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Heteroarylation of 1-Azulenyl Methyl Sulfide: Two-Step Synthetic Strategy for 1-Methylthio-3-(heteroaryl)azulenes Using the Triflate of *N*-Containing Heterocycles

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1-Azulenyl methyl sulfide reacts with highly electrophilic trifluoromethanesulfonates of *N*-heterocycles, that is, pyridine, isoquinoline, 1,10-phenanthroline, benzothiazole, quinoline, and acridine, to give 1-methylthio-3-(dihydroheteroaryl)azulenes in good yields. In the case of the reaction with the trifluoromethanesulfonate of pyridine, 1-methylthio-3-pyridylazulene was obtained directly under certain reaction conditions. Treatment of the 1-methylthio-3-(dihydroheteroaryl)azulenes with KOH or *t*BuOK afforded the corresponding 1-methylthio-3-(heteroaryl)azulenes in good yields. The redox behavior of these 1-methylthio-3-(heteroaryl)azulenes was examined by cyclic voltammetry and differential pulse voltammetry.

Introduction

Transition-metal-catalyzed aryl–aryl cross-coupling of aryl halides with organometallic reagents is one of the most powerful tools for the construction of biaryl compounds. A large number of transition-metal-catalyzed aryl–aryl cross-coupling reactions, such as the Stille,[1] Suzuki–Miyaura,[2] and Negishi[3] cross-coupling reactions, have been developed. Azulene ($C_{10}H_8$) has attracted the interest of many research groups owing to its unusual properties as well as its beautiful blue color.[4] We have recently reported the synthesis of several arylazulene derivatives by transition-metal-catalyzed cross-coupling reactions.[5] However, although many transition-metal-catalyzed aryl–aryl cross-coupling reactions have been developed, the synthesis of 1-arylazulenes by such methods might be difficult because of the instability of the 1-haloazulenes required. Moreover, the preparation of metal reagents for the coupling reaction is not easy for 1-azulenyl derivatives and the most promising 1-azulenylborane reagent is unstable, readily undergoing hydrolysis to afford hydrocarbon derivatives.[6] More recently, Oda and co-workers reported the efficient Suzuki–Miyaura and Stille coupling reactions of 1-halo- and 1,3-dihaloazulenes. However, these procedures require either an electron-withdrawing group on the azulene ring at the 3-position or an excess amount of arylborane or tin reagents.[7] To develop a facile method for the synthesis of 1-heteroarylazulenes, we have developed the reaction of azulenes with the triflates of *N*-heterocycles, which are readily available from the reaction of *N*-heterocycles with trifluoromethanesulfonic anhydride (Tf_2O), which gives 1-(dihydroheteroaryl)-, 1,3-bis(dihydroheteroaryl)-, and 5-(dihydroheteroaryl)azulenes. Transformation of the dihydroheteroarylazulenes to 1-(heteroaryl)-, 1,3-bis(heteroaryl)-, and 5-(heteroaryl)azulenes has led to a new two-step strategy for the heteroarylation of azulenes.[8] We have also reported a facile and efficient synthetic route to several 1-azulenyl methyl and phenyl sulfides and 1,3-bis(methylthio)- and 1,3-bis(phenylthio)azulenes via 1-azulenylsulfonium and 1,3-azulenediylsulfonium ions. We found that the products, 1-azulenyl sulfides, exhibit reversible redox behavior.[9] Thus, 1-(heteroaryl)azulenes bearing a sulfur moiety might exhibit special properties, especially in their redox behavior. Herein, we report the synthesis of 1-methylthio-3-(heteroaryl)azulenes using the triflates of *N*-heterocycles and their redox behavior was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

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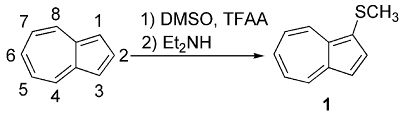
Results and Discussion

Synthesis

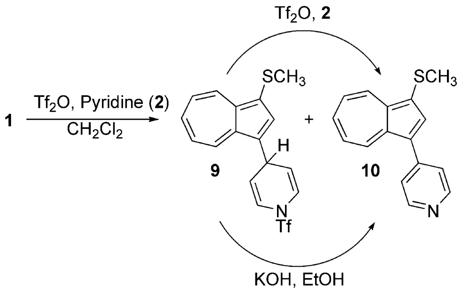
1-Azulenyl methyl sulfide (**1**) was prepared in 99% yield from azulene according to the procedure reported by us recently (Scheme 1).[9b]



Scheme 1.

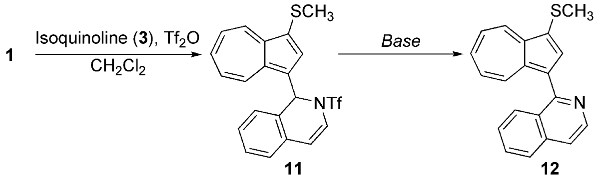
At the beginning of the investigation, we examined the reaction of **1** with trifluoromethanesulfonylpyridinium trifluoromethanesulfonate (TPT), which can be easily prepared by the reaction of Tf_2O with pyridine (**2**). Recently, we reported that the reaction of azulene with TPT prepared with an equimolar amount of Tf_2O and **2** gives 6-(1-azulenyl)-1-(trifluoromethylsulfonyl)-1-azahexa-1,3,5-triene as the main product by the attack of azulene on TPT at the 2-position.[7a] In contrast, when the reaction is carried out with a large excess of **2**, the reaction gives 1,3-bis(4-dihydropyridyl)azulene derivatives, which arise from the attack of azulene on TPT at the 4-position. Therefore, in the case of the reaction of azulene itself, excess **2** is required to obtain 1-(1,4-dihydropyridyl)azulene in good yield.

Thus, the reaction of **1** was carried out by using an equimolar amount of Tf_2O in the presence of excess **2** to afford 1-methylthio-3-(1,4-dihydropyridyl)azulene (**9**) in 62% yield. We found that the reaction of **1** with a two-fold excess of Tf_2O in the presence of excess **2** gives **9** and 1-methylthio-3-(4-pyridyl)azulene (**10**) in 24 and 64% yields, respectively (Scheme 2). We considered that the formation of **10** might be attributable to the excess pyridine, which should act as a base for the aromatization of the dihydropyridine moiety. Thus, we investigated the reaction of **9** with excess pyridine. However, the presumed aromatization reaction could not be observed and the reaction resulted in the complete recovery of the starting **9**. Aromatization of **9** to pyridine derivative **10** was observed in 82% yield when **9** was treated with TPT. Therefore, excess TPT should be responsible for the aromatization of **9** to **10**, although the reaction mechanism is unclear. Pyridylazulene derivative **10** was also obtained in 84% yield from **9** by reaction with KOH.



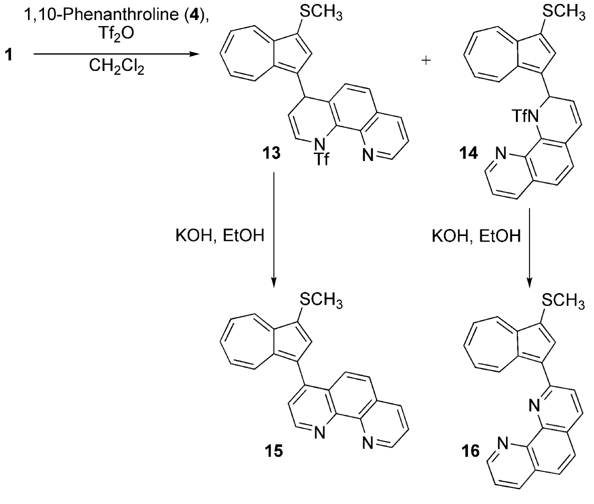
Scheme 2.

