Preparation and Stille cross-coupling reaction of the first organotin reagents of azulenes. Easy access to poly(azulen-6-yl)benzene derivatives

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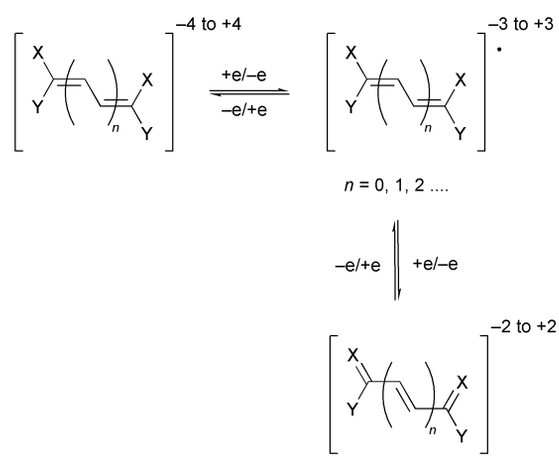
The first versatile organometallic reagents derived from azulenes, *i.e.*, 6-(tri-*n*-butylstannyl)azulene (**1a**) and its 1,3-diethoxycarbonyl derivative (**1b**), have been prepared by Pd(0)-catalyzed direct stannylation of 6-bromoazulenes with bis(tri-*n*-butyltin). We demonstrate the utility of the reagents in the Stille cross-coupling reaction with aryl, acyl and azulenyl halides to afford 6-aryl-, 6-acyl- and bi-azulenes in good yield. Furthermore, the methodology was applied to the synthesis of poly(azulen-6-yl)benzene derivatives. The reaction of **1b** with 1,4-di-, 1,3,5-tri-, 1,2,4,5-tetra- and hexabromobenzenes afforded 1,4-di-, 1,3,5-tri-, 1,2,4,5-tetra-, 1,2,4-tri- and 1,2,3,5-tetra(azulen-6-yl)benzene derivatives (**18**, **20**, **22**, **24** and **25**). The redox behavior of **18** and **22** was examined by cyclic voltammetry (CV) and compared with those of **20** and **24** reported previously. In contrast to the three-step reduction of **20**, the compound **18** exhibited a reversible one-step two-electron reduction wave at −1.30 V upon CV, which revealed the formation of a closed-shell dianion. The four azulen-6-yl substituents on benzene in a 1,2,4,5 relationship increased electron-accepting properties because of the formation of a closed-shell dianion stabilized by four azulen-6-yl groups. As expected, the compound **22** exhibited a color change during the electrochemical reduction. However, the reverse oxidation did not regenerate the spectrum of **22** due to the low stability of the presumed dianionic species under the conditions of the UV–vis measurement.

Introduction

Palladium-catalyzed cross-coupling reaction has become a widely used method for carbon–carbon bond formation in modern organic synthesis.[1] Several applications of this transition-metal catalyzed reaction in the chemistry of azulenes have also appeared in the literature, *e.g.*, palladium-catalyzed vinylation,[2] arylation,[3] ethynylation[4] and alkylation[5] of azulenyl halides or triflate. However, the lack of a versatile organometallic reagent for the transition-metal catalyzed reaction of azulene itself imposes restrictions[6] because of the synthetic inaccessibility of such a reagent due to the high reactivity of azulenes with organolithium and magnesium reagents to produce dihydroazulene derivatives.[7] From the viewpoint of the general usage of transition-metal catalyzed reactions in the chemistry of azulenes, we focused on the development of an organometallic reagent for the transition-metal catalyzed reaction of azulenes. Especially, application of the reagent would be a great advantage in multiple functionalization with azulenyl groups because the method does not require the preparation of troublesome polymetallic species.[8]

The Stille cross-coupling of organotin compounds with a variety of organic electrophiles, catalyzed by palladium, provides an efficient method for carbon–carbon bond formation.[1,9] Functionalization of azulene in the seven membered-ring is rather difficult so far, although that of the 1,3-positions of the system can be easily achieved by electrophilic substitution. Therefore, we examined the stannylation of azulenes in the seven-membered ring and the potential of the reagents for the Stille cross-coupling reaction. Herein we report in detail the preparation of the first versatile organometallic reagents of azulenes, 6-(tri-*n*-butylstannyl)azulene (**1a**) and its 1,3-diethoxycarbonyl derivative (**1b**) and the successful application to the Pd(0)-catalyzed Stille cross-coupling reaction of **1a** and **1b** with aryl, acyl and/or azulenyl halides to demonstrate the utility of the reagents for carbon–carbon bond formation.[10]

We also demonstrate easy access to poly(azulen-6-yl)benzene derivatives *via* the cross-coupling reaction of **1b** with aromatic polybromides promoted by the Pd(0)-catalyzed reaction. Recently, Hünig *et al.* have proposed the concept of violene–cyanine hybrids as stabilized organic electrochromics.[11] The hybrids contain the moiety X=C–Y, which represents a "cyanine"-type structure in fully reduced or oxidized form, as the end groups of violene. The system provides highly colored closed-shell systems such as cyanine dyes by an overall two-electron transfer (Scheme 1). We have recently proposed that the



Scheme 1

poly(azulen-6-yl)benzene derivatives could be considered as candidates for such a system.[12] Depending on the number and position of the azulen-6-yl substituents, the system could

