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ORIGINAL PAPER

Azulen-1-yl diazenes substituted at C-3 with phenyl-chalcogene moieties: dye synthesis, product characterization and properties

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Abstract Two synthesis strategies were used for the generation of azulene-1-yl diazenes substituted at C-3 with a phenyl-chalcogenyl moiety, the synthesis of azulenes substituted at C-3 followed by azo-coupling and azulene substitution at C-3 in azulene-azo dyes. The last synthetic route seems to give more satisfactory results for the synthesis of the desired chalcogenic derivatives. Another target of this study was to investigate the changes induced by the phenyl-chalcogenic substitution on the NMR and UV-vis spectra, and also to compare this effect with the one exerted by halogen atoms and by strongly electron donating groups such as AcNH or PhCOO. Whereas the latter groups exhibit a strong influence on the NMR and UV-vis spectra, PhS, PhSe, or PhTe groups as well as halogen atoms produce only a small effect because of the moderate change in electron distribution over the entire molecule.

Keywords Dyes · Chalcogenides · Electrophilic substitutions · Azulene · Diazenes

Introduction

In our studies on aromatic azo-dyes containing an azulenyl group, we were able to obtain several such compounds with one [1–6] or two diazenyl [7, 8] groups, as well as with one or two azulenyl moieties. In Scheme 1, such compounds with phenyl or phenylene as aromatic groups (compounds **I–III**) are represented. The synthesis of these dyes and several physico-chemical properties as well as the NLO [9, 10] and electrochemical [11, 12] behavior of the compounds were investigated. These studies proved the importance of the position of the N=N groups in the molecules and of the alkyl substitution at the azulenyl fragment for the properties of the compounds, e.g., on UV-vis or NMR spectra.

The goal of this study was to investigate the influence on the properties of the resulting products induced by the coupling of the five-member ring of the azulenyl moiety in compounds **I–III** with an electron-donating or -releasing group such as PhS, PhSe, PhTe, CH_3CONH or PhCOO. Our interest was sustained by the fact that a single piece of information is available so far on azulenic compounds containing the chalcogenic elements selenium or tellurium: 1-(selenocyanato)azulene and 1-(tellurocyanato)azulene were obtained in the reaction of azulene with KXCN (X = Se, Te) in the presence of Cu^{2+} ions (yields 42 and 7%, respectively) [13].

Results and discussion

Dye synthesis

For the generation of the azulenyl substituted compounds **I–III**, two synthetic routes are available, namely substitution of the azulene followed by the azo coupling with the corresponding diazotized anilines or the preparation of the compounds **I–III** and subsequently substitution of the azulenyl moiety. The first route involved electrophilic substitution at C-1 of the azulene for the formation of the compounds represented in Scheme 2. Compounds **1** [14], **2**

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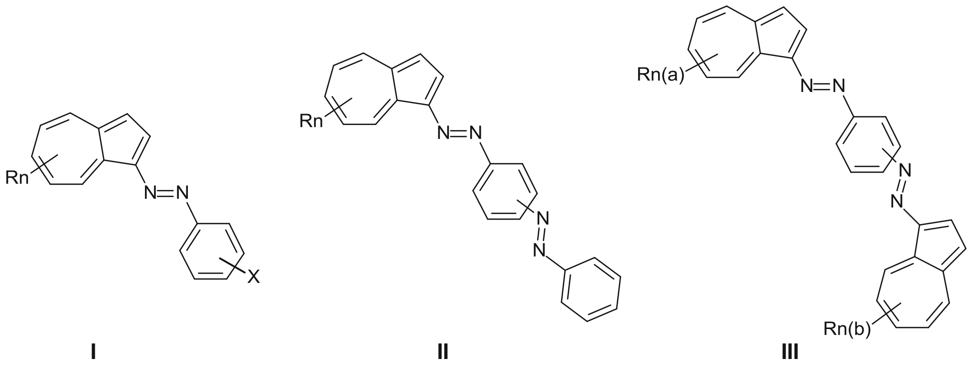
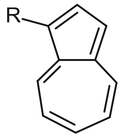
Scheme 1



Rn = H or alkyl
X = different substituents

meta- and *para*- isomers
Rn, Rn(a), Rn(b) = H, alkyl



1-5

R	AcNH	PhCOO	PhS	PhSe	PhTe
Azulene	**1**	**2**	**3**	**4**	**5**

Scheme 2

[15], and **3** [16, 17] were already obtained following this route and were fully characterized. The last compound was obtained in good yields in the reaction of azulene with PhSCl, although some problems arose in product isolation. However, our attempts to synthesize the corresponding selenium and tellurium compounds **4** and **5** using a similar reaction pathway encountered difficulties. Therefore, we have used only compounds **1–3** as starting reagents for the first reaction route.

*Synthesis starting from substituted azulenes **1–3***

The coupling reaction between azulenes **1–3** and diazonium salts obtained from (phenylazo)anilines **6** and **7** or (azulenylazo)anilines **14** and **15** occurred smoothly in moderate yields as shown in Scheme 3.

The yields were influenced to a small extent by the reciprocal position of amino and azo functions. Because of the poor results obtained starting from compound **3**, for the synthesis of the compounds substituted with PhS the second preparation route was also taken into account.

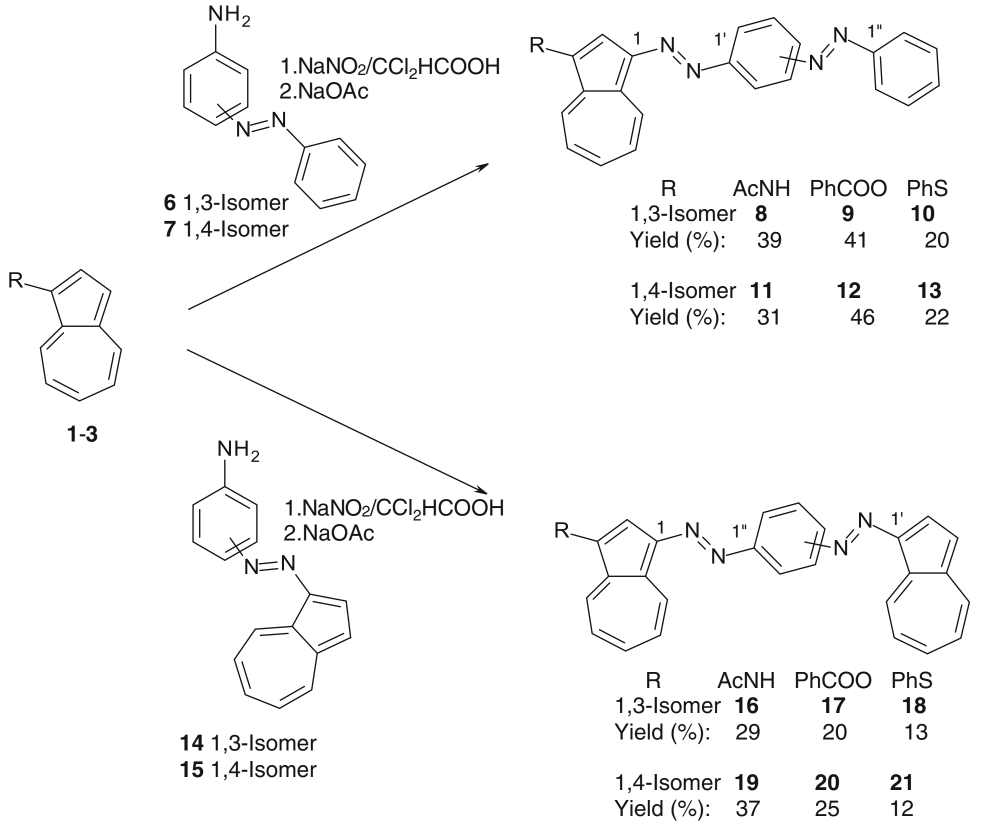
*Synthesis starting from the diazenes **I–III***

Investigation of the second reaction route started by introduction of the phenyl-chalogene group at the easily accessible dye 1-(4-methoxyphenylazo)azulene (**22**) [18], and the encouraging results are outlined in Scheme 4. Treatment of compound **22** with PhSCl at room temperature gave the desired compound **23** in good yield. For the substitution of the azulenyl moiety with a PhSe group, we have tried to use the commercially available reagent PhSeBr. The obtained reaction mixture contained nearly equal amounts of the products substituted with PhSe and Br, **24** and **27**, respectively, and a high amount of polymer. The introduction of the PhTe group was more difficult because the PhTeX reagents (X = Cl or Br) are not commercially available and they must be generated in situ. We tried to obtain PhTeX by oxidation of diphenyl ditelluride. The oxidation with bromine was unsuccessful; however, the use of SO_2Cl_2 as oxidant afforded the PhTeCl reagent, and hence, compound **25** was generated in 28% yield. The expected chlorinated by-product **26** was not detected in the reaction mixture.

The same reaction route was used starting from the *meta* and *para* mono-azulenyl bis-diazenes **28** and **29** (Scheme 4). When PhSeBr was used, the diazene conversion was about 50%, and the reaction afforded the dyes **30** and **32** along with the 3-bromo derivatives **34** and **35**. Replacing PhSeBr with PhSeCl, the reaction occurred more cleanly, and only the phenylseleno derivatives **30** and **32** were obtained in comparable yields (35 and 32%, respectively). For the synthesis of the corresponding compounds containing PhTe as substituent, a mixture of Ph_2Te_2 and SO_2Cl_2 was used, and the products **31** and **33** were formed in lower yields. It is interesting to note that when compounds **28** or **29** were treated with PhSCl, the products **10** and **13** were obtained in higher yields as compared with the first reaction route described above (results shown in Scheme 4 vs. Scheme 3). Due to the same reactivity of both azulenyl moieties in the bis-diazenes **36** and **37**, a complex composition of the reaction mixture generated by the substitution of these groups is expected. For the substitution with PhSe both PhSeBr and PhSeCl were used as starting reagents, and the results are shown in Scheme 5.

