

# Synthesis of 1,2'-Biazulenes by Palladium-Catalyzed Unusual Homo-coupling Reaction of 1-Haloazulenes in the Presence of Ferrocene

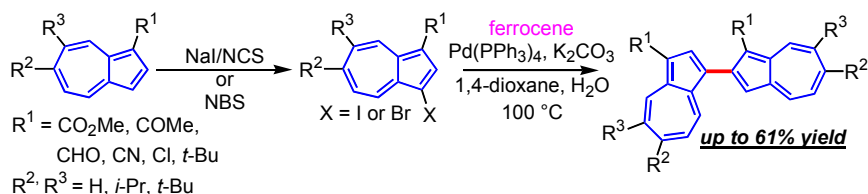
Taku Shoji,<sup>\*,a,b</sup>  
 Kanami Miyashita,<sup>a</sup>  
 Takanori Araki,<sup>a</sup>  
 Miwa Tanaka,<sup>a</sup>  
 Akifumi Maruyama,<sup>b</sup>  
 Ryuta Sekiguchi,<sup>c</sup>  
 Shunji Ito,<sup>c</sup>  
 Tetsuo Okujima,<sup>d</sup>

<sup>a</sup> Department of Chemistry, Faculty School of Science, Shinshu University, Matsumoto 390-8621, Nagano, Japan.  
 tshoji@shinshu-u.ac.jp

<sup>b</sup> Department of Material Science, Graduate School of Science and Technology, Shinshu University, Matsumoto 390-8621, Nagano, Japan.

<sup>c</sup> Graduate School of Science and Technology, Hirosaki University, Hirosaki 036-8561, Aomori, Japan.

<sup>d</sup> Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Ehime, Japan



Received:  
 Accepted:  
 Published online:  
 DOI:

**Abstract** The synthesis of 1,2'-biazulenes was established by palladium-catalyzed homo-coupling reactions of the corresponding 1-haloazulenes in the presence of ferrocene. The optical properties of the novel 1,2'-biazulenes were investigated by UV/Vis spectroscopy and theoretical calculations. The redox behaviors of 1,2'-biazulenes were also examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

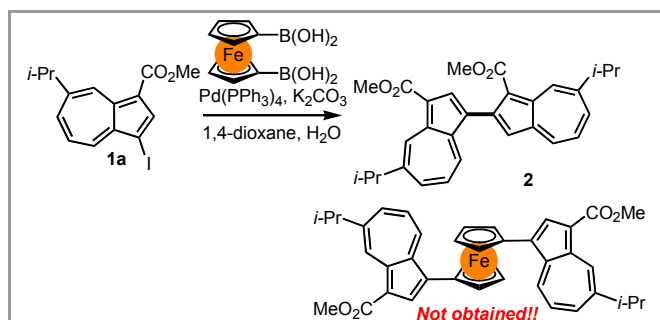
**Key words** azulene, 1,2'-biazulene, homo-coupling, UV/Vis spectrum, cyclic voltammetry

Azulene has attracted the interest of many research groups owing to its unusual properties as well as its beautiful blue color.<sup>1</sup> As well as azulene derivatives, biazulenes have also attracted much attention due to their characteristic electronic properties.<sup>2</sup> Although the synthesis of symmetrical 1,1',<sup>3</sup> 2,2',<sup>4</sup> 4,4',<sup>5</sup> 5,5'-<sup>6</sup> and 6,6'-biazulenes<sup>7</sup> appeared in the literatures, there are few reports for the preparation of unsymmetrically substituted biazulenes.<sup>8</sup> Especially, in the cases of 1,2'-biazulenes only four reports have been reported, so far. As a pioneering work, a 1,2'-biazulene derivative was synthesized by Morita and Takase by utilizing the Ullmann-type cross-coupling reaction of the corresponding haloazulenes, but the procedure produced a certain amount of symmetrically coupled biazulenes as by-products.<sup>9</sup> In 1997, Nozoe *et al.* reported the photolysis of 2-diazo-1,3-dicyanoazulene-6(2H)-one in the presence of azulene derivatives to afford 1,2'-biazulene derivatives, along with 2,5'-biazulenes.<sup>10</sup> Dyker *et al.* reported the reaction of parent azulene with stoichiometric amount of Pd(OAc)<sub>2</sub> to give 1,2'-biazulene in 10% yield.<sup>11</sup> In 2001, Murafuji *et al.* have also reported the preparation of a 1,2'-biazulene derivative by the reaction of parent azulene with a 6-azulenecarboxylic acid derivative in the presence of scandium(III) triflate in 10% yield.<sup>12</sup> The previous syntheses of the 1,2'-biazulene derivatives have undoubtedly contributed to the progress of azulene

chemistry. However, low yield and/or difficulty in the preparation of the precursor remains in the preparation of the 1,2'-biazulene derivatives by these methods.

Suzuki–Miyaura cross-coupling reaction is one of the efficient aryl–aryl bond-forming procedures.<sup>13</sup> We have also demonstrated the reaction of 2-azulenylboronate with several aryl halides to give the corresponding 2-arylazulenes.<sup>4a</sup> More recently, Oda and co-workers also reported the efficient synthesis of 1-aryl- and 1,3-diarylazulenes by the Suzuki–Miyaura cross-coupling reaction of 1-halo- and 1,3-dihaloazulenes with the corresponding arylboronic acids.<sup>14</sup> During the way to the synthesis of previously unknown 1,1'-di(1-azulenyl)ferrocene derivatives under the Suzuki–Miyaura cross-coupling conditions, we found an efficient synthetic procedure for the 1,2'-biazulene derivatives that may not be obtained by the normal palladium-catalyzed homo-coupling reaction of the corresponding aryl halides (Scheme 1). Since the 1-haloazulenes could be readily available, the catalytic procedure may become a convenient method for the preparation of 1,2'-biazulene derivatives.

Herein, we describe a novel synthetic procedure for the 1,2'-biazulenes by the palladium-catalyzed unusual homo-coupling reaction of the corresponding 1-haloazulenes. The optical and electronic properties of the new 1,2'-biazulene derivatives were also investigated by absorption spectroscopy, theoretical calculations, and electrochemical analysis.



**Scheme 1** Reaction of 1-iodoazulene **1a** with 1,1'-ferrocenediboronic acid under the Suzuki–Miyaura cross-coupling conditions.

We have encountered unexpected formation of 1,2'-biazulene derivative **2**, when the Suzuki–Miyaura cross-coupling reaction of 1-iodoazulene **1a** with 1,1'-ferrocenediboronic acid was carried out under the usual reaction conditions to synthesize a 1,1'-di(1-azulenyl)ferrocene derivative (Scheme 1). The product, 1,2'-biazulene derivative **2**, was obtained in only 11% yield, when the reaction was carried out using 10 mol%  $[\text{Pd}(\text{PPh}_3)_4]$  in 1,4-dioxane at 100 °C under an argon atmosphere (Table 1, Entry 1). The presumed 1,1'-di(1-azulenyl)ferrocene derivative could not be obtained at all in the reaction. However, we have realized the reaction might become a practical and facile synthetic procedure for the 1,2'-biazulene derivatives that have difficulty to access. Therefore, we have decided to optimize the reaction conditions for the palladium-catalyzed homo-coupling reaction utilizing 1-haloazulenes **1a** and **1b**.

To explore the reaction conditions, we have investigated the homo-coupling reaction of **1a** and **1b** in the absence of  $[\text{Pd}(\text{PPh}_3)_4]$  and/or ferrocene derivatives. The yield of the product **2**, amount of  $[\text{Pd}(\text{PPh}_3)_4]$  and ferrocene derivatives employed to the investigation are summarized in Table 1. In the initial attempt, the reaction of **1a** was carried out in the absence of 1,1'-ferrocenediboronic acid. However, the homo-coupling reaction was not observed without 1,1'-ferrocenediboronic acid and the starting halide was recovered even when the reaction was carried out with the other reagents (Entry 2). No reaction was also observed when the reaction of the halide **1a** was carried out without either or neither of  $\text{K}_2\text{CO}_3$  and  $[\text{Pd}(\text{PPh}_3)_4]$  (Entries 3, 4 and 5). When the reaction was performed in the presence of ferrocene, instead of 1,1'-ferrocenediboronic acid, the presumed product **2** was obtained in 9% yield (Entry 6). Thus, the addition of ferrocene derivative is essential with  $\text{K}_2\text{CO}_3$  and  $[\text{Pd}(\text{PPh}_3)_4]$  to give 1,2'-biazulene **2**. Since the ferrocene is recovered almost quantitatively after the usual workup process, ferrocene behaves catalytically under the reaction conditions.<sup>15</sup> We found the yield of the coupling reaction was significantly improved by increase of the palladium catalyst. In the presence of 10 mol%  $[\text{Pd}(\text{PPh}_3)_4]$  the reaction gave **2** in 37% yield (Entry 7). Increase of  $[\text{Pd}(\text{PPh}_3)_4]$  to 20 mol% further enhanced the product yield (48%), but using 50 mol%  $[\text{Pd}(\text{PPh}_3)_4]$  led to the complete decomposition of the product (Entries 8 and 9). Further improvement of the yield (61%) was established by the reaction with 1-bromoazulene **1b**<sup>16</sup> (Entry 10). The higher yield of the product might be attributed to the higher stability of **1b** under the reaction conditions than that of **1a**. In these investigations, a catalytic system using 20 mol%  $[\text{Pd}(\text{PPh}_3)_4]/\text{K}_2\text{CO}_3/\text{ferrocene}$  was found

to be the best condition with respect to the product yield of the homo-coupling reaction.

