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ORIGINAL PAPER

1-Phenylselanylazulenes: synthesis and selenium atom oxidation

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Abstract The phenylselanylation of azulene with PhSeCl or PhSeBr was reported. Clean electrophilic substitution of azulene in positions 1 and/or 3 occurred with the first reagent whereas with PhSeBr a complex mixture of products was generated suggesting a radicalic mechanism. The influence on the reaction route of the substituent attached at position 1 of azulene, or of the alkyl positions in alkylated azulenes was investigated. 1-Phenylselanylazulene and 1,3-bis(phenylselanyl)azulene were oxidized using sodium metaperiodate. The oxidation took place at selenium atom and afforded azulenes substituted with PhSe(O) and/or PhSe(O_2) groups in positions 1 and/or 3. The magnetic and electronic spectra as well as the electrochemical oxidation and reduction potentials of the obtained products were recorded and the results were briefly discussed.

Keywords Azulene · Selenides · Electrophilic substitutions · Oxidations · Ionization potentials

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Introduction

The organic compounds containing selenium atom(s) in the molecule are investigated for medical purposes as detoxifiant [1], cancer chemoprotectors [2–4], enzyme inhibitors, anti-inflammatory [5, 6], antitumor [7–9], biocide [10], or antioxidative stress agents [11]. Several data concerning the possibility of some aliphatic selenoxides to mimic the behavior of the enzyme glutathione peroxidase (GPx) [12] are known; some aromatic selenoxide derivatives have been also prepared and tested as GPx mimics [13]. However, similar to almost all drugs containing heavy atoms, the selenium containing compounds are considered "Janus compounds", the difference between good and evil effects being made by the administrated amount [14]. Excessive or inappropriate angiogenesis, as observed in some cancer diseases, were treated with diaryl derivatives of Se (IV and VI) [15]. Other similar selenium compounds were considered to participate in the biologic electron transfer, being tested as GPx mimics [16, 17]. Due to the several stable oxidation states, selenium develops a rich electrochemistry that has been recently reviewed by Jaworski [18].

Azulene represents one of the outstanding aromatic hydrocarbons due to its charge distribution over the molecular frame. The permanent electron density polarization toward the five-membered ring, reflected on the relatively high electric dipole, as well as its easy polarization under external factors fascinated the researchers. It is noteworthy to remind the increased azulene nucleophilicity at 1(3)-position as compared with other aromatic hydrocarbons. This property is improved by the presence of alkyl groups mainly in the seven-membered ring.

A remarkable effort was devoted to the study of the azulene derivatives containing sulfur atom(s) in molecule, in particular to those containing aryl- or alkyl-sulfenyl

group(s) [19–23]. The electrophilic substitution of azulenes was the reported route for the introduction of several sulfur-containing groups. Thus, the reaction of 4,6,8-trimethylazulene with PhSCl occurs in position 1 in 54 % yield for an equimolar ratio of azulene and PhSCl [24], and in both 1- and 3-positions (86 %) for a molar ratio PhSCl : azulene = 2 [25]. Until recently, less importance was given for the azulene compounds containing other chalcogen atoms, e.g., selenium or tellurium in their structures. However, during our exploration on (azulen-1-yl) diazenes, we were interested in the synthesis and properties of such compounds with azulenyl moiety substituted with groups containing chalcogen [26]. From the numerous explored strategies aiming the preparation of the aryl selenides [27–30] neither of them could be applied to azulene compounds. Therefore, we have adapted the procedure used for the synthesis of corresponding sulfur derivatives [24, 25]. Thus, the phenylselanylation of azulenic diazenes was accomplished with phenyl hypobromoselenoite (PhSeBr) or with phenyl hypochloroselenoite (PhSeCl). We established, however, that only the last reagent successfully affords the targeted products without undesirable by-products.

In the further research on azulenes phenylselanylation, we have decided to direct our preoccupations on the systematic investigation to the influence of alternative azulene substituents on this reaction. Because several alkylated azulenes are cheaper, more accessible, and even more stable than azulene itself, they were tested to see if they could give good results in this synthesis. Taking into account the possible use of selenoxides in the medical field, other target of our research was the study of the selenides oxidation. As part of our ongoing research, the magnetic and electronic spectra, as well as the electrochemical oxidation and reduction potentials of the obtained products, were recorded and the results were briefly discussed.

Results and discussion

Selenide synthesis

Starting from the azulene pattern, clean phenylselanylation was observed (Scheme 1) when PhSeCl was used at low temperatures (−40 °C) whereas a higher temperature produces advanced polymerization. The reaction mixture contained mainly 1-(phenylselanyl)azulene (**2**) and a minor amount of 1,3-bis(phenylselanylated) compound (**3**). A lower selectivity was observed in the presence of PhSeBr. The obtained reaction composition proved to be very complex containing compound **3** (34 %) and 1-bromoazulene (**5**, 23 %) as main products, together with small quantities of compound **2** (7 %) and 3-bromo-1-(phenylselanyl)azulene (**4**, 7 %), and traces of 1,3-dibromoazulene (Scheme 1). A small amount of undefined oligomers has also been detected. We have explained this difference of the reaction selectivity considering a modification of the mechanism from electrophilic in the case of PhSeCl to radicalic for the bromide correspondent.

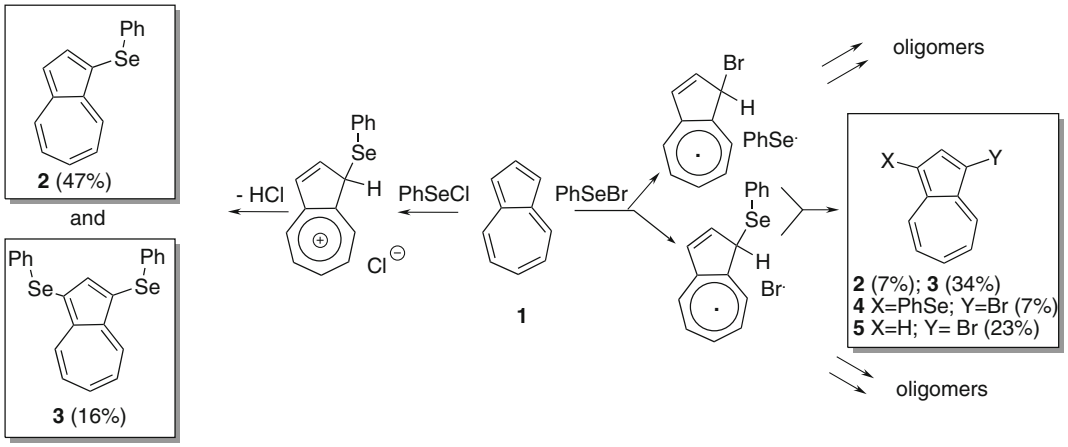
The net separation of compound **4** from the reaction mixture was very difficult for larger amounts; therefore, to characterize this new compound, it was synthesized by reaction of 1-(phenylselanyl)azulene with commercial *N*-bromosuccinimide. The resulted reaction mixture contained in this case mainly compound **4** (44 %), but unexpectedly also 1,3-bis(phenylselanyl)azulene (**3**, 22 %) and 1,3-dibromoazulene (24 %).

