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Palladium Mediated Strategies for Functionalizing the Dihydroazulene Photoswitch – Paving the Way for its Exploitation in Molecular Electronics

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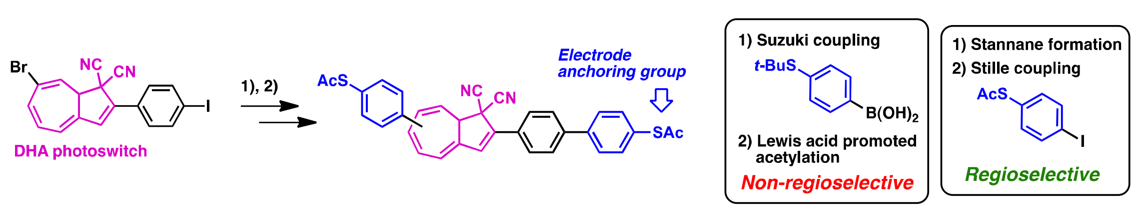
Graphical Abstract



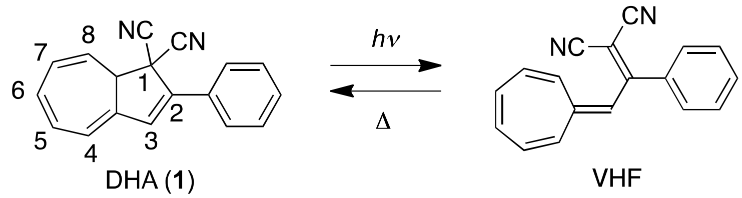
Abstract

The dihydroazulene (DHA) / vinylheptafulvene (VHF) photo/thermoswitch has attracted interest as a molecular switch for advanced materials and molecular electronics. We report here two synthetic approaches using palladium catalysis for synthesizing dihydroazulene (DHA) photoswitches with thioacetate anchoring groups for molecular electronics applications. The first methodology involves a Suzuki coupling using tert-butylthioether protecting groups. Conversion to the thioacetate using boron tribromide / acetyl chloride results in the formation of the product as a mixture of regioisomers mediated by a ring-opening reaction. The second approach circumvents isomerization by the synthesis of stannanes as intermediates and their use in a Stille coupling. Although fully unsaturated azulenes are formed as by-products during the synthesis of the DHA stannanes, this approach allowed the regioselective incorporation of the thioacetate anchoring group in either one of the two ends (positions 2 or 7) or at both.

Keywords: Dihydroazulene, Molecular wire, Photoswitch, Stille coupling, Suzuki coupling

Introduction

Dihydroazulene (DHA, **1**) is a fascinating molecule; it has photoswitching properties, whereby it undergoes a 10-electron retro-electrocyclization upon irradiation at ca. 360 nm to furnish a vinylheptafulvene (VHF) and is coupled with a thermally induced ring-closure reaction to revert back to the bicycle (Scheme 1).[1] The ring-closure itself is believed to proceed via a zwitterionic transition state.[2]



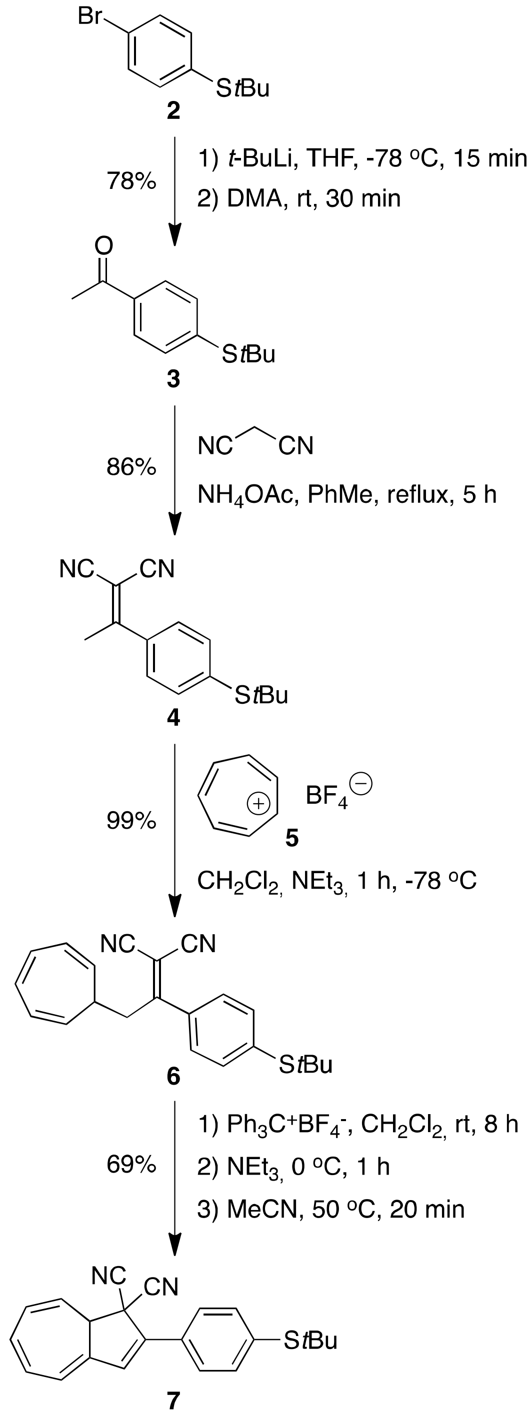
Scheme 1. Reversible DHA-VHF Interconversions.

Recent developments in DHA chemistry notably include the selective functionalization of the 7-position of the dihydroazulene core (for numbering, see Scheme 1) with bromine by the addition of elemental bromine and an elimination sequence using lithium hexamethyldisilazide (LiHMDS).[2, 3] The regioselective introduction of bromine to the 7-position has since been exploited by palladium catalyzed cross-coupling reactions, namely Sonogashira[2a,b] and to a greater extent Suzuki protocols[2c,3] to furnish DHAs bearing a variety of substituents at the 7-position. In addition, we have recently optimized the protocol for DHA synthesis to allow its preparation in multi-gram scale starting from acetophenone.[4] These synthetic developments have fuelled the exploitation of this photoactive compound in advanced systems; for example, suitable derivatives have recently been the subject of conductivity studies in single-molecule molecular electronics devices.[3, 5]

The most commonly used anchoring group to gold is the thiol.[6] This air sensitive group can be conveniently masked as the thioacetate, which can be easily liberated upon treatment with mild base and adhered to gold *in situ*. Recent studies have shown that a DHA incorporating an SAc anchoring group at the 2-position (via a tolane linker) can be assembled on a gold surface at which reversible DHA-VHF switchings were observed,[7] which warrants the further exploitation of these molecules in light-controlled devices. Yet, unlike other more commonly employed photoswitches, such as for example dithienylethenes,[8] a DHA bearing two acetyl-protected thiolate anchoring groups has not yet been reported. So far only the synthesis of a DHA functionalized with two SMe end-groups has been described.[3] The possibility for stronger thiolate anchoring at two specific positions, one in each end of the molecule, by cleavage of acetyl-protecting groups is desirable for controlling the positioning of molecules between for example two metal electrodes, although a strong coupling between electrode and molecule may in some cases quench photoactivity.[5] Here we present synthetic protocols for obtaining such derivatives, which is particularly challenging on account of the sensitive nature of the DHA system.