**Table 1** Palladium-catalyzed synthesis of 1,2'-biazulenes **2**.

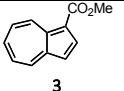
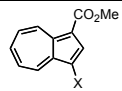
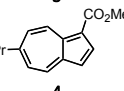
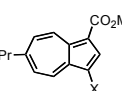
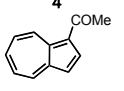
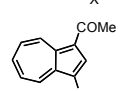
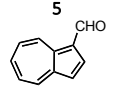
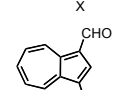
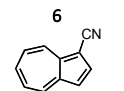
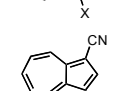
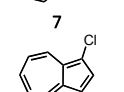
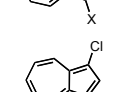
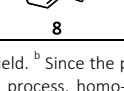
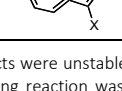
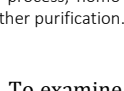
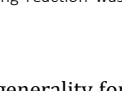
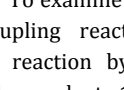
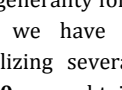
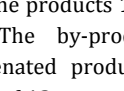
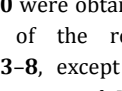
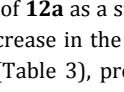
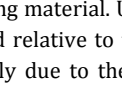
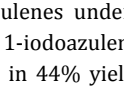
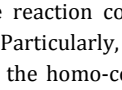
Entry	X	$[\text{Pd}(\text{PPh}_3)_4]$	additive	Yield [%]
1	I	10 mol%	0.5 eq. 1,1'-ferrocenediboronic acid	11
2	I	10 mol%	None	No reaction
3 <sup>a</sup>	I	None	1 eq. 1,1'-ferrocenediboronic acid	No reaction
4	I	None	1 eq. 1,1'-ferrocenediboronic acid	No reaction
5 <sup>a</sup>	I	10 mol%	1 eq. 1,1'-ferrocenediboronic acid	No reaction
6	I	5 mol%	1 eq. ferrocene	9
7	I	10 mol%	1 eq. ferrocene	37
8	I	20 mol%	1 eq. ferrocene	48
9	I	50 mol%	1 eq. ferrocene	Decomp.
10	Br	20 mol%	1 eq. ferrocene	61

<sup>a</sup> Reaction was performed in the absence of  $\text{K}_2\text{CO}_3$ .

Having optimized the reaction conditions as shown in Table 1, we have examined the scope of the homo-coupling reaction. For the investigation, we have prepared several 1-iodo- and 1-bromoazulenes, respectively (see experimental details in the Supporting Information). The results obtained for the reaction of azulene derivatives **3–8** with *N*-bromosuccinimide (NBS) or *N*-chlorosuccinimide (NCS) and NaI are summarized in Table 2. Iodination of azulene derivatives at the 1- and/or 3-positions are usually carried out by the reaction with *N*-iodosuccinimide (NIS). Since NIS is a rather expensive reagent, we have examined a new iodination procedure, which we have previously developed, by using NCS and NaI, to prepare the 1-iodoazulene derivatives **9a–14a**.<sup>17</sup> Thus, the reaction of azulenes with NCS/NaI in acetic acid at room temperature afforded the presumed 1-iodoazulenes **9a–12a** in 26–88% yields (Table 2). Low yield of **12a** might be attributable to the low reactivity of **6** toward ICl, the presumed reactive species in the NCS/NaI system, since **12a** has been prepared by Hafner and Elwahy by the reaction with NIS in 85% yield.<sup>18</sup> The reaction of **8** resulted in the decomposition due to the instability of **14a** under the conditions. However, no reaction of **7** was observed in the same conditions.<sup>18</sup> 1-Bromoazulenes **9b–14b** were prepared by the reaction of the corresponding azulenes **3–8** with NBS (Table 2).

**Table 2** Synthesis of 1-iodo- and 1-bromoazulenes.

Entry	Substrate	Product	Yield [%] <sup>a</sup>
	<b>3–8</b>	<b>9a–14a</b>	
	<b>3–8</b>	<b>9b–14b</b>	

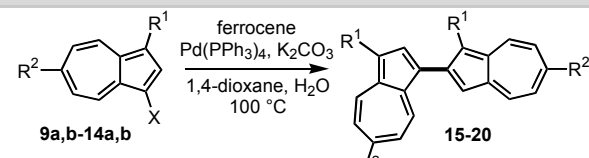
1			<b>9a</b> <sup>19</sup> (X = I), 88
2			<b>9b</b> <sup>20</sup> (X = Br), 99
3			<b>10a</b> (X = I), 87
4			<b>10b</b> (X = Br), 62
5			<b>11a</b> (X = I), 55
6			<b>11b</b> <sup>16b, 21</sup> (X = Br), 59
7			<b>12a</b> <sup>22</sup> (X = I), 26
8			<b>12b</b> <sup>23</sup> (X = Br), 82
9			<b>13a</b> (X = I), 0
10			<b>13b</b> <sup>17, 24</sup> (X = Br), 96
11			<b>14a</b> <sup>25</sup> (X = I), <sup>-b</sup>
12			<b>14b</b> <sup>26</sup> (X = Br), <sup>-b</sup>

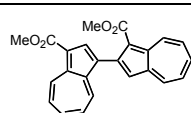
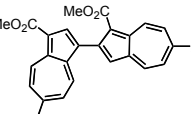
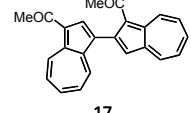
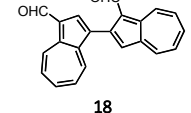
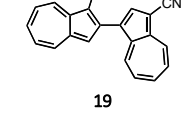
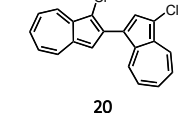
<sup>a</sup> Isolated yield. <sup>b</sup> Since the products were unstable and readily decomposed in the purification process, homo-coupling reaction was carried out using **14a** and **14b** without further purification.

To examine the generality for the palladium-catalyzed homo-coupling reaction, we have established the homo-coupling reaction by utilizing several 1-haloazulenes **9a,b–14a,b**. The products **15–20** were obtained in moderate to good yields. The by-product of the reaction was only the dehalogenated products **3–8**, except for the homo-coupling reaction of **12a** as a starting material. Using the bromides led to slight increase in the yield relative to that carried out with the iodides (Table 3), probably due to the chemical stability of 1-bromoazulenes under the reaction conditions compared with that of 1-iodoazulenes. Particularly, 1,2'-biazulene **18** was obtained in 44% yield by the homo-coupling of **12b**, although the reaction of **12a** led to the complete decomposition (entries 7 and 8). 1-Haloazulenes **14a** and **14b** reacted to give homo-coupling product **20** (from **14a**: 12%, from **14b**: 17%), in which the chlorine substituent retained at the 3-position (entries 10 and 11). Thus, the chlorine moiety should be inert to the homo-coupling reaction, in contrast to the bromine and iodine substituents. The substrate **21** possessing sterically bulky *tert*-butyl groups at the 1,6-positions afforded a mixture of 1,2'-biazulene **22** and 1,1'-biazulene **23** (18%, **22** : **23** = 1 : 1) (Scheme 2).<sup>27</sup> Formation of the 1,1'-biazulene **23** might indicate that bulky *tert*-butyl group at the 1-position prevents the 1,2-type homo-coupling, since the generation of 1,1'-biazulenes were not observed in the reaction of **9a,b–14a,b**.

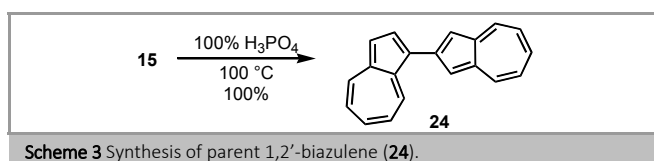
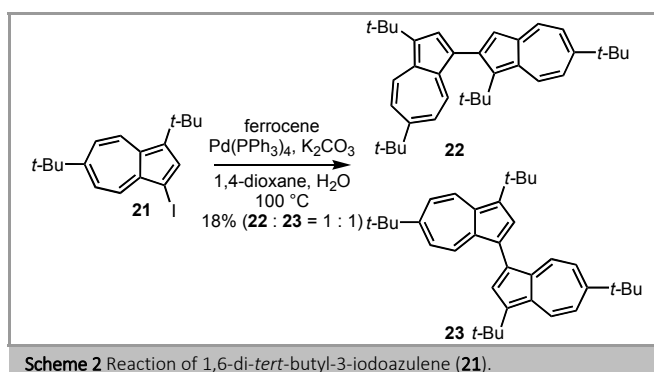
To further evaluate this new methodology, we have attempted the conversion of **15** into the parent 1,2'-biazulene **24**<sup>9</sup> (Scheme 3). Thus, the synthesis of **24** was established by the removal of the two ester functions from **24** by heating in 100% H<sub>3</sub>PO<sub>4</sub> in quantitative yield (100%). Compound **24** could be further functionalized by electrophilic substitution likewise a 1,6'-biazulene,<sup>8b</sup> because 1,3-positions of azulene derivative are the most reactive site toward the electrophilic reactions.