We extended the procedure to several *N*-heterocycles, that is, isoquinoline (**3**), 1,10-phenanthroline (**4**), benzothiazole (**5**), quinoline (**6**), and acridine (**7**). Similar to the reaction with **2**, the reactions of **1** with **3**–**7** were carried out in the presence of Tf_2O. The reaction of **1** with **3** in the presence of Tf_2O afforded 1-methylthio-3-(1,2-dihydroisoquinolyl)azulene (**11**) in 97% yield. The arylated product **12** was not obtained directly in the reaction with **3** even with excess of reagents. For the aromatization of **11** to **12**, we investigated the use of two bases, KOH and/or *t*BuOK, following a similar procedure to that reported by us previously.[8] The reaction of **11** with KOH in EtOH at reflux afforded 1-methylthio-3-(1-isoquinolyl)azulene (**12**) in 12% yield along with an inseparable complex mixture. The yield of **12** was improved by changing the reaction conditions to *t*BuOK in DMSO (43%) (Scheme 3).



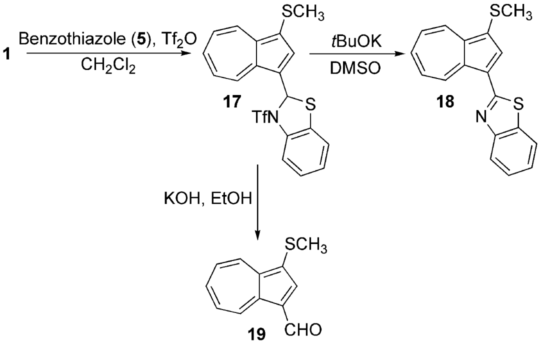
Scheme 3.

1,10-Phenanthroline (**4**) reacted with **1** in the presence of Tf_2O to give **13** and **14** both in yields of 45%. Although the reaction afforded a mixture of regioisomers **13** and **14**, they were easily separable by silica gel column chromatography. Aromatization of both **13** and **14** was established by treatment with KOH in EtOH to afford **15** and **16** in 51 and 87% yields, respectively (Scheme 4). Recently, Buchwald and co-workers reported that electron-rich 1,10-phenanthroline derivatives act as good ligands for the Cu-catalyzed synthesis of arylamines[10] and aryl ethers.[11] As the azulene moiety exhibits electron-donating properties at the 1-position, the products **15** and **16** might be expected to be good ligands for such a catalytic system.



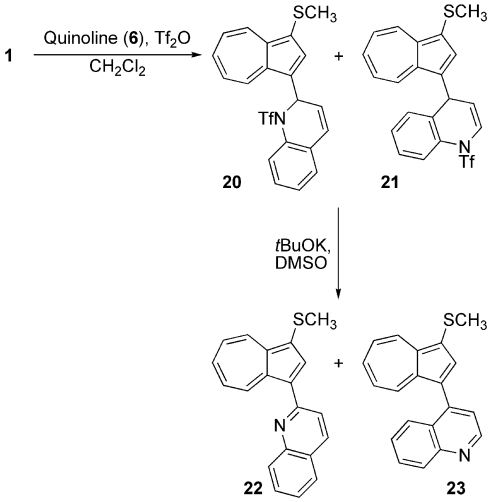
Scheme 4.

The Tf_2O-initiated heteroarylation reaction was also applied to benzothiazole (**5**). The reaction of **1** with **5** in the presence of Tf_2O afforded **17** in 96% yield. The product **17** reacted with *t*BuOK in DMSO to give the aromatized product **18** in 69% yield. When **17** was treated with KOH, hydrolysis of the dihydrobenzothiazole moiety proceeded to give 1-formyl-3-methylthioazulene (**19**) in 83% yield (Scheme 5), similar to the results for the formation of 1-formyl- and 1,3-diformylazulenes[11] by the reaction of azulene itself with **5** in the presence of Tf_2O.[8b]

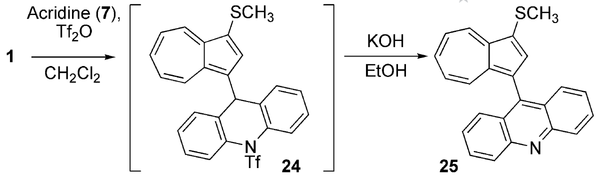


Scheme 5.

The reaction of **1** with quinoline (**6**) in the presence of Tf_2O afforded an inseparable mixture of **20** and **21** in 94% yield. All our attempts to separate these products were unsuccessful. Therefore, the mixture of **20** and **21** was treated with *t*BuOK in DMSO. The aromatized products were separated by silica gel column chromatography to give **22** and **23** in 27 and 29% yields, respectively (Scheme 6). The reaction of **1** with acridine (**7**) in the presence of Tf_2O afforded a complex mixture presumably containing **24**. Isolation of **24** was difficult, but the molecular-ion peak was observed in the crude product by HRMS spectroscopy. Therefore, the inseparable crude mixture was treated with KOH in EtOH to yield the presumed **25**, but the yield was significantly low (5% from **1**) in this case (Scheme 7).



Scheme 6.



Scheme 7.

Spectroscopic Properties

Compounds **9**–**25** were fully characterized by spectroscopic data, as shown in the Experimental Section. Mass spectra of **9**–**25** ionized by ESI showed the correct molecular-ion peaks. The characteristic stretching–vibration bands of the trifluoromethyl and sulfonyl groups of **9**, **11**, **13**, **14**, and **17** were observed at 1188–1224 and 1147–1186 cm^{-1}, respectively, in their IR spectra. These results are consistent with the structures of these products. The ^1H NMR chemical shifts of the azulene moiety of 1-methylthio-3-(heteroaryl)azulene derivatives are summarized in Table 1. In compounds **16**, **18**, and **22**, a significant low-field shift of the 4-H proton was observed. This may be attributable to the intramolecular interaction between the nitrogen atom of the heterocyclic rings and the proton of the azulene ring at the 4-position. However, a similar low-field shift was not observed in **12**. This can be attributed to the steric hindrance between the 2-H proton of the azulene ring and the 8-H proton of the isoquinoline moiety in **12**, which prevents a similar interaction between the nitrogen atom of the isoquinoline moiety and the 4-H proton of the azulene ring.

Table 1. ^1H NMR chemical shifts (δ values, ppm) of 1-methylthio-3-(heteroaryl)azulene derivatives in $CDCl_3$.

Sample	2-H	4-H	5-H	6-H	7-H	8-H
1	7.94	8.22	7.11	7.55	7.18	8.59
10	8.06	8.64	7.27	7.65	7.21	8.49
12	8.26	8.74	7.33	7.67	7.19	8.53
15	8.13	8.08	7.35	7.68	7.13	8.74
16	8.52	*10.20*	7.52	7.73	7.31	8.69
18	8.34	*9.90*	7.49	7.75	7.39	8.67
22	8.40	*9.84*	7.37	7.68	7.30	8.67
23	8.11	8.72	7.32	7.66	7.11	8.12
25	8.13	8.79	7.37	7.66	7.00	7.65

The absorption maxima and coefficients (log*ε*) for the 1-methylthio-3-(heteroaryl)azulenes are summarized in Table 2. The UV/Vis spectra of **10** in dichloromethane and in acetic acid are shown in Figure 1. The 1-methylthio-3-(dihydroheteroaryl)azulenes and 1-methylthio-3-(heteroaryl)azulenes in dichloromethane showed characteristic absorptions arising from the azulene system at 587–629 nm in the visible region. Compounds **16**, **18**, and **22** also exhibited relatively strong absorptions in the region of 404–411 nm, which may be attributable to charge transfer (CT) from the azulene ring to the substituted heterocycles. The relatively long wavelength of this absorption band should be due to the planar structure formed between the azulene ring and the substituted heterocycles, as expected from the analysis of the ^{1}H NMR chemical shift of the 4-H proton of the azulene ring.

Table 2. Absorption maxima and coefficients (logε) for the 1-methylthio-3-(heteroaryl)azulenes in dichloromethane and acetic acid.

