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Synthesis and Redox Behavior of 1-Azulenyl Sulfides and Efficient Synthesis of 1,1′-Biazulenes

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The reaction of azulenes with several sulfoxides in the presence of acid anhydrides to afford the corresponding 1-azulenylsulfonium and 1,3-azulenediyldisulfonium ions is reported. The subsequent conversion of these ions in high yields into 1-azulenyl methyl and phenyl sulfides and 1,3-bis(methyl- and phenylthio)azulenes through treatment with diethylamine is also described. Reaction of the 1-azulenyl sulfides with MCPBA afforded 1-azulenyl sulfoxides, which were then efficiently transformed into 1,1′-biazulene derivatives under acidic conditions. The redox properties of 1-azulenyl methyl and phenyl sulfides, 1,3-bis(methyl- and phenylthio)azulenes, and 1,1′-biazulene derivatives bearing methylthio or phenylthio substituents on each azulene ring are reported based on the results of cyclic voltammetry experiments.

Introduction

Recently, there has been considerable interest in sulfur-substituted aromatic compounds since there is a wide range of potential applications for these compounds, for example, in electroluminescent devices and as organic conductors, liquid crystals, and polymer stabilizers.[1] The development of general synthetic procedures and modification methods for sulfur-substituted aromatic compounds is, therefore, of vital importance. The existing methods tend to utilize nucleophilic substitution or a metal-catalyzed coupling reaction of thiols with aromatic compounds bearing halogen substituents. A major drawback of this sort of approach is that harsh reaction conditions, such as the use of strong bases, high reaction temperatures, and long reaction times, are often required.[1,2]

The synthesis of various sulfur-substituted compounds has been reported previously in the context of azulene chemistry.[3] Comparatively little attention has been paid to the development of a facile and selective synthetic method, however. Recently, we reported the synthesis of several azulenyl methyl sulfides via azulenethiols, but the methodologies require the use of a large number of reaction steps or tedious separation processes.[4] Balenkova and co-workers reported that dimethylsulfonium ditriflate (DMSD), prepared by the reaction of trifluoromethanesulfonic anhydride (Tf_2O) with dimethyl sulfoxide (DMSO), can react with nonactivated arenes as a highly reactive electrophile to introduce the sulfur moiety.[5] We, therefore, decided to explore the reaction of azulenes with several sulfoxides in the presence of acid anhydrides in detail. In this paper, we report a facile and efficient synthetic route to several 1-azulenyl methyl and phenyl sulfides and 1,3-bis(methyl- and phenylthio)azulenes via the formation of 1-azulenylsulfonium and 1,3-azulenediylsulfonium ions.

Recently, a number of transition-metal-mediated aryl–aryl coupling reactions (including the Stille,[6] Suzuki–Miyaura,[7] and Ullmann-type[8] coupling reactions) were developed to provide facile synthetic methodologies for biaryl compounds. In the case of azulene derivatives, Morita and Takase reported the synthesis of biazulenes using the Ullmann reaction. The main drawback, however, is that very high temperatures are required.[9] In 1985, Iyoda et al. reported a nickel-mediated synthesis of the parent 1,1′-biazulene. Unfortunately, the procedure also afforded 1,1′,3′,1′′-ter- and 1,1′:3′,1′′:3′′,1′′′-quaterazulenes as by-products.[10] Razus and co-workers subsequently reported that reaction of azulene-1-azoarenes[11a,11b] and *N*-(1-azulenylmethylene)arylamines[11c] with $FeCl_3$ afforded the corresponding 1,1′-biazulene derivatives under mild conditions. We also recently reported a transition-metal-catalyzed synthesis of arylazulenes.[12] This approach is highly chal-

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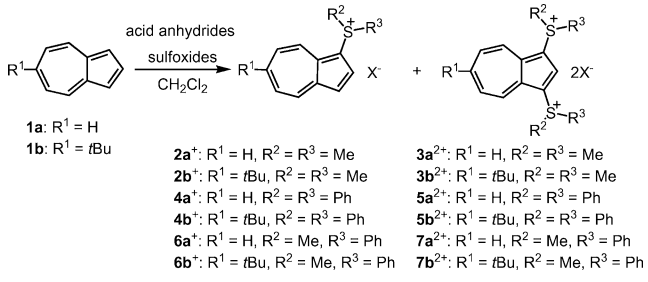
lenging in the case of 1,1′-biazulenes, however, due to the instability of the 1-haloazulenes which form a key part of the synthetic pathway. Moreover, preparation of the metal reagents is not straightforward. The most promising reagent, 1-azulenylborane, is unstable due to easy hydrolysis to a hydrocarbon derivative.[13] Herein, we report a novel transition-metal-free synthesis of 1,1′-biazulenes via 1-azulenyl methyl and phenyl sulfides[14] which may prove to have a number of significant advantages over these earlier approaches.

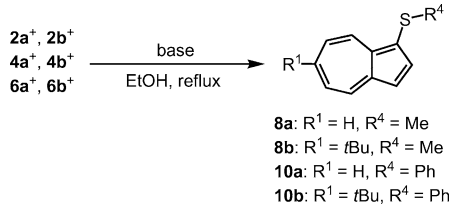
Results and Discussion

We initially explored the reaction of azulene (**1a**) with several sulfoxides in the presence of acid anhydrides (Scheme 1 and Table 1). When 1.2 equiv. of Tf_2O were used, the reaction proceeded at room temperature to afford **2a**$^+$·TfO^- and **3a**$^{2+}$·$2TfO^-$ in 55 and 24% yields, respectively. Compound **3a**$^{2+}$·was obtained in 95% yield as the sole product when the reaction was carried out with 2.4 equiv. of Tf_2O and excess DMSO (Entries 1 and 2). These results suggest that the reactivity of the DMSD reagent is too high with respect to electrophilic substitution of azulene for use in the selective synthesis of monosubstitution products such as **2a**$^+$. Tf_2O was, therefore, replaced with trifluoroacetic anhydride (TFAA) since the electrophile derived from TFAA and DMSO should be weaker. As anticipated, **2a**$^+$ was successfully prepared in a selective manner (Entry 3). The reaction of azulene with DMSO in the presence of acetic anhydride did not occur, however (Entry 4).

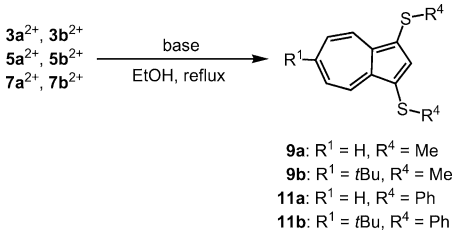
The reaction of azulene with diphenyl sulfoxide and methyl phenyl sulfoxide was attempted in the presence of a wide range of acid anhydrides to determine the applicability of this method. Azulene was found to react with diphenyl sulfoxide and methyl phenyl sulfoxide in the presence of TFAA or Tf_2O to afford the corresponding 1-azulenylsulfonium and 1,3-azulenediyldisulfonium ions in high yields (Table 1). We then proceeded to investigate the base-induced conversion of the 1-azulenylsulfonium ions into 1-azulenyl methyl and phenyl sulfides (Scheme 2, Scheme 3, and Table 2). Treatment of **2a**$^+$ with diethylamine in EtOH afforded the desired 1-azulenyl methyl sulfide (**8a**) in high yield, but the reaction was not efficient when KOH or NaOH was used as base (Table 2). Disulfonium ion **3a**$^{2+}$ was converted into the corresponding 1,3-bis(methylthio)-azulene (**9a**) quantitatively by treatment with Et_2NH. The reaction of **4a**$^+$ with Et_2NH afforded **10a** in 24% yield as part of a complex product mixture, but reaction with KOH and NaOH resulted in decomposition (Entry 8). In the case of **4b**$^+$, **5a**$^{2+}$, and **5b**$^{2+}$, base-induced conversion to the sulfide was also unsuccessful (Entries 9–12). The synthesis of 1-azulenyl phenyl sulfide (**10a**) via the (1-azulenyl)diphenylsulfonium ion (**4a**$^+$) is clearly quite challenging, therefore. Reaction of the (1-azulenyl)methylphenylsulfonium ion (**6a**$^+$) with Et_2NH proceeded smoothly to afford **10a**, however (Entry 13). The mechanism of these reactions is an S_N2 nucleophilic substitution of the base at the methyl group on the sulfonium ion with 1-azulenyl sulfide acting as a leaving group. It should be noted that nucleophilic substitution is much more efficient when the reaction center is an aliphatic carbon rather than an aromatic carbon atom.



Scheme 1.



Scheme 2.



Scheme 3.

Table 1. Synthesis of 1-azulenylsulfonium ions.

Entry	Sulfoxide	Acid anhydride, amount (equiv.)	Product, % yield	
1	DMSO	Tf_2O, 1.2	**2a**$^+$·TfO^-, 55	**3a**$^{2+}$·$2TfO^-$, 24
2	DMSO	Tf_2O, 2.4	**2a**$^+$·TfO^-, 0	**3a**$^{2+}$·$2TfO^-$, 95
3	DMSO	TFAA, 1.2	**2a**$^+$·$CF_3CO_2^-$, 99	**3a**$^{2+}$·$2CF_3CO_2^-$, 0
4	DMSO	Ac_2O, 2.4	no reaction	
5	Ph_2SO	TFAA, 1.2	**4a**$^+$·$CF_3CO_2^-$, 99	**5a**$^{2+}$·$2CF_3CO_2^-$, 0
6	Ph_2SO	Tf_2O, 2.4	**4a**$^+$·TfO^-, 0	**5a**$^{2+}$·$2TfO^-$, 92
7	PhMeSO	TFAA, 1.2	**6a**$^+$·$CF_3CO_2^-$, 99	**7a**$^{2+}$·$2CF_3CO_2^-$, 0
8	PhMeSO	Tf_2O, 2.4	**6a**$^+$·TfO^-, 0	**7a**$^{2+}$·$2TfO^-$, 89

The base-induced conversion of the sulfonium ions into sulfides is also more efficient when there are methyl substituents on the sulfonium ions rather than phenyl substituents. Isolation of the intermediate sulfonium ions during the reaction of 6-*tert*-butylazulene (**1b**) with sulfoxides in the presence of acid anhydrides is not straightforward and was not attempted (Entries 4, 6, 14, and 16).