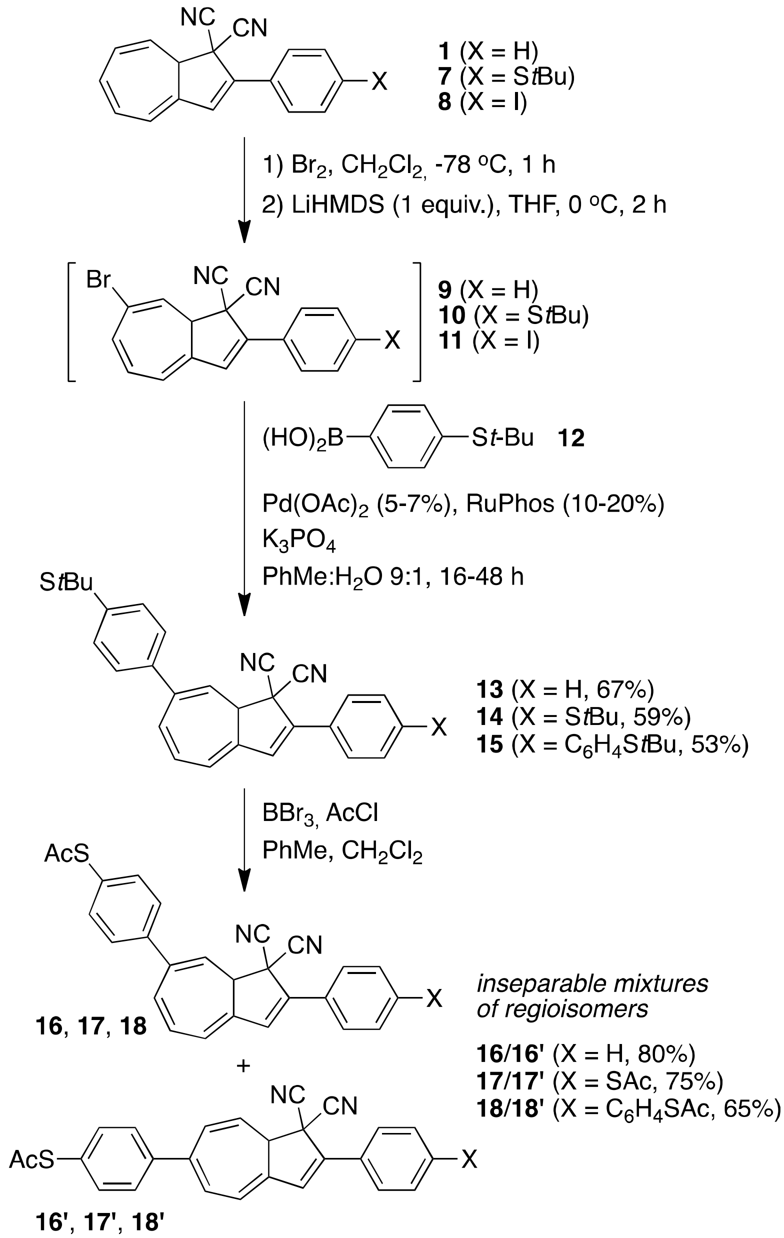
Results and Discussion

It was envisaged that using palladium catalysis, one could synthesize a system where the thioacetate moiety could be situated at opposing poles of the DHA. Our original Sonogashira coupling approach was discarded as we had previously experienced instability of compounds with an arylethynyl substituent group positioned at the 7-position of DHA if the aryl group did not include also methyl substituents at the ortho positions relative to the alkyne, which renders synthesis somewhat tedious.[2b] Instead, we turned first to the Suzuki reaction.[9] The Suzuki reaction too has its limits, in that not all functional groups are tolerated. A two-step strategy was investigated where a Suzuki reaction was employed to introduce the masked thiol, now as a tert-butylthioether at the 2- and 7-positions. The group was introduced at position 2 according to the route shown in Scheme 2. First, the known aryl bromide **2**[10] was lithiated and treated with *N*,*N*-dimethylacetamide (DMA) to furnish the acetophenone derivative **3**, which has previously been prepared by other routes.[11] A Knoevenagel condensation with malononitrile then afforded compound **4**, which by deprotonation with triethylamine reacted with tropylium tetrafluoroborate **5** to provide the product **6**. Finally, hydride abstraction followed by deprotonation gave the VHF intermediate, which converted to the DHA **7** upon heating.



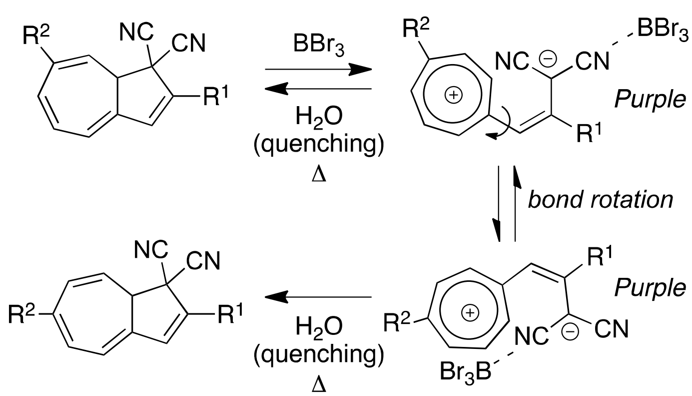
Scheme 2. Synthesis of DHA Functionalized with tert-butylthio Substituent. DMA = *N*,*N*-dimethylacetamide.

The three DHA compounds **1**, **7**, and **8**[12] (Scheme 3) were now subjected to the bromination-elimination protocol, which gave the 7-bromo-substituted intermediates **9**, **10**, and **11**[3]. To our delight, the thioether **7** was found to be compatible with these reaction conditions, despite the presence of the potentially oxidatively sensitive thioether and it seemed no side reactions had occurred during the bromination-elimination as verified by crude NMR analysis at each stage of the preparation of the 7-bromide. The three halogenated DHAs were then each treated with the known 4-(tert-butylsulfanyl)phenylboronic acid[13] (**12**) as coupling partner to furnish the final Suzuki products **13**, **14**, and **15** in reasonable yields over the three steps. In all systems the Suzuki chemistry was applicable at room temperature utilizing RuPhos / $Pd(OAc)_2$ as the catalytic system (RuPhos = 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl). Notably, the double Suzuki reaction furnished the product **15** in an overall yield of 53%.



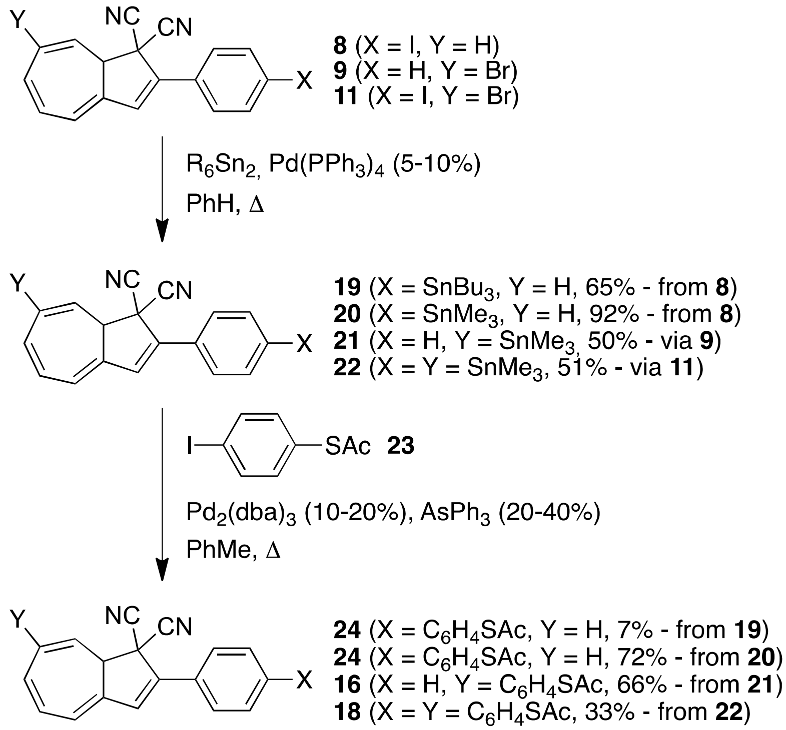
Scheme 3. Functionalization via Bromination-Elimination Protocol Followed by Suzuki Couplings and *S*-Protection Group Interconversions.

Treatment of each of these thioethers with the standard deprotection/acetylation conditions,[10] namely boron tribromide (BBr_3) and acetyl chloride (AcCl), resulted in the desired functional group transformation of the thioethers into thioacetates (Scheme 3), but in each case also resulted in the temporary ring opening to VHF. Strong Lewis acids have previously been observed to induce ring-opening of DHA to VHF.[14] All the reactions required a large excess of BBr_3 to ensure complete consumption of the starting material (ca. 5 equivalents per functional group). A sudden color change during the reaction to a brilliant purple was indicative of suspected VHF-BBr_3 complex formation (Scheme 4).[14a] As previously described, quenching with water breaks up such a complex to VHF, which ultimately converts thermally to DHA. To our dismay, in all cases, we isolated DHAs where scrambling had occurred to a mixture of the phenylthioacetate situated either on the 6- or the 7-position (compounds **16/16'** 4:5, **17/17'** 2:3, **18/18'** 1:2, ratios obtained from ^{1}H NMR spectra). This scrambling effect has been observed previously during light-heat cycle experiments (DHA→VHF→DHA),[2] but was in the present cases a result of the BBr_3 induced ring-opening of DHA to VHF as the reaction was conducted in the dark. The mechanism of the scrambling is due to the free rotation about the fulvene bond on account of its significant single-bond character; thus there are two possibilities of reforming the bicyclic DHA structure (Scheme 4). Separation of these sets of regioisomers was not accomplished (fractional crystallization proved fruitless, while tedious purification using column chromatography could potentially result in some isomeric enrichment).



Scheme 4. Lewis Acid Induced Isomerizations Between 7- and 6-Substituted DHAs. R^1 and R^2 Correspond to Aryl Groups.

It was decided to seek an alternate strategy to enforce a regioselective synthesis of **18**. It has been demonstrated in the literature that halogenated azulenes could be successfully transformed to their corresponding stannanes by heating in the presence of hexabutyltin and catalytic $Pd(PPh_3)_4$.[15] Indeed, unlike the Suzuki protocol, Stille coupling conditions have a greater tolerance of most functional groups,[16] and it was hoped that this methodology could be used to introduce the sulfur directly as the thioacetate in the final step. The added advantage of this strategy was the fact that a reactive coupling partner could be employed in the reaction, which was then not at the mercy of the sometimes seemingly unreactive bromine at the 7-position. To probe the Stille reaction, two standard tin end groups were chosen for this study, tributyl and trimethyl. Indeed, subjecting a series of halogenated DHAs (**8**, **9**, **11**) with hexaalkyldistannanes gave the *mono-* and *bis*-tin compounds **19-22** in moderate to excellent yields (Scheme 5). The use of hexabutylditin led to a lower yield of the stannane **19** and an increased amount of the corresponding fully unsaturated azulene by-product (vide infra). Azulenes result from the loss of hydrogen cyanide, which usually occurs under basic conditions.[2, 17] In addition, the metallation of the 7-position, although possible in moderate yield over three steps for the introduction of the trimethylstannyl moiety, did not allow for significant quantities of the tributyl analogues to be synthesized and was not further explored. All DHAs could be effectively separated from the azulenes using flash column chromatography in the dark (to avoid ring-opening of the DHA).



