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Electrophilic *ipso*-Substitution and Some Unique Reaction Behavior of 1,3,6-Tri-*tert*-butylazulene

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Electrophilic *ipso*-substitution reactions between 1,3,6-tri-*tert*-butylazulene (**2**) and several electrophilic reagents were examined. Friedel–Crafts and Vilsmeier reactions of **2** gave the corresponding *ipso*-substitution products in moderate to excellent yields. One of the *ipso*-substitution products, 1,6-di-*tert*-butyl-3-formylazulene (**5**), was converted in high yield into the synthetically more useful azulene derivative 1,6-di-*tert*-butylazulene (**1**) by decarbonylation on treatment with pyrrole in acetic acid. Treatment of **2** with *N*-[(trifluoromethyl)sulfonyl]pyridinium trifluoromethanesulfonate (TPT) unexpectedly afforded 1-trifluoromethylthioazulene **10** and 1(8*H*)-azulenone **11**. Compound **2** also reacted with tetracyanoethylene (TCNE) to give an excellent yield of cycloaddition product **13**, rather than the *ipso*-substitution reaction product.

Introduction

Electrophilic substitution is one of the most powerful and general methodologies for the functionalization of aromatic compounds.[1] Azulene ($C_{10}H_8$) has attracted the interest of many research groups both because of its unusual properties and because of its beautiful blue color. There are numerous reports of electrophilic substitution reactions of azulene derivatives at their 1- and/or 3-positions.[2] However, difficulties are frequently encountered in selective functionalization of azulene derivatives by electrophilic substitution because of their high reactivities toward electrophilic reagents at these positions. In 1962, Hafner and Moritz reported that 1,3-dialkylazulenes would undergo electrophilic *ipso*-substitution reactions such as Friedel–Crafts acylation and Vilsmeier formylation at their 1- and/or 3-positions.[3] In particular, Vilsmeier formylation of 1,3-di-*tert*-butylazulene is reported to afford the synthetically useful 1-*tert*-butyl-3-formylazulene as the sole product in excellent yield.[3] Still, little is known about the *ipso*-substitution reactions of azulene derivatives, although such azulene derivatives would be expected to show reactivities higher than those of benzene derivatives toward electrophilic reagents. Further investigation would thus have importance for evaluation of the reactivities of azulene derivatives toward *ipso*-substitution. Previously, we had reported the synthesis of 1,6-di-*tert*-butylazulene (**1**; Scheme 2, vide infra) by Friedel–Crafts alkylation of 6-*tert*-butylazulene with *tert*-butyl chloride in the presence of $AlCl_3$.[4] As would be expected, the reaction produced significant amounts of 1,3,6-tri-*tert*-butylazulene (**2**; Scheme 1) as a by-product. We were now able to put our hands on an azulene derivative suitable for the exploration of electrophilic *ipso*-substitution reactions. Electrophilic *ipso*-substitution of the unusual compound **2** should provide facile and efficient synthetic routes to functionalized azulene derivatives. Moreover, decarbonylation of 1-formylazulene derivatives should be readily achievable by treatment with pyrrole in acetic acid.[5] Vilsmeier formylation should therefore be one of the most promising reactions for exploration, because azulene derivatives unsubstituted at their 1- and/or 3-positions should by utilizable for further functionalization reactions.

Here we report efficient electrophilic *ipso*-substitution reactions between 1,3,6-tri-*tert*-butylazulene (**2**) and several electrophilic reagents, together with some reactivity unique to **2**, including cycloaddition reaction with TCNE.

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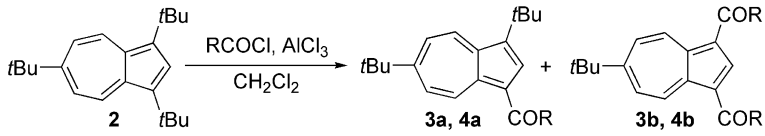


Scheme 1.

Results and Discussion

Two electrophilic reactions – Friedel–Crafts acylation and Vilsmeier formylation – of **2** were investigated as typical examples of *ipso*-substitution. Treatment with acetyl chloride and benzoyl chloride in the presence of aluminium chloride for Friedel–Crafts acylation was examined (Scheme 1), and the results are summarized in Table 1. Treatment of **2** with acetyl chloride (1.5 equiv.) in dichloromethane at room temperature gave 1-acetyl-3,6-di-*tert*-butylazulene (**3a**) in 31% yield together with 1,3-diacetyl-6-*tert*-butylazulene (**3b**) in 7% yield (Entry 1). Although the reaction afforded a mixture of **3a** and **3b**, these were easily separated by column chromatography on silica gel. When excess acetyl chloride was used for the reaction, the reaction went to completion at room temperature to afford **3b** in 77% yield as a sole product (Entry 2).

Table 1. Synthesis of 1-acetylazulene and 1-benzoylazulene derivatives **3a**, **3b**, **4a**, and **4b**.

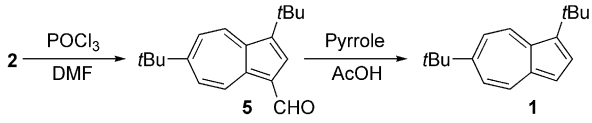
Entry	Reagent	Yield (%)	
1	1.5 equiv. CH_3COCl	**3a** (31)	**3b** (7)
2	5.0 equiv. CH_3COCl	**3a** (0)	**3b** (77)
3	1.5 equiv. PhCOCl	**4a** (19)	**4b** (24)
4	5.0 equiv. PhCOCl	**4a** (0)	**4b** (71)

Treatment of **2** with benzoyl chloride in the presence of aluminium chloride was also carried out, similarly to the reaction with acetyl chloride. Treatment with benzoyl chloride (1.5 equiv.) at room temperature afforded the presumed 1-benzoyl-3,6-di-*tert*-butylazulene (**4a**) in 19% yield together with 1,3-dibenzoyl-6-*tert*-butylazulene (**4b**) in 24% yield; these were also separable by silica gel column chromatography, similarly to the separation of **3a** and **3b** (Entry 3).

Product **4a** has also been prepared by us through the Vilsmeier–Haack reaction between **1** and *N*,*N*-dimethylbenzamide.[6] We also investigated the similar Vilsmeier–Haack reaction between **2** and *N*,*N*-dimethylbenzamide, but that reaction resulted in the complete recovery of the starting compound **2**.

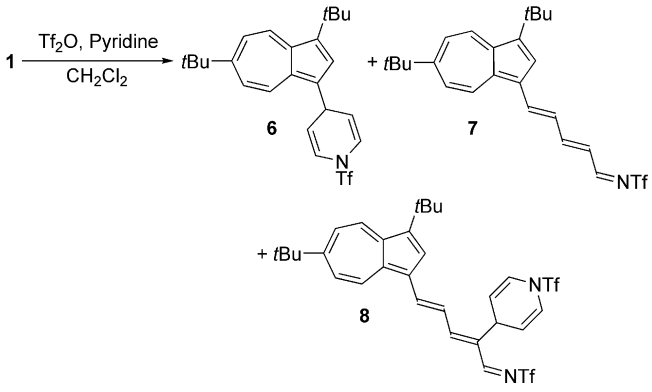
Treatment of **2** with excess benzoyl chloride also gave **4b** in 71% yield as the sole product (Entry 4). Friedel–Crafts reactions of **2** were thus found to be capable of allowing the selective synthesis of **3b** and **4b**, but the selective synthesis of **3a** and **4a** through Friedel–Crafts reactions of **2** was not straightforward, similarly to the results reported by Hafner et al.[3]

In contrast with the Friedel–Crafts reactions, selective *ipso*-formylation of **2** was established under normal Vilsmeier reaction conditions. Treatment of **2** with $POCl_3$ in DMF at 100 °C thus afforded 1,6-di-*tert*-butyl-3-formylazulene (**5**; Scheme 2)[7] in 98% yield as the sole product. Strikingly, 6-*tert*-butyl-1,3-diformylazulene was not produced in this case, even when the reaction temperature was raised to reflux in DMF. It is noteworthy that the yield of the reaction is comparable to that of the Vilsmeier formylation of **1**. This reactivity should be governed by the electron-withdrawing nature of the iminium intermediate for the Vilsmeier formylation reaction, which would hamper further *ipso*-substitution reaction. Although compound **1** could be an important synthetic intermediate,[8] the synthesis of **1** from 6-*tert*-butylazulene and *tert*-butyl chloride in the presence of $AlCl_3$ usually required a tedious separation process because of the formation of **2** as a by-product.[4] Thus, to evaluate this *ipso*-substitution reaction, we attempted the decarbonylation of the product **5** to give the useful compound **1** by treatment with pyrrole in acetic acid. Conversion of **5** into **1** in 83% yield was observed without any difficulties in the separation process (Scheme 2).