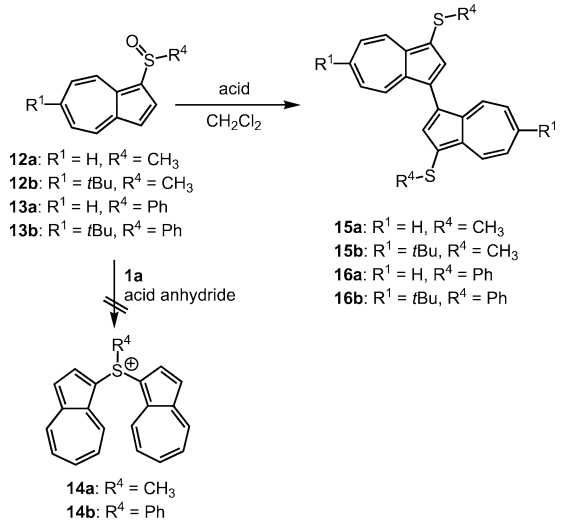
Table 2. Synthesis of 1-azulenyl sulfides.

Entry	Substrate	Base	Product, % yield
1	**2a**$^{+}$·$CF_3CO_2^-$	Et_2NH	**8a**, 99
2	**2a**$^{+}$·$CF_3CO_2^-$	KOH	**8a**, 58
3	**2a**$^{+}$·$CF_3CO_2^-$	NaOH	**8a**, 35
4	**2b**$^{+}$·2TfO$^-$	Et_2NH	**8b**, 96[a]
5	**3a**$^{2+}$·2TfO$^-$	Et_2NH	**9a**, 99
6	**3b**$^{2+}$·2TfO$^-$	Et_2NH	**9b**, 95[a]
7	**4a**$^{+}$·$CF_3CO_2^-$	Et_2NH	**10a**, 24
8	**4a**$^{+}$·$CF_3CO_2^-$	KOH	dec.
9	**4a**$^{+}$·$CF_3CO_2^-$	NaOH	dec.
10	**4b**$^{+}$·$CF_3CO_2^-$	KOH	dec.
11	**5a**$^{2+}$·2TfO$^-$	KOH	dec.
12	**5b**$^{2+}$·2TfO$^-$	KOH	dec.
13	**6a**$^{+}$·$CF_3CO_2^-$	Et_2NH	**10a**, 98
14	**6b**$^{+}$·$CF_3CO_2^-$	Et_2NH	**10b**, 94[a]
15	**7a**$^{2+}$·2TfO$^-$	Et_2NH	**11a**, 95
16	**7b**$^{2+}$·2TfO$^-$	Et_2NH	**11b**, 92[a]

[a] Yield from 6-*tert*-butylazulene (**1b**).

In the next set of experiments, we investigated the synthesis of bis(1-azulenyl)sulfonium ions. Recently, we reported the synthesis and properties of tris(1-azulenyl)methyl cations[15] and bis(1-azulenyl)-*p*-tolylamines.[16] As part of these studies, we attempted the preparation of bis(1-azulenyl)sulfonium ions. The preparation of these ions had been reported previously based on the reaction of diphenyl sulfoxide and benzene derivatives in the presence of TFAA.[17] We carefully examined the synthesis of bis(1-azulenyl)methylsulfonium ion (**14a**) using reaction conditions similar to those described previously. Previously, the 1-azulenyl methyl sulfoxide (**12a**) starting material was prepared by the reaction of **8a** with $NaIO_4$, using a relatively long reaction time.[3] We found that treatment of **8a** with MCPBA in CH_2Cl_2 at 0 °C readily afforded **12a** in 96% yield. Therefore, 1-azulenyl methyl and phenyl sulfides **8b**, **10a**, and **10b** were treated with MCPBA under the same conditions to afford the corresponding sulfoxides **12b**, **13a**, and **13b** in 98, 95, and 97% yields, respectively.

The reaction of 1-azulenyl sulfoxides **12a** and **13a** with acid anhydride, such as Tf_2O, TFAA, and Ac_2O, was then investigated. Initially, we anticipated the formation of bis(1-azulenyl)sulfonium ions **14a** and **14b**. The reaction of **12a** and **13a** with azulene in the presence of Tf_2O or TFAA did not afford **14a** and **14b**, however. Decomposition of **12a** and **13a** was observed instead. Sulfoxide **12a** also failed to react with azulene in the presence of Ac_2O. We eventually discovered that 1,1′-biazulene derivatives **15a** and **16a**, could be obtained by replacing the acid anhydrides with the corresponding acids (Scheme 4, Table 3). Reaction of **12a** with trifluoroacetic acid at 0 °C afforded 3,3′-bis(methylthio)-1,1′-biazulene (**15a**) in 89% yield (Entry 1). Similarly, **12a** reacted with 60% HPF_6 or HCl to give **15a** in 87 and 75% yields, respectively (Entries 2 and 3). The reaction of **12a** with trifluoromethanesulfonic acid also afforded **15a**, but the yield was relatively low. The presence of sulfuric acid was found to result in the decomposition of the azulene derivative, however, and no reaction was observed with trichloroacetic acid and acetic acid. Sulfoxides **13a**, **12b**, and **13b** were found to form the corresponding 1,1′-biazulenes under similar acidic conditions. Although details of the reaction mechanism remain unclear, the radical mechanism reported previously by Razus et al. is probably involved (Scheme 5).[11]

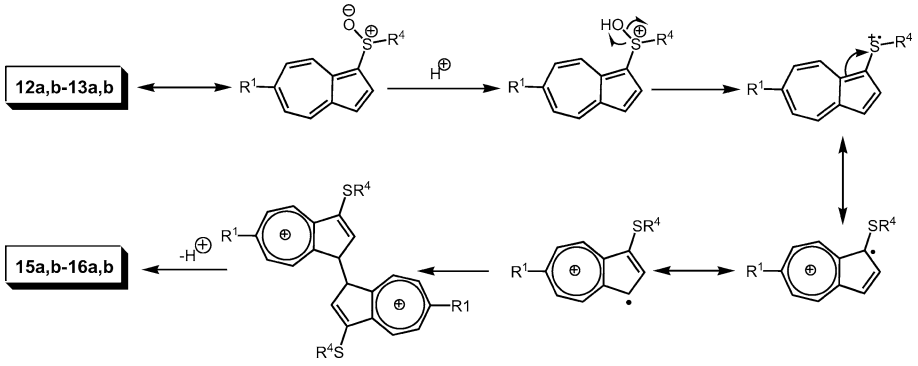


Scheme 4.

Table 3. Synthesis of 1,1′-biazulene derivatives.

Entry	Substrate	Acid	Product, % yield
1	**12a**	CF_3CO_2H	**15a**, 89
2	**12a**	HPF_6	**15a**, 87
3	**12a**	HCl	**15a**, 75
4	**12a**	TfOH	**15a**, 39
5	**12a**	H_2SO_4	dec.
6	**12a**	CCl_3CO_2H	no reaction
7	**12a**	CH_3CO_2H	no reaction
8	**12b**	CF_3CO_2H	**15b**, 80
9	**12b**	HPF_6	**15b**, 81
10	**13a**	CF_3CO_2H	**16a**, 51
11	**13a**	HPF_6	**16a**, 71
12	**13b**	CF_3CO_2H	**16b**, 56
13	**13b**	HPF_6	**16b**, 77

There have been several reports of the preparation of 1,1′-biazulenes, but the methods used involved high temperatures or metal reagents. The method described above proceeds under much milder conditions with very short reaction times and does not require tedious modification of the azulene prior to reaction, such as halogenation, borylation, or stannylation. This synthetic strategy may, therefore, prove to have considerable advantages.



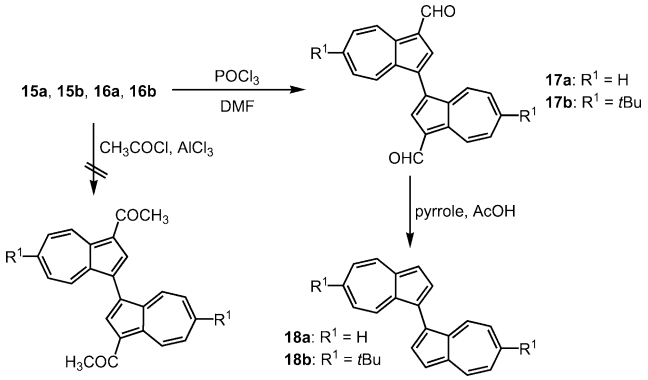
Scheme 5.

To further evaluate this new methodology, we attempted the conversion of **15a**, **15b**, **16a**, and **16b** into the 3,3′-unsubstituted 1,1′-biazulenes **18a** and **18b**. In 1962, Hafner and Moritz reported that 1,3-dialkylazulenes undergo electrophilic *ipso*-substitution (such as Friedel–Crafts acylation and Vilsmeier formylation) at the 1- and/or 1,3-positons.[18] We found that in an analogous manner to the reaction of 1,3-dialkylazulenes, 3,3′-formyl-1,1′-biazulene (**17a**)[11] could be obtained in 90% yield by the Vilsmeier formylation of **15a**. The reaction also proceeded with **15b**, **16a**, and **16b**, affording the corresponding 3,3′-formyl-1,1′-biazulenes **17a** and **17b** in 92, 65, and 72% yields (Table 4). This represents the first example in the field of azulene chemistry of methylthio and phenylthio substituents acting as leaving groups during electrophilic *ipso*-substitution. Thus, the methyl- and phenylthio groups can be regarded as a synthon of the formyl group which acts as a highly versatile functional group in organic synthesis. It should be noted, however, that Friedel–Crafts acylation of **15a**,**b** and **16a**,**b** with acetyl chloride in the presence of $AlCl_3$ led to the decomposition of these compounds. Conversion into the 3,3′-unsubstituted 1,1′-biazulenes **18a** and **18b** from the formyl compounds **17a** and **17b** was established by reaction with pyrrole in acetic acid;[19] 1,1′-biazulene (**18a**) and 6,6′-*tert*-butyl-1,1′-biazulene (**18b**) were obtained in 71 and 80% yields, respectively (Scheme 6).[20]

Table 4. Synthesis of 3,3′-formyl-1,1′-biazulene derivatives.

