FT-ICR, ditranol) *m/z* 358.12023 [M+Na$^+$], calcd. for ($C_{24}H_{17}NO$+Na$^+$) *m/z* 358.12024. **8b**: TLC (toluene): R_f = 0.17 ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (d, *J* = 10.0 Hz, 2H), 8.09 (t, *J* = 10.0 Hz, 1H), 8.06–8.03 (m, 2H), 7.87 (t, *J* = 10.0 Hz, 2H), 7.64–7.60 (m, 2H), 7.59–7.55 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.61, 145.44, 141.71, 138.14, 131.78, 131.67, 130.89, 129.65, 129.55, 116.10, 97.00 ppm. HRMS (ESP+, FT-ICR, TFA added) *m/z* 277.07438 [M+Na$^+$], calcd. for ($C_{18}H_{10}N_2$Na$^+$) *m/z* 277.07362.

3-(4'-Methoxyphenyl)-2-(4'-methylphenyl)azulene-1-carbonitrile (10). To a stirred solution of azulene **9** (64 mg, 0.20 mmol) in a mixture of toluene (14 mL) and water (2 mL) were added *p*-methoxyphenylboronic acid (71 mg, 0.467 mmol), K_3PO_4 (102 mg, 0.481 mmol), BrettPhos (46 mg, 0.086 mmol), and $Pd(OAc)_2$ (9.4 mg, 0.042 mmol). The reaction mixture was heated at 90 °C overnight, after which it was quenched with water and diluted with ether (100 mL). The organic layer was washed with water (3 × 50 mL), dried with $MgSO_4$, filtered, and the solvents were removed *in vacuo*. The residue was subjected to flash column chromatography (SiO_2 40–63 µm, loading: toluene, elution 20% EtOAc/heptane), which gave **10** (65 mg, 0.17 mmol, 94%) as a blue solid. TLC (toluene): R_f = 0.30, TLC (20% EtOAc/heptanes): R_f = 0.30. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 9.7 Hz, 1H), 8.34 (d, *J* = 9.7 Hz, 1H), 7.75 (t, *J* = 9.7 Hz, 1H), 7.50 (t, *J* = 9.7 Hz, 1H), 7.42–7.36 (m, 3H), 7.21–7.14 (m, 4H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 2.36 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.00, 151.24, 144.35, 140.41, 139.37, 138.68, 137.28, 135.92, 132.41, 131.33, 130.41, 129.44, 129.40, 127.86, 127.44, 127.23, 118.09, 114.23, 96.08, 55.42, 21.52 ppm. HRMS (ESP+, FT-ICR, TFA added) *m/z* 372.13648 [M+Na$^+$], calcd. for ($C_{25}H_{19}NO$Na$^+$) *m/z* 372.13589. Crystals suitable for X-ray crystallography were grown from CH_2Cl_2/heptane.