Taking into account the suitable results obtained at the selective phenylselanylation of azulene with PhSeCl, we have applied this protocol to other azulene derivatives (Scheme 2). Both the alkylated azulenes (compounds **7**) and those substituted with electron donor or acceptor groups in 1-position (compounds **6**) were submitted to phenylselanylation. As expected, the required reaction conditions were different for these compounds, being dependent on the azulene substituents. Thus, for azulene or azulenes with electron donor groups (e.g., R = $PhCO_2$ or AcNH) in 1-position, the reaction was performed at low temperatures in diethyl ether. Despite the mild reaction conditions, the obtained yields were moderate, possible due to the instability of the resulted products, especially at the work-up of reaction mixture. When 1-position was substituted with mild acceptors (e.g., R=$COCH_3$ or CO_2Me), the reaction occurred in dichloromethane (DCM) at room temperature with yields of about 80 %. The attack on the azulene substituted with NO_2 occurred difficultly because the nitro group strongly diminishes the nucleophilicity of the entire azulenic system. The reaction had to be carried out in DCM at reflux when both the starting 1-nitroazulene and the reaction product were partially destroyed dropping the yield to 55 %.

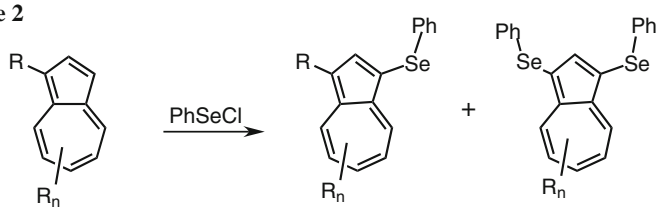
Whereas for unsubstituted azulene and 6-methylazulene (**7a**) mono and, to a lesser extent, double phenylselanylation were observed, for substrates with methyl groups in positions 4 and 8 (Scheme 2), as in 4,6,8-trimethylazulene (**7b**) or 6-*t*-butyl-4,8-dimethylazulene (**7c**), no double substitution was detected. At the same time, the phenylselanylation yield was diminished below 50 %. The position of methyl groups in these compounds is sufficiently close to the reaction center to suppress partially the first attack of the bulky selenium atom and to block the second substitution.

Taking into account the good overall yield obtained by Hafner et al. [23], when **7b** was reacted with two equivalents of PhSCl and hoping to increase the yield of phenylselanylation, we performed the reaction of 4,6,8-

Scheme 1



Scheme 2



[R_n=H];R=	AcNH	ThiCH=CH*	$PhCO_2$	PhS	CO_2Me	CHO	Ac	CF_3CO	NO_2
	8a	**8b**	**8c**	**8d**	**8e**	**8f**	**8g**	**8h**	**8i**
η/%	72	69	71	75	82	83	79	80	55

R=H; R_n=	H	6-Me	4,6,8-Me_3	4,8-Me_2-6-*t*Bu
	2/3	**9a/10a**	**9b**	**9c**
η/%	47/16	51/16	45	49

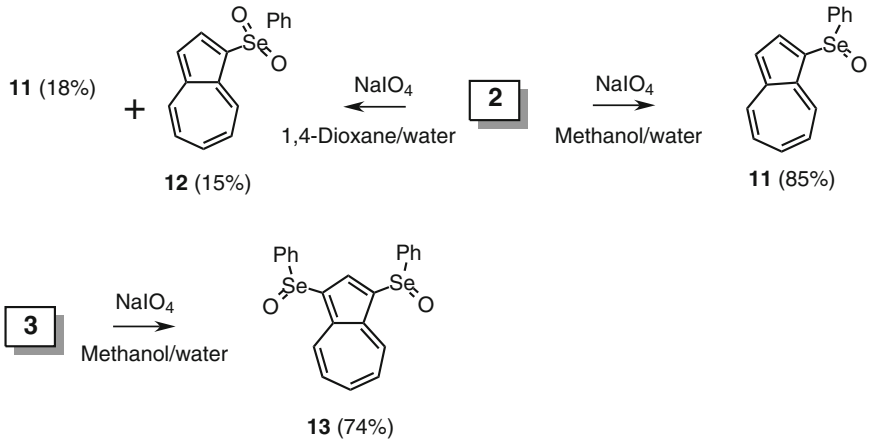
*Thi = Thien-2-yl

trimethylazulene using two equivalents of PhSeCl. Unfortunately, the reaction route followed in this case was much more complicated, and, additionally, the resulted products were altered on the chromatographic column during the separation procedure. The behavior of this compound, as well as that of guaiazulene, is currently investigated.

Selenides oxidation

The potential use of selenoxides in the medical field stimulated us to explore the oxidation of the obtained selenides and to determine their properties [31]. A large number of procedures for the selenides oxidation are described in the literature as for example the oxidation with hydrogen peroxide [32], ozone and peracetic acid [33], dinitrogen tetroxide [34], dichloroiodobenzene [35], *N*-bromosuccinimide, *N*-chlorosuccinimide or *t*-butyl hypochlorite [36], peroxo complexes of transitional metals, such as molybdenum [37]. Unfortunately, most of these reagents are not compatible with the azulenyl system. For example, hydrogen peroxide in acidic medium induces azulene polymerization. Other oxidizing agents, such as positively polarized halogens, lead to substitution in the position 3 of azulene. However, it is known that 1-azulenylsulfides can be oxidized to the corresponding sulfoxides or sulfones with sodium metaperiodate, a mild, neutral oxidant [23]. Several resemblances between the chemical behavior of arylsulfides and the corresponding selenides led us to use this reagent for the oxidation of selenium atom belonging to the phenylselanylated compounds. Thus, when the compound **2** was reacted with $NaIO_4$ one hour at reflux in a mixture of methanol and water, the corresponding 1-(phenylseleninyl) azulene (**11**) was obtained in 85 % yield (Scheme 3). It is interesting to note that the red-violet color of this compound resembles the color of the corresponding sulfur derivative and thus confirms our previous

Scheme 3



observation that the differences between the "chromophores" PhS and PhSe are almost insignificant for all azulene derivatives [25].

To obtain the 1-(phenylselenonyl) azulene (**12**), the reaction time was extended and an excess of $NaIO_4$ was added. It seems, however, that these conditions are not severe enough for selenium to reach the VI oxidation state [38]. Therefore, methanol was replaced with 1,4-dioxane to ensure a higher reflux temperature. In this way, the desired product **12** was obtained in 15 % yield together with the corresponding phenylseleninyl compound **11** and a high amount of polymeric tar. Despite its limited stability in solution (it was partially polymerized in time), the brown-colored compound **12** was separated by column chromatography. The oxidation of 1,3-bis(phenylselanyl)azulene in methanol/water gave 1,3-bis(phenylseleninyl) azulene (**13**) in good yield. The recorded NMR spectrum of bis-selenoxide **13** seems to indicate the presence of a mixture of the diastereoisomers, namely the enantiomeric pair and the mesostructure, which could not be separated. This assumption is in concordance with the reported chiral diaryl selenoxides prepared by oxidation of the corresponding selenides with hydrogen peroxide [39].