Sample	Solvent	λ_{max} [nm] (logε)
10	CH_2Cl_2	383 (3.67), 500 sh (2.31), 588 (2.37), 629 sh (2.34)
	AcOH	426 (3.89)
12	CH_2Cl_2	398 sh (3.91), 499 (2.24), 590 (2.53)
	AcOH	438 (3.91)
15	CH_2Cl_2	384 sh (3.82), 603 (2.45)
	AcOH	471 (3.86)
16	CH_2Cl_2	411 (4.16), 586 (2.63), 628 sh (2.59)
	AcOH	422 (4.13)
18	CH_2Cl_2	408 (4.19), 424 sh (4.16), 589 (2.70), 621 sh (2.68)
	AcOH	406 (4.16), 422 sh (4.12), 585 (2.81), 622 sh (2.78)
22	CH_2Cl_2	404 (4.13), 589 (2.60)
	AcOH	462 (4.15), 513 sh (3.97)
23	CH_2Cl_2	390 sh (3.85), 602 (2.52)
	AcOH	458 (3.92)
25	CH_2Cl_2	428 sh (3.69), 584 sh (2.53), 624 sh (2.54)
	AcOH	430 sh (3.56), 535 (3.73)

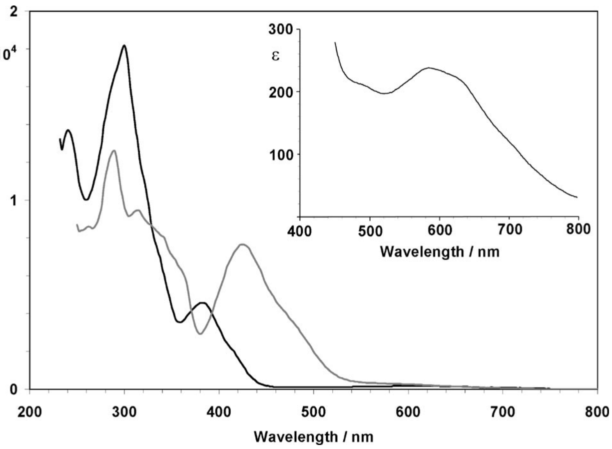
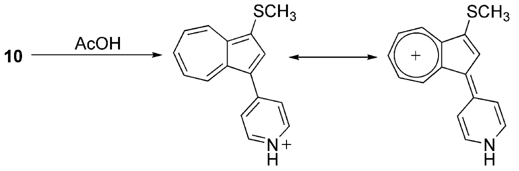


Figure 1. UV/Vis spectra of **10** in dichloromethane (black line) and in acetic acid (gray line).

Compound **10** in acetic acid exhibited a bathochromic shift and a higher absorption coefficient at 426 nm that arises from the development of a CT absorption that results from the protonation of the pyridine moiety (Scheme 8). A similar color change was also observed with the other 1-methylthio-3-(heteroaryl)azulenes, except for **18**, by changing the solvent from dichloromethane to acetic acid. Compound **12** showed a similar bathochromic shift (438 nm) in acetic acid that arises from protonation of the isoquinoline moiety. Compound **15** exhibited an absorption band at 471 nm in acetic acid. The absorption band of **16** showed a small shift from 411 to 422 nm by changing the solvent from dichloromethane to acetic acid. The quinoline derivatives **22** and **23** also exhibited a CT absorption at 462 and 458 nm, respectively, in acetic acid. The UV/Vis spectrum of **25** in dichloromethane exhibited an absorption at 428 (sh), 584 (sh), and 624 nm (sh) in the visible region. Compound **25** showed a broad CT absorption at 535 nm stretching to more than 700 nm in acetic acid. However, significant differences were not observed in the absorption spectrum of **18** by changing the solvent from dichloromethane to acetic acid. The basicity of the azulene-substituted benzothiazole moiety in **18** might be lower than the other heterocycles thus preventing the protonation of the nitrogen atom.



Scheme 8.

To study the theoretical aspects of the spectroscopic properties of these compounds, molecular orbital calculations were performed on **12** and **22** by using B3LYP/6-31G** density functional calculations.[12] The results depended on the geometry of 1-methylthio substituent on the azulene ring. With the 1-methylthio substituent as a planar geometry the UV/Vis spectra of these compounds were well reproduced, although the total energy was slightly higher than those of other geometries. The HOMOs and LUMOs with optimized structures resulting from the calculations are summarized in the Supporting Information

The geometries in which the nitrogen atom of the 3-heteroaryl substituent is located towards the seven-membered ring of the azulene skeleton are more stable, as expected by the analysis of ^{1}H NMR chemical shift of the 4-H proton of the azulene ring. The geometry optimizations revealed a substantial deviation from the planer structure of compound **12** due to the steric hindrance between the 2-H proton of the azulene ring and the 8-H proton of the isoquinoline moiety. However, the dihedral angle between the 3-heteroaryl ring and the azulene moiety in **22** is significantly small compared with that of **12**.

The HOMOs and LUMOs of **12** and **22** are concentrated mostly on the azulene moiety. Thus, it can be concluded that the longest weak absorption of these compounds is a HOMO–LUMO transition in the azulene skeleton. The LUMO+1 of these compounds is concentrated on the 3-heteroaryl substituent and includes the azulene moiety. Therefore, the relatively strong absorptions of these compounds in the region of 398–404 nm should include intramolecular CT from the azulene ring to the 3-heteroaryl group. Calculations on their protonated species should show that the LUMO is mostly concentrated on the 3-heteroaryl substituent. Thus, it can be concluded that the longest wavelength absorption in the visible region is an intramolecular CT transition in the cases of the protonated species.

Redox Behavior

To clarify the electrochemical properties of 1-methylthio-3-(heteroaryl)azulenes, the redox potentials of these products were measured by CV and DPV. The measurements were carried out by using a standard three-electrode configuration. Tetraethylammonium perchlorate (0.1 M) in benzonitrile was used as a supporting electrolyte with platinum wire as auxiliary and working electrodes. All measurements were taken under argon and potentials are referenced to the electrode formed from Ag/AgNO$_3$ (0.01 M) in acetonitrile containing nBu$_4$NClO$_4$ (0.1 M) with Fc/Fc$^+$ as an internal reference which discharges at +0.15 V under these conditions. The redox potentials (in V vs. Ag/AgNO$_3$) are summarized in Table 3. The cyclic voltammogram for **23** is shown in Figure 2.

Table 3. Redox potentials[a] of the 1-methylthio-3-(heteroaryl)azulenes.

Sample	E_{red}^1 [V]	E_{red}^2 [V]	E_{ox}^1 [V]	E_{ox}^2 [V]
1[9b]	(–1.83)	(–2.15)	(+0.34)	(+0.78)
10			+0.49	
	(–1.70)	(–2.02)	(+0.45)	(+0.63)
12[b]			+0.52	
	(–1.61)	(–1.87)	(+0.50)	(+1.02)
15			+0.50	
	(–1.68)	(–2.19)	(+0.48)	
16	(–1.71)	(–2.17)	(+0.37)	(+0.53)
18			+0.51	
	(–1.58)	(–2.16)	(+0.49)	(+0.96)
22			+0.42	
	(–1.70)	(–2.17)	(+0.40)	(+0.90)
23			+0.48	
	(–1.68)		(+0.46)	
25			+0.50	
	(–1.68)	(–1.85)	(+0.48)	(+1.04)

[a] Redox potentials were measured by CV and DPV [V vs. Ag/AgNO$_3$, 1 mM in benzonitrile containing Et$_4$NClO$_4$ (0.1 M), 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. The peak potentials measured by DPV are shown in parentheses. [b] The E_3^{red} value was observed at –2.16 V by DPV.