Scheme 2.

To examine the reactivity of **1** toward electrophilic reagents, we investigated its reaction with *N*-[(trifluoromethyl)-sulfonyl]pyridinium trifluoromethanesulfonate (TPT), which can be easily prepared by treatment of Tf_2O with pyridine. We have recently reported that treatment of azulene itself with TPT (prepared from equimolar amounts of Tf_2O and pyridine) gives as the main product 6-(azulen-1-yl)-1-[(trifluoromethyl)sulfonyl]-1-azahexa-1,3,5-triene, produced by attack of azulene on TPT at the 2-position. In contrast, when the reaction was carried out with a large excess of pyridine, it gave 1,3-bis(dihydropyridin-4-yl)azulene, the product of the attack of azulene on TPT selectively at the 4-position.[9] As in the case of the reaction between azulene and TPT, the proportions of azulene, Tf_2O, and pyridine are very important in determining the product distribution. Treatment of **1** with TPT in the presence of excess pyridine gave **6** in 88% yield, along with **7** in 5% yield. When equimolar amounts of pyridine and Tf_2O were used, compound **7** was obtained in 92% yield as the main product, along with **8** in 5% yield (Scheme 3). No such dihydropyridinylation of the triene moiety was observed in the case of the reaction between the parent azulene and TPT. The two *tert*-butyl groups on the azulene ring might thus enhance the reactivity of the triene moiety toward the attack of TPT. Compound **8** was also obtained, in 84% yield, by treatment of **7** with TPT.



Scheme 3.

Compounds **6**, **7**, and **8** were fully characterized by their spectroscopic data, as shown in the Experimental Section. The mass spectra of **6**, **7**, and **8** (ionized by ESI) showed the correct molecular ion peaks. The characteristic stretching vibration bands of the trifluoromethyl and sulfonyl groups of **6**, **7**, and **8** were observed by IR spectroscopy at 1184–1234 cm^{-1} and at 1157–1172 cm^{-1}, respectively. These results are consistent with the structures of these products. UV/Vis spectra of **7** and **8** in dichloromethane and in hexane are shown in Figures 1 and 2, respectively, whereas the solvent dependence of the absorption maxima and coefficients of **7** and **8** are summarized in Table 2. Compound **7** in dichloromethane exhibited strong absorption bands at 560 nm and 610 (sh) nm. These strong absorption bands should be attributable to CT absorption, as illustrated in the resonance structure shown in Scheme 4. When the UV/Vis spectrum of **7** was measured in hexane, compound **7** showed a hypsochromic shift of 34 nm on changing of the solvent. Compound **8** in dichloromethane showed strong absorption bands at 572 nm and 612 (sh) nm. The 572 nm absorption band of **8** exhibited a hypsochromic shift of 24 nm with the change in the solvent from dichloromethane to hexane.

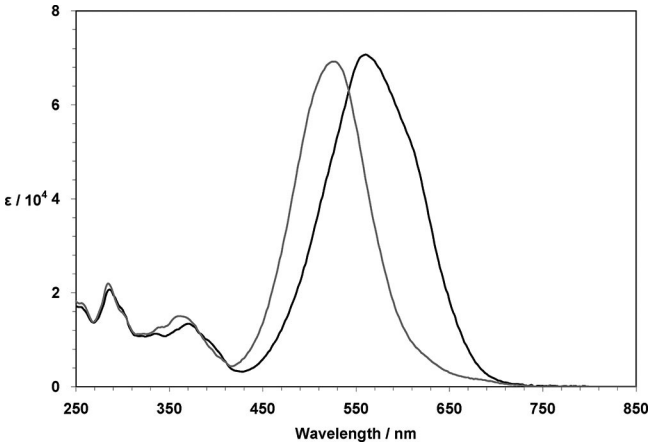


Figure 1. UV/Vis spectra of **7** in dichloromethane (black line) and in hexane (gray line).

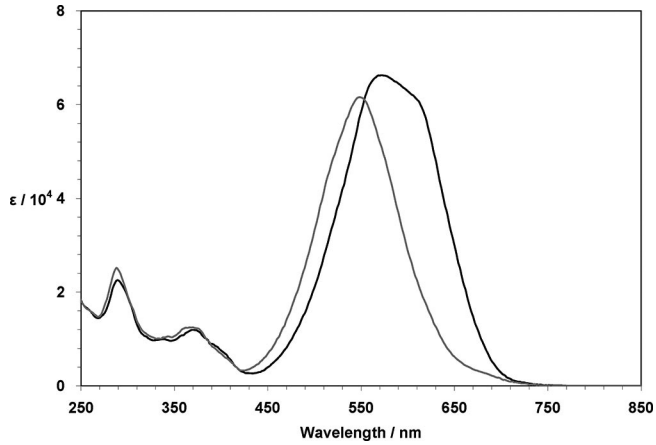
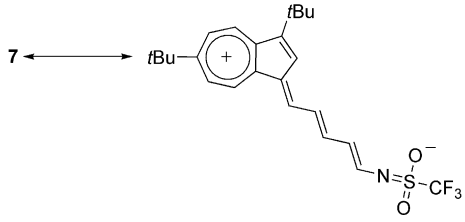


Figure 2. UV/Vis spectra of **8** in dichloromethane (black line) and in hexane (gray line).

Table 2. Absorption maxima of **7** and **8** and their coefficients in dichloromethane and hexane.

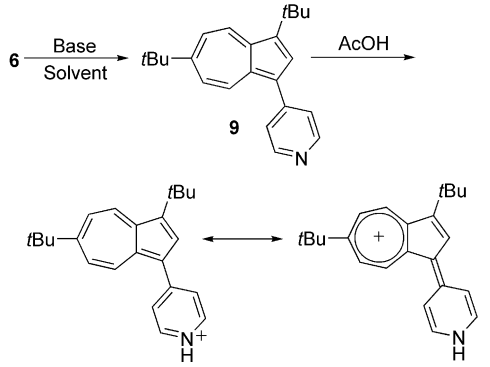
Sample	Solvent	λ_{max} [nm] (log ε)
7	CH_2Cl_2	560 (4.85), 610 sh (4.71)
	hexane	526 (4.84)
8	CH_2Cl_2	572 (4.82), 612 sh (4.78)
	hexane	548 (4.79)



Scheme 4. Resonance structure of **7**.

