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Tetrahedron 60 (2004) 5357–5366
Tetrahedron

Efficient preparation of 2-azulenylboronate and Miyaura-Suzuki cross-coupling reaction with aryl bromides for easy access to poly(2-azulenyl)benzenes

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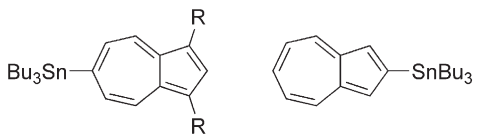
Received 9 February 2004; revised 22 April 2004; accepted 23 April 2004

Abstract—This paper describes an efficient preparation of 2-azulenylboronate (**6**) starting from 2-iodoazulene by halogen–metal exchange reaction using *n*-BuLi and subsequent quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The boronate **6** has been found to undergo Pd-catalyzed Miyaura-Suzuki cross-coupling reaction with a range of aryl bromides including aromatic poly bromides utilizing $Pd_2(dba)_3$–P(*t*-Bu)$_3$ as a catalyst and establishes a strategy to produce novel poly(2-azulenyl)benzenes, some of which are found to be insoluble in common organic solvents, however. The redox behavior of 2-arylazulenes and poly(2-azulenyl)benzenes was examined by cyclic voltammetry (CV) and compared with those of 6-azulenylbenzene derivatives reported previously.

1. Introduction

In recent years, there has been vital interest in transition-metal catalyzed cross-coupling reaction that can be used for carbon–carbon bond formation.[1] Several applications of the palladium-catalyzed reaction in the chemistry of azulene have appeared in the literature, for example, palladium-catalyzed vinylation,[2] arylation,[3] ethynylation,[4] and alkylation[5] of azulenyl halides or triflate. We have recently developed the first versatile organometallic reagents of azulenes, 6-(tri-*n*-butylstannyl)azulene (**1a**) and its 1,3-diethoxycarbonyl derivative (**1b**), which have been subjected to the Pd(0)-catalyzed Stille cross-coupling reaction with aryl, acyl, and/or azulenyl halides (Chart 1).[6] The study made up for the deficiency of the organometallic reagent for the transition-metal catalyzed reaction of azulene itself. Especially, application of the reagents is highly advantageous for multiple functionalization by azulenyl groups because the method does not require the troublesome preparation of a polymetallic species.[7] However, extension of the methodology to the functionalization of azulenes at the 2-position was so far hampered by the inefficiency of the



1a: R = H
1b: R = COOEt
2

Chart 1.

preparation of 2-(tri-*n*-butylstannyl)azulene (**2**) utilizing Pd-catalyzed direct stannylation of 2-bromoazulene (**3a**).[6b]

Boronate reagents also represent an important class of synthetic intermediates for the transition-metal catalyzed reaction. Miyaura-Suzuki cross-coupling of organoborane compounds with a variety of organic electrophiles, catalyzed by palladium, provides an efficient method for carbon–carbon bond formation.[8] Synthesis of the boronate reagents consists of conventional Pd-catalyzed cross-coupling of aryl bromides, iodides, or triflates with either alkoxyboron derivatives such as bis(pinacolato)diboron (**4**) or pinacolborane (**5**).[9,10] The direct boronate formation of 2-iodoazulene (**3b**) utilizing Pd-catalyst has been revealed to be a convenient method for preparing 2-azulenylboronate (**6**) (Scheme 1).[11] However, the yield of the boronate **6** remains so far at most 42%. More recently, Ir-catalyzed reaction of azulene (**7**) with bis(pinacolato)diboron (**4**) has

Keywords: Azulenylboronate; Palladium-catalyzed reaction; Miyaura-Suzuki cross-coupling; Redox property; Violene-cyanine hybrid.
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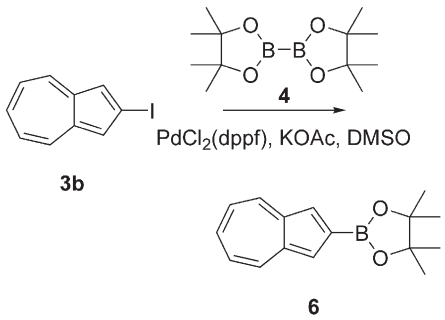
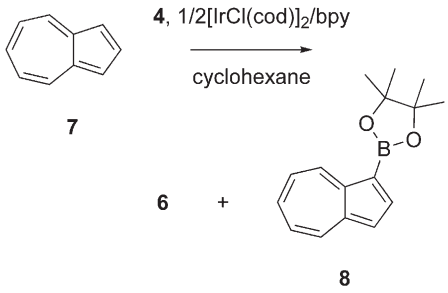
doi:10.1016/j.tet.2004.04.057



Scheme 1.

improved the yield of the desired 2-azulenylboronate (**6**) to 70%, in spite of the formation of undesirable 1-azulenylboronate (**8**) in a certain amount (10%) (Scheme 2).[12]



Scheme 2.

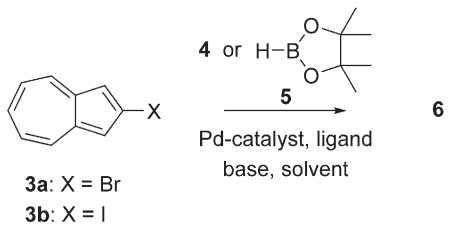
Herein, we report an efficient preparation of 2-azulenylboronate (**6**) and an efficient catalytic system for the Miyaura-Suzuki cross-coupling reaction of **6** with aryl bromides and the successful application to the Pd(0)-catalyzed cross-coupling reaction of **6** with aromatic poly bromides to afford poly(2-azulenyl)benzenes. We have recently proposed that the poly(6-azulenyl)benzene derivatives are considered to be a novel model compound of the violene-cyanine hybrid recently reported by Hünig et al.[13] Depending on the number and position of the 6-azulenyl substituents, the benzene derivatives provide a closed-shell cyanine-type substructure by an overall two-electron transfer.[14] The poly(2-azulenyl)benzenes might also provide a closed-shell system as a cyanine dye by an overall two-electron transfer, although the system does not provide a formal cyclopentadienide substructure in the closed-shell form. Herein, we also report the redox behavior of several 2-arylazulenes and poly(2-azulenyl)benzenes prepared by the cross-coupling reaction of **6**.

2. Results and discussion

2.1. Efficient synthesis of 2-azulenylboronate (6)

Employment of the reaction of 2-bromoazulene (**3a**)[15] with diboron **4** did not improve the yield of the desired 2-azulenylboronate (**6**) under the conditions originally described by Miyaura et al. (entry 1) (Table 1).[9] A slightly larger amount of the Pd-catalyst (5 mol%) in the reaction of 2-iodoazulene (**3b**)[15] with **4** was found to improve somewhat the yield of the desired 2-azulenylboronate (**6**) (entry 2), whereas a modified catalytic system of $PdCl_2$(dppf) with Et_3N in dioxane in the reaction of 2-haloazulenes (**3a** and **3b**) with pinacolborane (**5**) could not alter the situation (entries 3 and 4).[9,10]

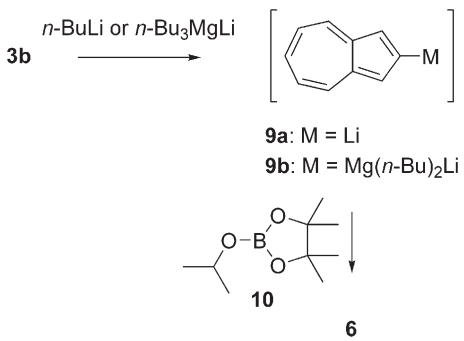
Table 1. Pd-catalyzed syntheses of 2-azulenylboronate (**6**)[a]