The reaction with PhSeBr afforded a very complex reaction mixture. Thus, along with the compounds with one or two PhSe groups (**38–41**), the mixture contained also the

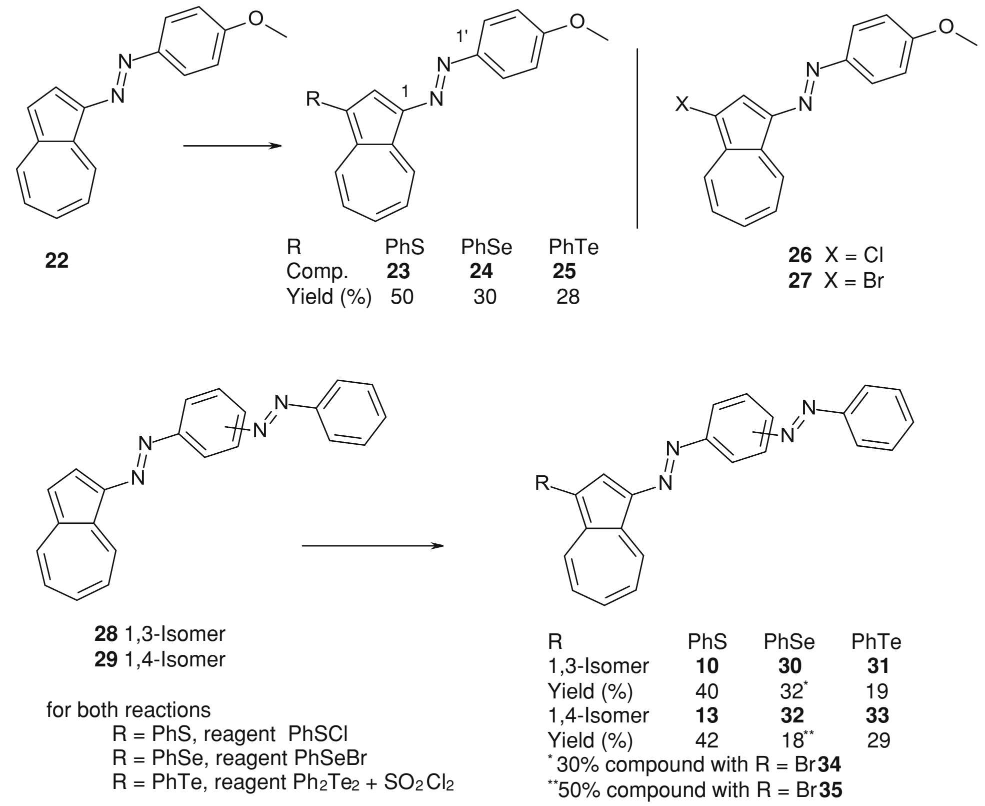
Scheme 3



R	AcNH	PhCOO	PhS
1,3-Isomer	**8**	**9**	**10**
Yield (%):	39	41	20
1,4-Isomer	**11**	**12**	**13**
Yield (%):	31	46	22

R	AcNH	PhCOO	PhS
1,3-Isomer	**16**	**17**	**18**
Yield (%):	29	20	13
1,4-Isomer	**19**	**20**	**21**
Yield (%):	37	25	12

Scheme 4



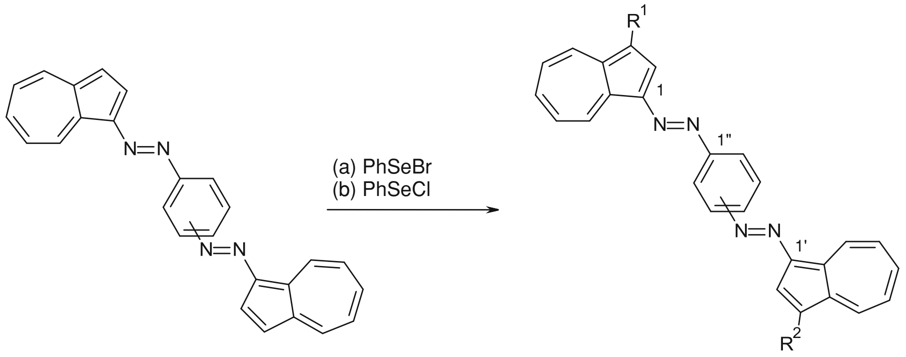
R	PhS	PhSe	PhTe
Comp.	**23**	**24**	**25**
Yield (%)	50	30	28

for both reactions
R = PhS, reagent PhSCl
R = PhSe, reagent PhSeBr
R = PhTe, reagent Ph_2Te_2 + SO_2Cl_2

R	PhS	PhSe	PhTe
1,3-Isomer	**10**	**30**	**31**
Yield (%)	40	32*	19
1,4-Isomer	**13**	**32**	**33**
Yield (%)	42	18**	29

*30% compound with R = Br **34**
50% compound with R = Br **35

Scheme 5



36 1,3-Isomer
37 1,4-Isomer

Resulted products using reagent (b) and yields (%)

R^1; R^2	PhSe; H	Yield	PhSe; PhSe	Yield
1,3-Isomer	**38**	32	**39**	21
1,4-Isomer	**40**	26	**41**	15

Brominated by-products resulted using reagent (a)

R^1; R^2	PhSe; Br	Br; H	Br; Br
1,3-Isomer	-	**42**	**43**
1,4-Isomer	**44**	**45**	**46**

by-products substituted with PhSe and Br (**44**) or only with Br (**42**, **43**, and **45**). The isolation and characterization of the obtained compounds were difficult because of the high number of generated products. However, for the structure assignment of the brominated products, these compounds were obtained by bromination of diazene **36** and **37**. The diazene **36** was brominated (55% conversion) to afford the compounds **42** (20%) and **43** (10%), while from **37** the compounds **45** (31%) and **46** (31%) (38% conversion) resulted. When PhSeCl was used as substitution reagent, only the phenylselenyl compounds **38–41** were generated in moderate yields (Scheme 5). Any attempts to introduce the phenyltelluro group at bis-diazenes **36** and **37** failed despite the successful substitution of mono-azulenyl diazenes **31** and **33**.

The influence on NMR spectra of diazenes by substitution with PhTe, PhSe, or PhS

The influence of the several substituents (as AcNH or –OCOR) at C-3 in 1-(phenylazo)azulenes with formula **I** [19] as well the general aspects of the NMR spectra recorded for the compounds with the structures **II** and **III** have already been detailed by us [7, 8]. Therefore, we have turned our attention mainly on the influence exerted on the proton chemical shifts δ_H by the chalcogene substituents because of the novelty of these compounds. We have focused our attention mainly on compounds **23–25** with more simple structure. The obtained data were compared with those of similar compounds substituted with halogen atoms (**26**, **27**, and **47**, Table 1), namely the atoms belonging to the same period of elements that contains the chalcogene elements. Thus, for the C-3 halogenated dyes the δ_H values of the same azulene protons are comparable and are slightly deshielded relative to the protons belonging to the corresponding compound **48** with a methyl group at C-3 (Table 1). As an exception, the proton at C-2 in the azulenyl moiety is deshielded by C-3 substitution in the order Cl < Br < I due to a superposition of the anisotropic, steric, and electronic effects of these atoms [20]. The azulenyl protons of the chalcogene compounds **23–25** are deshielded in comparison with the similar ones belonging to the halogenated diazenes. The phenyl-chalcogene group deshields the proton at C-2 more strongly in the order PhS < PhSe < PhTe. The same tendencies as described above were observed for the azulenyl protons of more complicated compounds with structures **II** or **III** substituted at C-3 in the azulene.

Table 1 ^{1}H NMR spectra of 3-substituted 1-(4-methoxyphenylazo)azulenes (δ in ppm)

3-Substituent (compound)	Azulenyl protons					
	2	4	5	6	7	8
Cl^{a} (**26**)	8.18	8.38	7.28	7.71	7.33	9.22
PhS (**23**)	8.37	8.59	7.30	7.70	7.40	9.27
Br^{a} (**27**)	8.28	8.33	7.30	7.71	7.35	9.19
PhSe^{b} (**24**)	8.52	8.68	7.48	7.78	7.38	9.35
I^{a} (**47**)	8.46	8.28	7.33	7.77	7.39	9.22
PhTe^{b} (**25**)	8.69	8.68	7.49	7.80	7.41	9.35
Me^{c} (**48**)	8.15	8.20	7.20	7.64	7.26	9.22

[a] NMR spectra at 300 MHz [21]

[b] NMR spectra at 400 MHz

[c] NMR spectra at 300 MHz [1]

As expected, the δ_H values of the phenyl and phenylene protons in the studied molecules were only little influenced

Table 2 Absorption maxima of the main visible band (λ_{max} in nm) of 3-substituted mono-azulenyl bis-diazenes and bis-azulenyl bis-diazenes in MeOH

Isom.	Substituent at C-3 in azulenyl moiety										
	Mono-azulenyl bis-diazene							Bis-azulenyl bis-diazene			
	H[a]	NHAc	BzO	PhS	PhSe	PhTe	Br	H[a]	NHAc	BzO	PhSe
1,3	428	460 (**8**)	440 (**9**)	429 (**10**)	431 (**22**)	430 (**23**)	434 (**26**)	442	462 (**30**)	448 (**31**)	444 (**38**)
1,4	469	504 (**11**)	483 (**12**)	475 (**13**)	472 (**32**)	474 (**33**)	471 (**35**)	520	538 (**19**)	520 (**20**)	523 (**40**)

[a] Data from Ref. [7, 8]

by the change in azulenyl substituents because they are too far from the substitution center. Several aspects regarding the δ_H values of the protons belonging to the compounds **II** and **III** were discussed in our previous papers [7, 8].

UV-vis spectra

The absorption maximum λ_{max} of the main visible band of 1-(4-methoxyphenylazo)azulene (**22**) showed a small bathochromic shift (6–8 nm) by substitution of the azulene at C-3 with PhTe, PhSe, or PhS as well as with halogen atoms [21]. However, the value was almost independent of the nature of the introduced substituent.

The modification of the λ_{max} values for mono-azulenyl bis-diazenes or bis-azulenyl bis-diazenes by the azulenyl substitution at C-3 with PhS, PhSe, PhTe, or halogens was also not significant (Table 2). As expected, the bathochromic effect exerted by the change in the position of the N=N groups from 1,3 to 1,4, observed in the parent compounds, was also maintained in all studied substituted compounds. The higher mobility of nonbonding electrons of the nitrogen or oxygen atoms in AcNH or PhCOO groups induced a bathochromic effect of over 30 nm for AcNH, whereas in the case of PhCOO it was limited to about 10 nm (Table 2).

In the visible region of the spectrum, a great number of small, poorly defined bands are also present between 500 and 700 nm. Due to their multitude and their low intensities, although they contribute to the final color of the compounds (brownish in solutions), these bands are difficult to interpret correctly.

