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Synthesis of 5-Heteroaryl- and 5,7-Bis(heteroaryl)azulenes by Electrophilic Substitution of 1,3-Di-*tert*-Butylazulene with Triflates of N-Containing Heterocycles

Taku Shoji,*[a] Shunji Ito,*[b] Kozo Toyota,[a] and Noboru Morita[a]

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An efficient synthesis of 5-heteroaryl- and 5,7-bis(heteroaryl)azulene derivatives was established for first time. The reaction proceeded through electrophilic substitution of 1,3-di-*tert*-butylazulene (**1**) with the triflates of N-containing heterocycles, in the presence of excess heterocycles, in good yields. The presumed intermediates, 5-(dihydroheteroaryl)-azulene derivatives were also available by the reaction with several N-containing heterocycles in the presence of Tf_2O under milder reaction conditions. Treatment of the 5-(dihydroheteroaryl)azulene derivatives with KOH readily gave the desired 5-(heteroaryl)azulene derivatives. Unexpectedly, *N*-(5-azulenyl)pyridinium triflate **17** was also obtained by the reaction of **1** with (trifluoromethylsulfonyl)pyridinium trifluoromethanesulfonate (TPT). 5-Heteroaryl- and 5,7-bis-(heteroaryl)azulene derivatives exhibited a significant color change in acetic acid compared to those in dichloromethane due to the development of intramolecular charge-transfer (CT) absorption bands. The redox behavior of these new azulene derivatives was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

Introduction

In recent years, there has been intense interest in transition-metal-catalyzed cross-coupling reactions that can be used for carbon–carbon bond formation in aromatic compounds.[1] In the chemistry of azulene, several applications of palladium-catalyzed reactions, for example, transition-metal-catalyzed vinylation,[2] arylation,[3] and ethynylation[4] utilizing azulenyl halides have appeared in the literature. We have also reported the palladium-catalyzed synthesis of various arylazulene derivatives.[5] However, the transition-metal-catalyzed aryl–aryl cross-coupling reaction of azulene derivatives at the 5- and 7-positions can cause difficulty because of the limited availability of 5- and 7-haloazulene derivatives.[6]

Electrophilic substitution reactions are a very important and general methodology for the functionalization of aromatic compounds. For azulene derivatives, there are numerous reports for the electrophilic substitution reactions at the 1- and 3-positions of the azulene ring.[7] Although the predicted electron density obtained by theoretical calculations on azulene suggests there should be sufficient reactivity toward electrophiles at the 5- and 7-positions of the azulene ring,[8] there are few reports on the functionalization of azulene derivatives at the seven-membered ring utilizing electrophilic substitution reactions. In 1962, Hafner and co-workers reported that 1,3-dialkyl-substituted azulene derivatives do undergo electrophilic substitution reactions such as Friedel–Crafts acylation and Vilsmeier formylation at the 5-position, but only with very low selectivity compared to *ipso*-substitution reactions at the 1-position.[9] We have also reported that the electrophilic substitution reactions of 1,3,6-tri-*tert*-butylazulene undergo selective *ipso*-substitution reaction at the 1- and 3-positions, in preference to electrophilic substitution reactions at the 5- and 7-positions of the azulene ring.[10] Although the stepwise synthesis of 5-phenylazulene[11] and 5,5′-biazulene[12] has appeared in the literature, there are no reports on the synthesis of 5-arylazulene derivatives by direct electrophilic arylation of the azulene ring. Recently, Morita and co-workers reported the efficient arylation of azulenes using Grignard reagents through nucleophilic addition reaction to the azulene ring, but at the 2-, 4-, and 6-positions.[13] Therefore, an efficient synthetic method for the preparation of 5-arylazulenes still remains a challenge for functionalization of azulene derivatives.

More recently, we have demonstrated that the reaction of azulene derivatives with the triflate of N-containing heterocycles, which are readily available from the reaction of N-containing heterocycles with trifluoromethanesulfonic anhydride (Tf_2O), gives the corresponding dihydroheteroarylazulene derivatives. Transformation of the dihydroheteroar-

[a] Department of Chemistry, Graduate School of Science, Tohoku University,
Sendai 980-8578, Japan
Fax: +81-22-795-7714
E-mail: shoji-azulene@m.tains.tohoku.ac.jp
[b] Graduate School of Science and Technology, Hirosaki University,
Hirosaki 036-8561, Japan
Fax: +81-172-39-3541
E-mail: itsnj@cc.hirosaki-u.ac.jp

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ylazulene derivatives to the corresponding heteroarylazulene derivatives opened a new, two-step strategy for the heteroarylation of azulene at the 1- and 3-positions.[14] If the triflates undergo comparable electrophilic substitution reactions at the 5- and 7-positions, a new and facile synthetic route to the 5- and 7-heteroarylazulene derivatives could be established.

Introduction of protecting groups at the highly reactive 1- and 3-positions of the azulene ring would be crucial to successful electrophilic substitution reactions at the 5- and 7-positions. We report herein the reaction of 1,3-di-*tert*-butylazulene (**1**), which is an azulene derivative that bears the required protecting groups at these highly reactive 1- and 3-positions, with the triflates of the N-containing heterocycles, and their transformation to the corresponding 5-heteroaryl- and 5,7-bis(heteroaryl)azulenes through an electrophilic substitution reaction. The newly obtained 5-heteroaryl- and 5,7-bis(heteroaryl)azulenes were characterized by absorption spectroscopy and electrochemical analysis.[15]

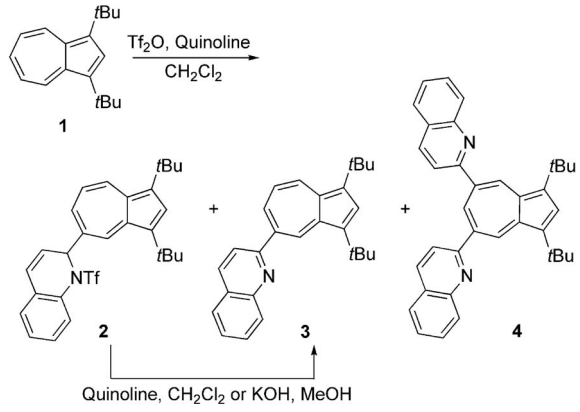
Results and Discussion

Synthesis

For the functionalization of azulene at the 5- and 7-positions, 1,3-di-*tert*-butylazulene (**1**), which is easily prepared by Friedel–Crafts alkylation of azulene with *tert*-butyl chloride/$AlCl_3$, was applied for the electrophilic substitution reaction with the triflates of several N-containing heterocycles.[16] The *tert*-butyl substituents at the 1- and 3-positions should suppress the highly reactive sites of the azulene ring and should also enable further functionalization by Hafner's electrophilic *ipso*-substitution reactions.[9,10] The results obtained for the reaction of **1** with quinoline in the presence of Tf_2O are summarized in Table 1 (Scheme 1). As expected, the reaction of **1** with quinoline at room temperature for 30 min in the presence of 1.5 equiv. of Tf_2O and excess quinoline provided 5-(dihydroquinolyl)azulene derivative **2** in 85% yield as the major product (Entry 3). However, when equimolar amounts of Tf_2O and quinoline were used, the yield of product **2** was significantly lower, probably due to decomposition of the azulene derivatives by the generated acid (Entry 1). These results suggest that basic conditions are necessary to obtain good product yields. We found that the reaction with 1.5 equiv. of Tf_2O and excess quinoline for 24 h afforded the aromatized product **3** in 70% yield instead of the 5-(dihydroquinolyl)azulene derivative **2**, along with the disubstituted derivative **4** in 6% yield (Entry 4). The direct heteroarylation might occur as a consequence of an electrophilic substitution reaction that takes place after the aromatization reaction under the basic conditions. Therefore, the sequence may be viewed as being equivalent to a one-pot electrophilic aryl–aryl cross-coupling reaction. To confirm the direct formation of **3**, treatment of **2** with excess quinoline was investigated. As expected, the presumed aromatization reaction was indeed observed; the reaction gave **3** in 94% yield. Therefore, it is reasonable to assume that the excess quinoline is responsible for the aromatization of **2** to **3**. Quinoline derivative **3** was also obtained in 97% yield by treatment of **2** with KOH, similar to the conversion of 1-(dihydroheteroaryl)-azulenes into 1-heteroarylazulenes.[14] The yield of 5,7-bis(2-quinolyl)azulene derivative **4** was increased to 77% when the reaction of **1** was carried out with 5.0 equiv. of Tf_2O and excess quinoline for 24 h (Entry 5).

Table 1. Synthesis of 5-quinolylazulene derivatives.

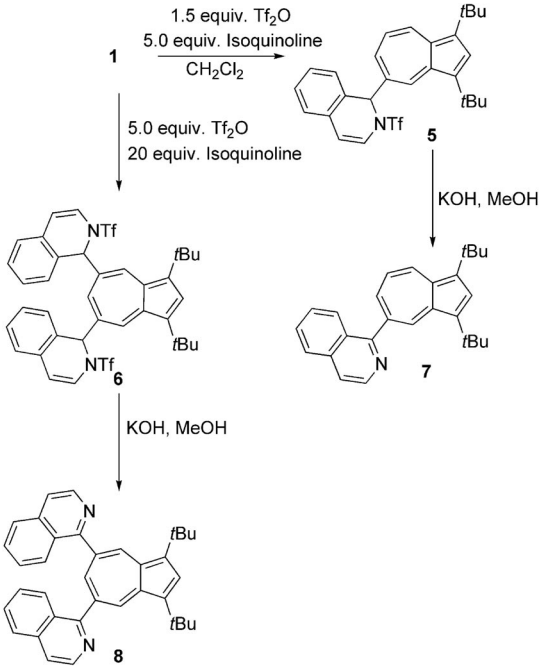
Entry	Ratio **1**/Tf_2O/quinoline	Reaction time	Yield [%] **2**	**3**	**4**
1	1.0:1.5:1.5	30 min	31	0	0
2	1.0:1.0:5.0	30 min	68	0	0
3	1.0:1.5:5.0	30 min	85	trace	0
4	1.0:1.5:10	24 h	trace	70	6
5	1.0:5.0:20	24 h	0	trace	77



Scheme 1.