Entry	X	Boron reagent	Catalyst	Base	Solvent	Yield (%)[b]	
						6	**3**
1	Br	**4**	$PdCl_2$(dppf)[c]	KOAc	DMSO	40	
2	I	**4**	$PdCl_2$(dppf)	KOAc	DMSO	53	
3	Br	**5**	$PdCl_2$(dppf)	Et_3N	Dioxane	5	52
4	I	**5**	$PdCl_2$(dppf)	Et_3N	Dioxane	38	

[a] Reactions of **3a** and **3b** (1 mmol) with bis(pinacolato)diboron (**4**) (1.1 mmol) were carried out at 80 °C for 5 h by using Pd-catalyst (5 mol%) and KOAc (3 mmol) in DMSO (6 mL). Reactions of **3a** and **3b** (1 mmol) with pinacolborane (**5**) (1.5 mmol) were carried out at 80 °C for 4 h by using Pd-catalyst (5 mol%) and triethylamine (3 mmol) in dioxane (6 mL).
[b] All yields are isolated yields.
[c] $PdCl_2$(dppf): [1,1′-bis(diphenylphosphino)ferrocene]palladium(II) dichloride.

The aryl boronate reagents could be also prepared by transmetalation between aryllithium or arylmagnesium reagents and boron compounds which have a good leaving group such as a halogen or an alkoxy group.[16] Synthetic inaccessibility of the metalated azulene due to the high reactivity of azulenes with organolithium and magnesium reagents to give dihydroazulene derivatives[17] hampered application to the transmetalation procedure. However, recently, generation of 2-azulenyllithium and magnesium reagents (**9a** and **9b**) has been accomplished by the transmetalation between 2-iodoazulene (**3b**) and *n*-BuLi or $(n\text{-Bu})_3MgLi$.[18] The 2-azulenylmagnesium reagent (**9b**) has been revealed to exhibit the envisaged borylation with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**) in 53% yield.[19,20] We found the borylation was much more effective by the use of 2-azulenyllithium reagent (**9a**) prepared by halogen–metal exchange reaction of 2-iodoazulene (**3b**) using *n*-BuLi at low temperature. Subsequent quenching of the reagent by **10** afforded the



Scheme 3.

desired 2-azulenylboronate reagent (**6**) in 78% yield as a single product (Scheme 3).

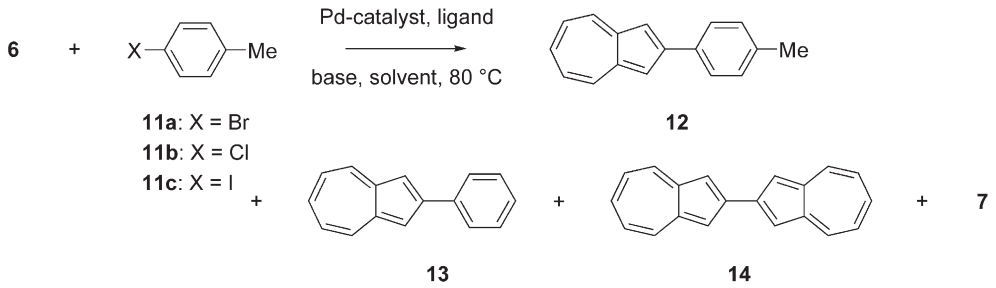
2.2. Miyaura-Suzuki cross-coupling reaction

To demonstrate the transformations utilizing **6**, the reaction with diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate has been conducted under the Miyaura-Suzuki cross-coupling reaction conditions.[11] However, in our initial experiments in the cross-coupling reaction with aryl halides, **6** was found to be inefficient under similar conditions to Miyaura-Suzuki's (Table 2). Concretely, the reaction of **6** with **11a** in the presence of $PdCl_2(PPh_3)_2$ catalyst produced the desired 2-(4-tolyl)azulene (**12**)[21] in mediocre yield (39%) together with undesired 2-phenylazulene (**13**)[21,22] (entry1) (Chart 1). The choice of the catalytic system was the key to the success of the reaction of **6** with aryl halides. The use of $Pd(PPh_3)_4$ as a catalyst instead of $PdCl_2(PPh_3)_2$ was also ineffective in this reaction (entry 2). Formation of the by-product **13** could be rationalized by an aryl–aryl exchange in the intermediate palladium(II) complex and subsequent coupling with the 2-azulenylboronate (**6**).[23] Indeed, substitution of the $Pd(PPh_3)_4$ catalyst with $Pd_2(dba)_3$–P(*t*-Bu)$_3$ in the catalytic protocol resulted in a significant increase of the desired cross-coupling product **12** in 73% yield (entry 3). The $Pd(OAc)_2$–P(*t*-Bu)$_3$ catalytic system was also effective in this reaction (entry 6). However, the use of P(*o*-Tol)$_3$ or PCy_3 as a ligand did not afford satisfactory results either with $Pd_2(dba)_3$ or $Pd(OAc)_2$ as a Pd-catalyst (entries 4, 5, 7 and 8). The addition of KF as a base in the catalytic protocol decreased significantly the conversion ratio of the catalytic reaction (entry 9).[24] Using the chloride **11b** or iodide **11c** instead of the bromide **11a** decreased the yield of the desired cross-coupling product **12** (entries 10 and 11). The formation of 2,2′-biazulene in significant amounts in the case of the reaction with chloride **11b** should be attributed to the homocoupling of **6** under the reaction conditions.[25]

2.3. Generality

To examine the generality of the reaction conditions, the cross-coupling reaction with several aryl bromides (**15a–c**) was conducted under the $Pd_2(dba)_3$–P(*t*-Bu)$_3$ reaction conditions. The results of the cross-coupling reaction of **6** with the aryl bromides are summarized in Table 3. The electron-deficient aryl bromide, 4-bromonitrobenzene (**15a**), was efficiently reacted with **6** to afford the coupled product **16a** in high yield (entry 1). However, the reaction of **6** with 4-bromoacetophenone (**15b**) afforded the desired coupled product **16b** in moderate yield (entry 2). The product **16b** contains enolizable keto-group. The relatively low yield of the product **16b** should be attributed to the side reaction arising from undesired aldol condensations. The yield of **16b** was slightly improved by the use of $Pd(PPh_3)_4$ as a catalyst (42%). In the case of the reaction of **6** with electron-rich bromide, 4-bromoanisole (**15c**), the reaction also proceeded smoothly to give the cross-coupling product **16c** in good yield (entry 3). On the whole, **6** reacted with several aryl bromides including an electron-rich one under the Pd-catalyzed conditions and the isolated yields of the cross-coupling product were generally high, except for **16b**.