Entry	Substrate	Product, % yield
1	**15a**	**17a**, 90
2	**15b**	**17b**, 92
3	**16a**	**17a**, 65
4	**16b**	**17b**, 72

Cyclic and differential pulse voltammetry (CV, DPV) were used to examine the redox behavior of **8a**,**b**–**11a**,**b** and to clarify the electrochemical properties of 1-azulenyl methyl and phenyl sulfides and 1,3-bis(methyl- and phenylthio)azulenes. The redox potentials (vs. $Ag/AgNO_3$) are summarized in Table 5 and the reduction and oxidation waves of **9b** are shown in Figure 1. The electrochemical reduction of 6-*tert*-butylazulene derivatives **8b**, **9b**, **10b**, and **11b** exhibits reversible reduction waves between –1.75 and



Scheme 6.

–1.97 V owing to the formation of a radical anion. In contrast, the electrochemical reduction of **8a**, **9a**, **10a**, and **11a** exhibits irreversible reduction waves between –1.60 and –1.83 V. The electrochemical oxidation of 1,3-bis(methyl- and phenylthio)azulenes **11a**, **11b**, **13a**, and **13b** results in reversible waves between +0.20 and +0.48 V arising from the oxidation of an azulene ring to give a radical cation species, while electrochemical oxidation of **8a**, **8b**, **10a**, and **10b** results in irreversible waves between +0.28 and +0.46 V. These results indicate that the *tert*-butyl group at the 6-position increases the persistence of the azulene radical anion, while 1,3-bis(methyl- and phenylthio) substituents stabilize the radical cation. Previously, Kurihara et al. reported oxidation potentials for 3-methylthio- and 3-butylthioguaiazulenes, with two-stage oxidation waves at +0.44 V and +1.01 to +1.06 V (vs. SCE).[21] Compounds **9a**,**b** and **11a**,**b** exhibit similar two-step oxidation behavior, but our results reveal the electrochemical reduction of these compounds for the first time. Since the reduction potential becomes less negative as the number of sulfur substituents on the five-membered ring increases, for example, **8a** (–1.83 V) and **9a** (–1.73 V), it is safe to assume that the addition of sulfur substituents increases the electron affinity of the azulene ring.

The redox potentials of 1,1′-biazulene derivatives **15a**, **15b**, **16a**, and **16b** obtained from CV and DPV experiments are summarized in Table 6 and the reduction and oxidation waves of **16b** are shown in Figure 2. The electrochemical

Table 5. Redox potentials[a] of compounds **8a**,**b**–**11a**,**b**.

Sample	E_1^{red} [V]	E_2^{red} [V]	E_1^{ox} [V]	E_2^{ox} [V]	E_3^{ox} [V]
8a	(–1.83)	(–2.15)	(+0.34)	–	–
8b	–1.97				
	(–1.93)	(–2.16)	(+0.28)	–	–
9a			+0.26		
	(–1.73)	(–2.15)	(+0.24)	(+0.70)	(+0.91)[b]
9b	–1.86		+0.20		
	(–1.84)	(–2.18)	(+0.19)	(+0.76)	–
10a	(–1.75)	(–2.16)	(+0.50)	–	–
10b	–1.91				
	(–1.88)	(–2.19)	(+0.42)	–	–
11a			+0.48		
	(–1.60)	(–2.18)	(+0.46)	(+0.70)	(+0.95)
11b	–1.75		+0.44		
	(–1.72)	(–2.20)	(+0.42)	(+0.80)	–

[a] Redox potentials were measured by CV and DPV [V vs. Ag/$AgNO_3$, 1 mM in benzonitrile containing 0.1 M Et_4NClO_4, Pt electrode (i.d.: 1.6 mm), scan rate: 100 mV s^{-1}, and Fc/Fc^+ = +0.15 V]. In the case of reversible waves, redox potentials measured by CV are presented. Peak potentials measured by DPV are shown in parentheses. [b] The E_4^{ox} value was observed at +1.18 V by DPV.

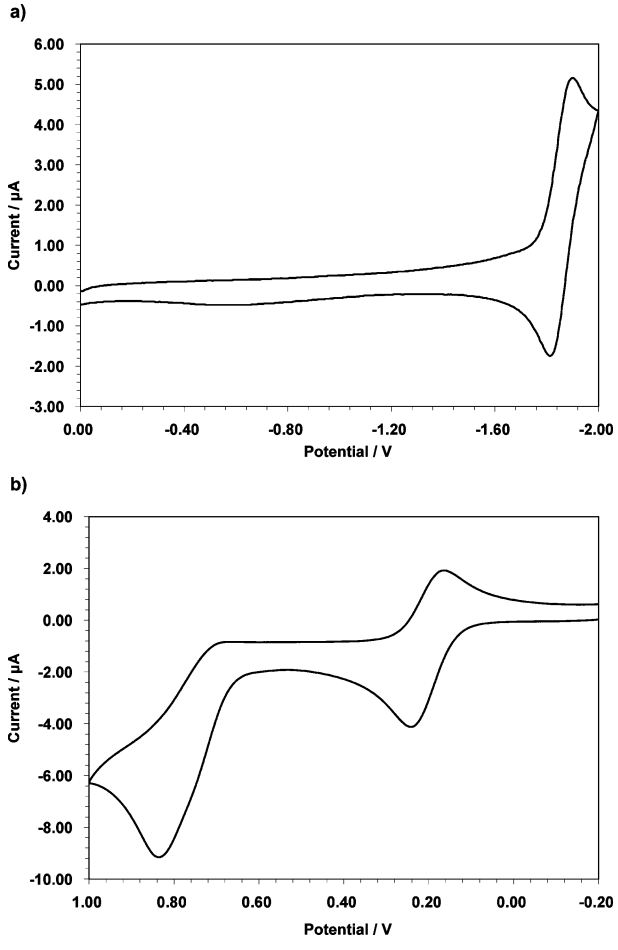


Figure 1. Cyclic voltammograms of (a) the reduction and (b) the oxidation of **9b** in benzonitrile containing 0.1 M Et_4NClO_4 as a supporting electrolyte.

reduction and oxidation of **16b** result in reversible redox waves arising from single-electron transfer to generate a radical anion and a radical cation species, respectively. The cyclic voltammograms of **15a**, **15b**, and **16a** contain a reversible oxidation wave, but an irreversible reduction wave is observed in the case of **15b** and **15a**. We recently reported that the cyclic voltammogram for the parent 1,1′-biazulene (**18a**) contains two-stage oxidation waves at +0.30 and +0.62 V with poor reversibility under similar conditions.[22] Compounds **15a** and **16a** exhibit first oxidation potentials

Table 6. Redox potentials[a] of 1,1′-biazulene derivatives **15a**,**b** and **16a**,**b**.

Sample	E_1^{red} [V]	E_2^{red} [V]	E_3^{red} [V]	E_1^{ox} [V]	E_2^{ox} [V]
15a				+0.17	
	(–1.87)	(–2.06)	(–2.16)	(+0.15)	(+0.38)
15b				+0.09	
	(–1.76)	(–2.04)	(–2.18)	(+0.06)	(+0.30)
16a					
	(–1.69)	(–1.96)	(–2.16)	(+0.33)	(+0.48)
16b	–1.88			+0.19	
	(–1.86)	(–2.14)	–	(+0.18)	(+0.74)

[a] Redox potentials were measured by CV and DPV [V vs. Ag/$AgNO_3$, 1 mM in benzonitrile containing 0.1 M Et_4NClO_4, Pt electrode (i.d.: 1.6 mm), scan rate: 100 mV s^{-1}, and Fc/Fc^+ = +0.15 V]. In the case of reversible waves, redox potentials measured by CV are presented. Peak potentials measured by DPV are shown in parentheses.

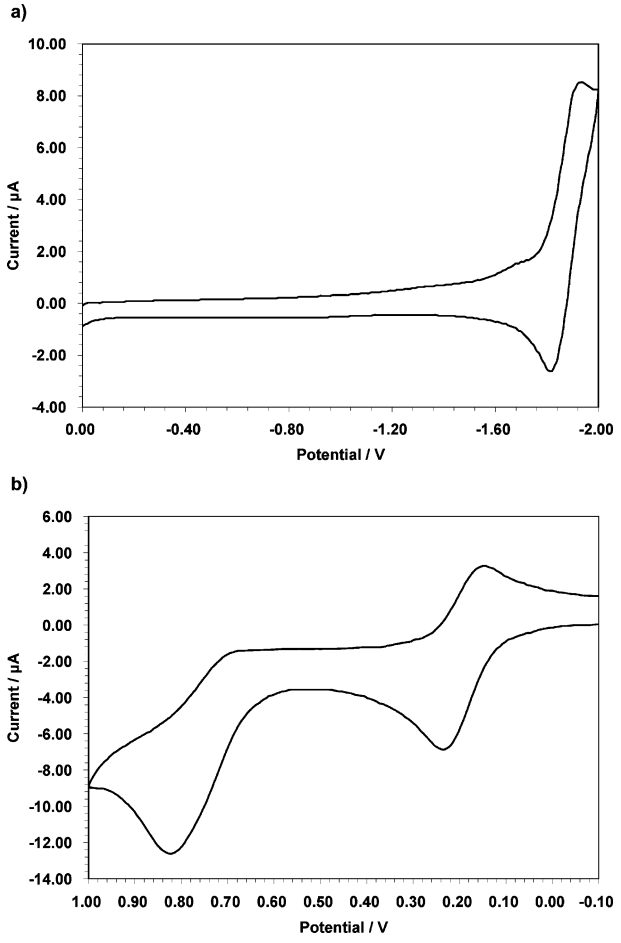


Figure 2. Cyclic voltammograms of (a) the reduction and (b) the oxidation of **16b** in benzonitrile containing 0.1 M Et_4NClO_4 as a supporting electrolyte.

at +0.15 and +0.33 V, respectively, with second potentials at +0.38 and +0.48 V. These results indicate that the π-donating properties are increased markedly by the presence of the methylthio groups, while the effect appears to be smaller in the case of the phenylthio groups. The two sulfur substituents increase the reversibility of the electrochemical oxidation reaction.

Conclusions

We have described a novel and efficient synthesis for 1-azulenyl methyl and phenyl sulfides, 1,3-bis(methyl- and phenylthio)azulenes, and 1,1′-biazulenes that offers a number of significant advantages over the methods reported previously. Azulenes react with sulfoxides in the presence of acid anhydrides to afford the corresponding 1-azulenylsulfonium ions. The reaction of 1-azulenylsulfonium ions with Et_2NH affords 1-azulenyl methyl and phenyl sulfides which then react with MCPBA to form 1-azulenyl methyl and phenyl sulfoxides. In a metal-free synthesis, the 1-azulenyl methyl and phenyl sulfoxides react with an acid to afford 1,1′-biazulene derivatives. The methyl- and phenylthio groups of the 1,1′-biazulene derivatives are readily converted into formyl groups by the Vilsmeier reaction. 3,3′-Formyl-1,1′-biazulenes react with pyrrole in acetic acid to afford 1,1′-biazulenes, including the unsubstituted 1,1′-biazulene. Further expansion of the π-electron systems using the 1,1′-biazulene core is now being investigated in our laboratory along with the physical properties of the new compounds formed.