Influence of selenium containing groups on the magnetic and electronic spectra

As results from the Table 1, a PhSe group placed in 1-position of azulene, compound **2**, deshields all azulenyl protons in the ^{1}H NMR spectrum. This effect, common with that exerted by the PhS group [26], can be assigned to the electron-withdrawing nature of the phenyl-chalcogen substituents. The chemical shift values δ_H for an azulenyl moiety substituted with phenyl-chalcogen groups range between those for azulenic compounds with electron-withdrawing groups (–E) and those for azulene itself. The

Table 1 Chemical shifts of azulenyl protons in ^{1}H NMR spectra of selenium containing compounds and other azulenyl derivatives

Compound	δ_H/ppm					
	H2	H4	H5	H6	H7	H8
1	7.81	8.23	7.05	7.45	7.05	8.23
2	8.12	8.42	7.30	7.70	7.32	8.72
1-Acetylazulene	8.30	8.48	7.47	7.81	7.61	9.91
Azulen-1-yl(phenyl)sulfane	8.04	8.38	7.29	7.68	7.29	8.69
11	7.92	8.45	7.39	7.78	7.43	8.90
1-(Phenylsulfinyl)azulene	7.89	8.42	7.40	7.79	7.46	9.00
12	8.30	8.59	7.58	7.95	7.65	9.49

deshielding observed for the proton H-8 in compound **11**, in its corresponding thio analog [27], as well as in compound **12** is due to the anisotropic effect of the double bond belonging to these substituents on H-8. This effect can be also induced by the C=O bond in 1-acetylazulene, where it is even more intense.

The electronic spectra of 1-phenylselanylazulenes contain two bands: one intense at $\lambda = 350$–400 nm and the second, less intense at 500–570 nm. As for other azulenic compounds, these values are influenced by the substituent at 3-position in azulene. As expected, by oxidation hypsochromic shifts were observed for the absorption maxima of compounds **11** and **13** as compared with the compound **2** and **3**.

Electrochemical properties

The oxidation potentials of some diaryl selenides were thoroughly investigated by several authors [40, 41]. The decrease of oxidation potentials for diphenyl chalcogenides in the order S > Se > Te [1.56 V > 1.38 V > 0.95 V (NHE)] [40, 42] proves the direct involvement of the

Table 2 The first oxidation and reduction potentials of azulene and azulenic compounds containing selenium atoms (from DPV experiments in acetonitrile with TBAP 10^{-1} M)

No	**1**	**2**	**8a**	**8c**	**8d**	**3**	**8g**	**8f**	**8i**	**11**	**12**
R		H	AcNH	$PhCO_2$	PhS	PhSe	Ac	CHO	NO_2	Se^{IV}	Se^{VI}
E_{ox}/V	0.61	0.36	0.28	0.39	0.38	0.38	0.62	0.71	0.76	0.41	0.64
E_{red}/V	−2.08	−1.82	−1.62	−1.70	−1.64	−1.65	−1.57	−1.43	−1.30	−1.35	−1.34

The potentials are reported to the Fc/Fc^+ couple, which is at 0.424 V vs. $Ag^+/AgCl$ (std)

heteroatom in the oxidation process. The quite high oxidation potential of diphenyl selenide attests that the selenium atom is the first part of the molecule that is oxidized to mono- and di-positive ions, which interact further with anions or with the starting materials [43–45]. The phenyl moiety is involved in charge delocalization only if it is substituted with strong electron donating groups [41, 46]. The study of an impressive number of disubstituted diaryl selenides revealed that their oxidation potentials are well correlated by Hammett equations [46].

Just as the chemistry of the investigated phenylselanylated azulenes, their electrochemistry is deeply influenced by this nonbenzenoid aromatic system with low values of oxidation and reduction potentials. As a result, in azulen-1-yl selenides, azulene moiety competes with selenium as the oxidation center.

The first oxidation and reduction peaks of azulene (**1**), as well as its above obtained selenium derivatives, are presented in Table 2. The substitution of azulene with PhSe group determines the decrease in the oxidation and the reduction potentials in compound **2** (in absolute value) in spite of the relatively high oxidation potential of PhSe group (which is 1.38 V vs. NHE in Ph_2Se). However, it is remarkable that the decrease in oxidation potential is also present for other 1-substituted azulenes, e.g., for the compounds **6** (R=Me, AcNH, PhS) [25, 47]. It is interesting to note that the second substituent introduced in compound **2** induces a variation of the redox potentials of compounds **8** in function of its nature. Whereas those possessing an -I effect (NHAc, $PhCO_2$, PhS, etc.) have no notable influence on the oxidation potential, the -E groups (Ac, CHO, and NO_2) are associated with an important increase of these potentials. If the second substituents introduced in the compound **2** contains relative easily reducible double bonds, as C=O and N=O, a decrease of the reduction potentials was observed. Higher oxidation states of selenium in compounds **11** and **12** increases also the oxidation potentials and diminish the reduction ones.

A very good correlation ($R = 0.984$) between the oxidation potential E_{ox} and Hammett σp constants was obtained (Fig. 1) for the azulene derivatives **8**, in agreement with that already reported for the diarylselenides [46].

Conclusions

The electrophilic substitution of azulene moiety with PhSe group, using PhSeCl as reagent, occurred at the five-membered azulene ring (position 1/3). Moderate yields were obtained for azulene and its alkylated derivatives. While an alkyl group in 8-position reduced the reaction yields, two methyl groups in 4- and 8-positions prevent the double phenylselanylation. Good yields in 3-phenylselanylated products were obtained starting from 1-substituted azulene with electron donor groups or with mild deactivating groups. A completely different phenylselanylation route was observed when PhSeBr was used as reagent, possible due to the change of the reaction mechanism. The oxidation of the compounds **2** and **3** with sodium metaperiodate, a mild and neutral oxidant, occurred at selenium atom and afforded azulenes with phenylseleninyl, PhSe(O) and/or phenylselenonyl, $PhSe(O_2)$ groups in 1- and/or 3- positions. Several data regarding electronic and nuclear magnetic spectra are also reported. Further investigations of the selanylation of other substituted azulene and of the influence of azulenes-/PhSeCl ratio on the reaction pathway are subjects of a future work.

In spite of the relatively high oxidation potential of PhSe group, a decrease of the oxidation and reduction potentials was observed at the substitution of azulene with this group in 1-position. This seems to be a general behavior for 1-substituted azulenes. For the disubstituted compounds **8**, the redox potentials are also influenced by the second azulene substituent. As expected, with the increasing of the oxidation states of selenium in the substituents PhSe(O) and/or $PhSe(O_2)$ of compounds **11** and **12**, the oxidation potentials rise while the reduction potentials decrease.