Conclusions

Years after Nefedov's report [13] on the azulene derivatives substituted with SeCN and TeCN, to our knowledge, this is the first investigation on the synthesis and characterization of azulen-1-yl selenyl and telluryl derivatives. Two synthetic strategies were tried for the generation of azulene-1-yl diazenes substituted at C-3 with PhX (X = S, Se, or Te), namely the synthesis of azulenes substituted at C-3 followed by azo-coupling and the substitution of azulene at C-3 in the azulene-azo dyes **I–III**. The last synthetic route seems to be more satisfactory for the synthesis of the desired chalcogenic derivatives. Unfortunately, the products were obtained in modest yields because of the high amount of by-products. However, the novelty of these compounds and the change that could result in their redox and other properties compensated this disadvantage. Another target of this study was to investigate the changes produced by phenyl-chalcogenic substitution at C-3 belonging to the azulen-1-yl group on the NMR and UV-vis spectra and to compare this effect with the one exerted by halogens and also by strongly electron-donating groups such as AcNH or PhCOO. Whereas the last groups exhibit a strong influence on the NMR and UV-vis spectra, PhS, PhSe, or PhTe groups as well as halogen atoms produce only a small effect because of moderate changes in the electron distribution over the molecule. Studies regarding the acido-basic behavior and several aspects on the redox properties of the synthesized diazenes are in progress.

Experimental

Melting points were measured on a Kofler apparatus (Reichert Austria). UV-vis spectra were recorded in methanol on a Varian Cary 100 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained on Bruker Avance DRX instruments (^{1}H: 400 MHz, ^{13}C: 75 MHz and 100.62 MHz); *J* values are given in Hz. COSY correlation experiments were used for the assignment of proton positions; the numbering of atom positions is shown in Schemes 3–5. Mass spectra were recorded on a Varian 1200L Quadrupole/MS/MS spectrometer by direct injection in ESI or APCI. Elemental analyses were obtained on a Perkin Elmer CHN 240B device and agreed satisfactorily (±0.2%) with calculated values. Column chromatography was carried out using silica gel. Dichloromethane (DCM) was distilled over CaH_2. Small samples from the compounds were crystallized for melting points from petroleum ether. 4-Aminoazobenzene, 1-(4-methoxyphenylazo)azulene, 3- and 4-(azulen-1-ylazo)azobenzenes, and compounds **I** (Rn=H) and **II** (Rn=H) were obtained as described in the literature [1–8].

Syntheses routes

Azocoupling reactions

To a stirred solution of aromatic amines (2 mmol) in 8 cm^3 dichloroacetic acid at 0 °C a solution of 140 mg sodium nitrite (2 mmol) in 1 cm^3 water was added slowly, maintaining the temperature below 5 °C. After 10 min the mixture was added at 0 °C to a very well-stirred solution of azulene **1**–**3**, **28**, or **29** (2 mmol), and 12 g potassium acetate in 100 cm^3 methanol. If the potassium acetate was not completely dissolved, the yields decreased significantly. The mixture was stirred at 0 °C for 1 h. The pH of the mixture was adjusted to neutral with sodium hydroxide solution, which was carefully added. The products were repeatedly extracted with DCM. The organic layers were washed with water, dried over sodium sulfate, and the solvent was removed in vacuum. The residue was fractionated by column chromatography on silica gel with a mixture *n*-hexane/DCM (gradient in DCM from 33 to 100% in volume). Sometimes the products were contaminated by oily by-products, and for purification they were washed several times with *n*-hexane.

Phenylselenation

The diazene **14**, **20**, **21**, **36**, or **37** (1 mmol) dissolved in 5 cm^3 DCM was treated with phenylselenyl bromide or chloride in small portions under stirring and nitrogen, and the stirring was continued for 1 h. The mixture was poured into a stirred mixture of 10 cm^3 DCM and 10 cm^3 20% Na_2CO_3 solution, and the layers were separated in a separatory funnel. The organic layer was washed with water and then dried over sodium sulfate. After removal of solvent the residue was fractionated by column chromatography on silica gel using a mixture *of n*-hexane/DCM. After removal of the solvent the residues were triturated with *n*-hexane for the elimination of oily by-products. When it was necessary the products were filtered on a silica gel pad.

Phenyltelluration

Under nitrogen atmosphere to 66 mg sulfuryl chloride (0.48 mmol), 164 mg diphenylditelluride (0.4 mmol) was added under stirring in small portions to avoid overheating, and the reaction mixture was stirred for 1 h. Then a solution of azo-azulene **20** or **21** (2 mmol) in 10 cm^3 DCM was added and the mixture was stirred for further 6 h, after which the reaction was worked up as above.

(E)-1-[3-(Acetylamino)azulen-1-yl]-2-[3-[(E)-phenyldiazenyl]phenyl]diazene (**8**, $C_{24}H_{19}N_5O$)

Dark brown crystals; m.p.: 208 °C; UV-vis (MeOH): λ_{max} (log ε) = 231 (4.34), 296 (4.44), 337 (sh, 4.33), 461 (4.25) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3 H, Me), 7.21 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.34 (t, ^3J = 9.8 Hz, 1 H, 7-H), 7.53 (t, ^3J = 7.1 Hz, 2 H, $3''$-H, $5''$-H), 7.55 (t, ^3J = 7.3 Hz, 1 H, $4''$-H), 7.64 (t, ^3J = 7.7 Hz, 1 H, $5'$-H), 7.71 (t, ^3J = 9.2 Hz, 1 H, 6-H), 7.93 (d, ^3J = 7.0 Hz, 1 H, $4'$-H), 7.97 (d, ^3J = 7.2 Hz, 2 H, $2''$-H, $6''$-H), 8.06 (d, ^3J = 7.6 Hz, 1 H, $6'$-H), 8.13 (d, ^3J = 9.6 Hz, 1 H, 4-H), 8.49 (s, 1 H, $2'$-H), 8.63 (s, 1 H, 2-H), 9.31 (d, ^3J = 9.4 Hz, 1 H, 8-H) ppm; ^{13}C NMR [75 MHz, $CDCl_3$ + TFA (5%)]: δ = 23.55, 110.9, 114.0, 121.6, 123.5, 124.2, 130.3, 131.7, 134.9, 138.9, 139.0, 140.0, 140.2, 142.1, 142.4, 142.5, 147.2, 147.3, 150.3, 151.3, 150.6, 174.1 ppm; MS (ESI): *m/z* = 394 [M + 1].

(E)-1-[3-(Benzoyloxy)azulen-1-yl]-2-[3-[(E)-phenyldiazenyl]phenyl]diazene (**9**, $C_{29}H_{20}N_4O_2$)

Dark brown crystals; m.p.: 106 °C; UV-vis (MeOH): λ_{max} (log ε) = 235 (4.53), 321 (4.41), 440 (4.38) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.42 (t, ^3J = 9.8 Hz, 1 H, 7-H), 7.52 (t, ^3J = 7.1 Hz, 1 H, $4''$-H), 7.56 (t, ^3J = 6.6 Hz, 2 H, $3''$-H, $5''$-H), 7.58 (d, ^3J = 7.8 Hz, 2 H, $3'''$-H, $5'''$-H), 7.65 (t, ^3J = 7.9 Hz, 1 H, $5'$-H), 7.70 (t, ^3J = 7.4 Hz, 1 H, $4'''$-H), 7.77 (t, ^3J = 9.9 Hz, 1 H, 6-H), 7.96 (d, ^3J = 7.9 Hz, 1 H, $4'$-H), 7.99 (d, ^3J = 7.0 Hz, 2 H, $2''$-H, $6''$-H), 8.09 (d, ^3J = 7.8 Hz, 1 H, $6'$-H), 8.34 (d, ^3J = 7.2 Hz, 2 H, $2'''$-H, $6'''$-H), 8.40 (d, ^3J = 9.3 Hz, 1 H, 4-H), 8.43 (s, 1 H, 2-H), 8.51 (bs, 1 H, $2'$-H), 9.41 (s, ^3J = 9.8 Hz, 1 H, 8-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.0, 116.0, 122.9, 123.0, 123.1, 125.5, 125.9, 126.6, 128.8, 129.2, 129.5, 130.3, 131.1, 133.8, 134.1, 140.1, 140.9, 143.9, 153.6, 154.9, 155.6, 164.2 ppm; MS (ESI): *m/z* = 457 [M + 1].

(E)-1-[3-[(E)-Phenyldiazenyl]phenyl]-2-[3-(phenylthio)-azulen-1-yl]diazene (**10**, $C_{28}H_{20}N_4S$)

Dark brown crystals; m.p.: 125 °C; UV-vis (MeOH): λ_{max} (log ε) = 234 (4.39), 304 (4.39), 431 (4.21) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (t, ^3J = 7.4 Hz, 1 H, $4'''$-H), 7.14 (d, ^3J = 7.2 Hz, 2 H, $2'''$-H, $6'''$-H), 7.20 (t, ^3J = 7.8 Hz, 2 H, $3'''$-H, $5'''$-H), 7.42 (t, ^3J = 9.8 Hz, 1 H, 5-H), 7.52 (t, ^3J = 8.8 Hz, 1 H, $4''$-H), 7.54 (m, 2 H, $3''$-H, $5''$-H), 7.56 (t, ^3J = 9.8 Hz, 1 H, 7-H), 7.66 (t, ^3J = 7.9 Hz, 1 H, $5'$-H), 7.83 (t, ^3J = 9.8 Hz, 1 H, 6-H), 7.97 (ddd, ^3J = 8.0 Hz, ^4J = 1.9 Hz, ^4J = 1.0 Hz, 1 H, $4'$-H), 7.99 (dd, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 2 H, $2''$-H, $6''$-H), 8.10 (ddd, ^3J = 7.9 Hz, ^4J = 1.9 Hz, ^4J = 1.1 Hz, 1 H, $6'$-H), 8.50 (s, 1 H, 2-H), 8.51 (t, ^3J = 1.9 Hz, 1 H, $2'$-H), 8.71 (d, ^3J = 9.4 Hz, 1 H, 4-H), 9.44 (d, ^3J = 9.8 Hz, 1 H, 8-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.0, 123.0, 123.3, 125.4, 125.5, 126.7, 127.2, 127.8, 128.2, 129.0, 129.4, 129.6, 131.3, 137.6, 139.6, 140.2, 140.7, 142.8, 143.8, 144.1, 152.8, 153.4, 154.8, 155.1 ppm; MS (ESI): *m/z* = 445 [M + 1].

