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Dihydroazulene/Vinylheptafulvene Photoswitch: Ultrafast Back Reaction Induced by Dihydronaphthalene Annulation

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The vinylheptafulvene (VHF) to dihydroazulene (DHA) electrocyclization is known to proceed from an s-*cis* conformation of VHF and cannot occur from the more stable s-*trans* conformation. Locking the VHF in the s-*cis* conformation by the introduction of a dihydronaphthalene (DHN) unit has been found to greatly enhance the speed of this reaction. Thus, the half-life was reduced by more than a factor of 150000 in cyclohexane and by a factor of approximately 950000 in ethanol. In addition, the characteristic absorption of the photoactive DHA isomer, now annulated to DHN, exhibited a desired redshift relative to the parent compound. Here, we present the synthesis and study of these DHN-DHA/VHFs, including a protocol for the incorporation of a pseudo-halide to enable the further functionalization of the molecule by metal-catalyzed cross-coupling reactions. For proof-of-concept, two different sulfur end-groups were incorporated as anchoring groups for potential molecular electronics applications.

Introduction

Photoswitches have been shown to exhibit many possible applications in both the materials and biological sciences. Although inherently different in switching mechanisms, the three most popular photoswitches, azobenzene,[1] dithienylethene,[2] and spiropyran,[3] have been successfully applied in these areas because of their reasonable quantum yields, high and tunable photostationary state ratios, good fatigue resistances, and synthetic accessibility. Recent impressive developments include the ability to turn on and off the catalytic function of artificial enzymes and to control peptide folding,[4] the modulation of the molecule conductance both on surfaces and in between electrodes,[5] and light-driven systems with machine-like functions such as molecular scissors or tweezers, pedals, lifts, and vehicles.[6]

Another example of a photochromic molecule is 1,8a-dihydroazulene-1,1-dicarbonitrile (DHA).[7] Following light irradiation at its lowest-energy absorption maximum (for DHA **1a**, ca. 353 nm), the molecule undergoes a retro-electrocyclization to vinylheptafulvene (VHF) (Scheme 1), which is evident by the formation of an often more intense and redshifted absorption maximum at around 470 nm. This light-induced ring-opening reaction from DHA to VHF induces a large change in the molecule's dipole moment,[8] elimination of the fluorescence of DHA,[9] a color change from yellow to red/purple,[9,10] and an increase in the system's single-molecule conductance.[11] The system is attractive as it rarely requires inconvenient precautions such as water- or oxygen-free conditions and no photostationary state is obtained as it is only photochromic in one direction (T-type photoswitch). Although the ring-opening (DHA → VHF) is fast (1.2 ps),[12] the ring-closure (VHF → DHA) is relatively slow ($t_{1/2}$ = 21–1545 min, 25 °C, in MeCN),[9,10,13] but for most derivatives complete conversion in both directions is usually ultimately observed. In connection with materials science and molecular electronics, a DHA molecule has been trapped between two silver electrodes in a single-molecule device operating in the Coulomb blockade regime, and, by using light/heat (or by regulating the bias potential), conductance modulation was observed.[11a,11b] Although light-induced switching from DHA to VHF in this device occurred almost instantaneously, the VHF → DHA back reaction took several minutes. A long half-life for this reaction could on one hand be advantageous for some molecular electronics components but on the other hand, relay components undergoing fast VHF → DHA conversions also present relevant targets.

The slow back-reaction is a consequence of the steric bulk of the two cyano groups rotating the two double bonds of the VHF out of the cycloheptatriene plane and thus pushing C8 and C1 out of proximity. Also a favorable s-*cis*-to-s-*trans* rotation around the single bond (C2–C3) is moving C8a and C1 further away from each other, thus pre-

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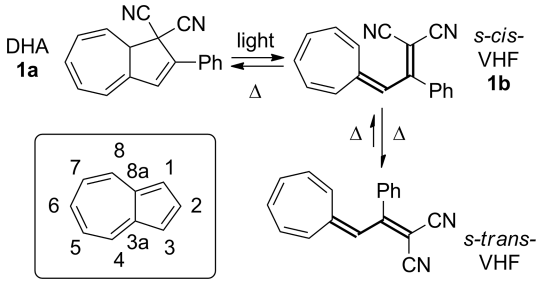
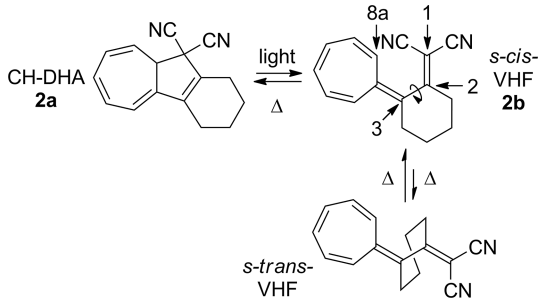


Scheme 1. Light-induced ring-opening of dihydroazulene (DHA) to its corresponding metastable VHF, most stable in its s-*trans* conformer. Inset: atomic numbering according to that of azulene.



Scheme 2. Light-induced ring-opening of CH-DHA **2a** to its corresponding sterically constrained metastable VHF **2b**; s-*cis*/s-*trans* rotation is inhibited.

venting the ring-closure reaction (Scheme 1; the s-*cis*/s-*trans* notation refers to the highlighted butadiene moiety of VHF).[14]

Despite this, by using a pulse-probe technique, it has been shown that by delaying a 530-nm laser pulse by 25 ps after a ring-opening 360-nm pulse, the resulting "VHF" structure could be returned to DHA.[12b] This was possible as the atoms are not allowed time to fully rearrange and are still located as they are in DHA. Although the life-time of the VHF can be fine-tuned by substitution with electron-withdrawing and/or -donating groups at each end of the molecule,[9a,10,13] a dramatic reduction of the life-time of the VHF was observed by tethering C2–C3 using a cyclohexane (CH) ring (Scheme 2).[15] Thus, steric constraints were thought to "lock" the VHF in its s-*cis* conformation and not only to inhibit rotation to its corresponding s-*trans* conformer, but also to keep C8a and C1 in close proximity, thereby accelerating the thermally induced back reaction. Thus, a light-induced conversion of CH-DHA **2a** into VHF **2b** could be identified only (on a second timescale) at a very low temperature (–60 °C in EtOH), at which too rapid a back reaction is prevented.[15] It seems that the cyclohexane ring has the appropriate length and geometry to enable the largest orbital overlap in the VHF state. Thus, neither VHFs with a fused cyclopentane nor a cycloheptane ring show such a fast ring-closure (half-lives $>$ 6 h in silicone[12a]). The photophysical properties of CH-DHA **2a** have not yet been investigated in detail, and for this reason the life-time of the VHF **2b** remains unknown. Because of this a more thorough study of the photophysical properties of such fast-switching DHA/VHFs was deemed necessary. We note that the use of steric constraints has successfully been used to significantly improve the switching speed of other photoswitches.[16]

Here, we report the synthesis of a dihydronaphthalene (DHN) annulated to DHA **3a**, combining the rate-enhancing features of the six-membered ring and the higher stability and redshift of the DHA absorption by forcing the phenyl ring into co-planarity with the five-membered ring. The rationale behind the design of the targeted DHN-DHA **3a** is the general trend that aryl-functionalized DHA/VHFs show greater fatigue resistance (as lower-energy light is required due to the redshifted absorption maximum) combined with the well-established synthetic procedures for the further functionalization of such systems. By employing UV/Vis absorption spectrophotometry at low temperatures, we were able to fully convert DHN-DHA (**3a**) into the corresponding VHF (**3b**) upon irradiation with light. This short-lived VHF showed a dramatic increase in the rate of ring-closure back to DHA of more than a factor of 150000 in cyclohexane and of approximately 950000 in EtOH compared with that of VHF **1b**. The DHA structures are shown in Figure 1.

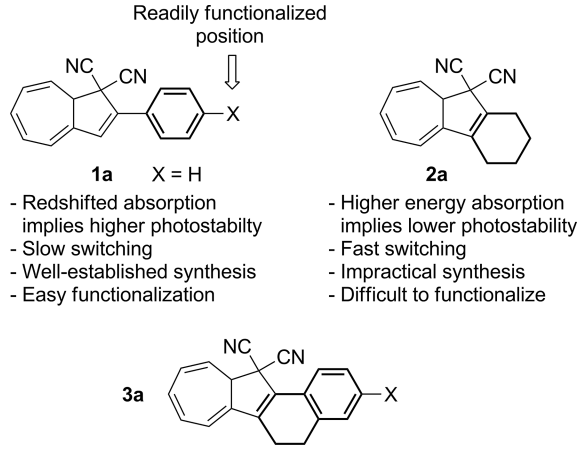


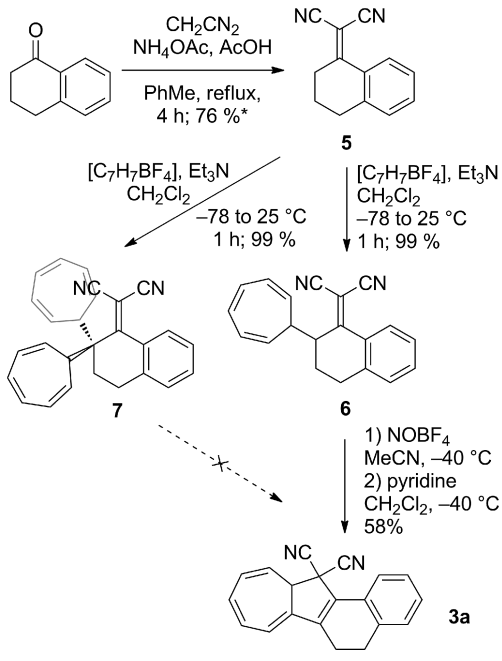
Figure 1. Structures of DHAs **1a**–**3a**.