Experimental

Melting points Kofler apparatus (Reichert Austria). Elemental analyses (C, H, and N) were conducted using the Elemental Analyzer XBO, their results were found to be in good agreement (± 0.3 %) with the calculated values. UV spectra in methanol and dioxane: Varian Cary Bio 100

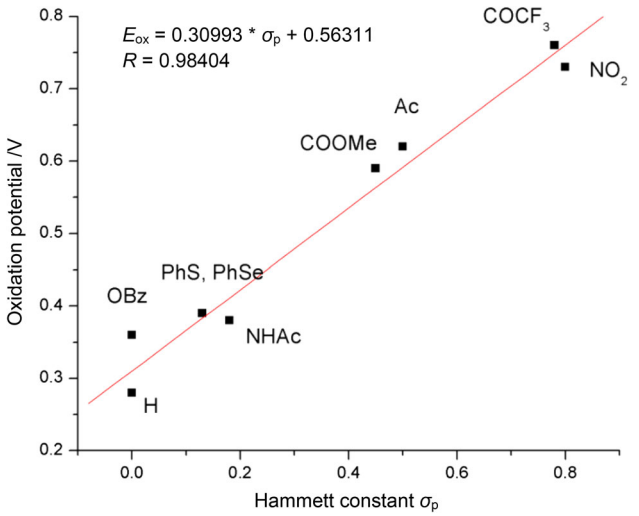


Fig. 1 Oxidation potential E_{ox}—Hammett σ_p constant correlation for compounds **8**R; data from DPV experiments in acetonitrile with TBAP 10^{-1} M; all potentials were referred to Fc/Fc^+ couple

spectrophotometer; λ values are given in nm, while log ε has no dimension; the molar extinction, ε, is expressed in M^{-1} cm^{-1} units. ^1H and ^{13}C NMR: Bruker Avance DRX 400 (^1H: 400 MHz, ^{13}C: 100.62 MHz), J values are given in Hz, TMS was used as internal standard in $CDCl_3$ as solvent; several signals were assigned on the basis of H–H COSY experiments. Mass spectra: Varian 1200 L Triple Quadrupole LC/MS/MS spectrometer by direct injection in ESI. For the column chromatography silica gel 60 or alumina (II–III Brockmann grade, 70–230 mesh ASTM) were used. The DCM was distilled over CaH_2 and the ether was preserved on sodium. The compounds nomenclature was obtained by the CambridgeSoft package of structure-to-name algorithm included with ChemBioDraw Ultra 11.

*Synthesis of azulen-1-yl(phenyl)selanes either unsubstituted or substituted with alkyl groups using phenylseleninyl halides (**2**, **3**, **9a–9c**, **10a**)—general procedure*

To a stirred solution of azulene (**1**) or alkylated azulenes **7** (1 mmol) in 2 cm^3 anhydrous ethyl ether, at −40 to −50 °C under a dry nitrogen atmosphere, an ethereal solution of 192 mg PhSeCl (1 mmol) was added in portions during 30 min (the reagent must be protected from moisture using a weighing bottle). After 20 min of stirring at −40 °C, the reaction mixture was allowed to warm slowly to room temperature with a temperature gradient of about 1 °C/min and was stirred for another 10 min. The blue- or green-colored solution was diluted to 10 cm^3 with ether, was washed with water, 1 N sodium carbonate solution, again with water and was dried over anhydrous Na_2SO_4. The solvent was removed in vacuum and the residue was chromatographed on silica gel, using *n*-pentane for the elution of unreacted azulenic compound, as a blue band. Then one or two large blue bands were eluted with a mixture of *n*-pentane-DCM (with DCM gradient): the first band consists of the mono-phenylselanylated product, while the second contained the 1,3-bis-phenylselanylated compound (only for azulene (**1**) and 6-methylazulene (**7a**)).

The same protocol as for the reaction with PhSeCl in ethyl ether at low temperature was used for reaction between azulene and PhSeBr. However, the chromatographic separation occurred using only *n*-pentane because the presence of a larger number of fractions that made the separation more difficult. First a very small band of 1,3-dibromoazulene was eluted, than eluted 1-bromoazulene followed by azulene, 3-bromo-1-(phenylselanyl)azulene, 1-(phenylselanyl)azulene, and 1,3-bis(phenylselanyl)-azulene.

1-(Phenylselanyl)azulene, (**2**, $C_{16}H_{12}Se$)
Blue-violet crystals; yield: 133 mg (47 %); m.p.: 79 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.08–7.14 (m, 5H, Ph), 7.30 (t, ^3J = 9.7 Hz, 1H, 5-H), 7.32 (t, ^3J = 9.7 Hz, 1H, 7-H), 7.50 (d, ^3J = 3.9 Hz, 1H, 3-H), 7.70 (t, ^3J = 9.9 Hz, 1H, 6-H), 8.12 (d, ^3J = 3.9 Hz, 1H, 2-H), 8.42 (d, ^3J = 9.6 Hz, 1H, 4-H), 8.72 (d, ^3J = 9.8 Hz, 1H, 8-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.3, 118.2, 124.4, 124.5, 125.6, 128.8, 129.0, 134.9, 136.9, 137.3, 138.3, 141.8, 142.1, 144.7 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 235 (4.35), 279 (4.61), 288 sh (4.48), 339 (3.62), 356 (3.60) nm; MS (ESI): m/z = 285 ($[M+1]^+$, ^{80}Se).

1,3-Bis(phenylselanyl)azulene (**3**, $C_{22}H_{16}Se_2$)
Blue-violet crystals; yield: 70 mg (16 %); m.p.: 115 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.10-7.16 (m, 10H, Ph), 7.42 (t, ^3J = 9.9 Hz, 2H, 5-H, 7-H), 7.77 (t, ^3J = 9.8 Hz, 1H, 6-H), 8.28 (s, 1H, 2-H), 8.76 (d, ^3J = 9.5 Hz, 2H, 4-H, 8-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.0, 125.8, 125.9, 129.0, 129.1, 134.3, 137.8, 139.4, 143.5, 151.7 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 236 (4.52), 259 (4.47), 282 (4.55), 293 (4.42), 360 (3.78), 567 (2.56) nm; MS (ESI): m/z = 441 ($[M+1]^+$, ^{80}Se).

(6-Methylazulen-1-yl)(phenyl)selane (**9a**, $C_{17}H_{14}Se$)
Blue-violet crystals; yield: 151 mg (51 %); m.p.: 88 °C; ^1H NMR (400 HMz, $CDCl_3$): δ = 2.66 (s, 3H, Me), 7.10–7.17 (m, 5H, Ph), 7.20 (d, ^3J = 9.4 Hz, 1H, 5-H), 7.21 (d, ^3J = 9.4 Hz, 1H, 7-H), 7.44 (d, ^3J = 3.2 Hz, 1H, 3-H), 8.02 (d, ^3J = 3.1 Hz, 1H, 2-H), 8.27 (d, ^3J = 10.4 Hz, 2H, 4-H), 8.58 (d, ^3J = 10.2 Hz, 2H, 8-H) ppm; ^{13}C NMR (100 HMz, $CDCl_3$): δ = 28.1, 112.0, 118.1, 125.4, 125.9, 128.6,

128.9, 135.1, 136.0, 136.3, 140.4, 140.6, 143.2, 150.3 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 234 (4.87), 283 (5.20), 294 (5.12), 336 (4.26), 343 (4.28), 358 (4.15), 552 (2.67) nm; MS (ESI): *m/z* = 299 ([M+1]$^+$, ^{80}Se).