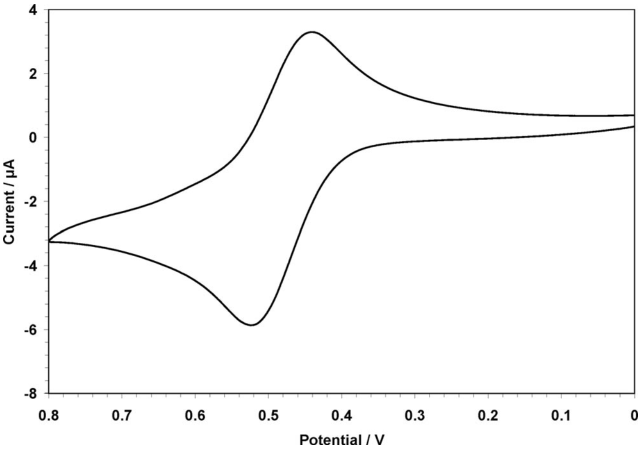


Figure 2. Cyclic voltammogram of **23** (1 mM) in benzonitrile containing Et$_4$NClO$_4$ (0.1 M) as the supporting electrolyte; scan rate: 100 mV s^{-1}.

Similar to the redox behavior of **1**,[9b] the electrochemical reduction of 1-methylthio-3-(heteroaryl)azulenes exhibited irreversible reduction waves in the range of –1.58 to –2.19 V by DPV. These results indicate the instability of the radical anionic states of these compounds. Electrochemical oxidation of **10** showed a reversible oxidation wave at +0.49 V due to the generation of radical cationic species upon CV. A reversible oxidation wave was also observed in **12** and **15** at +0.52 and +0.50 V, respectively, by CV, but **16** exhibited an irreversible oxidation wave due to the instability of its radical cation. Electrochemical oxidation of **18** also showed a reversible oxidation wave at +0.51 V owing to the generation of radical cationic species. Compound **22** showed a slightly less positive oxidation potential (+0.42 V) compared with that of **23** (+0.48 V), which indicates the 2-quinolyl moiety has greater π-donating properties than the 4-quinolyl group. Electrochemical oxidation of **25** also showed a reversible oxidation wave at +0.50 V.

Kurihara et al. have reported the oxidation potentials for sulfur-substituted guaiazulene derivatives **26**, **27**, and **28** (Figure 3), which exhibit two-stage oxidation waves at +0.40 to +0.44 V and +0.71 to +1.06 V (V vs. SCE).[13] Recently, we also reported that 1,3-bis(methylthio) and 1,3-bis(phenylthio) substituents stabilize the radical cationic state in the electrochemical oxidation.[9b] These results indicate that the heteroaryl groups at the 3-position of the azulene ring also stabilize the radical cationic states of azulene derivatives, similarly to the 1,3-bis(methylthio), 1,3-bis(phenylthio), and 1,3-dialkyl substituents, although 1-methylthio-3-(heteroaryl)azulenes exhibit slightly more positive first oxidation potentials.

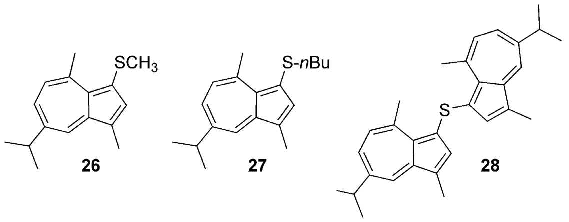


Figure 3. Guaiazulene derivatives **26**, **27**, and **28**.

Conclusions

Several 1-methylthio-3-(heteroaryl)azulenes have been prepared by the reaction of **1** with N-heterocycles in the presence of Tf$_2$O following the treatment with base. In the reaction of pyridine, 1-methylthio-3-(4-pyridyl)azulene was obtained without treatment with base. The UV/Vis spectra of the 1-methylthio-3-(heteroaryl)azulenes in acetic acid exhibit a significant color change compared with in DMSO due to intramolecular CT absorption. 1-Methylthio-3-(heteroaryl)azulenes **10**, **15**, **18**, **22**, **23**, and **25** showed an oxidation wave with high reversibility by CV due to the formation of stabilized radical cationic species.

Experimental Section

General: Melting points were determined with a Yanagimoto micro melting apparatus MP-S3 and are uncorrected. Mass spectra were obtained with a Hitachi M-2500 or a Bruker APEX II spectrometer. IR and UV/Vis spectra were measured with a Shimadzu FTIR-

8100M instrument. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded with a JEOL GSX 400 spectrometer at 400 MHz (100 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 solution of tetrabutylammonium perchlorate (0.1 M) in acetonitrile. Elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

1-Methylthio-3-[1-(trifluoromethylsulfonyl)-1,4-dihydropyridin-4-yl]azulene (9): Tf$_2$O (584 mg, 2.08 mmol) and **2** (1.37 g, 17.3 mmol) in CH$_2$Cl$_2$ (20 mL) were added at room temperature to a solution of **1** (303 mg, 1.74 mmol) in CH$_2$Cl$_2$ (5 mL). The resulting solution was stirred at the same temperature for 5 min. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$ and GPC with CHCl$_3$ to give **9** (419 mg, 62%) as blue crystals; m.p. 75.0–78.0 °C. HRMS (ESI): calcd. for $C_{17}H_{14}F_3NO_2S_2$ + Na$^+$ [M + Na]$^+$ 408.0310; found 408.0309. IR (KBr disk): $\tilde{\nu}_{max}$ = 1682 (m), 1576 (s), 1406 (s), 1387 (m), 1347 (m), 1287 (s), 1231 (s), 1202 (s), 1188 (s), 1159 (s), 1127 (s), 1075 (s), 1028 (m), 1017 (m), 941 (s), 874 (m), 787 (m), 766 (m), 750 (m), 739 (s), 696 (s), 598 (s), 581 (m), 567 (s), 523 (m), 465 (m) cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (logε) = 238 (4.38), 297 (4.55), 369 (3.79), 606 (2.55) nm. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.56 (d, J = 9.6 Hz, 1 H, 8-H), 8.22 (d, J = 9.6 Hz, 1 H, 4-H), 7.82 (s, 1 H, 2-H), 7.59 (t, J = 9.6 Hz, 1 H, 6-H), 7.17 (t, J = 9.6 Hz, 1 H, 7-H), 7.12 (t, J = 9.6 Hz, 1 H, 5-H), 6.57 (d, J = 7.2 Hz, 2 H, 2′,6′-H), 5.25 (d, J = 7.2 Hz, 2 H, 3′,5′-H), 4.80 (s, 1 H, 4′-H), 2.47 (s, 3 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 139.30, 139.08, 138.89, 135.84, 135.66, 132.94, 130.79, 123.22, 123.09, 121.49, 120.17, 119.70 (q, J = 323.2 Hz, CF$_3$), 112.89, 30.38, 19.94 ppm. $C_{17}H_{14}F_3NO_2S_2$ (385.43): calcd. C 52.98, H 3.66, N 3.63; found C 52.93, H 3.80, N 3.59.

1-Methylthio-3-(4-pyridyl)azulene (10): Tf$_2$O (327 mg, 1.16 mmol) and **2** (457 mg, 5.78 mmol) in CH$_2$Cl$_2$ (10 mL) was added at room temperature to a solution of **1** (101 mg, 0.581 mmol) in CH$_2$Cl$_2$ (5 mL). The resulting solution was stirred at the same temperature for 5 min. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$ and GPC with CHCl$_3$ to give **9** (64 mg, 24%) as blue crystals and **10** (90 mg, 64%) as green crystals.