**Table 3** Synthesis of 1,2'-biazulenes from 1-haloazulenes.



Entry	Substrate	Product	Yield [%] <sup>a</sup>
1	<b>9a</b>		19
2	<b>9b</b>	<b>15</b>	56
3	<b>10a</b>		35
4	<b>10b</b>	<b>16</b>	42
5	<b>11a</b>		21
6	<b>11b</b>	<b>17</b>	24
7	<b>12a</b>		0
8	<b>12b</b>	<b>18</b>	44
9	<b>13b</b>		14
10	<b>14a</b>		12
11	<b>14b</b>	<b>20</b>	17

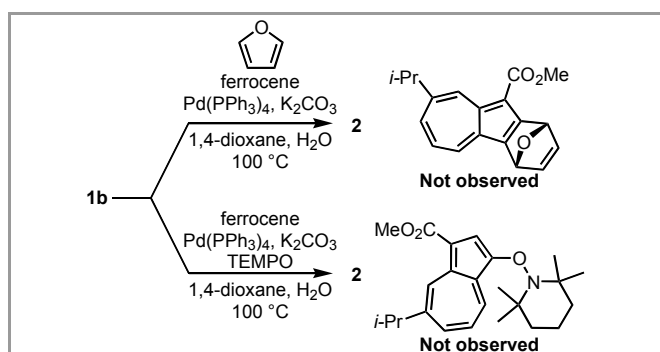
<sup>a</sup> Isolated yield.



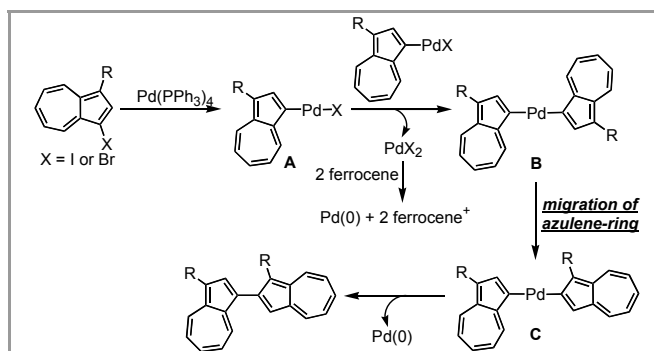
Since we have predicted the homo-coupling reaction proceed via azulene<sup>28</sup> or a radical mechanism as a reactive intermediate, the reaction was performed in the presence of

furan and 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as scavengers to investigate the reaction mechanism (Scheme 4). However, contrary to our prediction, only the 1,2'-biazulene **2** was obtained instead of the addition products.

Palladium-catalyzed homo-coupling reaction of aryl halides in the presence of a reducing agent, such as Cu powder, zinc dust and molecular hydrogen, to give biaryl compounds has been previously well-documented in the literatures.<sup>29</sup> Formic acid derivatives, 2-propanol, ascorbic acid,<sup>30</sup> and even other organic solvents<sup>31</sup> are used as milder reducing agents. Homo-coupling of aryl bromides and iodides has also been established by the palladium-catalyzed, fluoride-mediated reaction conditions.<sup>32</sup> In our cases the homo-coupling reaction catalyzed by palladium catalyst should require regeneration of the active metal catalyst in the zero oxidation state in the catalytic cycle. Thus, the ferrocenes act as a milder reducing agent that allows the second oxidative addition of 1-haloazulenes to the metal catalyst. Thus, we have supposed the reaction mechanisms, which include migration of azulene ring on the palladium atom as shown in Scheme 5. The catalytic cycle should involve homo-coupling of the 1-azulenylhalopalladium(II) species **A** formed by the oxidative addition of 1-haloazulenes to the palladium(0) species to form a symmetrically substituted di(1-azulenyl)palladium(II) species **B**. In this step Pd(II)X<sub>2</sub> should also be produced, which have to be reduced to palladium(0) species to form the catalytic cycle. Since the ferrocene is recovered almost quantitatively after the usual workup process, the catalytic cycle in the ferrocene/ferrocenium couple is also formed during the reaction. The high electron density on the 1-position of the substituted two azulene units may cause the migration of an azulene ring at the 2-position to give the palladium(II) species **C**. This would be consistent to the observation of the homo-coupling reaction of 1-haloazulene **21** with *tert*-butyl substituent at the 3-position, which may prevent the migration of the azulene ring at the 2-position, to form a symmetrical 1,1'-biazulene **23** in addition to the unsymmetrically substituted 1,2'-biazulene **22**.



Scheme 4 An attempt to trap the reactive intermediate by furan and TEMPO.



Scheme 5 Presumed reaction mechanism for the generation of 1,2'-biazulenes; PPh<sub>3</sub> ligands on Pd are omitted for clarity.

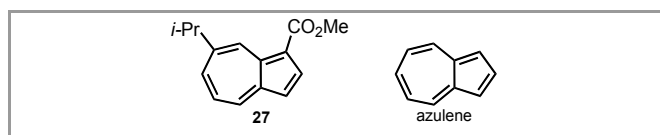
These new 1,2'-biazulene derivatives **2**, **15–20** and **24** were fully characterized by spectral data. The <sup>1</sup>H NMR spectroscopic assignment of the new compounds was confirmed by COSY experiments. Mass spectra of these compounds ionized by MALDI-TOF showed the correct molecular ion peaks. The characteristic stretching vibration band of the carbonyl groups of **2** and **15–18** was observed at  $\nu_{\max} = 1634\text{--}1688\text{ cm}^{-1}$  in their IR spectra. Compound **19** also exhibited a characteristic C≡N stretching band at  $\nu_{\max} = 2198\text{ cm}^{-1}$  on the IR spectrum. These results are consistent with the given structure of these products.

UV/Vis spectra of 1,2'-biazulenes **2**, **15–20** and **24**, as well as those of methyl 1-azulenecarboxylate **27**, azulene derivatives **3–8** and parent azulene, are shown in the Supporting Information. The absorption maxima and coefficients (log  $\epsilon$ ) of these compounds in CH<sub>2</sub>Cl<sub>2</sub> are summarized in Table 4. UV/Vis spectra of 1,2'-biazulenes **2**, **15–20** and **24** exhibited characteristic weak absorption bands arising from the azulene system in the visible region. The longest wavelength absorption maxima of **2**, **15–20** and **24** was almost equal to those of the corresponding azulenes **27**, **3–8** and parent azulene, although the extinction coefficients increased with the number of azulene rings substituted (Table 4). These results show less effective extension of the  $\pi$ -system in the biazulene structure probably due to the low planarity of the connected two-azulene rings. 1,2'-Biazulenes **2**, **15–20** and **24** also displayed relatively strong absorptions at around  $\lambda_{\max} = 420\text{--}460\text{ nm}$ , which may be attributable to intramolecular charge transfer (ICT) between the two-azulene rings, because these bands were not observed in those of the azulene derivatives **27**, **3–8** and parent azulene.

Table 4 Absorption maxima [nm]<sup>a</sup> and their coefficients (log  $\epsilon$ ) in visible region of 1,2'-biazulenes **2**, **15–20** and **24**, and the corresponding azulene derivatives in CH<sub>2</sub>Cl<sub>2</sub>.