In addition, we report the careful synthesis of a pseudo-halogenated (triflate) derivative of DHN-DHA (**4a**). As the initial attempt at incorporating an iodo substituent was not successful, a triflate substituent was used because triflates also present a versatile functional handle for further elaboration. It was included to enable further functionalization to ultimately allow, in future work, the exploitation of the ultrafast DHA/VHF couple in advanced systems. This could, as mentioned above, be in the field of molecular electronics. For proof-of-concept we have used this triflate functionality to incorporate such electrode anchoring groups as SMe and SAc by Suzuki cross-coupling and Pd-catalyzed S_NAr reaction protocols as these exact sulfur-containing functional groups have already successfully been used to incorporate DHA/VHF into a device.[11]

Results and Discussion

Synthesis

The synthesis of DHN-DHA **3a** is shown in Scheme 3. First, a Knoevenagel condensation between α-tetralone and malononitrile gave the malononitrile derivative **5** in 76% yield.[17] Next, treatment with tropylium tetrafluoroborate in the presence of Et_3N in CH_2Cl_2 at –78 °C yielded the VHF precursor **6** in quantitative yield. Its oxidation to VHF and subsequent ring-closure to DHA were achieved in a two-step one-pot reaction. Hydride abstraction using nitrosyl tetrafluoroborate ($NOBF_4$) in MeCN at –40 °C followed by the addition of pyridine in CH_2Cl_2 gave the VHF, which then immediately converted into the DHN-DHA **3a**. All other attempts to perform this step by using oxidants such as DDQ (with or without *p*TsOH), *m*- or *p*-chloranil, or tritylium tetrafluoroborate/Et_3N proved fruitless, giving no reaction or leading to complete decomposition. Also, the previously reported procedure,[14a] in which two cycloheptatrienyls were incorporated into the structure with one of these functions acting as a leaving group (i.e., tropylium) in the subsequent oxidation step, failed. Thus, although the intermediate **7** was readily obtainable, it could not be converted into **3a**.



Scheme 3. Synthesis of DHN-DHA **3a**; * known reaction.

The structures of the VHF precursor **6** and the final DHN-DHA **3a** were confirmed by X-ray crystallography, as shown in Figure 2. As found for parent DHA **1a**,[18] the seven-membered ring of **3a** adopts a boat-like structure with the C7–C8 double bond out of the plane and with the phenylene ring forced into planarity.

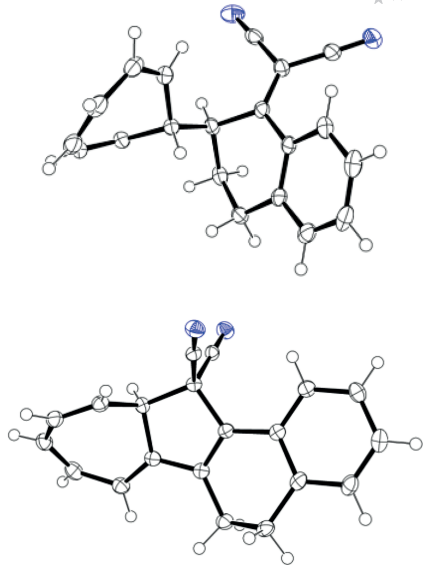
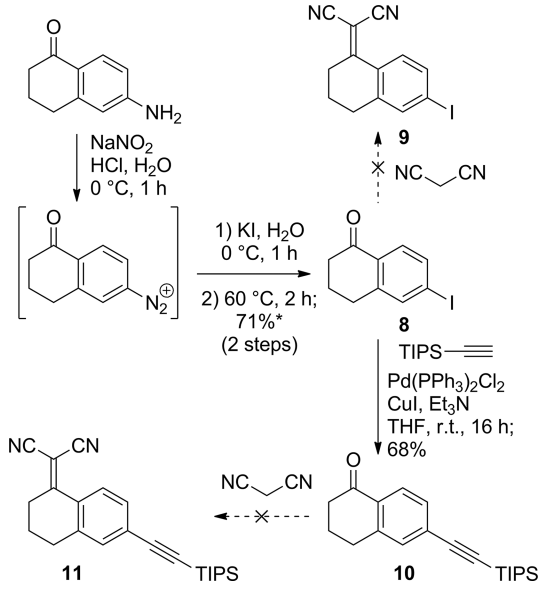


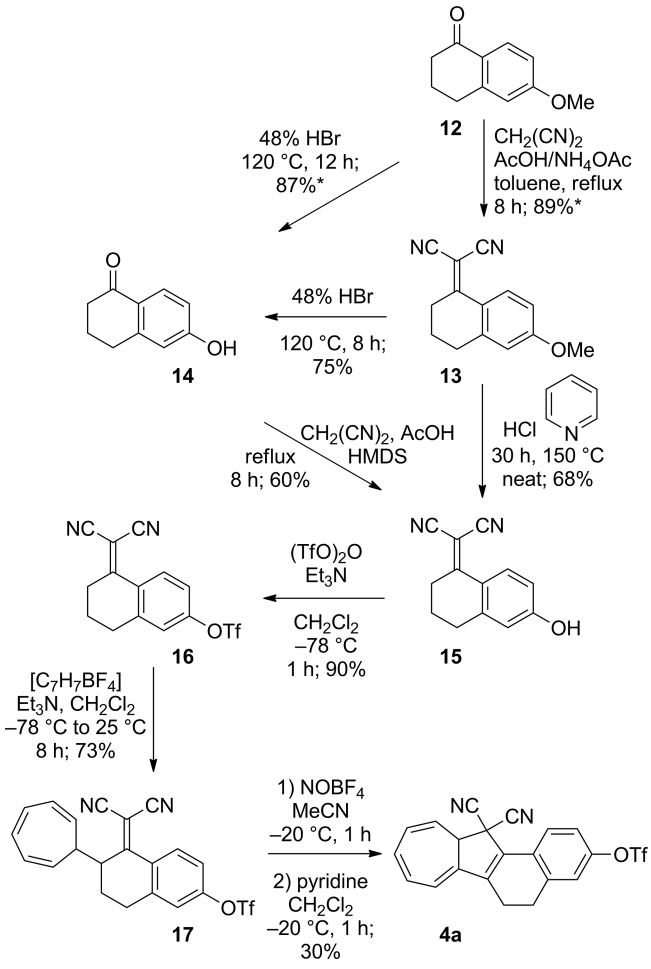
Figure 2. Molecular structures of **6** (crystals grown from $CHCl_3$/heptanes) and **3a** (crystals grown from EtOH) with displacement ellipsoids drawn at the 50% propbability level for non-hydrogen atoms.

To obtain a reactive handle for metal-catalyzed coupling reactions, the initial idea was to place an iodo substituent at the 6-position of the α-tetralone moiety, which corresponds to the "*para*" position of the DHA **1a** (relative to the DHA). First, the treatment of 6-amino-α-tetralone with $NaNO_2$ in aqueous HCl followed by the addition of KI gave 6-iodo-α-tetralone (**8**)[19] in 71% yield. This ketone **8** was then treated with malononitrile in a Knoevenagel condensation but the use of Al_2O_3 (with or without Et_3N) in CH_2Cl_2 or 1,2-dichloroethane, AcOH/NH_4OAc in toluene at reflux, or $TiCl_4$/pyridine in CH_2Cl_2 did not give the desired product **9**. Instead **8** was treated, in a Sonogashira cross-coupling reaction, with TIPS-acetylene to afford **10** in 68% yield. Unfortunately, this ketone did not show significant reactivity in a Knoevenagel condensation with malononitrile under a variety of conditions, including the use of either Al_2O_3 (with or without piperidine) in CH_2Cl_2 or 1,2-dichloroethane, piperidine in absolute EtOH, or AcOH/NH_4OAc in toluene at reflux, and only traces (<5% by NMR) of the desired product **11** could be observed. The attempted syntheses of **9** and **11** are shown in Scheme 4.

Instead, a different strategy towards inserting a reactive handle into the DHN-DHA was undertaken, focusing upon the incorporation of a pseudo-halogen (triflate) into the photoswitch. Commercially available 6-methoxy-α-tetralone (**12**) was treated with malononitrile in a Knoevenagel condensation using AcOH/NH_4OAc in toluene at reflux, yielding the malononitrile derivative **13**[20] in 89% yield (Scheme 5). This compound was then treated with 48% HBr at 120 °C,[21] which unfortunately resulted in an undesired retro-Knoevenagel condensation as well as the desired demethylation, with 6-hydroxy-α-tetralone (**14**) being isolated as the major product.[22] In an attempt to avoid this, **13** was instead treated with BBr_3 in CH_2Cl_2, but after 48 h



Scheme 4. Attempted synthesis of halogenated DHN-DHA; * known reaction.



Scheme 5. Synthesis of triflate-functionalized DHN-DHA **4a**; * known reaction.

at room temp., unfortunately only the starting material was regenerated after work-up. Nevertheless, a good result was finally obtained when **13** was dissolved in molten pyridinium hydrochloride at 150 °C for 30 h in a sealed container to give **15** in 68% yield (no retro-Knoevenagel observed).[23] Alternatively, **15** could also be obtained by first preparing compound **14** by the treatment of 6-methoxy-α-tetralone (**12**) with 48% HBr at reflux overnight. With **14**[21] in hand, Knoevenagel condensation with malononitrile was effected at reflux in AcOH/HMDS to give the desired compound **15** in 60% yield (the use of AcOH/NH_4OAc in toluene at reflux gave **15** in 22% yield). Conveniently, both methods could be performed on the gram scale and did not require chromatography for isolation of the products. In addition, the structure of **15** was confirmed by X-ray crystallography (Figure 3).

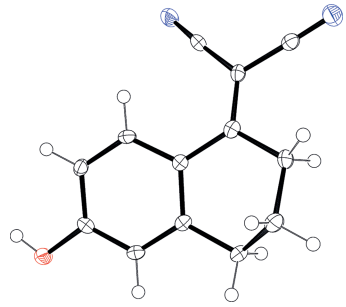


Figure 3. Molecular structure of **15** (crystals grown from $CHCl_3$) with displacement ellipsoids drawn at the 50% probability level for non-hydrogen atoms.