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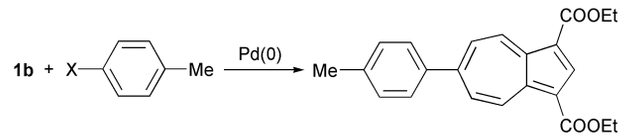
Table 1 Stille cross-coupling reaction of **1b** with **4a** and **4b**[a]



4a: X = Br
4b: X = I
5

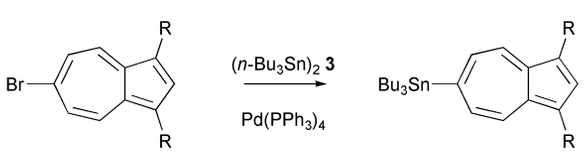
Entry	X	Catalyst	Ligand	Additive	Solvent	Yield/%[b]				
						5	**6**	**7b**	**8b**	**1b**
1	Br	$Pd(PPh_3)_4$			Toluene	16	52	12	5	0
2	I	$Pd(PPh_3)_4$			Toluene	8	30	25	2	11
3	Br	$Pd_2(dba)_3$	P(*t*-Bu)$_3$		Dioxane	45	—	11	14	0
4	Br	$Pd_2(dba)_3$	P(*t*-Bu)$_3$	CsF	Dioxane	74	—	8	5	0
5	I	$Pd_2(dba)_3$	P(*t*-Bu)$_3$		Dioxane	11	—	4	6	61
6	I	$Pd_2(dba)_3$	P(*t*-Bu)$_3$	CsF	Dioxane	61	—	4	6	22
7	Br	$Pd_2(dba)_3$	BINAP[c]		Dioxane	13	17	26	2	0
8	Br	$Pd_2(dba)_3$	BINAP[c]	CsF	Dioxane	35	17	5	2	0

[a] Reactions of **1b** (0.2 mmol) with **4a** or **4b** (0.6 mmol) were carried out at reflux temperature for 24 h by using 10 mol% Pd(0)-catalyst, ligand (Pd : P = 1 : 2), and 2.2 equiv of CsF in 20 ml of the solvent. [b] All yields are isolated yields. [c] BINAP: 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl.

provide a closed-shell cyanine-type structure by the two-electron reduction. Herein, we also report the redox behavior of several poly(azulen-6-yl)benzene derivatives prepared by the cross-coupling reaction of **1b** with aromatic polybromides.

Results and discussion

Traditionally, aryltin compounds have been prepared by reacting an aryllithium intermediate, generated by deprotonation or halogen–metal exchange, with trialkyltin compounds that have good leaving groups.[13] However, the azulen-6-yllithium intermediate was so far unknown and could not be easily generated by halogen–metal exchange. Therefore, the first 6-stannylazulenes (**1a** and **1b**) were synthesized from 6-bromoazulenes (**2a** and **2b**)[14] *via* Pd(0)-catalyzed direct stannylation with bis(tri-*n*-butyltin) (**3**).[15] The coupling reaction of **2a** with **3** in the presence of a catalytic amount of $Pd(PPh_3)_4$ in refluxing toluene for 1 d provided the desired 6-(tri-*n*-butylstannyl)-azulene (**1a**) in 49% yield. Likewise, diethyl 6-(tri-*n*-butylstannyl)azulene-1,3-dicarboxylate (**1b**) was prepared from **2b** with **3** in 69% yield (Scheme 2). These organotin compounds

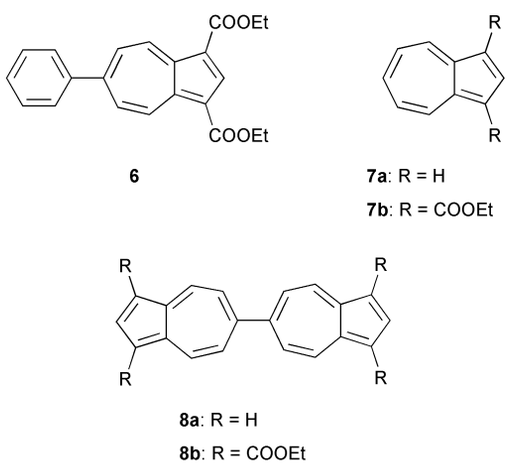


2a: R = H
2b: R = COOEt
1a: R = H
1b: R = COOEt

Scheme 2

are stable and are easily characterized by the usual spectroscopic analysis.

To demonstrate the transformations using **1a** and **1b**, we conducted the Stille cross-coupling reaction with aryl, acyl and azulenyl halides to produce 6-aryl-, 6-acyl- and bi-azulenes. The results of the reaction of **1b** with 4-bromo- and 4-iodotoluenes (**4a** and **4b**) are summarized in Table 1. In our initial experiments, **1b** proved to be inefficient in the cross-coupling reaction under typical conditions for the reaction with aryl halides.[16] The reaction of **1b** with **4a** in the presence of $Pd(PPh_3)_4$ catalyst produced the desired diethyl 6-(4-tolyl)azulene-1,3-dicarboxylate (**5**) in 16% yield together with a significant amount of undesired diethyl 6-phenylazulene-1,3-dicarboxylate (**6**),[17] diethyl azulene-1,3-dicarboxylate (**7b**)[18] and tetraethyl 6,6′-biazulene-1,1′,3,3′-tetracarboxylate (**8b**) (entry 1) (Chart 1).