Aromatization of the dihydropyridine moiety of **6** to a pyridine ring system was also investigated. We recently reported base-induced transformations of 1-(dihydroheteroaryl)-, 1,3-bis(dihydroheteroaryl)-, and 5-(dihydroheteroaryl)azulene derivatives to the corresponding (heteroaryl)azulene derivatives, which opened up a new two-step strategy for the heteroarylation of azulene.[10] For the aromatization of the dihydropyridine moiety of **6**, we investigated two bases, KOH and *t*BuOK, similarly to the procedure reported by us previously. Treatment of **6** with KOH in EtOH afforded 1,6-di-*tert*-butyl-3-(pyridin-4-yl)azulene (**9**) in 95% yield (Scheme 5). On changing the reaction conditions to *t*BuOK in DMSO, however, the yield of **9** was significantly decreased because of the generation of an inseparable complex mixture (Table 3).

The UV/Vis spectrum of **9** in dichloromethane showed a characteristic weak absorption arising from the azulene system at 594 nm (log ε = 2.57) in the visible region. In acetic acid, compound **9** exhibited a strong absorption at 438 nm (log ε = 4.40) arising from the development of CT absorption owing to protonation of the pyridine moiety, as shown in Scheme 5.

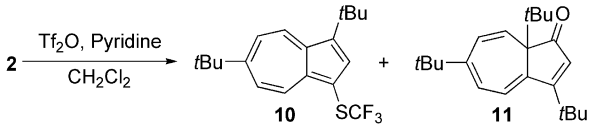


Scheme 5.

Table 3. Synthesis of 1,6-di-*tert*-butyl-3-(pyridin-4-yl)azulene (**9**).

Entry	Base	Solvent	Yield (%)
1	KOH	EtOH	95
2	*t*BuOK	DMSO	57

We extended the reaction with TPT to compound **2**. As with our results on the Friedel–Crafts and Vilsmeier reactions of **2**, we expected the formation of **6**, **7**, and **8** through *ipso*-substitution reactions. Contrarily to expectations, however, 1,6-di-*tert*-butyl-3-[(trifluoromethyl)thio]azulene (**10**) and 3,6,8a-tri-*tert*-butyl-(8a*H*)-azulen-1-one (**11**) were obtained in 51% and 38% yields, respectively (Scheme 6). The trifluoromethyl moiety appears widely in medicinal and agrochemical science.[11] Treatment of azulene with trifluoroacetic anhydride has already been reported to give 1-(trifluoroacetyl)azulene,[12] which exhibits tumor-specific cytotoxicity and apoptosis-inducing activity toward human cells.[13] Recently, we reported a facile and efficient synthetic route to several 1-azulenyl methyl and phenyl sulfides and 1,3-bis(methylthio and phenylthio)azulenes via 1-azulenylsulfonium and 1,3-azulenediylsulfonium ion intermediates.[14] However, this is the first example of a (trifluoromethyl)thio derivative of azulene. This procedure could provide a useful methodology for the synthesis of 1-[(trifluoromethyl)thio]azulene derivatives.



Scheme 6.

Compounds **10** and **11** were characterized by their spectroscopic data as shown in the Experimental Section. Assignment of peaks in the ^{1}H NMR spectra of **10** and **11** was accomplished by decoupling, NOE, and 2D COSY experiments. The mass spectra of **10** and **11**, ionized by EI and ESI, respectively, showed the correct molecular ion peaks. The characteristic stretching vibration band of the carbonyl group of **11** was observed at 1701 cm^{-1} in the IR spectrum. These results are consistent with the structures of these products. Single crystals of **11** suitable for X-ray crystallographic analysis were obtained by recrystallization from methanol, and an ORTEP drawing of the molecular structure of **11** is shown in Figure 3. These results are also consistent with the structure of **11**.

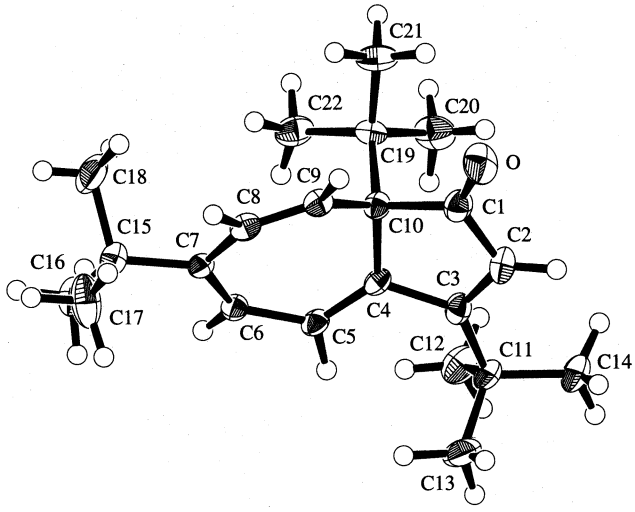
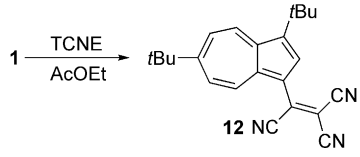


Figure 3. ORTEP drawing of the molecular structure of **11**.[15] Triclinic, a = 6.7426(19), b = 12.461(4), c = 12.566(4) Å, α = 73.681(11), β = 71.971(12), γ = 76.620(14)°, V = 951.4(5) Å^3, Z = 2, $D_{calcd.}$ = 1.091 g cm^{-3}, μ(Mo-K_α) = 0.641 cm^{-1}, R = 0.0595, Rw = 0.1348, $R1$ = 0.0468.

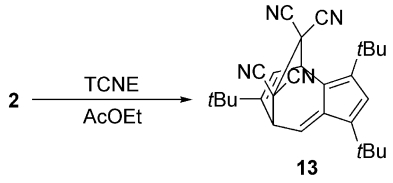
Unique reactivity of **2** was also observed in its reaction with tetracyanoethylene (TCNE). TCNE is known as a strong organic electron acceptor, and the high reactivity of TCNE toward nucleophiles or electron-rich reagents is frequently used to introduce strong acceptor moieties into organic molecules.[16] In the early days of azulene chemistry, Hafner et al. reported the reaction between azulene and TCNE, giving 1-(1,2,2-tricyanoethenyl)azulene via CT complex between azulene and TCNE.[17] As in the literature reported by Hafner et al., treatment of **1** with TCNE gave 1,6-di-*tert*-butyl-3-(1,2,2-tricyanoethenyl)azulene (**12**) in 94% yield (Scheme 7).



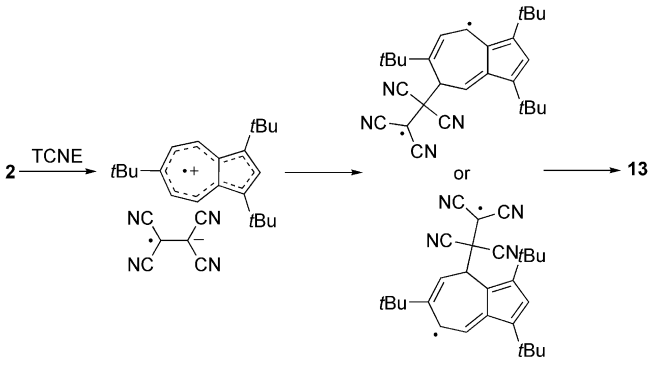
Scheme 7.

In contrast with the reaction behavior of **1**, treatment of **2** with TCNE in ethyl acetate afforded a quantitative yield of the unique cycloaddition product **13** (Scheme 8), rather than the *ipso*-substitution product. A retrocycloaddition reaction was also observed when the cycloadduct **13** was heated at reflux in ethyl acetate, giving the initial compound **2** quantitatively. Takekuma et al. recently reported that 1,2-bis(3-guaiazulenyl)ethylene and 2-(3-guaiazulenyl)-1,1-bis(4-methoxyphenyl)ethylene reacted with TCNE to give 1:2 cycloaddition products.[18] The reactions are believed to proceed via CT complexes of azulene and TCNE. The CT

complex is presumed to react with 2 equiv. TCNE at azulene and ethylene moieties to form 1:2 cycloaddition products. The reaction between **2** and TCNE should also proceed through the formation of CT complexes as illustrated in Scheme 9. However, compound **13**, to the best of our knowledge, would be the first example of a cycloaddition product of TCNE directly reacting with an azulene moiety.