1-Methylthio-3-(4-pyridyl)azulene (10): KOH (178 mg, 3.18 mmol) was added at room temperature to a solution of **9** (113 mg, 0.318 mmol) in EtOH (10 mL). The resulting solution was stirred at 50 °C for 50 min. The reaction mixture was poured into water, extracted with CH$_2$Cl$_2$, and dried with MgSO$_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc to give **10** (67 mg, 84%) as green crystals; m.p. 71.0–72.0 °C. HRMS (ESI): calcd. for $C_{16}H_{13}NS$ + Na$^+$ [M + Na]$^+$ 274.0661; found 274.0661. IR (KBr disk): $\tilde{\nu}_{max}$ = 1595 (s), 1574 (s), 1539 (m), 1510 (s), 1485 (m), 1448 (m), 1418 (s), 1397 (m), 1375 (s), 1348 (m), 1316 (m), 992 (m), 835 (m), 749 (s), 735 (s), 679 (m), 596 (m), 571 (m), 530 (m) cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (logε) = 240 (4.14), 284 sh (4.20), 300 (4.26), 334 sh (3.87), 383 (3.67), 500 sh (2.31), 588 (2.37), 629 sh (2.34) nm. UV/Vis (AcOH): λ_{max} (logε) = 261 (3.94), 288 (4.10), 313 (3.98), 338 sh (3.91), 360 sh (3.81), 426 (3.89) nm. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.67 (d, J = 4.8 Hz, 2 H, 2′,6′-H), 8.64 (d, J = 10.0 Hz, 1 H, 8-H), 8.49 (d, J = 10.0 Hz, 1 H, 4-H), 8.06 (s, 1 H, 2-H), 7.65 (t, J = 10.0 Hz, 1 H, 6-H), 7.48 (d, J = 4.8 Hz, 2 H, 3′,5′-H), 7.27 (t, J = 10.0 Hz, 1 H, 7-H), 7.21 (t, J = 10.0 Hz, 1 H, 5-H), 2.51 (s, 3 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 149.81, 144.38, 141.94, 139.92, 139.12, 136.97, 136.35, 135.41, 126.96, 125.10, 124.33, 124.01, 122.46, 20.05 ppm. $C_{16}H_{13}NS$ (251.35): calcd. C 76.46, H 5.21, N 5.57; found C 76.47, H 5.25, N 5.59.

Reaction of 9 with TPT: Tf$_2$O (564 mg, 2.00 mmol) and **2** (396 mg, 5.00 mmol) in CH$_2$Cl$_2$ (10 mL) were added at room temperature to a solution of **9** (385 mg, 1.00 mmol) in CH$_2$Cl$_2$ (10 mL). The resulting solution was stirred at the same temperature for 10 min. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$ and GPC with CHCl$_3$ to give **10** (206 mg, 82%) as green crystals.

1-Methylthio-3-[2-(trifluoromethylsulfonyl)-1,2-dihydroisoquinolin-1-yl]azulene (11): Tf$_2$O (977 mg, 3.46 mmol) and **3** (1.86 g, 14.4 mmol) in CH$_2$Cl$_2$ (10 mL) were added at room temperature to a solution of **1** (503 mg, 2.89 mmol) in CH$_2$Cl$_2$ (5 mL). The resulting solution was stirred at the same temperature for 5 min. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$ and GPC with CHCl$_3$ to give **11** (1.22 g, 97%) as blue crystals; m.p. 47.0–51.0 °C. HRMS (ESI): calcd. for $C_{21}H_{16}F_3NO_2S_2$ + Na$^+$ [M + Na]$^+$ 458.0467; found 458.0465. IR (KBr disk): $\tilde{\nu}_{max}$ = 1576 (m), 1453 (m), 1399 (s), 1248 (m), 1225 (s), 1194 (s), 1148 (s), 1117 (m), 1100 (m), 1028 (s), 907 (m), 777 (s), 739 (m), 708 (m), 679 (s), 633 (m), 623 (m), 592 (s), 575 (m), 488 (m) cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (logε) = 296 (4.51), 352 sh (3.75), 367 (3.78), 399 sh (3.33), 587 (2.54) nm. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.85 (d, J = 9.6 Hz, 1 H, 4-H), 8.60 (d, J = 9.6 Hz, 1 H, 8-H), 7.66 (s, 1 H, 6-H), 7.53 (s, 1 H, 1′-H), 7.34 (t, J = 9.6 Hz, 1 H, 5-H), 7.28–7.72 (m, 3 H, 3′,4′,5′-H), 7.26 (t, J = 9.6 Hz, 1 H, 7-H), 7.05 (d, J = 7.6 Hz, 1 H, 8′-H), 6.91 (s, 1 H, 2-H), 6.49 (d, J = 7.6 Hz, 1 H, 7′-H), 6.46 (d, J = 7.6 Hz, 1 H, 6′-H), 2.30 (s, 3 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 140.02, 139.88, 139.01, 135.96, 135.82, 134.03, 132.84, 128.85, 128.23, 128.00, 126.02, 125.99, 125.67, 124.70, 124.22, 122.27, 124.30, 119.83 (q, J = 324.0 Hz, CF$_3$), 116.96, 55.17, 20.15 ppm. $C_{21}H_{16}F_3NO_2S_2$ (435.48): calcd. C 57.92, H 3.70, N 3.22; found C 57.89, H 3.83, N 3.37.

1-Methylthio-3-(1-isoquinolyl)azulene (12): *t*BuOK (78.4 mg, 0.699 mmol) was added at room temperature to a solution of **11** (101.5 mg, 0.233 mmol) in DMSO (5 mL). The resulting solution was stirred at the same temperature for 15 min. The reaction mixture was poured into water, extracted with CH$_2$Cl$_2$, and dried with K$_2$CO$_3$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc to give **12** (30 mg, 43%) as dark-blue crystals; m.p. 99.0–107.0 °C. HRMS (ESI): calcd. for $C_{20}H_{15}NS$ + H$^+$ [M + H]$^+$ 302.0998; found 302.0998. IR (KBr disk): $\tilde{\nu}_{max}$ = 1574 (s), 1491 (m), 1453 (m), 1333 (m), 1314 (m), 1285 (m), 1248 (m), 1223 (s), 1192 (s), 1148 (s), 1117 (s), 1100 (m), 1028 (s), 967 (m), 947 (m), 905 (s), 876 (m), 839 (m), 777 (s), 708 (m), 679 (s), 633 (m), 592 (s), 575 (m), 544 (m), 529 (m), 488 (m) cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (logε) = 292 (4.46), 325 sh (4.21), 358 sh (4.05), 398 sh (3.91), 499 (2.24), 590 (2.53) nm. UV/Vis (AcOH): λ_{max} (logε) = 276 sh (4.29), 290 (4.31), 342 sh (4.04), 438 (3.91) nm. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.74 (d, J = 9.6 Hz, 1 H, 4-H), 8.68 (d, J = 5.6 Hz, 1 H, 3′-H), 8.53 (d, J = 9.6 Hz, 1 H, 8-H), 8.26 (s, 1 H, 2-H), 8.07 (d, J = 8.0 Hz, 1 H, 8′-H), 7.90 (d, J = 8.0 Hz, 1 H, 5′-H), 7.67 (t, J = 9.6 Hz, 1 H, 6-H), 7.71–7.64 (m, 2 H, 4′,6′-H), 7.50 (t, J = 8.0 Hz, 1 H, 7′-H), 7.33 (t, J = 9.6 Hz, 1 H, 5-H), 7.19 (t, J = 9.6 Hz, 1 H, 7-H), 2.53 (s, 3 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 156.88, 142.37, 141.57, 140.49, 139.27, 139.05, 136.96, 136.86, 136.13, 129.94, 128.16, 127.86, 127.15, 126.89, 125.16, 124.24, 121.29, 119.15, 20.44 ppm. $C_{20}H_{15}NS$ (301.41): calcd. C 79.22, H 5.05, N 4.62; found C 79.24, H 5.13, N 4.73.

1-Methylthio-3-(1-trifluoromethylsulfonyl-1,4-dihydro-1,10-phenanthrolin-4-yl)azulene (13) and 1-Methylthio-3-(1-trifluoromethylsulfonyl-1,2-dihydro-1,10-phenanthrolin-2-yl)azulene (14): Tf_2O (699 mg, 2.46 mmol) and **4** (1.62 g, 10.0 mmol) in CH_2Cl_2 (20 mL) were added at room temperature to a solution of **1** (344 mg, 1.97 mmol) in CH_2Cl_2 (20 mL). The resulting solution was stirred at the same temperature for 5 min. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **13** (429 mg, 45%) as blue crystals and **14** (432 mg, 45%) as blue crystals.