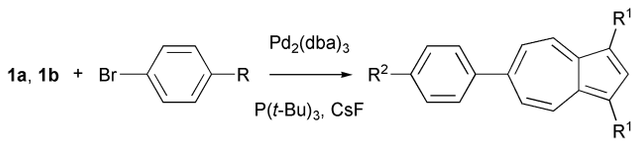
6
7a: R = H
7b: R = COOEt
8a: R = H
8b: R = COOEt

Chart 1

Using **4b** instead of **4a** increased the recovery of **1b** (entry 2). Formation of **6** in considerable yield is attributable to aryl–phenyl exchange with the triphenylphosphine ligand in the initial intermediate formed by oxidative addition of Pd(0) into the aryl halide.[19] Thus, the choice of the catalytic system was very important for the success of the reaction of **1b**. 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 **5** (entry 3). A fluoride-activation strategy,[20] which was utilized for the activation of the organotin compound, was effective for this Stille cross-coupling reaction. The addition of CsF in the catalytic protocol increased the desired coupling product **5** up to 74% yield (entry 4). While good conversions were obtained by using **4a**, the use of **4b** was unfavorable under the reaction conditions, which decreased the conversion ratio of the catalytic reaction significantly (entries 5 and 6). The use of BINAP as a ligand did not afford satisfactory results either in the presence or absence of CsF (entries 7 and 8).

To test the generality, the cross-coupling reaction with several aryl bromides was conducted under the reaction conditions. The results of the cross-coupling reaction of **1a** and **1b** with aryl bromides are summarized in Table 2. The electron-deficient aryl bromide, 4-bromonitrobenzene was efficiently reacted with **1b** to afford the coupled product **9a** in high yield (entry 1). Under similar conditions, the reaction of **1b** with 4-bromoacetophenone also afforded the desired coupling product **9b** in good yield (entry 2). In the case of the reaction of **1b** with

Table 2 Stille cross-coupling reaction of **1a** and **1b** with aryl bromides[a]



9a: R^1 = COOEt, R^2 = NO_2
9b: R^1 = COOEt, R^2 = COMe
9c: R^1 = COOEt, R^2 = OMe
9d: R^1 = H, R^2 = Me
9e: R^1 = H, R^2 = NO_2
9f: R^1 = H, R^2 = COMe
9g: R^1 = H, R^2 = OMe

Entry	Reagent	R	Time/h	Products (yield(%))[b]		
1	**1b**	NO_2	2	**9a** (84)	**7b** (5)	**8b** (10)
2	**1b**	COMe	2	**9b** (65)	**7b** (4)	**8b** (5)
3	**1b**	OMe	2	**9c** (64)	**7b** (5)	**8b** (3)
4	**1a**	Me	24	**9d** (60)	**7a** (5)	**8a** (12)
5[c]	**1a**	Me	24	**9d** (31)	**7a** (23)	**8a** (9)
6	**1a**	NO_2	2	**9e** (83)	**7a** (5)	**1a** (5)
7	**1a**	COMe	4	**9f** (67)	**7a** (0)	**1a** (1)
8	**1a**	OMe	6	**9g** (63)	**7a** (6)	**1a** (8)

[a] Reaction conditions: **1a** (0.3 mmol) or **1b** (0.2 mmol), aryl bromides (0.9 and 0.6 mmol, respectively), $Pd_2(dba)_3$ (10 mol%), P(*t*-Bu)$_3$ (40 mol%), CsF (2.2 eq), dioxane (30 and 20 ml, respectively), refluxed under an Ar atmosphere. [b] All yields are isolated yields. [c] The reaction was carried out without an addition of CsF.

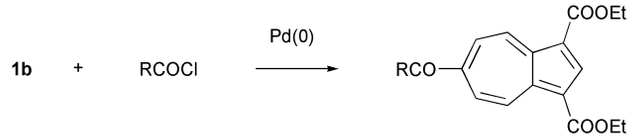
electron-rich bromide, 4-bromoanisole, the reaction also proceeded smoothly under our reaction conditions to give the cross-coupling product **9c** (entry 3).

The fluoride-activation strategy was also effective for the catalytic protocol of **1a** with **4a**. In the presence of CsF the reaction afforded the desired cross-coupling product **9d**[3b,21] in 60% yield, although the reaction without CsF did not afford satisfactory results (entries 4 and 5). On the whole, **1a** also reacted rapidly with a variety of aryl bromides including an electron-rich one under the Pd(0)-catalyzed conditions and generally the isolated yields of the cross-coupling product were above 60% (entries 6–8).

To demonstrate the scope of this procedure, attempts were made for the preparation of 6-acylazulenes, 6,6′- and 2,6′-biazulenes utilizing the cross-coupling reaction of **1b** with acyl chlorides, azulen-6-yl and azulen-2-yl bromides, respectively. Preparation of 6-actetylazulene **10c** has been achieved by multistep reaction from a tropolone derivative having an acetyl substituent.[22] However, several 6-acylazulene derivatives **10a–c** could be easily prepared by the cross-coupling reaction of **1b** with acyl chlorides under the Pd(0)-catalyzed reaction conditions. The results of the cross-coupling reaction of **1b** with acyl chlorides are summarized in Table 3. Benzoyl chloride was efficiently reacted with **1b** to afford the coupled product **10a** in high yield (entry 1). Under similar reaction conditions, the reaction of **1b** with *n*-heptanoyl chloride also afforded the desired coupling product **10b** in good yield together with a small amount of **7b** (entry 2). In the case of the reaction of **1b** with acetyl chloride, the reaction also proceeded smoothly under the reaction conditions, but the reaction did not give the coupled product **10c** in satisfactory yield due to the formation of a significant amount of **7b** (entry 3).