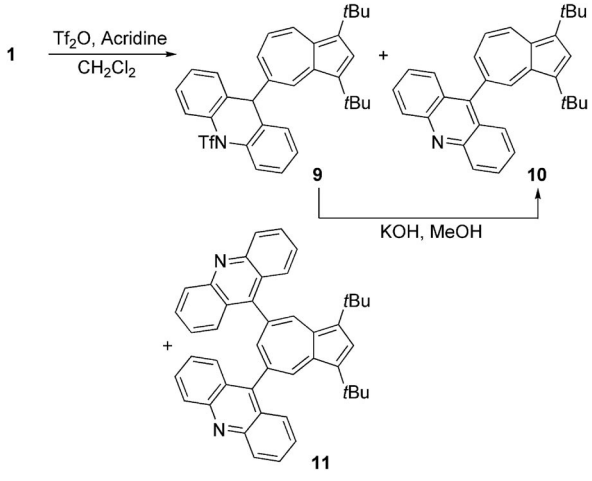
We applied the reaction to several N-containing heterocycles: isoquinoline, acridine, benzothiazole, benzimidazole, *N*-methylbenzimidazole, and *N*-methylimidazole. The N-containing heterocycles also reacted with **1** at room temperature in the presence of Tf_2O to afford the corresponding 5-(dihydroheteroaryl)azulene, 5-heteroaryl- and 5,7-bis(heteroaryl)azulene derivatives in good yields, except for the reaction with imidazole derivatives, such as benzimidazole, *N*-methylbenzimidazole, and *N*-methylimidazole.

Similar to the results described above for quinoline, the reaction of **1** with isoquinoline in the presence of Tf_2O gave dihydroisoquinoline derivatives **5** and **6**. Isoquinoline reacted with **1** in the presence of 1.5 equiv. Tf_2O to afford **5** in 89% yield. 5,7-Bis(isoquinolyl)azulene derivative **6** was also obtained in 96% yield when the reaction was carried out in the presence of excess Tf_2O and isoquinoline. In this case, although excess isoquinoline was used, formation of the aromatized products **7** and **8** was not observed. However, the reaction of **5** and **6** with KOH in MeOH afforded the corresponding isoquinoline derivatives **7** and **8** in 98% and 95% yield, respectively (Scheme 2).



Scheme 2.

The reaction of **1** with acridine in the presence of 1.5 equiv. of Tf_2O gave **9** in 91% yield. Aromatization of **9** was established by treatment with KOH in MeOH to afford the expected product **10** in 98% yield. 5,7-Bis(9′-acridyl)-azulene **11** was obtained in 76% yield when the reaction was carried out with 5.0 equiv. of Tf_2O and 20 equiv. of acridine (Scheme 3, Table 2).

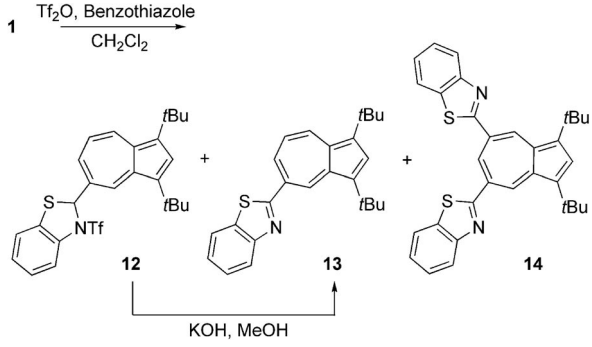


Scheme 3.

Table 2. Synthesis of 5-acridylazulene derivatives.

Entry	Ratio **1**/Tf_2O/acridine	Reaction time	Yield [%] **9**	**10**	**11**
1	1.0:1.5:5.0	30 min	91	0	0
2	1.0:1.5:10	24 h	0	71	8
3	1.0:5.0:20	24 h	0	0	76

The Tf_2O-initiated heteroarylation reaction was also applied to the reaction with benzothiazole. In this case, the presence of 1.5 equiv. of Tf_2O afforded **12** in 87% yield. As for other dihydroheteroaryl products, **12** reacted with KOH in MeOH to give the aromatized product **13** in 92% yield. When the reaction was carried out with excess benzothiazole, the aromatized products **13** and **14** were also obtained in good yield. Recently, we have reported that the treatment of 1-dihydrobenzothiazolyl- and 1,3-bis(dihydrobenzothiazolyl)azulenes with KOH gave 1-formyl- and 1,3-diformylazulenes, respectively, by hydrolysis of dihydrobenzothiazole moieties. However, base-induced hydrolysis to give the formylazulene derivatives was not observed in this case. These results might be attributable to the high acidity of the methyne proton binding to the 5-position of azulene derivative to afford the aromatized products **13** and **14** under basic conditions (Scheme 4, Table 3). Although benzimidazole smoothly reacted with the parent azulene at the 1- and 3-positions, other imidazole derivatives, such as benzimidazole, *N*-methylbenzimidazole, and *N*-methylimidazole, did not react with **1** in the presence of Tf_2O even under more severe reaction conditions such as heating to reflux in chloroform.[14a]



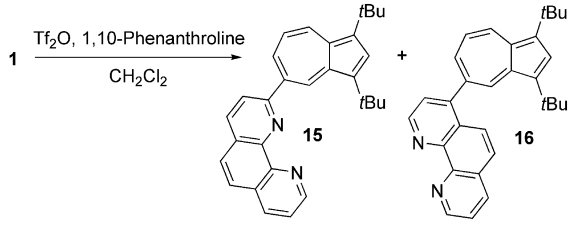
Scheme 4.

Table 3. Synthesis of 5-benzimidazolylazulene derivatives.

Entry	Ratio **1**/Tf_2O/benzothiazole	Reaction time	Yield [%] **12**	**13**	**14**
1	1.0:1.5:5.0	30 min	87	0	0
2	1.0:1.5:10	24 h	0	77	6
3	1.0:5.0:20	24 h	0	4	82

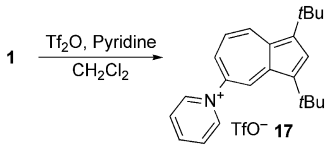
Remarkably, the reaction of **1** with the triflate of 1,10-phenanthroline gave only the aromatized products, 5-(1′,10′-phenanthrolin-2′-yl)azulene **15** and 5-(1′,10′-phenanthrolin-4′-yl)azulene **16**, in 12% and 71% yields, respectively, even when the reaction time was short (Scheme 5). The expected 5-(dihydrophenanthrolinyl)azulene derivatives were not obtained in this reaction. Moreover, 5,7-bis(1′,10′-phenanthrolin-4′-yl)azulene was not obtained when excess 1,10-phenanthroline and Tf_2O were used. Recently, Buchwald and co-workers have reported that electron-rich 4,7-dimethoxyphenanthroline is a good ligand for Cu-catalyzed amination to afford arylamines.[17] Since the 5-position of

azulene has an electron-donating propensity comparable to a methoxy substituent,[8] the products **15** and **16** might be expected to be good ligands for such a catalytic system.



Scheme 5.

Reaction of **1** with (trifluoromethylsulfonyl)pyridinium trifluoromethanesulfonate (TPT) was also investigated. In this case, we expected a similar electrophilic substitution reaction to occur as for the other N-containing heterocycles described above. However, instead of the expected 5-(dihydropyridyl)azulene derivative, the reaction produced the unexpected pyridinium compound **17** in 92% yield (Scheme 6). Compound **17** was fully characterized from its mass spectrometric data, which showed the expected ESI ion signals $[M - OTf]^+$ corresponding to the cationic structure of the product. ^{19}F NMR signals corresponding to the triflate anion were observed at $\delta = -78.12$ ppm, which also supported the cationic structure of the compound. Synthesis of *N*-(9-anthryl)pyridinium iodide has been reported to be formed through the reaction of 9-alkylanthracene with pyridine, in the presence of excess iodine, and its formation has been described as proceeding through a radical mechanism.[18] This is the first case described for this type of *N*-azulenylation of pyridine.



Scheme 6.

Properties

Compounds **2**–**17** were fully characterized by spectroscopic data as shown in the Experimental Section. The high-resolution mass spectra of **2**–**17** ionized by ESI showed the correct molecular ion peaks. The characteristic stretching-vibration bands of the trifluoromethyl and sulfonyl moieties of **2**, **5**, **6**, and **12** were observed at 1188–1224 cm^{-1} and 1147–1186 cm^{-1}, respectively, in their IR spectra. These results are consistent with the structure of these products.

^1H NMR chemical shifts of the azulene moiety of 5-heteroaryl- and 5,7-bis(heteroaryl)azulene derivatives are summarized in Table 4. Compounds **3**, **4**, **13**, **14**, and **15** showed significant low-field shifts of the 4-H and/or 8-H proton signals, which may be attributable to intramolecular interaction between the nitrogen atom of the heterocyclic rings and the protons of the azulene ring at the 4- and/or 8-positions. However, similar low-field shifts were not observed for compounds **7** and **8**, which could be attributable to the steric hindrance between the 6-H proton of the azulene ring and the 8-H proton of isoquinoline moiety in **7** and **8** that prevents a similar intramolecular interaction between the nitrogen atom of isoquinoline moiety and the 4-H and/or 8-H protons of the azulene ring.

Table 4. ^1H NMR chemical shifts of the azulene moiety in 5-heteroaryl- and 5,7-bis(heteroaryl)azulene derivatives in $CDCl_3$.

Sample	2-H	4-H	6-H	7-H	8-H
3	7.79	9.61	8.35	7.11	8.60
4	7.75	9.59	9.51	–	9.59
7	7.74	8.80	7.79	6.99	8.56
8	7.89	8.87	8.38	–	8.87
10	7.89	8.65	7.52	7.09	8.74
11	8.00	8.83	7.62	–	8.83
13	7.80	9.45	8.50	7.07	8.58
14	7.83	9.56	9.44	–	9.56
15	7.79	9.55	8.73	7.19	8.62
16	7.88	8.72	7.67	7.09	8.68

UV/Vis spectra absorption maxima and their coefficients for the 5-heteroaryl- and 5,7-bis(heteroaryl)azulene derivatives are summarized in Table 5. The UV/Vis spectra of **3** and **13** in dichloromethane and in acetic acid are shown in Figures 1 and 2, respectively.