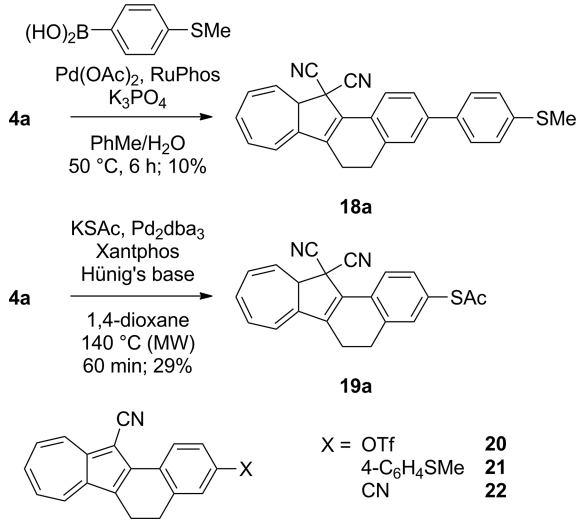
Intermediate **15** was then treated with triflic anhydride and Et_3N (pyridine was unsuccessful) in CH_2Cl_2 at –78 °C to yield **16** in 90% yield. Using the previously described procedure, compound **16** was treated with Et_3N in the presence of tropylium tetrafluoroborate to give the selectively alkylated VHF precursor **17** in almost quantitative yield (isolated analytically pure in 73% yield). Oxidation and subsequent ring-closure was facilitated by the treatment of **17** with $NOBF_4$ in MeCN at –20 °C followed by the addition of pyridine in MeCN/CH_2Cl_2 to give **4a** in 30% yield (Scheme 5).

The triflated species **16** and **17** are very sensitive to acid. Even on a TLC plate or in $CDCl_3$ solution, the triflates were cleaved, and for this reason TLC plates were pretreated with 5% Et_3N in CH_2Cl_2 and $CDCl_3$ with Al_2O_3.

Although the structures of the DHN-DHAs were easily confirmed by ^1H NMR spectroscopy, the presence of the triflate moiety was, in all three steps, confirmed by ^{13}C and ^{19}F NMR analyses, which showed a quartet at approximately 119 ppm, with a $J_{C,F}$ coupling constant of 321 Hz, and a resonance at approximately –71.5 ppm, respectively.

With the triflate-functionalized DHN-DHA (**4a**) in hand, we decided to evaluate whether this functionality was a suitable means to gaining access to functionalized DHN-DHAs. As the DHA/VHF system has already been successfully exploited in functional devices by using SMe and SAc

as anchoring groups, it was decided to investigate the possibility of using **4a** as a precursor for such compounds (Scheme 6). Gratifyingly, the triflate reacted under relatively mild conditions in a Suzuki cross-coupling reaction with methylthiophenylboronic acid and also rather easily in a palladium-catalyzed S_NAr reaction with KSAc, with the insertion of a methylthio (**18a**) and the acetyl-protected thiol **19a**, respectively. The amount of base added in both reactions was crucial as the corresponding azulenes **20**–**22** were isolated in significant amounts (see the Exp. Sect.). Nevertheless, the structures of both **18a** and **19a** were confirmed by X-ray crystallography, as shown in Figure 4.



Scheme 6. Insertion of SMe and SAc end-groups by palladium-catalyzed reactions. RuPhos = 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl; dba = dibenzylideneacetone; xantphos = 4,5-bis(diphenylphosphanyl)-9,9-dimethylxanthene; Hünig's base: diisopropylethylamine; MW = microwave.

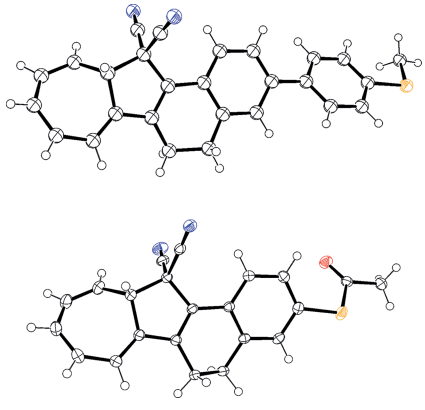


Figure 4. Molecular structures of **18** (crystals grown from $CHCl_3$/heptanes) and **19** (crystals grown from $CHCl_3$/heptanes) with displacement ellipsoids drawn at the 50% probability level for non-hydrogen atoms.

Spectroscopy and Kinetics

The four DHN-DHAs **3a**, **4a**, **18a**, and **19a** were studied in EtOH, MeCN, and/or cyclohexane solutions by UV/Vis absorption spectrophotometry. DHN-DHAs **3a** and **4a** both exhibit characteristic DHA absorption spectra, each with a lowest-energy absorption at approximately 365 nm, which is redshifted compared with those of CH-DHA **2a** (318 nm in EtOH)[15] and DHA **1a** (353 nm in MeCN).[18] This redshift is desirable because lower-energy light for photoisomerization should imply higher fatigue resistance. But irradiation with light corresponding to their absorption maxima, in both MeCN and EtOH at 25 °C, led to no changes in the absorption spectra (for details see the Supporting Information), which is explained by an extremely fast back reaction (VHF→DHA). However, irradiation in cyclohexane resulted in the formation of species with short-lived redshifted absorption bands at 455 and 460 nm, assigned to the VHF structures **3b** and **4b**, respectively. Very quickly after irradiation, a series of absorption spectra were acquired and, based on these measurements, half-lives of 0.9 and 0.3 s were estimated for **3b** and **4b**, respectively (the rate constants were determined by the decay of the absorptions of VHF). For VHF **3b**, this change in half-life corresponds to a dramatic more than 150000-fold decrease compared with that of VHF **1b** in cyclohexane.[18] Unfortunately, we do not have a point of reference for VHF **4b**. The UV/Vis absorption spectra resulting from an estimated 12 and 3% light-induced conversion of DHN-DHAs **3a** and **4a**, respectively, into their corresponding short-lived VHFs, and their conversion back into DHN-DHAs, including the kinetic details, are provided in the Supporting Information.

To acquire the absorption spectra of the short-lived VHFs, UV/Vis absorption spectrophotometry was performed at lower temperatures to retard the back reaction. Gratifyingly, irradiation (366 nm) of DHN-DHA **3a** in EtOH at –60 °C led to the appearance of an absorption band at 476 nm as a result of its conversion into VHF **3b** (Figure 5). At this temperature, the VHF isomer was relatively long-lived ($t_{1/2}$ = 13 min), and full conversion from DHA into VHF was hence accomplished. Similar values were obtained from a study of **4a**/**4b**, although the half-life of **4b** was significantly shorter, as expected because electron-withdrawing groups cause an increase in the rate of thermally induced ring-closure. The triflate-functionalized DHN-DHA **4a** was not studied in detail as the **4a**/**4b** system was not stable to multiple cycles of light and "heat" and a complex mixture was obtained. Five light/heat cycles were performed on a sample of DHN-DHA **3a** (in EtOH) without noticeable photodegradation. Although it is known that the quantum yield for the DHA→VHF conversion is temperature dependent[9a] (at lower temperatures the mechanism changes to relaxation by fluorescence instead of ring-opening), it is roughly estimated that the quantum yield for the DHN-DHA **3a**→VHF **3b** conversion is comparable to that of **1a**→**1b**. The absorption maxima of the DHA and VHF states are listed in Table 1.

After irradiation with light the sample was kept at –60 °C and the back reaction was monitored by acquiring an absorption spectrum every minute. By plotting the decay of the VHF absorption against time, the rate of ring-closure was determined (first-order kinetics). The UV/Vis absorp-

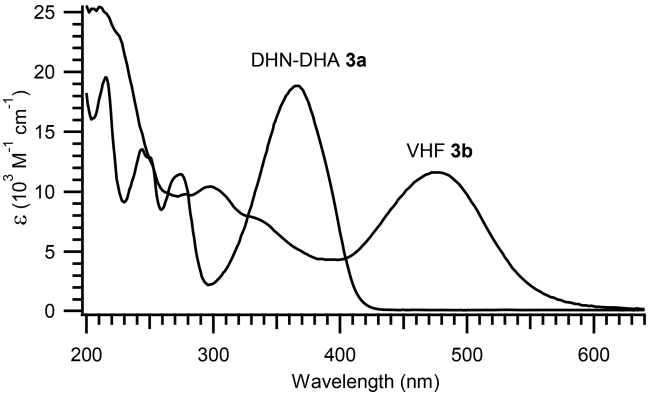


Figure 5. UV/Vis absorption spectra of DHN-DHA **3a** and the corresponding VHF **3b** in EtOH at –60 °C.

Table 1. Absorption maxima for DHAs **1a**–**4a** and VHFs **1b**–**4b** in various solvents at 25 °C, unless otherwise stated.

	Solvent	λ_{max} [nm] (ε [10^3 M^{-1}cm^{-1}])	
		DHA	VHF
1a/b[a]	EtOH	354 (13.9)	471 (18.2)
	MeCN	353 (17.9)	470 (34.4)
	CH	354 (13.6)	446 (24.6)
2a/b[b]	EtOH[c]	318 (6.3)	427 (7.9)
3a/b	EtOH[c]	365 (18.8)	476 (11.6)
	MeCN	365 (16.0)	–
	CH	364 (17.2)	455[d]
4a/b	EtOH[c]	366 (19.5)	486 (7.76)
	MeCN	365 (18.1)	–
	CH	364 (18.1)	460[d]
18a/b	EtOH[c]	388 (18.3)	482 (6.82)
19a/b	EtOH[c]	374 (23.5)	485 (8.72)

[a] Ref.[18]. [b] Ref.[15]. [c] Performed at –60 °C. [d] Estimated $\lambda_{max} \pm 5$ nm.

tion spectra acquired at intervals of 12 min are shown in Figure 6, and show the decay of VHF **3b** and the reformation of DHN-DHA **3a**.

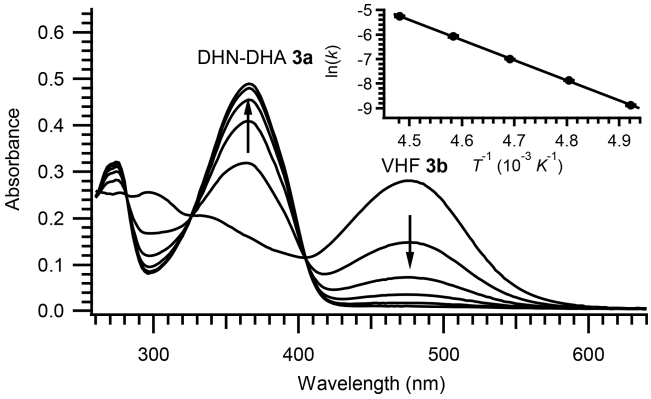


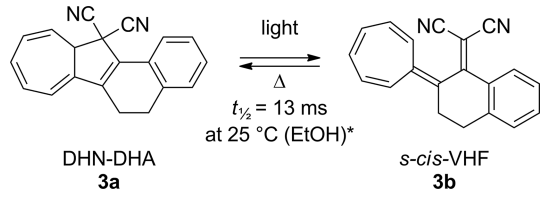
Figure 6. UV/Vis absorption spectra acquired during the VHF **3b**→DHN-DHA **3a** conversion (acquired every half-life) in EtOH (–60 °C). Inset: Arrhenius plot for the VHF **3b**→DHN-DHA **3a** conversion in EtOH. [k] = s^{-1}.