Preparation of biazulenes has been achieved by homo-coupling reaction of azulenyl halides[23] or stepwise reaction to prepare the two azulene rings.[24] However, selective synthesis of unsymmetrical biazulenes has been significantly difficult so far because of the restriction of the synthetic methods. The

Table 3 Stille cross-coupling reaction of **1b** with acyl chlorides[a]



10a: R = Ph
10b: R = *n*-Hexyl
10c: R = Me

Entry	R	Time/h	Products (yield(%))[b]	
1	Ph	2	**10a** (91)	**7b** (0)
2	*n*-Hexyl	3	**10b** (73)	**7b** (22)
3	Me	3	**10c** (26)	**7b** (50)

[a] Reaction conditions: **1b** (0.2 mmol), acyl chlorides (0.6 mmol), $Pd_2(dba)_3$ (10 mol%), P(*t*-Bu)$_3$ (40 mol%), CsF (2.2 eq), dioxane (20 ml), refluxed under an Ar atmosphere. [b] All yields are isolated yields.

coupling reaction of a mixture of azulenyl halides affords homo-coupling products in addition to the desired cross-coupled one. We then applied our new 6-stannylazulene **1b** to the selective synthesis of biazulenes including unsymmetrical ones. Under conditions analogous to those for the reaction with aryl bromides, **1b** reacted smoothly with **2a** and **2b** to afford 6,6′-biazulenes (**11** and **8b**) in 46% and 68% yields, respectively. Similarly, the present method could be applied to the selective synthesis of 2,6′-biazulene. The reaction of **1b** with 2-bromoazulene (**13**) under the Pd(0)-catalyzed conditions afforded 2,6′-biazulene **12** in 51% yield (Chart 2).

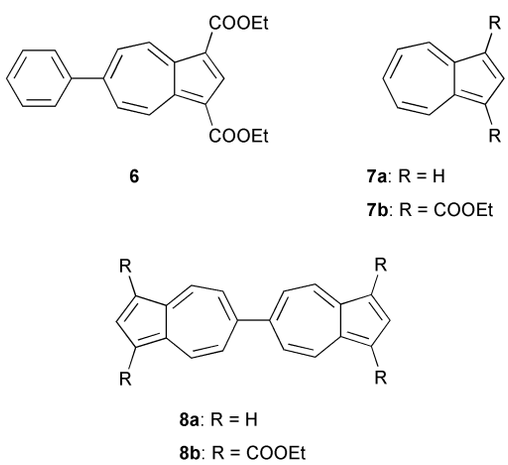
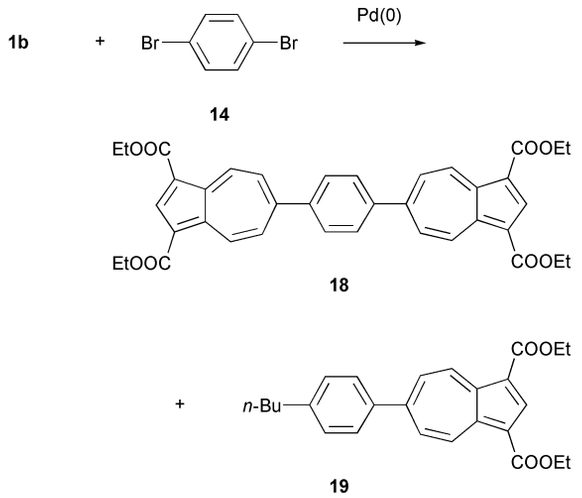


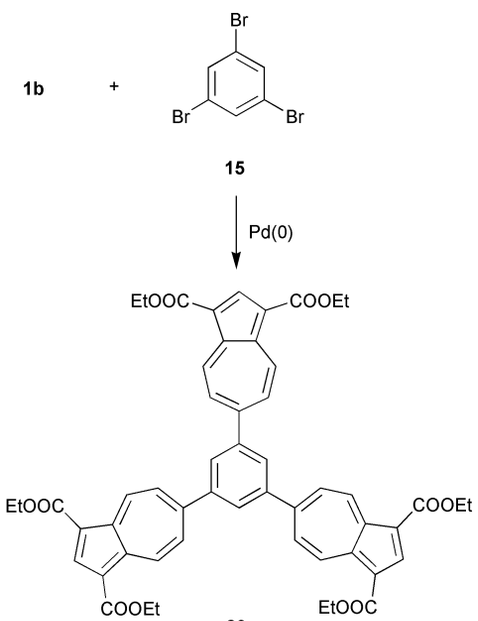
Chart 2

Finally, we demonstrated the use of the new 6-stannylazulene **1b** in the synthesis of poly(azulen-6-yl)benzene derivatives. We have recently reported the preparation of some azulen-6-ylbenzene derivatives utilizing Diels–Alder reaction of azulen-6-ylacetylenes with cyclopentadienone[4a] and Co-catalyzed cyclotrimerization of the azulen-6-ylacetylenes.[12] The reaction can introduce the azulen-6-yl groups to the aromatic core, but into limited positions. The scope of this methodology for multiple substitution was demonstrated utilizing the reaction of **1b** with di-, tri-, tetra- and hexabromobenzenes (**14**–**17**).