Scheme 8.



Scheme 9. Proposed reaction mechanism for the cycloaddition reaction between **2** and TCNE.

Mass spectra of **12** and **13**, ionized by ESI, showed the correct molecular ion peaks. The characteristic stretching vibration bands of the cyano groups of **12** and **13** were observed at 2210 and 2201 cm^{-1}, respectively, in their IR spectra. Neuenschwander and co-workers have reported the ^1H and ^{13}C NMR shifts of fulvene, and chemical shifts were observed in the olefinic region.[19] ^1H and ^{13}C NMR signals for **13** were also observed in the olefinic region, as with fulvene, so product **13** has the fused-ring structure between fulvene and seven-membered ring moieties. Single crystals of **13** suitable for X-ray crystallographic analysis were obtained by recrystallization from ethanol, and an ORTEP drawing of the molecular structure of **13** is shown in Figure 4. The C1–C10, C2–C3, and C4–C5 bond lengths are 1.358, 1.345, and 1.341 Å, respectively, which demonstrate the fulvene-like structure of **13**. The C11–C12 bond (1.605 Å) is relatively longer than the general single bond. The thermodynamic instability of **13** might be attributable to the strain in the molecule.

UV/Vis spectra of **12** in dichloromethane and in hexane are shown in Figure 5. Cyanovinyl compounds are well known to exhibit solvatochromic[21] and vapochromic behavior.[22] In the case of azulene derivatives, we have also reported that 1,1,4,4-tetracyano-2,3-bis[5-isopropyl-3-(methoxycarbonyl)-1-azulenyl]butadiene showed solvatochromism.[23] We examined the solvatochromic effect of **12** in eight solvents, and the solvent dependence of the absorp-

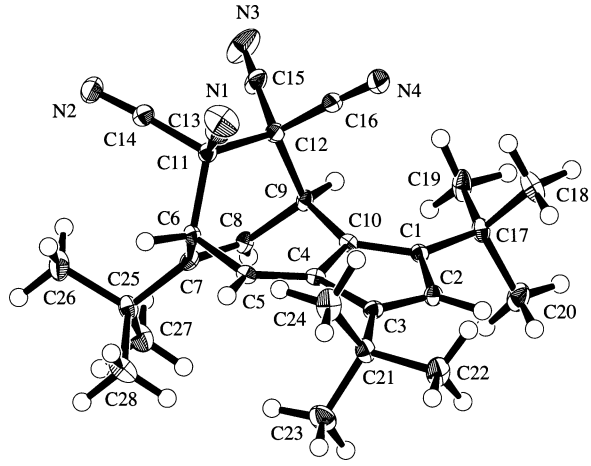


Figure 4. ORTEP drawing of the molecular structure of **13**.[20] Monoclinic, a = 11.7998(3), b = 22.7898(6), c = 19.3162(5) Å, β = 104.026(1)°, V = 5039.5(2) $Å^3$, Z = 8, $D_{calcd.}$ = 1.119 $g\,cm^{-3}$, μ(Mo-K_α) = 0.67 cm^{-1}, R = 0.049, Rw = 0.061, $R1$ = 0.049.

tion maxima and coefficients of **12** are summarized in Table 4. In its UV/Vis spectrum in dichloromethane, **12** showed strong absorption at 544 nm. The strong absorption might be attributable to CT absorption, depending on the contribution of the resonance structure as illustrated in Scheme 10. The largest solvent effect was observed when the solvent was changed from CH_2Cl_2 (λ_{max} = 544 nm) to hexane (λ_{max} = 508 nm). The UV/Vis spectrum of **13** in dichloromethane showed a characteristic absorption attributable to its fulvene-like structure in the visible region at 412 nm (log ε = 2.84).

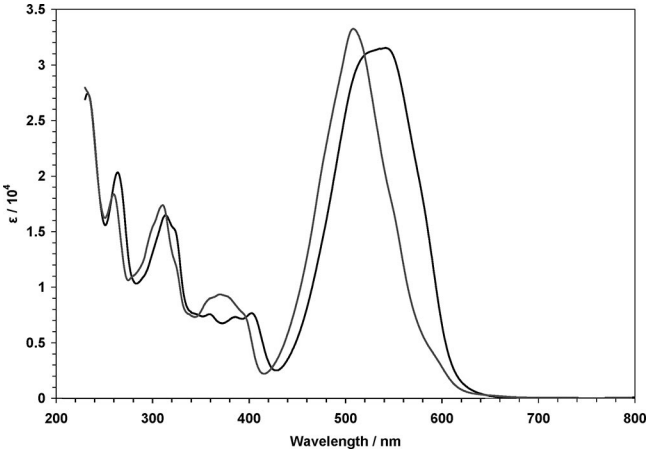
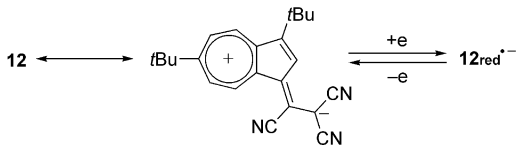


Figure 5. UV/Vis spectra of **12** in dichloromethane (black line) and in hexane (gray line).

To clarify the electrochemical properties of **2**, **6**, **7**, **8**, **9**, **12**, and **13**, the redox potentials of these products were measured by CV and DPV. The measurements were carried out with 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

Table 4. Solvatochromic data for the longest-wavelength absorptions of **12**.

Solvent	λ_{max} [nm] (log ε)	Solvent	λ_{max} [nm] (log ε)
CH_2Cl_2	544 (4.46)	EtOH	519 (4.48)
CH_3CN	535 (4.47)	THF	515 (4.49)
$CHCl_3$	527 (4.48)	AcOEt	513 (4.51)
MeOH	520 (4.47)	hexane	508 (4.52)



Scheme 10. Presumed electrochemical behavior of **12**.

formed from $Ag/AgNO_3$ (0.01 M) in acetonitrile containing nBu_4NClO_4 (0.1 M) with Fc/Fc^+, which discharges at +0.15 V under these conditions, as internal reference.

The redox potentials are summarized in Table 5. The electrochemical reduction of **2**, **6**, **7**, and **8** showed irreversible reduction waves at –0.90 to –2.14 V upon DPV. These results indicate instability of the radical anionic states of these compounds. Compounds **7** and **8** showed less negative first reduction potentials (**7**: –0.95 V; **8**: –0.90 V) than **2** (–2.14 V) and **6** (–2.00 V), which indicates that the substitution of electron-withdrawing triene moieties increased the π-accepting properties. A reversible reduction wave was observed in **9** at –1.96 V by CV. We have recently reported the redox behavior of 1-(methylthio)-3-(pyridin-4-yl)azulene, which shows an irreversible first reduction wave at –1.70 V by DPV.[10c] These results indicate that the *tert*-butyl groups on the azulene ring stabilize the radical anionic states of azulene derivatives relative to the methylthio group, although **9** shows a slightly more negative first reduction potential. The electrochemical reduction of **2**, **6**, **7**, **8**, and **9** showed irreversible oxidation waves at +0.46 to +0.64 V by DPV. These results indicate instability of radical cationic species of these compounds. Compounds **6**, **7**, **8**, and **9** showed slightly more positive oxidation potentials (**6**: +0.54 V; **7**: +0.55 V; **8**: +0.64 V; **9**: +0.59 V) than **2** (+0.46 V), which indicates the dihydropyridine or triene moieties acting as π-accepting substituents.

