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Synthesis and Redox Behavior of 1,3-Bis(methylthio-) and 1,3-Bis(phenylthio)azulenes Bearing 2- and 3-Thienyl Substituents by Palladium-Catalyzed Cross-Coupling Reaction of 2- and 6-Haloazulenes with Thienylmagnesium Ate Complexes

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Preparation of thienylazulenes **3**–**6** was established by the palladium-catalyzed cross-coupling reaction of the corresponding haloazulenes with thienylmagnesium ate complexes, which were readily prepared from the corresponding bromothiophenes. The reaction of **3**–**6** with several sulfoxides in the presence of Tf_2O, followed by treatment with triethylamine afforded the corresponding 1,3-bis(methylthio)- and 1,3-bis(phenylthio)-2- and 6-thienylazulenes **7**–**12** in good yields. Redox behavior of the novel azulene derivatives with 2- and 3-thienyl-substituted **3**–**12** was examined by cyclic voltammetry and differential pulse voltammetry, which revealed amphoteric redox behavior.

Introduction

The transition-metal-catalyzed cross-coupling reaction is one of the most important tools for the preparation of biaryl and/or polyaryl compounds in modern organic synthesis, because the structure is often found in a variety of compounds such as organic conductors, liquid crystals, and pharmaceutical and agrochemical compounds.[1] Therefore, many transition-metal-catalyzed aryl–aryl cross-coupling reactions, for example, Stille,[2] Suzuki–Miyaura,[3] Negishi,[4] and Ullmann-type reactions,[5] have been developed to construct or modify such compounds.

Azulene ($C_{10}H_8$) has attracted the interest of many research groups owing to its unusual properties as well as its beautiful blue color.[6] Recently, we reported the synthesis of *N*-containing 1-heteroaryl-, 1,3-bis(heteroaryl)-, and 5-heteroarylazulenes utilizing a two-step sequence involving an electrophilic substitution reaction, followed by a base-induced aromatization reaction.[7] However, preparation of 2- and 6-heteroarylazulenes utilizing the electrophilic substitution reaction might be difficult owing to the low reactivity of azulene towards electrophilic reagents at the 2- and 6-positions. We also reported the synthesis of several arylazulene derivatives by utilizing transition-metal-catalyzed cross-coupling reactions, for example, Suzuki–Miyaura and Stille coupling reactions, of azulenyl metal reagents.[8] Such azulenyl metal reagents might be useful for the multiple substitution by azulenyl groups. However, preparation of the metal reagents for transition-metal-catalyzed reactions are sometimes difficult for azulene derivatives and the most promising azulenylborane reagents are relatively unstable and undergo easy hydrolysis to afford hydrocarbon derivatives.[9] Therefore, development of a general and efficient method for the preparation of arylazulene derivatives from readily available reagents would be important if azulene derivatives were considered in the production of advanced materials. In 2003, Mongin et al. reported a one-pot procedure for the preparation of tri(quinolinyl)magnesium lithium ate complexes by a bromine–metal exchange reaction of bromoquinolines followed by subsequent palladium-catalyzed cross-coupling of the ate complexes with heteroaryl halides to give 2-, 3-, and 4-heteroarylquinolines.[10] Similar palladium-catalyzed cross-coupling reactions of 2- and 6-haloazulenes with tris(heteroaryl)magnesium lithium ate complexes will establish the new and efficient synthetic route to 2- and 6-heteroarylazulenes.[11]

Herein, we report the details of the palladium-catalyzed cross-coupling reaction of 2- and 6-haloazulenes with thienylmagnesium lithium ate complexes, which were prepared from commercially available 2- and 3-bromothiophenes, to afford 2- and 6-(2- and 3-thienyl)azulenes.[12]

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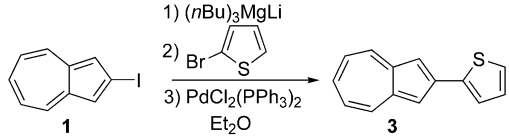
There has been considerable interest in sulfur-substituted aromatic compounds. There is a wide range of applications for these compounds, such as electroluminescent devices, organic conductors, liquid crystals, and polymer stabilizers.[13] Therefore, development of general synthetic procedures and modification methods for sulfur-substituted aromatic compounds would have vital importance. Nucleophilic substitution reactions or metal-catalyzed coupling reactions of aromatic compounds bearing halogen substituents with thiols are frequently utilized to prepare sulfur-substituted aromatic compounds. A major drawback of this sort of approach is that the reaction often required harsh conditions, such as strong basic conditions, high reaction temperatures, and longer reaction periods.[13,14] Although a variety of sulfur-substituted compounds has been synthesized previously in the context of azulene chemistry,[15] little attention has been paid to the development of a facile and selective synthetic method for the preparation of sulfur-substituted azulene derivatives. Recently, we also reported the synthesis of several azulenyl methyl sulfides via azulenethiols, but the procedure requires multiple reaction sequences and tedious separation processes.[16] More recently, we reported the novel synthesis of 1,3-bis(methylthio)- and 1,3-bis(phenylthio)azulenes, which exhibited reversible amphoteric redox properties upon cyclic voltammetry (CV).[17] Therefore, incorporation of 1,3-bis(methylthio) and 1,3-bis(phenylthio) substituents into (2- and 3-thienyl)azulenes is expected to induce novel multiple-redox properties in the 2- and 6-(2- and 3-thienyl)azulene derivatives.

Herein, we also report the reaction of 2- and 6-(2- and 3-thienyl)azulenes with several sulfoxides in the presence of trifluoromethanesulfonic anhydride (Tf_2O), followed by treatment with triethylamine to afford the corresponding 1,3-bis(methylthio)- and 1,3-bis(phenylthio)-2- and 6-thienylazulenes, and their redox properties were examined by CV and differential pulse voltammetry (DPV).

Results and Discussion

Synthesis of Thienylazulenes

Previously, we reported the preparation of azulenyllithium and magnesium reagents utilizing halogen–metal exchange reaction and their reactivities toward several electrophiles.[9] Lithium (2-thienyl)magnesate reagent was prepared in situ under similar reaction conditions utilizing the reaction of haloazulenes reported by us. To a solution of *n*-butylmagnesium chloride (*n*BuMgCl) in diethyl ether was added *n*-butyllithium (*n*BuLi) in hexane at 0 °C to give a lithium tri(*n*-butyl)magnesate reagent.[18] After the mixture was stirred at the same temperature for 30 min, 2-bromothiophene was added dropwise to the mixture at 0 °C. Then, a solution of 2-iodoazulene (**1**) and $PdCl_2(PPh_3)_2$ in diethyl ether was added dropwise to the mixture at 0 °C. The mixture was warmed to room temperature and stirred for 24 h to complete the cross-coupling reaction. The crude product was isolated and purified by the usual workup procedure to afford 2-(2-thienyl)azulene (**3**) in 94% yield (Scheme 1). To optimize the amount of the palladium catalyst, the reaction was examined by utilizing several catalytic amounts. Thus, to obtain the highest yield, at least 5 mol-% of palladium catalyst was required as shown in Table 1.