Scheme 5. Functionalizations via Stille Couplings. The starting materials **9** and **11** were freshly prepared from **1** and **8**, respectively, according to Scheme 3.

The stannanes were then subjected to Stille coupling conditions, using the catalytic system of $Pd_2(dba)_3$ (dba = dibenzylideneacetone) and $AsPh_3$ in refluxing toluene. Using 4-iodophenylthioacetate **23**[18] as the coupling partner resulted in rapid formation of the desired products **24**, **16**, and **18** in decent yields (except for the 7%-yield of **24** obtained by conversion of the tributylstannane **19**) and, gratifyingly, as single regioisomers. It has previously been shown that large rate enhancements of Stille couplings are obtained by using triphenylarsine as ligand;[19] indeed, fast reactions were desirable due to the somewhat sensitive nature of the thioacetate group. Usually, vinyl stannanes are more reactive than aryl stannanes,[20] but conversion of DHA stannanes **20-22** required the same reaction times (15 min). Particularly noteworthy is the synthesis of our main target molecule **18** (Figure 1) by the double Stille coupling. The down side is that a high catalyst loading was required for the reaction to be effective as reaction times needed to be short so as to minimalize competitive side reactions, which are likely a reflection of the lability of the thioacetate moiety and warrant further investigation.

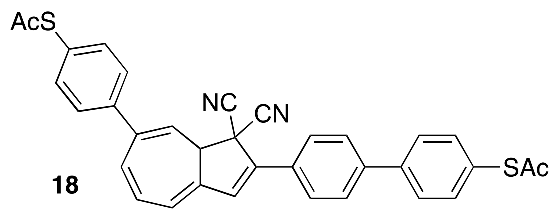
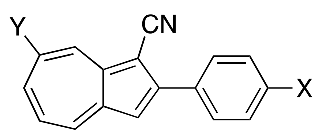


Figure 1. DHA End-capped with Two SAc Groups.

The fully unsaturated azulene by-products obtained from the stannation reactions all had a characteristic purple color and their structures (**25**-**28**) and isolated yields are shown in Figure 2. These compounds, which were all fully characterized, could be interesting precursors for further azulene scaffolding, targeting electrochromic materials.[21] Indeed, Stille cross-couplings have previously been used successfully for functionalization of azulenes at position 6.[15, 22] Compounds **27** and **28** present instead convenient precursors for coupling reactions at position 7. The yields of these by-products, were low, as desired in the present work in which high yields of the dihydroazulenes **19-22** were instead targeted, but as HCN is so easily eliminated from the dihydroazulenes, optimization of azulene formulation should be possible.



25 (X = $SnBu_3$, Y = H, 20% - from **8**)
26 (X = $SnMe_3$, Y = H, 3% - from **8**)
27 (X = H, Y = $SnMe_3$, 11% - via **9**)
28 (X = Y = $SnMe_3$, 1% - via **11**)

Figure 2. Azulene By-products Formed in the Stannation Reactions.

Conclusion

In summary, it is possible to introduce the thioacetate groups to the 2- and 7-positions of DHA using palladium catalysis. Future studies look to incorporate some of these compounds, in particular compound **18**, into break junction or other molecular electronics devices. Several techniques for entrapping and measuring electrical properties of molecules in metallic contact gaps exist[23] and the bent structure of **18** is not expected to pose a problem in this regard.[24] The Suzuki route gives rise to an inseparable mixture of 6- and 7-isomers after deprotection of the tert-butylthioether facilitated by the presence of BBr_3. In light of this finding, efforts are under way to induce regioselective control in ring closing reactions of substituted VHFs to afford an efficient synthesis of either the 6- or 7-isomer. The convenient synthesis of stannanes holds much potential for further development of DHA chemistry, although formation of fully unsaturated azulene by-products could not be avoided. Such by-products could, however, show promise as building blocks for development of new azulene derivatives. The Stille protocol worked particularly well for the trimethylstannanes, and in this synthetic approach, the Lewis acid BBr_3, inducing ring-opening of DHA, was conveniently avoided. The DHA stannanes could be versatile synthons not only just for the introduction of SAc groups to the DHA core, but possibly for introducing other anchoring groups, such as pyridyls or fullerenes, for introducing fluorine to the 7-position, or for generating dimeric structures of DHA, and hence molecules with potential for multimode switching.

Experimental

General Methods. Chemicals were used as purchased from commercial sources. THF was distilled from a sodium/benzophenone couple. Purification of products was carried out by flash chromatography on silica gel (40−63 μm, 60 Å). Thin-layer chromatography (TLC) was carried out using aluminum sheets precoated with silica gel. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on an instrument with a non-inverse cryoprobe using the residual solvent as the internal standard ($CDCl_3$, ^1H 7.26 ppm and ^{13}C 77.16 ppm) All chemical shifts are quoted on the δ scale (ppm), and all coupling constants (*J*) are expressed in Hz. In APT spectra, CH and CH_3 correspond to negative signals and C and CH_2 correspond to positive signals. Mass spectra (MS) were acquired either using an electrospray method of ionization or by FAB. HRMS spectra were obtained on a Q-TOF instrument. IR spectra were recorded of neat samples using the attenuated total reflectance (ATR) sampling technique. Melting points are uncorrected. For the stannanes, the *m/z* for the most intense signal is listed.

1-[4-(tert-Butylthio)phenyl]ethanone (3). To a stirring solution of the 4-bromophenyl tert-butyl sulfide **2** (6.50 g, 26.5 mmol) in dry THF (100 mL) at -78 ºC was slowly added tert-butyl lithium solution (34 mL, 1.7M in pentane, 57.8 mmol) and the resulting yellow solution was stirred for 15 min. DMA (5.0 mL, 54 mmol) was added in one portion and the contents of the vessel were allowed to reach rt, and stirring was allowed to continue for a further 30 min. The contents were cooled in an ice bath and 1M HCl (100 mL) was added to the vessel. The mixture was diluted with both water (200 mL) and diethyl ether (200 mL) and the phases separated. The aqueous phase was extracted once with ether (200 mL) and the combined organic phases were dried over $MgSO_4$, filtered and the solvent removed in vacuo. The crude oil was further purified by flash column chromatography (SiO_2, toluene) to afford the title compound (4.28 g, 78%) as a colorless oil. TLC (toluene): R_f = 0.35. ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 2.60 (s, 3H), 1.31 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 139.5, 137.0, 136.9, 128.3, 47.0, 31.2, 26.8 ppm. MS (ESP+): *m/z* = 247 [M+K$^+$]. Elem. anal. calc. for $C_{12}H_{16}OS$ (208.32): C: 69.20%, H: 7.75%, found: C: 69.10%, H: 7.84%.

2-[1-(4-(tert-Butylthio)phenyl)ethylidene]malononitrile (4). A mixture consisting of the acetophenone **3** (4.08 g, 19.6 mmol), malononitrile (5.62 g, 85.1 mmol), ammonium acetate (8.23 g, 107 mmol) in toluene (200 mL) and acetic acid (12 mL) was heated to reflux point using a Dean Stark apparatus for 5 h (oil bath temperature ca. 180 ºC). The vessel was allowed to cool and the contents diluted with ether (200 mL). The organic phase was washed with water (3 x 200 mL), then with saturated brine (200 mL) and dried over $MgSO_4$. Filtration and removal of the solvent under reduced pressure gave a crude residue, which was purified by flash column chromatography (SiO_2, toluene) to give **4** as a pale yellow oil (4.30 g, 86%). TLC (toluene): R_f= 0.43. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 2.63 (s, 3H), 1.33 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.5, 139.0, 137.2, 135.6, 127.4, 112.8, 84.9, 47.3, 31.2, 24.3 ppm, one carbon masked. MS (ESP+): m/z = 279 [$M+Na^+$]. Elem. anal. calc. for $C_{15}H_{16}N_2S$ (256.37): C: 70.27%, H: 6.29%, N: 10.93%, found: C: 70.20%, H: 6.19%, N: 10.71%.