Sample	$\lambda_{\max}$ (log $\epsilon$ )	Sample	$\lambda_{\max}$ (log $\epsilon$ )
<b>27</b>	540 (2.75)	<b>2</b>	438 (4.22), 538 sh (3.27), 565 sh (3.27)
<b>3</b>	536 (2.65)	<b>15</b>	428 (4.14), 538 (3.12), 565 sh (3.11)
<b>4</b>	521 (2.70)	<b>16</b>	432 (4.13), 525 (3.17), 552 sh (3.16)
<b>5</b>	538 (2.73)	<b>17</b>	394 sh (4.15), 433 sh (4.04), 552 (3.12)
<b>6</b>	533 (2.60)	<b>18</b>	440 sh (4.04), 534 (3.17), 557 sh (3.16)
<b>7</b>	544 (2.84)	<b>19</b>	422 sh (4.20), 444 sh (4.22), 541 sh (3.10), 563 (3.11)
<b>8</b>	599 (2.59)	<b>20</b>	447 (4.18), 601 (2.95)
azulene <sup>8a</sup>	576 (2.52)	<b>24</b>	446 (4.36), 463 (4.37), 564 (3.07), 605 (3.03), 665 sh (2.75)

<sup>a</sup> sh = shoulder peak



**Figure 1** Structure of methyl 1-azulenecarboxylate **27** and parent azulene.

To examine the theoretical aspects of the spectroscopic properties, time-dependent density functional theory (TD-DFT) calculations at the B3LYP/6-31G\*\* level<sup>33</sup> were carried out on azulene derivatives **3** and **8**, and the corresponding 1,2'-biazulenenes **15** and **20** as model compounds. The frontier Kohn-Sham orbitals of these compounds are shown in the Supporting Information. The calculations revealed that the longest wavelength absorption band of **3** and **8** in the visible region could be assigned as normal orbital types of HOMO → LUMO transition of the parent azulene<sup>34</sup> (Figures S-26 and S-27 in the Supporting Information). The relatively weak absorption bands at around  $\lambda_{\text{max}} = 540\text{--}600$  nm of **15** and **20** were confirmed to arise from the overlap of the  $\pi\text{-}\pi^*$  transitions of substituted azulene-rings themselves as shown in Table 5. The strong absorption band at  $\lambda_{\text{max}} = 428$  nm of **15** should be considered as the transition from the HOMO, that is mainly located on the 1-azulenyl group, to the LUMO, that is located on the azulene ring substituted by 2-position (Figure S-28). The calculation also revealed the contribution of transition between HOMO-1, which located on 2-azulenyl moiety, and LUMO+1, which located on 1-azulenyl moiety, is relatively low with respect to the oscillator strength. Thus, the absorption band could be assumed as the ICT from 1-azulenyl moiety to 2-azulenyl group. Similar with those of **15** the absorption maxima of **20** at  $\lambda_{\text{max}} = 447$  nm could be assigned to the transitions, which originated from the HOMO and HOMO-1 to the LUMO. Thus, the absorption band of **20** could be concluded to the ICT between 1-azulenyl moiety and 2-azulenyl group (HOMO → LUMO) in addition to  $\pi\text{-}\pi^*$  transition of 2-azulenyl moiety itself (HOMO-1 → LUMO) (Figure S-28).

**Table 5** Electronic transitions for azulenes **3** and **8**, and 1,2'-biazulenenes **15** and **20** derived from the computed values based on the B3LYP/6-31G\*\* method and experimental values

Sample	Experimental $\lambda_{\text{max}}$ (log $\epsilon$ )	Computed value $\lambda_{\text{max}}$ (strength)	Composition of band (amplitude)
<b>3</b>	536 (2.65)	485 (0.0093)	H → L (0.9703)
<b>8</b>	599 (2.59)	533 (0.0120)	H → L (0.9770)
<b>15</b>	428 (4.14)	426 (0.0001)	H-1 → L+1 (0.9908)
		440 (0.2592)	H → L (0.8949)
	538 (3.12)	483 (0.0211)	H-1 → L (0.8961)
			H → L (0.3121)
<b>20</b>	565 sh (3.11)	517 (0.0073)	H → L+1 (0.9668)
	447 (4.18)	458 (0.3934)	H-1 → L (0.2308)
			H → L (0.6805)
		489 (0.0009)	H-1 → L (0.6059)
		H-1 → L+1 (0.7749)	
	601 (2.95)	541 (0.0116)	H-1 → L (0.7312)
		578 (0.0092)	H → L (0.6374)
			H → L+1 (0.7319)

<sup>a</sup> H = HOMO, L = LUMO

To clarify the electrochemical properties, the redox behavior of 1,2'-biazulenenes **2**, **15–20** and **24** was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV).<sup>35</sup> The redox potentials (in V vs. Ag/AgNO<sub>3</sub>) of these compounds measured at a scan rate of 100 mVs<sup>-1</sup> are

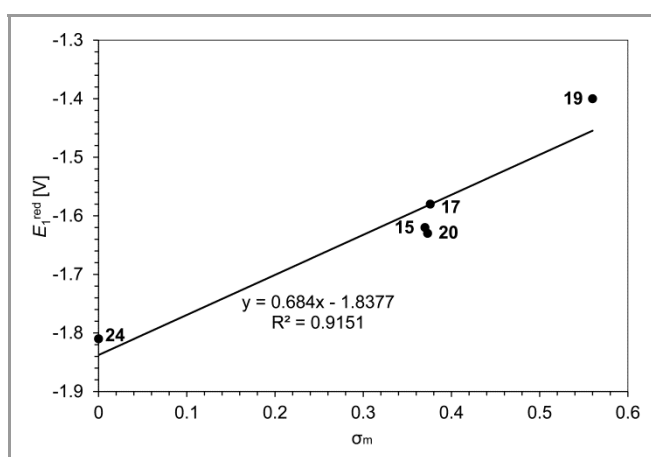
summarized in Table 6. The voltammograms of 1,2'-biazulenenes **2**, **15–20** and **24** measured by CV and DPV are summarized in the Supporting Information.

**Table 6** Redox potentials<sup>a,b</sup> of 1,2'-biazulenenes **2**, **15–20** and **24**.

Sample	Method	$E_1^{\text{ox}}$ [V]	$E_1^{\text{red}}$ [V]	$E_2^{\text{red}}$ [V]
<b>2</b>	CV	+0.83 ( $E_{\text{pa}}$ )	-1.71 ( $E_{\text{pc}}$ )	
	(DPV)	(+0.70)	(-1.65)	(-2.06)
<b>15</b>	CV	+0.85 ( $E_{\text{pa}}$ )	-1.62 ( $E_{\text{pc}}$ )	
	(DPV)	(+0.77)	(-1.59)	(-2.00)
<b>16</b>	CV	+0.79 ( $E_{\text{pa}}$ )	-1.77 ( $E_{\text{pc}}$ )	
	(DPV)	(+0.70)	(-1.71)	(-2.00)
<b>17</b>	CV	+0.90 ( $E_{\text{pa}}$ )	-1.58 ( $E_{\text{pc}}$ )	
	(DPV)	(+0.83)	(-1.53)	(-1.95)
<b>18</b>	CV	+0.95 ( $E_{\text{pa}}$ )	-1.50 ( $E_{\text{pc}}$ )	
	(DPV)	(+0.87)	(-1.42)	(-1.81)
<b>19</b>	CV	+1.02 ( $E_{\text{pa}}$ )	-1.40 ( $E_{\text{pc}}$ )	
	(DPV)	(+0.96)	(-1.35)	(-1.83)
<b>20</b>	CV	+0.70 ( $E_{\text{pa}}$ )	-1.63 ( $E_{\text{pc}}$ )	
	(DPV)	(+0.63)	(-1.60)	
<b>24</b>	CV	+0.52 ( $E_{\text{pa}}$ )	-1.81 ( $E_{\text{pc}}$ )	
	(DPV)	(+0.68)	(-1.76)	

<sup>a</sup> V vs. Ag/AgNO<sub>3</sub>, 1 mM in benzonitrile containing Et<sub>4</sub>NClO<sub>4</sub> (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate: 100 mVs<sup>-1</sup>, and internal reference Fc/Fc<sup>+</sup> = +0.15 V. The peak potentials ( $E_{\text{pa}}$  and  $E_{\text{pc}}$ ) measured by CV are presented. The peak potentials measured by DPV are shown in parentheses.

The oxidation and reduction waves of 1,2'-biazulene derivatives **2**, **15–20** and **24** were irreversible as measured by CV (see the Supporting Information). These results suggest the generation of unstable radical cationic and anionic species of **2**, **15–20** and **24** under the electrochemical conditions. The first reduction potential ( $E_{\text{pc}}$ ) measured by CV of 1,2'-biazulenenes **2**, **15–20** and **24** exhibited a good correlation of Hammett substitution constants  $\sigma_m$ <sup>36</sup> as shown in Figure 2, although the constants is defined by substituent on benzene-ring.<sup>37,38</sup> These results indicate that the first reduction potential of 1,2'-biazulenenes is directly affected by the substituent on 3- and 1'-positions in dependence on the Hammett substitution constants  $\sigma_m$ . The first reduction potential of **15** was observed noble side compared to that of isopropyl derivatives **2** and **16**, accompanying with the shift of the first oxidation potential to a more noble potential. This indicates that isopropyl group in **2** and **16** increases both HOMO and LUMO levels by its electron-donating nature.



**Figure 2** Correlation between Hammett substitution constants  $\sigma_m$  and the first reduction potentials  $E_1^{\text{red}}$  ( $E_{\text{pc}}$ )

In conclusion, we have described palladium-catalyzed, ferrocene-mediated synthesis of 1,2'-biazulene derivatives **2** and **15–20** with substituent on each azulene ring, which are usually difficult to prepare. Parent 1,2'-biazulene (**24**) was also prepared by the treatment of **15** with 100% H<sub>3</sub>PO<sub>4</sub> in quantitative yield. The substituent effect at the 3- and 1'-positions on 1,2'-biazulene derivatives was discussed by UV/Vis spectra, theoretical calculations and voltammetry experiments. These results revealed the effect of the substituent on 3- and 1'-positions to the optical and electrochemical properties of these compounds.