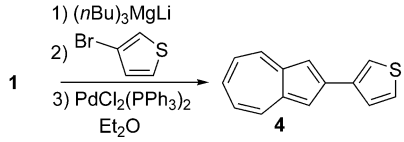


Scheme 1.

Table 1. Comparison of the amount of Pd catalyst with the yields of **3**.

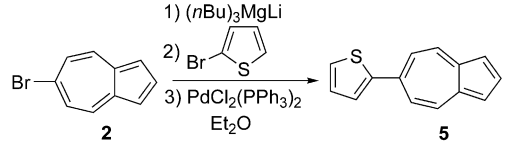
Entry	Catalyst	% Yield of **3**	% Recovery of **1**
1	none	0	99
2	1 mol-% $PdCl_2(PPh_3)_2$	16	79
3	3 mol-% $PdCl_2(PPh_3)_2$	64	33
4	5 mol-% $PdCl_2(PPh_3)_2$	94	0

The magnesium ate complex prepared from 3-bromothiophene was also treated with **1** efficiently to afford cross-coupling product **4** in 96% yield (Scheme 2).

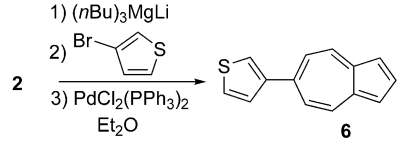


Scheme 2.

The cross-coupling reaction of 6-bromoazulene (**2**) with the thienylmagnesium ate complexes was also conducted under similar reaction conditions employed for the cross-coupling reaction of **1**. The magnesium ate complexes prepared from 2- and 3-bromothiophenes were efficiently treated with **2** to afford the corresponding coupling products **5** and **6** in 94 and 98% yield, respectively (Schemes 3 and 4). Thienylazulenes **3**–**6** possess fair solubility in common organic solvents, such as hexane, ethyl acetate, and



Scheme 3.



Scheme 4.

so on. Moreover, these compounds are stable and show no decomposition even after several weeks at room temperature.

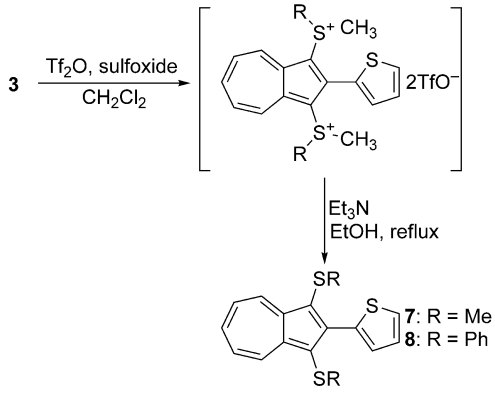
Preparation of 1,3-Bis(methylthio)- and 1,3-Bis(phenylthio)-thienylazulenes

We applied our synthetic procedure of 1-azulenyl methyl and phenyl sulfides and 1,3-bis(methylthio)- and 1,3-bis(phenylthio)azulenes via 1-azulenylsulfonium and 1,3-azulenediylsulfonium ions[17] to the synthesis 1,3-bis(methylthio)- and 1,3-bis(phenylthio)thienylazulenes. The results for the preparation of thienylazulenes from **3**–**6** with triflate and sulfoxide are summarized in Table 2.

Table 2. Synthesis of 1,3-bis(methylthio)- and 1,3-bis(phenylthio)-thienylazulenes **7**–**12**.

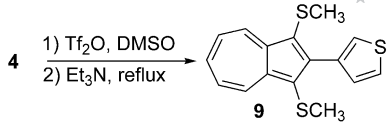
Entry	Substrate	Sulfoxide	Product, % Yield
1	**3**	DMSO	**7**, 87
2	**3**	MeS(O)Ph	**8**, 72
3	**4**	DMSO	**9**, 89
4	**4**	MeS(O)Ph	decomp.
5	**5**	DMSO	**10**, 84
6	**5**	MeS(O)Ph	decomp.
7	**6**	DMSO	**11**, 86
8	**6**	MeS(O)Ph	**12**, 73

The reaction of **3** with DMSO in the presence of Tf_2O (3 equiv.), followed by treatment with Et_3N afforded 1,3-bis(methylthio)-2-(2-thienyl)azulene (**7**) in 87% yield. 1,3-Bis(phenylthio)-2-(2-thienyl)azulene (**8**) was also prepared in 72% yield, when methyl phenyl sulfoxide was used as a reagent under similar reaction conditions (Scheme 5).



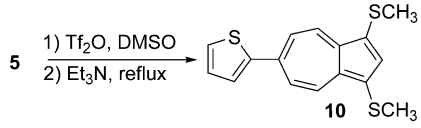
Scheme 5.

Compound **9** was obtained in 89% yield as a sole product, when the reaction of **4** was carried out with Tf_2O (3 equiv.) and an excess amount of DMSO (Scheme 6). However, the reaction of **4** with methyl phenyl sulfoxide as a reagent did not afford the presumed 1,3-bis(phenylthio)-2-(3-thienyl)azulene, but the reaction suffered from decomposition of the starting materials instead. These results would be attributable to the instability of the intermediate bis(sulfonium) ion, that is, the 2-(3-thienyl)azulene-1,3-diylbis(methylphenylsulfonium) ion.

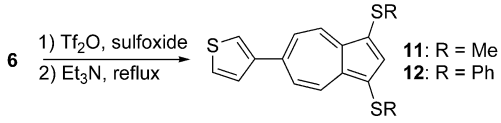


Scheme 6.

The similar reaction of thienylazulenes **5** and **6** with DMSO and methyl phenyl sulfoxide was also investigated to introduce the 1,3-bis(methylthio) and 1,3-bis(phenylthio) moieties into the azulene ring. The reaction of **5** and **6** with DMSO in the presence of Tf_2O, followed by treatment with triethylamine afforded **10** and **11** in 84 and 86% yield, respectively (Schemes 7 and 8). Compound **6** was also treated with methyl phenyl sulfoxide in the presence of Tf_2O to afford desired product **12** in 73% yield (Scheme 8), but the reaction of **5** with methyl phenyl sulfoxide in the presence of Tf_2O did not afford the presumed 1,3-bis(phenylthio)-6-(2-thienyl)azulene as similar with the reaction of **4** with methyl phenyl sulfoxide. New products **7**–**12** are stable and can be stored at room temperature.



Scheme 7.



Scheme 8.

Spectroscopic Properties

Compounds **3**–**12** were fully characterized by various spectroscopic techniques (see the Experimental Section). Mass spectra (EI or ESI) of **3**–**12** showed the correct molecular ion peaks. The UV/Vis spectra of **3**, **7**, **8** and **6**, **11**, **12** in dichloromethane are shown in Figures 1 and 2, respectively. Thienylazulene derivatives **3**–**12** in dichloromethane showed characteristic absorptions arising from the azulene skeleton in the visible region. The longest wavelength absorption maxima of **7**–**12** showed a bathochromic shift compared with those of thioazulenes **13**–**16** (Figure 3) [**13**; λ_{max} = 628 nm ($\log\varepsilon$ = 2.47), **14**; λ_{max} = 600 nm ($\log\varepsilon$ = 2.53), **15**; λ_{max} = 604 nm ($\log\varepsilon$ = 2.56), and **16**; λ_{max} = 560 nm ($\log\varepsilon$ = 2.63)],[17] probably due to expansion of π conjugation by the thienyl substituents.