5-Dihydroheteroaryl- and 5,7-bis(dihydroheteroaryl)azulene derivatives in dichloromethane showed characteristic weak absorptions in the visible region arising from the azulene system. 5-Heteroaryl- and 5,7-bis(heteroaryl)azulene derivatives in dichloromethane also exhibited relatively strong absorptions in the 388–432 nm region, which may be attributable to the charge-transfer (CT) absorption band from the azulene ring to the substituted heterocycles. The relatively longer wavelength of the absorption band could be due to the planar structure of the azulene ring and the substituted heterocycles; this is also indicated by the ^1H NMR chemical shifts of the 4-H and 8-H signals of the azulene ring. UV/Vis spectra of compounds **3** and **4** in acetic acid exhibited bathochromic shifts of their respective CT absorption bands at 484 nm and 482 nm, respectively, owing to protonation of the quinoline moieties (Figure 1).

With the exception of **13** and **14**, similar color changes were also observed for the other 5-heteroaryl- and 5,7-bis(heteroaryl)azulene derivatives upon changing the solvent from dichloromethane to acetic acid. Compounds **7** and **8** showed similar bathochromic shifts (**7**: 464 nm; **8**: 450 nm) in acetic acid due to protonation of the isoquinoline moiety, compared to those in dichloromethane (**7**: 401 nm; **8**: 412 nm). When the UV/Vis spectra of **10** and **11** were measured in dichloromethane, they exhibited weak absorption bands in the visible region. In contrast, the same compounds showed broad CT absorption bands at 562 nm and 546 nm, ranging to more than 700 nm in acetic acid. However, no significant difference was observed in the absorption spectra of **13** and **14** by changing the solvent from dichloromethane to acetic acid (Figure 2). In these cases, basicity of the azulene-substituted benzothiazole moiety

Table 5. UV/Vis absorption maxima [nm] and coefficients ($\log\varepsilon$) of 5-heteroaryl- and 5,7-bis(heteroaryl)azulene derivatives in dichloromethane and in acetic acid (sh = shoulder).

Sample	Solvent	λ_{max} ($\log\varepsilon$)
3	CH_2Cl_2	416 (4.22), 582 sh (2.67), 630 (2.81), 688 (2.75), 768 sh (2.31)
	AcOH	424 sh (3.88), 484 (4.06), 642 (3.09), 688 sh (2.96), 768 sh (2.48)
4	CH_2Cl_2	386 sh (3.92), 438 (4.28), 634 (2.84), 690 (2.82), 772 sh (2.43)
	AcOH	404 sh (4.00), 482 (4.25), 628 (3.43), 690 sh (3.33), 772 sh (3.10)
7	CH_2Cl_2	401 (3.98), 634 (2.62), 688 (2.54), 768 sh (2.02)
	AcOH	464 (3.80), 628 (2.73), 688 sh (2.60), 770 sh (2.00)
8	CH_2Cl_2	412 (4.21), 634 (2.80), 692 (2.75), 776 sh (2.30)
	AcOH	450 (4.11), 634 (2.81), 692 (2.71), 780 sh (2.23)
10	CH_2Cl_2	401 (3.83), 588 sh (2.38), 640 (2.51), 696 sh (2.40), 780 sh (1.59)
	AcOH	380 (3.88), 414 sh (3.68), 440 sh (3.43), 562 (3.53), 710 sh (2.93), 790 sh (2.31)
11	CH_2Cl_2	388 sh (4.22), 658 (2.86)
	AcOH	386 sh (4.15), 412 sh (4.09), 546 (3.85)
13	CH_2Cl_2	416 sh (4.57), 432 (4.66), 586 sh (2.78), 634 (2.92), 692 (2.87), 770 sh (2.47)
	AcOH	412 sh (4.28), 430 (4.39), 634 (2.93), 692 (2.87), 778 sh (2.42)
14	CH_2Cl_2	432 sh (4.54), 454 (4.75), 646 (2.97), 706 (2.95), 784 sh (2.57)
	AcOH	432 sh (4.55), 450 (4.74), 642 (3.04), 702 (3.02), 784 sh (2.62)
15	CH_2Cl_2	418 (3.93), 582 sh (2.47), 630 (2.59), 690 (2.52), 722 sh (2.29)
	AcOH	438 (3.91), 630 (2.61), 691 sh (2.52), 724 sh (2.29)
16	CH_2Cl_2	386 sh (3.73), 440 (3.47), 586 sh (2.38), 638 (2.51), 696 (2.41), 786 sh (1.85)
	AcOH	500 (3.61), 631 (2.79), 696 sh (2.65), 776 sh (2.16)

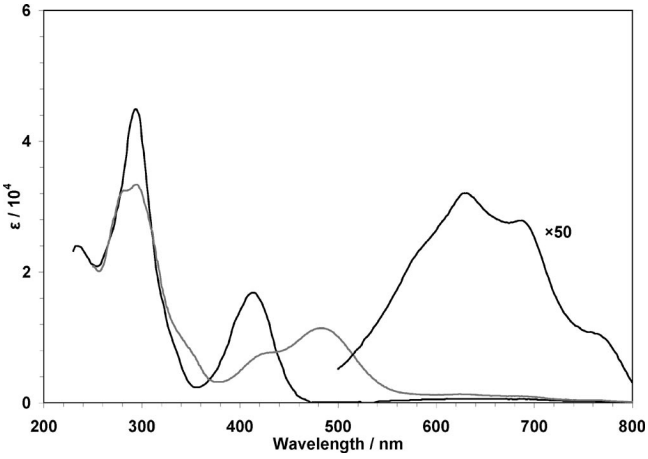


Figure 1. UV/Vis spectra of **3** in dichloromethane (black line) and in acetic acid (gray line).

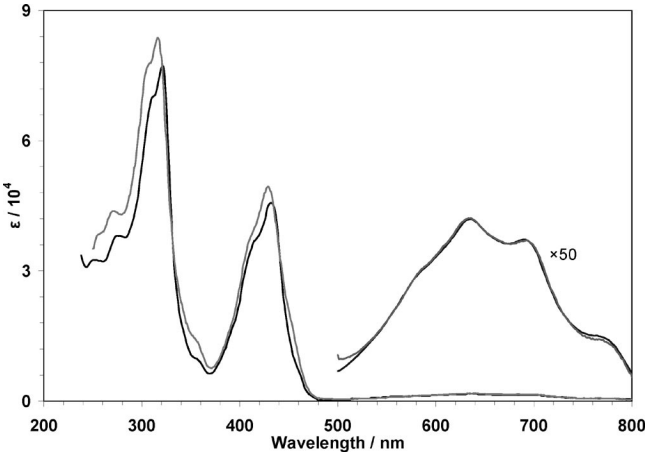


Figure 2. UV/Vis spectra of **13** in dichloromethane (black line) and in acetic acid (gray line).

might be lower than those of the other heterocycles and could be too low to establish any significant degree of protonation of the nitrogen atom in acetic acid.

To study the theoretical aspects of the spectroscopic properties of these compounds, molecular orbital calculations of **3** and **7** were performed by using B3LYP/6-31G** density functional calculations.[19] The HOMOs and LUMOs with optimized structures resulting from the calculations are summarized in the Supporting Information. The geometry in which the nitrogen atom of the 5-heteroaryl substituent in **3** is located towards the 4-H proton of the azulene skeleton, i.e. the *syn* form, is calculated to be more stable, as expected by analysis of ^{1}H NMR chemical shift of the 4-H proton on the azulene ring. The geometry optimization revealed a substantial deviation from the planer structure in compound **7** due to steric hindrance between the 6-H proton of the azulene ring and the 8-H proton of the isoquinoline moiety. The HOMOs and LUMOs of **3** and **7** 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 5-heteroaryl substituents and includes the azulene moiety. Therefore, the relatively strong absorption bands at around 400 nm for these compounds should involve intramolecular CT from the azulene ring to the 5-heteroaryl groups (see the Supporting Information).

Redox Behavior

To clarify the electrochemical behavior of 5-heteroaryl- and 5,7-bis(heteroaryl)azulene derivatives, redox potentials of these products were measured by cyclic voltammetry (CV) and differential pulse voltammetry (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 auxiliary and working electrodes. All measurements were run under argon, and potentials were related to the reference electrode formed from $Ag/AgNO_3$, by using Fc/Fc^+ as internal reference, which discharges at +0.15 V under these conditions. The redox potentials are summarized in Table 6. The cyclic voltammograms for the reduction and the oxidation of **4** are shown in Figure 3.

Table 6. Redox potentials[a] of 5-heteroaryl- and 5,7-bis(heteroaryl)azulene derivatives.

Sample	Method	E_{red}^1 [V]	E_{red}^2 [V]	E_{red}^3 [V]	E_{ox}^1 [V]	E_{ox}^2 [V]
3	CV				+0.53	
	(DPV)	(–1.93)	(–2.15)		(+0.51)	(+0.78)
4	CV	–1.87			+0.54	
	(DPV)	(–1.85)	(–2.15)		(+0.52)	(+1.19)
7	CV	–1.98			+0.56	
	(DPV)	(–1.96)	(–2.18)		(+0.54)	(+1.22)
8	CV	–1.90			+0.59	
	(DPV)	(–1.88)	(–2.18)		(+0.57)	
10	CV				+0.61	
	(DPV)	(–1.78)	(–2.07)	(–2.20)	(+0.59)	
11	CV				+0.67	
	(DPV)	(–1.72)	(–1.80)	(–2.07)[b]	(+0.65)	
13	CV				+0.62	
	(DPV)	(–1.82)	(–2.17)		(+0.60)	(+1.20)
14	CV	–1.67				
	(DPV)	(–1.65)	(–2.18)		(+0.67)	(+1.11)
15	CV				+0.52	
	(DPV)	(–1.72)	(–1.94)	(–2.17)	(+0.50)	
16	CV					
	(DPV)	(–1.69)	(–1.91)	(–2.21)	(+0.53)	
17	CV					
	(DPV)	(–1.29)	(–1.96)	(–2.16)	(+0.82)	(+1.48)

[a] Redox potentials were measured by CV and DPV [in V vs. $Ag/AgNO_3$, 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (i.d. 1.6 mm), scan rate 100 mVs^{-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] E_{red}^4 was observed at –2.21 V upon DPV.