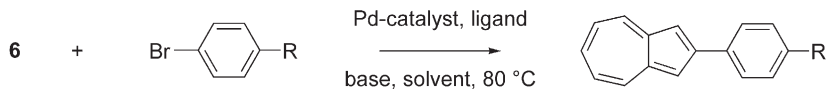
Table 2. Miyaura-Suzuki cross-coupling reaction of **6** with 4-tolyl halides **11a–c**[a]



Entry	X	Catalyst	Ligand	Base	Solvent	Yield (%) [b]				
						12	**13**	**14**	**7**	**6**
1[c]	Br	$PdCl_2(PPh_3)_2$		$Ba(OH)_2{\cdot}8H_2O$	DME/H_2O	39	21			
2	Br	$Pd(PPh_3)_4$		Cs_2CO_3	Dioxane	27	19			
3	Br	$Pd_2(dba)_3$[d]	P(*t*-Bu)$_3$	Cs_2CO_3	Dioxane	73				
4	Br	$Pd_2(dba)_3$	P(*o*-Tol)$_3$	Cs_2CO_3	Dioxane	54		5		5
5	Br	$Pd_2(dba)_3$	PCy_3	Cs_2CO_3	Dioxane	25				
6	Br	$Pd(OAc)_2$	P(*t*-Bu)$_3$	Cs_2CO_3	Dioxane	72			5	
7	Br	$Pd(OAc)_2$	P(*o*-Tol)$_3$	Cs_2CO_3	Dioxane	27		3	32	
8	Br	$Pd(OAc)_2$	PCy_3	Cs_2CO_3	Dioxane	42				
9	Br	$Pd_2(dba)_3$	P(*t*-Bu)$_3$	KF	Dioxane	7				74
10	Cl	$Pd_2(dba)_3$	P(*t*-Bu)$_3$	Cs_2CO_3	Dioxane	12		40	4	3
11	I	$Pd_2(dba)_3$	P(*t*-Bu)$_3$	Cs_2CO_3	Dioxane	51			4	22

[a] Reactions of **6** with 4-halotoluene (2 equiv.) were carried out at 80 °C for 24 h using Pd-catalyst (5 mol%), ligand (Pd:P=1:2–3), and 1.5 equiv. of base in solvent (6 mL/**6** (1 mmol)).
[b] All yields are isolated yields.
[c] Pd-catalyst (10 mol%) and 2.0 equiv. of base in DME:H_2O (50:1) (10 mL/**6** (0.4 mmol)) were used.
[d] $Pd_2(dba)_3$: tris(dibenzylideneacetone)dipalladium(0).

Table 3. Cross-coupling reaction of **6** with aryl bromides **15a**–**c**[a]



15a: R = NO_2
15b: R = COMe
15c: R = OMe

16a: R = NO_2
16b: R = COMe
16c: R = OMe

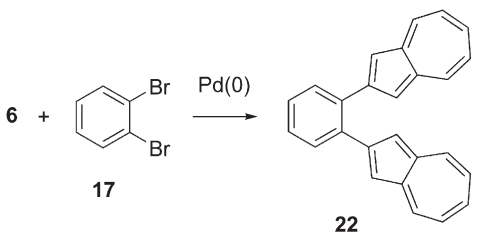
Entry	R	Catalyst	Ligand	Time (h)	Product (yield (%))[b]
1	NO_2	$Pd_2(dba)_3$	P(*t*-Bu)$_3$	6	**16a** (80)
2	COMe	$Pd_2(dba)_3$	P(*t*-Bu)$_3$	24	**16b** (34)
3	OMe	$Pd_2(dba)_3$	P(*t*-Bu)$_3$	19	**16c** (72)

[a] Reaction conditions: aryl bromides (2 equiv.), Cs_2CO_3 (1.5 equiv.), Pd-catalyst (5 mol%), ligand (Pd:P=1:3–4) in dioxane (3 mL/**6** (0.4 mmol)) at 80 °C.
[b] All yields are isolated yields.

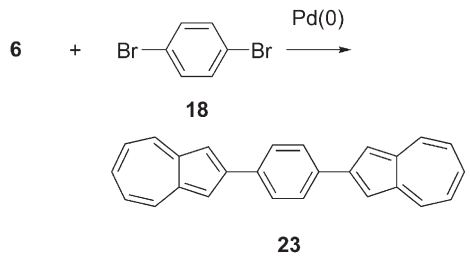
2.4. Polysubstitution

Finally, we demonstrated the intended use of the 2-azulenylboronate (**6**) in the synthesis of poly(2-azulenyl)benzenes. The scope of this methodology for multiple substitution was demonstrated utilizing the reaction of **6** with 1,2-di-, 1,4-di-, 1,3,5-tri-, 1,2,4-tri-, and 1,2,4,5-tetrabromobenzenes (**17**–**21**). The reaction of **6** with 1,2-dibromobenzene (**17**) afforded the desired coupling product, 1,2-bis(2-azulenyl)-benzene (**22**) in 33% yield (Scheme 4). Likewise, the reaction of **6** with 1,4-dibromobenzene (**18**) gave the expected 1,4-bis(2-azulenyl)benzene (**23**) in 44% yield, although the product **23** does not show any solubility in common organic solvents (Scheme 5). Sublimation could be used for the purification of the product **23** under reduced pressure. The insoluble material exhibited an ion peak at *m*/*z* 330 upon mass spectrum, which corresponds to the correct M^+ ion peak of 1,4-di(2-azulenyl)benzene (**23**).

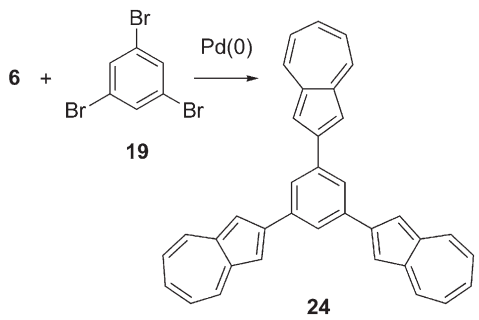
In the case of the reaction of **6** with 1,3,5-tri- and 1,2,4-tribromobenzenes (**19** and **20**), the desired *tris*-adducts **24** and **25** were obtained in 18 and 36% yields, respectively, (Schemes 6 and 7). The reaction of **6** with 1,2,4,5-tetrabromobenzenes (**21**) afforded an insoluble material (13%) in a common organic solvent along with 1,2,4-tris-adduct **25** in 13% yield (Scheme 8). The mass spectrum of the insoluble material showed the correct M^+ ion peak at *m*/*z* 582, which indicated the formation of the expected tetrakis-adduct **26**. The elimination of bromide was a side reaction for the multi-functionalization of benzene with 2-azulenyl substituents.



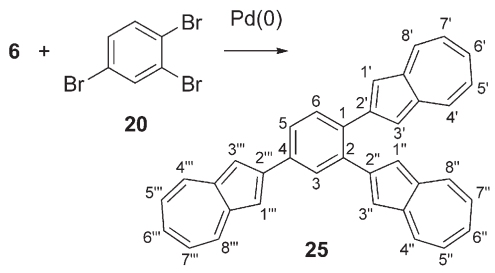
Scheme 4.



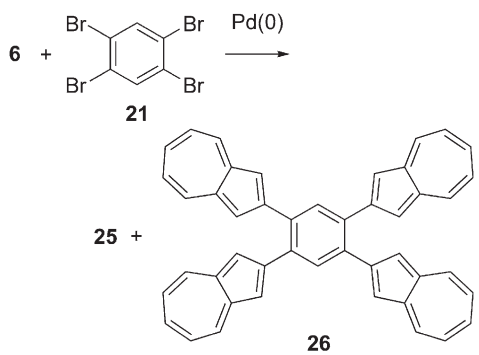
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

2.5. Redox behavior

The redox potentials (V vs Ag/Ag^+) of 2-arylazulenes (**12**, **13**, and **16a**–**c**) and poly(2-azulenyl)benzenes (**22**, **24**, and **25**) measured by CV along with those of 6-azulenylbenzene derivatives (**27**, **28**, and **29**)[14] are summarized in Table 4 (Chart 2). Insolubility of the products **23** and **26** in common organic solvents hampered the CV measurement of these compounds.