To evaluate the scope of this class of molecules investigated by this research, reactivity of the reported 1,2'-biazules are currently under investigation in our laboratory.

## Procedures

**General:** Melting points were determined with a Yanagimoto MPS3 micromelting apparatus, and the recrystallization solvent of the compounds was shown in the parenthesis. The HRMS data were obtained with a JEOL JMS-700 or Bruker Daltonics autoflex III TOF/TOF instrument. The IR and UV/Vis spectra were recorded with JASCO FTIR-4100 and Shimadzu UV-2550 spectrophotometers. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a JEOL ECA500 spectrometer at 500 and 125 MHz, respectively, or a JEOL LA400 spectrometer at 400 and 100 MHz, respectively.

### 1,2'-Bis(5-isopropyl-3-methoxycarbonyl)azulene (**2**):

**Reaction with 1-iodoazulene 1a:** To a solution of **1a** (182 mg, 0.514 mmol), ferrocene (94 mg, 0.505 mmol), and K<sub>2</sub>CO<sub>3</sub> (277 mg, 2.00 mmol) in 1,4-dioxane (5 mL) and H<sub>2</sub>O (0.5 mL) was added [Pd(PPh<sub>3</sub>)<sub>4</sub>] (116 mg, 0.100 mmol). The resulting mixture was stirred at 100 °C for 16 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4 : 1) to give **2** (56 mg 48%) as brown crystals.

**Reaction with 1-bromoazulene 1b:** To a solution of **1b** (162 mg, 0.527 mmol), ferrocene (98 mg, 0.527 mmol), and K<sub>2</sub>CO<sub>3</sub> (277 mg, 2.00 mmol) in 1,4-dioxane (5 mL) and H<sub>2</sub>O (0.5 mL) was added [Pd(PPh<sub>3</sub>)<sub>4</sub>] (117 mg, 0.101 mmol). The resulting mixture was stirred at 100 °C for 19 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4 : 1) to give **2** (73 mg 61%) as brown crystals. M.p. 75–78 °C (hexane/AcOEt); IR (KBr disk): ν<sub>max</sub> = 2959 (w), 1686 (s), 1575 (w), 1524 (m), 1485 (w), 1442 (s), 1417 (m), 1380 (m), 1335 (w), 1294 (w), 1264 (w), 1213 (s), 1168 (m), 1128 (m), 1058 (m), 1017 (m), 933 (w), 898 (m), 878 (w), 849 (w), 825 (m), 805 (m), 777 (m), 732 (m), 678 (w) cm<sup>-1</sup>; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 242 (4.60), 292 (4.72), 310 (4.69), 347 (4.46), 438 (4.22), 538 sh (3.27), 565 sh (3.27), 621 sh (2.99) nm; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 9.81 (d, 1H, J = 1.5 Hz, H8), 9.81 (d, 1H, J = 1.5 Hz, H8'), 8.54 (s, 1H, H2), 8.49 (d, 1H, J = 10.0 Hz, H4), 8.27 (d, 1H, J = 10.0 Hz, H4'), 7.73 (d, 1H, J = 10.0 Hz, H6), 7.67 (d, 1H, J = 10.0 Hz, H6'), 7.38 (dd, 1H, J = 10.0, 10.0 Hz, H5), 7.34 (dd, 1H, J = 10.0, 10.0 Hz, H5'), 3.98 (s, 3H, CO<sub>2</sub>Me), 3.60 (s, 3H, CO<sub>2</sub>Me), 3.27–3.21 (m, 2H, iPr), 1.45 (d, 12H, J = 6.5 Hz, iPr) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> = 166.79, 166.12, 149.48, 149.19, 148.17, 142.83, 142.47, 142.40, 142.25, 141.25, 138.49, 137.94, 136.84, 136.72, 135.72, 135.18, 127.27, 126.97, 126.01, 119.65, 114.86, 113.98, 51.16, 50.85, 39.43, 39.20, 24.80, 24.74 ppm; HRMS (MALDI-TOF): Calcd for C<sub>30</sub>H<sub>30</sub>O<sub>4</sub><sup>+</sup> [M]<sup>+</sup>, 454.2139; Found: 454.2143.

### 1,2'-Bis(3-methoxycarbonyl)azulene (**15**):

**Reaction with 1-iodoazulene 9a:** To a solution of **9a** (317 mg, 1.02 mmol), ferrocene (187 mg, 1.00 mmol), and K<sub>2</sub>CO<sub>3</sub> (557 mg, 4.03 mmol) in 1,4-dioxane (5 mL) and H<sub>2</sub>O (0.5 mL) was added [Pd(PPh<sub>3</sub>)<sub>4</sub>] (232 mg, 2.01 mmol). The resulting mixture was stirred at 100 °C for 16 h under an Ar

atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4 : 1) to give **15** (35 mg 19%) as brown crystals.

**Reaction with 1-bromoazulene 9b:** To a solution of **9b** (405 mg, 1.53 mmol), ferrocene (288 mg, 1.55 mmol), and K<sub>2</sub>CO<sub>3</sub> (850 mg, 6.15 mmol) in 1,4-dioxane (5 mL) and H<sub>2</sub>O (0.5 mL) was added [Pd(PPh<sub>3</sub>)<sub>4</sub>] (360 mg, 0.312 mmol). The resulting mixture was stirred at 100 °C for 22 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4 : 1) to give **15** (157 mg, 56%) as brown crystals. M.p. 162–163 °C (hexane/AcOEt); IR (KBr disk): ν<sub>max</sub> = 2945 (w), 1685 (s), 1574 (w), 1523 (m), 1493 (m), 1439 (m), 1414 (m), 1393 (m), 1380 (m), 1334 (w), 1309 (w), 1281 (w), 1219 (s), 1199 (s), 1161 (m), 1142 (m), 1105 (w), 1038 (m), 1018 (m), 944 (w), 926 (w), 867 (m), 838 (w), 791 (w), 774 (m), 745 (m), 734 (m), 672 (w) cm<sup>-1</sup>; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 236 (4.55), 288 (4.69), 307 (4.66), 345 sh (4.39), 428 (4.14), 538 (3.12), 565 sh (3.11), 621 sh (2.78) nm; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 9.70 (d, 1H, J = 10.0 Hz, H8), 9.50 (d, 1H, J = 10.0 Hz, H8'), 8.58 (d, 1H, J = 10.0 Hz, H4), 8.58 (s, 1H, H2), 8.39 (d, 1H, J = 10.0 Hz, H4'), 7.78 (dd, 1H, J = 10.0, 10.0 Hz, H6), 7.74 (dd, 1H, J = 10.0, 10.0 Hz, H6'), 7.56 (dd, 1H, J = 10.0, 10.0 Hz, H7), 7.55 (dd, 1H, J = 10.0, 10.0 Hz, H7'), 7.43 (dd, 1H, J = 10.0, 10.0 Hz, H5'), 7.40 (dd, 1H, J = 10.0, 10.0 Hz, H5), 3.98 (s, 3H, CO<sub>2</sub>Me), 3.60 (s, 3H, CO<sub>2</sub>Me) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> = 166.53, 165.91, 147.87, 142.91, 142.32, 142.12, 141.34, 139.62, 138.10, 138.06, 137.39, 137.06, 136.96, 128.25, 128.15, 127.46, 127.23, 126.80, 120.80, 116.07, 115.38, 51.29, 50.99 ppm; HRMS (MALDI-TOF): Calcd for C<sub>24</sub>H<sub>18</sub>O<sub>4</sub><sup>+</sup> [M]<sup>+</sup>, 370.1200; Found: 370.1202.

### 1,2'-Bis(6-isopropyl-3-methoxycarbonyl)azulene (**16**):

**Reaction with 1-iodoazulene 10a:** To a solution of **10a** (185 mg, 0.522 mmol), ferrocene (97 mg, 0.521 mmol), and K<sub>2</sub>CO<sub>3</sub> (281 mg, 2.03 mmol) in 1,4-dioxane (5 mL) and H<sub>2</sub>O (0.5 mL) was added [Pd(PPh<sub>3</sub>)<sub>4</sub>] (116 mg, 0.100 mmol). The resulting mixture was stirred at 100 °C for 17 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4 : 1) to give **16** (41 mg, 35%) as brown crystals.