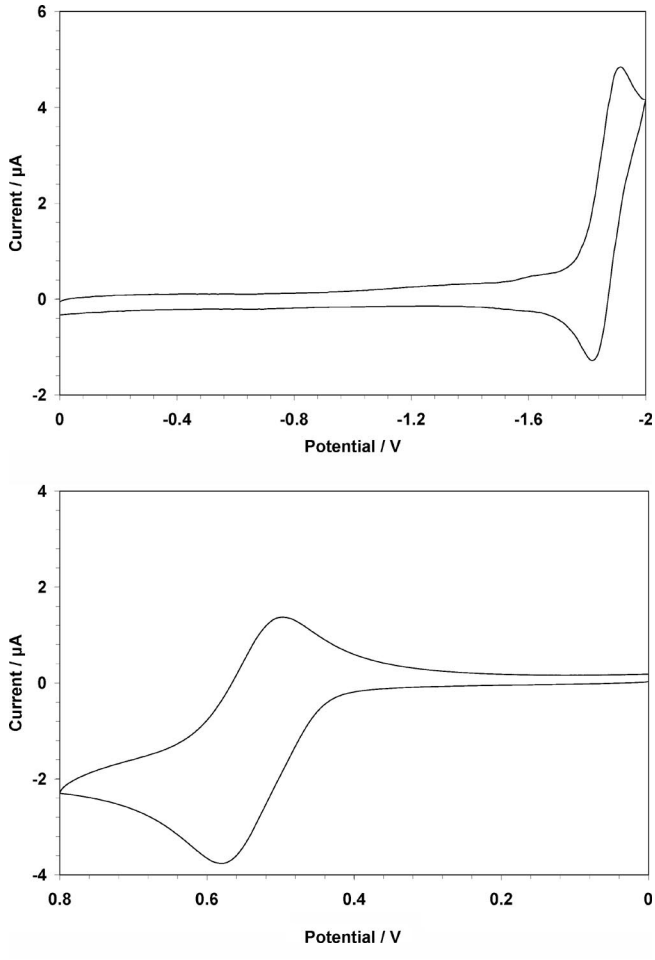


Figure 3. Cyclic voltammograms of (a) reduction and (b) oxidation of **4** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as supporting electrolyte; scan rate 100 mVs^{-1}.

Electrochemical reduction of **3** exhibited irreversible reduction waves at –1.93 V and –2.15 V upon DPV. These results indicate the formation of unstable radical anionic states in the compound. Electrochemical oxidation of **3** showed a reversible oxidation wave at +0.53 V due to the generation of radical cationic species upon CV. Reversible reduction and oxidation waves were observed in **4** at –1.87 V and +0.54 V upon CV, respectively (Figure 3). It is possible that the two quinoline moieties on the azulene ring stabilize the radical anionic species.

Electrochemical oxidation of **7** also showed reversible reduction and oxidation waves at –1.98 V and +0.56 V, respectively, owing to the generation of stable radical anionic and cationic species. Compound **8** showed a slightly less positive reduction potential (–1.90 V) compared with that of **7** (–1.98 V), which indicates that the isoquinoline moiety increases its π-accepting character.

Electrochemical oxidation of **10** and **11** also showed a reversible oxidation wave at +0.61 V and +0.67 V, respectively. Although the electrochemical reduction of **13** showed irreversible waves, compound **14** exhibited a reversible reduction wave at –1.67 V. In contrast to the electrochemical reduction, **13** showed a reversible wave at +0.62 V, although **14** exhibited an irreversible reduction wave. The electrochemical reduction of **17** exhibited irreversible reduction waves at –1.29 V upon DPV, which showed a relatively low reduction potential compared with those of the other 5-heteroarylazulenes. This might be attributable to the electron-withdrawing property of the *N*-pyridinium group in **17** and the low LUMO energy of the compound.

Conclusions

For the first time, an efficient synthesis of 5-heteroaryl- and 5,7-bis(heteroaryl)azulene derivatives through electrophilic substitution without using a transition-metal catalyst has been established. The intermediates, dihydroheteroarylazulene derivatives, were also obtained by reaction with N-containing heterocycles in the presence of Tf_2O under milder reaction conditions. Treatment of the 5-(dihydroheteroaryl)azulene derivatives with KOH gave the desired 5-heteroarylazulene derivatives efficiently. 5,7-Bis(heteroaryl)-azulene derivatives were also obtained when excess hetero-

cycle and Tf_2O were used in the reaction. Unexpectedly, *N*-(5-azulenyl)pyridinium triflate **17** was also obtained by the reaction of **1** with TPT. 5-Heteroaryl- and 5,7-bis(heteroaryl)azulene derivatives in acetic acid exhibit a significant color change compared with the same compounds dissolved in dichloromethane due to the development of an intramolecular CT absorption band.

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/Vis 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 G2000H6 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 $Ag/AgNO_3$ (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.1 M). Elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

1,3-Di-*tert*-butyl-5-[1-(trifluoromethylsulfonyl)-1,2-dihydroquinolin-2-yl]azulene (2): A mixture of Tf_2O (423 mg, 1.50 mmol) and quinoline (646 mg, 5.00 mmol) in CH_2Cl_2 (10 mL) was added at room temp. to a solution of **1** (254 mg, 1.00 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred at the same temperature for 1.5 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to give **2** (426 mg, 85%) as blue crystals; m.p. 115.0–117.0 °C. HRMS (ESI): calcd. for $C_{28}H_{30}F_3NO_2SNa$ $[M + Na]^+$ 524.1847; found 524.1846. IR (KBr): $\tilde{\nu}_{max}$ = 3105 (w), 3061 (w), 2963 (s), 2870 (w), 2870 (m), 1635 (w), 1603 (w), 1572 (s), 1518 (m), 1487 (s), 1456 (m), 1398 (s), 1365 (m), 1290 (m), 1226 (m), 1197 (m), 1142 (s), 1116 (m), 1072 (w), 1045 (m), 1028 (m), 993 (s), 922 (w), 870 (m), 835 (s), 802 (w), 779 (s), 754 (s), 731 (m), 692 (m), 675 (m), 607 (s), 572 (m), 526 (m), 505 (m), 459 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 288 (4.60), 368 (3.64), 386 (3.77), 588 sh (2.40), 634 (2.51), 690 sh (2.43), 774 sh (1.93) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.48 (d, J = 10.0 Hz, 1 H, 8-H), 8.42 (d, J = 1.2 Hz, 1 H, 4-H), 7.71 (s, 1 H, 2-H), 7.55 (d, J = 10.0 Hz, 1 H, 6-H), 7.45 (d, J = 8.0 Hz, 1 H, 8′-H), 7.23 (t, J = 8.0 Hz, 1 H, 5′-H), 7.20 (t, J = 8.0 Hz, 1 H, 6′-H), 7.13 (t, J = 8.0 Hz, 1 H, 7′-H), 6.93 (d, J = 9.2 Hz, 1 H, 4′-H), 6.28 (dd, J = 6.0, 9.2 Hz, 1 H, 3′-H), 6.04 (d, J = 6.0 Hz, 1 H, 2′-H), 1.52 (s, 9 H, *t*Bu), 1.32 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.44, 138.97, 137.70, 136.06, 135.90, 135.62, 135.40, 134.72, 131.12, 129.47, 129.23, 128.35, 128.18, 127.37, 126.67, 126.66, 126.32, 119.90, 117.26 (q, J = 413.6 Hz, CF_3), 63.67, 33.79 (*t*Bu), 33.44 (*t*Bu), 32.65 (*t*Bu), 32.49 (*t*Bu) ppm. $C_{28}H_{30}F_3NO_2S·0.25H_2O$ (501.60): calcd. C 66.45, H 6.07, N 2.77; found C 66.44, H 6.07, N 2.77.

2-(1,3-Di-*tert*-butylazulen-5-yl)quinoline (3): A mixture of Tf_2O (423 mg, 1.50 mmol) and quinoline (1.29 g, 10.0 mmol) in CH_2Cl_2 (10 mL) was added at room temp. to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). The resulting solution was stirred at the same temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina with CH_2Cl_2 to give **3** (257 mg, 70%) as green crystals and **4** (30 mg, 6%) as green crystals.