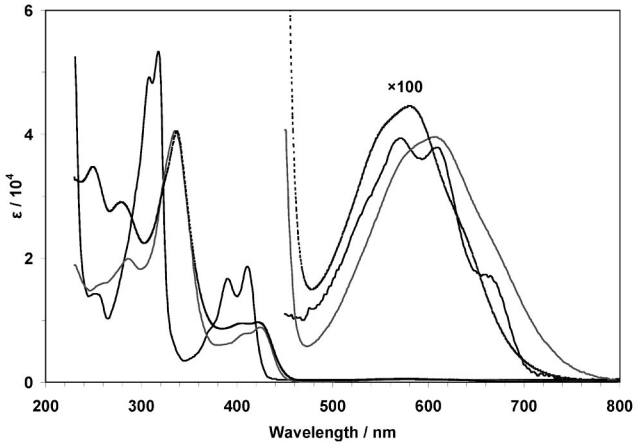


Figure 1. UV/Vis spectra of **3** (black line), **7** (gray line), and **8** (broken line) in dichloromethane.

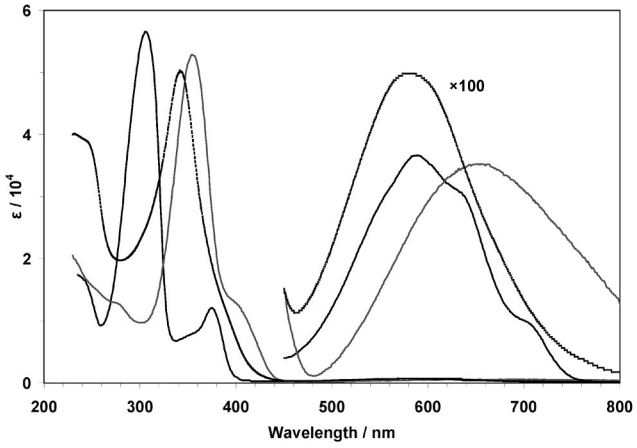
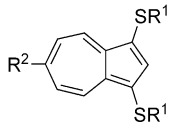


Figure 2. UV/Vis spectra of **6** (black line), **11** (gray line), and **12** (broken line) in dichloromethane.



13: R^1 = Me, R^2 = H
14: R^1 = Ph, R^2 = H
15: R^1 = Me, R^2 = *t*Bu
16: R^1 = Ph, R^2 = *t*Bu

Figure 3. 1,3-bis(methylthio)- and 1,3-bis(phenylthio)azulenes **13**–**16**.

^{1}H NMR spectroscopic analysis of thienylazulene derivatives **3**–**12** in $CDCl_3$ revealed characteristic chemical shifts attributable to the azulene and thiophene system in the aromatic region. Recently, we reported the low-field shift of the 4-H proton of the azulene ring upon binding of N-containing heterocycles with the azulene ring at the 1-position; this shift probably results from intramolecular interaction between the nitrogen atom of the heterocycles and the 4-H proton of the azulene ring.[17] In compounds **7**–**12**, chemical shifts of the 4,8-H protons were also observed at lower field compared with those of **3**–**6**. This may be attributable to the intramolecular interaction between the sulfur substituents at the 1,3-positions and the 4,8-H protons of the azulene ring, in a manner similar to that of the N-containing heterocycles.

Redox Behavior of Thienylazulene Derivatives

To clarify the electrochemical properties, the redox behavior of thienylazulene derivatives **3**–**12** was examined by CV and DPV. 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 carried out under an argon atmosphere and potentials were related to an $Ag/AgNO_3$ reference electrode and Fc/Fc^+ as an internal reference, which discharges at +0.15 V under these conditions. The redox potentials (in volts vs. $Ag/AgNO_3$) of thienylazulenes **3**–**6**, 1,3-bis(methylthio)- and 1,3-bis(phenylthio)thienylazulenes **7**–**12**, and 1,3-bis(methylthio)- and 1,3-bis(phenylthio)azulenes **13**–**16** are summarized in Table 3. The cyclic voltammograms for **6** and **11** are shown in Figures 4 and 5, respectively.

Table 3. Redox potentials [V][a] of **3**–**12**, 1,3-bis(methylthio)- and 1,3-bis(phenylthio)azulenes **13**–**16**, and guaiazulene derivatives **17**–**19**.[b]

Sample	E_1^{red}	E_2^{red}	E_1^{ox}	E_2^{ox}	E_3^{ox}	E_4^{ox}
3	–1.80					
	(–1.78)	(–2.13)	(+0.59)			
4	–1.87					
	(–1.85)	(–2.15)	(+0.56)			
5	–1.72					
	(–1.70)	(–2.15)	(+0.65)	(+0.99)		
6	–1.82					
	(–1.80)	(–2.15)	(+0.62)	(+0.97)		
7	(–1.62)	(–2.13)	(+0.56)	(+0.82)	(+1.00)	
8	(–1.53)	(–2.19)	(+0.76)	(+0.97)	(+1.30)	(+1.50)
9	(–1.68)	(–2.16)	(+0.51)	(+0.74)	(+0.97)	
10	–1.66		+0.23			
	(–1.64)	(–2.16)	(+0.21)	(+0.71)	(+1.35)	(+1.55)
11	–1.57		+0.23	+0.72		
	(–1.55)	(–2.12)	(+0.22)	(+0.72)	(+1.32)	(+1.50)
12	–1.54		+0.47			
	(–1.52)	(–2.19)	(+0.45)	(+0.77)	(+0.92)	(+1.53)
13[17]			+0.26			
	(–1.73)	(–2.15)	(+0.24)	(+0.70)	(+0.91)	(+1.18)
14[17]			+0.48			
	(–1.60)	(–2.18)	(+0.46)	(+0.70)	(+0.95)	
15[17]	–1.86		+0.20			
	(–1.84)	(–2.18)	(+0.19)	(+0.76)		
16[17]	–1.75		+0.44			
	(–1.72)	(–2.20)	(+0.42)	(+0.80)		
17[c][19]			+0.44	+1.01[d]		
18[c][19]			+0.44	+1.06[d]		
19[c][19]			+0.40	+0.71		

[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 (i.d. 1.6 mm), scan rate = 100 mV s^{-1}, and Fc/Fc^+ = +0.15 V]. In the case of reversible waves, redox potentials measured by CV are presented. The peak potentials measured by DPV are shown in parentheses. [b] Redox potentials were measured in acetonitrile. [c] V vs. SCE. [d] Irreversible waves.