13: M.p. 178.0–182.0 °C. HRMS (ESI): calcd. for $C_{24}H_{17}F_3NO_2S_2$ + Na^+ $[M + Na]^+$ 509.0576; found 509.0574. IR (KBr disk): $\tilde{\nu}_{max}$ = 1576 (m), 1453 (m), 1410 (m), 1393 (s), 1370 (m), 1337 (m), 1316 (m), 1213 (s), 1200 (s), 1183 (s), 1175 (m), 1142 (m), 1129 (m), 1103 (m), 1024 (m), 995 (m), 949 (m), 845 (s), 810 (m), 768 (m), 733 (m), 666 (m), 654 (m), 604 (s), 575 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 240 (4.63), 289 (4.50), 318 sh (4.23), 346 sh (394), 373 (3.79), 588 (2.50) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.87 (d, *J* = 9.6 Hz, 1 H, 4-H), 8.72 (dd, *J* = 4.4, 1.2 Hz, 1 H, 9′-H), 8.47 (d, *J* = 9.6 Hz, 1 H, 8-H), 8.01 (dd, *J* = 8.8, 1.2 Hz, 1 H, 7′-H), 7.74 (d, *J* = 4.0 Hz, 1 H, 6′-H), 7.67 (t, *J* = 9.6 Hz, 1 H, 6-H), 7.48 (d, *J* = 4.0 Hz, 1 H, 5′-H), 7.40 (t, *J* = 9.6 Hz, 1 H, 5-H), 7.34 (s, 1 H, 2-H), 7.28–7.21 (m, 2 H, 7,8′-H), 7.00 (d, *J* = 9.6 Hz, 1 H, 2′-H), 6.76 (d, *J* = 5.6 Hz, 1 H, 4′-H), 6.63 (dd, *J* = 9.6, 5.6 Hz, 1 H, 3′-H), 2.11 (s, 3 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.35, 144.02, 140.59, 139.56, 139.05, 137.62, 135.72, 135.33, 134.67, 132.11, 130.92, 128.80, 127.98, 125.30, 124.88, 124.45, 124.24, 121.26, 120.81 (q, *J* = 325.0 Hz, CF_3), 120.53, 120.47, 53.58, 20.07 ppm. $C_{24}H_{17}F_3NO_2S_2\cdot½H_2O$ (472.52): calcd. C 58.17, H 3.66, N 5.65; found C 58.31, H 3.62, N 5.87.

14: M.p. 159.5–162.0 °C. HRMS (ESI): calcd. for $C_{24}H_{17}F_3NO_2S_2$ + Na^+ $[M + Na]^+$ 509.0576; found 509.0573. IR (KBr disk): $\tilde{\nu}_{max}$ = 1619 (m), 1576 (m), 1499 (m), 1466 (m), 1433 (m), 1420 (m), 1387 (s), 1314 (m), 1262 (m), 1221 (m), 1202 (s), 1183 (s), 1138 (m), 1119 (s), 1065 (s), 1036 (m), 1011 (m), 995 (m), 968 (m), 938 (m), 922 (m), 884 (m), 878 (m), 845 (m), 833 (m), 787 (s), 772 (s), 749 (s), 735 (m), 723 (m), 714 (m), 669 (s), 646 (m), 606 (s), 586 (m), 573 (m), 559 (m), 546 (m), 529 (m), 450 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 238 (4.67), 296 (4.54), 318 sh (4.23), 355 sh (3.73), 370 (3.78), 396 sh (3.53), 591 sh (2.50), 625 (2.53) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.96 (dd, *J* = 4.0, 1.6 Hz, 1 H, 9′-H), 8.56 (d, *J* = 9.6 Hz, 1 H, 4-H), 8.20 (d, *J* = 8.4 Hz, 1 H, 8-H), 8.09 (dd, *J* = 8.0, 1.6 Hz, 1 H, 7′-H), 7.80 (s, 1 H, 2-H), 7.61 (t, *J* = 9.6 Hz, 1 H, 6-H), 7.55 (d, *J* = 8.4 Hz, 1 H, 6′-H), 7.44 (dd, *J* = 8.0, 4.0 Hz, 1 H, 8′-H), 7.21 (t, *J* = 9.6 Hz, 1 H, 5-H), 7.10 (t, *J* = 9.6 Hz, 1 H, 7-H), 6.93 (d, *J* = 8.4 Hz, 1 H, 5′-H), 6.87 (dd, *J* = 6.8, 1.2 Hz, 1 H, 2′-H), 6.05 (dd, *J* = 6.8, 3.6 Hz, 1 H, 3′-H), 5.45 (br. s, 1 H, 4′-H), 2.47 (s, 3 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.23, 141.03, 139.02, 138.90, 136.82, 136.21, 135.79, 135.47, 133.64, 131.36, 128.47, 127.61, 127.59, 126.81, 126.38, 126.22, 123.48, 123.30, 123.23, 122.25, 121.64, 120.62 (q, *J* = 325.0 Hz, CF_3), 36.60, 19.62 ppm. $C_{24}H_{17}F_3NO_2S_2\cdot H_2O$ (472.52): calcd. C 58.81, H 3.58, N 5.72; found C 58.77, H 3.61, N 5.95.

1-Methylthio-3-(1,10-phenanthrolin-4-yl)azulene (15): KOH (108 mg, 1.92 mmol) was added successively at room temperature to a solution of **14** (102 mg, 0.210 mmol) in a mixed solvent of EtOH (5 mL)/THF (5 mL). The resulting solution was stirred at the same temperature for 5 min and then poured into water, extracted with toluene, and dried with K_2CO_3. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ to give **16** (64 mg, 87%) as green crystals; m.p. 96.0–99.0 °C. HRMS (ESI): calcd. for $C_{23}H_{16}N_2S$ + H^+ $[M + H]^+$ 353.1107; found 353.1105. IR (KBr disk): $\tilde{\nu}_{max}$ = 1570 (s), 1553 (m), 1510 (m), 1499 (m), 1451 (m), 1424 (m), 1412 (m), 1397 (m), 1377 (m), 837 (m), 745 (m), 729 (m), 718 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 273 (4.55), 282 (4.55), 344 sh (3.95), 384 sh (3.82), 603 (2.45) nm. UV/Vis (AcOH): λ_{max} (logε) = 283 (4.55), 356 sh (3.87), 380 sh (3.74), 471 (3.86) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.25 (d, *J* = 4.4 Hz, 1 H, 2′-H), 9.24 (dd, *J* = 4.4, 1.6 Hz, 1 H, 9′-H), 8.74 (d, *J* = 9.6 Hz, 1 H, 4-H), 8.23 (dd, *J* = 8.0, 1.6 Hz, 1 H, 7′-H), 8.13 (s, 1 H, 2-H), 8.08 (d, *J* = 9.6 Hz, 1 H, 8-H), 7.79 (d, *J* = 9.2 Hz, 1 H, 6′-H), 7.68–7.63 (m, 4 H, 6,3′,5′,8′-H), 7.35 (t, *J* = 9.6 Hz, 1 H, 5-H), 7.13 (t, *J* = 9.6 Hz, 1 H, 7-H), 2.58 (s, 3 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.29, 149.49, 146.81, 146.48, 143.47, 140.60, 139.96, 139.53, 138.37, 136.36, 136.00, 135.74, 128.32, 127.98, 126.06, 125.54, 125.04, 124.85, 124.66, 124.20, 123.07, 122.11, 20.17 ppm. $C_{23}H_{16}N_2S\cdot½H_2O$ (352.45): calcd. C 76.43, H 4.74, N 7.75; found C 76.41, H 4.68, N 7.72.