2-[2-Cyclohepta-2,4,6-trienyl-1-(4'-(tert-butylthio)phenyl)ethylidene]malononitrile (6). To a stirring suspension of the crotonitrile **4** (4.21 g, 16.4 mmol) and freshly pulverized tropylium tetrafluoroborate **5** (3.50 g, 19.7 mmol) in dry CH_2Cl_2 (200 mL), at -78 ºC, was added dropwise NEt_3 (2.60 mL, 18.0 mmol) during the course of 1 h. The contents were stirred for a further 10 min and were then treated with 1M aqueous HCl (20 mL). The contents were then allowed to reach rt. The crude reaction mixture was washed with water (2 x 100 mL), dried over $MgSO_4$, filtered and the solvent was removed in vacuo. The residue, a yellowish oil, was essentially pure **4** (5.60 g, 99%), only containing minor impurities. A small sample (ca. 100 mg) was subjected to flash column chromatography (SiO_2, toluene) to give pure the title compound as a pale yellow oil. TLC (toluene): R_f= 0.44. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 6.60 - 6.59 (m, 2H), 6.21 - 6.17 (m, 2H), 5.15 (dd, J = 9.1, 6.5 Hz, 2H), 3.17 (d, J = 8.0 Hz, 2H), 2.03-1.98 (m, 1H), 1.32 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 138.4, 137.3, 134.5, 131.2, 127.4, 126.6, 122.9, 112.5, 112.5, 86.7, 47.2, 38.0, 37.9, 31.2 ppm. HR-MS (ESP-): *m*/*z* = 345.1447 $[M-H]^-$; calc. for ($C_{22}H_{21}N_2S^-$): *m*/*z* = 345.1431.

2-[4'-(tert-Butylthio)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (7). To a stirring solution of the crotonitrile **6** (5.60 g, 16.2 mmol) in CH_2Cl_2 (200 mL) was added tritylium tetrafluoroborate (5.90 g, 1.79 mmol) and the resulting mixture was stirred 8 h at rt, whilst protecting the vessel from light. The vessel was placed in an ice bath and NEt_3 (2.50 mL, 1.73 mmol) was added carefully over 10 min and the mixture was stirred for 1 h. The solvent was removed in vacuo and the crude residue was dissolved in acetonitrile (50 mL) and the vessel heated to 50 ºC for 20 min. The solvent was removed and the crude material was purified by flash column chromatography (SiO_2, 50% CH_2Cl_2 / heptane) to afford pure **7** as a yellow solid (3.85 g, 69%). This compound could be conveniently crystallized from CH_2Cl_2 / methanol. TLC (50% CH_2Cl_2 / heptane): R_f = 0.40. M.p. = 114.0 – 116.0 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 6.92 (s, 1H), 6.57 (dd, *J* = 11.3, 6.3 Hz, 1H), 6.49 (dd, *J* = 11.3, 6.1 Hz, 1H), 6.36 (br d, *J* = 6.3 Hz, 1H), 6.31 (ddd, *J* = 10.2, 6.1, 2.1 Hz, 1H), 5.82 (dd, *J* = 10.2, 3.8 Hz, 1H), 3.80 (dt, *J* = 3.8, 2.1 Hz, 1H), 1.33 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 138.6, 137.9, 135.7, 133.0, 131.2, 131.0, 130.6, 127.8, 126.1, 121.5, 119.6, 115.2, 112.8, 51.2, 47.0, 45.2, 31.2 ppm. MS (ESP+): *m*/*z* = 367 $[M+Na^+]$. Elem. anal. calc. for $C_{22}H_{20}N_2S$ (344.47): C: 76.71%, H: 5.85%, N: 8.13%, found: C: 76.42%, H: 5.78%, N: 8.21%. UV-Vis (MeCN): λ_{DHA} = 358 nm. λ_{VHF} = 478 nm.

2-[4'-(tert-Butylthio)phenyl]-7,8-dibromo-1,7,8,8a-tetrahydroazulene-1,1-dicarbonitrile (precursor to 10). To a stirring solution of the DHA **7** (342 mg, 0.993 mmol), at -78 ºC, was added dropwise a solution of Br_2 in CH_2Cl_2 (1.28 mL, 0.78M, 1.00 mmol) and the reaction contents were allowed to stir for 1 h. The solvent was removed in vacuo to give the title compound (500 mg, 100%), which was essentially pure, but very unstable, as grey / green powder. M.p. = 132 - 145 ºC (decomposes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.01 (s, 1H), 6.29 (dd, *J* = 7.6, 2.5 Hz, 1H), 6.10 (dd, *J* = 12.2, 7.6 Hz, 1H), 5.93 (dd, *J* = 12.2, 5.6 Hz, 1H), 5.33 – 5.31 (m, 1H), 5.05 (dt, *J* = 2.5, 1.2 Hz, 1H), 4.66 (br s, 1H), 1.34 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 139.0, 137.9, 136.1, 134.7, 130.2, 128.9, 126.3, 125.8, 121.7, 114.6, 111.7, 53.3, 51.5, 49.2, 47.4, 44.6, 31.2 ppm. Elem. anal. calc. for $C_{22}H_{20}N_2SBr_2$ (501.97): C: 52.40%, H: 4.00%, N: 5.56%, found: C: 52.29%, H: 4.13%, N: 5.55%.

7-Bromo-2-[4'-(tert-butylthio)phenyl]-1,8-dihydroazulene-1,1-dicarbonitrile (10). To a stirring solution of the DHA **7** (344 mg, 1.00 mmol) in CH_2Cl_2 (20 mL), at -78 ºC, was added dropwise a solution of bromine in CH_2Cl_2 (1.28 mL, 0.78M, 1.00 mmol) and the resulting solution was stirred for 1 h. The cold bath was removed and immediately the solvent was removed using a diaphragm pump, whilst keeping the vessel cold. The crude residue was dissolved in THF (20 mL) and cooled in an ice bath. To this solution was added LiHMDS (1.10 mL, 1.10 mmol, 1M in toluene) and the contents of the vessel stirred for 2 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl (5 mL) and diluted with both water (50 mL) and diethyl ether (50 mL). The phases were separated and the organic phase was dried over $MgSO_4$, filtered and the solvent removed in vacuo. The crude residue was purified by flash chromatography (SiO_2, gradient elution 50-75% toluene / heptane) to afford **10** (85 mg, 20%) as a bright yellow solid. TLC (60% toluene / heptane): R_f = 0.50. M.p. = 175 - 179 ºC (decomposes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 6.59 - 6.48 (m, 2H), 6.34 (d, *J* = 5.5 Hz, 1H), 6.12 (d, *J* = 4.4 Hz, 1H), 3.81 (dd, *J* = 4.4, 1.8 Hz, 1H), 1.34 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 140.9, 137.9, 136.5, 133.2, 132.2, 132.1, 130.1, 126.3, 120.5, 120.3, 120.0, 114.6, 112.4, 51.2, 47.2, 44.7, 31.2 ppm. MS (ESP+): m/z = 445 [M+Na$^+$]. Elem. anal. calc. for $C_{22}H_{19}BrN_2S$ (423.37): C: 62.41%, H: 4.52%, N: 6.62%, found: C: 62.69%, H: 4.47%, N: 6.69%.

7-[4-(tert-Butylthio)phenyl]-2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (13). To a stirring solution of the DHA **1** (512 mg, 2.00 mmol) in CH_2Cl_2 (30 mL), at -78 ºC, was added dropwise a solution of bromine in CH_2Cl_2 (2.56 mL, 0.78M, 2.00 mmol) and the resulting solution was stirred for 1 h. The cold bath was removed and immediately the solvent was removed using a diaphragm pump. The residue was dissolved in THF (30 mL) and cooled in an ice bath. To this solution was added LiHMDS (2.10 mL, 1M solution in toluene, 2.10 mmol) and the contents of the vessel stirred for 2 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl (5 mL) and was diluted with both diethyl ether (100 mL) and water (100 mL). The phases were separated and the aqueous phase extracted with diethyl ether (100 mL). The combined organics were dried over $MgSO_4$, filtered and the solvent removed in vacuo. Toluene (100 mL) and water (10 mL) were added to the residue (containing **9**) and the contents purged with argon. To this biphase was added 4-(tert-butylthio)phenylboronic acid **12** (625 mg, 2.97 mmol), K_3PO_4 (1.35 g, 6.36 mmol), $Pd(OAc)_2$ (25 mg, 0.11 mmol), and RuPhos (105 mg, 0.225 mmol). The mixture was allowed to stir in the dark for 16 h. The contents of the vessel were diluted with diethyl ether (100 mL) and water (100 mL) and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (100 mL). The combined organic phase was dried over Na_2SO_4, filtered and the solvent removed by rotary evaporation. The residue was subsequently purified by flash column chromatography (SiO_2, gradient elution 50-75% toluene / heptane) to afford **13** (561 mg, 67% over 3 steps) as a yellow crystalline solid. TLC (75% toluene / heptane): R_f = 0.53. M.p. = 150.5 - 152.5 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 2H), 7.54 - 7.43 (m, 5H), 7.37 (d, J = 8.2 Hz, 2H), 6.91 (s, 1H), 6.83 (dd, J = 11.5, 5.7 Hz, 1H), 6.77 (d, J = 11.5 Hz, 1H), 6.37 (br d, J = 5.7 Hz, 1H), 6.03 (d, J =

4.6 Hz, 1H), 3.85 (dd, *J* = 4.6, 1.5 Hz, 1H), 1.30 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 140.8, 140.4, 139.2, 137.7, 132.9, 132.8, 131.8, 131.7, 130.4, 129.4, 127.8, 126.5, 120.4, 116.8, 115.3, 113.1, 51.1, 46.4, 45.2, 31.1 ppm, one carbon masked. MS (FAB+): *m/z* = 420 [M^+]. Elem. anal. calc. for $C_{28}H_{24}N_2S$ (420.57): C: 79.96%, H: 5.75%, N: 6.66%, found: C: 79.92%, H: 5.54%, N: 6.72%.