Experimental Section

General: Melting points were determined with a Yanagimoto MP-S3 micro melting apparatus and are uncorrected. Mass spectra were obtained with a JEOL HX-110, a Hitachi M-2500, or a Bruker APEX II instrument, usually at 70 eV. IR and UV spectra were measured with a Shimadzu FTIR-8100M and a Hitachi U-3410 spectrophotometer, respectively. ^1H and ^{13}C NMR spectra were recorded with a JEOL GSX 400 (400 and 100 MHz), a JEOL JNM A500 (500 and 125 MHz), or a Bruker AM 600 spectrometer (600 and 150 MHz). Gel permeation chromatography (GPC) purification was performed with a TSKgel G2000H_6 instrument. Voltammetry measurements were carried out with a BAS 100B/W electrochemical workstation equipped with Pt working and auxiliary electrodes and a reference electrode formed from Ag/$AgNO_3$ (0.1 M) in a tetrabutylammonium perchlorate (0.1 M)/acetonitrile solution. Elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

(1-Azulenyl)dimethylsulfonium Trifluoroacetate ($2a^+ \cdot CF_3CO_2^-$): Trifluoroacetic anhydride (252 mg, 1.20 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of **1a** (128 mg, 1.00 mmol) and DMSO (1 mL) in CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature for 1 h. The solvent was removed under reduced pressure. The residue was washed several times with Et_2O to give $2a^+ \cdot CF_3CO_2^-$ (300 mg, 99%) as a purple oil. HRMS (ESI): calcd. for $C_{12}H_{13}S^+$ [M – $CF_3CO_2^-$]$^+$ 189.0738; found 189.0732. IR (KBr): $\tilde{\nu}_{max}$ = 3453 (s), 3400 (s), 3088 (m), 3044 (m), 3028 (m), 2901 (m), 1682 (s), 1585 (m), 1560 (w), 1537 (w), 1508 (w), 1485 (w), 1429 (m), 1325 (m), 1271 (w), 1209 (s), 1180 (s), 1128 (s), 1051 (m), 1041 (m), 1005 (m), 983 (w), 962 (w), 873 (w), 837 (m), 802 (m), 790 (s), 750 (s), 723 (m), 675 (w), 598 (w), 571 (w), 545 (w), 518 (w), 463 (w), 447 (s), 436 (w), 409 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 283 (4.39), 291 (4.40), 335 (3.59), 350 (3.53), 512 (3.05) nm. ^1H NMR (400 MHz, [D_6]acetone): δ = 8.82 (d, J = 10.0 Hz, 1 H, 8-H), 8.70 (d, J = 4.4 Hz, 1 H, 2-H), 8.62 (d, J = 10.0 Hz, 1 H, 4-H), 8.02 (t, J = 10.0 Hz, 1 H, 6-H), 7.73 (t, J = 10.0 Hz, 1 H, 7-H), 7.67 (t, J = 10.0 Hz, 1 H, 5-H), 7.62 (d, J = 4.4 Hz, 1 H, 4-H), 3.54 (s, 6 H, 1-S^+Me_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.41 (C=O), 144.43, 141.68, 141.64, 140.94, 136.95, 135.92, 129.00, 128.73, 120.98, 118.50 (q, J = 298.2 Hz, TfO^-), 104.92, 31.04 (1-S^+Me_2) ppm. $C_{14}H_{13}F_3O_2S \cdot H_2O$: C 53.39, H 4.61; found C 53.22, H 4.28.

1,3-Azulenediylbis(dimethylsulfonium) Bis(trifluoromethanesulfonate) ($3a^{2+} \cdot 2TfO^-$): Trifluoromethanesulfonic anhydride (677 mg, 2.4 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of **1a** (128 mg, 1.00 mmol) and DMSO (1 mL) in CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature for 2 h. The solvent was removed under reduced pressure. The residue was dissolved in a small amount of CH_2Cl_2 and then precipitated by the addition of excess Et_2O. The precipitate was collected by filtration and recrystallized from EtOH to give $3a^{2+} \cdot 2TfO^-$ (521 mg, 95%) as prism-shaped orange crystals; m.p. 178.0–178.5 °C (dec.). HRMS (ESI): calcd. for $C_{14}H_{18}S_2^{2+}$ [M – $2TfO^-$]$^{2+}$ 250.0850; found 250.0840. IR (KBr): $\tilde{\nu}_{max}$ = 3076 (m), 3030 (s), 2941 (m), 1585 (m), 1454 (m), 1437 (m), 1419 (s), 1334 (m), 1271 (m), 1257 (m), 1282 (s), 1224 (s), 1178 (s), 1209 (s), 1157 (s), 1143 (s), 1062 (m), 1030 (s), 1001 (m), 978 (w), 877 (w), 758 (m), 638 (s), 603 (w), 572 (m), 518 (m), 463 (w), 434 (w), 418 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 261 sh (4.28), 289 (4.72), 327 (3.94), 342 sh (3.76), 481 (3.00) nm. ^1H NMR (600 MHz, [D_6]acetone): δ = 9.76 (s, 1 H, 2-H), 9.29 (d, J = 10.0 Hz, 2 H, 4,8-H), 8.58 (t, J = 10.0 Hz, 1 H, 6-H), 8.28 (t, J = 10.0 Hz, 2 H, 5,7-H), 3.63 (s, 12 H, 1,3-S^+Me_2) ppm. $C_{16}H_{18}F_6O_6S_4$: C 35.03, H 3.31; found C 35.16, H 3.29.

(1-Azulenyl)diphenylsulfonium Trifluoroacetate ($4a^+ \cdot CF_3CO_2^-$): Trifluoroacetic anhydride (252 mg, 1.20 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of **1a** (128 mg, 1.00 mmol) and diphenyl sulfoxide (1.01 g, 5.00 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature for 1 h. The solvent was removed under reduced pressure. The residue was washed several times with Et_2O to give $4a^+ \cdot CF_3CO_2^-$ (422 mg, 99%) as a purple oil. HRMS (ESI): calcd. for $C_{22}H_{17}S^+$ [M – TfO^-]$^+$ 313.1051; found 313.1045. IR (KBr): $\tilde{\nu}_{max}$ = 3092 (w), 3065 (w), 1778 (s), 1738 (s), 1687 (s), 1538 (m), 1541 (w), 1477 (m), 1446 (m), 1402 (s), 1379 (m), 1313 (w), 1269 (m), 1194 (s), 1142 (s), 1070 (w), 1048 (w), 1022 (w), 999 (w), 873 (w), 792 (m), 746 (m), 708 (m), 684 (m), 613 (w), 592 (w), 561 (w), 505 (w), 486 (w), 466 (w), 443 (w), 426 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 300 (4.43), 335 sh (3.68), 358 (3.80), 405 (2.93), 512 (2.94) nm. ^1H NMR (400 MHz, [D_6]acetone): δ = 9.04 (d, J = 10.0 Hz, 1 H, 8-H), 8.74 (d, J = 10.0 Hz, 1 H, 4-H), 8.10 (d, J = 10.0 Hz, 1 H, 2-H), 7.99 (d, J = 4.4 Hz, 1 H, 2-H), 7.81 (t, J = 10.0 Hz, 1 H, 7-H), 7.75 (t, J = 10.0 Hz, 1 H, 5-H), 7.67–7.60 (m, 10 H, 1-S^+Ph_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.69, 143.24, 143.02, 142.10, 138.26, 134.26, 131.71, 130.73, 130.64, 130.41, 128.91, 122.16, 99.65 ppm. $C_{24}H_{17}F_3O_2S \cdot 1.15CH_2Cl_2$: C 57.63, H 3.71; found C 57.87, H 3.47.

1,3-Azulenediylbis(diphenylsulfonium) Bis(trifluoromethanesulfonate) ($5a^{2+} \cdot 2TfO^-$): Trifluoromethanesulfonic anhydride (677 mg,

2.40 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of **1a** (128 mg, 1.00 mmol) and diphenyl sulfoxide (1.01 g, 5.00 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature for 2 h. The solvent was removed under reduced pressure. The residue was dissolved in a small amount of CH_2Cl_2 and then precipitated by the addition of a large amount of Et_2O. The precipitate was collected by filtration and recrystallized from EtOH to give **5a**$^{2+}$·2TfO$^-$ (733 mg, 92%) as prism-shaped orange crystals; m.p. 208.0–210.0 °C (EtOH). HRMS (ESI): calcd. for $C_{34}H_{26}S_{22}^+$ [M – 2TfO$^-$]$^+$ 498.1476; found 498.1464. IR (KBr): $\tilde{\nu}_{max}$ = 3084 (w), 3061 (w), 3046 (w), 3034 (w), 1581 (w), 1537 (w), 1477 (w), 1446 (m), 1425 (m), 1379 (m), 1313 (w), 1273 (s), 1250 (s), 1236 (s), 1224 (s), 1178 (m), 1167 (m), 1149 (m), 1130 (m), 1101 (w), 1066 (w), 1030 (s), 1026 (s), 997 (w), 803 (w), 763 (m), 742 (m), 686 (m), 682 (m), 638 (s), 603 (w), 572 (w), 517 (m), 507 (m), 484 (w), 457 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 300 (4.65), 329 (4.03), 351 (3.98), 480 (3.05) nm. ^{1}H NMR (600 MHz, [D$_6$]-acetone): δ = 9.63 (d, J = 10.0 Hz, 2 H, 4,8-H), 8.75 (t, J = 10.0 Hz, 1 H, 6-H), 8.61 (s, 1 H, 2-H), 8.44 (t, J = 10.0 Hz, 2 H, 5,7-H), 7.99 (d, J = 7.3 Hz, 8 H, *o*-Ph), 7.83 (t, J = 7.3 Hz, 4 H, *p*-Ph), 7.75 (t, J = 7.3 Hz, 8 H, *m*-Ph) ppm. $C_{36}H_{26}F_6O_6S_4$: C 54.26, H 3.29; found C 54.27, H 3.51.