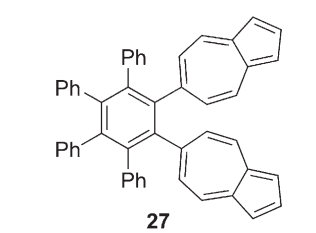
Table 4. Redox potentials[a] of 2-arylazulenes and poly(2- and 6-azulenyl)benzenes

Sample	E_1^{ox} (V)	E_2^{ox} (V)	E_1^{red} (V)	E_2^{red} (V)	E_3^{red} (V)	Ref.
12	(+1.07)	(+1.34)	(−1.85)			
13	(+1.07)	(+1.39)	(−1.82)			
16a	(+1.05)	(+1.38)	−1.33	−1.68		
16b	(+1.04)	(+1.33)	−1.65	(−2.17)		
16c	(+0.76)	(+1.02)	−1.87			
22	(+0.52)	(+0.89)	−1.82	−2.02		
24	(+0.69)	(+1.11)	(−1.72)[b]	(−1.85)[b]	(−2.01)[b]	
25	(+0.42)	(+1.10)	−1.71	−1.87	−2.11	
27[c]	(+0.81)		(−2.00)	(−2.20)		14
28[c]	(+0.73)	(+1.23)	(−1.75)[b]	(−1.87)[b]	(−2.00)[b]	14
29[c]	(+0.78)	(+1.29)	−1.74 (2e)	−2.15		14

[a] The redox potentials were measured by CV (0.1 M n-Bu_4NBF_4 in o-dichlorobenzene, Pt electrode, scan=100 mV s^{-1}, and F_c^+/F_c=0.27 V). In the case of irreversible waves, which are shown in parentheses, E_{ox} and E_{red} were calculated as E_{pa} (anodic peak potential)−0.03 and E_{pc} (cathodic peak potential)+0.03 V, respectively.

[b] The values are peak potentials measured by DPV.

[c] The potentials have been measured in 0.1 M n-Bu_4NBF_4 tetrahydrofuran solution (F_c^+/F_c=0.19 V).



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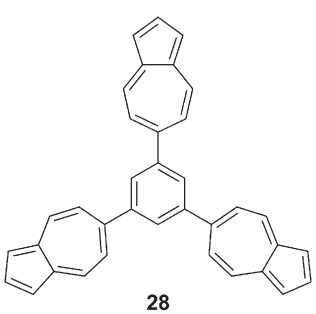

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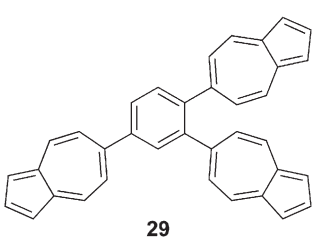

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Chart 2.

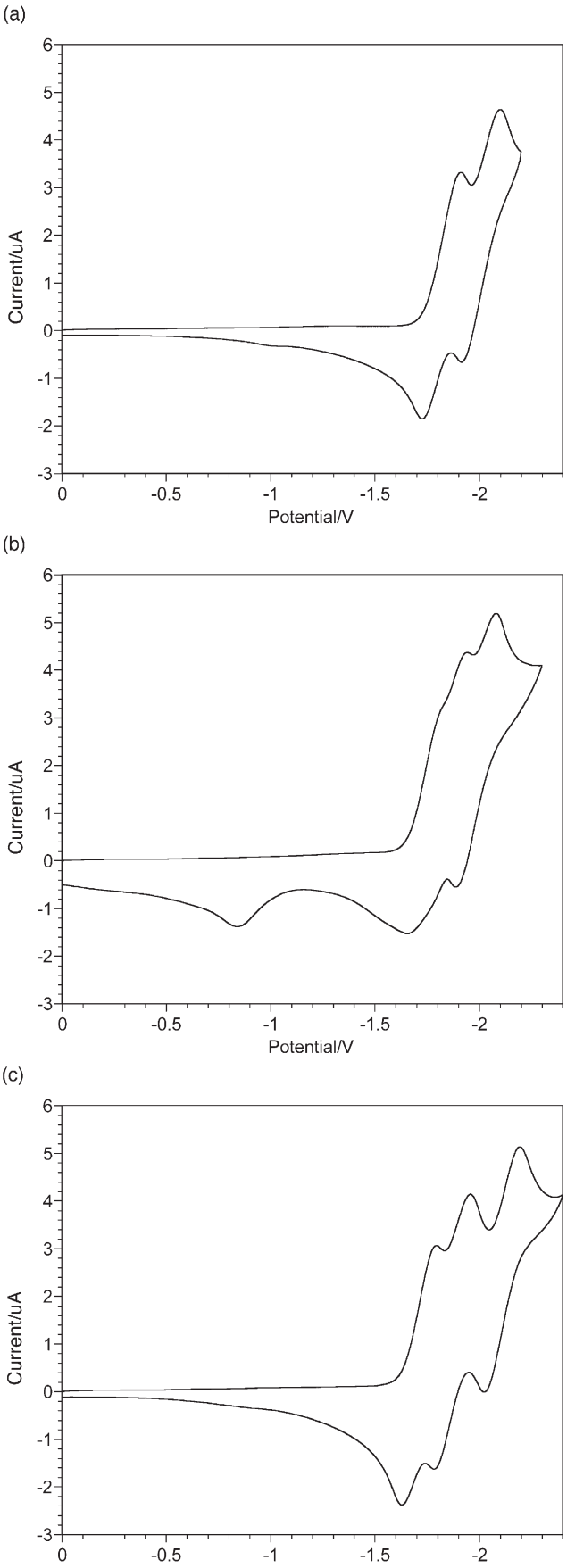
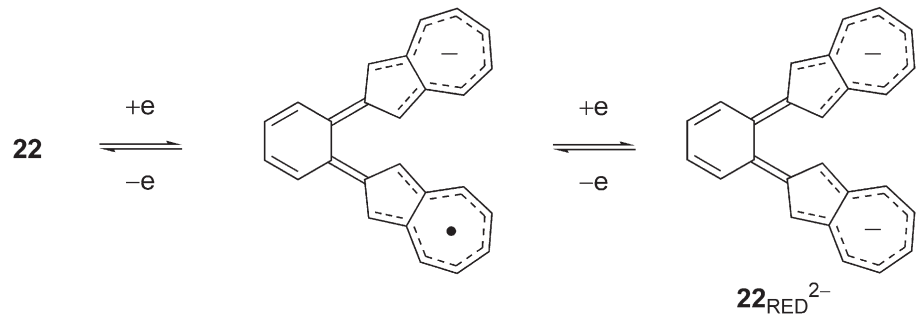


Figure 1. Cyclic voltammograms of (a) **22**, (b) **24**, and (c) **25** in o-dichlorobenzene containing n-Bu_4NBF_4 (0.1 M) as a supporting electrolyte; scan rate, 100 mV s^{-1}.



Scheme 9.