2,7-Bis[4-(tert-butylthio)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (14). To a stirring solution of the DHA **7** (1.32 g, 3.84 mmol) in CH_2Cl_2 (50 mL), at -78 ºC, was added dropwise a solution of bromine in CH_2Cl_2 (5.0 mL, 0.78M, 3.9 mmol) and the resulting solution was stirred for 1 h. The cold bath was removed and immediately the solvent was removed using a diaphragm pump. The residue was dissolved in THF (50 mL) and cooled in an ice bath. To this solution was added LiHMDS (4.0 mL, 1M solution in toluene, 4.0 mmol) and the contents of the vessel stirred for 2 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl (5 mL) and diluted with both diethyl ether (200 mL) and water (200 mL) and the phases separated. The organic phase was dried over $MgSO_4$, filtered and the solvent removed in vacuo. The residue (containing **10**) was taken up in toluene (100 mL) and water (10 mL) and the contents degassed with argon. To this solution was added 4-(tert-butylthio)phenylboronic acid **12** (1.37 g, 6.52 mmol), K_3PO_4 (2.76 g, 13.0 mmol), $Pd(OAc)_2$ (70 mg, 0.312 mmol), and RuPhos (276 mg, 0.591 mmol). The mixture was allowed to stir in the dark for 48 h. The contents of the vessel were diluted with diethyl ether (200 mL) and water (200 mL) and the phases separated. The aqueous phase was extracted with CH_2Cl_2 (100 mL) and the combined organic phase was dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The residue was subsequently purified by flash column chromatography (SiO_2, gradient elution 50-75% toluene / heptane) to afford **14** (1.15 g, 59% over the 3 steps) as a yellow orange powder. TLC (60% toluene / heptane): R_f = 0.43. M.p. = 140 - 142 ºC. ^{1}H NMR (500

MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6, 2H), 7.63 (d, *J* = 8.6, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.93 (s, 1H), 6.83 (dd, *J* = 11.4, 5.8 Hz, 1H), 6.78 (d, *J* = 11.4 Hz, 1H), 6.39 (d, 5.8 Hz, 1H), 6.02 (d, *J* = 4.7 Hz, 1H), 3.85 (dd, *J* = 4.7, 1.7 Hz, 1H), 1.34 (s, 9H), 1.29 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 140.4, 139.3, 137.9, 137.7, 136.0, 133.0, 132.7, 132.2, 132.1, 130.5, 127.8, 126.2, 120.8, 116.8, 115.1, 113.0, 51.1, 47.1, 46.4, 45.0, 31.2, 31.1 ppm; one carbon masked. MS (FAB+): *m/z* = 508 [M^+]. Elem. anal. calc. for $C_{32}H_{32}N_2S_2$ (508.74): C: 75.55%, H: 6.34%, N: 5.51%, found: C: 75.68%, H: 6.01%, N: 5.40%.

2-(4'-(tert-Butylthio)-[1,1'-biphenyl]-4-yl)-7-[4-(tert-butylthio)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (15). To a stirring solution of the DHA **8** (762 mg, 2.00 mmol) in CH_2Cl_2 (40 mL), at -78 ºC, was added dropwise a solution of bromine in CH_2Cl_2 (2.56 mL, 0.78M, 2.00 mmol) and the resulting solution was stirred for 1 h. The cold bath was removed and immediately the solvent was removed using a diaphragm pump. The crude mixture was dissolved in THF (50 mL) and cooled in an ice bath. To this solution was added LiHMDS (2.1 mL, 1M solution in toluene, 2.1 mmol) and the contents of the vessel stirred for 2 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl (5 mL), followed by water (100 mL) and diethyl ether (100 mL) and the phases separated. The organic phase was dried over $MgSO_4$, filtered and the solvent removed in vacuo. The crude residue (containing **11**) was taken up in toluene (100 mL) and water (10 mL) and degassed 15 min before adding $Pd(OAc)_2$ (45 mg, 0.20 mmol), RuPhos (188 mg, 0.403 mmol), and K_3PO_4 (2.35 g, 11.1 mmol) and 4-(tert-butylthio)phenylboronic acid **12** (1.13 g, 5.38 mmol). The biphasic mixture was then stirred for 16 h at rt. The contents of the vessel were diluted with water (100 mL) and diethyl ether (100 mL) and the phases separated. The aqueous phase was extracted with CH_2Cl_2 (100 mL) and the combined organic phases were dried over $MgSO_4$, filtered and the solvent removed in vacuo. The crude residue was subjected to flash column chromatography (SiO_2, gradient elution 50-75% toluene / heptane) to furnish **15**, which was crystallized from CH_2Cl_2 / ethanol giving **15** as a light yellow fibrous solid (626 mg, 53% over 3 steps). TLC (75% toluene / heptane): R_f = 0.43. M.p. = 169 - 171 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.6, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 6.96 (s, 1H), 6.84 (dd, J = 11.5, 6.0 Hz, 1H), 6.78 (d , J = 11.5 Hz, 1H), 6.40 (broad d, J = 6.0 Hz, 1H), 6.04 (d, J = 4.7 Hz, 1H), 3.87 (dd, J = 4.7, 1.6 Hz, 1H), 1.34 (s, 9H), 1.30 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 140.9, 140.8, 140.4, 140.1, 139.3, 133.0, 132.9, 132.8, 131.9, 131.6, 129.7, 128.0, 127.8, 127.1, 127.0, 120.5, 116.8, 115.3, 113.1, 51.1, 46.4, 46.4, 45.1, 31.2, 31.1 ppm; two carbons masked. MS (ESP+): m/z = 607 [M+Na$^+$]. Elem. anal. calc. for $C_{38}H_{36}N_2S_2$•$0.2CH_2Cl_2$ (584.84): C: 76.24%, H: 6.10%, N: 4.65%; found C 75.79%, H 6.02%, N 4.40%.

Mixture of 16 and 16'. To a degassed stirring solution of **13** (81 mg, 0.193 mmol) in CH_2Cl_2 (20 mL), toluene (2 mL) and acetyl chloride (1.0 mL) was added periodically over 3 h a solution of BBr_3 (1.0 mL, 1M in CH_2Cl_2, mmol). Ice was added to the reaction vessel and the mixture was diluted with water (100 mL) and CH_2Cl_2 (100 mL) and the phases separated. The aqueous phase was extracted with CH_2Cl_2 (50 mL) and the combined organics dried over Na_2SO_4. The solution was filtered and the solvent removed under reduced pressure and the crude residue purified by flash column chromatography (SiO_2, 0.8% ethyl acetate / toluene) to afford an isomeric mixture (5:4 ratio of the 6 isomer to the 7 isomer) as a viscous orange oil (63 mg, 80%). TLC (1% ethyl acetate / toluene): R_f= 0.38. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78-7.76 (m, 4H), 7.52-7.40 (m, 14H), 6.97 (d, J = 6.7 Hz, 1H), 6.95 (s, 1H), 6.91 (s, 1H), 6.83 (dd, J = 11.5, 6.0 Hz, 1H), 6.75 (d, J = 11.5 Hz, 1H), 6.53 (d, J = 10.4 Hz, 1H), 6.47 (dd, J = 6.9, 1.4 Hz, 1H), 6.37 (dd, J = 6.0, 1.4 Hz, 1H), 6.04-6.01 (m, 2H), 3.85-3.82 (m, 2H), 2.45 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 194.0, 194.0, 142.3, 142.0, 141.5, 141.2, 140.7, 139.6, 139.1, 134.8, 134.7, 132.9, 132.1, 131.6, 131.6, 130.5, 130.4, 130.3, 129.4, 128.9, 128.6, 128.4, 127.9, 127.8, 127.5, 126.5, 126.4, 120.8, 120.6, 120.3, 117.1, 115.2, 115.2, 113.0, 112.9, 51.1, 51.1, 45.1, 45.1, 30.4, 30.4 ppm; three carbons masked. MS (ESP+): *m/z* = 429 [M+Na$^+$]. HRMS ($C_{26}H_{18}N_2OSNa^+$): calcd 429.1032; found 429.1032 [M+Na$^+$].