Phenyl(4,6,8-trimethylazulen-1-yl)selane (**9b**, $C_{19}H_{18}Se$)
Blue-violet crystals; yield: 146 mg (45 %); m.p.: 42 °C; ^{1}H NMR (400 HMz, $CDCl_3$): δ = 2.61 (s, 3H, 6-Me), 2.89 (s, 3H, 4-Me), 3.25 (s, 3H, 8-Me), 7.06 (s, 1H, 5-H), 7.08 (s, 1H, 7-H), 7.10–7.21 (m, 5H, Ph), 7.39 (d, ^3J = 4.1 Hz, 1H, 3-H), 7.74 (d, ^3J = 4.1 Hz, 1H, 2-H) ppm; ^{13}C NMR (100 HMz, $CDCl_3$): δ = 25.7, 27.8, 28.5, 111.0, 116.5, 125.6, 128.2, 129.1, 129.4, 130.6, 135.9, 136.7, 139.0, 143.3, 145.8, 147.1, 148.7 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 245 (4.39), 290 (4.46), 300 sh (4.35), 368 sh (3.47), 545 (2.60) ppm; MS (ESI): *m/z* = 327 ([M+1]$^+$, ^{80}Se).

(6-tert-Butyl-4,8-dimethylazulen-1-yl)(phenyl)selane (**9c**, $C_{22}H_{24}Se$)
Blue-violet crystals; yield: 180 mg (49 %); m.p.: 80 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.50 (s, 9H, *t*Bu), 2.97 (s, 3H, Me), 3.33 (s, 3H, Me), 7.13–7.25 (m, 5H, Ph), 7.34 (bs, 1H, 5-H), 7.37 (bs, 1H, 7-H), 7.41 (d, ^3J = 4.1 Hz, 1H, 3-H), 7.81 (d, ^3J = 4.1 Hz, 1H, 2-H) ppm; ^{13}C NMR ($CDCl_3$): δ = 26.3, 28.4, 32.0, 38.6, 110.2, 116.1, 125.0, 125.5, 127.4, 129.1, 129.3, 136.2, 136.9, 139.2, 144.1, 145.5, 148.4, 159.1 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 246 (4.58), 290 (4.67), 300 (4.60), 361 sh (3.77), 541 (2.81) nm; MS (ESI): *m/z* = 369 ([M+1]$^+$, ^{80}Se).

(6-Methylazulene-1,3-diyl)bis(phenylselane) (**10a**, $C_{23}H_{18}Se_2$)
Blue-violet crystals; yield: 72 mg (16 %); m.p.: 82 °C; ^{1}H NMR (400 HMz, $CDCl_3$): δ = 2.68 (s, 3H, Me), 7.10–7.11 (m, 10H, Ph), 7.32 (d, ^3J = 10.3 Hz, 2H, 5-H, 7-H), 8.17 (s, 1H, 2-H), 8.60 (d, ^3J = 10.4 Hz, 2H, 4-H, 8-H) ppm; ^{13}C NMR (100 HMz, $CDCl_3$): δ = 28.3, 112.6, 125.7, 127.5, 128.9, 129.0, 134.5, 136.8, 142.1, 150.3, 151.7 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 235 (4.65), 258 (4.59), 287 (4.72), 300 (4.65), 353 (3.90), 364 (3.92), 368 (3.90), 553 (2.69) nm; MS (ESI): *m/z* = 453 ([M+1]$^+$, ^{80}Se).

*Synthesis of azulen-1-yl(phenyl)selanes 3-substituted with electron donating groups using phenylseleninyl chlorides (**8a–8d**)—general procedure*

To a stirred solution of 3-substituted azulene **7** (1 mmol) in 2 cm^3 anhydrous ethyl ether at −40 to −50 °C and under a dry nitrogen atmosphere, 192 mg PhSeCl (1 mmol) was added in portions as solution in 1 cm^3 anhydrous ether during 30 min (the reagent must be protected from moisture using a weighing bottle). After 20 min of stirring at −40 °C, the reaction mixture was allowed to warm slowly to room temperature with a temperature gradient of about 1 °C/min and was stirred for another 10 min. The blue- or green-colored solution was diluted to 10 cm^3 with ether, was washed with water, 1 N sodium carbonate solution, again with water and was dried over anhydrous Na_2SO_4. The solvent was removed in vacuum and the residue was chromatographed on silica gel, using a mixture of *n*-pentane-DCM (with DCM gradient). Usually only one colored band is eluted containing the desired product.

N-[3-(Phenylselanyl)azulen-1-yl]acetamide (**8a**, $C_{18}H_{15}NOSe$)
Green crystals; yield: 245 mg (72 %); m.p.: 149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of two conformers a and b with the ratio a/b = 10/3, resulted from the signal integrals; the structure of the conformers was not studied): δ = 1.90 (s, 3H, Me_b), 2.29 (s, 3H, Me_a), 7.08-7.14 (m, 5H, Ph), 7.18 (t, ^3J = 9.9 Hz, 2H, 5-H_a, 7-H_a), 7.35 (t, ^3J = 9.7 Hz, 1H, 5-H_b), 7.36 (t, ^3J = 9.8 Hz, 1H, 7-H_b), 7.61 (t, ^3J = 9.9 Hz, 1H, 6-H_a), 7.76 (t, ^3J = 9.8 Hz, 1H, 6-H_b), 8.37 (s, 1H, 2-H_a), 7.90 (s, 1H, 2-H_b), 8.11 (d, ^3J = 9.7 Hz, 1H, 8-H_a), 8.31 (d, ^3J = 9.7 Hz, 1H, 8-H_b), 8.59 (d, ^3J = 9.5 Hz, 1H, 4-H_a), 9.62 (d, ^3J = 9.5 Hz, 1H, 4-H_b) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.8(b), 24.0(a), 110.6(a), 111.1(b), 124.7(b), 125.1(a), 125.6(b), 125.9(a,b), 126.1(a), 129.1(a,b), 129.2(a,b), 130.7(a), 132.1(b), 133.5(a), 134.2(b), 134.5(a), 135.8(b), 138.1(b), 138.3(b), 138.7(b), 139.1(a), 140.0(a), 140.2(b), 140.3(a), 141.7(a), 168.7(a), 173.9(b) ppm; In time it improved in one isomer as can be seen in the ^{13}C NMR spectrum attached in the Supplementary Material: 23.2, 109.5, 122.3, 123.2, 125.7, 126.6, 128.5, 128.6, 129.2, 133.4, 133.9, 136.4, 137.1, 138.2, 139.5, 167.9 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 239 (4.57), 289 (4.70), 299 sh (4.61), 368 (3.92), 625 (2.45) nm; MS (ESI): *m/z* = 341 (M$^+$, ^{80}Se).