(1-Azulenyl)methylphenylsulfonium Trifluoroacetate (6a$^+$·CF$_3$CO$_2^-$): Trifluoroacetic anhydride (252 mg, 1.20 mmol) was added to a solution of **1a** (128 mg, 1.00 mmol) and methyl phenyl sulfoxide (420 mg, 3.00 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature for 10 min. The solvent was removed under reduced pressure. The residue was washed several times with Et_2O to give **6a**$^+$·$CF_3CO_2^-$ (362 mg, 99%) as a purple oil. HRMS (ESI): calcd. for $C_{17}H_{15}S^+$ [M – $CF_3CO_2^-$]$^+$ 251.0894; found 251.0889. IR (KBr): $\tilde{\nu}_{max}$ = 3096 (w), 3032 (w), 2937 (w), 1778 (s), 1740 (s), 1686 (m), 1583 (m), 1541 (w), 1487 (w), 1477 (w), 1456 (w), 1448 (m), 1402 (m), 1381 (m), 1317 (w), 1304 (w), 1271 (w), 1186 (s), 1147 (s), 1074 (w), 1043 (w), 983 (w), 873 (w), 810 (m), 794 (m), 746 (m), 706 (m), 684 (m), 638 (w), 609 (w), 594 (w), 569 (w), 551 (w), 518 (w), 486 (w), 449 (w), 428 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 286 sh (4.62), 294 (4.67), 334 (3.90), 354 (3.95), 514 (2.87), 538 sh (2.83) nm. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 9.17 (d, J = 10.0 Hz, 2 H, 8-H), 8.94 (d, J = 10.0 Hz, 1 H, 4-H), 8.72 (d, J = 4.8 Hz, 1 H, 2-H), 8.27 (t, J = 10.0 Hz, 1 H, 6-H), 8.09 (dd, J = 6.8, 1.2 Hz, 2 H, *o*-Ph), 4.08 (s, 3 H, 1-S$^+$Me) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 207.41 (C=O), 145.87, 143.25, 143.08, 142.46, 137.48, 136.75, 134.68, 132.23, 131.43, 130.80, 130.48, 130.10, 122.43, 117.66 (q, J = 284.2 Hz, TfO$^-$), 103.19, 31.28 (1-S$^+$Me) ppm. $C_{19}H_{15}F_3O_2S$·1.10CH_2Cl_2: C 52.73, H 3.79; found C 53.03, H 3.49.

1,3-Azulenediylbis(methylphenylsulfonium) Bis(trifluoromethanesulfonate) (7a^{2+}·2TfO$^-$): Trifluoromethanesulfonic anhydride (667 mg, 2.40 mmol) was added to a solution of **1a** (128 mg, 1.00 mmol) and methyl phenyl sulfoxide (841 mg, 6.00 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature for 1 h. The solvent was removed under reduced pressure. The residue was washed several times with Et_2O to give **7a**$^{2+}$·2TfO$^-$ (600 mg, 89%) as prism-shaped orange crystals; m.p. 150.0–152.0 °C (MeOH). HRMS (ESI): calcd. for $C_{24}H_{22}S_2^{2+}$ [M – 2TfO$^-$]$^+$ 374.1163; found 374.1152. IR (KBr): $\tilde{\nu}_{max}$ = 3076 (m), 3032 (m), 2932 (m), 1583 (m), 1537 (w), 1479 (m), 1448 (s), 1419 (s), 1383 (s), 1224 (s), 1155 (s), 1072 (w), 1030 (s), 997 (m), 985 (m), 877 (w), 835 (w), 758 (s), 748 (s), 684 (m), 638 (s), 601 (w), 572 (m), 518 (w), 499 (w), 480 (w), 468 (m), 455 (w), 439 (w), 414 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 226 (4.61), 290 (4.69), 324 (3.97), 342 (3.89), 476 (3.03) nm. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 9.85 (s, 1 H, 2-H), 9.53 (d, J = 9.6 Hz, 2 H, 4,8-H), 8.66 (t, J = 9.6 Hz, 1 H, 6-H), 8.35 (t, J = 9.6 Hz, 2 H, 5,7-H), 8.26 (dd, J = 6.8, 1.2 Hz, 4 H, *o*-Ph), 7.71 (m, 6 H, *m*- and *p*-Ph), 4.18 (s, 6 H, 1,3-S$^+$Me) ppm. $C_{26}H_{22}F_6O_6S_4$: C 46.42, H 3.30; found C 46.51, H 3.42.

1-Azulenyl Methyl Sulfide (8a):[3] Et_2NH (10 mL) was added to a solution of **2a**$^+$·$CF_3CO_2^-$ (302 mg, 1.00 mmol) in EtOH (10 mL). The solution was refluxed for 30 min. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel with hexane/AcOEt (4:1) as eluent to give **8a** (173 mg, 99%) as a dark-blue oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, J = 9.6 Hz, 1 H, 8-H), 8.22 (d, J = 9.6 Hz, 1 H, 4-H), 7.94 (d, J = 4.0 Hz, 1 H, 2-H), 7.55 (t, J = 9.6 Hz, 1 H, 6-H), 7.34 (d, J = 4.0 Hz, 1 H, 3-H), 7.18 (t, J = 9.6 Hz, 1 H, 7-H), 7.11 (t, J = 9.6 Hz, 1 H, 5-H), 2.45 (s, 3 H, -SCH$_3$) ppm. ^{13}C NMR (100MHz, $CDCl_3$): δ = 142.01, 140.28, 139.24, 138.76, 137.40, 135.75, 124.04, 123.53, 122.20, 117.77, 20.96 ppm.

6-*tert*-Butyl-1-azulenyl Methyl Sulfide (8b): Trifluoroacetic anhydride (504 mg, 2.40 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **1b** (184 mg, 1.00 mmol) and DMSO (390 mg, 5.00 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature for 30 min. The solvent was removed under reduced pressure. EtOH (10 mL) and Et_2NH were added to the residue and the mixture was refluxed for 30 min. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4:1) as eluent to give **8b** (225 mg, 96% from **1b**) as a dark-blue oil. MS (EI): *m*/*z* (%) = 230 (100) [M]$^+$, 215 (77), 200 (10), 185 (10), 167 (9). IR (KBr): $\tilde{\nu}_{max}$ = 2964 (m), 1581 (s), 1549 (w), 1477 (m), 1400 (s), 1368 (w), 1304 (w), 1253 (w), 1236 (w), 1057 (w), 997 (w), 966 (w), 929 (w), 841 (m), 821 (w), 765 (w), 711 (w), 675 (w), 453 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 253 (4.05), 290 sh (4.48), 296 (4.51), 335 (3.62), 351 (3.65), 588 (2.53) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, J = 10.0 Hz, 1 H, 8-H), 8.22 (d, J = 10.0 Hz, 1 H, 4-H), 7.86 (d, J = 3.6 Hz, 1 H, 2-H), 7.43 (dd, J = 10.0, 1.2 Hz, 1 H, 7-H), 7.35 (dd, J = 10.0, 1.2 Hz, 1 H, 5-H), 7.28 (d, J = 3.6 Hz, 1 H, 3-H), 2.46 (s, 3 H, 1-SMe), 1.46 (s, 9 H, 6-*t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 140.0, 138.9, 137.4, 135.7, 134.0, 121.2, 120.9, 120.8, 116.6, 38.2 (s, 6-*t*Bu), 31.5 (q, 6-*t*Bu), 20.4 (1-SMe) ppm. $C_{15}H_{18}S$: C 78.21, H 7.88; found C 78.21, H 7.99.

1,3-Bis(methylthio)azulene (9a):[3] Et_2NH (10 mL) was added to a solution of **3a**$^{2+}$·2TfO$^-$ (548 mg, 1.00 mmol) in EtOH (10 mL). The solution was refluxed for 30 min. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel with hexane/AcOEt (4:1) as eluent to give **9a** (219 mg, 99%) as a dark-blue oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, J = 9.6 Hz, 2 H, 4,8-H), 7.98 (s, 1 H, 2-H), 7.62 (t, J = 9.6 Hz, 1 H, 6-H), 7.21 (t, J = 9.6 Hz, 2 H, 5,7-H), 2.48 (s, 6 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.41, 139.75, 139.00, 135.29, 123.48, 121.29, 20.07 ppm.

6-*tert*-Butyl-1,3-bis(methylthio)azulene (9b): Trifluoromethanesulfonic anhydride (677 mg, 2.40 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **1b** (184 mg, 1.00 mmol) and DMSO (390 mg, 5.00 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature for 30 min. The solvent was removed under reduced pressure. EtOH (10 mL) and Et_2NH (10 mL) were added to the residue and the mixture was refluxed for 30 min. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4:1) as eluent to give **9b** (265 mg, 95% from **1b**) as dark-blue crystals; m.p. 49.0–51.0 °C. HRMS (ESI): calcd. for $C_{16}H_{20}S_2^+$ [M]$^+$ 276.1006;

found 276.1001. IR (KBr): $\tilde{\nu}_{max}$ = 2964 (s), 2914 (s), 2866 (m), 2824 (w), 1581 (s), 1547 (w), 1475 (s), 1435 (m), 1404 (s), 1383 (m), 1361 (s), 1292 (m), 1253 (m), 1232 (w), 1196 (w), 1180 (w), 1107 (w), 1062 (m), 1018 (w), 968 (m), 922 (w), 875 (m), 846 (m), 819 (m), 702 (w), 677 (m), 615 (m), 482 (w), 468 (w), 451 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 240 (4.28), 304 (4.48), 322 sh (4.28), 346 sh (3.91), 376 sh (3.72), 406 (3.51), 604 (2.56) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 10.0 Hz, 2 H, 4,8-H), 7.84 (s, 1 H, 2-H), 7.41 (d, J = 10.0 Hz, 2 H, 5,7-H), 2.46 (s, 6 H, 1-SMe), 1.45 (s, 9 H, 6-*t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.75, 141.80, 139.38, 135.02, 122.45, 121.13, 39.16 (s, 6-*t*Bu), 32.36 (q, 6-*t*Bu), 20.97 (1-SMe) ppm. $C_{16}H_{20}S_2$: calcd. C 69.51, H 7.29; found C 69.61, H 7.11.