1-Methylthio-3-(1,10-phenanthrolin-2-yl)azulene (16): KOH (68 mg, 1.2 mmol) was added at room temperature to a solution of **14** (60 mg, 0.12 mmol) in EtOH (3 mL) and THF (2 mL). The resulting solution was stirred at the same temperature for 23 h. The reaction mixture was poured into water, extracted with CH_2Cl_2, and dried with K_2CO_3. The solvent was removed under reduced pressure and the residue was purified by column chromatography on Al_2O_3 with CH_2Cl_2 and GPC with $CHCl_3$ to give **16** (22 mg, 51%) as green crystals; m.p. 176.5–177.5 °C. HRMS (ESI): calcd. for $C_{23}H_{16}N_2S$ + H^+ $[M + H]^+$ 353.1107; found 353.1106. IR (KBr disk): $\tilde{\nu}_{max}$ = 1584 (s), 1572 (m), 1512 (s), 1456 (m), 1408 (m), 1387 (s), 1370 (m), 849 (m), 774 (m), 745 (m), 741 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 235 (4.66), 264 (4.60), 285 sh (4.54), 300 sh (4.48), 336 sh (4.28), 411 (4.16), 586 (2.63), 628 sh (2.59) nm. UV/Vis (AcOH): λ_{max} (logε) = 264 (4.56), 283 sh (4.48), 310 sh (4.43), 422 (4.13) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 10.20 (d, *J* = 9.6 Hz, 1 H, 4-H), 9.21 (dd, *J* = 4.4, 2.0 Hz, 1 H, 9′-H), 8.69 (d, *J* = 9.6 Hz, 1 H, 8-H), 8.52 (s, 1 H, 2-H), 8.25 (d, *J* = 8.4 Hz, 1 H, 4′-H), 8.23 (dd, *J* = 8.4, 2.0 Hz, 1 H, 7′-H), 8.09 (d, *J* = 8.4 Hz, 1 H, 3′-H), 7.78 (d, *J* = 8.8 Hz, 1 H, 6′-H), 7.73 (t, *J* = 9.6 Hz, 1 H, 6-H), 7.72 (d, *J* = 8.4 Hz, 1 H, 5′-H), 7.62 (dd, *J* = 8.4, 4.4 Hz, 1 H, 8′-H), 7.52 (t, *J* = 9.6 Hz, 1 H, 5-H), 7.31 (t, *J* = 9.6 Hz, 1 H, 7-H), 2.54 (s, 3 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.86, 150.20, 146.44, 146.21, 142.03, 140.04, 139.54, 139.20, 138.93, 136.13, 136.01, 135.80, 128.98, 127.32, 127.13, 126.37, 126.27, 125.39, 124.77, 122.95, 122.72, 121.81, 20.38 ppm. $C_{23}H_{16}N_2S$ (352.45): calcd. C 78.38, H 4.58, N 7.95; found C 78.13, H 4.62, N 7.92.

1-Methylthio-3-[1-(trifluoromethylsulfonyl)-2,3-dihydrobenzothiazol-2-yl]azulene (17): Tf_2O (351 mg, 1.24 mmol) and **5** (681 mg, 5.04 mmol) in CH_2Cl_2 (15 mL) were added at room temperature to a solution of **1** (183 mg, 1.05 mmol) in CH_2Cl_2 (15 mL). The resulting solution was stirred at the same temperature for 5 min. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **17** (445 mg, 96%) as dark-green crystals; m.p. 35.0–40.0 °C. HRMS (ESI): calcd. for $C_{19}H_{14}F_3NO_2S_3$ + Na^+ $[M + Na]^+$ 464.0031; found 464.0030. IR (KBr disk): $\tilde{\nu}_{max}$ = 1576 (m), 1462 (m), 1451 (m), 1401 (s), 1225 (s), 1202 (s), 1136 (s), 1063 (m), 1028 (m), 997 (m), 965 (m), 722 (m), 604 (s), 571 (m), 525 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 239 (4.39), 288 (4.48), 324 sh (4.03), 366

(3.75), 399 sh (3.34), 604 (2.56) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (d, J = 9.6 Hz, 1 H, 8-H), 8.41 (d, J = 9.6 Hz, 1 H, 4-H), 7.76 (s, 1 H, 2-H), 7.72 (t, J = 9.6 Hz, 1 H, 6-H), 7.57 (br. s, 1 H, 2′-H), 7.36–7.19 (m, 4 H, 4′,5′,6′,7′-H), 7.33 (t, J = 9.6 Hz, 2 H, 5,7-H), 2.35 (s, 3 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.21, 139.09, 137.27, 136.23, 134.73, 134.29, 133.21, 131.44, 127.40, 125.91, 125.85, 124.47, 124.46, 123.01, 121.64, 119.90 (q, J = 325.0 Hz, CF_3), 118.53, 63.97, 19.92 ppm. $C_{19}H_{14}F_3NO_2S_3\cdot{}^1/_3H_2O$ (441.51): calcd. C 50.99, H 3.30, N 3.13; found C 50.81, H 3.27, N 3.44.

1-Methylthio-3-(benzothiazol-2-yl)azulene (18): *t*BuOK (182 mg, 1.63 mmol) was added at room temperature to a solution of **17** (213 mg, 0.48 mmol) in DMSO (10 mL). The resulting solution was stirred at the same temperature for 30 min and then the reaction mixture was poured into water, extracted with toluene, and dried with K_2CO_3. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **18** (101 mg, 69%) as dark greenish-blue crystals; m.p. 115.0–116.0 °C. HRMS (ESI): calcd. for $C_{18}H_{13}NS_2$ + H^+ $[M + H]^+$ 308.0562; found 308.0560. IR (KBr disk): $\tilde{\nu}_{max}$ = 1574 (m), 1518 (s), 1489 (m), 1437 (m), 1406 (s), 1372 (s), 880 (m), 750 (m), 739 (s), 725 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 238 (4.48), 276 (4.34), 315 (4.44), 343 sh (4.27), 408 (4.19), 424 sh (4.16), 589 (2.70), 621 sh (2.68) nm. UV/Vis (AcOH): λ_{max} (logε) = 275 sh (4.31), 314 (4.42), 336 sh (4.29), 406 (4.16), 422 sh (4.12), 585 (2.81), 622 sh (2.78) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.90 (d, J = 9.6 Hz, 1 H, 4-H), 8.67 (d, J = 9.6 Hz, 1 H, 8-H), 8.34 (s, 1 H, 2-H), 8.07 (d, J = 8.0 Hz, 1 H, 7′-H), 7.89 (d, J = 8.0 Hz, 1 H, 4′-H), 7.75 (t, J = 9.6 Hz, 1 H, 6-H), 7.52–7.45 (m, 1 H, 6′-H), 7.49 (t, J = 9.6 Hz, 1 H, 5-H), 7.39 (t, J = 9.6 Hz, 1 H, 7-H), 7.39–7.32 (m, 1 H, 5′-H), 2.54 (s, 3 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.05, 154.70, 142.54, 140.39, 140.31, 138.83, 137.77, 136.78, 134.19, 127.62, 126.06, 125.92, 124.39, 122.96, 122.51, 121.23, 120.63, 20.07 ppm. $C_{18}H_{13}NS_2\cdot H_2O$ (307.43): calcd. C 69.51, H 4.34, N 4.50; found C 69.67, H 4.35, N 4.44.

1-Methylthio-3-[1-(trifluoromethylsulfonyl)-1,2-dihydroquinolin-2-yl]azulene (20) and 1-Methylthio-3-[1-(trifluoromethylsulfonyl)-1,4-dihydroquinolin-4-yl]azulene (21): Tf_2O (346 mg, 1.22 mmol) and **6** (646 mg, 5.00 mmol) in CH_2Cl_2 (10 mL) were added at room temperature to a solution of **1** (177 mg, 1.02 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred at the same temperature for 5 min. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give a mixture of **20** and **21** (419 mg, 94%). HRMS (ESI): calcd. for $C_{21}H_{16}F_3NO_2S_2$ + Na^+ $[M + Na]^+$ 458.0467; found 458.0466. $C_{21}H_{16}F_3NO_2S_2$ (435.48): calcd. C 57.92, H 3.70, N 3.22; found C 57.67, H 3.82, N 3.26.