The rate constants for the back reaction of VHF→DHA were determined at various temperatures in ethanol, and from an Arrhenius plot (Figure 6, inset) the rate of ring-closure of **3b** to **3a** at 25 °C was estimated by extrapolation to be 54 s^{-1} ($t_{1/2}$ = 0.013 s), which corresponds to a dramatic approximate 950000-fold increase compared with that of **1b** ($k = 5.72 \times 10^{-5}$ s^{-1}, $t_{1/2}$ = 12118 s). This larger rate-enhancement in the more polar solvent (EtOH) compared with that in cyclohexane is related to the presence of a highly polarized or zwitterionic transition state, which would be stabilized to a higher degree in a polar solvent.[7c] Also, the activation energy (E_a) and the pre-exponential factor (A) were determined from the Arrhenius plot to be 68.2 ± 0.6 kJ/mol and 4.71×10^{13} s^{-1}, respectively. Using the Eyring equation, ΔG^{TS} was calculated to be 63.1 ± 0.2 kJ/mol. For DHA/VHFs **18a/b** and **19a/b**, both the absorption and kinetics data are very similar to those of **3a/b**. With absorption maxima in EtOH of 388 and 374 nm for **18a** and **19a**, respectively, and 482 and 485 nm for **18b** and **19b**, respectively, both couples exhibit redshifted absorptions as expected. Also, the ring-closure for **18b** and **19b** are slightly faster than that of **3b**, in agreement with our previously published data,[10] which suggests that both the 4-C_6H_4SMe and SAc substituents are mildly electron-withdrawing (rate of back reaction compared at –60 °C). The kinetic data are listed in Table 2 and the switching event is depicted for **3a/3b** in Scheme 7.

Table 2. Kinetic data for VHF→DHA conversions for VHFs **1b**, **3b**, and **4b** in various solvents and at various temperatures.

	Solvent	Temp. [°C]	k [s^{-1}]	$t_{1/2}$ [s]
1b[a]	EtOH	25	5.72×10^{-5}	12118
	MeCN	25	5.36×10^{-5}	12932
	CH	25	0.495×10^{-5}	140030
3b	EtOH	–70	0.139×10^{-3}	4991
	EtOH	–65	0.384×10^{-3}	1806
	EtOH	–60	0.911×10^{-3}	761
	EtOH	–55	2.29×10^{-3}	302
	EtOH	–50	5.22×10^{-3}	133
	CH	25	0.7(41)	0.9(35)
4b	CH	25	2(.20)	0.3(15)
18b	EtOH	–60	1.23×10^{-3}	565
19b	EtOH	–60	2.00×10^{-3}	347
	EtOH	–70	3.09×10^{-3}	2244

[a] Ref.[18]



Scheme 7. Fast light/heat-induced interconversion between DHN-DHA **3a** and VHF **3b**; * value estimated by extrapolation.

With molar absorptivities between 11.6×10^3 and 6.82×10^3 M^{-1}cm^{-1} for the VHFs **3b**, **4b**, **18b**, and **19b**, and a molar absorptivity of 7.9×10^3 M^{-1}cm^{-1} previously reported for **2b**,[15] it appears that the absorptions of the s-*cis* VHFs are significantly lower than those of the s-*trans* VHFs. This is in perfect agreement with the high molar absorptivity previously found for the cyclopentane-

annulated VHF ($\varepsilon = 27 \times 10^3$ M^{-1}cm^{-1} in acetone), which, with a half-life of >6 h in silicone,[12a] is thought to exist in a less sterically congested VHF conformer in solution. Thus, it seems reasonable to conclude that the VHFs **3b**, **4b**, **18b**, and **19b** exist in their congested s-*cis*-VHF conformers, which results in a significantly faster VHF→DHA ring-closure.

Conclusions

We have developed a protocol for the synthesis of dihydronaphthalene-annulated DHAs. For unknown reasons, iodo- and ethynyl-substituted α-tetralones were reluctant to undergo Knoevenagel condensation with malononitrile. We therefore turned to another synthetic strategy in which ultimately a triflate functionality was incorporated. This pseudo-halogen enabled further functionalization of the system by metal-catalyzed cross-coupling reactions, and suitable derivatives as potential components for molecular electronics devices were synthesized as proof-of-concept. These DHN-DHAs were shown by kinetics studies (UV/Vis absorption spectrophotometry) to have great potential, with respect to both the forward and backward reactions, for the development of ultrafast photoswitches. The half-life of the VHF→DHA conversion was decreased 150000-fold in cyclohexane and almost 950000-fold in EtOH!

Experimental Section

General Methods: All reactions were performed under nitrogen (using a gas bubbler) or argon (balloon technique). Coupling reactions using palladium catalysts were performed in a solvent flushed with argon by allowing the argon to flow through the solvent for at least 20 min while exposed to ultrasound. All chemicals and solvents were used as received, unless otherwise stated. Acetonitrile was purified and dried using activated Al_2O_3. THF and 1,4-dioxane were purified and dried by distillation from a Na/benzophenone couple. $CDCl_3$ was purified by passing through activated Al_2O_3. TLC was carried out on commercially available precoated plates (silica 60) with fluorescence indicator. Chromatographic purifications were performed on silica (SiO_2) with a pore size of 60 Å and a particle size of 15–40 μm using the dry-column vacuum chromatography method, as described previously, and with a particle size of 40–63 μm for flash column chromatography.[13d,14a,24] All spectroscopic measurements (including photolysis) were performed in a 1-cm path length quartz cuvette. UV/Vis absorption spectra were recorded in the range 800–200 nm. Photoswitching experiments were performed by 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 (linewidth ± 2.5 nm). The thermal back reaction was performed by heating the sample (cuvette) by using a Peltier unit in the UV/Vis spectrophotometer (temperature kept at 25 ± 0.1 °C) or, at a low temperature, in a cryostat (–70 to –50 ± 0.1 °C). All photoswitching experiments were performed in non-deoxygenated solvents as it has been shown that this does not significantly improve stability.[3] Mass spectra were recorded with an ESP-MALDI-FT-ICR spectrometer equipped with a 7 T magnet (prior to the experiments, the instrument was calibrated using NaTFA cluster ions) or a MicrOTOF-QII spectrometer using ESP (calibrated using formic acid). All NMR spectra were recorded with a 500-MHz instrument equipped with a (non-inverse) cryoprobe (500.1300/125.7578 MHz) or, in a few examples, with a 300-MHz (300.0787 Hz) or 500-MHz (499.9704 MHz) instrument with a penta-probe. All ^{1}H and ^{13}C chemical shifts are referenced to the residual solvent peak ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; [D$_6$]DMSO: δ_H = 2.50 ppm, δ_C = 39.52 ppm). The ^{19}F chemical shifts are referenced to TFA (δ_F = –76.55 ppm), which was present in a lock-tube inside the NMR tube during acquisition. All chemical shifts are given in ppm to two decimal places (signal widths: ^{13}C: approximately 0.004 ppm, 0.5 Hz; ^{19}F: approximately 0.01 ppm, 3 Hz). In the case of compounds **14** and **15**, the free phenol did move some peaks in ^{13}C NMR depending on the concentration and water content. Elemental analyses were performed at the Department of Chemistry, University of Copenhagen or at London Metropolitan University.

CCDC-1009627 (for **6**), -1009628 (for **3a**), -1009626 (for **15**), -1050396 (for **18a**), and -1050395 (for **19a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Experimental Procedures

5,6-Dihydronaphtho[2,1-*a*]azulene-12,12(11a*H*)-dicarbonitrile (3a): $NOBF_4$ (324 mg, 2.77 mmol) was added (see Note 1 below) to a stirred solution of **6** (393 mg, 1.38 mmol) in dry acetonitrile (30 mL) at –40 °C. The resulting yellow or light-brown reaction mixture was stirred for 30 min, after which it was diluted with cold dry CH_2Cl_2 (20 mL) and at –40 °C, a solution of pyridine (0.22 mL, 2.8 mmol) in cold dry CH_2Cl_2 (10 mL) was added dropwise. The reaction mixture was stirred for an additional 30 min in which it turned darker brown. The reaction mixture was poured into water (50 mL) and the reaction mixture extracted with both CH_2Cl_2 (3 × 20 mL) and water (3 × 10 mL). The combined organic and aqueous extracts were separated and the organic phase washed with water (3 × 25 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by dry column chromatography (SiO_2, 12.6 cm^2, 0–60% $CHCl_3$/heptanes, 10% steps, 40 mL fractions) gave **3a** (227 mg, 0.800 mmol, 58%, Note 2) as a bright-yellow solid. Crystals suitable for X-ray crystallography were grown from EtOH. TLC (60% CH_2Cl_2/heptanes): R_f = 0.52 ($UV_{254\,nm}$), m.p. 175–178 °C (EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, J = 7.6 Hz, 1 H), 7.38–7.33 (m, 1 H), 7.29 (td, J = 7.4, 1.2 Hz, 1 H), 7.25 (dd, J = 7.4, 0.8 Hz, 1 H), 6.62 (dd, J = 11.2, 6.4 Hz, 1 H), 6.50 (dd, J = 11.2, 6.1 Hz, 1 H), 6.32 (app. ddd, J = 10.2, 6.1, 2.2 Hz, 1 H), 6.26 (app. dd, J = 6.4, 1.4 Hz, 1 H), 5.86 (dd, J = 10.2, 3.8 Hz, 1 H), 3.78 (app. dt, J = 3.8, 1.9 Hz, 1 H), 2.99 (t, J = 8.3 Hz, 2 H), 2.67–2.52 (m, 2 H) ppm (Note 3). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.98, 138.63, 136.51, 134.12, 130.97, 129.37, 128.47, 128.42, 127.63, 127.47, 123.32, 119.82, 118.12, 115.18, 112.90, 51.24, 42.72, 27.45, 21.37 ppm (one signal missing due to overlap). HRMS (ESP$^+$): calcd. for $[C_{20}H_{15}N_2]^+$ 283.1230 $[MH]^+$; found 283.1235. $C_{20}H_{14}N_2$ (282.34): calcd. C 85.08, H 5.00, N 9.92; found C 84.97, H 4.96, N 9.98. Notes: 1) The temperature was kept at –40 °C (±5 °C). 2) When the reaction was performed on an approximately 6 mmol scale, the isolated yield was about 50%. 3) A correlation between the signal at δ = 3.78 ppm and the signals at δ = 6.26 and 6.32 ppm, with coupling constants of 1.4 and 2.2 Hz, gives a broadening of the apparent doublet of triplets with an apparent coupling constant of 1.9 Hz.