(E)-1-[3-(Acetylamino)azulen-1-yl]-2-[4-[(E)-phenyldiazenyl]phenyl]diazene (**11**, $C_{24}H_{19}N_5O$)
Dark brown crystals; m.p.: 270 °C; UV-vis (MeOH): λ_{max} (log ε) = 230 (4.40), 297 (4.38), 364 (4.37), 504 (4.51) nm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 2.14$ (s, 3 H Me), 7.21 (t, $^3J = 9.6$ Hz, 1 H, 5-H), 7.35 (t, $^3J = 9.8$ Hz, 1 H, 7-H), 7.45 (t, $^3J = 6.7$ Hz, 1 H, 4″-H), 7.49 (t, $^3J = 7.2$ Hz, 2 H, 3″-H, 5″-H), 7.73 (t, $^3J = 9.7$ Hz, 1 H, 6-H), 7.85 (d, $^3J = 7.8$ Hz, 2 H, 2″-H, 6″-H), 7.98 (d, $^3J = 9.0$ Hz, 2 H, 2′-H, 6′-H), 8.04 (d, $^3J = 9.0$ Hz, 2 H, 3′-H, 5′-H), 8.48 (d, $^3J = 9.3$ Hz, 1 H, 4-H), 8.74 (s, 1 H, 2-H), 9.23 (d, $^3J = 9.9$ Hz, 1 H, 8-H) ppm; ^{13}C NMR [100 MHz, CDCl$_3$ + TFA (5%)]: $\delta = 23.83$, 113.5, 118.5, 123.1, 130.1, 130.2, 133.7, 133.8, 139.8, 140.0, 140.5, 143.6, 147.6, 148.2, 148.8, 151.1, 173.8 ppm; MS (ESI): *m/z* = 394 [M + 1].

(E)-1-[3-(Benzoyloxy)azulen-1-yl]-2-[4-[(E)-phenylazo]phenyl]diazene (**12**, $C_{29}H_{20}N_4O_2$)
Dark brown crystals; m.p.: 73 °C; UV-vis (MeOH): λ_{max} (log ε) = 230 (4.53), 295 (4.37), 354 (4.29), 483 (4.54) nm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.30$ (t, $^3J = 9.7$ Hz, 1 H, 5-H), 7.47 (t, $^3J = 9.8$ Hz, 1 H, 7-H), 7.53 (t, $^3J = 7.6$ Hz, 1 H, 4″-H), 7.54 (t, $^3J = 7.6$ Hz, 2 H, 3″-H, 5″-H), 7.59 (d, $^3J = 7.7$ Hz, 2 H, 3‴-H, 5‴-H), 7.70 (t, $^3J = 7.4$ Hz, 1 H, 4‴-H), 7.76 (t, $^3J = 9.9$ Hz, 1 H, 6-H), 7.97 (d, $^3J = 7.2$ Hz, 2 H, 2″-H, 6″-H), 8.08 (d, $^3J = 8.9$ Hz, 2 H, 2′-H, 6′-H), 8.12 (d, $^3J = 8.9$ Hz, 2 H, 3′-H, 5′-H), 8.35 (d, $^3J = 7.2$ Hz, 2 H, 2‴-H, 6‴-H), 8.41 (d, $^3J = 9.4$ Hz, 1 H, 4-H), 8.44 (s, 1 H, 2-H), 9.41 (d, $^3J = 9.7$ Hz, 1 H, 8-H) ppm; ^{13}C NMR [100 MHz, CDCl$_3$ + TFA (5%)]: $\delta = 114.6$, 123.0, 123.1, 123.9, 127.7, 128.3, 128.8, 129.1, 129.5, 130.3, 131.0, 133.8, 134.2, 136.6, 141.0, 143.1, 145.6, 149.6, 149.9, 153.0, 164.2 ppm; MS (ESI): *m/z* = 457 [M + 1].

(E)-1-[4-[(E)-Phenyldiazenyl]phenyl]-2-[3-(phenylthio)-azulen-1-yl]diazene (**13**, $C_{28}H_{20}N_4S$)
Dark brown crystals; m.p.: 129 °C; UV-vis (MeOH): λ_{max} (log ε) = 237 (4.49), 289 (4.34), 353 (4.29), 475 (4.49) nm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.13$–7.15 (m, 3 H, 3‴-H, 4‴-H, 5‴-H), 7.20 (d, $^3J = 7.3$ Hz, 2 H, 2‴-H, 6‴-H), 7.44 (t, $^3J = 10.0$ Hz, 1 H, 5-H), 7.58 (t, $^3J = 10.0$ Hz, 1 H, 7-H), 7.51 (t, $^3J = 7.0$ Hz, 1 H, 4″-H), 7.53 (t, $^3J = 6.9$ Hz, 2 H, 3″-H, 5″-H), 7.85 (t, $^3J = 9.8$ Hz, 1 H, 6-H), 7.97 (d, $^3J = 6.9$ Hz, 2 H, 2″-H, 6″-H), 8.08 (d, $^3J = 8.7$ Hz, 2 H, 2′-H, 6′-H), 8.12 (d, $^3J = 8.4$ Hz, 2 H, 3′-H, 5′-H), 8.71 (d, $^3J = 9.5$ Hz, 1 H, 4-H), 8.48 (s, 1 H, 2-H), 9.43 (d, $^3J = 9.9$ Hz, 1 H, 8-H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 120.4$, 123.0, 123.1, 123.9, 125.7, 127.3, 128.0, 128.3, 129.0, 129.1, 131.1, 136.1, 137.7, 140.6, 140.9, 143.2, 144.1, 152.8, 152.9, 155.4 ppm; MS (ESI): *m/z* = 445 [M + 1].

(E)-1-[3-(Acetylamino)azulen-1-yl]-2-[3-[(E)-phenyldiazenyl]phenyl]diazene (**16**, $C_{28}H_{21}N_5O$)
Dark brown crystals; m.p.: 227 °C; UV-vis (MeOH): λ_{max} (log ε) = 232 (4.60), 281 (4.55), 339 (4.46), 415 (sh, 4.54), 462 (4.63) nm; ^{1}H NMR (400 MHz, acetone-*d$_6$*): $\delta = 2.28$ (s, 3 H, Me), 7.31 (t, $^3J = 10.0$ Hz, 1 H, 5-H), 7.47 (t, $^3J = 9.6$ Hz, 1 H, 7-H), 7.53 (d, $^3J = 9.8$ Hz, 1 H, 5′-H), 7.58 (d, $^3J = 4.6$ Hz, 1 H, 3′-H), 7.68 (t, $^3J = 9.8$ Hz, 1 H, 7′-H), 7.71 (t, $^3J = 7.9$ Hz, 1 H, 5″-H), 7.84 (t, $^3J = 9.9$ Hz, 1 H, 6-H), 7.96 (t, $^3J = 9.8$ Hz, 1 H, 6′-H), 8.04 (ddd, $^3J = 7.0$ Hz, $^4J = 1.9$ Hz, $^4J = 1.0$ Hz, 1 H, 4″-H), 8.06 (ddd, $^3J = 7.0$ Hz, $^4J = 1.9$ Hz, $^4J = 1.0$ Hz, 1 H, 6″-H), 8.36 (d, $^3J = 4.6$ Hz, 1 H, 2′-H), 8.54 (d, $^3J = 1.8$ Hz, 1 H, 2″-H), 8.57 (d, $^3J = 9.2$ Hz, 1 H, 4-H), 8.60 (d, $^3J = 9.8$ Hz, 1 H, 4′-H), 8.92 (s, 1 H, 2-H), 9.38 (d, $^3J = 9.7$ Hz, 1 H, 8-H), 9.49 (d, $^3J = 9.7$ Hz, 1 H, 8′-H) ppm; ^{13}C NMR [75 MHz, CDCl$_3$ + TFA (5%)]: $\delta = 23.38$, 106.9, 114.6, 117.4, 117.9, 127.9, 132.3, 134.3, 137.8, 138.9, 139.9, 140.1, 140.2, 140.3, 141.6, 142.0, 142.8, 143.7, 146.5, 147.3, 147.5, 150.9, 152.4, 156.4 ppm; MS (ESI): *m/z* = 444 [M + 1].

(E)-1-[3-[(E)-Azulen-1-yldiazenyl]phenyl]-2-[3-(benzoyloxy)azulen-1-yl]diazene (**17**, $C_{33}H_{22}N_4O_2$)
Dark brown crystals; m.p.: 110 °C; UV-vis (MeOH): λ_{max} (log ε) = 231 (4.63), 281 (4.53), 332 (4.43), 448 (4.66) nm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.26$ (t, $^3J = 9.8$ Hz, 1 H, 5-H), 7.33 (t, $^3J = 9.8$ Hz, 1 H, 5′-H), 7.40 (t, $^3J = 9.8$ Hz, 1 H, 7-H), 7.45 (d, $^3J = 4.6$ Hz, 1 H, 3′-H), 7.48 (t, $^3J = 9.8$ Hz, 1 H, 7′-H), 7.58 (t, $^3J = 7.7$ Hz, 2 H, 3‴-H, 5‴-H), 7.64 (t, $^3J = 7.8$ Hz, 1 H, 5″-H), 7.69 (t, $^3J = 7.4$ Hz, 1 H, 4‴-H), 7.75 (t, $^3J = 9.9$ Hz, 1 H, 6-H) 7.76 (t, $^3J = 9.9$ Hz, 1 H, 6′-H) 8.02 (ddd, $^3J = 7.0$ Hz, $^4J = 1.8$ Hz, $^4J = 1.0$ Hz, 1 H, 4″-H), 8.04 (ddd, $^3J = 7.0$ Hz, $^4J = 1.8$ Hz, $^4J = 1.0$ Hz, 1 H, 6″-H), 8.35–8.37 (m, 3 H, 2‴-H, 6‴-H, 4-H), 8.38 (d, $^3J = 9.3$ Hz, 1 H, 4′-H), 8.40 (d, $^3J = 4.8$ Hz, 1 H, 2′-H), 8.47 (s, 1 H, 2-H), 8.57 (t, $^4J = 1.8$ Hz, 1 H, 2″-H), 9.43 (s, $^3J = 9.8$ Hz, 2 H, 8-H, 8′-H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 115.0$, 116.0, 120.0, 122.9, 123.1, 125.4, 125.7, 126.4, 126.6, 126.7, 126.8, 128.8, 129.3, 130.3, 133.8, 134.0, 134.5, 135.7, 136.6, 138.5, 139.0, 139.5, 140.1, 140.6, 140.8, 144.0, 144.1, 155.0, 155.1, 164.2 ppm; MS (ESI): *m/z* = 507 [M + 1].