Mixture of 17 and 17'. To a degassed stirring solution of **14** (135 mg, 0.265 mmol) in dry CH_2Cl_2 (50 mL), toluene (5 mL) and acetyl chloride (2.0 mL) was added a solution of BBr_3 periodically over 6 h (2.8 mL, 1.0M in CH_2Cl_2, 2.8 mmol). Ice was added to the vessel, followed by water (100 mL) and CH_2Cl_2 (100 mL) and the phases separated. The organic phase was dried over Na_2SO_4, filtered and the solvent removed in vacuo. The crude residue was purified by column chromatography (SiO_2, 2% ethyl acetate / toluene) to afford an isomeric mixture (3:2 ratio of the 6 isomer to the 7 isomer) (96 mg, 75%) as a yellow solid. TLC (2% ethyl acetate / toluene): R_f = 0.39. M.p. = 138-141 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83-7.80 (m, 4H), 7.57-7.45 (m, 12H), 7.02 (s, 1H), 7.00 (d, *J* = 6.9 Hz, 1H), 6.98 (s, 1H), 6.86 (dd, *J* = 11.5, 6.0 Hz, 1H), 6.80 (d, *J* = 11.5 Hz, 1H), 6.56 (d, *J* = 10.3 Hz, 1H), 6.53 (dd, *J* = 6.9, 1.4 Hz, 1H), 6.43 (dd, *J* = 6.0, 1.4 Hz, 1H), 6.07-6.04 (m, 2H), 3.88-3.86 (m, 2H), 2.49 (s, 3H), 2.49 (s, 3H), 2.48 (s, 3H), 2.46 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.0, 193.1, 193.1, 142.4, 142.2, 141.1, 140.4, 140.4, 139.6, 139.2, 139.2, 135.1, 134.8, 134.7, 133.2, 132.9, 132.8, 132.0, 131.4, 131.3, 130.6, 130.5, 128.8, 128.6, 128.5, 128.0, 127.9, 127.5, 126.9, 126.9, 121.6, 121.1, 120.6, 117.1, 115.0, 115.0, 112.8, 112.7, 51.0, 51.0, 45.0, 45.0, 30.5, 30.4, 30.4 ppm; three carbons masked. MS (ESP+): *m/z* = 503 [M+Na$^+$]. Elem. anal. calc. for $C_{28}H_{20}N_2S_2O_2$ (480.60): C: 69.97%, H: 4.19%, N: 5.83%, found C 69.68%, H 4.05%, N 5.61%.

Mixture of 18 and 18'. To a degassed stirring solution of **15** (202 mg, 0.368 mmol) in dry CH_2Cl_2 (65 mL), toluene (5 mL) and acetyl chloride (2.0 mL) was added a solution of BBr_3 (3.8 mL, 1.0M in CH_2Cl_2, 3.8 mmol) and the resulting solution was stirred 16 h at rt. Ice was added to quench the reaction, followed by the addition of water (100 mL) and CH_2Cl_2 (100 mL). The phases were separated and the aqueous component was extracted with CH_2Cl_2 (50 mL). The combined organics were dried over $MgSO_4$, filtered and the solvent removed in vacuo. The crude residue was purified by column chromatography (SiO_2, 2% ethyl acetate / toluene) to afford an isomeric mixture (2:1 ratio of the 6 isomer to the 7 isomer) (125 mg, 65%) as an orange yellow solid. TLC (2% ethyl acetate / toluene): R_f = 0.37. M.p. = 213-225 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.84 (m, 4H), 7.73-7.70 (m, 4H), 7.68-7.66 (m, 4H), 7.53-7.50 (m, 6H), 7.46-7.41 (m, 6H), 6.99 (s, 1H), 6.98 (d, *J* = 6.9 Hz, 1H), 6.96 (s, 1H), 6.84 (dd, *J* = 11.5, 6.0 Hz, 1H), 6.76 (d, *J* = 11.5 Hz, 1H), 6.54 (d, *J* = 10.3 Hz, 1H), 6.49 (dd, *J* = 6.9, 1.3 Hz, 1H), 6.39 (dd, *J* = 6.0, 1.4 Hz, 1H), 6.06-6.03 (m, 2H), 3.87-3.84 (m, 2H), 2.47 (s, 3H), 2.46 (s, 3H), 2.45 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.0, 194.0, 194.0, 142.3, 142.1, 141.9, 141.8, 142.1, 141.0, 140.9, 140.7, 140.2, 139.5, 139.1, 135.1, 134.8, 134.7, 132.9, 132.1, 131.7, 131.7, 129.9, 129.8, 128.8, 128.6, 128.4, 128.1, 127.9, 127.9, 127.9, 127.5, 127.0, 126.9, 121.0, 120.6, 117.1, 115.2, 115.2, 113.0, 112.9, 51.1, 51.0, 45.0, 45.0, 30.4, 30.4, 30.4 ppm; nine carbons masked. MS (ESP+): *m/z* = 579 [M+Na$^+$]. Elem. anal. calc. for $C_{34}H_{24}N_2S_2O_2$ (556.70): C: 73.36%, H: 4.35%, N: 5.04%, found C: 73.18%, H: 3.91%, N: 4.75%.

2-[4-(Tributylstannyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (19). To an argon degassed solution consisting of DHA **8** (383 mg, 1.00 mmol) and Bu_6Sn_2 (1.0 mL, 2.29 mmol) in dry benzene (50 mL) was added $Pd(PPh_3)_4$ (80 mg, 0.0692 mmol) and the resulting solution was heated at reflux point until either TLC had indicated consumption of starting material or 16 h. The solvent was removed in vacuo and the crude residue was purified by flash column chromatography (SiO_2, gradient elution of 25% toluene / heptane to toluene) to afford **19** as an orange oil (355 mg, 65%), and the corresponding azulene **25** as a dark purple oil (104 mg, 20%). **DHA 19**: TLC (50% toluene / heptane): R_f = 0.50. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H, Sn satellites J_{SnH} = 36.5, 34.9 Hz), 6.90 (s, 1H), 6.57 (dd, J = 11.3, 6.4 Hz, 1H), 6.47 (dd, J = 11.3, 6.1 Hz, 1H), 6.34-6.29 (m, 2H), 5.83 (dd, J = 10.2, 3.8 Hz, 1H), 3.79 (dt, J = 3.8, 2.0 Hz, 1H), 1.61-1.51 (m, 6H), 1.35 (h, J = 7.3 Hz, 6H), 1.16-1.04 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3 (Sn satellites J_{SnC} = 361, 345 Hz), 140.8, 139.0, 137.4 (Sn satellites J_{SnC} = 30 Hz), 131.9, 131.1, 130.9, 129.9, 127.8, 125.3 (Sn satellites J_{SnC} = 40 Hz), 120.8, 119.6, 115.4, 113.0, 51.3, 45.2, 29.2 (Sn satellites J_{SnC} = 21 Hz), 27.5 (Sn satellites J_{SnC} = 58, 56 Hz), 13.8 , 9.8 (Sn satellites J_{SnC} = 342, 327 Hz) ppm. MS (ESP+): m/z = 569 [M+Na$^+$]. Elem. anal. calc. for $C_{30}H_{38}N_2Sn$ (545.35): C: 66.05%, H: 7.03%, N: 5.14%, found C: 65.93%, H: 7.09%, N: 5.18%. **2-[4-(Tributylstannyl)phenyl]azulene-1-carbonitrile (25)**: TLC (50% toluene / heptane): R_f = 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, J = 9.8 Hz, 1H), 8.40 (d, J = 9.8 Hz, 1H), 8.03 (d, J = 8.1 Hz, 2H), 7.77 (t, J = 9.8 Hz, 1H), 7.65 (d, J = 8.1 Hz, 2H, Sn satellites J_{SnH} = 37.5, 36.0 Hz), 7.56 (s, 1H), 7.53 (t, J = 9.8 Hz, 1H), 7.47 (t, J = 9.8 Hz, 1H), 1.63-1.54 (m, 6H), 1.36 (h, J = 7.3 Hz, 6H), 1.18-1.04 (m, 6H), 0.91 (t, J = 7.3 Hz, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6, 145.9, 145.0 (Sn satellites J_{SnC} = 369, 354 Hz), 142.7, 138.8, 137.9, 137.4 (Sn satellites J_{SnC} = 30 Hz), 135.7, 133.9, 128.0, 127.9, 127.8 (Sn satellites J_{SnC} = 40 Hz), 118.3, 116.5, 94.3, 29.3 (Sn satellites J_{SnC} = 20 Hz), 27.6 (Sn satellites J_{SnC} = 57, 56 Hz), 13.8, 9.8 (Sn satellites J_{SnC} = 341, 326 Hz) ppm. MS (ESP+): m/z = 542 [M+Na$^+$]. Elem. anal. calc. for $C_{29}H_{37}NSn$ (518.32): C: 67.18%, H: 7.20%, N: 2.70%, found C: 67.01%, H: 6.90%, N: 2.51%.