12,12-Dicyano-5,6,11a,12-tetrahydronaphtho[2,1-*a*]azulen-3-yl Trifluoromethanesulfonate (4a): $NOBF_4$ (904 mg, 7.74 mmol) was added to a stirred solution of **17** (1.67 g, 3.87 mmol; Note 1) in dry MeCN (160 mL) at –20 °C. The color of the solution changed slowly from colorless to bright yellow or green. After stirring for 1 h with the temperature maintained below –20 °C (Note 2), cold dry CH_2Cl_2 (140 mL) was added. The temperature was again kept at around –20 °C. A solution of dry pyridine (0.62 mL, 7.7 mmol) in cold dry CH_2Cl_2 (20 mL) was added and the resulting dark-yellow solution was stirred for 1 h. The reaction mixture was then poured into water (100 mL) and extracted with CH_2Cl_2 (3× 100 mL). The extract was dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by dry-column vacuum chromatography (SiO_2, 15–40 μm, 0–50% toluene/heptanes, 10% steps, 50–100% toluene/heptanes, 8.3% steps, 40 mL fractions) gave **4** (500 mg, 1.16 mmol, 30%; Note 3) as a yellow oil, which solidified under high vacuum. TLC (toluene): R_f = 0.64 ($UV_{254\,nm}$), m.p. 129–130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (d, J = 8.5 Hz, 1 H), 7.25 (dd, J = 8.5, 2.4 Hz, 1 H), 7.20–7.28 (m, 1 H), 6.63 (dd, J = 11.2, 6.4 Hz, 1 H), 6.54 (dd, J = 11.2, 6.0 Hz, 1 H), 6.34 (ddd, J = 10.2, 6.0, 2.0 Hz, 1 H), 6.33–6.30 (m, 1 H), 5.84 (dd, J = 10.2, 3.8 Hz, 1 H), 3.78 (dt, J = 3.8, 2.0 Hz, 1 H), 3.04 (t, J = 8.3 Hz, 2 H), 2.72–2.62 (m, 1 H), 2.67–2.55 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 149.33, 144.55, 139.31, 137.83, 132.30, 131.75, 130.84, 128.80, 127.83, 121.71, 120.25, 119.83, 119.35, 119.34, 118.86 (q, J = 320.9 Hz), 114.78, 112.56, 51.09, 42.73, 27.56, 21.00 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –71.52 (s, 3 F) ppm. HRMS (MALDI$^+$ FT-ICR, ditranol): calcd. for $[C_{21}H_{13}F_3N_2O_3SNa]^+$ 453.04912 $[MNa]^+$; found 453.04964. $C_{21}H_{13}F_3N_2O_3S$ (430.40): calcd. C 58.60, H 3.04, N 6.51; found C 58.48, H 2.98, N 6.44. Notes: 1) We found that the attempted synthesis of **4** from crude **17** was unsuccessful. 2) Starting material consumed, new spot observed. TLC (toluene): R_f = 0.64 ($UV_{254\,nm}$). 3) When the reaction was performed on an approximately. 1 mmol scale, the isolated yield was around 50%.

2-[2,3-Dihydronaphthalen-4(1*H*)-ylidene]malononitrile (5):[17] Acetic acid (2.1 g, 2.0 mL, 35 mmol) and NH_4OAc (501 mg, 6.5 mmol) were added to a stirred solution of malononitrile (2.11 g, 32.0 mmol) and 3,4-dihydronaphthalen-1(2*H*)-one (4.09 g, 28.0 mmol) in toluene (20 mL), and the flask was equipped with a Dean–Stark trap. The reaction mixture was heated at reflux for 4 h (Note 1), after which it was poured into brine (100 mL). Diethyl ether (100 mL) was added and the organic layer was separated, dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was recrystallized from ethanol (Note 2), which gave **5** (4.12 g, 21.2 mmol, 76%) as colorless crystals. TLC (toluene): R_f = 0.50 ($UV_{254\,nm}$), m.p. 110.1–111.2 °C (EtOH) [ref.[17] 115.3–117.8 °C (EtOH)]. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.21 (dd, J = 8.0, 0.7 Hz, 1 H), 7.50 (td, J = 7.5, 1.2 Hz, 1 H), 7.35 (ddd, J = 8.0, 1.2, 0.7 Hz, 1 H), 7.29 (br. d, J = 7.5 Hz, 1 H), 3.03 (t, J = 6.4 Hz, 2 H), 2.89 (t, J = 6.4 Hz, 2 H), 2.04–1.97 (p, J = 6.4 Hz, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 172.67, 142.15, 133.86, 130.18, 129.61, 128.11, 127.01, 114.13, 113.54, 79.95, 33.19, 29.86, 22.29 ppm. Notes: 1) TLC (toluene): R_f = 0.30 (starting material). 2) Colorless crystals were obtained by treatment with activated carbon.

2-[2-Cyclohepta-2′,4′,6′-trienyl-2,3-dihydronaphthalen-4(1*H*)-ylidene]malononitrile (6): Et_3N (0.64 mL, 4.6 mmol) was added dropwise over 1 h to a stirred suspension of finely powdered tropylium tetrafluoroborate (816 mg, 4.59 mmol) and **5** (810 mg, 4.17 mmol) in dry CH_2Cl_2 (50 mL) under argon at –78 °C, and the temperature was then allowed to rise to room temp. The solution was stirred for 10 min (Note 1) and aqueous 2 M HCl (25 mL) was added. The organic phase was washed with water (2× 250 mL), dried with $MgSO_4$, and evaporation of the solvents gave **6** (1.19 g, 4.17 mmol, 99%) as a colorless foam that solidified. TLC (60% CH_2Cl_2/heptanes): R_f = 0.42 ($UV_{254\,nm}$), m.p. 102.5–103.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (dd, J = 8.0, 0.7 Hz, 1 H), 7.46 (td, J = 7.6, 1.2 Hz, 1 H), 7.30 (dddt, J = 8.0, 7.6, 1.2, 0.7 Hz, 1 H), 7.21 (br. d, J = 7.6 Hz, 1 H), 6.67–6.57 (m, 2 H), 6.31 (dd, J = 9.5, 5.3 Hz, 1 H), 6.23 (dd, J = 9.4, 5.3 Hz, 1 H), 5.31 (dd, J = 9.5, 6.7 Hz, 1 H), 5.16 (dd, J = 9.4, 6.7 Hz, 1 H), 3.50 (app. t, J = 3.7 Hz, 1/2 H), 3.47 (app. t, J = 3.7 Hz, 1/2 H), 2.90 (d, J = 4.1 Hz, 1 H), 2.88 (d, J = 4.3 Hz, 1 H), 2.39 (app. d, J = 7.8, 4.3 Hz, 1/2 H), 2.36 (app. q, J = 4.8, 3.7 Hz, 1/2 H), 2.10–2.00 (m, 2 H) ppm (Note 2). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.95, 140.12, 133.56, 131.53, 130.67, 129.66, 129.19, 128.52, 127.08, 126.90, 122.12, 121.80, 113.94, 113.41, 81.05, 42.22, 39.77, 25.04, 24.59 ppm (one signal missing). MS [ESP$^+$]: m/z = 91 $[C_7H_7]^+$, 285 $[MH]^+$, 307 $[MNa]^+$. HRMS (ESP$^+$): calcd. for $[C_{20}H_{16}N_2Na]^+$ 307.1206; found 307.1203 $[MNa]^+$. $C_{20}H_{16}N_2$ (284.35): calcd. C 84.48, H 5.67, N 9.85; found C 84.05, H 5.56, N 9.81. Notes: 1) All the tropylium tetrafluoroborate dissolved and a clear, almost colorless solution was observed. 2) The signals are reported as observed. Not all spin systems could be paired.

6-Iodo-3,4-dihydronaphthalen-1(2*H*)-one (8):[19] A solution of $NaNO_2$ (2.57 g, 37.2 mmol) in H_2O (11 mL) was added over the course of an hour to a stirred solution of 6-amino-3,4-dihydronaphthalen-1(2*H*)-one (5.00 g, 31.0 mmol) in approx. 15% HCl (25 mL) at 0 °C. The temperature was monitored and kept below 5 °C. The reaction mixture changed from a light-yellow suspension to a brown mixture with precipitation. A solution of KI (6.18 g, 37.2 mmol) in H_2O (20 mL) was added in portions of 4 mL over the course of around 10 min while carefully monitoring the evolution of N_2 gas and mechanically stirring the reaction mixture by hand. After the addition, the temperature was allowed to reach room temp. and the mixture was then stirred for 16 h. A heavy brown-black precipitate was formed in an otherwise clear yellow aqueous reaction mixture. The contents of the reaction vessel were extracted with Et_2O (3× 100 mL) and CH_2Cl_2 (3× 100 mL), and the combined organic extracts were then washed with a mixture of saturated aqueous $Na_2S_2O_4$ (40 mL) and H_2O (160 mL). The formation of emulsions was minimized by the addition of a little brine, and the organic phase was separated and dried with Na_2SO_4, filtered, and concentrated in vacuo. The red residue was dissolved in CH_2Cl_2 and concentrated in vacuo onto Celite and purification by dry-column vacuum chromatography (SiO_2 15–40 μm, 0–20% EtOAc/heptanes, 2.5% steps, 80 mL fractions) gave **8** (6.01 g, 22.1 mmol, 71%) as a light-red solid. The ^{1}H NMR spectroscopic data are in accordance with the literature.[19]

6-Triisopropylsilylethynyl-α-tetralone (10): CuI (18.8 mg, 98.5 μmol, 2 mol-%), $[Pd(PPh_3)_2Cl_2]$ (173 mg, 246 mmol, 5 mol-%), Et_3N (6.86 mL, 49.3 mmol), and TIPS-acetylene (3.29 mL, 14.8 mmol, 3 equiv.) were added to a stirred solution of 6-iodo-α-tetralone (**8**; 1.34 mg, 4.92 mmol) in argon-flushed THF (50 mL), and the reaction mixture was stirred overnight. The reaction mixture was poured into water (100 mL), extracted twice with diethyl ether (100 mL), and the combined organic phases were washed with water (3× 100 mL), saturated aqueous NH_4Cl (100 mL), and brine (100 mL), after which it was dried with $MgSO_4$, filtered, and concentrated in vacuo. Purification by dry-column vacuum chromatography (SiO_2, 15–40 μm) gave **10** (1.10 g, 33.7 mmol, 68%) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, J = 8.1 Hz, 1 H), 7.38 (d, J = 8.1 Hz, 1 H), 7.36 (br. s, 1 H), 2.93 (t, J = 6.1 Hz, 2 H), 2.69–2.60 (m, 2 H), 2.13 (dt, J = 12.6, 6.4 Hz, 2 H), 1.13 (s, 21 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 197.71, 144.23, 132.16,

131.94, 130.18, 128.47, 127.08, 106.29, 94.57, 39.10, 29.48, 23.11, 18.66, 11.28 ppm. GC–MS (EI^+): m/z = 326.3 [$M^{\cdot+}$]. HRMS (ESI^+ FT-ICR): calcd. for $[C_{21}H_{31}OSi]^+$ 327.21387 $[MH]^+$; found 327.21381.