(E)-1-[3-[(E)-Azulen-1-yldiazenyl]phenyl]-2-[3-(phenylthio)azulen-1-yl]diazene (**18**, $C_{32}H_{22}N_4S$)
Dark brown crystals; m.p.: 80 °C; UV-vis (MeOH): λ_{max} (log ε) = 232 (4.64), 281 (4.54), 332 (4.38), 434 (4.62) nm;

^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.11$ (t, $^3J = 7.0$ Hz, 1 H, 4‴-H), 7.13 (d, $^3J = 7.0$ Hz, 2 H, 2‴-H, 6‴-H), 7.20 (t, $^3J = 7.2$ Hz, 2 H, 3‴-H, 5‴-H), 7.35 (t, $^3J = 9.5$ Hz, 1 H, 5′-H), 7.43 (t, $^3J = 9.5$ Hz, 1 H, 5-H), 7.46 (d, $^3J = 4.6$ Hz, 1 H, 3′-H), 7.49 (t, $^3J = 9.8$ Hz, 1 H, 7′-H), 7.58 (t, $^3J = 9.7$ Hz, 1 H, 7-H), 7.65 (t, $^3J = 7.9$ Hz, 1 H, 5″-H), 7.77 (t, $^3J = 9.8$ Hz, 1 H, 6′-H), 7.84 (t, $^3J = 9.8$ Hz, 1 H, 6-H), 8.02 (ddd, $^3J = 8.0$ Hz, $^4J = 1.9$ Hz, $^4J = 1.0$ Hz, 1 H, 4″-H), 8.05 (ddd, $^3J = 7.9$ Hz, $^4J = 1.9$ Hz, $^4J = 1.1$ Hz, 1 H, 6″-H), 8.39 (d, $^3J = 9.8$ Hz, 1 H, 4′-H), 8.40 (d, $^3J = 4.5$ Hz, 1 H, 2′-H), 8.53 (s, 1 H, 2-H), 8.57 (t, $^4J = 1.8$ Hz, 1 H, 2″-H), 8.72 (d, $^3J = 9.4$ Hz, 1 H, 4-H), 9.42 (d, $^3J = 9.7$ Hz, 1 H, 8′-H), 9.48 (d, $^3J = 9.7$ Hz, 1 H, 8-H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 115.8$, 116.0, 120.1, 123.0, 123.3, 125.4, 125.5, 126.5, 126.6, 126.7, 127.2, 127.6, 127.9, 129.0, 129.4, 131.3, 135.5, 135.7, 136.1, 137.6, 138.5, 139.6, 140.1, 140.7, 142.8, 143.8, 144.0, 144.1, 154.9, 155.1 ppm; MS (ESI): *m/z* = 495 [M + 1].

(E)-1-[3-(Acetylamino)azulen-1-yl]-2-[4-[(E)-azulen-1-yldiazenyl]phenyl]diazene (**19**, C$_{28}$H$_{21}$N$_5$O)
Dark brown crystals; dec. without melting; UV-vis (MeOH): $\lambda_{\max}$ (log ε) = 232 (4.49), 285 (4.47), 355 (4.08), 426 (4.16), 538 (4.60) nm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 2.22$ (s, 3 H, Me), 7.30 (t, $^3J = 10.0$ Hz, 1 H, 5-H), 7.45 (t, $^3J = 9.8$ Hz, 1 H, 5′-H), 7.52 (t, $^3J = 9.6$ Hz, 1 H, 7-H), 7.57 (d, $^3J = 4.6$ Hz, 1 H, 3′-H), 7.64 (t, $^3J = 9.6$ Hz, 1 H, 7′-H), 7.83 (t, $^3J = 10.2$ Hz, 1 H, 6-H), 7.95 (t, $^3J = 9.6$ Hz, 1 H, 6′-H), 8.15 (bs, 4 H, 2″-H, 3″-H, 5″-H, 6″-H), 8.34 (d, $^3J = 4.5$ Hz, 1 H, 2′-H), 8.56 (d, $^3J = 9.0$ Hz, 1 H, 4-H), 8.58 (d, $^3J = 9.0$ Hz, 1 H, 4′-H), 8.88 (s, 1 H, 2-H), 9.35 (d, $^3J = 10.3$ Hz, 1 H, 8-H), 9.45 (d, $^3J = 9.9$ Hz, 1 H, 8′-H) ppm; ^{13}C NMR [75 MHz, CDCl$_3$ + TFA (5%)]: $\delta = 23.48$, 114.6, 120.0, 120.4, 127.4, 134.4, 138.8, 138.9, 140.1, 140.4, 140.7, 141.1, 141.5, 141.6, 141.7, 142.0, 142.1, 142.5, 143.8, 146.7, 147.0, 147.6, 150.7, 152.2, 156.3 ppm; MS (ESI): *m/z* = 444 [M + 1].

(E)-1-[4-[(E)-Azulen-1-yldiazenyl]phenyl]-2-[3-(benzoyloxy)azulen-1-yl]diazene (**20**, C$_{33}$H$_{22}$N$_4$O$_2$)
Dark brown crystals; m.p.: 130 °C; UV-vis (MeOH): $\lambda_{\max}$ (log ε) = 234 (4.55), 281 (4.43), 337 (4.07), 418 (sh, 4.07), 520 (4.52) nm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.26$ (t, $^3J = 9.7$ Hz, 1 H, 5-H), 7.34 (t, $^3J = 9.7$ Hz, 1 H, 5′-H), 7.41 (t, $^3J = 9.7$ Hz, 1 H, 7-H), 7.45 (d, $^3J = 4.8$ Hz, 1 H, 3′-H), 7.48 (t, $^3J = 9.8$ Hz, 1 H, 7′-H), 7.59 (t, $^3J = 7.6$ Hz, 2 H, 3‴-H, 5‴-H), 7.70 (td, $^3J = 7.3$ Hz, $^4J = 1.3$ Hz, 1 H, 4‴-H), 7.76 (t, $^3J = 10.0$ Hz, 2 H, 6-H, 6′-H), 8.13 (bs, 4 H, 2″-H, 6″-H, 3″-H, 5″-H), 8.34 (d, $^3J = 9.0$ Hz, 1 H, 4-H), 8.35 (dd, $^3J = 8.4$ Hz, $^4J = 1.4$ Hz, 2 H, 2‴-H, 6‴-H), 8.36 (d, $^3J = 4.5$ Hz, 1 H, 2′-H), 8.37 (d, $^3J = 9.1$ Hz, 1 H, 4′-H), 8.44 (s, 1 H, 2-H), 9.39 (d, $^3J = 9.8$ Hz, 1 H, 8-H), 9.40 (d, $^3J = 9.5$ Hz, 1 H, 8′-H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 115.0$, 120.4, 122.8, 123.1, 123.2, 125.9, 126.5, 126.8, 128.8, 129.3, 130.3, 132.7, 133.8, 134.0, 136.6, 137.1, 139.6, 140.9, 144.0, 152.2, 152.2, 164.2 ppm; MS (ESI): *m/z* = 507 [M + 1].

(E)-1-[4-[(E)-Azulen-1-yldiazenyl]phenyl]-2-[3-(phenylthio)azulen-1-yl]diazene (**21**, C$_{32}$H$_{22}$N$_4$S)
Dark brown crystals; m.p.: 129 °C; UV-vis (MeOH): $\lambda_{\max}$ (log ε) = 230 (4.43), 284 (4.43), 338 (4.11), 464 (4.53) nm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.10$–7.14 (m, 3 H, 3‴-H, 4‴-H, 5‴-H), 7.19 (dd, $^3J = 7.2$ Hz, $^4J = 1.0$ Hz, 2 H, 2‴-H, 6‴-H), 7.34 (t, $^3J = 9.7$ Hz, 1 H, 5′-H), 7.35 (t, $^3J = 9.6$ Hz, 1 H, 5-H), 7.46 (d, $^3J = 4.6$ Hz, 1 H, 3′-H), 7.49 (t, $^3J = 9.7$ Hz, 1 H, 7′-H), 7.56 (t, $^3J = 9.5$ Hz, 1 H, 7-H), 7.77 (t, $^3J = 10.0$ Hz, 1 H, 6′-H), 7.84 (t, $^3J = 10.0$ Hz, 1 H, 6-H), 8.13 (bs, 4 H, 2″-H, 6″-H, 3″-H, 5″-H), 8.35 (d, $^3J = 10.0$ Hz, 1 H, 4′-H), 8.37 (d, $^3J = 4.6$ Hz, 1 H, 2′-H), 8.50 (s, 1 H, 2-H), 8.71 (d, $^3J = 9.4$ Hz, 1 H, 4-H), 9.39 (d, $^3J = 9.7$ Hz, 1 H, 8′-H), 9.44 (d, $^3J = 9.8$ Hz, 1 H, 8-H) ppm; MS (ESI): *m/z* = 495 [M + 1].

(E)-1-[4-(Methoxyphenyl)]-2-[3-(phenylthio)azulen-1-yl]diazene (**23**, C$_{23}$H$_{18}$N$_2$OS)
Green crystals; m.p.: 159 °C; UV-vis (MeOH): $\lambda_{\max}$ (log ε) = 230 (4.42), 278 (4.33), 341 (4.07), 428 (4.28), 446 (sh, 4.24) nm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 3.99$ (s, 3 H, OMe), 7.03 (d, $^3J = 9.0$ Hz, 2 H, 3′-H, 5′-H), 7.00 (t, $^3J = 7.1$ Hz, 1 H, 4″-H), 7.09 (d, $^3J = 7.3$ Hz, 2 H, 2″-H, 6″-H), 7.17 (t, $^3J = 8.6$ Hz, 2 H, 3″-H, 5″-H), 7.38 (t, $^3J = 9.8$ Hz, 1 H, 5-H), 7.48 (t, $^3J = 9.8$ Hz, 1 H, 7-H), 7.78 (t, $^3J = 9.8$ Hz, 1 H, 6-H), 7.97 (d, $^3J = 9.0$ Hz, 2 H, 2′-H, 6′-H), 8.45 (s, 1 H, 2-H), 8.67 (d, $^3J = 9.5$ Hz, 1 H, 4-H), 9.35 (d, $^3J = 9.9$ Hz, 1 H, 8-H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 55.7$, 114.3, 118.9, 124.0, 125.4, 127.0, 127.1, 127.2, 128.9, 131.2, 135.8, 137.3, 138.8, 139.2, 140.4, 142.8, 143.3, 148.3, 161.1 ppm; MS (ESI): *m/z* = 371 [M + 1].