1,8a-Dihydro-3-(4'-nitrophenyl)-2-phenylazulene-1,1-dicarbonitrile (11b). To a stirring solution of **16b** (1.18 g, 3.10 mmol) at -40 °C in dry MeCN (25 mL) was added $NOBF_4$ (788 mg, 6.75 mmol). The resulting light brown solution was stirred at -40 °C (± 5°C) until no starting material was left judged by TLC (approximately 1 h). Then, by cannula, the solution was diluted with cold CH_2Cl_2 (80 mL) and at -40 °C a solution of pyridine (0.55 mL, 6.8 mmol) in cold CH_2Cl_2 (20 mL) was dropwise added. Upon the first drop, the solution changed color to the distinct red color of VHF. The reaction mixture was stirred for an additional 3 h while letting the temperature voluntarily increase to rt in which the reaction mixture turned brownish. The reaction mixture was quenched with H_2O (100 mL) and extracted with CH_2Cl_2 (3 x 50 mL), dried with $MgSO_4$, filtered, and the solvents were removed *in* vacuo. The residue was redissolved in CH_2Cl_2, Celite was added and the mixture was concentrated *in vacuo*. Purification by dry column vacuum chromatography (SiO_2, 15–40 µm, 12.6 cm^2, toluene/heptane, 0−100% 10% steps, followed by neat toluene, 40 mL fractions) gave **11b** (205 mg, 0.543 mmol, 17%) as a yellow solid. TLC (toluene): R_f = 0.53. ppm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.9 Hz, 2H), 7.39–7.31 (m, 7H), 6.61–6.56 (m, 2H), 6.41–6.35 (m, 1H), 6.00 (dd, *J* = 3.8, 1.7 Hz, 1H), 5.84 (dd, *J* = 9.8, 4.0 Hz, 1H), 3.76 (dt, *J* = 4.0, 1.8 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.14, 143.47, 139.39, 138.78, 138.31, 131.71, 130.99, 130.82, 130.63, 130.16, 129.23, 129.00, 127.94, 124.24, 121.11, 119.66, 115.32, 112.58, 50.25, 47.58 ppm. Elem. anal. calc. for $C_{24}H_{15}N_3O_2$ (377.12): C: 76.38%, H: 4.01%, N: 11.13%, found: C: 76.23%, H: 3.85%, N: 10.94%. HRMS (ESP+, FT-ICR, TFA added) *m/z* 376.10816 [M+H$^+$], calcd. for ($C_{24}H_{14}N_3O_2^+$) 376.10805.

1,8a-Dihydro-2-(4'-methoxyphenyl)-3-(4'-nitrophenyl)azulene-1,1-dicarbonitrile (11c). To a stirring solution of **16c** (821 mg, 2.01 mmol) at -40 °C in dry MeCN (25 mL) was added $NOBF_4$ (500 mg, 4.28 mmol). The resulting light brown solution was stirred at -40 °C (± 5°C) until no starting material was left as judged by TLC (approximately 1 h). Then, by cannula the solution was diluted with cold CH_2Cl_2 (80 mL) and at -40 °C a solution of pyridine (0.35 mL, 4.3 mmol) in cold CH_2Cl_2 (20 mL) was added dropwise. Upon addition of the first drop, the solution changed color to the distinct red color of VHF. The reaction mixture was stirred for an additional 3 h while letting the temperature voluntarily increase to rt in which the reaction mixture turned brownish. The reaction mixture was quenched with H_2O (100 mL) and extracted with CH_2Cl_2 (3 x 50 mL), dried with $MgSO_4$, filtered, and the solvents were removed *in vacuo*. The crude residue was dissolved in CH_2Cl_2, Celite was added and the mixture was concentrated *in vacuo*. Purification by dry column vacuum chromatography (SiO_2 15-40 µm, 12.6 cm^2, CH_2Cl_2/heptane, 0−100% 10% steps, followed by neat CH_2Cl_2, 40 mL fractions) gave **11c** (52 mg, 0.13 mmol, 6%) as a yellow solid. TLC (75% CH_2Cl_2/heptanes), R_f = 0.36 ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 8.9 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 6.59–6.51 (m, 2H), 6.39–6.34 (m, 1H), 5.98–5.94 (m, 1H), 5.82 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.80 (s, 3H), 3.74 (dt, *J* = 4.0, 1.8 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.86, 148.05, 141.82, 139.88, 139.04, 138.16, 131.28, 131.06, 130.68, 130.44, 127.87, 124.31, 122.96, 120.39, 119.49, 115.52, 114.68, 112.81, 55.46, 50.27, 47.34 ppm. Elem. anal. calc. for $C_{25}H_{17}N_3O_3$ (407.13): C: 73.70%, H: 4.21%, N: 10.31%, found: C: 73.41%, H: 3.99%, N: 10.16%. HRMS (ESP+, FT-ICR, TFA added) *m/z* 406.11889 [M-H$^-$], calcd. for ($C_{25}H_{16}N_3O_3^+$) *m/z* 406.11862.