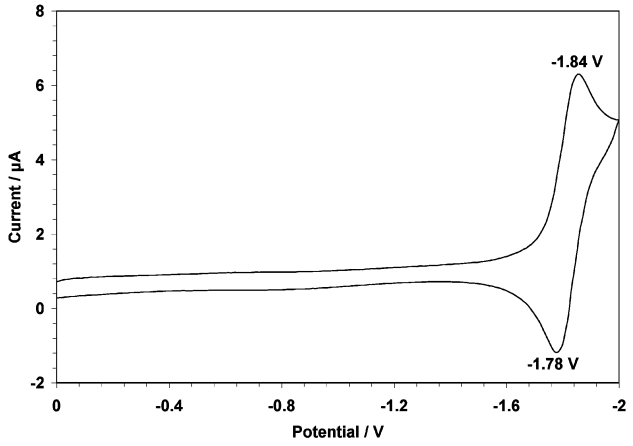


Figure 4. Cyclic voltammogram of the reduction of **6** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

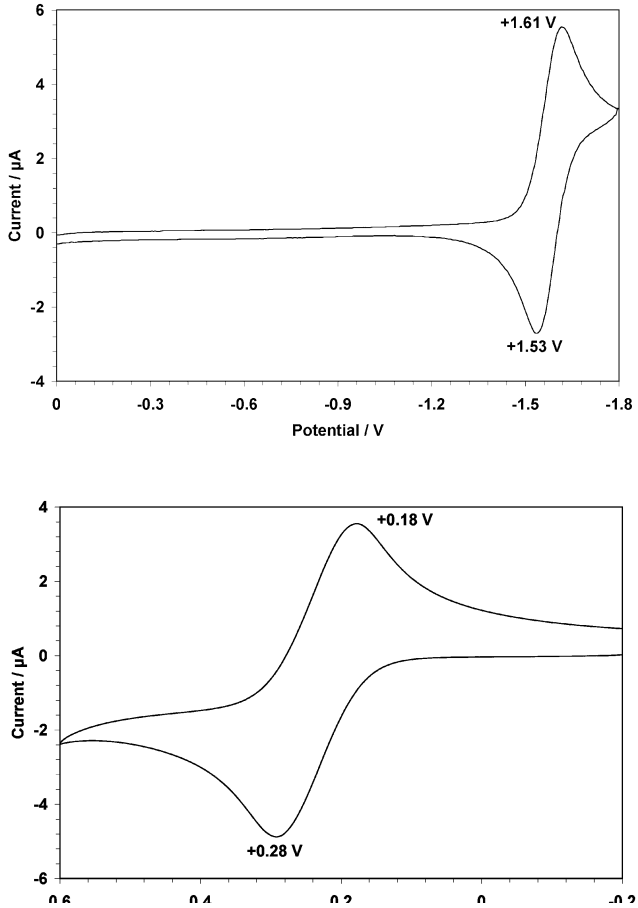


Figure 5. Cyclic voltammograms of (top) reduction and (bottom) oxidation of **11** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

Thienylazulenes **3**–**6** exhibit a reversible reduction wave upon CV. Electrochemical reduction of **3** showed a reversible reduction wave at a half-wave potential of –1.80 V upon CV, which can be ascribed to the formation of a radical anionic species produced by the reduction of the azulene moiety. Further electrochemical reduction produced an irreversible wave at –2.15 V upon DPV. Compound **4** exhibited reversible and irreversible reduction waves, whose potentials were identified at –1.85 and –2.15 V, respectively, upon DPV attributable to the formation of a radical anionic and a dianionic species. The electrochemical reduction of **5** also exhibited reversible and irreversible reduction waves, whose potentials were identified at –1.70 and –2.15 V, respectively, upon DPV. Electrochemical reduction of **6** showed a reversible reduction wave at half-wave potential of –1.82 V upon CV, which can be ascribed to the formation of a radical anionic species (Figure 4). Further electrochemical reduction also produced an irreversible wave at –2.15 V upon DPV.

The redox behaviors of 1,3-bis(methylthio)- and (phenylthio)thienylazulenes **7**–**12** were also examined by CV and DPV. Electrochemical reduction and oxidation of **7** exhibited irreversible waves upon CV. Their potentials were determined by DPV as shown in Table 3. As similar with **7**, electrochemical reduction and oxidation of 2-thienylazulene derivatives **8** and **9** also showed irreversible waves, although 2-thienylazulenes **3** and **4** showed reversible reduction waves upon CV. These results were attributable to the instability of radical cationic and anionic species of 1,3-bis(methylthio)- and 1,3-bis(phenylthio)-2-thienylazulene derivatives **7**–**9**. 6-Thienylazulene derivatives **10**–**12** exhibited reversible reduction and oxidation waves upon CV. Electrochemical reduction of **10** showed a reversible wave at half-wave potential of –1.66 V upon CV and an irreversible reduction wave, whose potential was identified at –2.16 V upon DPV. A reversible oxidation wave of **10** was observed at +0.23 V upon CV due to the generation of a radical cationic species. Electrochemical reduction and oxidation of **11** and **12** also showed reversible redox waves owing to the generation of a stable radical anionic and cationic species (Figure 5, top and bottom). These results indicate that the thienyl substituent at the 6-position of azulene ring stabilizes the radical anionic and cationic states compared with those at the 2-position.

Previously, Kurihara et al. reported the oxidation potentials for sulfur-substituted guaiazulene derivatives **17**, **18**, and **19** (Figure 6), which exhibit two-step oxidation waves at +0.40 to +0.44 V and +0.71 to +1.06 V (V vs. SCE).[19] Recently, we also reported that 1,3-bis(methylthio)- and 1,3-bis(phenylthio)azulenes **13**–**16** exhibit multistep oxidation waves at relatively lower first oxidation potentials upon CV within these compounds as similar with those of guaiazulene derivatives **17**–**19**. Although 2-thienylazulene derivatives **7** and **8** did not show a decrease in the oxidation potentials with sulfur substituents at the 1- and 3-positions, 6-thienylazulene derivatives **10**–**12** showed reversible oxidation waves at the similar lower potential region with those of **13**–**16**. The more positive first oxidation potentials of **7**–**9** should be ascribed to the less effective conjugation of the 1- and 3-sulfur substituents owing to steric interaction of the 2-thienyl group with the azulene ring. Moreover, the first reduction waves of **10**–**12** exhibited slightly less negative potentials compared with those of **13**–**16**. These

results indicate that the thienyl substituents on the azulene ring at the 6-position decrease the LUMO level and the 1,3-bis(methylthio)- and 1,3-bis(phenylthio) substituents increase the HOMO level. Consequently, compounds **10**–**12** show high amphoteric redox properties within these compounds. Comparison of the first oxidation potentials of compounds **11** (+0.23 V) and **12** (+0.47 V) shows the methylthio moiety has greater electron-donating properties than the phenylthio group on azulene ring at the 1- and 3-positions. Therefore, compounds **10** and **11** exhibit the highest amphoteric redox properties within these compounds.

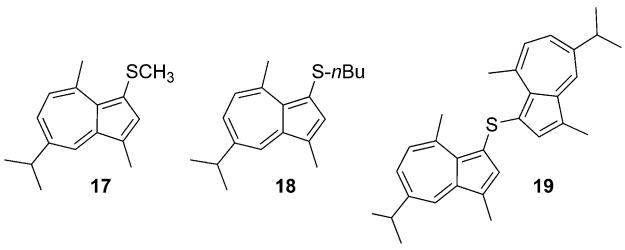


Figure 6. Sulfur-substituted guaiazulene derivatives **17**, **18**, and **19**.