3: M.p. 192.0–193.0 °C. HRMS (ESI): calcd. for $C_{27}H_{30}N$ $[M + H]^+$ 368.2378; found 368.2373. IR (KBr): $\tilde{\nu}_{max}$ = 3103 (w), 3057 (m), 2963 (m), 2951 (w), 2903 (m), 2866 (m), 1618 (m), 1595 (s), 1570 (m), 1556 (m), 1504 (s), 1477 (w), 1458 (m), 1425 (w), 1414 (m), 1388 (m), 1363 (m), 1309 (m), 1275 (m), 1240 (m), 1203 (s), 1143 (m), 1113 (w), 1026 (w), 1014 (w), 1001 (w), 972 (w), 951 (w), 924 (w), 906 (m), 877 (m), 848 (m), 827 (s), 794 (m), 783 (m), 754 (m), 694 (m), 667 (w), 625 (m), 607 (w), 590 (w), 547 (m), 534 (w), 476 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 236 (4.38), 294 (4.65), 416 (4.22), 582 sh (2.67), 630 (2.81), 688 (2.75), 768 sh (2.31) nm. UV/Vis (AcOH): λ_{max} (log ε) = 282 (4.51), 294 (4.52), 424 sh (3.88), 484 (4.06), 642 (3.09), 688 sh (2.96), 768 sh (2.48) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.61 (d, J = 1.2 Hz, 1 H, 4-H), 8.60 (d, J = 9.6 Hz, 1 H, 8-H), 8.35 (d, J = 9.6 Hz, 1 H, 6-H), 8.22 (d, J = 8.8 Hz, 1 H, 8′-H), 8.17 (d, J = 8.8 Hz, 1 H, 4′-H), 7.93 (d, J = 8.8 Hz, 1 H, 3′-H), 7.83 (d, J = 8.8 Hz, 1 H, 5′-H), 7.79 (s, 1 H, 2-H), 7.73 (t, J = 8.8 Hz, 1 H, 7′-H), 7.52 (d, J = 8.8 Hz, 1 H, 6′-H), 7.11 (t, J = 9.6 Hz, 1 H, 7-H), 1.68 (s, 9 H, *t*Bu), 1.61 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.76, 148.69, 140.84, 139.17, 137.16, 137.05, 136.44, 135.99, 135.83, 135.76, 135.35, 131.11, 130.17, 130.09, 127.78, 127.02, 126.47, 119.89, 119.87, 33.91 (*t*Bu), 33.86 (*t*Bu), 32.92 (*t*Bu), 32.69 (*t*Bu) ppm. $C_{27}H_{29}N·0.2H_2O$ (367.53): calcd. C 87.38, H 7.98, N 3.77; found C 87.47, H 8.01, N 3.77.

4: M.p. 248.0–251.0 °C. HRMS (ESI): calcd. for $C_{36}H_{35}N_2$ $[M + H]^+$ 495.2800; found 495.2795. IR (KBr): $\tilde{\nu}_{max}$ = 3055 (w), 2960 (s), 2929 (w), 2902 (w), 2866 (m), 1618 (w), 1595 (s), 1571 (m), 1556 (m), 1502 (s), 1475 (w), 1458 (m), 1421 (m), 1388 (m), 1363 (m), 1301 (m), 1261 (w), 1240 (w), 1201 (w), 1145 (w), 1031 (w), 948 (w), 921 (w), 902 (w), 879 (w), 827 (s), 792 (w), 756 (m), 698 (m), 624 (w), 574 (w), 474 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 266 sh (4.45), 306 (4.61), 386 sh (3.92), 438 (4.28), 634 (2.84), 690 (2.82), 772 sh (2.43) nm. UV/Vis (AcOH): λ_{max} (log ε) = 286 (4.58), 304 (4.59), 404 sh (4.00), 482 (4.25), 628 (3.43), 690 sh (3.33), 772 sh (3.10) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.59 (d, J = 2.0 Hz, 2 H, 4,8-H), 9.51 (s, 1 H, 6-H), 8.20 (d, J = 8.8 Hz, 2 H, 4′,4′′-H), 8.14 (d, J = 8.8 Hz, 2 H, 8′,8′′-H), 7.99 (d, J = 8.8 Hz, 2 H, 3′,3′′-H), 7.79 (d, J = 8.8 Hz, 2 H, 5′,5′′-H), 7.75 (s, 1 H, 2-H), 7.68 (t, J = 8.8 Hz, 2 H, 7′,7′′-H), 7.67 (t, J = 8.8 Hz, 2 H, 6′,6′′-H), 1.63 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.23, 148.64, 142.60, 137.43, 137.30, 136.88, 136.09, 135.28, 130.64, 130.18, 130.14, 127.80, 127.08, 126.56, 120.15, 34.05 (*t*Bu), 32.94 (*t*Bu) ppm. $C_{36}H_{34}N_2·0.75H_2O$ (494.67): calcd. C 85.09, H 7.04, N 5.51; found C 85.19, H 7.14, N 5.47.

2-(1,3-Di-*tert*-butylazulen-5-yl)quinoline (3): KOH (560 mg, 10.0 mmol) was added at room temp. to a solution of **2** (502 mg, 1.00 mmol) in MeOH (10 mL). The resulting solution was stirred at 50 °C for 1 h. The reaction mixture was poured into water, extracted with CH_2Cl_2 and dried with $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina with CH_2Cl_2 to give **3** (345 mg, 94%) as green crystals.

1,3-Di-*tert*-butyl-5,7-bis(quinol-2′-yl)azulene (4): A mixture of Tf_2O (1.41 g, 5.00 mmol) and quinoline (2.58 g, 20.0 mmol) in CH_2Cl_2 (10 mL) was added at room temp. to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). The resulting solution was stirred at the same temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column

chromatography on alumina with CH_2Cl_2 to give **4** (326 mg, 77%) as green crystals.

1,3-Di-*tert*-butyl-5-[2-(trifluoromethylsulfonyl)-1,2-dihydroisoquinolin-1-yl]azulene (5): A mixture of Tf_2O (423 mg, 1.50 mmol) and isoquinoline (646 mg, 10.0 mmol) in CH_2Cl_2 (10 mL) was added at room temp. to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). The resulting solution was stirred at the same temperature for 30 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 **5** (446 mg, 89%) as blue crystals; m.p. 127.0–132.0 °C. HRMS (ESI): calcd. for $C_{28}H_{30}F_3NO_2SNa$ $[M + Na]^+$ 524.1847; found 524.1846. IR (KBr): $\tilde{\nu}_{max}$ = 3104 (w), 2961 (s), 2907 (w), 2870 (w), 1632 (w), 1572 (m), 1520 (m), 1462 (w), 1454 (w), 1396 (w), 1388 (w), 1365 (m), 1333 (w), 1288 (w), 1226 (m), 1197 (m), 1151 (s), 1116 (s), 1095 (w), 1074 (w), 1037 (s), 945 (m), 900 (s), 879 (w), 854 (w), 829 (w), 794 (w), 777 (w), 769 (w), 748 (m), 681 (m), 671 (m), 630 (w), 599 (m), 588 (m), 561 (w), 547 (w), 530 (w), 515 (w), 480 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 290 (4.69), 368 sh (3.71), 389 (3.81), 590 sh (2.37), 634 (2.50), 690 sh (2.39), 784 sh (1.57) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 9.6 Hz, 1 H, 8-H), 8.18 (d, J = 1.2 Hz, 1 H, 4-H), 7.61 (s, 1 H, 2-H), 7.50 (dd, J = 1.2, 9.6 Hz, 1 H, 6-H), 7.28–7.24 (m, 3 H, 5′,6′,7′-H), 7.07 (d, J = 7.2 Hz, 1 H, 8′-H), 6.83 (t, J = 9.6 Hz, 1 H, 7-H), 6.44 (d, J = 7.6 Hz, 1 H, 3′-H), 6.31 (d, J = 7.6 Hz, 1 H, 4′-H), 6.30 (s, 1 H, 1′-H), 1.45 (s, 9 H, *t*Bu), 1.24 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.45, 138.74, 137.30, 135.77, 135.73, 134.19, 131.55, 130.01, 129.65, 129.45, 129.27, 126.66, 122.79, 119.67, 118.76 (q, J = 325.7 Hz, CF_3), 65.40, 33.73 (*t*Bu), 33.31 (*t*Bu), 32.60 (*t*Bu), 32.33 (*t*Bu) ppm. $C_{28}H_{30}F_3NO_2S$ (501.60): calcd. C 67.04, H 6.03, N 2.79; found C 66.74, H 6.25, N 2.79.

1,3-Di-*tert*-butyl-5,7-bis[2-(trifluoromethylsulfonyl)-1,2-dihydroisoquinolin-1-yl]azulene (6): A mixture of Tf_2O (1.41 g, 5.00 mmol) and isoquinoline (2.58 mg, 20.0 mmol) in CH_2Cl_2 (10 mL) was added at room temp. to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). The resulting solution was stirred at the same temperature for 30 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 **6** (732 mg, 96%) as blue crystals; m.p. 148.0–151.0 °C. HRMS (ESI): calcd. for $C_{38}H_{36}F_6N_2O_4S_2Na$ $[M + Na]^+$ 785.1918; found 785.1913. IR (KBr): $\tilde{\nu}_{max}$ = 3107 (w), 2964 (m), 2907 (w), 2872 (w), 1637 (w), 1576 (w), 1518 (w), 1491 (w), 1464 (m), 1402 (s), 1365 (w), 1228 (s), 1197 (s), 1149 (s), 1118 (m), 1037 (s), 949 (w), 900 (m), 775 (s), 748 (m), 681 (s), 609 (m), 590 (s), 557 (w), 498 (w), 488 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 264 sh (4.52), 290 (4.71), 378 (3.86), 396 (4.01), 636 (2.50), 698 sh (2.83), 788 sh (2.36) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.38 (s, 2 H, 4,8-H), 7.66 (s, 1 H, 6-H), 7.45–7.29 (m, 7 H, 2, 5′, 7′, 8′, 5′′, 7′′, 8′′-H), 7.11 (d, J = 7.6 Hz, 2 H, 6′, 6′′-H), 6.44 (dd, J = 7.6, 7.6 Hz, 2 H, 3′, 3′′-H), 6.34–6.26 (m, 4 H, 1′, 4′, 1′′, 4′′-H), 1.36 (s, 18 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.64, 136.94, 136.09, 135.67, 133.77, 130.87, 129.23, 128.86, 127.14, 126.47, 122.13, 119.90 (q, J = 325.3 Hz, CF_3), 65.35, 33.03 (*t*Bu), 31.97 (*t*Bu) ppm. $C_{38}H_{36}F_6N_2O_4S_2$ (762.83): calcd. C 59.83, H 4.76, N 3.67; found C 59.88, H 4.76, N 3.69.