The reaction of **1b** with **14** afforded the desired coupled product, 1,4-bis[1,3-bis(ethoxycarbonyl)azulen-6-yl]benzene (**18**) in 32% yield along with 1-[1,3-bis(ethoxycarbonyl)azulen-6-yl]-4-butylbenzene (**19**) in 11% yield (Scheme 3). The reaction of **1b** with **15** also gave the desired tris-adduct **20**[12] in 28% yield together with 1,3-bis[1,3-bis(ethoxycarbonyl)azulen-6-yl]-5-butylbenzene (**21**) in 13% yield (Scheme 4). Therefore, transfer of an *n*-butyl group from the organotin reagent **1b** was the

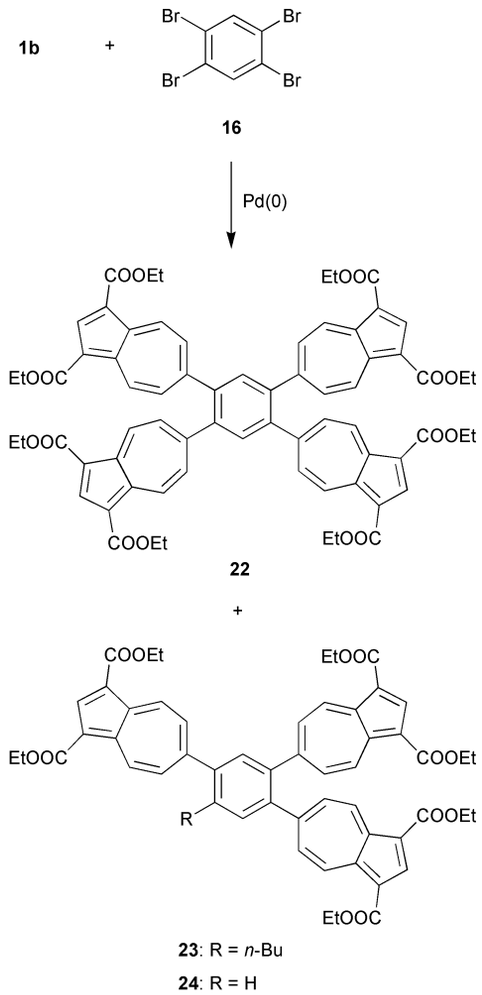


Scheme 3



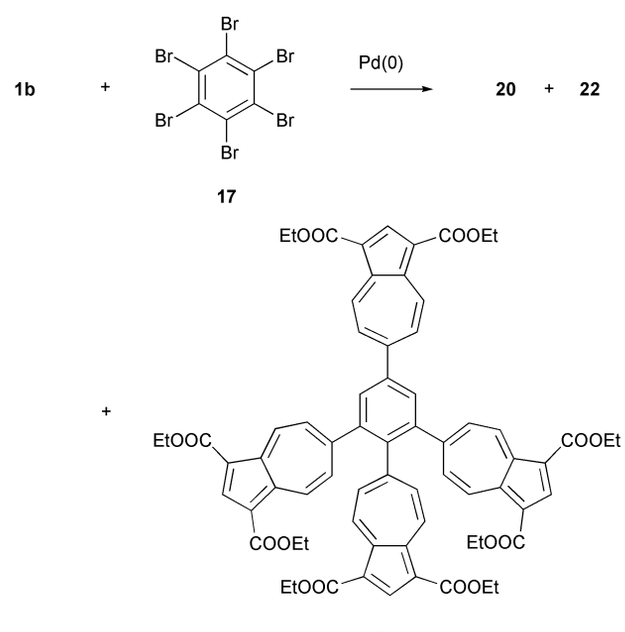
Scheme 4

side reaction for the multi-functionalization of benzene with azulen-6-yl substituents. Likewise, the reaction of **1b** with **16** afforded the expected tetrakis-adduct **22** in 13% yield together with 5-butyl-1,2,4-tris[1,3-bis(ethoxycarbonyl)azulen-6-yl]benzene (**23**) and 1,2,4-tris[1,3-bis(ethoxycarbonyl)azulen-6-yl]benzene (**24**)[12] in 5% and 6% yields, respectively (Scheme 5). On increasing the steric hindrance, the reduction of bromide also took place in addition to the transfer of an *n*-butyl group. In the