As seen from Table 4, 2-phenylazulene (**13**) showed an irreversible one-electron transfer at −1.82 V upon CV. As expected, the electron-donating group on the phenyl group, that is, 4-methyl (**12**) and 4-methoxy (**16c**), slightly decreases the electron affinity of the azulene ring. In contrast to the one-electron transfer of **12**, **13**, and **16c**, compounds **16a** and **16b** showed two-stage, one-electron reductions due to the redox reaction of the electron-withdrawing substituents such as 4-nitro and 4-acetyl groups. In addition to the two-stage reductions, compounds **16a** and **16b** showed improvement of the reversibility of the CV waves due to the stabilization of the radical anionic state.

Poly(2-azulenyl)benzenes (**22**, **24**, and **25**) revealed multi-electron redox properties. 1,2-Di(2-azulenyl)benzene (**22**) exhibited a well-resolved two-step reduction wave at $E_{1/2}$=−1.82 and −2.02 V, upon CV (Fig. 1(a)). The first reduction potential and even the second one of **22** are almost comparable with those of **12**, **13**, and **16c**. Therefore, the two 2-azulenyl substituents on a benzene ring exhibit multiple electron affinity similarly to the reduction of 6-azulenyl derivative (**27**). Thus, the redox system of **22** could be considered to be that of violene as illustrated in Scheme 9. 1,3,5-Tri(2-azulenyl)benzene (**24**) exhibited a quasi-reversible three-step reduction wave at around −1.90 V, upon CV (Fig. 1(b)). The wave was identified as the superimposition of three independent waves at −1.72, −1.85, and −2.01 V, by differential pulse voltammetry (DPV) (Fig. 2) similarly to the reduction of 6-azulenyl derivative (**28**). Therefore, the three 2-azulenyl substituents on the benzene ring are concluded to result in an increase of the multiplicity of electron affinity due to the reduction of the respective azulene chromophore. The three-step reduction exhibits the existence of the redox interaction among the three 2-azulenyl groups. Similarly to the three-step reduction of **24**, 1,2,4-tri(2-azulenyl)benzene (**25**) also showed a three-step reduction wave with excellent reversibility upon CV (Fig. 1(c)), although the reduction of **25** is expected to show a one-step, two-electron transfer as observed in the reduction of 6-azulenyl derivative (**29**). Consequently, the redox property of tri(2-azulenyl)-benzenes (**24** and **25**) does not depend on the position of the 2-azulenyl substituents on the benzene ring and the redox system of **25** could be depicted in Scheme 10.

3. Conclusion

We have demonstrated an efficient preparation of 2-azulenylboronate reagent (**6**) which has been found to undergo Pd-catalyzed coupling with a range of aryl halides, and herein established a strategy to produce novel poly(2-azulenyl)benzene derivatives. The reaction of **6** with 1,2-di-, 1,4-di-, 1,3,5-tri-, 1,2,4-tri-, and 1,2,4,5-tetrabromobenzenes afforded 1,2-di-, 1,4-di-, 1,3,5-tri-, 1,2,4-tri-, and 1,2,4,5-tetra(2-azulenyl)benzene derivatives (**22**, **23**, **24**, **25** and **26**). These results provide a straightforward methodology for the carbon–carbon bond formation at the 2-position of azulene. Although 2-azulenyl substituents do not possess the formal cyclopentadienide substructure in the electrochemically reduced form, the redox behaviors examined by CV of these compounds clarified the presumed multiple-electron transfer under the electrochemical conditions.

4. Experimental

4.1. General

Melting points were determined on a Yanagimoto micro melting apparatus MP-S3 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 on a Shimadzu FTIR-8100M and a Hitachi U-3410 spectrophotometer, respectively. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded on a JEOL GSX 400 at 400 MHz (100 MHz), a JEOL JNM A500 at 500 MHz (125 MHz), or a Bruker AM 600 spectrometer at 600 MHz (150 MHz). Gel permeation chromatography (GPC) purification was performed on a TSKgel G2000H$_6$. 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, 1 M=1 mol dm^{-3}) in a tetrabutylammonium perchlorate (0.1 M) acetonitrile solution. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

4.1.1. 2-(2-Azulenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6). To a solution of *n*-butyllithium (1.5 mL, 1.6 M solution in hexane, 2.4 mmol) in ether (10 mL) was added dropwise at −100 °C a solution of 2-iodoazulene (**3b**) (256 mg, 1.01 mmol) in ether (20 mL). The mixture was allowed to react at −80 °C for 30 min. A solution of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**) (563 mg, 3.03 mmol) in ether (5 mL) was added dropwise to the cooled mixture. The mixture was allowed to warm to

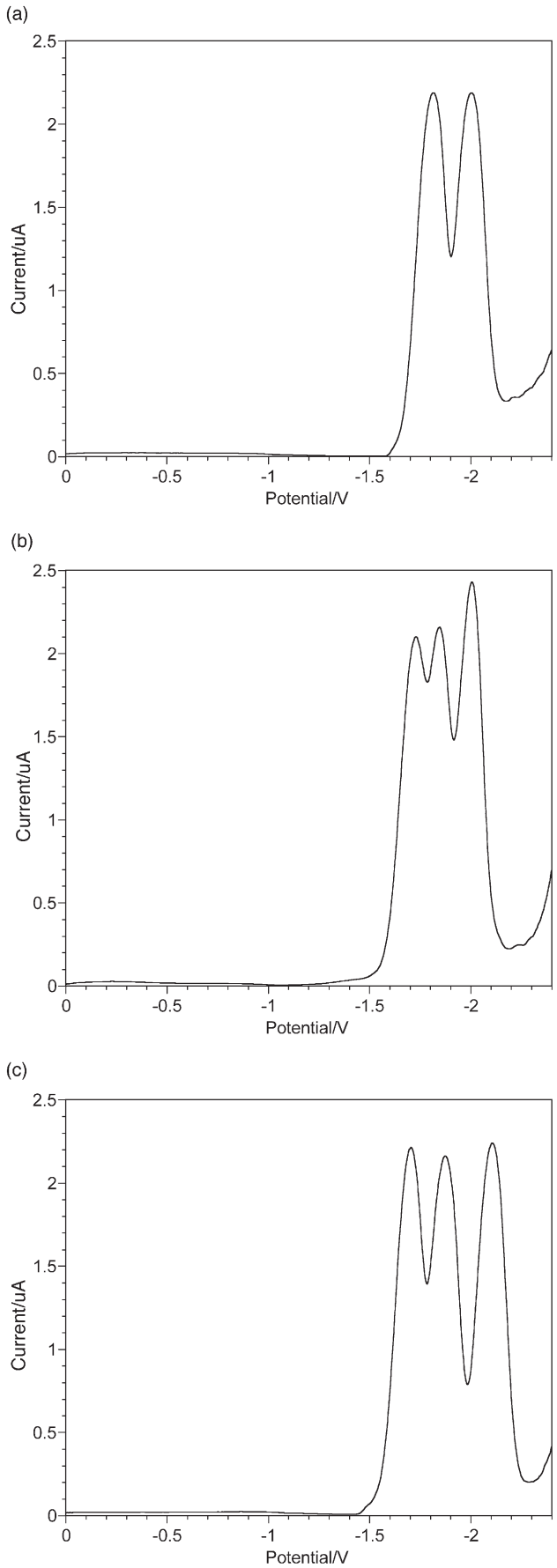


Figure 2. Differential pulse voltammograms of (a) **22**, (b) **24**, and (c) **25** in *o*-dichlorobenzene containing *n*-Bu_4NBF_4 (0.1 M) as a supporting electrolyte; scan rate, 20 mV s^{-1}.