1-Azulenyl Phenyl Sulfide (10a):[3] Et_2NH (10 mL) was added to a solution of **6a**$^+$·$CF_3CO_2^-$ (364 mg, 1.00 mmol) in EtOH (10 mL). The solution was refluxed for 30 min. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel with hexane/AcOEt (4:1) as eluent to give **10a** (231 mg, 98%) as dark-blue crystals; m.p. 80.0–81.5 °C (ref.[3] 84–84.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, J = 9.6 Hz, 1 H, 8-H), 8.38 (d, J = 9.6 Hz, 1 H, 4-H), 8.03 (d, J = 3.6 Hz, 1 H, 2-H), 7.69 (t, J = 9.6 Hz, 1 H, 6-H), 7.46 (d, J = 3.6 Hz, 1 H, 3-H), 7.33–7.24 (m, 2 H, 5,7-H), 7.13 (t, J = 7.6 Hz, 2 H, *m*-Ph), 7.03 (t, J = 7.6 Hz, 1 H, *p*-Ph), 6.95 (d, J = 7.6 Hz, 2 H, *o*-Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.49, 142.30, 141.49, 138.60, 137.26, 135.77, 131.00, 129.16, 128.69, 125.88, 124.72, 124.52, 117.78, 114.88 ppm.

6-*tert*-Butyl-1-azulenyl Phenyl Sulfide (10b): Trifluoroacetic anhydride (756 mg, 3.60 mmol) in CH_2Cl_2 (20 mL) was added to a solution of **1b** (184 mg, 1.00 mmol) and methyl phenyl sulfoxide (1.26 g, 9.00 mmol) in CH_2Cl_2 (30 mL). The resulting solution was stirred at room temperature for 30 min. The solvent was removed under reduced pressure. EtOH (20 mL) and Et_2NH (20 mL) were added to the residue and the mixture was refluxed for 10 min. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/CH_2Cl_2 (4:1) as eluent to give **10b** (274 mg, 94%) as a purple oil. HRMS (ESI): calcd. for $C_{20}H_{20}S^+$ $[M]^+$ 292.1286; found 292.1280. IR (KBr): $\tilde{\nu}_{max}$ = 3071 (w), 2964 (m), 2905 (w), 2868 (w), 1583 (s), 1551 (w), 1477 (s), 1439 (w), 1402 (s), 1363 (w), 1304 (w), 1250 (w), 1236 (w), 1180 (w), 1157 (w), 1080 (w), 1024 (w), 1005 (w), 931 (w), 895 (w), 843 (m), 821 (w), 769 (w), 736 (m), 713 (w), 690 (m), 675 (w), 617 (w), 605 (w), 484 (w), 449 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 236 (4.40), 286 (4.68), 296 (4.68), 350 sh (3.82), 368 sh (3.57), 556 (2.62), 590 sh (2.58), 656 sh (2.14) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (d, J = 10.0 Hz, 1 H, 8-H), 8.33 (d, J = 10.0 Hz, 1 H, 4-H), 7.94 (d, J = 4.0 Hz, 1 H, 2-H), 7.49 (dd, J = 10.0, 1.2 Hz, 2 H, 5,7-H), 7.37 (d, J = 4.0 Hz, 1 H, 3-H), 7.13 (t, J = 8.0 Hz, 2 H, *m*-Ph), 7.13 (d, J = 8.0 Hz, 1 H, *p*-Ph), 6.96 (d, J = 8.0 Hz, 2 H, *o*-Ph), 1.46 (s, 9 H, 6-*t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.21, 143.14, 141.49, 141.26, 140.82, 136.81, 135.19, 129.117, 129.115, 126.24, 125.03, 123.29, 117.60, 114.36, 39.22 (s, 6-*t*Bu), 32.35 (q, 6-*t*Bu) ppm. $C_{20}H_{20}S$: C 82.14, H 6.89; found C 82.00, H 6.85.

1,3-Bis(phenylthio)azulene (11a):[3] Et_2NH (10 mL) was added to a solution of **7a**$^{2+}$·2TfO^- (548 mg, 1.00 mmol) in EtOH (10 mL). The solution was refluxed for 30 min. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel with hexane/AcOEt (4:1) as eluent to give **11a** (210 mg, 95%) as dark-blue crystals; m.p. 121.0–123.0 °C (ref.[3] 127–128.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, J = 9.6 Hz, 2 H, 4,8-H), 8.17 (s, 1 H, 2-H), 7.74 (t, J = 9.6 Hz, 1 H, 6-H), 7.38 (t, J = 9.6 Hz, 2 H, 5,7-H), 7.15 (t, J = 7.6 Hz, 4 H, *m*-Ph), 7.05 (t, J = 7.6 Hz, 2 H, *p*-Ph), 7.01 (d, J = 7.6 Hz, 4 H, *o*-Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.97, 143.80, 140.35, 140.06, 136.93, 129.30, 126.70, 126.69, 125.56, 115.88 ppm.

6-*tert*-Butyl-1,3-bis(phenylthio)azulene (11b): Trifluoromethanesulfonic anhydride (667 mg, 2.40 mmol) in CH_2Cl_2 (20 mL) was added to a solution of **1b** (184 mg, 1.00 mmol) and methyl phenyl sulfoxide (841 mg, 6.00 mmol) in CH_2Cl_2 (20 mL). The resulting solution was stirred at room temperature for 10 min. The solvent was removed under reduced pressure. EtOH (20 mL) and Et_2NH (20 mL) were added to the residue and the mixture was refluxed for 10 min. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as eluent to give **11b** (369 mg, 92%) as purple crystals; m.p. 125.0–130.0 °C. HRMS (ESI): calcd. for $C_{26}H_{24}S_2^+$ $[M]^+$ 400.1319; found 400.1314. IR (KBr): $\tilde{\nu}_{max}$ = 3071 (w), 3053 (w), 2951 (w), 2864 (w), 1579 (s), 1475 (s), 1437 (m), 1410 (s), 1394 (w), 1360 (m), 1327 (w), 1296 (w), 1250 (w), 1234 (w), 1178 (w), 1101 (w), 1080 (w), 1022 (m), 997 (w), 922 (w), 898 (w), 844 (m), 819 (w), 736 (m), 688 (m), 675 (w), 613 (w), 595 (w), 490 (w), 464 (w), 447 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 238 (4.45), 254 sh (4.39), 290 (4.49), 302 (4.49), 370 sh (3.75), 560 (2.63) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, J = 10.8 Hz, 2 H, 4,8-H), 8.09 (s, 1 H, 2-H), 7.59 (d, J = 10.8 Hz, 2 H, 5,7-H), 7.15 (t, J = 8.0 Hz, 4 H, *m*-Ph), 7.04 (t, J = 8.0 Hz, 2 H, *p*-Ph), 7.01 (d, J = 8.0 Hz, 4 H, *o*-Ph), 1.44 (s, 9 H, 6-*t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.82, 149.30, 142.64, 140.46, 135.88, 129.23, 126.51, 125.35, 124.99, 114.79, 39.43 (s, 6-*t*Bu), 32.27 (q, 6-*t*Bu) ppm. $C_{20}H_{20}S$: C 77.95, H 6.04; found C 77.65, H 5.85.

1-Azulenyl Methyl Sulfoxide (12a):[3] 70% MCPBA (260 mg) in CH_2Cl_2 (20 mL) was added to a solution of **8a** (174 mg, 1.00 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at 0 °C for 5 min. The reaction mixture was poured into 10% $NaHCO_3$, extracted with CH_2Cl_2, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by reversed-phase column chromatography (ODS with 70% MeOH) to give **12a** (183 mg, 96%) as a purple oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.83 (d, J = 9.5 Hz, 1 H, 8-H), 8.43 (d, J = 9.5 Hz, 1 H, 4-H), 8.31 (d, J = 4.5 Hz, 1 H, 2-H), 7.76 (t, J = 9.5 Hz, 1 H, 6-H), 7.44 (d, J = 4.5 Hz, 1 H, 3-H), 7.40 (t, J = 9.5 Hz, 1 H, 7-H), 7.37 (t, J = 9.5 Hz, 1 H, 5-H), 2.97 [s, 3 H, 1-S(O)Me] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.91, 139.20, 138.76, 137.38, 134.16, 133.33, 127.69, 125.93, 125.65, 118.30, 42.02 [1-S(O)Me] ppm.

6-*tert*-Butyl-1-azulenyl Methyl Sulfoxide (12b): 70% MCPBA (260 mg) in CH_2Cl_2 (20 mL) was added to a solution of **8b** (230 mg, 1.00 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at 0 °C for 5 min. The reaction mixture was poured into 10% $NaHCO_3$, extracted with CH_2Cl_2, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by reversed-phase column chromatography (ODS with 70% MeOH) to give **12b** (241 mg, 98%) as a purple oil. HRMS (ESI): calcd. for $C_{15}H_{18}OS$ + Na^+ $[M + Na]^+$ 269.0976; found 269.0971. IR (KBr): $\tilde{\nu}_{max}$ = 2966 (m), 2870 (w), 1585 (s), 1552 (w), 1402 (s), 1294 (s), 1240 (w), 1190 (w), 1172 (m), 1126 (s), 1024 (m), 964 (m), 848 (m), 760 (m), 758 (m), 713 (w), 711 (w), 677 (w), 584 (w), 534 (m), 501 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 256 (3.66), 289 sh (4.60), 298 (4.66), 321 (3.66), 345 (3.77), 357 (3.49), 520 (2.86) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (d, J = 10.0 Hz, 1 H, 8-H), 8.42 (d, J = 10.0 Hz, 1 H, 4-H), 8.22 (d, J = 4.4 Hz, 1 H, 2-H), 7.64 (dd, J = 10.0, 1.2 Hz, 1 H, 7-H), 7.60 (dd, J = 10.0, 1.2 Hz, 1 H, 5-H), 7.37 (d, J = 4.4 Hz, 1 H, 3-H), 2.46 [s, 3 H, 1-S(O)Me], 1.48 (s, 9 H, 6-*t*Bu) ppm. ^{13}C

NMR (100 MHz, $CDCl_3$): δ = 163.88, 141.72, 137.85, 136.41, 133.35, 132.51, 127.03, 124.18, 124.05, 117.75, 42.04 [1-S(O)Me], 38.79 (s, 6-*t*Bu), 31.68 (q, 6-*t*Bu) ppm. $C_{15}H_{18}OS$: C 73.13, H 7.36; found C 73.17, H 7.48.