2-[6-Methoxy-3,4-dihydronaphthalen-1(2*H*)-ylidene]malononitrile (13):[20] Acetic acid (40 mL, 0.70 mol) and NH_4OAc (30 g, 39 mmol) were added to a stirred mixture of 6-methoxy-α-tetralone (**12**; 17.26 g, 97.95 mmol) and malononitrile (12.80 g, 193.8 mmol) in toluene (500 mL), and the reaction mixture was heated at reflux for 8 h (Note 1). The resulting light-brown solution was cooled and poured into a mixture of water (250 mL) and Et_2O (250 mL). The phases were separated and the organic phase washed with water (3 × 250 mL) and brine (250 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The resulting light-yellow crystalline solid was recrystallized from boiling 96% EtOH (400 mL), which gave **13** (19.50 g, 86.95 mmol, 89%) as off-white to light-grey needle-shaped crystals. TLC (CH_2Cl_2): R_f = 0.59. Note: TLC (CH_2Cl_2): R_f = 0.21 (starting material, orange-red by treatment with 2,4-dinitrophenylhydrazine (DNP). ^1H NMR spectroscopic data are in accordance with literature data.[20]

6-Hydroxy-α-tetralone (14)

Method 1: A mixture of **13** (3.516 g, 15.68 mmol) and 48% aqueous HBr (20 mL, 0.18 mol) was stirred at 120 °C for 8 h. The resulting dark-yellow solution was poured into water (200 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were washed with water (100 mL) and saturated $NaHCO_3$ (50 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by dry-column vacuum chromatography (SiO_2, 15–40 μm, 0–100% $CHCl_3$/heptanes, 10% steps, 0–13% EtOAc/$CHCl_3$, 1% steps, 40 mL fractions) gave **14** (1.91 g, 11.8 mmol, 75%) as an off-white crystalline solid.

Method 2:[21] A mixture of 6-methoxy-α-tetralone (**12**; 6.01 g, 34.1 mmol) and 48% HBr (21 mL, 0.19 mol) was stirred at 120 °C for 12 h (Note 1). The resulting black solution was cooled to room temp. after which water was added and **14** (5.26 g, 32.4 mmol, 95%) was isolated as a dark-red crystalline solid, which was washed with plenty of water and dried in a desiccator. The compound was recrystallized from boiling toluene (80 mL), a black oil was discarded, and **14** (4.79 g, 29.5 mmol, 87%) was collected as an off-white to bright-red needle-shaped crystals (Note 2). TLC (10% EtOAc/$CHCl_3$): R_f = 0.22–0.31 (UV_{254nm} and orange by treatment with anisaldehyde or DNP stain and gentle heating, red with vanillin stain and gentle heating), m.p. 153.7–155.2 °C (toluene). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.6 Hz, 1 H), 6.76 (dd, J = 8.6, 2.5 Hz, 1 H), 6.68 (d, J = 2.5 Hz, 1 H), 5.77–5.43 (m, 1 H), 2.90 (t, J = 6.3 Hz, 2 H), 2.62 (app. t, J = 6.3 Hz, 2 H), 2.11 (app. pent, J = 6.3 Hz, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 198.63, 160.27, 147.60, 130.27, 126.57, 114.58, 114.52, 39.01, 30.09, 23.43 ppm. HRMS ($MALDI^+$ FT-ICR, ditranol): calcd. for $[C_{10}H_{10}O_2]^+$ 163.07536 $[MH]^+$; found 163.07537. $C_{10}H_{10}O_2$ (162.19): calcd. C 74.06, H 6.21; found C 74.00, H 6.03. Notes: 1) TLC (10% EtOAc/$CHCl_3$): R_f = 0.94 (starting material). 2) No noticeable difference in purity by NMR was observed.

2-[6-Hydroxy-3,4-dihydronaphthalen-1(2*H*)-ylidene]malononitrile (15)

Method 1: In a glass-container suitable for high-pressure reactions, **13** (1.52 g, 6.80 mmol) and pyridine hydrochloride (3.49 g, 30.2 mmol) were mixed and heated to 150 °C for 30 h (sealed vessel, note 1). While still melted, the content of the vessel was poured into water (100 mL), which was then extracted with CH_2Cl_2 (3 × 100 mL, note 2). The combined extracts were washed with water (100 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo to give a yellow crystalline solid. Recrystallization from boiling EtOH (40 mL) gave **15** (330 mg, 1.57 mmol, 23%) as a bright-yellow crystalline solid. The mother liquor was concentrated in vacuo and the residue recrystallized from boiling EtOH (30 mL) to give **15** (222 mg, 1.06 mmol, 16%) as a bright-yellow crystalline solid. The mother liquor was concentrated in vacuo and purification by dry-column vacuum chromatography (SiO_2, 15–40 μm, 0–100% $CHCl_3$/heptanes, 20% steps, 0–11%, EtOAc/$CHCl_3$, 1% steps, 40 mL fractions) gave **15** (420 mg, 2.00 mmol, 29%) as an off-white solid. Notes: 1) A cylinder-shaped glass container, usually used for microwave heating, with a super-seal was heated using an aluminum mantle. The part of the glass that was over the heating mantle was from time to time covered in pyridinium hydrochloride because of sublimation, which was then melted back into the mixture by using a heat gun. 2) On a larger scale (8 g), the content of the reaction vessel was poured (if necessary with the help from a heat gun) into a mixture of water (0.5 L) and CH_2Cl_2 (1.5 L) and stirred overnight.

Method 2.1: While stirring, AcOH (7.0 mL, 0.12 mol, 10 equiv.) was added slowly to HMDS (2.6 mL, 12 mmol, 1 equiv.). 6-Hydroxy-α-tetralone (**14**; 2.02 g, 12.5 mmol) and malononitrile (1.63 g, 24.7 mmol) were added to the resulting clear, colorless solution, and the mixture heated near reflux for 8 h (Note 1). The reaction mixture was cooled to room temp., then poured into water (100 mL), and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed with saturated aqueous NH_4Cl (100 mL), water (100 mL), and brine (100 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo. The resulting dark-yellow solid residue was recrystallized from boiling toluene (250 mL) to give **15** (1.56 g, 7.41 mmol, 60%) as yellow-to-green needle-shaped crystals. Note 1) The reaction did not go to completion.

Method 2.2: AcOH (0.65 mL, 11 mmol) was added to a stirred mixture of 6-hydroxy-α-tetralone (**14**; 1.84 g, 11.3 mmol), malononitrile (2.99 g, 45.3 mmol), and NH_4OAc (0.437 mg, 5.67 mmol) in toluene (75 mL), and the mixture was heated at reflux overnight. While still hot, the resulting light-brown solution was filtered or decanted from the dark-red oil, which was formed in the reaction, and the reaction mixture was cooled slowly to 5 °C to give a grey precipitate. Recrystallization from boiling toluene (75 mL) gave **15** (532 mg, 2.53 mmol, 22%) as off-white needle-shaped crystals. Crystals suitable for X-ray crystallography were grown from $CHCl_3$. TLC (10% EtOAc/CH_2Cl_2): R_f = 0.45–0.53 (UV_{254nm}, and yellow → black upon treatment with DNP stain), m.p. 210–213 °C, darkens >170 °C (ethanol). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.25 (d, J = 8.8 Hz, 1 H), 6.80 (dd, J = 8.8, 2.7 Hz, 1 H), 6.74 (br. d, J = 2.7 Hz, 1 H), 5.78 (br. s, 1 H), 2.99 (dd, J = 6.7, 6.2 Hz, 2 H), 2.83 (t, J = 6.3 Hz, 2 H), 1.96 (dt, J = 12.7, 6.3 Hz, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.58, 160.67, 145.64, 130.81, 123.15, 116.03, 114.92, 114.56, 114.07, 33.30, 30.36, 22.11 ppm (one signal is missing due to overlap with $CDCl_3$). ^1H NMR (500 MHz, [D_6]DMSO): δ = 10.79 (br. s, 1 H), 8.12 (d, J = 8.8 Hz, 1 H), 6.81 (dd, J = 8.8, 2.6 Hz, 1 H), 6.74 (d, J = 2.6 Hz, 1 H), 2.94 (t, J = 6.2 Hz, 2 H), 2.76 (t, J = 6.2 Hz, 2 H), 1.82 (app. pent, J = 6.2 Hz, 2 H) ppm. ^{13}C NMR (126 MHz, [D_6]DMSO): δ = 172.20, 162.93, 146.16, 130.25, 120.98, 115.57, 115.43, 114.60, 114.32, 73.57, 32.62, 29.49, 21.44 ppm. HRMS (ESP^+ FT-ICR): calcd. for $[C_{13}H_{10}N_2ONa]^+$ 233.06853 $[MNa]^+$; found 233.06856. $C_{13}H_{10}N_2O$ (210.24): calcd. C 74.27, H 4.79, N 13.33; found C 74.26, H 4.44, N 13.19.