**Reaction with 1-bromoazulene 10b:** To a solution of **10b** (156 mg, 0.508 mmol), ferrocene (99 mg, 0.532 mmol), and K<sub>2</sub>CO<sub>3</sub> (284 mg, 2.04 mmol) in 1,4-dioxane (5 mL) and H<sub>2</sub>O (0.5 mL) was added [Pd(PPh<sub>3</sub>)<sub>4</sub>] (123 mg, 0.106 mmol). The resulting mixture was stirred at 100 °C for 16 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4 : 1) to give **16** (49 mg, 42%) as brown crystals. M.p. 78–81 °C (hexane/AcOEt); IR (KBr disk): ν<sub>max</sub> = 2961 (w), 1688 (s), 1581 (w), 1526 (w), 1487 (w), 1439 (s), 1419 (m), 1378 (m), 1324 (w), 1288 (w), 1253 (w), 1204 (s), 1112 (w), 1056 (m), 1018 (w), 988 (w), 919 (w), 902 (w), 848 (m), 796 (w), 775 (w), 735 (w), 701 (w), 673 (w) cm<sup>-1</sup>; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 234 (4.46), 294 (4.67), 314 (4.68), 348 sh (4.40), 432 (4.13), 525 (3.17), 552 sh (3.16) nm; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 9.61 (d, 1H, J = 10.5 Hz, H4), 9.43 (d, 1H, J = 10.5 Hz, H4'), 8.53 (d, 1H, J = 10.5 Hz, H8), 8.48 (s, 1H, H2), 8.33 (d, 1H, J = 10.5 Hz, H8'), 7.50 (d, 2H, J = 10.5 Hz, H5,5'), 7.38 (d, 1H, J = 10.5 Hz, H7'), 7.34–7.33 (m, 2H, H7 and H1'), 3.97 (s, 3H, CO<sub>2</sub>Me), 3.61 (s, 3H, CO<sub>2</sub>Me), 3.19–3.09 (m, 2H, iPr), 1.40 (d, 6H, J = 7.0 Hz, iPr), 1.37 (d, 6H, J = 7.0 Hz, iPr) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> = 166.67, 166.07, 162.16, 160.44, 146.94, 141.68, 141.15, 141.10, 140.82, 140.11, 137.72, 137.12, 136.63, 127.34, 126.76, 126.72, 126.55, 120.49, 115.72, 115.01, 51.17, 50.87, 39.79, 39.76, 24.43, 24.37 ppm. Two signals are overlapped with other signals; HRMS (MALDI-TOF): Calcd for C<sub>30</sub>H<sub>30</sub>O<sub>4</sub><sup>+</sup> [M]<sup>+</sup>, 454.2139; Found: 454.2122.

### 1,2'-Bis(3-acetyl)azulene (**17**):

**Reaction with 1-iodoazulene 11a:** To a solution of **11a** (139 mg, 0.469 mmol), ferrocene (93 mg, 0.500 mmol), and  $K_2CO_3$  (272 mg, 1.97 mmol) in 1,4-dioxane (5 mL) and  $H_2O$  (0.5 mL) was added  $[Pd(PPh_3)_4]$  (107 mg, 0.0926 mmol). The resulting mixture was stirred at 100 °C for 20 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with  $Na_2SO_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4 : 1) to give **17** (17 mg, 21%) as brown crystals.

**Reaction with 1-bromoazulene 11b:** To a solution of **11b** (91 mg, 0.365 mmol), ferrocene (73 mg, 0.392 mmol), and  $K_2CO_3$  (205 mg, 1.48 mmol) in 1,4-dioxane (5 mL) and  $H_2O$  (0.5 mL) was added  $[Pd(PPh_3)_4]$  (86 mg, 0.0744 mmol). The resulting mixture was stirred at 100 °C for 16 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with  $Na_2SO_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (4 : 1) to give **17** (15 mg, 24%) as brown crystals. M.p. 171–172 °C ( $CH_2Cl_2/EtOH$ ); IR (KBr disk):  $\nu_{max}$  = 2924 (w), 2854 (w), 1634 (s), 1590 (w), 1574 (m), 1531 (m), 1507 (w), 1486 (w), 1449 (m), 1416 (s), 1391 (s), 1376 (s), 1284 (m), 1225 (m), 1208 (m), 1096 (w), 1016 (m), 996 (m), 918 (m), 889 (m), 873 (m), 832 (m), 803 (m), 754 (s), 707 (m), 694 (m), 679 (m), 664 (m)  $cm^{-1}$ ; UV/Vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (log  $\epsilon$ ) = 236 (4.56), 270 sh (4.46), 296 (4.67), 313 (4.68), 352 (4.34), 394 sh (4.15), 433 sh (4.04), 552 (3.12) nm;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta_H$  = 9.98 (d, 1H,  $J$  = 10.0 Hz, H4), 9.45 (d, 1H,  $J$  = 10.0 Hz, H4'), 8.60 (d, 1H,  $J$  = 10.0 Hz, H8), 8.45 (d, 1H,  $J$  = 10.0 Hz, H8'), 8.42 (s, 1H, H2), 7.88 (dd, 1H,  $J$  = 10.0, 10.0 Hz, H6), 7.79 (dd, 1H,  $J$  = 10.0, 10.0 Hz, H6'), 7.68 (dd, 1H,  $J$  = 10.0, 10.0 Hz, H5), 7.60 (dd, 1H,  $J$  = 10.0, 10.0 Hz, H5'), 7.49 (dd, 1H,  $J$  = 10.0, 10.0 Hz, H7'), 7.48 (dd, 1H,  $J$  = 10.0, 10.0 Hz, H7), 7.42 (s, 1H, H1'), 2.77 (s, 3H, COMe), 2.01 (s, 3H, COMe) ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta_C$  = 198.97, 195.62, 147.11, 142.68, 141.96, 141.36, 140.87, 140.80, 140.54, 138.71, 137.89, 137.48, 130.26, 129.14, 128.62, 127.41, 126.78, 126.72, 124.72, 120.62, 31.19, 29.40 ppm. Two peaks are overlapped with other signals; HRMS (MALDI-TOF): Calcd for  $C_{24}H_{18}O_2^+$  [ $M$ ] $^+$ , 338.1301; Found: 338.1284.

**1,2'-Bis(3-formyl)azulene (18):** To a solution of **12b** (237 mg, 1.01 mmol), ferrocene (187 mg, 1.01 mmol), and  $K_2CO_3$  (556 mg, 4.02 mmol) in 1,4-dioxane (5 mL) and  $H_2O$  (0.5 mL) was added  $[Pd(PPh_3)_4]$  (240 mg, 0.208 mmol). The resulting mixture was stirred at 100 °C for 43 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with  $Na_2SO_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with  $CH_2Cl_2/AcOEt$  (10 : 1) to give **18** (68 mg, 44%) as brown crystals. M.p. 225–227 °C ( $EtOH$ ); IR (KBr disk):  $\nu_{max}$  = 2956 (w), 2923 (w), 2851 (w), 1641 (s), 1590 (w), 1577 (w), 1524 (m), 1507 (w), 1488 (w), 1453 (m), 1427 (s), 1411 (m), 1393 (s), 1374 (m), 1359 (m), 1313 (w), 1295 (m), 1280 (m), 1220 (w), 1155 (w), 1113 (w), 1094 (w), 1027 (w), 974 (w), 952 (w), 925 (w), 886 (w), 874 (w), 827 (w), 809 (m), 790 (w), 744 (s), 701 (w), 687 (w), 670 (w)  $cm^{-1}$ ; UV/Vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (log  $\epsilon$ ) = 269 sh (4.35), 296 (4.54), 317 (4.61), 359 (4.43), 440 sh (4.04), 534 (3.17), 557 sh (3.16), 610 sh (2.83) nm;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta_H$  = 10.46 (s, 1H, CHO), 10.26 (s, 1H, CHO), 9.84 (d, 1H,  $J$  = 10.0 Hz, H8), 9.76 (d, 1H,  $J$  = 10.0 Hz, H8'), 8.82 (d, 1H,  $J$  = 10.0 Hz, H4), 8.51 (d, 1H,  $J$  = 10.0 Hz, H4'), 8.47 (s, 1H, H2), 7.94 (t, 1H,  $J$  = 10.0 Hz, H6), 7.86 (t, 1H,  $J$  = 10.0 Hz, H6'), 7.74 (t, 1H,  $J$  = 10.0 Hz, H7'), 7.71 (t, 1H,  $J$  = 10.0 Hz, H7), 7.61 (t, 1H,  $J$  = 10.0 Hz, H5 or H5'), 7.59 (t, 1H,  $J$  = 10.0 Hz, H5 or H5') ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta_C$  = 188.20, 186.95, 150.66, 144.99, 144.86, 143.59, 141.92, 141.67, 141.21, 139.18, 138.91, 138.60, 138.16, 137.98, 131.10, 130.78, 129.65, 129.18, 125.67, 125.35, 122.37, 120.31 ppm; HRMS (MALDI-TOF): Calcd for  $C_{22}H_{14}O_2^+$  [ $M$ ] $^+$ , 310.0988; Found: 310.0993.