(E)-2-[2-(3-(Phenylselanyl)azulen-1-yl]vinyl)thiophene (**8b**, $C_{22}H_{16}SSe$)
Green crystals; yield: 270 mg (69 %); m.p.: 77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.02 (dd, ^3J = 5.1 Hz, ^3J = 3.6 Hz, 1H, 4_{Thi}-H), 7.07 (d, ^3J = 3.5 Hz, 1H, 3_{Thi}-H), 7.09-7.17 (m, 5H, Ph), 7.16 (t, ^3J = 10.0 Hz, 1H, 5-H), 7.19 (d, ^3J = 4.8 Hz, 1H, 5_{Thi}-H), 7.22 (t, ^3J = 10.0 Hz, 1H, 7-H), 7.32 (d, ^3J = 15.8 Hz, 1H, TfC*H* =), 7.47 (d, ^3J = 15.9 Hz, 1H, AzC*H* =), 7.61 (t, ^3J = 9.8 Hz, 1H, 6-H), 8.39 (s, 1H, 2-H), 8.48 (d, ^3J = 9.8 Hz, 1H, 8-H), 8.55 (d, ^3J = 9.5 Hz, 1H, 4-H) ppm; ^{13}C NMR (100 HMz, $CDCl_3$): δ = 114.2, 119.7, 120.7, 123.6, 124.2, 125.1, 125.3, 125.8, 127.1, 127.7, 129.0, 129.1, 133.2, 133.9, 137.2, 137.6, 139.3, 141.0, 143.7, 143.8 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 266

(4.45), 323 (4.47), 368 (4.37), 388 (4.37), 405 sh (4.32), 643 (2.59) nm; MS (ESI): $m/z = 393$ ($[M+1]^+$, ^{80}Se).

3-(Phenylselanyl)azulen-1-yl benzoate (**8c**, $C_{23}H_{16}O_2Se$)
Green crystals; yield: 286 mg (71 %); m.p.: 103 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.10–7.20$ (m, 5H, PhSe), 7.22 (t, $^3J = 9.7$ Hz, 1H, 7-H), 7.25 (t, $^3J = 9.8$ Hz, 1H, 5-H), 7.57 (t, $^3J = 7.7$ Hz, 2H, $PhCO_{2,m}$), 7.68 (t, $^3J = 7.7$ Hz, 1H, $PhCO_{2,p}$), 7.68 (t, $^3J = 9.8$ Hz, 1H, 6-H), 8.18 (s, 1H, 2-H), 8.33 (dd, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz, 2H, $PhCO_{2,o}$), 8.38 (d, $^3J = 9.7$ Hz, 1H, 8-H), 8.69 (d, $^3J = 9.6$ Hz, 1H, 4-H) ppm; ^{13}C NMR (100 MHZ, $CDCl_3$): $\delta = 109.1$, 123.6, 124.2, 125.8, 128.7, 129.0, 129.1, 129.2, 129.5, 130.2, 132.6, 133.7, 134.5, 135.1, 137.5, 137.9, 138.7, 139.6, 164.7 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 235 (4.60), 281 (4.62), 292 (4.51), 361 (3.77), 598 (2.65) nm; MS (ESI): $m/z = 405$ ($[M+1]^+$, ^{80}Se).

Phenyl[3-(phenylselanyl)azulen-1-yl]sulfane
(**8d**, $C_{22}H_{16}SSe$)
Blue crystals; yield: 293 mg (75 %); m.p.: 116 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.01$ (bd, $^3J = 8.5$ Hz, 2H, Ph), 7.07 (bt, $^3J = 7.2$ Hz, 1H, Ph), 7.10–7.19 (m, 7-H, Ph), 7.41 (t, $^3J = 9.8$ Hz, 1H, 5-H), 7.43 (t, $^3J = 9.7$ Hz, 1H, 7-H), 7.78 (t, $^3J = 9.8$ Hz, 1H, 6-H), 8.23 (s, 1H, 2-H), 8.75(bd, $^3J = 9.8$ Hz, 2H, 4-H, 8-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 112.6$, 116.0, 125.2, 125.9, 126.0, 126.1, 126.4, 128.8, 129.1, 134.2, 136.2, 138.1, 139.6, 139.7, 143.2, 143.7, 150.6 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 236 (4.54), 253 (4.47), 282 (4.52), 294 (4.42), 363 (3.76), 571 (2.60) nm; MS (ESI): $m/z = 393$ ($[M+1]^+$, ^{80}Se).

*Synthesis of azulen-1-yl(phenyl)selanes substituted with electron-withdrawing groups using phenylseleninyl chloride (**8e–8h**)—general procedure*

To a stirred solution of compound **6** with electron acceptor substituents (1 mmol) in 2 cm^3 dry DCM protected from atmosphere by an oil trap at room temperature was slowly added 192 mg PhSeCl (1 mmol) during 3–5 min as a solution in 2 cm^3 dry DCM. The reaction was stirred for 2 hours and is worked up as above. The column separation was made on silica gel with *n*-pentane-DCM (with DCM gradient). After the first colored fraction which contained an undefined product (probably diphenyldiselenide), the second fraction was formed from the desired product and the third, contained the unreacted starting material.

Methyl 3-(phenylselanyl)azulene-1-carboxylate
(**8e**, $C_{18}H_{14}O_2Se$)
Red crystals; yield: 280 mg (82 %); m.p.: 78 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.88$ (s, 3H, Me), 6.91-7.04 (m, 5H, Ph), 7.44 (t, $^3J = 9.8$ Hz, 1H, 5-H), 7.54 (t, $^3J = 9.8$ Hz, 1H, 7-H), 7.77 (t, $^3J = 9.8$ Hz, 1H, 6-H), 8.48 (s, 1H, 2-H), 8.71 (dd, $^3J = 9.8$ Hz, $^4J = 0.6$ Hz, 1H, 4-H), 9.62 (dd, $^3J = 10.0$ Hz, $^4J = 0.5$ Hz, 1H, 8-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 51.2$, 112.7, 116.9, 125.9, 128.0, 129.0, 129.1, 133.8, 138.0, 139.0, 140.0, 142.2, 145.7, 147.8, 165.3 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 233 (4.49), 260 (4.36), 287 (4.52), 298 (4.48), 361 (3.76), 368 (3.80), 533 (2.66) nm; MS (ESI): $m/z = 343$ ($[M+1]^+$, ^{80}Se).

3-(Phenylselanyl)azulene-1-carbaldehyde
(**8f**, $C_{17}H_{12}OSe$)
Red-brownish crystals; yield: 258 mg (83 %); m.p.: 110 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.11–7.20$ (m, 5H, Ph), 7.64 (t, $^3J = 9.8$ Hz, 1H, 5-H), 7.72 (t, $^3J = 9.8$ Hz, 1H, 7-H), 7.94 (t, $^3J = 9.8$ Hz, 1H, 6-H), 8.46 (s, 1H, 2-H), 8.85 (d, $^3J = 9.9$ Hz, 1H, 4-H), 9.69 (d, $^3J = 9.8$ Hz, 1H, 8-H), 10.35 (s, 1H, CHO) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 114.5$, 125.9, 126.2, 129.2, 129.4, 129.5, 130.9, 133.2, 138.1, 139.9, 140.8, 141.5, 147.0, 149.7, 186.4 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 235 (4.40), 275 (4.35), 294 (4.38), 305 (4.35), 368 sh (3.74), 376 (3.77), 384 sh (3.74), 504 (2.81) nm; MS (ESI): $m/z = 313$ ($[M+1]^+$, ^{80}Se).