4-Nitrophenyl acid chloride (13). *p*-Nitrophenyl acetic acid **12** (40.4 g, 223 mmol) was dissolved in $CHCl_3$ (120 mL) in a 500 mL 3-necked flask fitted with stoppers and a condenser connected with Dreschel bottles containing an aqueous solution of NaOH (1 equiv.). $SOCl_2$ (24 mL, 330 mmol) was added, and the solution was allowed to reflux until no gas formation could be seen at the bubble counter. The reaction mixture was cooled to rt and the excess $SOCl_2$ was removed under vacuum affording a brown gel containing the acid chloride **13**. This compound was dissolved in CS_2 (200 mL) and the solution was split in two halves, which were carried forward to the synthesis of **14b** and **14c**, respectively.

2-(4'-Nitrophenyl)-1-phenylethanone (14b). A solution of **13** (111 mmol) in CS_2 (100 mL) was cooled to 0 °C, and benzene (12 mL, 135 mmol) was added. Then, $AlCl_3$ (18 g, 135 mmol) was added portionwise at 0 °C. After the addition of $AlCl_3$, the mixture was allowed to reach rt and stirred for 14 h. The reaction mixture was cooled to 0 °C and quenched with ice-cold water. The organic layer was separated and dried with $MgSO_4$, filtered, and concentrated *in vacuo*. Fractional recrystallization from CH_2Cl_2/heptanes gave compound **14b** (24.5 g, 102 mmol, 91% calculated from **12**) as a white solid. M.p. 136−138 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 4.42 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.11, 147.23, 142.15, 136.31, 133.88, 130.78, 129.03, 128.59, 123.91, 45.09 ppm. HRMS (MALDI+ FT-ICR, ditranol) *m/z* 272.09187 [M+H$^+$], calcd. for ($C_{14}H_{12}NO_3^+$) *m/z* 272.09173.

1-(4'-Methoxyphenyl)-2-(4'-nitrophenyl)-1-ethanon (14c). A solution of **13** (111 mmol) in CS_2 (100 mL) was cooled to 0 °C, and anisole (14 mL, 130 mmol) was added. Then, anhydrous $AlCl_3$ (18 g, 135 mmol) was added portionwise at 0 °C resulting in an intense red coloration of the mixture. After the addition of $AlCl_3$, the mixture was allowed to reach rt and stirred for 14 h. The reaction mixture was cooled to 0 °C and quenched with ice-cold water. The organic layer was separated and dried with $MgSO_4$, filtered, and concentrated *in vacuo*. Then fractional recrystallization from CH_2Cl_2/heptane and recrystallization from boiling 96% ethanol (500 mL) gave **14c** (20.3 g, 74.7 mmol, 67% calculated from **12**) as white crystals. M.p. 117−118 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.99 (d, *J* = 8.9 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H),

6.96 (d, *J* = 8.9 Hz, 2H), 4.35 (s, 2H), 3.88 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.65, 164.11, 147.14, 142.62, 130.96, 130.70, 129.31, 123.87, 114.18, 55.70, 44.82 ppm. HRMS (ESP+, FT-ICR, TFA added) *m/z* 272.09187 [M+H$^+$], calcd. for ($C_{15}H_{14}NO_4^+$) 272.09173.

2-(2-(4'-Nitrophenyl)-1-phenylethylidene)malononitrile (15b). To a stirring solution of **14b** (9.62 g, 40.7 mmol) and malononitrile (13.2 g, 199 mmol) in toluene (240 mL) were added NH_4OAc (15.4 g, 199 mmol) and glacial acetic acid (29 mL, 507 mmol). The reaction vessel was equipped with a Dean−Stark trap and refluxed for 48 h. When still warm, the reaction mixture was decanted to discard an insoluble black oil and then concentrated *in vacuo*. Et_2O (300 mL) was added to this residue, which was then washed with water (3 × 150 mL), dried with $MgSO_4$ and the organic phase was concentrated *in vacuo*. The crude residue was dissolved in CH_2Cl_2, Celite was added and the mixture was concentrated *in vacuo*. Purification by dry column vacuum chromatography (SiO_2 15−40 µm, 113 cm^2 CH_2Cl_2/heptanes, 0−100%, 10% steps, then neat CH_2Cl_2 to collect product, 100 mL fractions) gave **15b** (8.09 g, 27.7 mmol, 70%) as a thick dark oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.8 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 4.38 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.39, 147.65, 141.62, 134.14, 132.70, 129.82, 129.58, 127.96, 124.42, 112.69, 112.26, 86.70, 42.81 ppm. HRMS (ESP+, FT-ICR, TFA added) *m/z* 290.09279 [M+H$^+$], calcd. for ($C_{17}H_{12}N_3O_2^+$) *m/z* 290.09240.