5-(Dicyanomethylene)-5,6,7,8-tetrahydronaphthalen-2-yl Trifluoromethanesulfonate (16): Et_3N (3.43 mL, 24.6 mmol, 2.2 equiv.) fol-

lowed by triflic anhydride (4.19 mL, 22.4 mmol, 2.0 equiv.) were added dropwise to a mixture of **15** (2.35 g, 11.2 mmol) and dry CH_2Cl_2 (120 mL) at –78 °C (an immediate yellow coloration was observed that slowly faded). The reaction mixture was stirred for 1 h and the resulting orange-to-red reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (3 × 150 mL). The combined organic phases were dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by dry-column vacuum chromatography (SiO_2, 15–40 μm, 0–100% $CHCl_3$/heptanes, 12.5% steps, then neat $CHCl_3$, 40 mL fractions) gave **16** (3.45 g, 10.1 mmol, 90%) as a colorless oil (Note 1). TLC ($CHCl_3$): R_f = 0.42. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.30 (d, J = 8.8 Hz, 1 H), 7.26 (dd, J = 8.8, 2.6 Hz, 1 H), 7.23 (d, J = 2.6 Hz, 1 H), 3.05 (dd, J = 6.9, 6.2 Hz, 2 H), 2.95 (t, J = 6.3 Hz, 2 H), 2.05 (dt, J = 12.8, 6.4 Hz, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.28, 152.18, 145.12, 130.40, 130.20, 122.33, 119.98, 118.79 (q, J = 320.8 Hz), 113.47, 112.84, 81.88, 32.84, 29.97, 21.90 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –71.55 (s, 3 F) ppm. HRMS (MALDI$^+$ FT-ICR, ditranol): calcd. for $[C_{14}H_9F_3N_2O_3SNa]^+$ 365.01782 $[MNa]^+$; found 365.01781. $C_{14}H_9F_3N_2O_3S$ (342.29): calcd. C 49.12, H 2.65, N 8.18; found C 49.23, H 2.53, N 8.06. Note 1) The neat oil was unstable and changed color to brown over the course of a few weeks.

6-(Cyclohepta-2,4,6-trienyl)-5-(dicyanomethylene)-5,6,7,8-tetrahydronaphthalen-2-yl Trifluoromethanesulfonate (17): Et_3N (0.842 mL, 6.04 mmol) was added dropwise to a stirred mixture of **16** (2.05 g, 5.98 mmol) and finely powdered tropylium tetrafluoroborate (1.07 g, 6.04 mmol) in CH_2Cl_2 (150 mL) at –78 °C over the course of 1 h. The reaction mixture was stirred at –78 °C for 2 h and then allowed to slowly rise to room temp. over the course of 6 h. The resulting yellow solution of **17** (Note 1) was poured into a saturated aqueous NH_4Cl solution (50 mL), the phases separated, and the aqueous layer extracted once with CH_2Cl_2 (50 mL). The combined organic layers were washed with saturated aqueous NH_4Cl (50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The brown residue was purified by dry-column vacuum chromatography [SiO_2, 15–40 μm, 1) 0–75% toluene/heptanes, 12.5% steps, 40 mL fractions, 2) 75–100% toluene/heptanes, 6.25% steps, 40 mL fractions] to give **17** (1.89 g, 4.37 mmol, 73%) as an almost colorless oil that slowly changes to bright-yellow. TLC ($CHCl_3$): R_f = 0.52; TLC (toluene): R_f = 0.45. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.09 (d, J = 8.8 Hz, 1 H), 7.23 (dd, J = 8.8, 2.5 Hz, 1 H), 7.15 (d, J = 2.5 Hz, 1 H), 6.65 (dd, J = 9.6, 5.5 Hz, 2 H), 6.34 (dd, J = 9.6, 5.5 Hz, 1 H), 6.26 (dd, J = 9.6, 5.5 Hz, 1 H), 5.31 (dd, J = 9.5, 6.9 Hz, 1 H), 5.13 (dd, J = 9.5, 6.9 Hz, 1 H), 3.50 (t, J = 3.7 Hz, 1/2 H), 3.48 (t, J = 3.7 Hz, 1/2 H), 2.97–2.92 (m, 2 H), 2.42–2.34 (m, 1 H), 2.05–2.01 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.36, 152.10, 143.30, 131.59, 130.82, 130.67, 129.17, 127.46, 127.27, 122.34, 121.55, 121.26, 119.91, 118.75 (q, J = 320.7 Hz), 113.31, 112.73, 82.84, 41.78, 39.64, 24.93, 24.59 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –71.61 (s, 3 F) ppm (in the crude mixture, signals of BF_4^- salts were also observed at δ = –149.58 and –149.64 ppm). HRMS (MALDI$^+$ FT-ICR, ditranol): calcd. for $[C_{21}H_{16}F_3N_2O_3S]^+$ 433.08282 $[MH]^+$; found 433.08293. $C_{21}H_{15}F_3N_2O_3S$ (432.42): calcd. C 58.33, H 3.50, N 6.48; found C 58.12, H 3.36, N 6.43.Note 1) The complete conversion from **16** to **17** was observed by TLC and ^{19}F and ^{1}H NMR spectroscopy; the triethylammonium salt and traces of cycloheptatriene were observed.

3-[4-(Methylthio)phenyl]-5,6-dihydronaphtho[2,1-*a*]azulene-12,12(11a*H*)-dicarbonitrile (18a): K_3PO_4 (99.3 mg, 468 μmol, 1.5 equiv.), $Pd(OAc)_2$ (9.1 mg, 41 μmol, 0.13 equiv.), and RuPhos (29.3 mg, 63 μmol, 0.20 equiv.) were added to a mixture of [4-(methylthio)phenyl]boronic acid (104 mg, 618 μmol, 2 equiv.) and DHN-DHA **4a** (133 mg, 309 μmol) and argon-flushed toluene (36 mL) and water (4 mL), and the reaction mixture was stirred at 50 °C for 6 h (Note 1). Saturated aqueous NH_4Cl (50 mL) was added to the resulting black-green reaction mixture, which was then extracted with CH_2Cl_2 (100 mL). The extract was dried with $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash column chromagraphy (SiO_2, 40–63 μm, toluene, note 2) gave **18a** (12.5 mg, 30.9 μmol, 10%) as a yellow-to-green solid, 12-cyano-5,6-dihydronaphtho[2,1-*a*]azulen-3-yl trifluoromethanesulfonate (**20**) (11.2 mg, 27.8 μmol, 9%) as a greenish blue solid (blue band on column), and 3-[4-(methylthio)phenyl]-5,6-dihydronaphtho[2,1-*a*]-azulene-12-carbonitrile (**21**; 30.5 mg, 80.8 μmol, 26%) as a green solid (greenish blue band on column) and, presumably, 5,6-dihydronaphtho[2,1-*a*]azulene-3,12-dicarbonitrile (**22**; 24.9 mg, 88.8 μmol, 29%) as a green solid (blue band on column). Crystals of **18a** suitable for X-ray crystallography were grown from $CHCl_3$/heptanes. Data for **18a**: TLC (toluene): R_f = 0.50 (purple by treatment with H_2SO_4 in EtOH), m.p. 188–190 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.0 Hz, 1 H), 7.57–7.52 (m, 3 H), 7.46 (s, 1 H), 7.34 (d, J = 7.5 Hz, 2 H), 6.62 (dd, J = 11.2, 6.4 Hz, 1 H), 6.50 (dd, J = 11.2, 6.1 Hz, 1 H), 6.34–6.31 (m, 1 H), 6.27 (d, J = 6.4 Hz, 1 H), 5.86 (dd, J = 10.1, 3.7 Hz, 1 H), 3.81–3.79 (m, 1 H), 3.05 (t, J = 8.2 Hz, 2 H), 2.72–2.64 (m, 1 H), 2.63–2.55 (m, 1 H), 2.54 (s, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.79, 141.45, 138.69, 138.59, 137.14, 137.00, 134.02, 130.99, 130.97, 127.71, 127.42, 127.41, 127.00, 126.85, 125.75, 123.79, 119.89, 118.14, 115.21, 112.93, 51.31, 42.75, 27.75, 21.47, 15.90 ppm. HRMS (MALDI$^+$ FT-ICR ditranol): calcd. for $[C_{27}H_{20}N_2S]^{\cdot+}$ 357.10561 $[M]^{\cdot+}$; found 404.13417. $C_{27}H_{20}N_2S$ (404.53): calcd. C 80.17, H 4.98, N 6.92; found C 80.07, H 4.94, N 7.02. Data for **20**: TLC (toluene): R_f = 0.37 (blue-purple), m.p. 167–169 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.58 (dd, J = 9.6, 0.9 Hz, 1 H), 8.55 (d, J = 8.5 Hz, 1 H), 8.33 (dd, J = 9.6, 0.6 Hz, 1 H), 7.75 (tt, J = 9.6, 1.0 Hz, 1 H), 7.48 (t, J = 9.6 Hz, 1 H), 7.44 (t, J = 9.6 Hz, 1 H), 7.31–7.26 (m, 2 H), 3.26–3.21 (m, 2 H), 3.16–3.11 (m, 2 H) ppm (Note 3). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 149.83, 146.04, 143.75, 141.75, 139.49, 137.71, 135.98, 135.41, 131.56, 128.02, 127.66, 127.28, 126.75, 121.74, 120.33, 118.81 (q, J = 320.8 Hz), 118.30, 90.81, 29.88, 20.79 ppm. HRMS (MALDI$^+$ FT-ICR ditranol): calcd. for $[C_{20}H_{12}F_3NO_3S]^{\cdot+}$ 403.04845 $[M]^{\cdot+}$; found 403.04859. $C_{20}H_{12}F_3NO_3S$ (403.37): calcd. C 59.55, H 3.00, N 3.47, S 7.95; found C 59.51, H 3.03, N 3.47, S 7.86. Data for **21**: An analytically pure sample obtained by recrystallization from boiling $CHCl_3$/heptanes gave **21** as a fluffy dark-blue solid. TLC (toluene): R_f = 0.30 (green), m.p. >260 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.55 (d, J = 8.5 Hz, 1 H), 8.54 (d, J = 9.8 Hz, 1 H), 8.29 (d, J = 9.8 Hz, 1 H), 7.68 (t, J = 9.8 Hz, 1 H), 7.63–7.60 (m, 1 H), 7.60 (d, J = 8.6 Hz, 2 H), 7.57 (br. s, 1 H), 7.43 (t, J = 9.8 Hz, 1 H), 7.39 (t, J = 9.8 Hz, 1 H), 7.36 (d, J = 8.6 Hz, 2 H), 3.27–3.22 (m, 2 H), 3.19–3.14 (m, 2 H), 2.55 (s, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.34, 145.86, 141.89, 139.67, 138.51, 138.44, 137.62, 137.28, 134.90, 134.49, 130.16, 127.50, 127.34, 127.07, 127.02, 126.97, 126.89, 125.99, 118.72, 90.56, 30.01, 21.28, 15.95 ppm (one signal missing due to overlap). HRMS (MALDI$^+$ FT-ICR ditranol): calcd. for $[C_{26}H_{19}SNa]^+$ 400.11304 $[MNa]^+$; found 400.11373. $C_{26}H_{19}NS$ (377.51): calcd. C 82.72, H 5.07, N 3.71, S 8.49; found C 82.98, H 5.06, N 3.81, S 8.40. Data for **22**: M.p. 241–242 °C ($CHCl_3$/heptanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.61 (d, J = 9.8 Hz, 1 H), 8.56 (d, J = 8.0 Hz, 1 H), 8.36 (d, J = 9.8 Hz, 1 H), 7.79 (t, J = 9.8 Hz, 1 H), 7.68 (d, J = 8.0 Hz, 1 H), 7.63 (br. s, 1 H), 7.50 (t, J = 9.8 Hz, 1 H), 7.46 (t, J = 9.8 Hz, 1 H), 3.24 (dd, J = 8.3, 6.2 Hz, 2 H), 3.14 (dd, J = 8.3, 6.2 Hz, 2 H) ppm. ^{13}C NMR