(E)-1-[4-(Methoxyphenyl)]-2-[3-(phenylseleno)azulen-1-yl]diazene (**24**, C$_{23}$H$_{18}$N$_2$OSe)
Green crystals; m.p.: 178 °C; UV-vis (MeOH): $\lambda_{\max}$ (log ε) = 227 (4.40), 248 (sh, 4.35), 283 (4.33), 340 (4.13), 426 (4.32), 447 (sh, 4.28) nm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 3.90$ (s, 3 H, OMe), 7.03 (d, $^3J = 9.0$ Hz, 2 H, 3′-H, 5′-H), 7.11–7.17 (m, 3 H, 3″-H, 4″-H, 5″-H), 7.18 (dd, $^3J = 7.9$ Hz, $^4J = 1.6$ Hz, 2 H, 2″-H, 6″-H), 7.38 (t, $^3J = 9.8$ Hz, 1 H, 5-H), 7.48 (t, $^3J = 9.8$ Hz, 1 H, 7-H), 7.78 (t, $^3J = 9.8$ Hz, 1 H, 6-H), 7.97 (d, $^3J = 9.0$ Hz, 2 H, 2′-H, 6′-H), 8.52 (s, 1 H, 2-H), 8.68 (d, $^3J = 9.5$ Hz, 1 H, 4-H), 9.35 (d, $^3J = 9.8$ Hz, 1 H, 8-H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 55.6$, 114.3, 116.0, 124.0, 126.1,

127.0, 127.1, 129.1, 129.6, 132.5, 135.5, 139.0, 140.2, 143.2, 143.9, 148.4, 161.1 ppm; MS (ESI): *m/z* = 419 [M + 1]; isotopic composition: 413 (17.3%), 414 (9.2%), 415 (25.5%), 416 (23.4%), 417 (50.0%), 418 (10.0%), 419 (100%), 420 (30.7%), 421 (23.1%).

(E)-1-[4-(Methoxyphenyl)]-2-[3-(phenyltelluro)azulen-1-yl]diazene (**25**, $C_{23}H_{18}N_2OTe$)
Green crystals; m.p.: 188 °C; UV-vis (MeOH): λ_{max} (log ε) = 225 (4.34), 287 (4.33), 336 (4.07), 426 (4.29), 445 (sh, 4.25) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (s, 3 H, OMe), 7.03 (d, ^3J = 9.0 Hz, 2 H, 3′-H, 5′-H), 7.08 (t, ^3J = 7.2 Hz, 2 H, 3″-H, 5″-H), 7.14 (t, ^3J = 7.3 Hz, 1 H, 4″-H), 7.41 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.42 (dd, ^3J = 7.2 Hz, ^4J = 1 Hz, 2H, 2″-H, 6″-H), 7.49 (t, ^3J = 9.8 Hz, 1 H, 7-H), 7.79 (t, ^3J = 9.9 Hz, 1 H, 6-H), 7.98 (d, ^3J = 9.0 Hz, 2 H, 2′-H, 6′-H), 8.68 (d, ^3J = 9.8 Hz, 1 H, 4-H), 8.69 (s, 1 H, 2-H), 9.35 (d, ^3J = 9.8 Hz, 1 H, 8-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 102.1, 114.4, 124.1, 127.1, 127.2, 129.5, 135.1, 135.3, 137.6, 139.2, 140.0, 142.4, 144.8, 146.6, 161.2 ppm; MS (ESI): *m/z* = 467 [M + 1]; isotopic composition: 461 (9%), 462 (4.7%), 463 (21.9%), 464 (18.6%), 465 (67.8%), 466 (11.5%), 467 (100.0%), 468 (16.2%), 469 (92.0%), 470 (22.6%), 471 (4.1%).

(E)-1-[3-[(E)-Phenyldiazenyl]phenyl]-2-[3-(phenylseleno)azulen-1-yl]diazene (**30**, $C_{28}H_{20}N_4Se$)
Dark brown crystals; m.p.: 120 °C; UV-vis (MeOH): λ_{max} (log ε) = 230 (4.42), 306 (4.43), 431 (4.25) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13–7.18 (m, 3 H, 3‴-H, 4‴-H, 5‴-H), 7.24–7.28 (m, 2 H, 2‴-H, 6‴-H), 7.44 (t, ^3J = 9.8 Hz, 1 H, 5-H), 7.52 (t, ^3J = 7.0 Hz, 1 H, 4″-H), 7.56 (t, ^3J = 7.5 Hz, 2 H, 3″-H, 5″-H), 7.56 (t, ^3J = 9.6 Hz, 1 H, 7-H), 7.66 (t, ^3J = 8.0 Hz, 1 H, 5′-H), 7.84 (t, ^3J = 9.8 Hz, 1 H, 6-H), 7.98 (ddd, ^3J = 8.0 Hz, ^4J = 1.9 Hz, ^4J = 1.1 Hz, 1 H, 4′-H), 7.99 (dd, ^3J = 7.3 Hz, ^4J = 1.5 Hz, 2 H, 2″-H, 6″-H), 8.10 (ddd, ^3J = 7.9 Hz, ^4J = 1.9 Hz, ^4J = 1.1 Hz, 1 H, 6′-H), 8.52 (t, ^4J = 1.9 Hz, 1 H, 2′-H), 8.56 (s, 1 H, 2-H), 8.72 (d, ^3J = 9.4 Hz, 1 H, 4-H), 9.45 (d, ^3J = 9.8 Hz, 1 H, 8-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.0, 116.9, 123.0, 123.4, 125.4, 126.3, 127.7, 128.0, 129.1, 129.2, 129.5, 129.8, 131.3, 132.6, 135.8, 139.3, 140.2, 140.5, 143.2, 144.4, 152.7, 153.5, 154.8 ppm; MS (ESI): *m/z* = 493 [M + 2]; isotopic composition: 489 (17%), 490 (8%), 491 (54%), 493 (100%), 494 (23%), 495 (17%), 496 (7%), 497 (3%).

(E)-1-[3-[(E)-Phenyldiazenyl]phenyl]-2-[3-(phenyltelluro)azulen-1-yl]diazene (**31**, $C_{28}H_{20}N_4Te$)
Dark brown crystals; m.p.: 128 °C; UV-vis (MeOH): λ_{max} (log ε) = 226 (4.42), 309 (4.48), 431 (4.16) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10–7.16 (m, 3 H, 3‴-H, 4‴-H, 5‴-H), 7.46 (dd, ^3J = 8.2 Hz, ^4J = 1.3 Hz, 2 H, 2‴-H, 6‴-H), 7.47 (t, ^3J = 9.4 Hz, 1 H, 5-H), 7.52 (t, ^3J = 7.0 Hz, 1 H, 4″-H), 7.56 (t, ^3J = 7.5 Hz, 2 H, 3″-H, 5″-H), 7.56 (t, ^3J = 9.4 Hz, 1 H, 7-H), 7.66 (t, ^3J = 7.8 Hz, 1 H, 5′-H), 7.86 (t, ^3J = 9.8 Hz, 1 H, 6-H), 7.97 (ddd, ^3J = 7.9 Hz, ^4J = 1.1 Hz, 1 H, 4′-H), 7.99 (dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz, 2 H, 2″-H, 6″-H), 8.10 (ddd, ^3J = 7.9 Hz, ^4J = 1.9 Hz, ^4J = 1.1 Hz, 1 H, 6′-H), 8.52 (t, ^4J = 1.9 Hz, 1 H, 2′-H), 8.73 (d, ^3J = 9.5 Hz, 1 H, 4-H), 8.75 (s, 1 H, 2-H), 9.45 (d, ^3J = 9.9 Hz, 1 H, 8-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 102.8, 116.2, 117.4, 123.1, 123.5, 125.5, 127.3, 127.8, 128.2, 129.3, 129.5, 129.7, 131.3, 135.4, 135.6, 137.7, 140.3, 142.7, 144.9, 152.9, 153.7, 155.0 ppm; MS (ESI): *m/z* = 541 [M + 1]; isotopic composition: 535 (13.2%), 536 (6.6%), 537 (19.0%), 538 (45.6%), 539 (57.3%), 540 (21.0%), 541 (100.0%), 542 (34.0%), 543 (84.6%), 544 (22.3%).

(E)-1-[4-[(E)Phenyldiazenyl]phenyl]-2-[3-(phenylseleno)azulen-1-yl]diazene (**32**, $C_{28}H_{20}N_4Se$)
Dark brown crystals; m.p.: 126 °C; UV-vis (MeOH): λ_{max} (log ε) = 233 (4.60), 284 (4.38), 354 (4.27), 475 (4.52) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13–7.20 (m, 3 H, 3‴-H, 4‴-H, 5‴-H), 7.27 (d, ^3J = 7.2 Hz, ^4J = 2.4 Hz, 2 H, 2‴-H, 6‴-H), 7.45 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.57 (t, ^3J = 9.8 Hz, 1 H, 7-H), 7.51 (t, ^3J = 7.0 Hz, 1 H, 4″-H), 7.55 (t, ^3J = 7.7 Hz, 2 H, 3″-H, 5″-H), 7.84 (t, ^3J = 9.8 Hz, 1 H, 6-H), 7.97 (dt, ^3J = 7.0 Hz, ^4J = 1.8 Hz, 2 H, 2″-H, 6″-H), 8.08 (d, ^3J = 8.6 Hz, 2 H, 2′-H, 6′-H or 3′-H, 5′-H), 8.12 (d, ^3J = 8.9 Hz, 2 H, 3′-H, 5′-H or 2′-H, 6′-H), 8.55 (s, 1 H, 2-H), 8.71 (d, ^3J = 9.5 Hz, 1 H, 4-H), 9.42 (d, ^3J = 9.8 Hz, 1 H, 8-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 117.4, 123.0, 123.1, 123.9, 126.3, 127.9, 128.2, 129.1, 129.2, 129.9, 131.1, 132.6, 133.1, 135.8, 139.3, 140.5, 140.6, 143.7, 144.7, 152.8, 152.9, 155.4 ppm; MS (ESI): *m/z* = 493 [M + 2]; isotopic composition: 489 (19%), 490 (9%), 491 (52%), 493 (100%), 494 (24%), 495 (15%), 496 (8%), 497 (3%).