**1,2'-Bis(3-cyano)azulene (19):** To a solution of **13b** (117 mg, 0.504 mmol), ferrocene (96 mg, 0.516 mmol), and  $K_2CO_3$  (280 mg, 2.03 mmol) in 1,4-dioxane (5 mL) and  $H_2O$  (0.5 mL) was added  $[Pd(PPh_3)_4]$  (120 mg, 0.104 mmol). The resulting mixture was stirred at 100 °C for 16 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with  $Na_2SO_4$ , and concentrated under reduced pressure. The residue was

purified by column chromatography on silica gel with hexane/AcOEt (4 : 1) to give **19** (11 mg, 14%) as brown crystals. M.p. 274–276 °C (hexane); IR (KBr disk):  $\nu_{max}$  = 3089 (w), 2926 (w), 2198 (s), 1577 (w), 1530 (m), 1490 (w), 1452 (w), 1418 (s), 1372 (m), 1294 (w), 1223 (w), 1160 (w), 1107 (w), 1035 (w), 999 (w), 943 (w), 887 (w), 820 (m), 737 (s), 724 (s), 689 (m), 676 (m)  $cm^{-1}$ ; UV/Vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (log  $\epsilon$ ) = 233 (4.52), 274 sh (4.55), 281 (4.59), 313 (4.60), 340 (4.44), 422 sh (4.20), 444 sh (4.22), 541 sh (3.10), 563 (3.11), 624 sh (2.82) nm;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta_H$  = 8.95 (d, 1H,  $J$  = 10.0 Hz, H4), 8.77 (d, 1H,  $J$  = 10.0 Hz, H4'), 8.69 (d, 1H,  $J$  = 10.0 Hz, H8), 8.62 (s, 1H, H2), 8.46 (d, 1H,  $J$  = 10.0 Hz, H8'), 7.96 (dd, 1H,  $J$  = 10.0, 10.0 Hz, H6), 7.82 (dd, 1H,  $J$  = 10.0, 10.0 Hz, H6'), 7.66–7.52 (m, 5H, H5,7,1',5',7') ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta_C$  = 146.94, 145.37, 145.26, 142.89, 141.45, 140.91, 139.20, 138.89, 138.68, 137.73, 135.67, 129.01, 128.40, 128.35, 128.13, 124.64, 118.16, 117.68, 116.72, 98.94, 96.65 ppm. One signal was overlapped with other signals; HRMS (MALDI-TOF): Calcd for  $C_{22}H_{12}N_2^+$  [ $M$ ] $^+$ , 304.0995; Found: 304.0976.

### 1,2'-Bis(3-chloro)azulene (20):

**Reaction with 1-iodoazulene 14a:** To a solution of crude **14a** (279 mg, 0.996 mmol), ferrocene (190 mg, 1.02 mmol), and  $K_2CO_3$  (555 mg, 4.02 mmol) in 1,4-dioxane (5 mL) and  $H_2O$  (0.5 mL) was added  $[Pd(PPh_3)_4]$  (233 mg, 0.202 mmol). The resulting mixture was stirred at 100 °C for 21 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with  $Na_2SO_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (10 : 1) to give **20** (20 mg, 12%) as green crystals.

**Reaction with 1-bromoazulene 14b:** To a solution of crude **14b** (281 mg, 1.16 mmol), ferrocene (218 mg, 1.17 mmol), and  $K_2CO_3$  (647 mg, 4.68 mmol) in 1,4-dioxane (5 mL) and  $H_2O$  (0.5 mL) was added  $[Pd(PPh_3)_4]$  (267 mg, 0.231 mmol). The resulting mixture was stirred at 100 °C for 19 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with brine, dried with  $Na_2SO_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (10 : 1) to give **20** (32 mg, 17%) as green crystals. M.p. 138–140 °C ( $CH_2Cl_2/EtOH$ ); IR (KBr disk):  $\nu_{max}$  = 3022 (w), 2922 (w), 2851 (w), 1577 (s), 1538 (m), 1536 (m), 1523 (m), 1484 (m), 1482 (m), 1466 (w), 1434 (w), 1389 (s), 1356 (m), 1286 (m), 1259 (w), 1219 (w), 1170 (w), 1091 (w), 1029 (w), 927 (s), 888 (w), 867 (w), 862 (m), 820 (w), 785 (m), 741 (s), 726 (s), 716 (m), 713 (m), 681 (w), 657 (w)  $cm^{-1}$ ; UV/Vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (log  $\epsilon$ ) = 239 (4.47), 271 (4.60), 278 sh (4.58), 299 (4.50), 314 (4.63), 348 sh (4.23), 447 (4.18), 601 (2.95), 640 sh (2.91), 700 (2.59) nm;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta_H$  = 8.68 (d, 1H,  $J$  = 10.0 Hz, H4), 8.46–8.44 (m, 2H, H8,4'), 8.33 (s, 1H, H2), 8.25 (d, 1H,  $J$  = 10.0 Hz, H8'), 7.68 (dd, 1H,  $J$  = 10.0, 10.0 Hz, H6), 7.59 (dd, 1H,  $J$  = 10.0, 10.0 Hz, H6'), 7.55 (s, 1H, H1'), 7.30–7.19 (m, 4H, H5,7,5',7') ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta_C$  = 141.25, 139.97, 138.90, 137.44, 137.42, 136.41, 136.14, 135.52, 135.16, 133.45, 125.03, 124.33, 124.25, 123.99, 122.53, 117.59, 116.49, 114.91 ppm. Two signals are overlapped with other signals; HRMS (MALDI-TOF): Calcd for  $C_{20}H_{12}Cl_2^+$  [ $M$ ] $^+$ , 322.0311; Found: 322.0322.

**1,2'-Bis(3,6-di-tert-butyl)azulene (22) and 1,1'-bis(3,6-di-tert-butyl)azulene (23):** To a solution of **21** (183 mg, 0.50 mmol), ferrocene (93 mg, 0.50 mmol), and  $K_2CO_3$  (276 mg, 2.00 mmol) in 1,4-dioxane (5 mL) and  $H_2O$  (0.5 mL) was added  $[Pd(PPh_3)_4]$  (115 mg, 0.10 mmol). The resulting mixture was stirred at 100 °C for 14 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with hexane. The organic layer was washed with brine, dried with  $Na_2SO_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane to give a mixture of **22** and **23** (22 mg, 18%). HRMS (MALDI-TOF): Calcd for  $C_{36}H_{46}^+$  [ $M$ ] $^+$ , 478.3594; Found: 478.3613.

**1,2'-Biazulene (24):** A solution of **15** (100 mg, 0.270 mmol) in 100%  $H_3PO_4$  (15 mL) was stirred at 100 °C for 30 min. The reaction mixture was cooled, poured into water, and extracted with toluene. The organic layer was washed with brine, dried with  $Na_2SO_4$ , and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with toluene as an eluent to afford **24** (68 mg, 100%) as



green crystals. M.p. 146–147°C (CH<sub>2</sub>Cl<sub>2</sub>/MeOH), lit. 144–145 °C; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 236 (4.43), 267 (4.58), 312 (4.68), 446 (4.36), 463 (4.37), 564 (3.07), 605 (3.03), 665 sh (2.75) nm; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 9.07 (d, J = 10.0 Hz, 1H, H8), 8.35 (s, 1H, H2), 8.34 (d, J = 10.0 Hz, 1H, H4), 8.29 (d, J = 9.5 Hz, 2H, H4',8'), 7.76 (s, 2H, H1,3), 7.63 (t, J = 10.0 Hz, 1H, H6), 7.49 (d, J = 10.0 Hz, 1H, H5), 7.48 (d, J = 9.5 Hz, 1H, H6'), 7.28 (t, J = 10.0 Hz, 1H, H7), 7.21 (d, J = 4.0 Hz, 1H, H3), 7.18 (t, J = 9.5 Hz, 2H, H5',7') ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> = 146.72, 143.60, 141.33, 138.63, 138.55, 137.32, 136.30, 135.17, 134.60, 127.25, 124.50, 124.23, 123.85, 119.01, 116.55 ppm, One signal is overlapped with other signals.

## Acknowledgment

This work was supported by JSPS KAKENHI Grant Number 25810019, Grant-in-Aid for Young Scientists (B), to T.S.