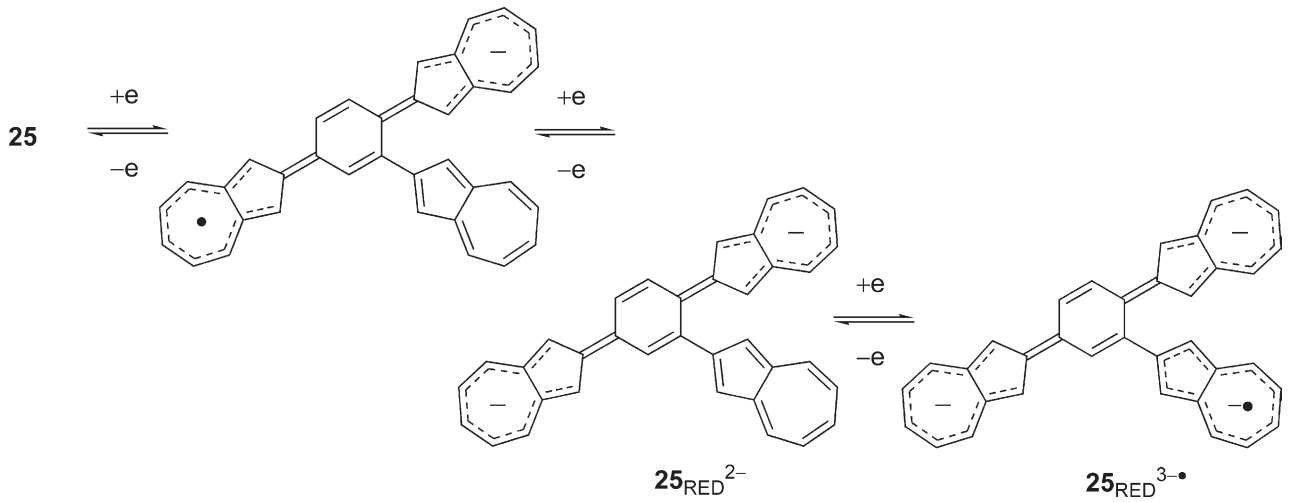
room temperature to react for 1.5 h. The reaction was quenched with water, and the organic layer was separated, washed with brine, and dried with $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ to afford **6** (201 mg, 78%). blue prisms; mp 97–100 °C (sublimation) [lit.[11] mp 99–101 °C].

4.1.2. General procedure for the Pd-catalyzed reaction of 2-azulenylboronate (6). To a degassed solution of **6**, aryl halides, and base in solvent was added Pd-catalyst and ligand. The resulting mixture was heated at 80 °C under an Ar atmosphere. The reaction mixture was poured into water and then extracted with toluene or CH_2Cl_2. The organic layer was washed with water, dried with $MgSO_4$, and concentrated under reduced pressure. The products were isolated by column chromatography on silica gel and/or gel permeation chromatography (GPC) with $CHCl_3$.

4.1.3. 2-Tolylazulene (12). The general procedure was followed by using 2-azulenylboronate (**6**) (252 mg, 0.992 mmol), 4-bromotoluene (**11a**) (340 mg, 1.99 mmol), Cs_2CO_3 (479 mg, 1.47 mmol), $Pd_2(dba)_3$ (45 mg, 0.049 mmol), and P(*t*-Bu)$_3$ (57 mg, 0.28 mmol) in dioxane (6 mL). Column chromatography on silica gel with 10% ethyl acetate/hexane and GPC afforded **12** (157 mg, 73%). blue plates; mp 216–217 °C [lit.[21] mp 214 °C]; MS (70 eV) *m*/*z* (relative intensity) 218 (M^+, 100%); IR (KBr disk) ν_{max} 1406, 806, 723 and 505 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 246 (4.18), 275 sh (4.37), 288 sh (4.56), 301 (4.79), 312 (4.83), 345 sh (3.68), 361 (3.90), 378 (4.17), 397 (4.23), 435 (2.26), 534 sh (2.47), 573 (2.62), 613 (2.60), and 666 sh (2.25); ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.24 (d, *J*=9.9 Hz, 2H, H-4,8), 7.85 (d, *J*=8.3 Hz, 2H, H-2′,6′), 7.64 (s, 2H, H-1,3), 7.47 (t, *J*=9.9 Hz, 1H, H-6), 7.26 (d, *J*=8.3 Hz, 2H, H-3′,5′), 7.13 (dd, *J*=9.9 Hz, 2H, H-5,7), and 2.40 (s, 3H, 4′-Me).

4.1.4. 2-(4-Nitrophenyl)azulene (16a). The general procedure was followed by using 2-azulenylboronate (**6**) (100 mg, 0.393 mmol), 4-bromonitrobenzene (**15a**) (161 mg, 0.797 mmol), Cs_2CO_3 (198 mg, 0.608 mmol), $Pd_2(dba)_3$ (18 mg, 0.020 mmol), and P(*t*-Bu)$_3$ (35 mg, 0.17 mmol) in dioxane (3 mL) at 80 °C for 6 h. Column chromatography on silica gel with CH_2Cl_2 afforded **16a** (78 mg, 80%). green needles; mp 249–255 °C decomp. (hexane wash) [lit.[21] mp 248–249 °C]; MS (70 eV) *m*/*z* (relative intensity) 249 (M^+, 100%) and 202 (57); IR (KBr disk) ν_{max} 1514, 1509, 1347, 1331, 808 and 756 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 237 (4.27), 265 (4.16), 296 sh (4.50), 312 (4.58), 368 sh (4.26), 381 (4.45), 399 (4.46), 544 sh (2.54), 587 (2.70), 627 (2.70), and 683 sh (2.39); ^{1}H NMR (600 MHz, $CDCl_3$) δ=8.36 (d, *J*=9.9 Hz, 2H, H-4,8), 8.32 (d, *J*=9.0 Hz, 2H, H-3′,5′), 8.08 (d, *J*=9.0 Hz, 2H, H-2′,6′), 7.71 (s, 2H, H-1,3), 7.61 (t, *J*=9.9 Hz, 1H, H-6), and 7.22 (dd, *J*=9.9, 9.9 Hz, 2H, H-5,7); ^{13}C NMR (150 MHz, $CDCl_3$) δ=147.2 (C-1′), 146.5 (C-2), 143.0 (C-4′), 141.4 (C-3a,8a), 138.2 (C-6), 137.7 (C-4,8), 128.0 (C-2′,6′), 124.4 (C-5,7), 124.3 (C-3′,5′), and 115.0 (C-1,3). Anal. Calcd for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Found: C, 76.83; H, 4.65; N, 5.55.