A cyclic voltammogram of **12** is shown in Figure 6. Electrochemical reduction showed a reversible reduction wave at the halfwave potential of –0.94 V by CV, probably due to the formation of a stabilized radical anion species. The electrochemical behavior of **12** could thus be explained as shown in Scheme 10. The electrochemical reduction also exhibited irreversible waves at –2.00 and –2.14 V by DPV, probably due to the reduction of the substituted azulene ring. The reduction of **13** showed three irreversible reduction waves at –1.70, –1.90, and –2.17 V by DPV. The first reduction wave of **13** is slightly less negative than that of **2**, which indicates that the fulvene derivative **13** has a lower LUMO level than **2**. The electrochemical oxidation

Table 5. Redox potentials[a] of **2**, **6**, **7**, **8**, **9**, **12**, and **13**.

Sample	E^1_{red} [V]	E^2_{red} [V]	E^3_{red} [V]	E^1_{ox} [V]	E^2_{ox}[V]
2	(–2.14)			(+0.46)	
6	(–2.00)	(–2.14)		(+0.54)	(+0.64)
7	(–0.95)	(–1.99)	(–2.14)	(+0.55)	
8	(–0.90)	(–1.96)	(–2.12)	(+0.64)	
9	–1.94				
	(–1.92)	(–2.14)		(+0.59)	(+0.84)
12	–0.94				
	(–0.92)	(–2.00)	(–2.14)	(+1.10)	
13	(–1.70)	(–1.90)	(–2.17)	(+1.24)	

[a] Redox potentials were measured by CV and DPV [V vs. $Ag/AgNO_3$, 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (1.6 mm i.d.), 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.

of **12** and **13** showed irreversible oxidation waves at +1.10 to +1.24 V, respectively, by DPV. These results indicate instability of the radical cation species of these compounds.

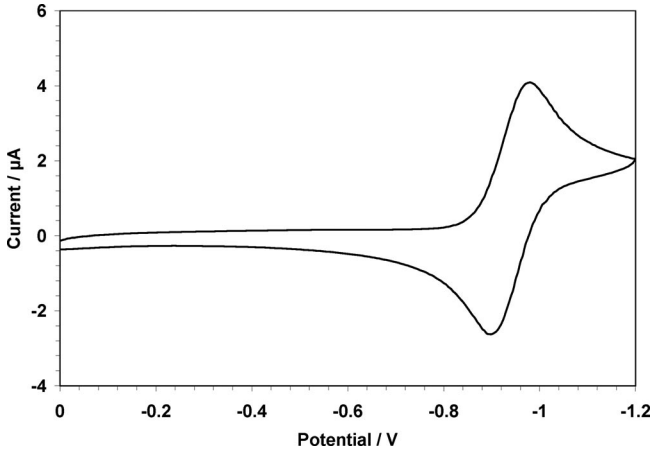


Figure 6. Cyclic voltammogram for the reduction of **12** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

Conclusions

We report *ipso*-substitution (i.e., by Friedel–Crafts reactions and Vilsmeier formylations) and some unique reactivity characteristics of **1** and **2**. Friedel–Crafts reactions between **2** and acetyl chloride and benzoyl chloride in the presence of aluminium chloride gave the corresponding *ipso*-substitution products, although selective monosubstitution was not established. In contrast, Vismeier formylation of **2** with $POCl_3$ in DMF afforded **5** in excellent yield. Compound **5** was readily converted into **1** by decarbonylation with pyrrole in acetic acid. We also examined the reactivity of **1** toward some electrophiles. Treatment of **1** with TPT gave **6**, **7**, and **8**, depending on the proportions of the amounts of reagents used. The preparation of **8** by treatment of **7** with TPT was also established. In contrast, the reaction between **2** and TPT unexpectedly afforded

compounds **10** and **11**. Although **1** reacted with TCNE to give the substitution reaction product **12**, compound **2** afforded the fulvene-like 1:1 cycloaddition product **13** in excellent yield on treatment with TCNE.

Experimental Section

General: Melting points were determined with a Yanagimoto MP-S3 micro melting apparatus and are uncorrected. Mass spectra were obtained with a Hitachi M-2500 or a Bruker APEX II instrument. IR and UV/Vis spectra were measured with a Shimadzu FTIR-8100M and a Hitachi U-3410 spectrophotometer, respectively. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded with a JEOL GSX 400 instrument at 400 MHz (100 MHz) or a Bruker AVANCE 400 instrument at 400 MHz (100 MHz). Gel permeation chromatography (GPC) purification was performed with a TSKgel G2000H$_6$ instrument. Elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

1-Acetyl-3,6-di-*tert*-butylazulene (3a) and 1,3-Diacetyl-6-*tert*-butylazulene (3b): Acetyl chloride (236 mg, 3.00 mmol) and $AlCl_3$ (800 mg, 6.00 mmol) were added at room temperature to a solution of **2** (592 mg, 2.00 mmol) in CH_2Cl_2 (20 mL). The resulting mixture was stirred at the same temperature for 30 min. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4:1) to give **3a** (175 mg, 31%) as purple crystals and **3b** (38 mg, 7%) as red crystals.

Compound 3a: M.p. 119.0–120.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.82 (d, J = 10.8 Hz, 1 H, 8-H), 8.78 (d, J = 10.8 Hz, 1 H, 4-H), 8.10 (s, 1 H, 2-H), 7.70 (dd, J = 10.8, 1.6 Hz, 1 H, 7-H), 7.61 (dd, J = 10.8, 1.6 Hz, 1 H, 5-H), 2.69 (s, 3 H, 1-COMe), 1.59 (s, 9 H, *t*-Bu), 1.46 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.99, 163.46, 140.44, 139.03, 138.13, 137.98, 137.81, 136.41, 126.82, 123.95, 122.19, 38.47, 32.85, 31.69, 29.07 ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 2961 (s), 2868 (m), 1636 (s), 1578 (s), 1475 (m), 1460 (m), 1437 (s), 1398 (m), 1381 (s), 1364 (m), 1350 (m), 1232 (s), 1209 (m), 1182 (m), 949 (m), 847 (m), 602 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 229 (4.28), 240 (4.28), 272 (4.15), 309 sh (4.53), 318 (4.62), 388 (sh) (3.97), 401 (4.00), 546 (2.76), 588 (sh) (2.66), 652 (sh) (2.10) nm. HRMS (ESI): calcd. for $C_{20}H_{26}O$ + Na^+ [M + Na]$^+$ 305.1876; found 305.1875. $C_{20}H_{26}O{\cdot}0.1H_2O$ (282.42): calcd. C 84.52, H 9.29; found C 84.58, H 9.25.

Compound 3b: M.p. 190.5–195.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.97 (d, J = 11.6 Hz, 2 H, 4,8-H), 8.59 (s, 1 H, 2-H), 8.04 (d, J = 11.6 Hz, 2 H, 5,7-H), 2.73 (s, 6 H, 1,3-COMe), 1.51 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.26, 167.03, 143.07, 142.61, 140.10, 131.01, 123.44, 39.07, 31.73, 28.86 ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 1649 (m), 1632 (s), 1583 (m), 1574 (m), 1508 (m), 1427 (s), 1400 (s), 1364 (m), 1221 (s), 1192 (m), 976 (m), 924 (m), 874 (m), 596 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 242 (4.49), 292 (4.70), 313 (4.57), 378 (sh) (4.02), 391 (4.04), 491 (2.97), 515 (sh) (2.92), 571 (sh) (2.33) nm. HRMS (ESI): calcd. for $C_{18}H_{20}O_2$ + Na^+ [M + Na]$^+$ 291.1356; found 291.1355. $C_{18}H_{20}O_2{\cdot}0.2H_2O$ (268.35): calcd. C 79.50, H 7.56; found C 79.50, H 7.56.