(126 MHz, $CDCl_3$): δ = 146.06, 143.20, 140.10, 139.68, 137.77, 136.56, 135.97, 135.38, 132.07, 131.42, 127.82, 127.52, 127.44, 126.55, 118.96, 118.13, 112.56, 91.18, 29.46, 20.78 ppm. IR (neat, film): $\tilde{\nu}$ = 2226 (w, CN), 2194 (w, CN), 1276 (m), 1261 (m), 764 (s), 750 (s) cm^{-1}. HRMS (MALDI$^+$ FT-ICR ditranol): calcd. for $[C_{20}H_{10}N_2Na]^+$ 303.08927 $[MNa]^+$; found 303.08921. No satisfactory elemental analysis was obtained. Notes: 1) TLC (toluene): R_f = 0.53 (**4a**, brown by treatment with H_2SO_4 in EtOH). 2) Alternatively, purification could be accomplished by repeated dry-column vacuum chromatography [SiO_2, 15–40 μm, 1) 0–100% toluene/heptanes, 5% steps, 40 mL fractions, 2) 0–100% $CHCl_3$/heptanes, 5% steps, 40 mL fractions]. 3) The signals are reported as observed. Not all spin systems could be paired.

***S*-(12,12-Dicyano-5,6,11a,12-tetrahydronaphtho[2,1-*a*]azulen-3-yl) Ethanethioate (19a):** DHN-DHA **4a** (131 mg, 304 μmol), potassium thioacetate (69.5 mg, 609 μmol, 2 equiv.), [Pd_2dba_3] (15.8 mg, 15.2 μmol, 5 mol-%), and Xantphos (17.6 mg, 30.4 μmol, 10 mol-%) were introduced into a glass container suitable for microwave heating, and the container was charged with argon. Freshly distilled argon-flushed 1,4-dioxane (5 mL) was added and the mixture was further flushed with argon with exposure to ultrasound for 10 min and then diisopropylethylamine (0.1 mL, 0.6 mmol, 2 equiv.) was added. The septum was replaced with an unpunctured one and the reaction mixture heated by using microwaves at 140 °C for 60 min (ca. 77 W, 3 bar). The contents of the reaction vessel were transferred through the use of CH_2Cl_2 (50 mL) into water (100 mL) and the phases were separated. The aqueous layer was extracted twice with CH_2Cl_2 (50 mL) and the combined organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by repeated flash column chromatography [SiO_2, 40–63 μm, 1) 50% CH_2Cl_2/heptanes to neat CH_2Cl_2, 2) 10–20% EtOAc/heptanes, note) gave **19a** (31.1 mg, 87.8 μmol, 29%) as a fluffy yellow solid. Crystals suitable for X-ray crystallography were grown from $CHCl_3$/heptanes. TLC ($CHCl_3$): R_f = 0.61 (purple by treatment with H_2SO_4 in EtOH), m.p. 162–163 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.0 Hz, 1 H), 7.39 (br. d, J = 8.0 Hz, 1 H), 7.31 (br. s, 1 H), 6.62 (dd, J = 11.2, 6.4 Hz, 1 H), 6.52 (dd, J = 11.2, 6.1 Hz, 1 H), 6.32 (ddd, J = 10.2, 6.1, 2.0 Hz, 1 H), 6.29 (br. d, J = 6.4 Hz, 1 H), 5.84 (dd, J = 10.2, 3.9 Hz, 1 H), 3.78 (dt, J = 3.8, 2.0 Hz, 1 H), 3.00 (t, J = 8.3 Hz, 2 H), 2.71–2.62 (m, 1 H), 2.62–2.53 (m, 1 H), 2.45 (s, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 193.73, 144.34, 138.25, 137.25, 134.18, 133.37, 133.27, 131.43, 130.90, 129.49, 128.90, 127.72, 123.74, 119.93, 118.89, 114.97, 112.71, 51.20, 42.68, 30.47, 27.35, 21.28 ppm. HRMS (MALDI$^+$ FT-ICR ditranol): calcd. for $[C_{22}H_{17}N_2OS]^+$ 357.10561 $[MH]^+$; found 357.10556. Note: Alternatively, purification can be accomplished by repeated dry-column vacuum chromatography [SiO_2, 15–40 μm, 1) 0–100% toluene/heptanes, 10% steps, followed by neat toluene, 40 mL fractions, 2) 0–100% $CHCl_3$/heptanes, 10% steps, followed by neat $CHCl_3$, 40 mL fractions, 3) 0–40% EtOAc/heptanes, 2.5% steps, 40 mL fractions].

Photoswitching of DHN-DHA 3a: A sample of **3a** (1.09 mg, 0.00386 mmol) was dissolved in MeCN (10.0 mL). From this stock solution, a sample of 0.100 mL was further diluted with MeCN (2.60 mL). A UV/Vis absorption spectrum was acquired (see Figure S46, left, red curve) by using the following settings: window: 200–800 nm, interval: 1 nm, scan rate: 600 nm/min. The settings were then adjusted to quickly scan the region between 200–800 nm in less than 1 s (window: 200–800 nm, interval: 5 nm, scan rate: 48000 nm/min). The sample was then exposed to light at 364 nm for 10 min (a sample of DHA **1a** with the same concentration took less than 1 min to fully convert into VHF **1b**). No change in the absorption spectrum was observed. A new sample, with the same concentration, was prepared in cyclohexane. A UV/Vis absorption spectrum was acquired (see Figure S47, left, red curve). The settings were then adjusted to quickly scan the region between 200 and 800 nm in less than 1 s. The sample was then exposed to light at 364 nm for 10 min. As quickly as possible, a series of five UV/Vis absorption spectra were acquired with an approximate 1 s delay between them (see Figure S48, left). In the first scan, shortly after light irradiation, an absorption band appeared at 455 nm (assigned to VHF **3b**) and the original band had disappeared (88% of original absorption). After 5 s, the original spectrum had reappeared and the VHF absorption had disappeared. The decay of the VHF absorption could be followed at 450, 455, and 460 nm, as shown in Figure S49, and the rate of the back reaction estimated.

Photoswitching DHN-DHA 4a: A sample of **4a** (2.54 mg, 0.00590 mmol) was dissolved in MeCN (10.0 mL). From this stock solution, a sample of 0.050 mL was further diluted with MeCN (2.60 mL). A UV/Vis absorption spectrum was acquired (see Figure S46, left, black curve) by using the following settings: window: 200–800 nm, interval: 1 nm, scan rate: 600 nm/min. The settings were then adjusted to quickly scan the region between 200–800 nm in less than 1 s (window: 200–800 nm, interval: 5 nm, scan rate: 48000 nm/min). The sample was then exposed to light at 364 nm (a sample of DHA **1a** with the same concentration took less than 1 min to fully convert to VHF **1b**). No change in the absorption spectrum was observed after 1 min of irradiation, but conversion into an unknown species was observed after prolonged irradiation (see Figure S46, right, red). A new sample, with the same concentration, was prepared in cyclohexane. A UV/Vis absorption spectrum was acquired (see Figure S47, left, black curve). The settings were then adjusted to quickly scan the region between 200 and 800 nm in less than 1 s. The sample was then exposed to light at 364 nm for 10 min. As quickly as possible, a series of three UV/Vis absorption spectra were acquired with an approximate 1 s delay between them (see Figure S48, right). In the first scan, shortly after light irradiation, an absorption band appeared at 460 nm (assigned to VHF **4b**) and the original band had disappeared (97% of original absorption). After 5 s, the original spectrum reappeared and the VHF absorption had disappeared. The decay of the VHF absorption could be followed at 455, 460, and 465 nm, as shown in Figure S50, and the rate of the back reaction estimated.

Low-Temperature Photoswitching of DHN-DHA 3a: Using a cryostat placed inside a UV/Vis spectrophotometer, absolute EtOH in a cuvette was cooled to –40, –50, –60, and –70 °C and baseline spectra were acquired. From a stock solution of **3a** (3.86×10^{-4} M) in MeCN, a sample of 0.200 mL was taken and the solvent blown off by using a stream of nitrogen gas. The solid sample was dissolved in absolute EtOH and cooled to, for example, –70 °C. The settings were then adjusted to quickly scan the region between 200 and 800 nm in less than 5 s (window: 200–800 nm, interval: 2 nm, scan rate 2400 nm/min). The sample (inside the cryostat) was then exposed to UV light (366 nm) for 3–5 min and the conversion from DHA to VHF was monitored. When fully converted, the back reaction was monitored by acquiring a UV/Vis absorption spectrum every minute until the DHN-DHA was fully reformed. The decay of VHF was followed at 476 nm. This experiment was repeated at –65, –60, –55, and –50 °C using the same sample.

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