1-[3-(Phenylselanyl)azulen-1-yl]ethanone
(**8g**, $C_{18}H_{14}OSe$)
Red-violet crystals; yield: 257 mg (79 %); m.p.: 101 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.71$ (s, 3H, Me), 7.12 (s, 5H, Ph), 7.59 (t, $^3J = 9.7$ Hz, 1H, 5-H), 7.71 (t, $^3J = 9.7$ Hz, 1H, 7-H), 7.90 (t, $^3J = 9.8$ Hz, 1H, 6-H), 8.50 (s, 1H, 2-H), 8.83 (d, $^3J = 9.8$ Hz, 1H, 4-H), 9.96 (d, $^3J = 9.9$ Hz, 1H, 8-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 29.2$, 112.5, 125.1, 126.0, 128.7, 128.9, 129.2, 130.7, 133.8, 139.4, 139.8, 140.5, 141.5, 146.2, 148.4, 195.2 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 236 (4.42), 272 (4.38), 292 (4.38), 303 (4.35), 370 sh (3.73), 385 (3.75), 531 (2.69) nm; MS (ESI): $m/z = 327$ ($[M+1]^+$, ^{80}Se).

2,2,2-Trifluoro-1-[3-(phenylselanyl)azulen-1-yl]ethanone
(**8h**, $C_{18}H_{11}F_3OSe$)
Red crystals; yield: 303 mg (80 %); m.p.: 94 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.14–7.18$ (m, 5H, Ph), 7.78 (t, $^3J = 10.6$ Hz, 1H, 5-H), 7.88 (t, $^3J = 10.6$ Hz, 1H, 7-H), 8.04 (t, $^3J = 9.8$ Hz, 1H, 6-H), 8.60 (q, $^{CF}J = 2.3$ Hz, 1H, 2-H), 8.90 (dd, $^3J = 9.9$ Hz, $^4J = 1.0$ Hz, 1H, 4-H), 9.95 (dd, $^3J = 9.9$ Hz, $^4J = 1.0$ Hz, 1H, 8-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 115.3$, 117.3, 126.4, 129.3, 131.2, 132.7, 132.8, 139.8, 140.2, 141.6, 145.1, 148.0, 148.5, 175.7 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 233 (4.46), 279 (4.42), 291 (4.40), 299

(4.38), 309 (4.36), 396 (3.86), 504 (2.89) nm; MS (ESI): $m/z = 381$ ($[M+1]^+$, ^{80}Se).

*(3-Nitroazulen-1-yl)(phenyl)selane (**8i**, $C_{16}H_{11}NO_2Se$)*
To a stirred mixture of 173 mg 1-nitroazulene (**6i**, 1 mmol) in 2 cm^3 dry DCM protected from atmosphere by an oil trap was added 192 mg PhSeCl (1 mmol). The reaction mixture was stirred 2 h at room temperature and supplementary for 1 h at the reflux. The work-up was similar to that described above. On silica gel, a brownish-red band eluted containing 180 mg (55 %) compound **8i**, isolated as red crystals; m.p.: 126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.15$–7.19 (m, 3H, $Ph_{m,p}$), 7.22–7.24 (m, 2H, Ph_o), 7.75 (tt, $^3J = 9.2$ Hz, $^4J = 0.6$ Hz, 1H, 7-H), 7.86 (tt, $^3J = 10.0$ Hz, $^4J = 0.8$ Hz, 1H, 5-H), 8.05 (tt, $^3J = 9.8$ Hz, $^4J = 1.0$ Hz, 1H, 6-H), 8.68 (s, 1H, 2-H), 8.93 (dd, $^3J = 9.9$ Hz, $^4J = 1.1$ Hz, 1H, 8-H), 9.81 (dd, $^3J = 9.6$ Hz, $^4J = 0.6$ Hz, 1H, 4-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 113.5$, 126.7, 129.4, 130.0, 130.6, 132.1, 132.3, 135.3, 138.2, 141.3, 141.8, 141.9, 144.5 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 219 (4.34), 234 (4.29), 278 (4.28), 306 (4.18), 405 (3.81), 544 sh (2.95) nm; MS (ESI): $m/z = 330$ ($[M + 1]^+$, ^{80}Se).

(3-Bromoazulen-1-yl)(phenyl)selane (**4**, $C_{16}H_{11}BrSe$)
To a magnetically stirred solution of 283 mg 1-(phenylselanyl)azulene (**2**, 1 mmol) in 10 cm^3 DCM at 0 °C, protected from atmosphere by an oil trap, 180 mg unpurified NBS (1 mmol) was added in portions. Then, the reaction mixture was stirred at 0 °C for about 15 min and then 30 min at room temperature. The solvent was removed in vacuum and the residue was chromatographed on silica gel using petroleum ether as eluent. The first blue-green colored fraction was 1,3-dibromoazulene (70 mg, 24 %), the second, blue one, contained the brominated compound **4** (160 mg, 44 %) and the third, blue-violet band, was bis-selanylated compound **3** (100 mg, 22 %). Compound **4** was isolated as dark blue crystals. Yield: 160 mg (44 %); m.p.: 84 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.12$–7.15 (m, 5H, Ph), 7.34 (t, $^3J = 9.8$ Hz, 1H, 5-H), 7.38 (t, $^3J = 9.8$ Hz, 1H, 7-H), 7.73 (t, $^3J = 9.9$ Hz, 1H, 6-H), 8.03 (s, 1H, 2-H), 8.43 (d, $^3J = 9.8$ Hz, 1H, 4-H), 8.65 (d, $^3J = 9.7$ Hz, 1H, 8-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 104.3$, 111.9, 125.0, 125.1, 126.0, 129.1, 129.2, 134.2, 136.4, 137.6, 138.0, 139.7, 141.6, 144.8 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 236 (4.41), 250 sh (4.36), 285 (4.45), 296 sh (4.36), 368 (3.60), 587 (1.75), 633 sh (1.68) nm; MS (ESI): $m/z = 363/365$ ($[M + 1]^+$, ^{80}Se).