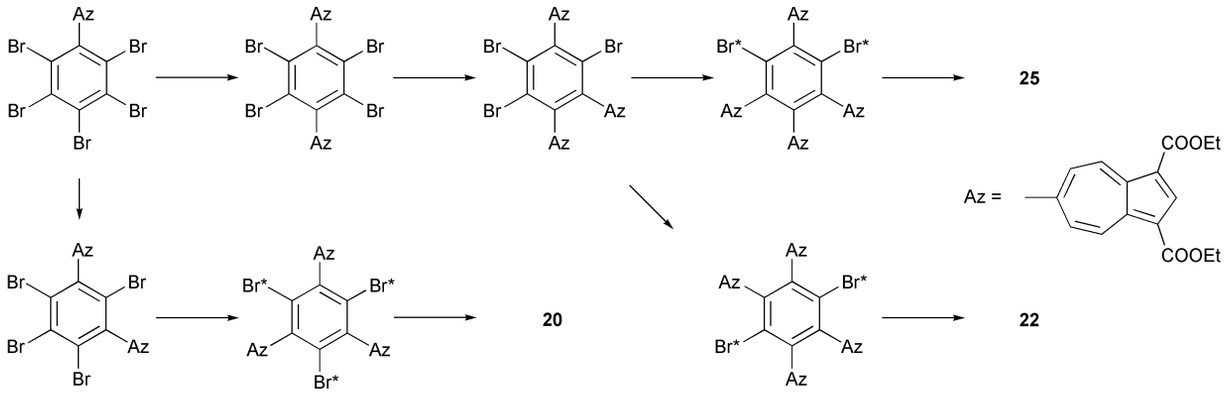


Scheme 5

case of the reaction of **1b** with **17**, the reaction afforded **20** and a mixture (1.6 : 1) of **22** and 1,2,3,5-tetrakis[1,3-bis(ethoxycarbonyl)azulen-6-yl]benzene (**25**) in 16% and 8% yields, respectively, instead of the desired hexa(azulen-6-yl)benzene derivative **26** (Scheme 6). Separation of the products **22** and **25** was attempted by repeated silica gel preparative TLC, but we



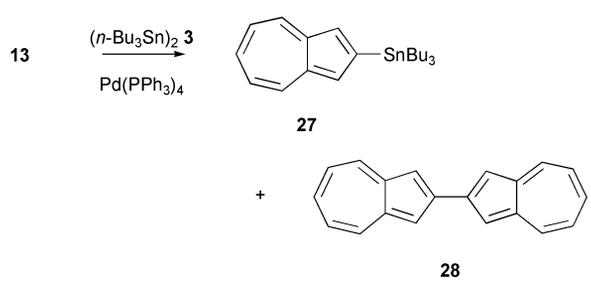
Scheme 6



Scheme 7

could not separate **22** and **25**, completely. The ratio of **22** and **25** could be increased up to 1 : 12 and the characterization of **25** was accomplished by both ^{1}H and ^{13}C NMR spectroscopy. Formation of the products **20**, **22** and **25** indicates that the transfer of azulen-6-yl groups does not occur at the positions pointed out by asterisks in Scheme 7, which are interposed by two azulen-6-yl groups. Since 1,2-disubstitution is unfavorable for steric reasons, therefore, a plausible pathway for the formation of these compounds could be depicted as in Scheme 7.

The methodology was then applied to functionaliaztion at the 2-position of azulenes. However, the reaction of 2-bromoazulene (**13**) with **3** under similar Pd(0)-catalyzed conditions afforded the desired 2-stannylazulene (**27**) in only 11% yield together with 2,2′-biazulene (**28**) in 48% yield (Scheme 8).[25] The



Scheme 8

high reactivity of either the desired product **27** with **13** or homocoupling[26] of **27** under the reaction conditions leads to the formation of **28** in significant amounts. For functionalization at the 2-position, use of azulen-2-yl borate, which could be prepared by the same strategy,[27] was more effective for similar Pd(0)-catalyzed reactions.[28]

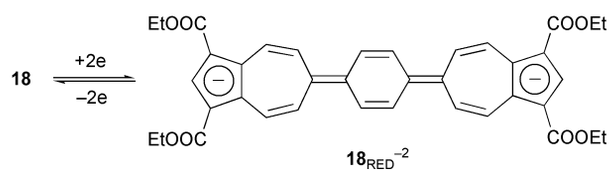
The redox behavior of the benzene derivatives **18** and **22** represented the presumed multi-electron redox properties. The reduction potentials (V *vs.* Ag/Ag^{+}) of **18** and **22**, along with those of **20** and **24**, measured by CV are summarized in Table 4. In contrast to the three-step reduction of the 1,3,5-tri(azulen-6-yl)benzene **20**,[12] compound **18** showed a reversible one-step two-electron reduction wave at −1.30 V upon CV (Fig. 1a). The relatively less negative reduction potential of **18** compared with that of **20** is attributable to the stabilization of the dianion by the formation of a closed-shell dianionic structure $\mathbf{18}_{\mathbf{RED}}{}^{-2}$. Therefore, the two azulen-6-yl substituents on the benzene ring in a 1,4 relationship increased the electron-accepting properties. Thus, the redox system of **18** can be depicted as illustrated in Scheme 9.

The voltammogram of **22** was characterized by a reversible wave at −1.27 V and the next barely separated irreversible one centered at −1.61 V upon CV (Fig. 1b). The first reversible wave for **22** should be due to the one-step two-electron reduction to form dianion $\mathbf{22}_{\mathbf{RED}}{}^{-2}$ and the second one could be attributed to the stepwise redox reaction of $\mathbf{22}_{\mathbf{RED}}{}^{-2}$ to produce

Table 4 Reduction potentials[a] of the poly(azulen-6-yl)benzene derivatives

Sample	E_1^{red}/V	E_2^{red}/V	E_3^{red}/V	Ref.
18	−1.30 (2e)			
20	(−1.38)[b]	(−1.46)[b]	(−1.55)[b]	12
22	−1.27 (2e)	(−1.57)[b]	(−1.62)[b]	
24	−1.31 (2e)	−1.63 (1e)		12

[a] The reduction potentials were measured by CV (0.1 M n-Bu_4NBF_4 in tetrahydrofuran, Pt electrode, scan rate = 100 mV s^{-1}, and Fc/Fc^{+} = 0.19 V). In the case of irreversible waves, which are shown in parentheses, E_{red} were calculated as E_{pc} (cathodic peak potential) + 0.03 V. [b] The values are peak potentials measured by DPV.