1-Methylthio-3-(2-quinolyl)azulene (22) and 1-Methylthio-3-(4-quinolyl)azulene (23): *t*BuOK (122 mg, 1.09 mmol) was added at room temperature to a solution of the mixture of **21** and **22** (228 mg, 0.52 mmol) in DMSO (10 mL). The resulting solution was stirred at the same temperature for 10 min. The reaction mixture was poured into water, extracted with CH_2Cl_2, and dried with K_2CO_3. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **22** (43 mg, 27%) as greenish-blue crystals and **23** (46 mg, 29%) also as greenish-blue crystals.

22: M.p. 121.5–123.0 °C. HRMS (ESI): calcd. for $C_{20}H_{16}NS$ + H^+ $[M + H]^+$ 302.0998; found 302.0997. IR (KBr disk): $\tilde{\nu}_{max}$ = 1597 (s), 1570 (s), 1509 (s), 1408 (m), 1399 (s), 1375 (s), 961 (m), 961 (m), 831 (s), 760 (s), 739 (s) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 239 (4.51), 290 (4.56), 358 sh (4.05), 404 (4.13), 589 (2.60) nm. UV/Vis (AcOH): λ_{max} (logε) = 281 (4.39), 297 (4.38), 339 (4.16), 372 sh (3.96), 462 (4.15), 513 sh (3.97) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.84 (d, J = 9.6 Hz, 1 H, 4-H), 8.67 (d, J = 9.6 Hz, 1 H, 8-H), 8.40 (s, 1 H, 2-H), 8.17 (d, J = 8.4 Hz, 1 H, 8′-H), 8.14 (d, J = 8.4 Hz, 1 H, 4′-H), 7.85 (d, J = 8.4 Hz, 1 H, 3′-H), 7.77 (d, J = 8.4 Hz, 1 H, 5′-H), 7.70 (t, J = 8.4 Hz, 1 H, 7′-H), 7.68 (t, J = 9.6 Hz, 1 H, 6-H), 7.47 (t, J = 8.4 Hz, 1 H, 6′-H), 7.37 (t, J = 9.6 Hz, 1 H, 5-H), 7.30 (t, J = 9.6 Hz, 1 H, 7-H), 2.50 (s, 3 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.78, 148.29, 141.91, 140.10, 139.65, 138.73, 138.36, 136.16, 136.10, 129.44, 129.21, 127.44, 126.95, 126.52, 126.25, 125.64, 124.76, 121.89, 121.74, 20.37 ppm. $C_{20}H_{15}NS$ (301.41): calcd. C 79.70, H 5.02, N 4.65; found C 79.87, H 5.17, N 4.74.

23: M.p. 103.5–104.5 °C. HRMS (ESI): calcd. for $C_{20}H_{16}NS$ + H^+ $[M + H]^+$ 302.0998; found 302.0997. IR (KBr disk): $\tilde{\nu}_{max}$ = 1570 (s), 1530 (w), 1507 (s), 1493 (m), 1431 (s), 1397 (m), 1377 (m), 857 (s), 776 (s), 743 (s) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 290 (4.45), 322 sh (4.19), 356 sh (3.96), 390 sh (3.85), 602 (2.52) nm. UV/Vis (AcOH): λ_{max} (logε) = 288 (4.36), 315 sh (4.16), 342 sh (4.00), 380 sh (3.76), 458 (3.92) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.99 (d, J = 4.4 Hz, 1 H, 2′-H), 8.72 (d, J = 9.6 Hz, 1 H, 8-H), 8.21 (d, J = 8.4 Hz, 1 H, 8′-H), 8.12 (d, J = 9.6 Hz, 1 H, 4-H), 8.11 (s, 1 H, 2-H), 7.82 (dd, J = 8.4, 1.2 Hz, 1 H, 5′-H), 7.73 (ddd, J = 8.4, 6.8, 1.2 Hz, 1 H, 7′-H), 7.66 (t, J = 9.6 Hz, 1 H, 6-H), 7.46 (dd, J = 8.4, 1.2 Hz, 1 H, 6′-H), 7.44 (d, J = 4.4 Hz, 1 H, 3′-H), 7.32 (t, J = 9.6 Hz, 1 H, 5-H), 7.11 (t, J = 9.6 Hz, 1 H, 7-H), 2.60 (s, 3 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.77, 148.82, 143.36, 140.55, 139.93, 139.47, 138.38, 136.25, 135.98, 129.79, 129.31, 127.99, 126.51, 126.37, 125.60, 124.55, 124.08, 122.89, 121.97, 20.19 ppm. $C_{20}H_{15}NS$ (301.41): calcd. C 79.70, H 5.02, N 4.65; found C 79.50, H 5.11, N 4.70.

1-Methylthio-3-(acridin-9-yl)azulene (25): Tf_2O (287 mg, 1.01 mmol) and **7** (180 mg, 1.01 mmol) in CH_2Cl_2 (20 mL) were added at room temperature to a solution of **1** (172 mg, 0.989 mmol) in CH_2Cl_2 (5 mL). The resulting solution was stirred at the same temperature for 5 min. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ to give a crude product containing **24** (34.5 mg). KOH (81 mg, 1.44 mmol) was added to a solution of the crude product containing **24** in EtOH (15 mL) at room temperature. The resulting solution was stirred at the same temperature for 3 h. The reaction mixture was poured into water, extracted with CH_2Cl_2, and dried with K_2CO_3. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **25** (18 mg, 5% from **1**) as dark-green crystals; m.p. 225.0–226.0 °C. HRMS (ESI): calcd. for $C_{24}H_{17}NS$ + H^+ $[M + H]^+$ 352.1154; found 352.1153. IR (KBr disk): $\tilde{\nu}_{max}$ = 1572 (m), 1557 (m), 1514 (m), 1497 (m), 1449 (m), 1431 (m), 1402 (m), 1300 (m), 762 (s), 745 (s) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 252 (5.05), 296 (4.44), 323 sh (4.06), 346 sh (4.05), 361 (4.17), 388 sh (3.96), 428 sh (3.69), 584 sh (2.53), 624 sh (2.54) nm. UV/Vis (AcOH): λ_{max} (logε) = 257 (4.98), 292 (4.40), 319 sh (4.05), 342 sh (4.09), 358 (4.27), 393 sh (3.82), 430 sh (3.56), 535 (3.73) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, J = 10.0 Hz, 1 H, 4-H), 8.32 (d, J = 8.8 Hz, 2 H, 1′,8′-H), 8.13 (s, 1 H, 2-H), 7.77 (dd, J = 8.4, 1.2 Hz, 2 H, 2′,7′-H), 7.66 (t, J = 10.0 Hz, 1 H, 6-H), 7.65 (d, J = 10.0 Hz, 1 H, 8-H), 7.57 (d, J = 8.4 Hz, 2 H, 4′,5′-H), 7.38–7.34 (m, 2 H, 3′,6′-H), 7.37 (t, J = 10.0 Hz, 1 H, 5-H), 7.00 (t, J = 10.0 Hz, 1 H, 7-H), 2.61 (s, 3 H, 1-SMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.86, 142.69, 141.57, 139.71, 139.37, 139.31, 136.38, 136.23, 129.91, 129.70, 127.30, 126.60, 125.58, 124.36, 124.05, 123.47, 122.08, 20.20 ppm.

$C_{24}H_{17}NS$ (351.46): calcd. C 82.02, H 4.88, N 3.99; found C 81.89, H 4.93, N 3.96.

Supporting Information (see also the footnote on the first page of this article): Cyclic voltammograms and UV/Vis spectra of reported compounds, and B3LYP/6-31G** calculations for **12** and **22**.

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