1,3-Diacetyl-6-*tert*-butylazulene (3b): Acetyl chloride (785 mg, 10.0 mmol) and $AlCl_3$ (2.67 g, 20.0 mmol) were added at room temperature to a solution of **2** (592 mg, 2.00 mmol) in CH_2Cl_2 (20 mL). The resulting mixture was stirred at the same temperature for 2 h. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/AcOEt (4:1) to give **3b** (413 mg, 77%).

1-Benzoyl-3,6-di-*tert*-butylazulene (4a) and 1,3-Dibenzoyl-6-*tert*-butylazulene (4b):[6] Benzoyl chloride (422 mg, 3.00 mmol) and $AlCl_3$ (800 mg, 6.00 mmol) were added at room temperature to a solution of **2** (592 mg, 2.00 mmol) in CH_2Cl_2 (20 mL). The resulting mixture was stirred at the same temperature for 2 h. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/AcOEt (4:1) to give **4a** (130 mg, 19%) as purple crystals and **4b** (188 mg, 24%) as red needles.

Compound 4a: M.p. 78.0–81.0 °C (ref.[6] 80.9–81.9 °C).

Compound 4b: M.p. 168.0–169.0 °C (AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.81 (d, J = 10.4 Hz, 2 H, 4,8-H), 8.17 (s, 1 H, 2-H), 8.08 (d, J = 10.4 Hz, 2 H, 5,7-H), 7.48 (dd, J = 6.8, 1.6 Hz, 4 H, *o*-Ph), 7.52 (ddd, J = 6.8, 1.6, 1.6 Hz, 2 H, *p*-Ph), 7.46 (ddd, J = 6.8, 1.6, 1.6 Hz, 4 H, *m*-Ph), 1.53 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.67, 167.14, 146.12, 143.88, 140.44, 139.62, 131.51, 130.64, 129.43, 128.12, 123.45, 39.14, 31.71 ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 237 (4.47), 309 (4.69), 322 (4.64), 386 (sh) (4.15), 399 (4.17), 487 (3.02) nm. HRMS (ESI): calcd. for $C_{28}H_{24}O_2$ + Na^+ [M + Na]$^+$ 415.1674; found 415.1669. $C_{28}H_{24}O_2{\cdot}0.25H_2O$ (392.49): calcd. C 84.71, H 6.22; found C 84.75, H 6.31.

1,3-Dibenzoyl-6-*tert*-butylazulene (4b): Benzoyl chloride (1.40 g, 10.0 mmol) and $AlCl_3$ (2.67 g, 20.0 mmol) were added at room temperature to a solution of **2** (592 mg, 2.00 mmol) in CH_2Cl_2 (20 mL). The resulting mixture was stirred at the same temperature for 2 h. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/AcOEt (4:1) to give **4b** (557 mg, 71%).

1,6-Di-*tert*-Butyl-3-formylazulene (5):[7] $POCl_3$ (613 mg, 4.00 mmol) was added at room temperature to a solution of **2** (296 mg, 1.00 mmol) in DMF (20 mL). The resulting mixture was stirred at 100 °C for 12 h. The reaction mixture was poured into NaOH (1 M) and extracted with toluene. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/AcOEt (1:1) to give **5** (262 mg, 98%) as purple crystals. M.p. 95.0–99.0 °C (ref.[7] 96.0–99.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.33 (s, 1 H, 3-CHO), 9.44 (d, J = 10.8 Hz, 1 H, 4-H), 8.80 (d, J = 10.8 Hz, 1 H, 8-H), 8.12 (s, 1 H, 2-H), 7.75–7.66 (m, 2 H, 5,7-H), 1.59 (s, 9 H, *t*Bu), 1.48 (s, 9 H, *t*Bu) ppm.

1,6-Di-*tert*-butylazulene (1):[4] Pyrrole (10 mL) was added to a solution of **5** (2.68 g, 10.0 mmol) in acetic acid (50 mL). The mixture was stirred at room temperature for 24 h. The reaction mixture was poured into water and extracted with hexane. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane to afford **1** (1.99 g, 83%) as blue crystals. M.p. 40.5–45.0 °C (ref.[4] 42.0–44.0 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.61 (d, J = 10.5 Hz, 1 H, 8-H), 8.19 (d, J = 10.5 Hz, 1 H, 4-H), 7.74 (d, J = 4.0 Hz, 1 H, 2-H), 7.25 (dd, J = 10.5, 2.0 Hz, 1 H, 7-

H), 7.22 (dd, J = 10.5, 2.0 Hz, 1 H, 5-H), 7.19 (d, J = 4.0 Hz, 1 H, 3-H), 1.59 (s, 9 H, *t*Bu), 1.44 (s, 9 H, *t*Bu) ppm.

1,6-Di-*tert*-butyl-3-{1-[(trifluoromethyl)sulfonyl]-1,4-dihydropyridin-4-yl}azulene (6): Tf_2O (339 mg, 1.20 mmol) and pyridine (396 mg, 5.00 mmol) in CH_2Cl_2 (10 mL) were added at room temperature to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (10 mL). The resulting mixture 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** (379 mg, 88%) as blue crystals. M.p. 128.0–130.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (d, J = 10.8 Hz, 1 H, 4-H), 8.17 (d, J = 10.8 Hz, 1 H, 8-H), 7.62 (s, 1 H, 2-H), 8.02 (s, 1 H, 2-H), 7.24 (d, J = 10.8 Hz, 1 H, 7-H), 7.22 (d, J = 10.8 Hz, 1 H, 5-H), 6.55 (d, J = 8.4 Hz, 2 H, 2′,4′-H), 5.28 (dd, J = 8.4, 3.2 Hz, 2 H, 5′-H), 4.78 (s, 1 H, 4′-H), 1.57 (s, 9 H, *t*Bu), 1.45 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.45, 135.34, 134.84, 134.53, 133.82, 131.34, 129.02, 128.21, 125.28, 119.88, 119.86, 119.82 (q, $J_{C,F}$ = 323.9 Hz), 119.07, 113.63, 38.32, 33.30, 32.13, 31.78 ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 2965 (m), 2957 (m), 2907 (m), 2872 (m), 1580 (m), 1410 (s), 1368 (m), 1285 (m), 1233 (s), 1196 (s), 1159 (s), 1076 (m), 949 (s), 810 (m), 696 (s), 594 (s), 569 (m), 525 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 243 (4.20), 261 (4.02), 293 (4.70), 303 (4.75), 345 (sh) (3.64), 355 (3.78), 367 (3.49), 372 (3.64), 458 (sh) (1.87), 598 (2.53), 648 (sh) (2.42) nm. HRMS (ESI): calcd. for $C_{24}H_{28}F_3NO_2S$ + Na^+ [M + Na]$^+$ 474.1690; found 474.1685. $C_{24}H_{28}F_3NO_2S$ (451.55): calcd. C 63.84, H 6.25, N 3.10; found C 63.77, H 6.15, N 3.14.

6′-(1,6-Di-*tert*-butylazulen-3-yl)-1′-[(trifluoromethyl)sulfonyl]-1′-azahexa-1′,3′,5′-triene (7) and 6′-(1,6-Di-*tert*-butylazulen-3-yl)-3′-{1′′-[(trifluoromethyl)sulfonyl]-1′′,4′′-dihydropyridin-4′′-yl}-1′-[(trifluoromethyl)sulfonyl]-1′-azahexa-1′,3′,5′-triene (8): Tf_2O (339 mg, 1.20 mmol) and pyridine (119 mg, 1.50 mmol) in CH_2Cl_2 (10 mL) were added at room temperature to a solution of **1** (240 mg, 1.00 mmol) in CH_2Cl_2 (10 mL). The resulting mixture 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_2Cl_2 to give **7** (415 mg, 92%) as metallic-green needles and **8** (33 mg, 5%) as metallic-green needles.