Scheme 9

tetraanion diradical $\mathbf{22}_{\mathbf{RED}}{}^{\bullet\bullet-4}$, by analogy with those of 1,2,4-tri(azulen-6-yl)benzene derivative **24**.[12] Indeed, the second wave was identified as two waves that were barely separated, at −1.57 and −1.62 V, by differential pulse voltammetry (DPV). Thus, the four azulen-6-yl substituents on benzene in a 1,2,4,5 relationship increased the electron-accepting properties because of the formation of a closed-shell dianionic structure $\mathbf{22}_{\mathbf{RED}}{}^{-2}$. Consequently, the redox system of **22** could be illustrated as a violene–cyanine hybrid and could exhibit a significant color change with a change to a different oxidation state (Scheme 10).

Electrochemical reduction of **22** was examined to clarify the formation of colored species arising from dianion $\mathbf{22}_{\mathbf{RED}}{}^{-2}$ by visible spectroscopy under the electrochemical reduction conditions. When the visible spectra of **22** were measured under the electrochemical reduction conditions in benzonitrile containing Et_4NClO_4 (0.1 M) at room temperature, a new absorption in the visible region was gradually developed as shown in Fig. 2. The color of the solution of **22** gradually changed from pink to brown during the electrochemical reduction. However, the reverse oxidation of the colored solution did not regenerate the spectrum of the neutral **22**, although good reversibility was observed upon CV. The color of the solution changed to orange during the electrochemical oxidation. These results demonstrate the low stability of the dianionic species under the conditions of the measurement, although the dianions $\mathbf{22}_{\mathbf{RED}}{}^{-2}$ are stabilized by four azulen-6-yl substituents.

Conclusion

As stated above, the first organotin reagents of azulenes, 6-stannylazulenes (**1a** and **1b**), were prepared by Pd(0)-catalyzed

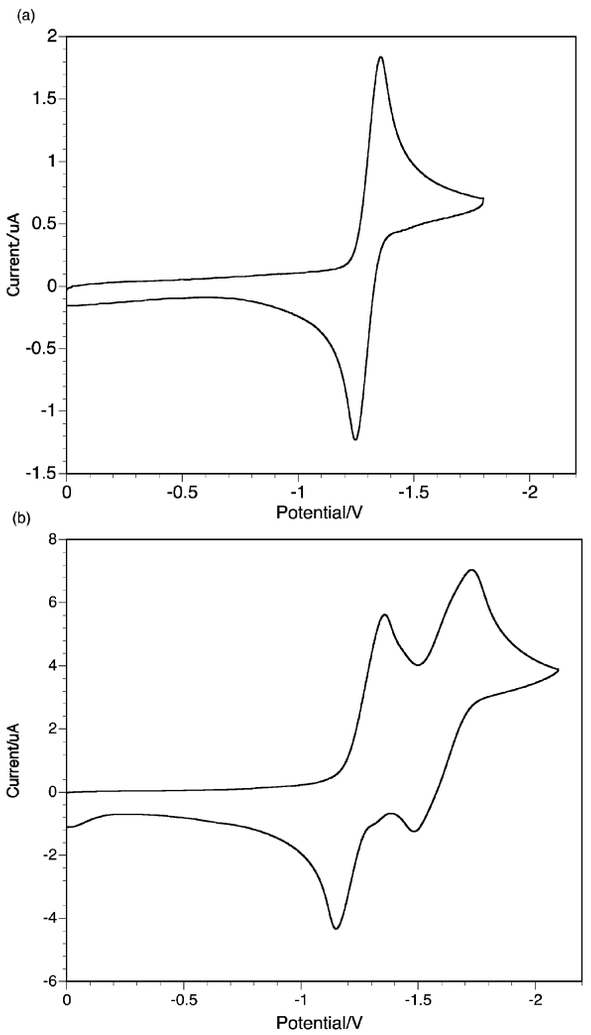


Fig. 1 Cyclic voltammograms of (a) **18** and (b) **22** in THF containing *n*-Bu_4NBF_4 (0.1 M) as a supporting electrolyte.

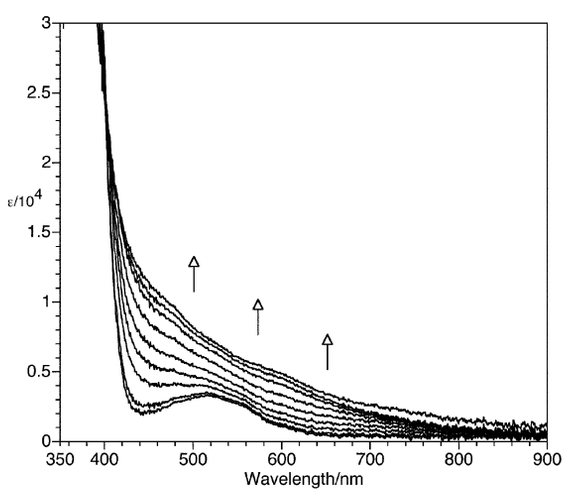
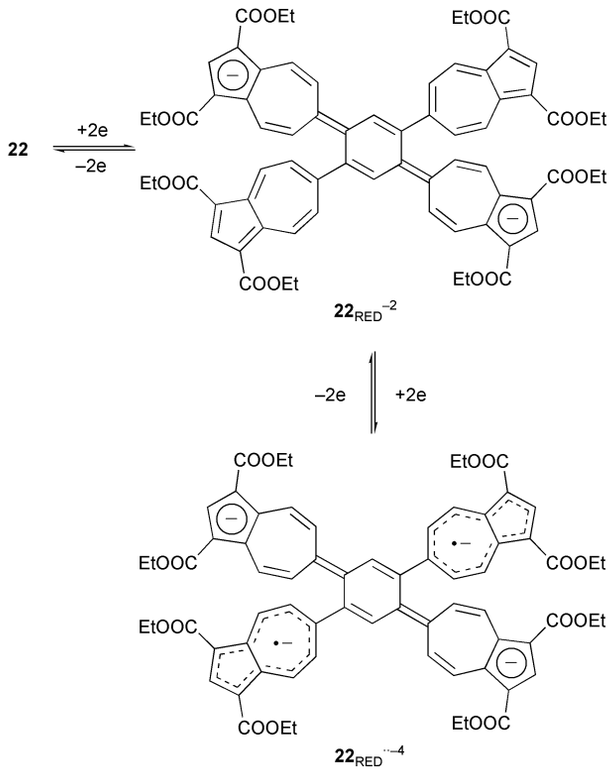