(E)-1-[4-[(E)Phenyldiazenyl]phenyl]-2-[3-(phenyltelluro)azulen-1-yl]diazene (**33**, $C_{28}H_{20}N_4Te$)
Dark brown crystals; m.p.: 134 °C; UV-vis (MeOH): λ_{max} (log ε) = 290 (4.37), 343 (4.28), 475 (4.48); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (t, ^3J = 7.3 Hz, 2 H, 3‴-H, 5‴-H), 7.17 (t, ^3J = 7.3 Hz, 1 H, 4‴-H), 7.46 (d, ^3J = 7.6 Hz, 2 H, 2‴-H, 6‴-H), 7.50 (t, ^3J = 9.7 Hz, 1 H, 5-H), 7.52 (t, ^3J = 7.9 Hz, 1 H, 4″-H), 7.54 (t, ^3J = 7.9 Hz, 2 H, 3″-H, 5″-H), 7.59 (t, ^3J = 9.7 Hz, 1 H, 7-H), 7.86 (t, ^3J = 9.7 Hz, 1 H, 6-H), 7.97 (d, ^3J = 8.0 Hz, 2 H, 2″-H, 6″-H), 8.08 (d, ^3J = 8.8 Hz, 2 H, 2′-H, 6′-H or 3′-H, 5′-H), 8.13 (d, ^3J = 8.7 Hz, 2 H, 3′-H, 5′-H or 2′-H, 6′-H), 8.72 (d, ^3J = 9.9 Hz, 1 H, 4-H), 8.73 (s, 1 H, 2-H), 9.42 (d, ^3J = 9.9 Hz, 1 H, 8-H) ppm;

^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 103.3$, 123.1, 123.3, 124.0, 127.3, 128.0, 128.4, 129.3, 129.5, 131.2, 135.4, 135.6, 137.7, 140.4, 140.6, 142.7, 145.3, 147.4, 152.9, 153.0, 155.6 ppm; MS (ESI): *m/z* = 541 [M + 1]; isotopic composition: 535 (10.5%), 536 (6.2%), 537 (17.0%), 538 (38.7%), 539 (55.6%), 540 (13.2%), 541 (100.0%), 542 (34.8%), 543 (91.1%), 544 (29.4%).

(E)-1-[3-(Bromoazulen-1-yl)]-2-[3-[(E)-phenyldiazenyl]phenyl]diazene (**34**, C$_{22}$H$_{15}$BrN$_4$)
Dark brown crystals; m.p.: 139 °C; UV-vis (MeOH): λ_{max} (log ε) = 233 (4.41), 288 (4.37), 326 (4.40), 434 (4.39) nm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.43$ (t, $^3J = 9.8$ Hz, 1 H, 5-H), 7.51 (t, $^3J = 10.1$ Hz, 1 H, 7-H), 7.54 (t, $^3J = 7.3$ Hz, 1 H, 4″-H), 7.56 (t, $^3J = 7.5$ Hz, 2 H, 3″-H, 5″-H), 7.66 (t, $^3J = 7.8$ Hz, 1 H, 5′-H), 7.82 (t, $^3J = 9.8$ Hz, 1 H, 6-H), 7.97 (ddd, $^3J = 7.9$ Hz, $^4J = 1.8$ Hz, $^4J = 1.1$ Hz, 1 H, 4′-H), 7.99 (dd, $^3J = 8.1$ Hz, $^4J = 1.5$ Hz, 2 H, 2″-H, 6″-H), 8.08 (ddd, $^3J = 7.8$ Hz, $^4J = 1.8$ Hz, $^4J = 1.1$ Hz, 1 H, 6′-H), 8.37 (s, 1 H, 2-H), 8.44 (d, $^3J = 9.5$ Hz, 1 H, 4-H), 8.49 (t, $^4J = 1.8$ Hz, 1 H, 2′-H), 9.35 (d, $^3J = 9.8$ Hz, 1 H, 8-H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 109.4$, 116.0, 123.0, 123.5, 125.4, 126.3, 126.9, 127.3, 129.2, 129.6, 131.2, 136.0, 138.1, 138.3, 138.3, 139.5, 140.9, 142.3, 153.5, 154.7 ppm; MS (ESI): *m/z* = 415 [M + 1], 417 [M + 3].

(E)-1-[3-(Bromoazulen-1-yl)]-2-[4-[(E)-phenyldiazenyl]phenyl]diazene (**35**, C$_{22}$H$_{15}$BrN$_4$)
Dark brown crystals; m.p.: 160 °C; UV-vis (MeOH): λ_{max} (log ε) = 232 (4.42), 288 (4.24), 354 (4.28), 471 (4.50) nm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.44$ (t, $^3J = 9.8$ Hz, 1 H, 5-H), 7.48–7.56 (m, 4 H, 7-H, 3″-H, 4″-H, 5″-H), 7.82 (t, $^3J = 9.8$ Hz, 1 H, 6-H), 7.96 (d, $^3J = 7.4$ Hz, 2 H, 2″-H, 6″-H), 8.07 (d, $^3J = 8.9$ Hz, 1 H, 2′-H, 6′-H or 3′-H, 5′-H), 8.10 (d, $^3J = 8.9$ Hz, 1 H, 3′-H, 5′-H or 2′-H, 6′-H), 8.36 (s, 1 H, 2-H), 8.44 (d, $^3J = 9.2$ Hz, 1 H, 4-H), 9.33 (d, $^3J = 9.6$ Hz, 1 H, 8-H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 104.8$, 123.0, 123.9, 126.3, 127.2, 127.5, 129.1, 131.1, 136.0, 138.1, 139.2, 141.0, 142.8, 152.8, 152.9, 154.6 ppm; MS (ESI): *m/z* = 415 [M + 1], 417 [M + 3].

(E)-1-[3-[(E)Azulen-1-yldiazenyl]phenyl]-2-[3-(phenylseleno)azulen-1-yl]diazene (**38**, C$_{32}$H$_{22}$N$_4$Se)
Dark brown crystals; m.p.: 160 °C; UV-vis (MeOH): λ_{max} (log ε) = 230 (4.60), 280 (4.55), 336 (4.43), 444 (4.61) nm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.12$–7.19 (m, 3 H, 3‴-H, 4‴-H, 5‴-H), 7.26 (dd, $^3J = 7.6$ Hz, $^4J = 2.0$ Hz, 2 H, 2‴-H, 6‴-H), 7.35 (t, $^3J = 9.6$ Hz, 1 H, 5′-H), 7.43 (t, $^3J = 9.7$ Hz, 1 H, 5-H), 7.46 (d, $^3J = 4.1$ Hz, 1 H, 3′-H), 7.48 (t, $^3J = 9.8$ Hz, 1 H, 7′-H), 7.56 (t, $^3J = 9.7$ Hz, 1 H, 7-H), 7.64 (t, $^3J = 7.8$ Hz, 1 H, 5″-H), 7.77 (t, $^3J = 9.8$ Hz, 1 H, 6′-H), 7.83 (t, $^3J = 9.8$ Hz, 1 H, 6-H), 8.02 (ddd, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, $^4J = 0.8$ Hz, 1 H, 4″-H), 8.05 (ddd, $^3J = 7.9$ Hz, $^4J = 1.6$ Hz, $^4J = 0.8$ Hz, 1 H, 6″-H), 8.36 (d, $^3J = 9.3$ Hz, 1 H, 4′-H), 8.40 (d, $^3J = 4.5$ Hz, 1 H, 2′-H), 8.57 (d, $^4J = 1.8$ Hz, 1 H, 2″-H), 8.60 (s, 1 H, 2-H), 8.72 (d, $^3J = 9.4$ Hz, 1 H, 4-H), 9.42 (d, $^3J = 9.7$ Hz, 1 H, 8′-H), 9.47 (d, $^3J = 9.9$ Hz, 1 H, 8-H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 116.2$, 116.8, 120.1, 123.1, 123.4, 124.9, 125.5, 126.3, 126.8, 127.6, 127.9, 129.0, 129.3, 129.5, 129.9, 131.1, 132.8, 135.8, 135.9, 138.6, 139.3, 139.7, 140.1, 140.5, 143.4, 144.2, 144.5, 155.0, 155.2 ppm; MS (ESI): *m/z* = 543 [M + 2]; isotopic composition: 539 (24.7%), 540 (21.9%), 541 (50.2%), 542 (12.8%), 543 (100%), 544 (34.1%), 545 (17.9%), 546 (6.5%), 548 (2.2%).

(E)-1-[3-[(E)-[3-(Phenylseleno)Azulen-1-yl]-diazenyl]phenyl]-2-[3-(phenylseleno)azulen-1-yl]diazene (**39**, C$_{38}$H$_{26}$N$_4$Se$_2$)
Dark brown crystals; m.p.: 167 °C; UV-vis (MeOH): λ_{max} (log ε) = 230 (4.67), 283 (4.58), 336 (4.39), 445 (4.52); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.11$–7.19 (m, 6 H, 3$_{Ph}$-H, 4$_{Ph}$-H, 5$_{Ph}$-H), 7.26 (dd, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz, 4 H, 2$_{Ph}$-H, 6$_{Ph}$-H), 7.45 (t, $^3J = 9.8$ Hz, 2 H, 5-H and 5′-H), 7.57 (t, $^3J = 9.8$ Hz, 2 H, 7-H and 7′-H), 7.65 (t, $^3J = 7.8$ Hz, 1 H, 5″-H), 7.85 (t, $^3J = 9.8$ Hz, 2 H, 6-H and 6′-H), 8.04 (dd, $^3J = 7.9$ Hz, $^4J = 1.7$ Hz, 2 H, 4″-H, 6″-H), 8.56 (t, $^4J = 1.6$ Hz, 1 H, 2″-H), 8.59 (s, 2 H, 2-H and 2′-H), 8.73 (d, $^3J = 9.5$ Hz, 2 H, 4-H and 4′-H), 9.47 (d, $^3J = 9.7$ Hz, 2 H, 8-H and 8′-H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 116.2$, 123.5, 126.4, 127.7, 128.0, 129.5, 129.6, 130.0, 132.8, 133.5, 136.0, 139.4, 140.6, 143.4, 144.5, 155.1 ppm; MS (ESI): *m/z* = 699 [M + 3]; isotopic composition: 691 (6.0%), 692 (1.8%), 693 (19.8%), 694 (6.6%), 695 (46.1%), 696 (36.1%), 697 (67.8%), 698 (3.5%), 699 (100%), 700 (32.6%), 701 (19.3%), 702 (9.1%), 703 (2.4%), 704 (1.9%).