4.1.5. 2-(4-Acetylphenyl)azulene (16b). The general



Scheme 10.

procedure was followed by using 2-azulenylboronate (**6**) (110 mg, 0.433 mmol), 4-bromoacetophenone (**15b**) (150 mg, 0.754 mmol), Cs_2CO_3 (195 mg, 0.598 mmol), and $Pd(PPh_3)_4$ (27 mg, 0.023 mmol) in dioxane (3 mL) at 80 °C for 24 h. Column chromatography on silica gel with CH_2Cl_2 afforded **16b** (45 mg, 42%). blue plates; mp 247–256 °C decomp. (ethyl acetate); MS (70 eV) *m*/*z* (relative intensity) 246 (M^+, 100%); IR (KBr disk) ν_{max} 1647 (C=O), 1271, and 808 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 242 (4.16), 303 sh (4.80), 314 (4.91), 360 sh (4.14), 376 (4.38), 396 (4.40), 542 sh (2.57), 582 (2.70), 623 (2.68), and 676 sh (2.39); ^1H NMR (600 MHz, $CDCl_3$) δ=8.34 (d, *J*=9.9 Hz, 2H, H-4,8), 8.05 (m, 2H, H-3′,5′), 8.05 (m, 2H, H-2′,6′), 7.72 (s, 2H, H-1,3), 7.56 (t, *J*=9.9 Hz, 1H, H-6), 7.20 (dd, *J*=9.9, 9.9 Hz, 2H, H-5,7), and 2.66 (s, 3H, 4′-COMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ=197.7 (s, 4′-COMe), 148.0 (C-2), 141.3 (C-3a,8a), 141.0 (C-4′), 137.4 (C-6), 136.9 (C-4,8), 136.3 (C-1′), 129.0 (C-2′,6′), 127.6 (C-3′,5′), 124.1 (C-5,7), 114.9 (C-1,3), and 26.7 (q, 4′-COMe). Anal. Calcd for $C_{18}H_{14}O$: C, 87.78; H, 5.73. Found: C, 87.38; H, 5.92.

4.1.6. 2-(4-Methoxyphenyl)azulene (16c). The general procedure was followed by using 2-azulenylboronate (**6**) (100 mg, 0.393 mmol), 4-bromoanisole (**15c**) (164 mg, 0.877 mmol), Cs_2CO_3 (193 mg, 0.592 mmol), $Pd_2(dba)_3$ (18 mg, 0.020 mmol), and P(*t*-Bu)$_3$ (20 mg, 0.099 mmol) in dioxane (3 mL) at 80 °C for 19 h. Column chromatography on silica gel with CH_2Cl_2 and GPC afforded **16c** (66 mg, 72%). blue plates; mp 229–234 °C decomp.; MS (70 eV) *m*/*z* (relative intensity) 234 (M^+, 100%); IR (KBr disk) ν_{max} 1605, 1478, 1258, 1183, 1030 and 810 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 248 sh (4.16), 275 (4.40), 307 (4.74), 317 (4.81), 369 sh (4.01), 388 (4.25), 405 (4.29), 533 sh (2.53), 569 (2.64), 608 (2.60), and 658 sh (2.29); ^1H NMR (500 MHz, $CDCl_3$) δ=8.25 (d, *J*=9.8 Hz, 2H, H-4,8), 7.92 (d, *J*=8.9 Hz, 2H, H-2′,6′), 7.62 (s, 2H, H-1,3), 7.47 (t, *J*=9.8 Hz, 1H, H-6), 7.15 (dd, *J*=9.8, 9.8 Hz, 2H, H-5,7), 7.01 (d, *J*=8.9 Hz, 2H, H-3′,5′), and 3.88 (s, 3H, 4′-OMe); ^{13}C NMR (125 MHz, $CDCl_3$) δ=160.0 (C-4′), 149.8 (C-2), 141.4 (C-3a,8a), 135.7 (C-6), 135.2 (C-4,8), 129.2 (C-1′), 128.9 (C-2′,6′), 123.7 (C-5,7), 114.4 (C-3′,5′), 113.8 (C-1,3), and 55.4 (4′-OMe). Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.85; H, 6.17.

4.1.7. 1,2-Di(2-azulenyl)benzene (22). The general procedure was followed by using 2-azulenylboronate (**6**) (203 mg, 0.799 mmol), 1,2-dibromobenzene (**17**) (95 mg, 0.40 mmol), Cs_2CO_3 (394 mg, 1.21 mmol), $Pd_2(dba)_3$ (42 mg, 0.046 mmol), P(*t*-Bu)$_3$ (65 mg, 0.32 mmol), and dioxane (5 mL) at 80 °C for 24 h. Chromatographic purification on silica gel with CH_2Cl_2 and GPC afforded **22** (43 mg, 33%), 2-phenylazulene (**13**) (11 mg, 7%), and azulene (**7**) (4 mg, 4%).

Compound **22**. Blue crystals; mp 188–189 °C; MS (70 eV) *m*/*z* (relative intensity) 330 (M^+, 88%), 329 (53), 327 (69), 326 (M^+−4H, 100), 314 (49), and 313 (57); IR (KBr disk) ν_{max} 1456, 1401, 826, 762 and 731 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 238 sh (4.44), 281 (4.93), 314 sh (4.60), 322 (4.62), 393 (4.14), 544 sh (2.65), 579 (2.88), 621 (2.75), and 673 sh (2.42); ^1H NMR (500 MHz, $CDCl_3$) δ=8.07 (d, *J*=9.9 Hz, 4H, H-4′,8′), 7.71 (m, 2H, H-3,6), 7.44 (m, 2H, H-4,5), 7.43 (t, *J*=9.9 Hz, 2H, H-6′), 7.18 (s, 4H, H-1′,3′), and 7.03 (dd, *J*=9.9, 9.9 Hz, 4H, H-5′,7′); ^{13}C NMR (125 MHz, $CDCl_3$) δ=151.3 (C-2′), 140.2 (C-3a,8a), 136.9 (C-1,2), 136.3 (C-6′), 135.9 (C-4′,8′), 131.8 (C-3,6), 127.8 (C-4,5), 123.0 (C-5′,7′), and 118.5 (C-1′,3′); HRMS Calcd for $C_{26}H_{18}$—e 330.1403, found 330.1401. Anal. Calcd for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.23; H, 5.65.

4.1.8. 1,4-Di(2-azulenyl)benzene (23). Following the general procedure, the reaction of 2-azulenylboronate (**6**) (204 mg, 0.803 mmol) of 1,4-dibromobenzene (**18**) (93 mg, 0.39 mmol) in dioxane (5 mL) at 80 °C for 24 h in the presence of Cs_2CO_3 (400 mg, 1.23 mmol), $Pd_2(dba)_3$ (40 mg, 0.044 mmol), and P(*t*-Bu)$_3$ (47 mg, 0.23 mmol) afforded an insoluble material in CH_2Cl_2. Mass spectrum of the insoluble material showed a peak at *m*/*z* 330, which corresponded to a correct M^+ ion peak of **23** (57 mg, 44%). After the insoluble material was removed by filtration, the organic layer was worked up. Column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ afforded

2-phenylazulene (**13**) (2 mg, 2%) and azulene (**7**) (2 mg, 2%).

Compound **23**. Green crystals; mp >300 °C; MS (70 eV) *m/z* (relative intensity) 330 (M^+, 100%); IR (KBr disk) ν_{max} 1410 and 808 cm^{-1}; HRMS Calcd for $C_{26}H_{18}$—e 330.1403, found 330.1409. Anal. Calcd for $C_{26}H_{18}\cdot 1/4H_2O$: C, 93.24; H, 5.57. Found: C, 93.53; H, 5.63.