1-Azulenyl Phenyl Sulfoxide (13a):[3] 70% MCPBA (260 mg) in CH_2Cl_2 (20 mL) was added to a solution of **10a** (236 mg, 1.00 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at 0 °C for 5 min. The reaction mixture was poured into 10% $NaHCO_3$, extracted with CH_2Cl_2, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/AcOEt (1:1) as eluent to give **13a** (240 mg, 95%) as a purple oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.00 (d, *J* = 10.0 Hz, 1 H, 8-H), 8.42 (d, *J* = 10.0 Hz, 1 H, 4-H), 7.89 (d, *J* = 4.0 Hz, 1 H, 2-H), 7.79 (d, *J* = 10.0 Hz, 1 H, 6-H), 7.65 (dd, *J* = 7.0, 1.5 Hz, 2 H, *o*-Ph), 7.46 (t, *J* = 10.0 Hz, 1 H, 7-H), 7.42–7.40 (m, 3 H, *m*- and *p*-Ph), 7.40 (t, *J* = 10.0 Hz, 1 H, 5-H), 7.34 (d, *J* = 4.0 Hz, 1 H, 3-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.48, 143.41, 139.37, 138.92, 138.88, 136.13, 134.64, 129.95, 128.81, 128.20, 126.46, 126.37, 124.50, 118.47 ppm.

6-*tert*-Butyl-1-azulenyl Phenyl Sulfoxide (13b): 70% MCPBA (260 mg) in CH_2Cl_2 (20 mL) was added to a solution of **10b** (230 mg, 1.00 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at 0 °C for 5 min. The reaction mixture was poured into 10% $NaHCO_3$, extracted with CH_2Cl_2, dried with $MgSO_4$, and concentrated under reduced pressure. The residure was purified by column chromatography on silica gel with CH_2Cl_2 as eluent and reversed-phase column chromatography (ODS with 70% MeOH) to give **13b** (300 mg, 97%) as purple crystals; m.p. 99.0–102.0 °C. HRMS (ESI): calcd. for $C_{20}H_{20}OS + Na^+$ $[M + Na]^+$ 331.1133; found 331.1127. IR (KBr): $\tilde{\nu}_{max}$ = 3055 (w), 2964 (m), 2907 (w), 2868 (w), 1583 (s), 1551 (w), 1475 (m), 1442 (m), 1400 (s), 1365 (w), 1304 (w), 1282 (w), 1257 (w), 1238 (w), 1186 (w), 1161 (m), 1147 (w), 1082 (w), 1035 (s), 1022 (s), 997 (w), 925 (w), 898 (w), 844 (m), 821 (w), 746 (m), 736 (m), 713 (w), 692 (m), 675 (w), 617 (w), 599 (w), 528 (w), 480 (m), 451 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 290 sh (4.63), 298 (4.74), 348 (3.89), 360 sh (3.65), 526 (2.65), 558 sh (2.59), 614 sh (2.12) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (d, *J* = 10.4 Hz, 1 H, 8-H), 8.36 (d, *J* = 10.4 Hz, 1 H, 4-H), 7.79 (d, *J* = 4.0 Hz, 1 H, 2-H), 7.65 (m, 3 H, 7-H, *o*-Ph), 7.42 (t, *J* = 8.0 Hz, 1 H, *m*-Ph), 7.38 (t, *J* = 8.0 Hz, 1 H, *m*-Ph), 7.24 (d, *J* = 4.0 Hz, 1 H, 3-H), 1.45 (s, 9 H, 6-*t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.25, 148.00, 144.34, 140.21, 137.50, 135.95, 132.05, 131.00, 129.62, 127.03, 126.81, 126.76, 125.60, 120.12, 41.13 (s, 6-*t*Bu), 34.00 (q, 6-*t*Bu) ppm. $C_{20}H_{20}OS \cdot H_2O$: C 76.98, H 6.59; found C 76.77, H 6.33.

3,3′-Bis(methylthio)-1,1′-biazulene (15a)

Reaction with CF_3CO_2H: CF_3CO_2H (10 mL) was added to a solution of **12a** (190 mg, 1.00 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at 0 °C for 5 min. The reaction mixture was poured into 1 M NaOH and extracted with toluene, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4:1) as eluent to give **15a** (154 mg, 89%) as brown crystals.

Reaction with 60% HPF_6: 60% HPF_6 (5 mL) was added to a solution of **12a** (190 mg, 1.00 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at 0 °C for 5 min. The reaction mixture was poured into 1 M NaOH and extracted with toluene, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4:1) as eluent to give **15a** (151 mg, 87%) as brown crystals.

Reaction with TfOH: TfOH (1 mL) was added to a solution of **12a** (190 mg, 1.00 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was poured into 1 M NaOH and extracted with toluene, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4:1) as eluent to give **15a** (68 mg, 39%) as brown crystals; m.p. 138.0–140 °C (hexane). HRMS (ESI): calcd. for $C_{30}H_{20}N_2 + H^+$ $[M + H]^+$ 409.1705; found 409.1699. MS (EI): *m*/*z* (%) = 345 (100) $[M]^+$, 330 (45), 315 (19), 300 (12), 282 (12), 239 (10), 158 (19), 109 (20), 84 (10). IR (KBr): $\tilde{\nu}_{max}$ = 3038 (w), 2918 (w), 1568 (s), 1483 (m), 1444 (w), 1396 (s), 1298 (m), 1263 (w), 1211 (w), 985 (w), 960 (w), 941 (w), 927 (m), 860 (m), 735 (s), 572 (w), 557 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 242 (4.43), 278 (4.56), 402 (4.07), 638 (2.81) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (d, *J* = 10.4 Hz, 1 H, 8-H), 8.24 (d, *J* = 10.4 Hz, 1 H, 4-H), 8.11 (s, 1 H, 2-H), 7.59 (t, *J* = 10.4 Hz, 1 H, 6-H), 7.20 (t, *J* = 10.4 Hz, 1 H, 7-H), 7.06 (t, *J* = 10.4 Hz, 1 H, 5-H), 2.56 (s, 3 H, 3,3′-SMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.45, 139.55, 139.17, 138.23, 136.45, 135.65, 125.13, 123.68, 123.14, 121.63, 20.29 (3,3′-SMe) ppm. $C_{22}H_{18}S_2$: C 76.26, H 5.24; found C 75.98, H 5.46.

6,6′-Di-*tert*-butyl-3,3′-bis(methylthio)-1,1′-biazulene (15b)

Reaction with CF_3CO_2H: CF_3CO_2H (10 mL) was added to a solution of **12b** (246 mg, 1.00 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was poured into 1 M NaOH and extracted with toluene, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4:1) as eluent to give **15b** (183.5 mg, 80%) as green crystals.

Reaction with 60% HPF_6: 60% HPF_6 (5 mL) was added to a solution of **12b** (246 mg, 1.00 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was poured into 1 M NaOH and extracted with toluene, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4:1) as eluent to give **15b** (210 mg, 81%) as green crystals; m.p. 93.0–95.0 °C (hexane). MS (EI): *m*/*z* (%) = 458 (17) $[M]^+$, 412 (29), 276 (49), 261 (35), 84 (100). IR (KBr): $\tilde{\nu}_{max}$ = 2963 (m), 2916 (w), 2868 (w), 1576 (s), 1477 (m), 1406 (s), 1361 (m), 1304 (w), 1252 (m), 1061 (w), 1018 (w), 964 (m), 935 (m), 870 (w), 837 (m), 821 (w), 677 (w), 619 (w), 582 (w), 451 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 290 (4.66), 303 sh (4.62), 367 (3.98), 407 (4.17), 499 (1.96), 625 (2.87) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 10.4 Hz, 1 H, 8-H), 8.25 (d, *J* = 10.4 Hz, 1 H, 4-H), 8.02 (s, 1 H, 2-H), 7.38 (dd, *J* = 10.4, 1.2 Hz, 1 H, 7-H), 7.25 (dd, *J* = 10.4, 1.2 Hz, 1 H, 5-H), 2.53 (s, 3 H, 3,3′-SMe), 1.45 (s, 9 H, 6-*t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.04, 139.74, 138.38, 136.90, 135.51, 134.53, 124.90, 121.80, 121.24, 120.77, 38.60 (s, 6-*t*Bu), 31.77 (q, 6-*t*Bu), 20.47 (3,3′-SMe) ppm. $C_{30}H_{34}S_2$: C 78.55, H 7.47; found C 78.56, H 7.55.

3,3′-Bis(phenylthio)-1,1′-biazulene (16a)

Reaction with CF_3CO_2H: CF_3CO_2H (10 mL) was added to a solution of **13a** (252 mg, 1.00 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at 0 °C for 5 min. The reaction mixture was poured into 1 M NaOH and extracted with toluene, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/CH_2Cl_2 (4:1) as eluent to give **16a** (120 mg, 51%) as green crystals.

Reaction with 60% HPF_6: 60% HPF_6 (5 mL) was added to a solution of **13a** (252 mg, 1.00 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at 0 °C for 5 min. The reaction mixture was poured into 1 M NaOH and extracted with toluene, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/CH_2Cl_2 (4:1) as eluent to give **15a** (167 mg, 71%) as green crystals; m.p. 187.0–

189.0 °C. HRMS (ESI): calcd. for $C_{32}H_{22}S_2$ + Na^+ $[M + Na]^+$ 493.1061; found 493.1055. MS (EI): *m*/*z* (%) = 470 (100) $[M]^+$, 235 (7). IR (KBr): $\tilde{\nu}_{max}$ = 3059 (w), 3017 (w), 1570 (s), 1475 (m), 1406 (w), 1394 (s), 1350 (w), 1327 (w), 1300 (w), 1290 (w), 1263 (w), 1211 (w), 1178 (w), 1149 (w), 1095 (w), 1078 (w), 1022 (w), 997 (w), 949 (w), 935 (w), 900 (w), 893 (w), 873 (w), 835 (w), 731 (s), 687 (m), 578 (w), 515 (w), 499 (w), 478 (w), 453 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 242 (4.43), 278 (4.56), 402 (4.07), 638 (2.81) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.71 (d, *J* = 9.6 Hz, 2 H, 8,8′-H), 8.41 (d, *J* = 9.6 Hz, 2 H, 4,4′-H), 8.24 (s, 2 H, 2,2′-H), 7.66 (t, *J* = 9.6 Hz, 2 H, 6,6′-H), 7.27 (t, *J* = 9.6 Hz, 2 H, 7,7′-H), 7.20 (t, *J* = 9.6 Hz, 2 H, 5,5′-H), 7.16 (t, *J* = 7.6 Hz, 4 H, *m*-Ph), 7.09–7.04 (m, 6 H, *o*- and *p*-Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.25, 142.18, 140.06, 139.53, 139.12, 136.63, 136.27, 128.81, 128.80, 126.17, 125.29, 124.94, 124.94, 114.91 ppm. $C_{32}H_{22}S_2$: C 81.66, H 4.71; found C 81.61, H 4.81.