Conclusions

We have described a novel and efficient synthetic method for thienylazulenes **3**–**6** that offers a number of advantages over the methods reported previously. Haloazulenes reacted with thienylmagnesium ate complexes in the presence of a palladium catalyst to afford the corresponding thienylazulenes **3**–**6** under mild reaction conditions. The reaction of thienylazulenes with sulfoxides in the presence of Tf_2O followed by treatment with triethylamine afforded 1,3-bis(methylthio)- and 1,3-bis(phenylthio)azulenes **7**–**12**. Thienylazulenes **3**–**6** showed a reversible one-stage reduction wave due to the formation of a stable radical anionic species. Although, 1,3-bis(methylthio)- and 1,3-bis(phenylthio)-2-thienylazulenes **7**–**9** did not display reversible redox waves, 1,3-bis(methylthio)- and 1,3-bis(phenylthio)-6-thienylazulenes **10**–**12** exhibited oxidation and reduction waves with high reversibility upon CV probably due to the formation of stabilized radical cationic and anionic species.

Experimental Section

General Remarks: Melting points were determined with a Yanagimoto MPS3 micromelting apparatus and are uncorrected. Mass spectra were obtained with a JEOL HX-110, a Hitachi M-2500, or a Bruker APEX II instrument, usually at 70 eV. IR and UV spectra were measured with a Shimadzu FTIR-8100M and a Hitachi U-3410 spectrophotometer, respectively. ^1H and ^{13}C NMR spectra were recorded with a JEOL GSX 400 a Bruker Avance 400 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.

2-(2-Thienyl)azulene (3): To a solution of *n*BuMgCl (0.9 M in THF, 1.4 mL) in diethyl ether (10 mL) was added *n*BuLi (1.6 M in hexane, 1.5 mL) at 0 °C. After the mixture was stirred at the same temperature for 30 min, 2-bromothiophene (179 mg, 1.10 mmol) was added dropwise. The resulting mixture was stirred at 0 °C for 1 h. To the mixture was dropwise added a solution of **1** (254 mg, 1.00 mmol) and $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol) in diethyl ether (20 mL) at 0 °C, and 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 washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene to give **3** (198 mg, 94%) as blue crystals. M.p. 143.0–144.0 °C (decomp.). MS (70 eV): *m*/*z* (%) = 210 (100) [M^+]. IR (KBr): $\tilde{\nu}$ = 3053 (w), 2924 (w), 1576 (m), 1537 (m), 1471 (m), 1410 (m), 1400 (w), 1223 (w), 1205 (m), 1034 (w), 947 (m), 898 (m), 835 (m), 808 (s), 725 (m), 690 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ (logε) = 309 (4.69), 318 (4.72), 371 (sh., 3.92), 392 (4.21), 412 (4.27), 571 (2.60), 609 (2.58), 666 (sh., 2.23) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 10.0 Hz, 2 H, 4,8-H), 7.58 (dd, *J* = 4.0, 1.2 Hz, 1 H, 5′-H), 7.53 (s, 2 H, 1,3-H), 7.47 (t, *J* = 10.0 Hz, 1 H, 6-H), 7.36 (dd, *J* = 4.0, 1.2 Hz, 1 H, 3′-H), 7.14 (t, *J* = 10.0 Hz, 2 H, 5,7-H), 7.13 (dd, *J* = 4.0, 1.2 Hz, 1 H, 4′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.70, 141.75, 141.39, 136.48, 135.87, 128.80, 126.92, 126.08, 124.55, 114.43 ppm. $C_{14}H_{10}S$ (210.30): calcd. C 79.96, H 4.79; found C 79.73, H 4.87.

2-(3-Thienyl)azulene (4): To a solution of *n*BuMgCl (0.9 M in THF, 1.4 mL) in diethyl ether (10 mL) was added *n*BuLi (1.6 M in hexane, 1.5 mL) at 0 °C. After the mixture was stirred at the same temperature for 30 min, 3-bromothiophene (179 mg, 1.10 mmol) was added dropwise. The resulting mixture was stirred at 0 °C for 1 h. To the mixture was dropwise added a solution of **1** (254 mg, 1.00 mmol) and $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol) in diethyl ether (20 mL) at 0 °C, and 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 washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene to give **4** (202 mg, 96%) as blue crystals. M.p. 132.0–133.0 °C (decomp.). MS (70 eV): *m*/*z* (%) = 210 (100) [M^+]. IR (KBr): $\tilde{\nu}_{max}$ = 3096 (m), 1578 (m), 1543 (m), 1466 (m), 1412 (m), 1388 (m), 1350 (w), 1296 (w), 1267 (w), 1211 (m), 1174 (w), 1086 (w), 1014 (w), 949 (m), 897 (w), 870 (m), 816 (m), 783 (s), 725 (m), 688 (w), 667 (w), 617 (w), 580 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ (logε) = 299 (4.80), 309 (4.78), 359 (sh., 3.86), 376 (4.10), 393 (4.19), 570 (2.90), 600 (2.90), 665 (sh., 2.50) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 10.0 Hz, 2 H, 4,8-H), 7.77 (dd, *J* = 4.8, 0.8 Hz, 1 H, 2′-H), 7.62 (dd, *J* = 4.8, 0.8 Hz, 1 H, 4′-H), 7.55 (s, 2 H, 1,3-H), 7.48 (t, *J* = 10.0 Hz, 1 H, 6-H), 7.41 (dd, *J* = 4.8, 0.8 Hz, 1 H, 5′-H), 7.14 (t, *J* = 10.0 Hz, 2 H, 5,7-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.52, 141.28, 138.82, 136.00, 135.51, 135.50 127.04, 126.18, 123.81, 122.73 ppm. $C_{14}H_{10}S{\cdot}1/10H_2O$ (210.30): calcd. C 79.28, H 4.85; found C 79.31, H 4.99.

6-(2-Thienyl)azulene (5): To a solution of *n*BuMgCl (0.9 M in THF, 1.4 mL) in diethyl ether (10 mL) was added *n*BuLi (1.6 M in hexane, 1.5 mL) at 0 °C. After the mixture was stirred at the same temperature for 30 min, 2-bromothiophene (179 mg, 1.10 mmol) was added dropwise. The mixture was stirred at 0 °C for 1 h. To the mixture was dropwise added a solution of **2** (207 mg, 1.00 mmol) and $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol) in diethyl ether (20 mL) at 0 °C and stirred at room temperature for 24 h. The reaction mixture was poured into water and extracted with hexane. 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 to give **5** (198 mg, 94%) as blue crystals. M.p. 160.0–161.0 °C. MS (70 eV): *m*/*z* (%) = 210 (100) [M^+]. IR (KBr): $\tilde{\nu}$ = 3053 (w), 2924 (w), 1576 (m), 1537 (m), 1471 (m), 1410 (m), 1400 (w), 1223 (w), 1205 (m), 1034 (w), 947 (m), 898 (m), 835 (m), 808 (s), 725 (m), 690 (m), 653 (w), 586 (w), 493 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ ($\log\varepsilon$) = 296 (sh., 4.37), 326 (4.51), 390 (4.14), 598 (2.49), 647 (sh., 2.40), 728 (sh., 1.83) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 10.0 Hz, 2 H, 4,8-H), 7.82 (t, *J* = 4.0 Hz, 1 H, 2-H), 7.53 (d, *J* = 10.0 Hz, 2 H, 5,7-H), 7.47 (dd, *J* = 4.4, 1.2 Hz, 1 H, 5′-H), 7.38 (dd, *J* = 4.4, 1.2 Hz, 1 H, 3′-H), 7.34 (d, *J* = 4.0 Hz, 2 H, 1,3-H), 7.11 (t, *J* = 4.4 Hz, 1 H, 4′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.01, 142.82, 138.82, 136.81, 135.66, 128.47, 127.32, 125.92, 121.33, 118.81 ppm. $C_{14}H_{10}S$ (210.30): calcd. C 79.96, H 4.79; found C 79.67, H 4.87.