Compound 7: M.p. 210.0–218.0 °C (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (d, J = 10.5 Hz, 1 H, 4-H), 8.63 (d, J = 10.5 Hz, 1 H, 2′-H), 8.46 (d, J = 10.5 Hz, 1 H, 8-H), 8.04 (s, 1 H, 2-H), 7.81 (d, J = 14.5 Hz, 1 H, 6′-H), 7.66 (t, J = 10.5 Hz, 1 H, 4′-H), 7.58 (d, J = 10.5, 2.0 Hz, 1 H, 5-H), 7.55 (d, J = 10.5, 2.0 Hz, 1 H, 7-H), 7.13 (dd, J = 14.5, 10.5 Hz, 1 H, 5′-H), 6.57 (dd, J = 14.5, 10.5 Hz, 1 H, 3′-H), 1.59 (s, 9 H, *t*Bu), 1.48 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.90, 164.45, 143.62, 141.75, 141.51, 141.03, 136.67, 132.86, 132.18, 125.85, 124.97, 124.16, 122.79, 122.49, 121.13, 119.47 (q, $J_{C,F}$ = 310.2 Hz), 38.76, 33.27, 31.65, 31.50 ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 2964 (m), 1570 (s), 1498 (s), 1439 (m), 1394 (m), 1338 (m), 1184 (s), 1157 (s), 1115 (s), 1070 (m), 1022 (m), 831 (s), 796 (m), 769 (m), 758 (m), 630 (m), 571 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 236 (4.35), 258 (sh) (4.22), 286 (4.32), 372 (4.13), 394 (sh) (3.64), 355 (3.78), 367 (3.49), 372 (3.64), 560 (4.85), 610 (sh) (4.71) nm. UV/Vis (hexane): λ_{max} (log ε) = 236 (4.35), 258 (sh) (4.22), 286 (4.33), 302 (sh) (4.18), 362 (4.18), 526 (4.84) nm. HRMS (ESI): calcd. for $C_{24}H_{28}F_3NO_2S$ + Na^+ [M + Na]$^+$ 474.1690; found 474.1685. $C_{24}H_{28}F_3NO_2S$ (451.55): calcd. C 63.84, H 6.25, N 3.10; found C 64.11, H 6.44, N 3.09.

Compound 8: M.p. 171.0–176.0 °C (AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, J = 10.4 Hz, 1 H, 4-H), 8.49 (d, J = 10.4 Hz, 1 H, 8-H), 8.48 (s, 1 H, 2′-H), 7.96 (s, 1 H, 2-H), 7.76 (d, J = 13.6 Hz, 1 H, 6′-H), 7.66–7.51 (m, 4 H, 5,7,4′,5′-H), 6.65 (d, J = 6.8 Hz, 2 H, 2′′,6′′-H), 5.12 (dd, J = 6.8, 3.2 Hz, 2 H, 3′′,5′′-H), 4.85 (s, 1 H, 4′′-H), 1.58 (s, 9 H, *t*Bu), 1.49 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.92, 142.85, 142.63, 142.35, 136.96, 132.97, 132.60, 126.64, 125.81, 124.98, 124.56, 121.86, 121.56, 119.12, 111.83, 111.55, 38.86, 33.25, 31.67, 31.42 ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 1573 (m), 1494 (s), 1436 (m), 1413 (m), 1394 (m), 1371 (m), 1223 (m), 1172 (s), 1116 (s), 1072 (m), 887 (m), 839 (s), 796 (m), 769 (m), 705 (m), 680 (m), 617 (m), 590 (m), 578 (m), 447 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 238 (4.36), 288 (4.40), 360 (sh) (4.09), 378 (sh) (4.07), 548 (4.79) nm. UV/Vis (hexane): λ_{max} (log ε) = 236 (4.35), 258 (sh) (4.22), 286 (4.33), 302 (sh) (4.18), 362 (4.18), 526 (4.84) nm. HRMS (ESI): calcd. for $C_{30}H_{32}F_6N_2O_4S_2$ + Na^+ [M + Na]$^+$ 685.1605; found 685.1600. $C_{30}H_{32}F_6N_2O_4S_2$ (662.71): calcd. C 54.37, H 4.87, N 4.23; found C 54.34, H 5.02, N 4.26.

6′-(1,6-Di-*tert*-butylazulen-3-yl)-3′-{1′′-[(trifluoromethyl)sulfonyl]-1′′,4′′-dihydropyridin-4′′-yl}-1′-[(trifluoromethyl)sulfonyl]-1′-azahexa-1′,3′,5′-triene (8): Tf_2O (282 mg, 1.00 mmol) and pyridine (95 mg, 1.2 mmol) in CH_2Cl_2 (5 mL) were added at room temperature to a solution of **7** (227 mg, 0.503 mmol) in CH_2Cl_2 (5 mL). The resulting mixture 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 **8** (278 mg, 84%).

1,6-Di-*tert*-butyl-3-(pyridin-4-yl)azulene (9)

Treatment of 6 with KOH in EtOH: KOH (561 mg, 10.0 mmol) was added at room temperature to a solution of **6** (451 mg, 1.00 mmol) in EtOH (20 mL). The resulting mixture was heated at reflux for 30 min, 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 silica gel with AcOEt to give **9** (323 mg, 95%) as blue crystals.

Treatment of 6 with *t*BuOK in DMSO: *t*BuOK (336 mg, 3.00 mmol) was added at room temperature to a solution of **6** (451 mg, 1.00 mmol) in DMSO (20 mL). The resulting mixture was stirred at the same temperature for 10 min, poured into water, extracted with toluene, and dried with $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel with AcOEt and by GPC with $CHCl_3$ to give **9** (194 mg, 57%).

Compound 9: M.p. 126.0–127.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, J = 10.8 Hz, 1 H, 8-H), 8.64 (d, J = 5.6 Hz, 2 H, 2′,6′-H), 8.50 (d, J = 10.8 Hz, 1 H, 4-H), 7.89 (s, 1 H, 2-H), 7.52 (d, J = 5.6 Hz, 2 H, 3′,5′-H), 7.35 (dd, J = 10.8, 2.0 Hz, 1 H, 7-H), 7.33 (dd, J = 10.8, 2.0 Hz, 1 H, 5-H), 1.62 (s, 9 H, *t*Bu), 1.46 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.36, 149.68, 145.14, 138.92, 136.16, 135.75, 135.44, 134.60, 133.82, 124.95, 123.93, 122.08, 120.28, 38.31, 33.13, 31.99, 31.67 ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = = 3067 (s), 3030 (s), 2963 (s), 2905 (s), 1593 (s), 1578 (s), 1545 (m), 1518 (m), 1495 (m), 1460 (m), 1427 (m), 1390 (m), 1365 (m), 1240 (m), 1217 (m), 1199 (m), 835 (s), 825 (s), 692 (m), 617 (m), 557 (m), 416 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 246 (4.30), 263 (4.10), 289 (4.40), 317 (4.49), 347 (3.79), 358 (sh) (3.83), 389 (4.04), 473 (1.96), 594 (2.57), 641 (2.47), 715 (1.93) nm. UV/Vis (AcOH): λ_{max} (log ε) = 292 (4.48), 338 (sh) (4.24), 350 (4.31), 438 (4.40) nm. HRMS (ESI): calcd. for $C_{23}H_{27}N$ + H^+ [M + H]$^+$ 318.2222; found 318.2216. $C_{23}H_{27}N$ (317.47): calcd. C 87.02, H 8.57, N 4.41; found C 86.86, H 8.46, N 4.40.