2-[4-(Trimethylstannyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (20). To a degassed solution consisting of the DHA **8** (382 mg, 1.00 mmol) and Me_6Sn_2 (0.50 mL, 2.4 mmol) in dry benzene (50 mL) was added $Pd(PPh_3)_4$ (62 mg, 0.0537 mmol) and the resulting solution was heated at reflux point for 16 h. The solvent was removed in vacuo and the crude residue was purified by column chromatography (SiO_2, 3% THF / heptane) to afford **20** as a yellow oil (386 mg, 92%) and the corresponding azulene **26** as a dark purple solid (12 mg, 3%). **DHA 20**: TLC (30% THF / heptane): R_f = 0.54. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, J = 9.7 Hz, 1H), 8.39 (d, J = 9.7 Hz, 1H), 8.03 (d, J = 8.1 Hz, 2H), 7.76 (t, J = 9.7 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H, Sn satellites J_{SnH} = 42.0, 40.2 Hz), 7.54-7.50 (m, 2H), 7.46 (t, J = 9.7 Hz, 1H), 0.36 (s, 9H, Sn satellites J_{SnH} = 55.5, 53.0 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2 (Sn satellites J_{SnC} = 437, 418 Hz), 140.6, 138.9, 136.7 (Sn satellites J_{SnC} = 36 Hz), 132.1, 131.0, 127.8, 125.5 (Sn satellites J_{SnC} = 44 Hz), 121.0, 119.6, 115.3, 112.9, 51.2, 45.2, -9.4 (Sn satellites J_{SnC} = 355, 339 Hz) ppm. MS (ESP+): m/z = 443 [M+Na$^+$]. Elem. anal. calc. for $C_{21}H_{20}N_2Sn$ (419.11): C: 60.16%, H: 4.81%, N: 6.69%, found C: 60.27%, H: 4.82%, N: 6.29%. **2-[4-(Trimethylstannyl)phenyl]azulene-1-carbonitrile (26)**: TLC (30% THF / heptane): R_f = 0.40. M.p. = 123 - 126 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, J = 9.7 Hz, 1H), 8.39 (d, J = 9.7 Hz, 1H), 8.03 (d, J = 8.1 Hz, 2H), 7.76 (t, J = 9.7 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H, Sn satellites J_{SnH} = 43.2, 41.3 Hz), 7.76 (t, J = 9.7 Hz, 1H), 7.54 (s, 1H), 7.54 (t, J = 9.7 Hz, 1H), 7.46 (t, J = 9.7 Hz, 1H), 0.36 (s, 9H, Sn satellites J_{SnH} = 55.5, 53.0 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5, 145.8, 144.9 (Sn satellites J_{SnC} = 445, 426 Hz), 142.6, 138.9, 137.9, 136.7 (Sn satellites J_{SnC} = 36 Hz), 135.7, 134.2, 128.1, 128.0, 127.8, 118.2, 116.6, 94.3, -9.4 (Sn satellites J_{SnC} = 353, 337 Hz) ppm. MS (ESP+): m/z = 807 [2M+Na$^+$], 416 [M+Na$^+$]). Elem. anal. calc. for $C_{20}H_{19}NSn$ (392.08): C: 61.25%, H: 4.89%, N: 3.57%, found C: 61.05%, H: 4.61%, N: 3.53%.

2-Phenyl-7-(trimethylstannyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (21). To a stirring solution of DHA **1** (512 mg, 2.00 mmol) in CH_2Cl_2 (30 mL), at -78 ºC, was added dropwise a solution of bromine in CH_2Cl_2 (2.56 mL, 0.78M, 2.00 mmol) and the resulting solution was stirred for 1 h. The cold bath was removed and immediately the solvent was removed using a diaphragm pump. The crude mixture was dissolved in THF (20 mL) and cooled in an ice bath. To this solution was added LiHMDS (2.1 mL, 1.0M in toluene, 2.1 mmol) and the contents of the vessel stirred for 2 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl and the phases separated. The organic phase was dried over $MgSO_4$, filtered and the solvent removed in vacuo. The residue (containing **9**) was taken up in dry benzene (100 mL) and hexamethylditin (0.90 mL, 4.34 mmol) was introduced to the vessel and the contents purged with argon. To this solution was added $Pd(PPh_3)_4$ (165 mg, 0.143 mmol) and the contents of the vessel heated to reflux point for 16 h. The vessel was allowed to cool to rt and the solvent was removed by rotary evaporation. The residue was subsequently purified by flash column chromatography (SiO_2, 50% toluene / heptane) to afford **21** (420 mg, 50% over 3 steps) as an orange oil. Additionally, the corresponding azulene **27** (85 mg, 11%) was isolated as a purple solid. **DHA 21:** TLC (50% toluene / heptane): R_f = 0.35. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 7.3 Hz, 2H), 7.49-7.42 (m, 3H), 6.86 (s, 1H), 6.66 (d, J = 10.7 Hz, 1H, Sn satellites J_{SnH} = 28.1 Hz), 6.51 (dd, J = 10.7, 6.2 Hz, 1H), 6.34 (broad d, J = 6.2 Hz, 1H), 5.67 (d, J = 4.1 Hz, 1H, Sn satellites J_{SnH} = 57.1 Hz), 3.48 (dd, J = 4.1, 1.6 Hz, 1H), 0.26 (s, 9H, Sn satellites J_{SnH} = 55.2, 52.8 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9 (Sn satellites J_{SnC} = 399, 382 Hz). 140.6, 137.6, 136.9 (Sn satellites J_{SnC} = 32 Hz), 132.2, 130.8, 130.0, 129.4, 128.1 (Sn satellites J_{SnC} = 44 Hz), 126.3, 123.6 (Sn satellites J_{SnC} = 43 Hz), 120.3, 115.5, 113.2, 52.7 (Sn satellites J_{SnC} = 58, 56 Hz), 44.6, -8.9 (Sn satellites J_{SnC} = 352, 336 Hz) ppm. MS (ESP+): m/z = 443 [$M+Na^+$]. Elem. anal. calc. for $C_{21}H_{20}N_2Sn$ (419.11): C: 60.16%, H: 4.81%, N: 6.69%, found C: 60.21%, H: 4.95%, N: 6.71%. **2-Phenyl-7-(trimethylstannyl)azulene-1-carbonitrile**

(27): M.p. = 120 - 122 ºC. TLC (50% toluene / heptane): R_f = 0.18. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (s,1H, Sn satellites J_{SnH} = 50.7 Hz), 8.31 (d, J = 9.6 Hz, 1H), 8.08-8.06 (m, 2H), 7.92 (d, J = 9.6 Hz, 1H, Sn satellites J_{SnH} = 53.1 Hz), 7.55-7.52 (m, 2H), 7.48 (s, 1H), 7.47-7.43 (m, 1H), 7.40 (t, J = 9.6 Hz, 1H, Sn satellites J_{SnH} = 5.2 Hz), 0.47 (s, 9H, Sn satellites J_{SnH} = 55.0, 52.6 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 146.6 (Sn satellites J_{SnC} = 416, 397 Hz), 146.3 (Sn satellites J_{SnC} = 38 Hz), 145.0 (Sn satellites J_{SnC} = 61, 59 Hz), 142.6 (Sn satellites J_{SnC} = 44 Hz), 142.6, 137.4, 134.7, 129.4, 129.2, 128.7, 127.6 (Sn satellites J_{SnC} = 58, 57 Hz), 118.4, 116.0, 93.4, -8.3 (Sn satellites J_{SnC} = 352, 337 Hz) ppm. MS (ESP+): m/z = 807 [2M+Na^+], 416 [M+Na^+]. Elem. anal. calc. for $C_{20}H_{19}NSn$ (392.08): C: 61.25%, H: 4.89%, N: 3.57%, found C: 61.56%, H: 4.89%, N: 3.50%.

7-(Trimethylstannyl)-2-[4-(trimethylstannyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (22). To a stirring solution of the DHA **8** (1.43 g, 3.74 mmol) in CH_2Cl_2 (50 mL), at -78 ºC, was added dropwise a solution of bromine in CH_2Cl_2 (4.9 mL, 0.78M, 3.8 mmol) and the resulting solution was stirred for 1 h. The cold bath was removed and immediately the solvent was removed using a diaphragm pump. The crude mixture was dissolved in THF (50 mL) and cooled in an ice bath. To this solution was added LiHMDS (4.0 mL, 1.0M in toluene, 4.0 mmol) and the contents of the vessel stirred for 2 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl and the phases separated. The organic phase was dried over $MgSO_4$, filtered and the solvent removed in vacuo. The residue (containing **11**) was taken up in dry benzene (100 mL) and hexamethylditin (3.2 mL, 15.4 mmol) was introduced to the vessel and the contents purged with argon. To this solution was added $Pd(PPh_3)_4$ (435 mg, 0.376 mmol) and the reaction vessel was set to reflux point for 16 h. The vessel was allowed to cool to rt and the solvent as removed by rotary evaporation. The residue was subsequently purified by flash column chromatography (SiO_2, 2%