6,6′-Di-*tert*-butyl-3,3′-bis(phenylthio)-1,1′-biazulene (16b)

Reaction with CF_3CO_2H: CF_3CO_2H (10 mL) was added to a solution of **13b** (308 mg, 1.00 mmol) in CH_2Cl_2 (20 mL). The solution was stirred at 0 °C for 5 min. The reaction mixture was poured into 1 M NaOH and extracted with toluene, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/CH_2Cl_2 (4:1) as eluent to give **15b** (152 mg, 56%) as green crystals.

Reaction with 60% HPF_6: 60% HPF_6 (5 mL) was added to a solution of **13b** (308 mg, 1.00 mmol) in CH_2Cl_2 (20 mL). The solution was stirred at 0 °C for 5 min. The reaction mixture was poured into 1 M NaOH and extracted with toluene, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/CH_2Cl_2 (4:1) as eluent to give **15b** (223 mg, 77%) as green crystals; m.p. 112.0–115.0 °C. HRMS (ESI): calcd. for $C_{40}H_{38}S_2^+$ $[M]^+$ 582.2415; found 582.2409. IR (KBr): $\tilde{\nu}_{max}$ = 3071 (w), 2964 (m), 2905 (w), 2868 (w), 1583 (s), 1551 (w), 1477 (s), 1439 (w), 1402 (s), 1363 (w), 1304 (w), 1250 (w), 1236 (w), 1180 (w), 1157 (w), 1080 (w), 1024 (w), 1005 (w), 931 (w), 895 (w), 843 (m), 821 (w), 769 (w), 736 (m), 713 (w), 690 (m), 675 (w), 617 (w), 605 (w), 484 (w), 449 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 246 (4.70), 278 (4.78), 312 (4.70), 398 (4.22), 604 (2.97) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 10.0 Hz, 2 H, 8,8′-H), 8.43 (d, *J* = 10.0 Hz, 2 H, 4,4′-H), 8.16 (s, 2 H, 2,2′-H), 7.45 (dd, *J* = 10.0, 1.2 Hz, 2 H, 7,7′-H), 7.40 (dd, *J* = 10.0, 1.2 Hz, 2 H, 5,5′-H), 7.17 (t, *J* = 8.0 Hz, 4 H, *o*-Ph), 7.07 (d, *J* = 8.0 Hz, 4 H, *m*-Ph), 7.05 (t, *J* = 8.0 Hz, 2 H, *p*-Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.06, 143.78, 141.41, 141.01, 138.23, 136.13, 135.55, 129.17, 126.39, 125.50, 125.12, 123.54, 123.20, 114.23, 39.19 (s, 6-*t*Bu), 32.23 (q, 6-*t*Bu) ppm. $C_{40}H_{38}S_2$: C 82.43, H 6.57; found C 82.19, H 6.84.

1,1′-Biazulene-3,3′-dicarbaldehyde (17a)[11]

Vilsmeier Reaction of 15a: $POCl_3$ (613 mg, 4.00 mmol) was added to a solution of **15a** (346 mg, 1.00 mmol) in DMF (20 mL). The solution was stirred at 50 °C for 24 h. The reaction mixture was poured into 1 M NaOH and extracted with AcOEt, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/AcOEt (1:1) as eluent to give **17a** (280 mg, 90%) as brown crystals.

Vilsmeier Reaction of 16a: $POCl_3$ (767 mg, 5.00 mmol) was added to a solution of **16a** (235 mg, 0.50 mmol) in DMF (10 mL). The solution was stirred at 50 °C for 24 h. The reaction mixture was poured into 1 M NaOH and extracted with AcOEt, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/AcOEt (1:1) as eluent to give **17a** (101 mg, 65%) as brown crystals; m.p. 247.0–251.0 °C (ref.[11] 254–256 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 10.45 (s, 2 H, 3,3′-CHO), 9.63 (d, *J* = 9.6 Hz, 2 H, 4-H), 8.46 (d, *J* = 9.6 Hz, 2 H, 8-H), 8.40 (s, 2 H, 2-H), 7.89 (t, *J* = 9.6 Hz, 2 H, 6-H), 7.66 (t, *J* = 9.6 Hz, 2 H, 5-H), 7.47 (t, *J* = 9.6 Hz, 2 H, 7-H) ppm. ^{13}C NMR (100 MHz. $CDCl_3$): δ = 186.25 (s, 3,3′-CHO), 143.16, 142.48, 141.08, 140.66, 137.93, 137.74, 129.72, 128.49, 125.61, 125.00 ppm.

6,6′-Di-*tert*-butyl-1,1′-biazulene-3,3′-dicarbaldehyde (17b)

Vilsmeier Reaction of 15b: $POCl_3$ (613 mg, 4.00 mmol) was added to a solution of **15b** (458 mg, 1.00 mmol) in DMF (20 mL). The solution was stirred at 50 °C for 24 h. The reaction mixture was poured into 1 M NaOH and extracted with AcOEt, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/AcOEt (1:1) as eluent to give **17b** (388 mg, 92%) as brown needle-shaped crystals.

Vilsmeier Reaction of 16b: $POCl_3$ (613 mg, 4.00 mmol) was added to a solution of **16b** (583 mg, 1.00 mmol) in DMF (20 mL). The solution was stirred at 50 °C for 24 h. The reaction mixture was poured into 1 M NaOH and extracted with AcOEt, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/AcOEt (1:1) as eluent to give **17b** (388 mg, 72%) as brown needle-shaped crystals; m.p. 147.0–148.0 °C (acetone). HRMS (ESI): calcd. for $C_{30}H_{30}O_2$ + Na^+ $[M + Na]^+$ 445.2143; found 445.2138. IR (KBr): $\tilde{\nu}_{max}$ = 2964 (m), 2872 (w), 2723 (w), 1651 (s), 1579 (s), 1294 (s), 1500 (m), 1460 (m), 1437 (m), 1419 (m), 1400 (m), 1363 (m), 1288 (m), 1244 (m), 1190 (w), 1163 (w), 1128 (w), 1074 (w), 877 (w), 846 (w), 814 (w), 792 (w), 675 (w), 659 (w), 559 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 240 (4.52), 298 (4.85), 318 sh (4.79), 424 sh (4.10), 546 (3.12) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 10.46 (s, 2 H, 3,3′-CHO), 8.57 (d, *J* = 10.4 Hz, 2 H, 8-H), 8.49 (d, *J* = 10.4 Hz, 2 H, 4-H), 8.36 (s, 1 H, 2-H), 7.86 (dd, *J* = 10.4, 1.2 Hz, 2 H, 7-H), 7.70 (dd, *J* = 10.4, 1.2 Hz, 2 H, 5-H), 1.45 (s, 18 H, 6,6′-*t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.20 (s, 3,3′-CHO), 165.58, 142.21, 141.39, 140.15, 137.02, 136.86, 127.77, 127.14, 125.53, 124.88, 39.06 (s, 6,6′-*t*Bu), 31.81 (q, 6,6′-*t*Bu) ppm. $C_{30}H_{30}O_2 \cdot ½H_2O$: C 83.49, H 7.24; found C 83.49, H 7.18.

1,1′-Biazulene (18a):[9] Pyrrole (5 mL) was added to a solution of **17a** (100 mg, 0.32 mmol) in acetic acid (5 mL). The solution was stirred at room temperature for 24 h. The reaction mixture was poured into water and extracted with hexane, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/CH_2Cl_2 (4:1) to afford **18a** (62 mg, 71%) as green crystals; m.p. 102–104 °C (ref.[9] 104–105 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 10.0 Hz, 2 H, 4,8-H), 8.03 (d, *J* = 4.0 Hz, 1 H, 2-H), 7.46 (d, *J* = 10.0 Hz, 1 H, 6-H), 7.44 (d, *J* = 4.0 Hz, 1 H, 3-H), 7.04 (t, *J* = 10.0 Hz, 1 H, 5-H), 6.95 (t, *J* = 10.0 Hz, 1 H, 7-H) ppm.

6,6′-Di-*tert*-butyl-1,1′-biazulene (18b): Pyrrole (3 mL) was added to a solution of **17b** (60 mg, 0.14 mmol) in acetic acid (3 mL). The solution was stirred at room temperature for 24 h. The reaction mixture was poured into water and extracted with hexane, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/CH_2Cl_2 (4:1) to afford **18b** (41 mg, 80%) as green crystals; m.p. 75.0–77.0 °C. HRMS (EI): calcd. for $C_{28}H_{30}^+$ $[M]^+$ 366.2348; found 366.2344. IR (KBr): $\tilde{\nu}_{max}$ = 2963 (s), 2903 (m), 2866 (m), 1576 (s), 1549 (m), 1481 (m), 1460 (m), 1402 (s), 1361 (m), 1304 (w), 1252 (w), 1234 (w), 1196 (w), 1093 (w), 1057 (w), 1020 (w), 997 (w), 908 (w), 837 (s), 819 (m), 769 (m), 711 (w), 675 (w), 617

(w), 542 (w), 449 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 244 (4.43), 268 (4.67), 312 (4.61), 386 (4.20), 432 sh (3.82), 612 (2.81) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, J = 10.0 Hz, 1 H, 4-H), 8.20 (d, J = 10.4 Hz, 1 H, 8-H), 7.94 (d, J = 4.0 Hz, 1 H, 2-H), 7.35 (d, J = 4.0 Hz, 1 H, 3-H), 7.20 (dd, J = 10.0, 1.6 Hz, 1 H, 7-H), 7.15 (dd, J = 10.0, 1.6 Hz, 1 H, 7-H), 1.35 (s, 9 H, 6-*t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.29, 140.45, 137.96, 136.37, 135.75, 135.68, 126.98, 121.38, 121.17, 117.44, 38.96 (s, 6-*t*Bu), 32.33 (q, 6-*t*Bu) ppm. $C_{28}H_{30}$: C 91.75, H 8.25; found C 91.70, H 8.11.

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