Treatment of 2 with TPT: Tf_2O (677 mg, 2.40 mmol) and pyridine (791 mg, 10.0 mmol) in CH_2Cl_2 (10 mL) were added at room tem-

perature to a solution of **2** (296 mg, 1.00 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred at the same temperature for 12 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel with hexane/AcOEt (4:1) to give 1,6-di-*tert*-butyl-3-[(trifluoromethyl)thio]azulene (**10**, 174 mg, 51%) as purple crystals and 3,6,8a-tri-*tert*-butyl-1(8a*H*)-azulenone (**11**, 119 mg, 38%) as yellow prisms.

Compound 10: M.p. 104.0–105.0 °C (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, J = 10.4 Hz, 1 H, 8-H), 8.66 (d, J = 10.4 Hz, 1 H, 4-H), 7.87 (s, 1 H, 2-H), 7.57 (dd, J = 10.4, 2.0 Hz, 1 H, 7-H), 7.50 (dd, J = 10.4, 2.0 Hz, 1 H, 5-H), 1.60 (s, 9 H, *t*Bu), 1.48 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.87, 143.18, 141.67, 138.95, 136.90, 135.97, 134.65, 129.40 (q, $J_{C,F}$ = 308.6 Hz), 123.27, 122.01, 103.03, 38.65, 33.27, 31.98, 31.83 ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = = 2907 (s), 2872 (s), 1587 (s), 1578 (m), 1549 (m), 1500 (m), 1475 (m), 1460 (m), 1410 (m), 1392 (m), 1379 (m), 1363 (m), 1261 (m), 1244 (m), 1217 (m), 1201 (m), 1068 (m), 978 (m), 873 (m), 841 (m), 750 (m), 677 (m), 636 (m), 478 (m), 451 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 239 (4.32), 262 (3.97), 296 (4.74), 304 (4.79), 323 (3.65), 350 sh (3.83), 354 (3.82), 363 (3.68), 372 (3.79), 561 (2.66), 598 (sh) (2.60), 663 (2.11) nm. HRMS (EI): calcd. for $C_{19}H_{23}F_3S^+$ [M]$^+$ 340.1473; found 340.1469. $C_{19}H_{23}F_3S$ (340.45): calcd. C 67.03, H 6.81; found C 67.14, H 6.94.

Compound 11: M.p. 109.0–110.0 °C (MeOH). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.69 (d, J = 7.7 Hz, 1 H, 4-H), 6.33 (dd, J = 11.7, 1.6 Hz, 1 H, 7-H), 6.15 (dd, J = 7.7, 1.6 Hz, 1 H, 5-H), 5.82 (d, J = 11.7 Hz, 1 H, 8-H), 5.71 (s, 1 H, 2-H), 1.38 (s, 9 H, *t*Bu), 1.16 (s, 9 H, *t*Bu), 0.80 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 209.17 (1-C), 180.61 (3-C), 153.02 (6-C), 136.06 (3a-C), 128.78 (8-C), 127.31 (7-C), 124.43 (2-C), 123.46 (4-C), 121.19 (5-C), 63.58 (8a-C), 42.84 (*t*Bu), 36.44 (*t*Bu), 34.71 (*t*Bu), 30.28 (*t*Bu), 29.76 (*t*Bu), 25.76 (*t*Bu) ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 2872 (s), 1701 (s, C=O), 1394 (m), 1363 (m), 1315 (m), 1246 (m), 1196 (m), 1159 (m), 877 (m), 846 (m), 773 (m), 659 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 244 (4.25), 271 (sh) (3.76), 301 (3.03), 383 (3.49), 323 (3.65), 350 (sh) (3.83), 380 (3.49), 404 (3.48) nm. HRMS (ESI): calcd. for $C_{22}H_{32}O$ + Na^+ [M + Na]$^+$ 335.2351; found 335.2345. $C_{22}H_{32}O$·0.25H_2O (312.49): calcd. C 83.45, H 10.62; found C 83.45, H 10.62.

1,6-Di-*tert*-butyl-3-(1,2,2-tricyanoethenyl)azulene (12): TCNE (154 mg, 1.20 mmol) was added at room temperature to a solution of **1** (240 mg, 1.00 mmol) in AcOEt (5 mL). The resulting mixture was stirred at the same temperature for 2 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel with toluene/AcOEt (4:1) to give **12** (321 mg, 94%) as reddish-purple crystals. M.p. 209.0–211.0 °C (EtOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.19 (d, J = 10.8 Hz, 1 H, 4-H), 8.86 (d, J = 10.8 Hz, 1 H, 8-H), 8.50 (s, 1 H, 2-H), 7.97 (dd, J = 10.8, 2.0 Hz, 1 H, 5-H), 7.93 (dd, J = 10.8, 2.0 Hz, 1 H, 7-H), 1.58 (s, 9 H, *t*Bu), 1.53 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.39, 144.73, 144.71, 143.24, 137.91, 135.74, 135.52, 130.09, 130.03, 129.52, 118.08, 115.30, 115.04, 114.23, 39.23, 33.32, 31.63, 31.11 ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 2970 (m), 2210 (m, C≡N), 1581 (m), 1491 (s), 1466 (m), 1444 (m), 1400 (m), 1383 (m), 1361 (m), 1107 (m), 557 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) 235 (4.41), 266 (4.29), 316 (4.20), 324 (sh) (4.16), 363 (sh) (3.86), 388 (sh) (3.85), 405 (3.87), 524 (sh) (4.45), 544 (4.46) nm. UV/Vis (hexane): λ_{max} (log ε) = 260 (4.26), 311 (4.24), 370 (3.97), 508 (4.52) nm. HRMS (ESI): calcd. for $C_{23}H_{23}N_3$ + Na^+ [M + Na]$^+$ 364.1790; found 364.1785. $C_{23}H_{23}N_3$ (341.45): calcd. C 80.90, H 6.79, N 12.31; found C 80.91, H 6.91, N 12.12.

3,5,9-Tri-*tert*-butyltricyclo[6.2.2.0^{2,6}]dodeca-2,4,6,9-tetraene-11,11,12,12-tetracarbonitrile (13): TCNE (384 mg, 3.00 mmol) was added at room temperature to a solution of **2** (593 mg, 2.00 mmol) in AcOEt (10 mL). The resulting mixture was stirred at the same temperature for 15 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 **13** (837 mg, 100%) as orange prisms. M.p. 151.0–152.0 °C (decomp.). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.87 (d, J = 8.8 Hz, 1 H, 7-H), 6.20 (dd, J = 7.9, 1.4 Hz, 1 H, 10-H), 6.13 (s, 1 H, 4-H), 4.97 (d, J = 7.9 Hz, 1 H, 1-H), 4.10 (dd, J = 8.8, 1.4 Hz, 1 H, 8-H), 1.34 (s, 9 H, *t*Bu), 1.23 (s, 9 H, *t*Bu), 1.16 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 156.15 (3-C), 155.65 (9-C), 148.16 (2-C), 145.80 (5-C), 129.75 (7-C), 128.83 (4-C), 120.22 (10-C), 115.94 (2-C), 112.98 (CN), 112.53 (CN), 111.44 (CN), 111.13 (CN), 46.27 (12-C), 45.30 (11-C), 44.82 (1-C), 43.51 (8-C), 35.10 (*t*Bu), 34.38 (*t*Bu), 32.86 (*t*Bu), 31.52 (*t*Bu), 30.91 (*t*Bu), 27.54 (*t*Bu) ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 2968 (s), 2907 (m), 2872 (m), 2201 (m, C≡N), 1632 (m), 1479 (m), 1466 (m), 1394 (m), 1365 (m), 1252 (m), 1199 (m), 852 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 250 (4.04), 277 (3.89), 412 (2.84) nm. HRMS (ESI): calcd. for $C_{28}H_{32}N_4$ + Na^+ [M + Na]$^+$ 447.2525; found 447.2519. $C_{28}H_{32}N_4$ (424.58): calcd. C 79.21, H 7.60, N 13.20; found C 79.33, H 7.69, N 13.19.

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