6-(3-Thienyl)azulene (6): To a solution of *n*BuMgCl (0.9 M in THF, 1.4 mL) in diethyl ether (10 mL) was added *n*BuLi (1.6 M in hexane, 1.5 mL) at 0 °C. After the mixture was stirred at the same temperature for 30 min, 3-bromothiophene (179 mg, 1.10 mmol) was added dropwise. The resulting mixture was stirred at 0 °C for 1 h. To the mixture was dropwise added a solution of **2** (207 mg, 1.00 mmol) and $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol) in diethyl ether (20 mL) at 0 °C, and 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 washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene to give **6** (206 mg, 98%) as blue crystals. M.p. 180.0–181.0 °C. MS (70 eV): *m*/*z* (%) = 210 (100) [M^+]. IR (KBr): $\tilde{\nu}$ = 3100 (m), 1572 (s), 1554 (m), 1508 (m), 1457 (s), 1444 (w), 1402 (s), 1346 (m), 1304 (w), 1255 (m), 1217 (m), 1199 (w), 1182 (m), 1093 (m), 1055 (m), 983 (w), 970 (w), 891 (m), 862 (m), 841 (s), 781 (s), 754 (s), 690 (m), 667 (m), 609 (m), 572 (w), 543 (w), 505 (m), 461 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ ($\log\varepsilon$) = 307 (4.75), 376 (4.07), 589 (2.56), 635 (sh., 2.48), 705 (sh., 1.99) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 10.8 Hz, 2 H, 4,8-H), 7.82 (t, *J* = 4.0 Hz, 1 H, 2-H), 7.58 (dd, *J* = 4.4, 1.6 Hz, 1 H, 2′-H), 7.49–7.41 (m, 4 H, 5,7,4′,5′-H), 7.38 (d, *J* = 4.0 Hz, 2 H, 1,3-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.65, 145.23, 139.33, 137.11, 136.33, 127.97, 126.94, 123.65, 122.72, 118.88 ppm. $C_{14}H_{10}S{\cdot}1/10H_2O$ (210.30): calcd. C 79.28, H 4.85; found C 79.42, H 4.89.

1,3-Bis(methylthio)-2-(2-thienyl)azulene (7): Trifluoromethanesulfonic anhydride (338 mg, 1.20 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **3** (105 mg, 0.50 mmol) and DMSO (195 mg, 2.50 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure. To the residue was added EtOH (10 mL) and Et_3N (10 mL), and the mixture was heated at reflux for 30 min. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with toluene as an eluent to give **7** (132 mg, 87%) as green crystals. M.p. 91.0–93.0 °C. HRMS (ESI): calcd. for $C_{16}H_{14}NaS_3$ [M + Na]$^+$ 325.0155; found 325.0150. IR (KBr): $\tilde{\nu}$ = 3089 (w), 2979 (w), 2914 (w), 1573 (m), 1508 (m), 1433 (s), 1404 (s), 1361 (w), 1342 (w), 1278 (w), 1215 (w), 1124 (w), 1055 (w), 962 (w), 935 (w), 883 (w), 848 (m), 736 (s), 707 (s), 586 (w), 574 (w), 507 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ ($\log\varepsilon$) = 255 (sh., 4.19), 286 (4.30), 337 (4.61), 407 (sh., 3.87), 424 (3.95), 576 (sh., 2.56), 608 (2.60) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 10.0 Hz, 2 H, 4,8-H), 8.30 (dd, *J* = 4.4, 1.2 Hz, 1 H, 5′-H), 7.64 (t, *J* = 10.0 Hz, 1 H, 6-H), 7.36 (dd, *J* = 5.2, 1.2 Hz, 1 H, 3′-H), 7.39 (t, *J* = 10.0 Hz, 2 H, 5,7-H), 7.13 (dd, *J* = 5.2, 4.4 Hz, 1 H, 4′-H), 2.11 (s, 6 H, Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.80, 142.97, 137.83, 136.65, 135.66, 130.03, 128.59, 126.98, 125.91, 118.49, 20.51 ppm. $C_{16}H_{14}S_3$ (302.48): calcd. C 63.53, H 4.67; found C 63.32, H 4.78.

1,3-Bis(phenylthio)-2-(2-thienyl)azulene (8): Trifluoromethanesulfonic anhydride (423 mg, 1.50 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **3** (105 mg, 0.50 mmol) and methyl phenyl sulfoxide (350 mg, 2.50 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure. To the residue was added EtOH (10 mL) and Et_3N (10 mL), and the mixture was heated at reflux for 30 min. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with toluene as an eluent to give **8** (154 mg, 72%) as green crystals. M.p. 182.0–186.0 °C. HRMS (ESI): calcd. for $C_{26}H_{18}NaS_3$ [M + Na]$^+$ 449.0468; found 449.0463. IR (KBr): $\tilde{\nu}$ = 3068 (w), 3030 (w), 3001 (w), 1577 (s), 1510 (m), 1477 (s), 1433 (s), 1407 (s), 1340 (w), 1326 (w), 1217 (w), 1157 (w), 1126 (w), 1078 (m), 1056 (w), 1024 (m), 997 (w), 896 (w), 883 (w), 848 (m), 827 (w), 732 (s), 707 (s), 686 (s), 617 (w), 570 (w), 511 (w), 464 (w), 435 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ ($\log\varepsilon$) = 250 (4.54), 280 (4.46), 337 (4.61), 403 (3.98), 424 (3.99), 550 (sh., 2.61), 582 (2.65) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.83 (d, *J* = 9.6 Hz, 2 H, 4,8-H), 7.92 (dd, *J* = 4.0, 0.8 Hz, 1 H, 5′-H), 7.69 (t, *J* = 9.6 Hz, 1 H, 6-H), 7.45 (t, *J* = 9.6 Hz, 2 H, 5,7-H), 7.42 (dd, *J* = 4.8, 0.8 Hz, 1 H, 3′-H), 7.14 (t, *J* = 8.0 Hz, 4 H, *m*-Ph), 7.05–7.01 (m, 3 H, *p*-Ph and 4′-H), 6.93 (dd, *J* = 8.0, 1.2 Hz, 4 H, *o*-Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.66, 145.28, 139.63, 138.46, 136.28, 135.77, 131.05, 129.64, 128.91, 127.81, 127.04, 125.42, 124.77, 112.43 ppm. $C_{26}H_{18}S_3$ (426.62): calcd. C 73.20, H 4.25; found C 73.11, H 4.29.