## Supporting Information

YES (this text will be updated with links prior to publication)

## Primary Data

NO (this text will be deleted prior to publication)

## References

- Zeller, K.-P. *Azulene in Houben-Weyl: Methoden der Organischen Chemie*, 4th ed., ed. by Kropf, H. Georg Thieme, Stuttgart, **1985**, Vol. V, Part 2c, p. 127.
- (a) Kurihara, T.; Suzuki, T.; Wakabayashi, H.; Ishikawa, S.; Shindo, K.; Shimada, Y.; Chiba, H.; Miyashi, T.; Yasunami, M.; Nozoe, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2003. (b) Hünig, S.; Ort, B. *Liebigs Ann. Chem.* **1984**, 1959. (c) Hünig, S.; Ort, B. *Liebigs Ann. Chem.* **1984**, 1936.
- (a) Razus, A. C. *J. Chem. Soc., Perkin Trans. 1* **2000**, 981. (b) Razus, A. C.; Nitu, C. *J. Chem. Soc., Perkin Trans. 1* **2000**, 989. (c) Razus, A. C.; Nitu, C.; Carvacu, S.; Birzan, L.; Razus, S. A.; Pop, M.; Tarko, L. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1227. (d) Shoji, T.; Ito, S.; Toyota, K.; Yasunami, M.; Morita, N. *Tetrahedron Lett.* **2007**, *48*, 4999. (e) Shoji, T.; Higashi, J.; Ito, S.; Toyota, K.; Asao, T.; Yasunami, M.; Fujimori, K.; Morita, N. *Eur. J. Org. Chem.* **2008**, 1242. (f) Shoji, T.; Shimomura, E.; Inoue, Y.; Maruyama, M.; Yamamoto, A.; Fujimori, K.; Ito, S.; Yasunami, M.; Morita, N. *Heterocycles* **2013**, *87*, 303. (g) Shoji, T.; Maruyama, A.; Maruyama, M.; Ito, S.; Okujima, T.; Higashi, J.; Toyota, K.; Morita, N. *Bull. Chem. Soc. Jpn.* **2014**, *87*, 141.
- (a) Ito, S.; Terazono, T.; Kubo, T.; Okujima, T.; Morita, N.; Murafuji, T.; Sugihara, Y.; Fujimori, K.; Kawakami, J.; Tajiri, A. *Tetrahedron* **2004**, *60*, 5357. (b) Shibasaki, T.; Ooishi, T.; Yamanouchi, N.; Murafuji, T.; Kurotobi, K.; Sugihara, Y. *J. Org. Chem.* **2008**, *73*, 7971. (c) Shoji, T.; Maruyama, A.; Ito, S.; Okujima, T.; Yasunami, M.; Higashi, J.; Morita, N. *Heterocycles*, **2014**, *89*, 2588.
- Crombie, A. L.; Kane, J. L. Jr.; Shea, K. M.; Danheiser, R. L. *J. Org. Chem.* **2004**, *69*, 8652.
- Hanke, M.; Jutz, C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 214.
- (a) Okujima, T.; Ito, S.; Morita, N. *Tetrahedron Lett.* **2002**, *43*, 1261. (b) Ito, S.; Okujima, T.; Morita, N. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1896. (c) Maher, T. R.; Spaeth, A. D.; Neal, B. M.; Berrie, C. L.; Thompson, W. H.; Day, V. W.; Barybin, M. V. *J. Am. Chem. Soc.* **2010**, *132*, 15924.
- (a) Kurotobi, K.; Tabata, H.; Miyauchi, M.; Murafuji, T.; Sugihara, Y. *Synthesis* **2002**, 1013. (b) Shoji, T.; Yamamoto, A.; Shimomura, E.; Maruyama, M.; Ito, S.; Okujima, T.; Toyota, K.; Morita, N. *Chem. Lett.* **2013**, *42*, 638. (c) Yamaguchi, Y.; Ogawa, K.; Nakayama, K.; Ohba, Y.; Katagiri, H. *J. Am. Chem. Soc.* **2013**, *135*, 19095.
- Morita, T.; Takase, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1144.
- Lin, S.-J.; Jiang, S.-Y.; Huang, T.-C.; Dai, C.-S.; Tsai, P.-F.; Takeshita, H.; Lin, Y.-S.; Nozoe, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 3071.
- Dyker, G.; Borowski, S.; Heiermann, J.; Körning, J.; Opwis, K.; Henkel, G.; Köckerling, M. *J. Organomet. Chem.* **2000**, *606*, 108.
- Kurotobi, K.; Takakura, K.; Murafuji, T.; Sugihara, Y. *Synthesis* **2001**, 1346.
- (a) Miyauchi, N.; Suzuki, A. *J. Chem. Soc., Chem. Commun.* **1979**, 866. (b) Miyauchi, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (c) Martin, R.; Buchwald, S. L. *Acc. Chem. Res.* **2008**, *41*, 1461.
- (a) Thanh, N. C.; Ikai, M.; Kajioka, T.; Fujikawa, H.; Taga, Y.; Ogawa, S.; Zhang, T.; Shimada, H.; Miyahara, Y.; Kuroda, S.; Oda, M. *Tetrahedron* **2006**, *62*, 11227. (b) Oda, M.; Thanh, N. C.; Ikai, M.; Fujikawa, H.; Nakajima, K.; Kuroda, S. *Tetrahedron* **2007**, *63*, 10608.
- A little amount of ferrocene was sublimated in evaporation process of solvent.
- Nozoe, T.; Ishikawa, S.; Shindo, K. *Chem. Lett.* **1989**, *2*, 353.
- (a) Shoji, T.; Higashi, J.; Ito, S.; Okujima, T.; Yasunami, M.; Morita, N. *Chem. Eur. J.* **2011**, *17*, 5116. (b) Shoji, T.; Shimomura, E.; Maruyama, M.; Maruyama, A.; Ito, S.; Okujima, T.; Toyota, K.; Morita, N. *Eur. J. Org. Chem.* **2013**, 7785. (c) Shoji, T.; Ito, S.; Okujima, T.; Morita, N. *Chem. Eur. J.* **2013**, *19*, 5721.
- No reaction was also observed in the reaction of **7** with NIS.
- (a) Ueno, T.; Toda, H.; Yasunami, M.; Yoshifuji, M. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1645. (b) Ito, S.; Nomura, A.; Morita, N.; Kabuto, C.; Kobayashi, H.; Maejima, S.; Fujimori, K.; Yasunami, M. *J. Org. Chem.* **2002**, *67*, 7295.
- (a) McDonald, R. N.; Reitz, R. R.; Richmond, J. M. *J. Org. Chem.* **1976**, *41*, 1822. (b) Yamashiro, S.; Imafuku, K. *J. Heterocyclic Chem.* **2002**, *39*, 671.
- Anderson, A. G., Jr.; Gale, D. J.; McDonald, R. N.; Anderson, R. G.; Rhodes, R. C. *J. Org. Chem.* **1964**, *29*, 1373.
- Elwahi, A. H. M.; Hafner, K. *Eur. J. Org. Chem.* **2010**, 265.
- Lash, T. D.; Lammer, A. D.; Idate, A. S.; Colby, D. A.; White, K. *J. Org. Chem.* **2012**, *77*, 2368.
- Nefedov, V. A.; Tarygina, L. K. *Zh. Org. Khim.* **1976**, *12*, 1763.
- Compound **14a** was prepared by the reaction of **7** with NIS, according to the literature. Dubovik, J.; Bredihhin, A. *Synthesis* **2015**, *47*, 2663.
- Anderson, A. G., Jr.; Nelson, J. A.; Tazuma, J. J. *J. Am. Chem. Soc.* **1953**, *75*, 4980.
- Since attempts to the separation of **22** and **23** by both silica gel column chromatography and GPC were unsuccessful, ratio of the products were determined by <sup>1</sup>H NMR spectral measurement.
- Lu, Y.; Lemal, D. M.; Jasinski, J. P. *J. Am. Chem. Soc.* **2000**, *122*, 2440.
- Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359.
- Ram, R. M.; Singh, V. *Tetrahedron Lett.* **2006**, *47*, 7625.
- Silverira, P. B.; Lando, V. R.; Dupont, J.; Monteiro, A. L. *Tetrahedron Lett.* **2002**, *43*, 2327.
- Seganish, W. M.; Mowery, M. E.; Riggelman, S.; DeShong, P. *Tetrahedron*, **2005**, *61*, 2117.
- The B3LYP/6-31G\*\* time-dependence density functional calculations were performed with Spartan'10, Wavefunction, Irvine, CA.
- Ito, S.; Yamazaki, S.; Kudo, S.; Sekiguchi, R.; Kawakami, J.; Takahashi, M.; Matsuhashi, T.; Toyota, K.; Morita, N. *Tetrahedron* **2014**, *70*, 2796.
- The voltammetry measurements were performed with a BAS 100B/W electrochemical workstation equipped with a standard three-electrode configuration and all measurements were carried out under an Ar atmosphere. Tetraethylammonium perchlorate (0.10 M) in benzonitrile was used as a supporting electrolyte, with a platinum wire auxiliary and disk working electrodes. Reference electrode was formed from Ag/AgNO<sub>3</sub> (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.10 M). The half-wave potential of the ferrocene/ferrocenium ion couple (Fc/Fc<sup>+</sup>) under these conditions using this reference electrode was observed at +0.15V on CV. Accuracy of the reference electrode was confirmed by CV measurements of the couple in each sample as an internal ferrocene standard.
- McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* **1958**, *23*, 420.



- (37) Since the 3-position of azulene should be correspond to the *meta*-position of the azulene ring, Hammett substitution constants  $\sigma_m$  was applied in this case.
- (38) Correlation between Hammett substitution constants and redox potential of ferrocene derivatives are previously reported: Komenda, J.; Tirouflet, J. *Compt. Rend.* **1962**, *254*, 3093.