1-(1,3-Di-*tert*-butylazulen-5-yl)isoquinoline (7): KOH (560 mg, 10.0 mmol) was added at room temp. to a solution of **5** (502 mg, 1.00 mmol) in MeOH (10 mL). The resulting solution was heated at reflux for 1 h. The reaction mixture was poured into water, extracted with hexane, and dried with $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina with CH_2Cl_2 to give **7** (360 mg, 98%) as green crystals; m.p. 76.0–79.0 °C. HRMS (ESI): calcd. for $C_{27}H_{30}N$ $[M + H]^+$ 368.2378; found 368.2373. IR (KBr): $\tilde{\nu}_{max}$ = 3105 (w), 3049 (m), 2963 (w), 2951 (w), 2903 (m), 2866 (m), 1581 (w), 1568 (w), 1554 (s), 1518 (w), 1498 (m), 1475 (w), 1460 (m), 1415 (w), 1387 (s), 1363 (s), 1346 (m), 1313 (m), 1242 (m), 1215 (m), 1201 (s), 1161 (w), 1018 (w), 964 (w), 904 (s), 875 (s), 823 (s), 806 (w), 796 (w), 789 (w), 750 (s), 733 (m), 690 (s), 671 (w), 652 (m), 611 (w), 576 (w), 547 (w), 522 (w), 463 (w), 436 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 239 sh (4.32), 296 (4.66), 326 sh (4.04), 401 (3.98), 634 (2.62), 688 (2.54), 768 sh (2.02) nm. UV/Vis (AcOH): λ_{max} ($\log\varepsilon$) = 294 (4.66), 332 sh (3.99), 464 (3.80), 628 (2.73), 688 sh (2.60), 770 sh (2.00) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, J = 1.2 Hz, 1 H, 4-H), 8.56 (d, J = 10.0 Hz, 1 H, 8-H), 8.53 (d, J = 5.6 Hz, 1 H, 3′-H), 8.02 (dd, J = 0.8, 8.0 Hz, 1 H, 6′-H), 7.79 (dd, J = 1.2, 10.0 Hz, 1 H, 6-H), 7.74 (s, 1 H, 2-H), 7.56–7.53 (m, 2 H, 4′,6′-H), 7.40 (t, J = 8.0 Hz, 1 H, 7′-H), 6.99 (t, J = 10.0 Hz, 1 H, 7-H), 1.53 (s, 9 H, *t*Bu), 1.42 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.93, 142.73, 139.61, 139.51, 138.63, 138.13, 137.54, 136.45, 135.97, 135.81, 134.69, 130.91, 130.44, 128.22, 127.56, 127.55, 127.14, 120.05, 119.92, 33.95 (*t*Bu), 33.87 (*t*Bu), 33.00 (*t*Bu), 32.77 (*t*Bu) ppm. $C_{27}H_{29}N{\cdot}0.33H_2O$ (367.53): calcd. C 86.82, H 8.01, N 3.75; found C 86.84, H 8.01, N 3.75.

1,3-Di-*tert*-butyl-5,7-bis(isoquinol-1′-yl)azulene (8): KOH (1.12 g, 20.0 mmol) was added at room temp. to a solution of **6** (763 mg, 1.00 mmol) in MeOH (10 mL). The resulting solution was heated at reflux for 2 h. The reaction mixture was poured into water, extracted with hexane, and dried with $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina with CH_2Cl_2 to give **8** (470 mg, 95%) as green crystals; m.p. 194.0–195.5 °C. HRMS (ESI): calcd. for $C_{36}H_{35}N_2$ $[M + H]^+$ 495.2800; found 495.2795. IR (KBr): $\tilde{\nu}_{max}$ = 3049 (w), 2962 (s), 2952 (s), 2902 (w), 2866 (w), 1620 (w), 1581 (m), 1554 (s), 1514 (w), 1498 (w), 1477 (w), 1417 (w), 1377 (s), 1363 (m), 1344 (s), 1313 (w), 1242 (m), 1217 (m), 1199 (w), 1164 (w), 1139 (w), 916 (w), 893 (w), 873 (w), 825 (s), 796 (w), 750 (m), 692 (m), 655 (m), 611 (w), 432 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 298 (4.72), 326 sh (4.40), 412 (4.21), 634 (2.80), 692 (2.75), 776 sh (2.30) nm. UV/Vis (AcOH): λ_{max} ($\log\varepsilon$) = 294 (4.72), 328 (4.40), 340 sh (4.37), 450 (4.11), 634 (2.81), 692 (2.71), 780 sh (2.23) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.87 (d, J = 1.2 Hz, 2 H, 4,8-H), 8.60 (d, J = 5.6 Hz, 2 H, 3′,3′′-H), 8.38 (br. s, 1 H, 6-H), 8.20 (d, J = 8.4 Hz, 2 H, 8′,8′′-H), 7.90 (d, J = 8.4 Hz, 2 H, 5′,5′′-H), 7.89 (s, 1 H, 2-H), 7.68 (dd, J = 0.8, 8.4 Hz, 2 H, 6′,6′′-H), 7.65 (d, J = 5.6 Hz, 2 H, 4′,4′′-H), 7.52 (dd, J = 0.8, 8.4 Hz, 2 H, 7′,7′′-H), 1.56 (s, 18 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.44, 142.04, 141.34, 140.53, 137.93, 137.14, 136.07, 134.43, 130.09, 129.85, 127.87, 127.25, 127.07, 126.71, 119.77, 33.48 (*t*Bu), 32.50 (*t*Bu) ppm. $C_{36}H_{34}N_2{\cdot}0.1H_2O$ (494.67): calcd. C 87.09, H 6.94, N 5.64; found C 87.09, H 7.15, N 5.56.

1,3-Di-*tert*-butyl-5-[10-(trifluoromethylsulfonyl)-9,10-dihydroacridin-9-yl]azulene (9): A mixture of Tf_2O (423 mg, 1.50 mmol) and acridine (896 mg, 5.00 mmol) in CH_2Cl_2 (10 mL) was added at room temp. to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). The resulting solution was stirred at the same temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel with CH_2Cl_2 to give **9** (502 mg, 91%) as blue crystals; m.p. 167.0–168.0 °C. HRMS (ESI): calcd. for $C_{32}H_{32}F_3NO_2S^+$ $[M]^+$ 551.2106; found 551.2100. IR (KBr): $\tilde{\nu}_{max}$ = 2870 (m), 1568 (w), 1471 (m), 1458 (m), 1402 (s), 1388 (m), 1365 (m), 1296 (w), 1232 (s), 1203 (s), 1194 (s), 1167 (w), 1142 (m), 1120 (w), 972 (w), 883 (w), 854 (w), 825 (w), 798 (m), 700 (w), 681 (w), 655 (w), 611 (m), 580 (w), 536

(w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 252 (4.29), 292 (4.69), 344 sh (3.50), 362 (3.73), 380 (3.80), 588 sh (2.38), 630 (2.49), 688 sh (2.40), 774 sh (1.83) nm. $C_{32}H_{32}F_3NO_2S$ (551.66): calcd. C 69.67, H 5.85, N 2.54; found C 69.70, H 6.01, N 2.32. All ^1H and ^{13}C NMR signals were broadened and, consequently, the assignment of signals was problematic.

9-(1,3-Di-*tert*-butylazulen-5-yl)acridine (10): A mixture of Tf_2O (423 mg, 1.50 mmol) and acridine (1.79 g, 10.0 mmol) in CH_2Cl_2 (10 mL) was added at room temp. to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). The resulting solution was stirred at the same temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina with CH_2Cl_2 to give **10** (296 mg, 71%) as green crystals and **11** (48 mg, 8%) as green crystals.

10: M.p. 140.0–145.0 °C. HRMS (ESI): calcd. for $C_{31}H_{32}N$ [M + H]$^+$ 418.2535; found 418.2529. IR (KBr): $\tilde{\nu}_{max}$ = 2963 (s), 2903 (w), 2868 (m), 1558 (s), 1543 (w), 1516 (m), 1460 (m), 1437 (w), 1408 (m), 1388 (m), 1363 (s), 1242 (m), 1215 (m), 1010 (w), 908 (w), 889 (m), 819 (w), 758 (s), 731 (w), 681 (m), 636 (w), 623 (w), 542 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 269 sh (4.47), 293 (4.65), 401 (3.83), 588 sh (2.38), 640 (2.51), 696 sh (2.40), 780 sh (1.59) nm. UV/Vis (AcOH): λ_{max} (log ε) = 256 (4.94), 294 (4.75), 344 sh (3.98), 362 (4.25), 380 (3.88), 414 sh (3.68), 440 sh (3.43), 562 (3.53), 710 sh (2.93), 790 sh (2.31) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, J = 9.6 Hz, 1 H, 8-H), 8.65 (s, 1 H, 4-H), 8.53 (d, J = 8.8 Hz, 2 H, 1′,8′-H), 7.90 (d, J = 8.8 Hz, 1 H, 4′,5′-H), 7.89 (s, 1 H, 2-H), 7.78 (t, J = 8.8 Hz, 2 H, 2′,7′-H), 7.52 (d, J = 9.6 Hz, 1 H, 6-H), 7.43 (t, J = 8.8 Hz, 2 H, 3′,6′-H), 7.09 (t, J = 10.0 Hz, 1 H, 7-H), 1.68 (s, 9 H, *t*Bu), 1.43 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.57, 149.51, 139.64, 139.36, 138.75, 138.14, 136.70, 136.51, 135.72, 134.53, 130.44, 130.21, 127.35, 126.72, 126.23, 125.74, 119.51, 33.91 (*t*Bu), 33.77 (*t*Bu), 32.85 (*t*Bu), 32.78 (*t*Bu) ppm. $C_{31}H_{31}N{\cdot}0.5H_2O$ (417.58): calcd. C 87.28, H 7.56, N 3.28; found C 87.34, H 7.68, N 3.16.