1,3-Bis(methylthio)-2-(3-thienyl)azulene (9): Trifluoromethanesulfonic anhydride (423 mg, 1.50 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **4** (105 mg, 0.50 mmol) and DMSO (195 mg, 2.50 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure. To the residue was added EtOH (10 mL) and Et_3N (10 mL), and the mixture was heated at reflux for 30 min. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with toluene as an eluent to give **9** (135 mg, 89%) as green crystals. M.p. 122.0–124.0 °C. HRMS (ESI): calcd. for $C_{16}H_{14}NaS_3$ [M + Na]$^+$ 325.0155; found 325.0150. IR (KBr): $\tilde{\nu}$ = 3105 (w), 3087 (w), 3053 (w), 3022 (w), 2910 (m), 2844 (w), 2819 (w), 1581 (m), 1448 (m), 1438 (m), 1417 (m), 1402 (s), 1359 (m), 1305 (w), 1284 (m), 1201 (m), 1139 (w), 1076 (w), 1004 (w), 956 (m), 902 (m), 854 (s), 792 (s), 736 (s), 711 (s), 696 (m), 686 (m), 617 (w), 599 (w), 578 (w), 503 (w), 422 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ ($\log\varepsilon$) = 248 (4.37), 323 (4.61), 385 (sh., 3.78), 412 (sh., 3.51), 580 (sh., 2.53), 607 (2.54) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, *J* = 10.0 Hz, 2 H, 4,8-H), 8.06 (dd, *J* = 3.2, 1.2 Hz, 1 H, 2′-H), 7.86 (dd, *J* = 4.8, 1.2 Hz, 1 H, 5′-H), 7.65 (t, *J* = 10.0 Hz, 1 H, 6-H), 7.36 (dd, *J* = 4.8, 3.2 Hz, 1 H, 4′-H), 7.37 (t, *J* = 10.0 Hz, 2 H, 5,7-H), 2.11 (s, 6 H, Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.63, 142.36, 138.03, 136.00, 135.59, 129.40, 126.30, 125.43, 124.28, 119.18, 20.31 ppm. $C_{16}H_{14}S_3$ (302.48): calcd. C 63.53, H 4.67; found C 63.44, H 4.69.

1,3-Bis(methylthio)-6-(2-thienyl)azulene (10): Trifluoromethanesulfonic anhydride (423 mg, 1.50 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **5** (105 mg, 0.50 mmol) and DMSO (195 mg, 2.50 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure. To the residue was added EtOH (10 mL) and Et_3N (10 mL), and the mixture was heated at reflux for 30 min. The solvent was removed under reduced pressure. The residue was

purified by column chromatography on silica gel with toluene as an eluent to give **10** (127 mg, 84%) as green oil. HRMS (ESI): calcd. for $C_{16}H_{14}NaS_3$ $[M + Na]^+$ 325.0155; found 325.0150. IR (KBr): $\tilde{\nu}$ = 3095 (w), 2979 (w), 2914 (w), 1568 (s), 1512 (w), 1471 (w), 1434 (w), 1398 (m), 1371 (w), 1352 (w), 1311 (w), 1292 (w), 1251 (w), 1232 (w), 1215 (w), 1184 (w), 1116 (w), 1014 (w), 960 (m), 881 (w), 860 (m), 839 (m), 775 (s), 707 (w), 690 (w), 673 (w), 642 (w), 626 (w), 607 (w), 511 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ ($\log\varepsilon$) = 248 (sh., 4.29), 341 (4.71), 394 (sh., 3.92), 636 (2.48) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.48 (d, J = 10.8 Hz, 2 H, 4,8-H), 7.89 (s, 1 H, 2-H), 7.61 (dd, J = 4.4, 1.2 Hz, 1 H, 5′-H), 7.48 (d, J = 10.8 Hz, 2 H, 5,7-H), 7.46–7.43 (m, 2 H, 3′,4′-H), 2.49 (s, 6 H, Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.65, 145.61, 140.98, 138.57, 134.74, 127.33, 126.75, 123.84, 123.00, 121.96, 20.24 ppm. $C_{16}H_{14}S_3 \cdot 1/10H_2O$ (302.48): calcd. C 63.16, H 4.70; found C 63.20, H 4.88.

1,3-Bis(methylthio)-6-(3-thienyl)azulene (11): Trifluoromethanesulfonic anhydride (423 mg, 1.50 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **6** (105 mg, 0.50 mmol) and DMSO (195 mg, 2.50 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure. To the residue was added EtOH (10 mL) and Et_3N (10 mL), and the mixture was heated at reflux for 30 min. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with toluene as an eluent to give **11** (130 mg, 86%) as brown crystals. M.p. 73.0–76.0 °C. HRMS (ESI): calcd. for $C_{16}H_{14}NaS_3$ $[M + Na]^+$ 325.0155; found 325.0150. IR (KBr): $\tilde{\nu}$ = 2914 (w), 1573 (s), 1562 (s), 1512 (w), 1477 (w), 1419 (w), 1402 (s), 1371 (m), 1350 (m), 1323 (w), 1294 (w), 1249 (m), 1232 (m), 1180 (w), 1055 (w), 1014 (w), 975 (m), 958 (m), 837 (s), 815 (s), 794 (w), 748 (w), 705 (s), 657 (w), 626 (w), 511 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ ($\log\varepsilon$) = 280 (sh., 4.10), 354 (4.72), 404 (sh., 4.09), 656 (2.55) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, J = 10.8 Hz, 2 H, 4,8-H), 7.85 (s, 1 H, 2-H), 7.55–7.51 (m, 3 H, 5,7,2′-H), 7.42 (d, J = 4.0 Hz, 1 H, 5′-H), 7.38 (d, J = 4.8, 4.0 Hz, 1 H, 4′-H), 2.48 (s, 6 H, Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.33, 144.69, 140.80, 138.38, 134.50, 128.63, 127.95, 126.45, 122.42, 121.91, 20.15 ppm. $C_{16}H_{14}S_3$ (302.48): calcd. C 63.53, H 4.67; found C 63.50, H 4.62.

1,3-Bis(phenylthio)-6-(3-thienyl)azulene (12): Trifluoromethanesulfonic anhydride (423 mg, 1.50 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **6** (105 mg, 0.50 mmol) and methyl phenyl sulfoxide (350 mg, 2.50 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure. To the residue was added EtOH (10 mL) and Et_3N (10 mL), and the mixture was heated at reflux for 30 min. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with toluene as an eluent to give **12** (156 mg, 73%) as green crystals. M.p. 97.0–99.5 °C. HRMS (ESI): calcd. for $C_{16}H_{14}NaS_3$ $[M + Na]^+$ 325.0155; found 325.0150. IR (KBr): $\tilde{\nu}$ = 3101 (w), 3053 (w), 1579 (s), 1506 (m), 1475 (s), 1436 (m), 1409 (s), 1359 (s), 1294 (w), 1272 (w), 1257 (w), 1238 (w), 1220 (w), 1184 (w), 1155 (w), 1091 (w), 1078 (m), 1024 (m), 970 (w), 873 (w), 860 (m), 842 (m), 779 (s), 740 (s), 690 (s), 609 (w), 516 (m), 486 (w), 462 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ ($\log\varepsilon$) = 248 (sh., 4.58), 344 (4.70), 583 (2.70) nm. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.67 (d, J = 10.4 Hz, 2 H, 4,8-H), 8.08 (s, 1 H, 2-H), 7.66 (d, J = 10.4 Hz, 2 H, 5,7-H), 7.60 (br. s, 1 H, 2′-H), 7.42–7.41 (m, 2 H, 4′,5′-H), 7.16 (t, J = 8.0 Hz, 4 H, *m*-Ph), 7.07–7.02 (m, 6 H, *o*-, *p*-Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.79, 147.41, 145.16, 141.88, 139.67, 135.66, 128.82, 127.23, 127.08, 126.22, 125.44, 125.05, 124.44, 115.75 ppm. $C_{26}H_{18}S_3$ (426.62): calcd. C 73.20, H 4.25; found C 73.06, H 4.38.