(E)-1-[4-[(E)-Azulen-1-yldiazenyl]phenyl]-2-[3-(phenylseleno)azulen-1-yl]diazene (**40**, C$_{32}$H$_{22}$N$_4$Se)
Dark brown crystals; m.p.: 146 °C; UV-vis (MeOH): λ_{max} (log ε) = 232 (4.49), 281 (4.45), 340 (4.07), 523 (4.53) nm; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.12$–7.19 (m, 3 H, 3‴-H, 4‴-H, 5‴-H), 7.24–7.28 (m, 2 H, 2‴-H, 6‴-H), 7.35 (t, $^3J = 9.8$ Hz, 1 H, 5′-H), 7.43 (t, $^3J = 9.6$ Hz, 1 H, 5-H), 7.46 (d, $^3J = 4.5$ Hz, 1 H, 3′-H), 7.48 (t, $^3J = 9.8$ Hz, 1 H, 7′-H), 7.55 (t, $^3J = 9.7$ Hz, 1 H, 7-H), 7.77 (t, $^3J = 9.8$ Hz, 1 H, 6′-H), 7.83 (t, $^3J = 9.8$ Hz, 1 H, 6-H), 8.13 (bs, 4 H, 2″-H, 3″-H, 5″-H, 6″-H), 8.34 (d, $^3J = 9.8$ Hz, 1 H, 4′-H), 8.37 (t, $^3J = 3.0$ Hz, 1 H, 2′-H), 8.57 (s, 1 H, 2-H), 8.70 (d, $^3J = 9.5$ Hz, 1 H, 4-H), 9.38 (d, $^3J = 9.8$ Hz, 1 H, 8′-H), 9.42 (d, $^3J = 9.7$ Hz, 1 H, 8-H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 117.1$, 120.6, 123.2, 123.4, 125.4, 126.3, 127.0, 127.1, 127.8, 128.0, 129.3, 129.9, 132.7, 135.8,

135.9, 138.7, 139.2, 139.3, 139.8, 140.2, 140.6, 143.9, 144.4, 144.6, 144.7, 154.3, 154.8 ppm; MS (ESI): *m/z* = 545 [M + 2].

(E)-1-[4-[(E)-[(3-Phenylseleno)azulen-1-yl]diazenyl]phenyl]-2-[(3-phenylseleno)azulen-1-yl]-diazene (**41**, $C_{38}H_{26}N_4Se_2$)
Dark brown crystals; m.p.: 237 °C; UV-vis (MeOH): λ_{max} (log ε) = 227 (4.72), 281 (4.55), 531 (4.47) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14–7.17 (m, 3 H, 3_{Ph}-H, 4_{Ph}-H, 5_{Ph}-H), 7.24–7.28 (m, 2 H, 2_{Ph}-H, 6_{Ph}-H), 7.44 (t, ^{3}J = 9.6 Hz, 1 H, 5-H and 5′-H), 7.57 (t, ^{3}J = 9.7 Hz, 1 H, 7-H and 7′-H), 7.84 (t, ^{3}J = 9.8 Hz, 1 H, 6-H and 6′-H), 8.13 (bs, 4 H, 2″-H, 3″-H, 5″-H, 6″-H), 8.57 (s, 2 H, 2-H and 2′-H), 8.71 (d, ^{3}J = 9.5 Hz, 1 H, 4-H and 4′-H), 9.44 (d, ^{3}J = 9.7 Hz, 1 H, 8-H and 8′-H) ppm; ^{13}C NMR [75 MHz, $CDCl_3$ + TFA (5%)]: δ = 119.7, 125.5, 127.0, 130.2, 130.6, 135.3, 139.3, 140.6, 140.7, 140.8, 141.5, 141.8, 142.0, 146.3, 152.4, 153.3 ppm; MS (ESI): *m/z* = 699 [M + 3].

(E)-1-[3-[(E)-Azulen-1-yldiazenyl]phenyl]-2-[3-bromoazulen-1-yl]diazene (**42**, $C_{26}H_{17}BrN_4$)
Dark brown crystals; m.p.: 213 °C; UV-vis (MeOH): λ_{max} (log ε) = 225 (4.60), 281 (4.54), 331 (4.43), 443 (4.57) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (t, ^{3}J = 9.6 Hz, 1 H, 5′-H), 7.43 (t, ^{3}J = 9.8 Hz, 1 H, 5-H), 7.46 (d, ^{3}J = 4.6 Hz, 1 H, 3′-H), 7.49 (t, ^{3}J = 9.8 Hz, 1 H, 7′-H), 7.50 (t, ^{3}J = 9.9 Hz, 1 H, 7-H), 7.64 (t, ^{3}J = 7.8 Hz, 1 H, 5″-H), 7.78 (t, ^{3}J = 9.8 Hz, 1 H, 6-H), 7.82 (t, ^{3}J = 9.8 Hz, 1 H, 6′-H), 8.01 (ddd, ^{3}J = 7.9 Hz, ^{4}J = 1.8 Hz, ^{4}J = 1.1 Hz, 2 H, 4″-H), 8.05 (ddd, ^{3}J = 7.8 Hz, ^{4}J = 1.8 Hz, ^{4}J = 1.0 Hz, 1 H, 6″-H), 8.37 (d, ^{3}J = 9.3 Hz, 1 H, 4-H), 8.39 (d, ^{3}J = 4.6 Hz, 1 H, 2′-H), 8.40 (s, 1 H, 2-H), 8.45 (d, ^{3}J = 9.8 Hz, 1 H, 4′-H), 8.55 (d, ^{4}J = 1.9 Hz, 1 H, 2″-H), 9.39 (d, ^{3}J = 9.8 Hz, 1 H, 8-H), 9.43 (d, ^{3}J = 9.8 Hz, 1 H, 8′-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.4, 116.2, 120.3, 123.1, 123.4, 125.2, 125.5, 126.4, 126.9, 127.3, 129.5, 135.8, 136.1, 137.9, 138.2, 138.7, 139.4, 139.7, 140.7, 141.0, 143.2, 145.9, 154.1, 154.9 ppm; MS (ESI): *m/z* = 465 [M + 1], 467 [M + 3].

(E)-1-[3-[(E)-(3-Bromoazulen-1-yl)diazenyl]phenyl]-2-(3-bromoazulen-1-yl)diazene (**43**, $C_{26}H_{16}Br_2N_4$)
Dark brown crystals; m.p.: 245 °C; UV-vis (MeOH): λ_{max} (log ε) = 226 (4.57), 283 (4.52), 335 (4.42), 446 (4.55) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (t, ^{3}J = 9.8 Hz, 2 H, 5-H and 5′-H), 7.51 (t, ^{3}J = 9.8 Hz, 2 H, 7-H and 7′-H), 7.64 (t, ^{3}J = 7.9 Hz, 2 H, 5″-H), 7.82 (t, ^{3}J = 9.9 Hz, 2 H, 6-H and 6′-H), 8.02 (dd, ^{3}J = 7.9 Hz, ^{4}J = 1.9 Hz, 2 H, 4″-H, 6″-H), 8.39 (s, 2 H, 2-H and 2′-H), 8.46 (d, ^{3}J = 9.5 Hz, 2 H, 4-H and 4′-H), 8.56 (t, ^{4}J = 1.9 Hz, 1 H, 2″-H), 9.38 (d, ^{3}J = 9.8 Hz, 2 H, 8-H and 8′-H) ppm; ^{13}C NMR [100 MHz, $CDCl_3$ + TFA (5%)]: δ = 108.9, 117.5, 125.8, 128.4, 132.4, 139.3, 139.6, 141.6, 142.2, 142.3, 142.8, 147.2, 150.9, 151.9 ppm; MS (ESI): *m/z* = 543 [M + 1], 545 [M + 3], 547 [M + 5].

(E)-1-[4-[(E)-(3-Bromoazulen-1-yl)diazenyl]phenyl]-2-[3-(phenylseleno)azulen-1-yl]diazene (**44**, $C_{32}H_{21}BrN_4Se$)
Dark brown crystals (in mixture); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.17 (m, 3 H, 3_{Ph}-H, 4_{Ph}-H, 5_{Ph}-H), 7.25–7.27 (m, 2 H, 2_{Ph}-H, 6_{Ph}-H), 7.45 (t, ^{3}J = 9.7 Hz, 1 H, 5-H or 5′-H), 7.46 (t, ^{3}J = 9.6 Hz, 1 H, 5′-H or 5-H), 7.52 (t, ^{3}J = 9.7 Hz, 1 H, 7-H or 7′-H), 7.59 (t, ^{3}J = 9.5 Hz, 1 H, 7′-H or 7-H), 7.83 (t, ^{3}J = 10.0 Hz, 1 H, 6-H or 6′-H), 7.86 (t, ^{3}J = 10.0 Hz, 1 H, 6′-H or 6-H), 8.12 (bs, 4 H, 2″-H, 3″-H, 5″-H, 6″-H), 8.37 (s, 1 H, 2′-H), 8.45 (d, ^{3}J = 9.4 Hz, 1 H, 4′-H), 8.55 (s, 1 H, 2-H), 8.72 (d, ^{3}J = 9.5 Hz, 1 H, 4-H), 9.35 (d, ^{3}J = 9.8 Hz, 1 H, 8′-H), 9.43 (d, ^{3}J = 9.8 Hz, 1 H, 8-H) ppm; ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.2, 117.1, 117.9, 119.5, 126.1, 126.3, 127.7, 127.8, 127.9, 128.2, 129.5, 130.0, 132.8, 133.1, 135.8, 136.0, 138.1, 139.2, 139.3, 140.5, 140.6, 141.0, 142.2, 142.9, 143.7, 144.7, 151.0, 153.6 ppm; MS (ESI): *m/z* = 623 [M + 3], 625 [M + 5].

(E)-1-[4-[(E)-Azulen-1-yldiazenyl]phenyl]-2-(3-bromoazulen-1-yl)diazene (**45**, $C_{26}H_{17}BrN_4$)
Dark brown crystals; m.p.: 193 °C; UV-vis (MeOH): λ_{max} (log ε) = 232 (4.48), 283 (4.41), 333 (4.10), 415 (sh, 4.04), 521 (4.53) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (t, ^{3}J = 9.8 Hz, 1 H, 5′-H), 7.42 (t, ^{3}J = 9.6 Hz, 1 H, 5-H), 7.46 (d, ^{3}J = 4.5 Hz, 1 H, 3′-H), 7.49 (t, ^{3}J = 9.7 Hz, 2 H, 7-H, 7′-H), 7.75 (t, ^{3}J = 9.8 Hz, 1 H, 6′-H), 7.82 (t, ^{3}J = 9.8 Hz, 1 H, 6-H), 8.13 (bs, 4 H, 2″-H, 3″-H, 5″-H, 6″-H), 8.36 (d, ^{3}J = 9.8 Hz, 1 H, 4′-H), 8.38 (s, 1 H, 2′-H), 8.44 (d, ^{3}J = 9.5 Hz, 1 H, 4-H), 8.38 (s, 1 H, 2-H), 9.35 (d, ^{3}J = 9.8 Hz, 1 H, 8-H), 9.39 (d, ^{3}J = 9.8 Hz, 1 H, 8′-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.6, 120.5, 123.1, 123.3, 125.4, 126.3, 126.9, 127.0, 127.2, 135.7, 136.0, 138.0, 138.1, 138.6, 139.5, 139.7, 141.0, 142.9, 143.1, 144.4, 150.7, 151.6 ppm; MS (ESI): *m/z* = 465 [M + 1], 467 [M + 3].

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