11: M.p. >300.0 °C. HRMS (ESI): calcd. for $C_{44}H_{39}N_2$ [M + H]$^+$ 595.3113; found 595.3108. IR (KBr): $\tilde{\nu}_{max}$ = 3060 (w), 3045 (w), 2962 (m), 2904 (w), 2868 (w), 1627 (w), 1608 (w), 1558 (m), 1542 (m), 1515 (m), 1460 (w), 1417 (w), 1404 (w), 1388 (w), 1363 (w), 1342 (w), 1259 (w), 1240 (w), 1176 (w), 1149 (w), 1132 (w), 1012 (w), 948 (w), 896 (w), 756 (s), 686 (w), 636 (w), 599 (w), 555 (w), 432 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 250 (5.34), 2.98 (4.78), 350 sh (4.33), 362 (4.40), 388 sh (4.22), 658 (2.86) nm. UV/Vis (AcOH): λ_{max} (log ε) = 296 (4.87), 344 sh (4.34), 358 (4.56), 386 sh (4.15), 412 sh (4.09), 546 (3.85) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.83 (d, J = 1.2 Hz, 2 H, 4,8-H), 8.53 (d, J = 8.8 Hz, 4 H, 1′,1′′,8′,8′′-H), 7.90 (d, J = 8.8 Hz, 4 H, 4′,4′′,5′,5′′-H), 8.00 (s, 1 H, 2-H), 7.77 (ddd, J = 8.8, 1.2, 1.2 Hz, 4 H, 2′,2′′,7′,7′′-H), 7.62 (br. s, 1 H, 6-H), 7.43 (t, J = 8.8, 1.2, 1.2 Hz, 4 H, 3′,3′′,6′,6′′-H), 1.53 (s, 18 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.52, 148.95, 141.36, 140.38, 137.92, 137.50, 134.50, 129.98, 129.88, 126.50, 126.05, 125.59, 125.20, 33.51 (*t*Bu), 32.40 (*t*Bu) ppm. $C_{44}H_{38}N_2{\cdot}1.5H_2O$ (594.79): calcd. C 84.99, H 6.65, N 4.51; found C 85.05, H 6.45, N 4.37.

9-(1,3-Di-*tert*-butylazulen-5-yl)acridine (10): KOH (560 mg, 10.0 mmol) was added at room temp. to a solution of **9** (552 mg, 1.00 mmol) in MeOH (10 mL). The resulting solution was heated at reflux for 1 h. The reaction mixture was poured into water, extracted with CH_2Cl_2, and dried with $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina with CH_2Cl_2 to give **10** (409 mg, 98%) as green crystals.

5,7-Bis(acridin-9′-yl)-1,3-di-*tert*-butylazulene (11): A mixture of Tf_2O (1.41 g, 5.00 mmol) and acridine (3.58 g, 20.0 mmol) in CH_2Cl_2 (10 mL) was added at room temp. to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). The resulting solution was stirred at the same temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina with CH_2Cl_2 to give **11** (452 mg, 76%) as green crystals.

2-(1,3-Di-*tert*-butylazulen-5-yl)-3-(trifluoromethylsulfonyl)-2,3-dihydrobenzothiazole (12): A mixture of Tf_2O (423 mg, 1.50 mmol) and benzothiazole (676 mg, 10.0 mmol) in CH_2Cl_2 (10 mL) was added at room temp. to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). The resulting solution was stirred at the same temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina with CH_2Cl_2 to give **12** (442 mg, 87%) as blue crystals; m.p. 66.0–68.0 °C. HRMS (ESI): calcd. for $C_{26}H_{28}F_3NO_2S_2Na$ [M + Na]$^+$ 530.1411; found 530.1406. IR (KBr): $\tilde{\nu}_{max}$ = 3065 (w), 2964 (s), 2905 (w), 2870 (w), 1572 (m), 1518 (w), 1464 (m), 1406 (s), 1365 (m), 1338 (w), 1277 (w), 1226 (m), 1201 (w), 1140 (s), 1088 (w), 1064 (m), 1012 (m), 970 (m), 879 (w), 831 (m), 794 (w), 769 (w), 748 (m), 717 (w), 698 (w), 673 (w), 621 (w), 605 (s), 571 (m), 524 (m), 432 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 258 (4.33), 290 (4.67), 370 sh (3.75), 386 (3.86), 636 (2.62), 690 (2.55), 780 (2.04) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.58 (d, J = 1.2 Hz, 1 H, 4-H), 8.39 (d, J = 10.0 Hz, 1 H, 8-H), 7.62 (s, 1 H, 2-H), 7.49 (d, J = 7.6 Hz, 1 H, 4′-H), 7.33 (d, J = 1.2, 10.0 Hz, 1 H, 6-H), 7.20 (dd, J = 1.2, 7.6 Hz, 1 H, 7′-H), 7.11–7.03 (m, 2 H, 5′,6′-H), 6.75 (t, J = 10.0 Hz, 1 H, 7-H), 6.68 (s, 1 H, 2′-H), 1.41 (s, 9 H, *t*Bu), 1.20 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.00, 139.80, 136.39, 136.04, 135.67, 135.31, 135.29, 135.28, 132.89, 131.56, 130.40, 129.20 (q, J = 357.0 Hz, CF_3), 128.00, 127.98, 126.76, 119.31, 118.98, 74.30, 33.85 (*t*Bu), 33.39 (*t*Bu), 32.63 (*t*Bu), 32.46 (*t*Bu) ppm. $C_{26}H_{28}F_3NO_2S_2$ (507.63): calcd. C 61.52, H 5.56, N 2.76; found C 61.52, H 5.86, N 2.68.

2-(1,3-Di-*tert*-butylazulen-5-yl)benzothiazole (13): A mixture of Tf_2O (423 mg, 1.50 mmol) and benzothiazole (1.35 g, 10.0 mmol) in CH_2Cl_2 (10 mL) was added at room temp. to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). The resulting solution was stirred at the same temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina with CH_2Cl_2 to give **13** (287 mg, 77%) as green crystals and **14** (30 mg, 6%) as green crystals.

13: M.p. 147.0–149.0 °C. HRMS (ESI): calcd. for $C_{25}H_{28}NS$ [M + H]$^+$ 374.1942; found 374.1937. IR (KBr): $\tilde{\nu}_{max}$ = 2964 (w), 2953 (w), 2903 (w), 2868 (w), 1570 (m), 1520 (w), 1471 (m), 1458 (w), 1427 (w), 1410 (w), 1388 (w), 1365 (m), 1313 (m), 1286 (w), 1242 (m), 1196 (s), 1012 (w), 945 (w), 895 (w), 879 (w), 846 (w), 789 (w), 758 (s), 727 (m), 684 (m), 669 (w), 628 (w), 580 (w), 418 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 250 sh (4.51), 276 (4.58), 312 sh (4.85), 322 (4.89), 358 sh (3.97), 416 sh (4.57), 432 (4.66), 586 sh (2.78), 634 (2.92), 692 (2.87), 770 sh (2.47) nm. UV/Vis (AcOH): λ_{max} (log ε) = 272 (4.34), 310 sh (4.59), 316 (4.62), 412 sh (4.28), 430 (4.39), 634 (2.93), 692 (2.87), 778 sh (2.42) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.45 (d, J = 2.0 Hz, 1 H, 4-H), 8.58 (d, J = 10.0 Hz, 1 H, 8-H), 8.50 (d, J = 1.2, 10.0 Hz, 1 H, 6-H), 8.05 (d, J = 8.0 Hz, 1 H, 4′-H), 7.89 (d, J = 8.0 Hz, 1 H, 7′-H), 7.80 (s, 1 H, 2-H), 7.48 (t, J = 8.0 Hz, 1 H, 5′-H), 7.35 (t, J = 8.0 Hz, 1 H, 6′-H), 7.07 (t, J = 10.0 Hz, 1 H, 7-H), 1.69 (s, 9 H, *t*Bu), 1.60 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.75, 155.04, 142.76, 141.31, 136.51, 136.32, 135.97, 135.83, 135.58, 134.40, 126.71, 125.21, 124.52, 123.33, 121.79, 119.82, 115.17, 34.04 (*t*Bu),

33.97 (*t*Bu), 33.04 (*t*Bu), 32.67 (*t*Bu) ppm. $C_{25}H_{27}NS·0.17H_2O$ (373.55): calcd. C 79.74, H 7.32, N 3.72; found C 79.75, H 7.33, N 3.81.

14: M.p. 283.0–285.0 °C. HRMS (ESI): calcd. for $C_{32}H_{31}N_2S_2$ [M + H]$^+$ 507.1929; found 507.1923. IR (KBr): $\tilde{\nu}_{max}$ = 2964 (m), 2902 (w), 2868 (w), 1577 (m), 1494 (m), 1471 (w), 1458 (m), 1434 (m), 1388 (w), 1363 (m), 1313 (m), 1282 (w), 1191 (s), 1159 (w), 1147 (w), 1124 (w), 1103 (w), 1064 (w), 1014 (w), 906 (m), 896 (m), 756 (s), 727 (s), 698 (w), 684 (w), 669 (w), 565 (w), 434 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 250 (4.61), 324 (4.89), 356 sh (4.71), 432 sh (4.54), 454 (4.75), 646 (2.97), 706 (2.95), 784 sh (2.57) nm. UV/Vis (AcOH): λ_{max} (log ε) = 254 (4.56), 318 (4.90), 350 sh (4.72), 432 sh (4.55), 450 (4.74), 642 (3.04), 702 (3.02), 784 sh (2.62) nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.54 (d, *J* = 1.6 Hz, 2 H, 4,8-H), 9.44 (dd, *J* = 1.6, 1.6 Hz, 1 H, 6-H), 8.13 (dd, *J* = 8.0, 0.8 Hz, 2 H, 4′,4′′-H), 7.93 (dd, *J* = 8.0, 0.8 Hz, 2 H, 7′,7′′-H), 7.83 (s, 1 H, 2-H), 7.52 (ddd, *J* = 8.0, 0.8, 0.8 Hz, 2 H, 5′,5′′-H), 7.39 (ddd, *J* = 8.0, 0.8, 0.8 Hz, 2 H, 6′,6′′-H), 1.71 (s, 18 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.93, 154.61, 145.75, 137.09, 135.75, 135.63, 135.02, 134.38, 126.34, 124.99, 123.74, 123.28, 121.42, 33.89 (*t*Bu), 32.63 (*t*Bu) ppm. $C_{32}H_{30}N_2S_2·H_2O$ (506.72): calcd. C 73.24, H 6.15, N 5.34; found C 73.32, H 6.10, N 5.33.