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[1] a) J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359–1469; b) J.-P. Corbet, G. Mignani, *Chem. Rev.* **2006**, *106*, 2651–2710; c) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133–173.

[2] a) D. Milstein, J. K. Stille, *J. Am. Chem. Soc.* **1978**, *100*, 3636–3638; b) P. Espinet, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2004**, *43*, 4704–4734.

[3] a) N. Miyaura, A. Suzuki, *J. Chem. Soc., Chem. Commun.* **1979**, 866–867; b) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483.

[4] a) A. O. King, N. Okukado, E. Negishi, *J. Chem. Soc., Chem. Commun.* **1977**, 683–684; b) E. Negishi, A. O. King, N. Okukado, *J. Org. Chem.* **1977**, *42*, 1821–1823; c) E. Negishi, *Acc. Chem. Res.* **1982**, *15*, 340–348; d) E. Erdik, *Tetrahedron* **1992**, *48*, 9577–9648.

[5] a) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359–1470; b) S. V. Ley, A. W. Thomas, *Angew. Chem. Int. Ed.* **2003**, *42*, 5400–5449.

[6] K.-P. Zeller, "Azulene" in *Methoden der Organischen Chemie* (*Houben-Weyl*) (Ed.: H. Kropf), 4th ed., Thieme, Stuttgart, Germany, **1985**, vol. V, part 2c, pp. 127–418.

[7] a) T. Shoji, R. Yokoyama, S. Ito, M. Watanabe, K. Toyota, M. Yasunami, N. Morita, *Tetrahedron Lett.* **2007**, *48*, 1099–1103; b) T. Shoji, S. Ito, M. Watanabe, K. Toyota, M. Yasunami, N. Morita, *Tetrahedron Lett.* **2007**, *48*, 3009–3012; c) J. Higashi, T. Shoji, S. Ito, K. Toyota, M. Yasunami, N. Morita, *Eur. J. Org. Chem.* **2008**, 5823–5831; d) T. Shoji, S. Ito, T. Okujima, J. Higashi, R. Yokoyama, K. Toyota, M. Yasunami, N. Morita, *Eur. J. Org. Chem.* **2009**, 1554–1563.

[8] a) S. Ito, H. Inabe, T. Okujima, N. Morita, M. Watanabe, N. Harada, K. Imafuku, *J. Org. Chem.* **2001**, *66*, 7090–7101; b) S. Ito, A. Nomura, N. Morita, C. Kabuto, H. Kobayashi, S. Maejima, K. Fujimori, M. Yasunami, *J. Org. Chem.* **2002**, *67*, 7295–7302; c) S. Ito, T. Okujima, N. Morita, *Tetrahedron Lett.* **2002**, *43*, 1261–1264; d) S. Ito, T. Okujima, N. Morita, *J. Chem. Soc. Perkin Trans. 1* **2002**, 1896–1905; e) S. Ito, H. Inabe, N. Morita, K. Ohta, T. Kitamura, K. Imafuku, *J. Am. Chem. Soc.* **2003**, *125*, 1669–1680; f) S. Ito, T. Terazono, T. Kubo, T. Okujima, N. Morita, T. Murafuji, Y. Sugihara, K. Fujimori, J. Kawakami, A. Tajiri, *Tetrahedron* **2004**, *60*, 5357–5366.

[9] S. Ito, T. Kubo, N. Morita, Y. Matsui, T. Watanabe, A. Ohta, K. Fujimori, T. Murafuji, Y. Sugihara, A. Tajiri, *Tetrahedron Lett.* **2004**, *45*, 2891–2894.

[10] a) S. Dumouchel, F. Mongin, F. Trécourt, G. Quéguiner, *Tetrahedron Lett.* **2003**, *44*, 2033–2035; b) S. Dumouchel, F. Mongin, F. Trécourt, G. Quéguiner, *Tetrahedron Lett.* **2003**, *44*, 3877–3880; c) S. Dumouchel, F. Mongin, F. Trécourt, G. Quéguiner, *Tetrahedron* **2003**, *59*, 8629–8640.

[11] Part of this work was recently published in preliminary form: T. Shoji, S. Kikuchi, S. Ito, N. Morita, *Heterocycles* **2005**, *66*, 91–94.

[12] Transition-metal-catalyzed coupling of 1,3-thienylazulene derivatives was recently reported: a) F. Wang, M.-Y. Han, K.-Y. Mya, Y. Wang, Y.-H. Lai, *J. Am. Chem. Soc.* **2005**, *127*, 10350–10355; b) M. Oda, N. C. Thanh, M. Ikai, H. Fujikawa, K. Nakajima, S. Kuroda, *Tetrahedron* **2007**, *63*, 10608–10614.

[13] M. Gingras, J. Raimundo, Y. M. Chabre, *Angew. Chem. Int. Ed.* **2006**, *45*, 1686–1712.

[14] T. Kondo, T. Mitsudo, *Chem. Rev.* **2000**, *100*, 3205–3220.

[15] a) A. G. Anderson Jr, R. N. McDonald, *J. Am. Chem. Soc.* **1959**, *81*, 5669–5674; b) L. L. Replogle, R. M. Arluck, J. R. Maynard, *J. Org. Chem.* **1965**, *30*, 2715–2718; c) L. L. Replogle,

J. R. Maynard, *J. Org. Chem.* **1967**, *32*, 1909–1915; d) L. L. Replogle, G. C. Peters, J. R. Maynard, *J. Org. Chem.* **1969**, *34*, 2022–2024.
[16] T. Asao, S. Ito, N. Morita, *Tetrahedron Lett.* **1989**, *30*, 6345–6348.
[17] a) T. Shoji, S. Ito, K. Toyota, M. Yasunami, N. Morita, *Tetrahedron Lett.* **2007**, *48*, 4999–5002; b) T. Shoji, H. Higashi, S. Ito, K. Toyota, M. Yasunami, N. Morita, *Eur. J. Org. Chem.* **2008**, 1242–1252.
[18] a) A. Inoue, K. Kitagawa, H. Shinokubo, K. Oshima, *J. Org. Chem.* **2001**, *66*, 4333–4339; b) T. Iida, T. Wada, K. Tomimoto, T. Mase, *Tetrahedron Lett.* **2001**, *42*, 4841–4844.
[19] T. Kurihara, T. Suzuki, H. Wakabayashi, S. Ishikawa, K. Shindo, Y. Shimada, H. Chiba, T. Miyashi, M. Yasunami, T. Nozoe, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2003–2008.

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