2-(1-(4'-Methoxyphenyl)-2-(4'-nitrophenyl)ethylidene)malononitrile (15c). To a stirring solution of **14c** (9.82 g, 36.2 mmol) and malononitrile (11.3 g, 171 mmol) in toluene (240 mL) were added NH_4OAc (13.2 g, 171 mmol) and glacial acetic acid (25 mL, 437 mmol). The reaction vessel was equipped with a Dean−Stark trap and refluxed for 96 h. When still warm, the reaction mixture was decanted to discard an insoluble black oil and then concentrated *in vacuo*. Et_2O (300 mL) was added to this residue, which was then washed with water (3 × 150 mL), dried with $MgSO_4$ and the organic phase was concentrated *in vacuo*. The crude residue was dissolved in CH_2Cl_2, Celite was added and the mixture was concentrated *in vacuo*. Purification by dry column vacuum chromatography (SiO_2 15−40 µm 113 cm^2, CH_2Cl_2/heptanes, 0−50%, 10% steps, 50-70%, 5%, 70−90 3% steps. 100 mL fractions) gave **15c** (7.55 g, 23.6 mmol, 65%) as white crystals. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 4.37 (s, 2H), 3.86 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.06, 163.43, 147.47, 142.33, 130.44, 129.63, 125.98, 124.33, 114.99, 113.32, 113.16, 83.94, 55.73, 42.13 ppm. Elem. anal. calc. for $C_{18}H_{13}N_3O_3$ (319.32): C: 67.71%, H: 4.10%, N: 13.16%, found: C: 67.58%, H: 3.98%, N: 13.03%. HRMS (MALDI+ FT-ICR, ditranol) *m/z* 320.10364 [M+H$^+$], calcd. for ($C_{18}H_{14}N_3O_3^+$) *m/z* 320.10297.

2-(2-(Cyclohepta-2,4,6-trien-1-yl)-2-(4'-nitrophenyl)-1-phenylethylidene)malononitrile (16b). To a stirring suspension of **15b** (2.08 g, 7.19 mmol) and freshly mortared tropylium tetrafluoroborate (1.34 g, 7.55 mmol) in CH_2Cl_2 (125 mL) kept at -78 °C was added Et_3N (1.30 mL, 9.35 mmol) in CH_2Cl_2 (30 mL) slowly over 2 h (Note 1). The reaction mixture was stirred at -78 °C for 4h, 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 (50 mL) and brine (50 mL), dried with $MgSO_4$, filtered, and concentrated *in vacuo*, which gave **16b** (2.55 g, 6.72 mmol, 93%) as a slightly yellow solid. TLC (75% CH_2Cl_2/heptanes), R_f = 0.56. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.7 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.84 (dd, *J* = 11.0, 5.8 Hz, 1H), 6.73 (dd, *J* = 11.0, 5.8 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 2H), 6.50 (dd, *J* = 9.3, 5.3 Hz, 1H), 6.18 (dd, *J* = 9.3, 5.8 Hz, 1H), 5.42 (dd, *J* = 9.3, 6.2 Hz, 1H), 4.97 (dd, *J* = 9.3, 6.2 Hz, 1H), 4.90 (d, *J* = 12.0 Hz, 1H), 2.42 (dt, *J* = 12.0, 6.2 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.35, 147.96, 142.75, 132.54, 131.74, 131.32, 130.86, 130.39, 128.85, 127.33, 126.47, 124.16, 121.51, 120.87, 112.02, 111.32, 90.58, 75.00, 53.28, 39.77 ppm. HRMS (MALDI+ FT-ICR, ditranol) *m/z* 380.13951 [M+H$^+$], calcd. for ($C_{24}H_{18}N_3O_2^+$) *m/z* 380.13935. Note 1) The addition of Et_3N must be slow to avoid a build-up of a strongly colored red anion.