THF / heptanes) to afford **22** (1.11 g, 51% over 3 steps) as an orange oil. Additionally, the corresponding azulene **28** (22 mg, 1%) was isolated as a purple solid. **DHA 22:** TLC (30% THF / heptane): R_f = 0.58. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H, Sn satellites J_{SnH} = 42.2, 40.3 Hz), 6.87 (s, 1H), 6.65 (d, J = 10.6 Hz, 1H, Sn satellites J_{SnH} = 28.3 Hz), 6.51 (dd, J = 10.6, 6.0 Hz, 1H), 6.33 (broad d, J = 6.0 Hz, 1H), 5.67 (d, J = 4.1 Hz, 1H, Sn satellites J_{SnH} = 57.3 Hz), 3.48 (dd, J = 4.1, 1.6 Hz, 1H, Sn satellites J_{SnH} = 11.0 Hz), 0.33 (s, 9H, Sn satellites J_{SnH} = 55.6, 53.2 Hz), 0.25 (s, 9H, Sn satellites J_{SnH} = 55.2, 52.7 Hz) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.0 (Sn satellites J_{SnC} = 439, 419 Hz), 141.9 (Sn satellites J_{SnC} = 399, 382 Hz), 140.9, 137.8, 136.8 (Sn satellites J_{SnC} = 32 Hz), 136.7 (Sn satellites J_{SnC} = 36 Hz), 131.8, 130.4 (Sn satellites J_{SnC} = 11 Hz), 128.2 (Sn satellites J_{SnC} = 44 Hz), 125.4 (Sn satellites J_{SnC} = 45 Hz), 123.7 (Sn satellites J_{SnC} = 44 Hz), 120.2, 115.6, 113.3, 52.7 (Sn satellites J_{SnC} = 58, 56 Hz), 44.5, -8.9 (Sn satellites J_{SnC} = 351, 336 Hz), -9.4 (Sn satellites J_{SnC} = 355, 339 Hz) ppm. MS (ESP+): m/z = 605 [M+Na$^+$]. Elem. anal. calc. for $C_{24}H_{28}N_2Sn_2$ (581.91): C: 49.51%, H: 4.85%, N: 4.81%, found C: 49.47%, H: 4.85%, N: 4.69%. **7-(Trimethylstannyl)-2-[4-(trimethylstannyl)phenyl]azulene-1-carbonitrile (28)**: TLC (30% THF / heptane): R_f = 0.52. M.p. = 135 - 137 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H, Sn satellites J_{SnH} = 50.7 Hz), 8.32 (d, J = 9.5 Hz, 1H), 8.03 (d, J = 8.1 Hz, 2H), 7.92 (d, J = 9.5 Hz, 1H, Sn satellites J_{SnH} = 53.0 Hz), 7.68 (d, J = 8.1 Hz, 2H, Sn satellites J_{SnH} = 42.4 Hz), 7.50 (s, 1H), 7.41 (t, J = 9.5 Hz, 1H), 0.46 (s, 9H, Sn satellites J_{SnH} = 55.0, 52.6 Hz), 0.35 (s, 9H, Sn satellites J_{SnH} = 55.3, 53.1 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 146.6 (Sn satellites J_{SnC} = 416, 398 Hz), 146.3 (Sn satellites J_{SnC} = 38 Hz), 145.1 144.8 (Sn satellites J_{SnC} = 447, 427 Hz), 142.7, 142.6 (Sn satellites J_{SnC} = 44 Hz), 137.4, 136.7 (Sn satellites J_{SnC} = 36 Hz), 134.5 (Sn satellites J_{SnC} = 11 Hz), 128.1 (Sn satellites J_{SnC} = 45 Hz), 127.5 (Sn satellites J_{SnC} = 57 Hz), 118.4, 116.0, 93.5, -8.3 (Sn satellites J_{SnC} = 352, 337 Hz), -9.4 (Sn satellites J_{SnC} = 353, 337 Hz) ppm. MS (ESP+): *m/z* = 578 ($[M+Na]^+$). HRMS ($C_{23}H_{27}NSn_2Na^+$): calcd 578.0073; found 578.0079 $[M+Na^+]$.

***S*-[4'-(1,1-Dicyano-1,8a-dihydroazulen-2-yl)-(1,1'-biphenyl)-4-yl] ethanethioate (24).** To a stirring mixture of 4-iodophenylthioacetate **23** (80 mg, 0.288 mmol), Pd_2dba_3 (32 mg, 0.0349 mmol) and $AsPh_3$ (43 mg, 0.140 mmol) under an argon atmosphere in a microwave tube was added a degassed toluene solution of the stannane **19** (94 mg in 4 mL, 0.172 mmol). The resulting solution was heated to 110 ºC for 30 min. The cooled reaction mixture was directly loaded onto a flash column and eluted (SiO_2, 1% ethyl acetate / toluene) to afford **24** (8 mg, 7%) as a yellow solid. M.p. = 155 - 157 ºC. TLC (1% ethyl acetate / toluene): R_f = 0.33. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 6.94 (s, 1H), 6.58 (dd, *J* = 11.3, 6.2 Hz, 1H), 6.49 (dd, *J* = 11.3, 5.7 Hz, 1H), 6.37 (broad d, *J* = 5.7 Hz, 1H), 6.32 (ddd, *J* = 10.2, 6.2, 2.1 Hz, 1H), 5.84 (dd, *J* = 10.2, 3.8 Hz, 1H), 3.82 (dt, *J* = 3.8, 2.1 Hz, 1H) 2.46 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.0, 141.7, 141.0, 139.7, 138.8, 135.0, 132.5, 131.1, 131.0, 129.9, 128.0, 127.9, 127.8, 126.9, 121.3, 119.6, 115.3, 112.9, 51.2, 45.3, 30.4 ppm; one carbon masked. MS (ESP+): *m/z* = 429 $[M+Na^+]$. Elem. anal. calc. for $C_{26}H_{18}N_2OS$ (406.50): C: 76.83%, H: 4.47%, N: 6.90%, found C: 77.09%, H: 4.22%, N: 6.64%.

***S*-[4'-(1,1-Dicyano-1,8a-dihydroazulen-2-yl)-(1,1'-biphenyl)-4-yl] ethanethioate (24).** To a stirring mixture of 4-iodophenylthioacetate **23** (140 mg, 0.503 mmol), Pd_2dba_3 (63 mg, 0.0688 mmol) and $AsPh_3$ (79 mg, 0.258 mmol) under an argon atmosphere in a microwave tube was added a degassed toluene solution of the stannane **20** (140 mg in 4 mL, 0.334 mmol). The resulting solution was heated to 110 ºC for 15 min. The cooled reaction mixture was directly loaded onto a flash column and eluted with 1% ethyl acetate / toluene to afford **24** (98 mg, 72%) as a yellow solid.

***S*-[4-(3,3-Dicyano-2-phenyl-3,3a-dihydroazulen-5-yl)phenyl] ethanethioate (16).** A thoroughly degassed solution of the stannane **21** (67 mg, 0.160 mmol) in toluene (4 mL) was added via cannula to a deoxygenated microwave vessel containing 4-iodophenylthioacetate **23** (70 mg, 0.252 mmol), Pd_2dba_3 (32 mg, 0.0349 mmol) and $AsPh_3$ (39 mg, 0.127 mmol). The resulting solution was heated to 110 °C for 15 min and then allowed to cool to ambient temperature. The solution was subjected to flash column chromatography (SiO_2, 2% ethyl acetate / toluene) to afford **16** (43 mg, 66%) as a yellow solid. M.p. = 132 - 134 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.51-7.40 (m, 7H), 6.91 (s, 1H), 6.83 (dd, *J* =11.4, 6.0 Hz, 1H), 6.76 (d, *J* = 11.4 Hz, 1H), 6.37 (dd, *J* = 6.0, 1.6 Hz, 1H), 6.02 (d, *J* = 4.7 Hz, 1H), 3.84 (dd, *J* = 4.7, 1.6 Hz, 1H), 2.43 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.0, 141.5, 141.2, 140.8, 139.1, 134.7, 132.9, 131.6, 130.4, 129.4, 128.6, 126.5, 120.3, 117.1, 115.2, 113.0, 51.1, 45.1, 30.4 ppm; three carbons masked. MS (ESP+): *m/z* = 429 [M+Na$^+$]. Elem. anal. calc. for $C_{26}H_{18}N_2OS$ (406.11): C: 76.83%, H: 4.47%, N: 6.90%, found C: 76.93%, H: 4.48%, N 7.06%.

***S*-{4-[2-(4'-(Acetylthio)-[1,1'-biphenyl]-4-yl)-3,3-dicyano-3,3a-dihydroazulen-5-yl]phenyl} ethanethioate (18).** A thoroughly degassed solution of **22** (52 mg, 0.0894 mmol) in toluene (4 mL) was added via cannula to a deoxygenated microwave vial containing 4-iodophenylthioacetate **23** (80 mg, 0.288 mmol), Pd_2dba_3 (34 mg, 0.0371 mmol) and $AsPh_3$ (43 mg, 0.140 mmol). The resulting solution was heated to 110 °C for 15 min and then allowed to cool to ambient temperature. The solution was then subjected to flash column chromatography (SiO_2, 2% ethyl acetate / toluene) to result in the isolation of **18** (16 mg, 33%) as a yellow solid. M.p. = 208 - 211 ºC. IR (ATR): ν 2920w, 2852vw, 1418w, 1396m, 1350w, 11116m, 1092m, 1014w, 1004m, 943m, 916w, 902w, 853w, 839w, 757m, 544m cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J*

= 8.6 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 6.96 (s, 1H), 6.84 (dd, *J* = 11.5, 6.0 Hz, 1H), 6.77 (d, *J* = 11.5 Hz, 1H), 6.40 (dd, *J* = 6.0, 1.5 Hz, 1H), 6.04 (d, *J* = 4.7 Hz, 1H), 3.87 (dd, *J* = 4.7, 1.5 Hz, 1H), 2.46 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.9, 193.8, 141.8, 141.1, 140.9, 140.8, 140.6, 139.0, 134.9, 134.6, 132.8, 131.6, 129.7, 128.4, 128.0, 127.8, 127.8, 126.9, 120.4, 117.0, 115.1, 112.9, 50.9, 44.9, 30.3, 30.3 ppm; two carbons masked. HRMS ($C_{34}H_{24}N_2O_2S_2Na^+$): calcd 579.1171; found 579.1172 [M+Na$^+$].

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Supporting Information Available: NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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