4.1.9. 1,3,5-Tri(2-azulenyl)benzene (24). The general procedure was followed by using 2-azulenylboronate (**6**) (301 mg, 1.18 mmol), 1,3,5-tribromobenzene (**19**) (128 mg, 0.407 mmol), Cs_2CO_3 (596 mg, 1.83 mmol), $Pd_2(dba)_3$ (66 mg, 0.072 mmol), P(*t*-Bu)$_3$ (49 mg, 0.24 mmol), dioxane (7 mL) at 80 °C for 24 h. Chromatographic purification on silica gel with CH_2Cl_2 and GPC afforded **24** (32 mg, 18%), azulene (**7**) (46 mg, 30%), and the recovered **6** (22 mg, 7%).

Compound **24**. Greenish blue microneedles; mp >300 °C; MS (70 eV) *m/z* (relative intensity) 456 (M^+, 100%); IR (KBr disk) ν_{max} 1505, 1453, 1399 and 801 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 245 (4.54), 301 (5.16), 314 (5.16), 381 (4.69), 399 (4.73), 541 sh (2.92), 575 (3.05), 615 (3.03), and 664 sh (2.67); ^{1}H NMR (600 MHz, $CDCl_3$) δ=8.54 (s, 3H, H-2,4,6), 8.39 (d, *J*=9.8 Hz, 6H, H-4′,8′), 7.89 (s, 6H, H-1′,3′), 7.57 (t, *J*=9.8 Hz, 3H, H-6′), and 7.23 (dd, *J*=9.8, 9.8 Hz, 6H, H-5′,7′); ^{13}C NMR (150 MHz, $CDCl_3$) δ=149.8 (C-2′), 141.4 (C-3′a,8′a), 137.8 (C-1,3,5), 136.6 (C-6′), 136.2 (C-4′,8′), 126.9 (C-2,4,6), 123.9 (C-5′,7′), and 114.8 (C-1′,3); HRMS Calcd for $C_{36}H_{24}$—e 456.1873, found 456.1874. Anal. Calcd for $C_{36}H_{24}\cdot 1/2H_2O$: C, 92.87; H, 5.41. Found: C, 92.73; H, 5.40.

4.1.10. 1,2,4-Tri(2-azulenyl)benzene (25). The general procedure was followed by using 2-azulenylboronate (**6**) (254 mg, 1.00 mmol), 1,2,4-tribromobenzene (**20**) (105 mg, 0.334 mmol), Cs_2CO_3 (587 mg, 1.80 mmol), $Pd_2(dba)_3$ (59 mg, 0.064 mmol), P(*t*-Bu)$_3$ (72 mg, 0.36 mmol), and dioxane (7 mL) at 80 °C for 24 h. Chromatographic purification on silica gel with CH_2Cl_2 and GPC afforded **25** (55 mg, 36%) and azulene (**7**) (3 mg, 2%).

Compound **25**. Green crystals; mp 238.5–239 °C decomp.; MS (70 eV) *m/z* (relative intensity) 456 (M^+, 100%) and 439 (49); IR (KBr disk) ν_{max} 1455, 1401 and 810 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 236 (4.58), 274 (4.80), 316 (5.04), 386 sh (4.53), 408 (4.61), 430 sh (4.53), 537 sh (2.94), 579 (3.05), 618 (3.01), and 670 sh (2.68); ^{1}H NMR (600 MHz, $CDCl_3$) δ=8.32 (d, *J*=9.7 Hz, 2H, H-4‴,8‴), 8.30 (d, *J*=1.9 Hz, 1H, H-3), 8.18 (d, *J*=9.7 Hz, 2H, H-4″,8″), 8.11 (d, *J*=9.7 Hz, 2H, H-4′,8′), 8.06 (dd, *J*=8.1, 1.9 Hz, 1H, H-5), 7.86 (d, *J*=8.1 Hz, 1H, H-6), 7.79 (s, 2H, H-1‴,3‴), 7.53 (t, *J*=9.9 Hz, 1H, H-6‴), 7.51 (t, *J*=9.9 Hz, 1H, H-6″), 7.46 (t, *J*=9.9 Hz, 1H, H-6′), 7.32 (s, 2H, H-1″,3″), 7.22 (s, 2H, H-1′,3′), 7.18 (dd, *J*=9.9, 9.7 Hz, 2H, H-5‴,7‴), 7.11 (dd, *J*=9.9, 9.7 Hz, 2H, H-5″,7″), and 7.07 (dd, *J*=9.9, 9.7 Hz, 2H, H-5′,7′); ^{13}C NMR (150 MHz, $CDCl_3$) δ=151.5 (C-2″), 150.8 (C-2′), 149.3 (C-2‴), 141.4 (C-3‴a,8‴a), 140.3 (C-3′a,8′a or C-3″a,8″a), 140.2 (C-3′a,8′a or C-3″a,8″a), 137.7 (C-2), 136.7 (C-1), 136.5 (2C, C-6′, C-6″, and/or C-6‴), 136.3 (C-6′, C-6″, or C-6‴), 136.1 (2C, C-4′,8′, C-4″,8″, and/or C-4‴,8‴), 136.0 (C-4′,8′, C-4″,8″, or C-4‴,8‴), 135.9 (C-4), 132.5 (C-6), 131.2 (C-3), 126.9 (C-5), 123.8 (C-5‴,7‴), 123.2 (C-5′,7′ or C-5″,7″), 123.1 (C-5′,7′ or C-5″,7‴), 118.6 (C-1″,3″), 118.4 (C-1′,3′), and 114.6 (C-1‴,3‴); HRMS Calcd for $C_{36}H_{24}$—e 456.1873, found 456.1874. Anal. Calcd for $C_{36}H_{24}\cdot 1/2H_2O$: C, 92.87; H, 5.41. Found: C, 92.78; H, 5.64.

4.1.11. 1,2,4,5-Tetra(2-azulenyl)benzene (26). Following the general procedure, the reaction of 2-azulenylboronate (**6**) (417 mg, 1.64 mmol) with 1,2,4,5-tetrabromobenzene (**21**) (147 mg, 0.374 mmol) in dioxane (10 mL) at 80 °C for 24 h in the presence of Cs_2CO_3 (802 mg, 2.46 mmol), $Pd_2(dba)_3$ (74 mg, 0.081 mmol), and P(*t*-Bu)$_3$ (96 mg, 0.47 mmol) afforded an insoluble material in CH_2Cl_2. Mass spectrum of the insoluble material showed a peak at *m/z* 582, which corresponded to a correct M^+ ion peak of **26** (29 mg, 13%). After the insoluble material was removed by filtration, the organic layer was worked up. Column chromatography on silica gel with CH_2Cl_2 and GPC afforded 1,2,4-tri(2-azulenyl)benzene (**25**) (23 mg, 13%) and azulene (**7**) (9 mg, 4%).

Compound **26**. Green microneedles; mp >300 °C; MS (70 eV) *m/z* (relative intensity) 582 (M^+, 66%), 565 (45), 490 (41), 489 (55), 466 (49), 465 (100), 454 ($M^+-C_{10}H_8$, 69), 453 (47), 439 (41), 328 ($M^+-2C_{10}H_7$, 51), 291 ($M^+/2$, 53), and 265 (78); IR (KBr disk) ν_{max} 1574, 1453, 1399, 1383, 820 and 812 cm^{-1}; HRMS Calcd for $C_{46}H_{30}$—e 582.2342, found 582.2358. Anal. Calcd for $C_{46}H_{30}\cdot 2/3H_2O$: C, 92.90; H, 5.31. Found: C, 92.75; H, 5.36.

Acknowledgements

The present work was supported by a Grant-in-Aid for Scientific Research (No. 14540486 to S. I.) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and notes

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