2-(1,3-Di-*tert*-butylazulen-5-yl)benzothiazole (13): KOH (560 mg, 10.0 mmol) was added at room temp. to a solution of **12** (508 mg, 1.00 mmol) in MeOH (10 mL). The resulting solution was heated at reflux for 1 h. The reaction mixture was poured into water, extracted with hexane, and dried with $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina with CH_2Cl_2 to give **13** (343 mg, 92%) as green crystals.

5,7-Bis(benzothiazol-2′-yl)-1,3-di-*tert*-butylazulene (14): A mixture of Tf_2O (1.41 g, 5.00 mmol) and benzothiazole (2.70 g, 20.0 mmol) in CH_2Cl_2 (10 mL) was added at room temp. to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). The resulting solution was stirred at the same temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina with CH_2Cl_2 to give **14** (416 mg, 82%) as green crystals and **13** (15 mg, 4%) as green crystals.

1,3-Di-*tert*-butyl-5-(1′,10′-phenanthrolin-2′-yl)azulene (15) and 1,3-Di-*tert*-butyl-5-(1′,10′-phenanthrolin-4′-yl)azulene (16): A mixture of Tf_2O (423 mg, 1.50 mmol) and 1,10-phenanthroline (901 mg, 5.00 mmol) in CH_2Cl_2 (10 mL) was added at room temp. to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). The resulting solution was stirred at the same temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina with CH_2Cl_2 to give **15** (50 mg, 12%) as a green oil and **16** (297 mg, 71%) as a green oil.

15: HRMS (ESI): calcd. for $C_{30}H_{30}N_2Na$ [M + Na]$^+$ 441.2307; found 441.2301. IR (KBr): $\tilde{\nu}_{max}$ = 2955 (s), 2868 (m), 1558 (m), 1541 (m), 1516 (m), 1458 (m), 1406 (m), 1388 (w), 1363 (m), 1242 (w), 1213 (w), 889 (w), 758 (s), 681 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 286 (4.53), 322 sh (4.08), 378 sh (3.64), 418 (3.93), 582 sh (2.47), 630 (2.59), 690 (2.52), 722 sh (2.29) nm. UV/Vis (AcOH): λ_{max} (log ε) = 289 (4.50), 305 sh (4.37), 379 (3.53), 438 (3.91), 630 (2.61), 691 sh (2.52), 724 sh (2.29) nm. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.55 (d, *J* = 1.9 Hz, 1 H, 4-H), 9.23 (dd, *J* = 1.6, 5.9 Hz, 1 H, 9′-H), 8.73 (dd, *J* = 1.9, 9.5 Hz, 1 H, 6-H), 8.62 (d, *J* = 9.5 Hz, 1 H, 8-H), 8.32 (d, *J* = 8.4 Hz, 1 H, 4′-H), 8.25 (dd, *J* = 1.6, 5.9 Hz, 1 H, 7′-H), 8.14 (d, *J* = 8.4 Hz, 1 H, 3′-H), 7.82 (d, *J* = 8.8 Hz, 1 H, 5′-H), 7.79 (s, 1 H, 2-H), 7.76 (d, *J* = 8.8 Hz, 1 H, 6′-H), 7.19 (t, *J* = 9.5 Hz, 1 H, 7-H), 1.70 (s, 9 H, *t*Bu), 1.62 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.68, 150.24, 146.39, 146.00, 140.11, 138.59, 137.58, 136.85, 136.00, 135.93, 135.71, 135.58, 135.16, 134.85, 130.90, 129.13, 126.83, 125.94, 122.85, 121.06, 119.91, 33.47 (*t*Bu), 33.42 (*t*Bu), 32.53 (*t*Bu), 32.29 (*t*Bu) ppm. $C_{30}H_{30}N_2$ (418.57): calcd. C 86.08, H 7.22, N 6.69; found C 85.96, H 7.34, N 6.58.

16: HRMS (ESI): calcd. for $C_{30}H_{30}N_2Na$ [M + Na]$^+$ 441.2307; found 441.2301. IR (KBr): $\tilde{\nu}_{max}$ = 3105 (s), 2985 (m), 2968 (m), 1616 (w), 1585 (m), 1568 (m), 1552 (w), 1504 (m), 1479 (w), 1442 (w), 1414 (m), 1388 (s), 1368 (m), 1300 (m), 1265 (m), 1242 (m), 1203 (s), 1115 (s), 1066 (m), 1032 (w), 1011 (w), 902 (w), 877 (w), 860 (w), 846 (w), 775 (m), 740 (m), 684 (w), 655 (w), 625 (w), 605 (m), 571 (w), 547 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 250 (4.96), 290 (4.61), 344 sh (3.90), 362 (3.99), 374 sh (3.87), 386 sh (3.73), 440 (3.47), 586 sh (2.38), 638 (2.51), 696 (2.41), 786 sh (1.85) nm. UV/Vis (AcOH): λ_{max} (log ε) = 295 (4.62), 350 sh (3.70), 500 (3.61), 631 (2.79), 696 sh (2.65), 776 sh (2.16) nm. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.26–9.24 (m, 2 H, 2′,9′-H), 8.72 (d, *J* = 1.8 Hz, 1 H, 4-H), 8.68 (d, *J* = 9.5 Hz, 1 H, 8-H), 8.25 (dd, *J* = 1.6, 5.9 Hz, 1 H, 7′-H), 7.98 (d, *J* = 9.0 Hz, 1 H, 5′-H), 7.88 (s, 1 H, 2-H), 7.73 (d, *J* = 9.0 Hz, 1 H, 6′-H), 7.69 (d, *J* = 4.4 Hz, 1 H, 3′-H), 7.67–7.64 (m, 2 H, 6,8′-H), 7.09 (t, *J* = 9.5 Hz, 1 H, 7-H), 1.65 (s, 9 H, *t*Bu), 1.51 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.22, 150.42, 149.76, 146.90, 146.53, 139.38, 138.63, 138.31, 137.10, 136.29, 135.83, 135.19, 134.23, 128.68, 128.36, 126.98, 126.26, 124.40, 123.75, 123.17, 119.34, 33.45 (*t*Bu), 33.36 (*t*Bu), 32.37 (*t*Bu), 32.25 (*t*Bu) ppm. $C_{30}H_{30}N_2·0.5H_2O$ (418.57): calcd. C 84.27, H 7.31, N 6.55; found C 84.20, H 7.34, N 6.49.

***N*-(1,3-Di-*tert*-butylazulen-5-yl)pyridinium Triflate (17):** A mixture of Tf_2O (423 mg, 1.50 mmol) and pyridine (391 mg, 10.0 mmol) in CH_2Cl_2 (10 mL) was added at room temp. to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (5 mL). The resulting solution was stirred at the same temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel with EtOAc to give **17** (430 mg, 92%) as green crystals; m.p. 240.0–241.0 °C (MeOH). HRMS (ESI): calcd. for $C_{22}H_{25}N^+$ [M – OTf]$^+$ 318.2222; found 318.2217. IR (KBr): $\tilde{\nu}_{max}$ = 3103 (w), 3057 (m), 2963 (m), 2951 (w), 2903 (m), 2866 (m), 1618 (m), 1595 (s), 1570 (m), 1556 (m), 1504 (s), 1477 (w), 1458 (m), 1425 (w), 1414 (m), 1388 (m), 1363 (m), 1309 (m), 1275 (m), 1240 (m), 1203 (s), 1143 (m), 1113 (w), 1026 (w), 1014 (w), 1001 (w), 972 (w), 951 (w), 924 (w), 906 (m), 877 (m), 848 (m), 827 (s), 794 (m), 783 (m), 754 (m), 694 (m), 667 (w), 625 (m), 607 (w), 590 (w), 547 (m), 534 (w), 476 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 291 (4.77), 351 (3.60), 463 (3.64), 645 (2.56), 710 sh (2.43), 800 sh (1.93) nm. UV/Vis (MeOH): λ_{max} (log ε) = 288 (4.78), 344 sh (3.58), 428 (3.67), 637 (2.56), 703 sh (2.43), 793 sh (1.93) nm. UV/Vis (MeCN): λ_{max} (log ε) = 284 (4.74), 340 sh (3.53), 413 (3.68), 640 (2.54), 705 sh (2.43), 798 sh (1.91) nm. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.02 (d, *J* = 5.7 Hz, 2 H, 2′,6′-H), 8.69 (d, *J* = 5.7 Hz, 1 H, 4′-H), 8.69 (d, *J* = 9.7 Hz, 1 H, 8-H), 8.55 (d, *J* = 2.6 Hz, 1 H, 4-H), 8.35 (t, *J* = 5.7 Hz, 2 H, 3′,5′-H), 8.00 (s, 1 H, 2-H), 7.70 (dd, *J* = 2.6, 9.7 Hz, 1 H, 6-H), 7.07 (t, *J* = 9.7 Hz, 1 H, 7-H), 1.60 (s, 9 H, *t*Bu), 1.55 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 146.10 (4′-C), 144.81 (2′,6′-C), 144.00 (3-C), 142.70 (1-C), 138.98 (2-C), 136.67 (8a-C), 136.29 (8-C), 133.84 (5-C), 132.47 (6-C), 131.26 (3a-C), 129.91 (4-C), 129.28 (3′,5′-C), 119.20 (q, *J* = 325.7 Hz, CF_3), 33.57 (*t*Bu), 33.54 (*t*Bu), 32.19 (*t*Bu) ppm. ^{19}F NMR (560 MHz, $CDCl_3$): δ = –78.12 (s, CF_3) ppm. $C_{24}H_{28}F_3NO_3S$ (467.54): calcd. C 61.65, H 6.04, F 12.19, N 3.00, S 6.86; found C 61.64, H 6.14, F 12.27, N 2.97, S 6.86.

Supporting Information (see footnote on the first page of this article): UV/Vis spectra of reported compounds; B3LYP/6-31G** calculations for **3** and **7**.

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[19] The B3LYP/6-31G** density functional calculations were performed by using *Spartan 04*, Wavefunction, Inc., Irvine, CA.

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