1-(Phenylseleninyl)azulene (**11**, $C_{16}H_{12}SeO$)
To the solution of 283 mg 1-(phenylselanyl)azulene (**2**, 1 mmol) in a mixture of MeOH—water (15–10 cm^3), protected from atmosphere by an oil trap, was added 214 mg sodium metaperiodate (1 mmol) and the mixture was refluxed for 1 h. Water was added and the mixture was extracted with DCM. The organic extract was washed with water, dried on anhydrous $MgSO_4$, and the solvent was removed in vacuum. The residue was chromatographed on alumina. The first blue-colored band, which eluted with DCM, represented the unreacted selenide while the second red-violet band, which was eluted with DCM–MeOH, contained the product **11**. It was isolated as red crystals. Yield: 254 mg (85 %); m.p.: 111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.37$ (d, $^3J = 4.4$ Hz, 1H, 3-H), 7.39 (t, $^3J = 10.0$ Hz, 1H, 5-H), 7.43 (t, $^3J = 10.0$ Hz, 1H, 7-H), 7.43–7.47 (m, 3H, $Ph_{m,p}$), 7.75 (dd, $^3J = 7.9$ Hz, $^4J = 2.5$ Hz, 2H, Ph_o), 7.78 (t, $^3J = 9.9$ Hz, 1H, 6-H), 7.92 (d, $^3J = 4.1$ Hz, 1H, 2-H), 8.45 (d, $^3J = 9.5$ Hz, 1H, 4-H), 8.90 (d, $^3J = 9.7$ Hz, 1H, 8-H) ppm; ^{13}C NMR (100 HMz, $CDCl_3$): $\delta = 117.3$, 124.6, 125.1, 125.2, 125.6, 128.4, 129.7, 134.4, 136.5, 137.7, 138.3, 138.5, 141.3, 142.6 ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 228 (4.38), 286 sh (4.53), 295 (4.59), 333 (3.72), 339 (3.77), 355 (3.72) nm; MS (ESI): $m/z = 301$ ($[M+1]^+$, ^{80}Se).

1-(Phenylselenonyl)azulene (**12**, $C_{16}H_{12}SeO_2$)
To a solution of 283 mg 1-(phenylselanyl)azulene (**2**, 1 mmol) in a mixture of dioxane–water (15–10 cm^3), protected from atmosphere by an oil trap, 535 mg sodium metaperiodate (2.5 mmol) was added and the solution was refluxed for 8 h. Then, the mixture was diluted with water and was extracted with DCM. The organic solution was washed with water, dried on anhydrous $MgSO_4$, and the solvent was removed in vacuum. The residue was chromatographed on silica gel. The first blue-colored band, eluted with DCM, was the unreacted selenide, the second brown-colored band, eluted with DCM–EtOH, represented compound **11** and the third, red-violet band, eluted also with DCM–EtOH and contained compound **12**. It was isolated as brown crystals. Yield: 47 mg (15 %); m.p.: 121 °C; ^{1}H NMR (400 HMz, $CDCl_3$): $\delta = 7.43$ (d, $^3J = 4.3$ Hz, 1H, 3-H), 7.59 (t, $^3J = 10.0$ Hz, 1H, 5-H), 7.65 (d, $^3J = 9.9$ Hz, 1H, 7-H), 7.56–7.61 (m, 3H, $Ph_{m,p}$), 8.04 (dd, $^3J = 8.1$ Hz, $^4J = 2.5$ Hz, 2H, Ph_o), 7.95 (t, $^3J = 9.9$ Hz, 1H, 6-H), 8.30 (d, $^3J = 4.3$ Hz, 1H, 2-H), 8.59 (d, $^3J = 9.6$ Hz, 1H, 4-H), 9.49 (d, $^3J = 9.9$ Hz, 1H, 8-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 117.9$, 126.5, 127.9, 128.5, 129.8, 130.0, 133.5, 137.3, 137.4, 138.6, 140.1, 140.7, 144.0, 145.2 ppm; UV–Vis (dioxane, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 235 (4.39), 287 (4.48), 294 (4.50), 354 (3.84), 368 (3.70), 373 (3.68), 664 (2.43) nm; MS (ESI): $m/z = 317$ ($[M + 1]^+$, ^{80}Se).

*1,3-Bis(phenylseleninyl)azulene (**13**, $C_{22}H_{16}Se_2O_2$), mixture of diastereoisomers a and b in the ratio 1:1*
To the solution of 283 mg 1,3-bis(phenylselanyl)azulene (**3**, 1 mmol) in a mixture of MeOH–water (15–10 cm^3),

protected from atmosphere by an oil trap, was added 428 mg sodium metaperiodate (2 mmol) and the mixture was refluxed for 1 h. Water was added and the mixture was extracted with DCM. The organic extract was washed with water, dried on anhydrous $MgSO_4$, and the solvent was removed in vacuum. The residue was chromatographed on alumina. Compound **13**, which represented the main fraction, was isolated as red crystals. Yield: 353 mg (75 %); m.p.: 130 °C; ^{1}H NMR (400 HMz, $CDCl_3$): $\delta = 7.43$–7.48 (m, 6H, $Ph_{a,b(m,p)}$), 7.57 (t, $^3J = 10.3$ Hz, 2H, 5-H_b, 7-H_b), 7.59 (t, $^3J = 10.3$ Hz, 2H, 5-H_a, 7-H_a), 7.64–7.66 (m, 2H, $Ph_{b(o)}$), 7.68-7.70 (m, 2H, $Ph_{a(o)}$), 7.85 (s, 1H, 2-H_b), 7.92 (t, $^3J = 9.7$ Hz, 1H, 6-H_b), 7.95 (t, $^3J = 9.7$ Hz, 1H, 6-H_a), 8.03 (s, 1H, 2-H_a), 9.06 (d, $^3J = 7.7$ Hz, 2H, 4-H_b, 8-H_b), 9.07 (d, $^3J = 7.7$ Hz, 2H, 4-H_a, 8-H_a) ppm; ^{13}C NMR (100 HMz, $CDCl_3$): $\delta = 125.6, 126.0, 126.4, 126.5, 129.0, 129.1, 129.6, 129.7, 131.1, 131.2, 137.7, 137.9, 138.2, 141.5, 141.6, 141.7, 142.1, 142.2$ ppm; UV–Vis (methanol, $c = 3 \times 10^{-5}$ mol dm^{-3}): λ_{max} (log ε) = 230 (4.51), 290 (4.54), 298 (4.59), 333 (3.79), 356 (3.77) nm; MS (ESI): $m/z = 473$ ($[M+1]^+$, ^{80}Se). The ratio between the two conformers (resulted from the signal integrals) was "a":"b" = 10:3. The structure of the resulted conformers was not studied.

Electrochemical experiments

Acetonitrile (Rathburn, HPLC grade) and tetra *n*-butylammonium perchlorate (TBAP) from Fluka were used as received for solvent and supporting electrolyte, respectively. Differential pulse voltammetry (DPV) experiments were conducted in a conventional three-electrode cell under argon atmosphere at 25 °C using a PGSTAT 12 AUTOLAB potentiostat. The working electrode was a glassy carbon disk (3-mm diameter from CH Instruments) polished with 0.1 μm diamond paste. The Ag/10 mM $AgNO_3$ in acetonitrile +0.1 M TBAP system was used as reference electrode. All potentials were referred to the potential of ferrocene/ferrocenium (Fc/Fc^+), which was 0.07 V with our experimental conditions. DPV curves were recorded at 10 mV/s with a pulse height of 25 mV and a step time of 0.2 s. The potentials were measured in acetonitrile with 0.1 M TBAP as supporting electrolyte in millimolar solutions of azulenic derivatives. The evidenced peaks correspond to the oxidation and reduction processes, which occur during scanning.

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