2-(2-(Cyclohepta-2,4,6-trien-1-yl)-1-(4'-methoxyphenyl)-2-(4'-nitrophenyl)ethylidene)malononitrile (16c). To a stirring suspension of **15c** (2.09 g, 6.55 mmol) and freshly mortared tropylium tetrafluoroborate (1.17 g, 6.58 mmol) in CH_2Cl_2 (125 mL) kept at -78 °C was added Et_3N (0.92 mL, 6.55 mmol) in CH_2Cl_2 (30 mL) slowly over 2 h. 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 organic layer was separated and washed with water (50 mL) and brine (50 mL), dried with $MgSO_4$, filtered, and concentrated *in vacuo*, which gave **16c** (2.20 g, 5.37 mmol, 82%) as a fluffy purple solid. TLC (75% CH_2Cl_2/heptanes), R_f = 0.53. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.84–6.79 (m, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.73 (dd, *J* = 10.9, 5.7 Hz, 1H), 6.66 (d, *J* = 8.9 Hz, 2H), 6.46 (dd, *J* = 9.4, 5.7 Hz, 1H), 6.19 (dd, *J* = 9.4, 5.7 Hz, 1H), 5.36 (dd, *J* = 9.4, 6.2 Hz, 1H), 4.99 (dd, *J* = 9.4, 6.2 Hz, 1H), 4.88 (d, *J* = 12.1 Hz, 1H), 3.79 (s, 3H), 2.43 (dt, *J* = 12.1, 6.2 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.35, 161.73, 147.94, 143.18, 131.74, 131.34, 130.35, 129.29, 127.24, 126.43, 124.74, 124.21, 121.72, 120.92, 114.43, 112.40, 111.88, 89.80, 55.50, 53.41, 39.87 ppm. HRMS (MALDI+ FT-ICR, ditranol) *m/z* 410.150177 [M+H$^+$], calcd. for ($C_{25}H_{20}N_3O_3^+$) *m/z* 410.14992.

Supporting Information

NMR spectra, X-ray crystallographic data, additional details on the switching studies, and calculated structures and energies.

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Keywords: Cyclization • Donor-acceptor systems • Fused-ring systems • Kinetics • Photochromism

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Entry for the Table of Contents

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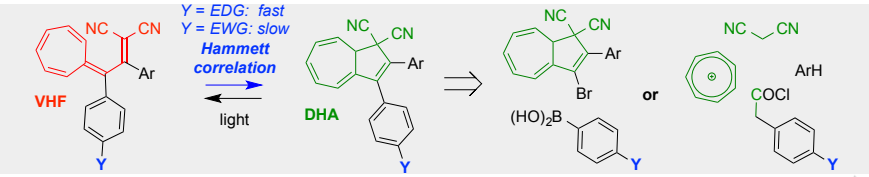

A selection of 2,3-diarylated dihydroazulenes (DHAs) was prepared and converted upon irradiation to vinylheptafulvenes (VHFs). The kinetics of the ring-closure reaction of the VHFs was found to follow Hammett correlations.

Hammett Correlations

Martin Drøhse Kilde, Mia Harring Hansen, Søren Lindbæk Broman, Kurt V. Mikkelsen, Mogens Brøndsted Nielsen**

Page No. – Page No.

Expanding the Hammett Correlations for the Vinylheptafulvene Ring-Closure Reaction