Fig. 2 Continuous change in visible spectrum of **22** (2 cm^3; 2.0 × 10^{-4} M) in benzonitrile containing Et_4NClO_4 (0.1 M) upon constant-current electrochemical reduction (100 uA) at 3 min interval.

direct stannylation of 6-bromoazulenes (**2a** and **2b**) and their application in Pd(0)-catalyzed Stille cross-coupling reaction with aryl, acyl and azulenyl halides was investigated. In fact, our new stannylazulenes were effective in the Stille cross-coupling reaction to afford 6-aryl-, 6-acyl- and bi-azulenes. This study shows the potential utility of the new transition-metal catalyzed reaction for the difficult functionalization of azulenes in the seven-membered ring. Indeed, the methodology was



Scheme 10

applied to the synthesis of several poly(azulen-6-yl)benzene derivatives (**18**–**25**). The redox behavior of **18** and **22** was examined by cyclic voltammetry (CV) and compared with those of **20** and **24** reported previously. We could not detect the colored closed-shell dianion of azulene-substituted benzene derivatives by UV–vis spectroscopy due to the instability of the species. However, the redox behavior examined by CV represented the presumed multi-electron redox properties under the electrochemical conditions used.

Experimental

General

Mps were determined on a Yanagimoto micro melting point apparatus MP-S3 and are uncorrected. Mass spectra were obtained with a JEOL HX-110 or a Hitachi M-2500 instrument usually at 70 eV. IR and UV spectra were measured on a Shimadzu FTIR-8100M and a Hitachi U-3410 spectrophotometers, respectively. ^1H NMR spectra (^{13}C NMR spectra) were recorded on a JEOL GSX 400 at 400 MHz (100 MHz) or a JEOL A500 at 500 MHz (125 MHz). Gel permeation chromatography (GPC) was performed on a TSKgel $G2000H_6$. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

6-(Tri-*n*-butylstannyl)azulene 1a

To a degassed solution of **2a** (829 mg, 4.00 mmol) and **3** (4.65 g, 8.02 mmol) in dry toluene (50 cm^3) was added $Pd(PPh_3)_4$ (239 mg, 0.207 mmol). After the resulting mixture was refluxed for 24 h under an Ar atmosphere, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel and medium-pressure liquid column chromatography on silica gel with hexane to afford **1a** (817 mg, 49%) as a blue oil (Found: C, 63.3; H, 8.1. Calc. for $C_{22}H_{34}Sn$: C, 63.3; H, 8.2%); λ_{max} (CH_2Cl_2)/nm 238 (log ε 4.16), 286 (4.74), 332 (3.70), 339 (3.67), 347 (3.83), 575 (2.51), 620 (2.44) and 682 (2.01); ν_{max} (neat)/cm^{-1} 2960, 2924, 2868, 2852, 1578, 1464, 1446, 1396, 814 and 746; δ_H (400 MHz, $CDCl_3$) 8.22

(d, *J* 9.3, 2H, 4,8-H), 7.88 (t, *J* 3.8, 1H, 2-H), 7.36 (d, *J* 3.8, 2H, 1,3-H), 7.35 (d, *J* 9.3, 2H, 5,7-H), 1.57 (m, 6H, 2′-H), 1.35 (tq, *J* 7.3 and 7.3, 6H, 3′-H), 1.14 (m, 6H, 1′-H) and 0.89 (t, *J* 7.3, 9H, 4′-H); δ_C (100 MHz, $CDCl_3$) 159.8 (C-6), 139.7 (C-3a,8a), 137.0 (C-2), 134.5 (C-4,8), 130.6 (C-5,7), 117.4 (C-1,3), 29.0 (C-2′), 27.4 (C-3′), 13.7 (C-4′) and 10.4 (C-1′); *m*/*z* (EI) 418 (M^+, 50%), 361 ($M^+ - Bu$, 86), 305 ($M^+ - 2Bu+H$, 56) and 247 ($M^+ - 3Bu$, 100).

Diethyl 6-(tri-*n*-butylstannyl)azulene-1,3-dicarboxylate 1b

The same procedure as was used for the preparation of **1a** was adopted. The reaction of **2b** (3.49 g, 9.94 mmol) with **3** (11.52 g, 19.86 mmol) in dry toluene (200 cm^3) in the presence of $Pd(PPh_3)_4$ (569 mg, 0.492 mmol) followed by chromatographic purification on silica gel with hexane and CH_2Cl_2 and medium-pressure column chromatography on silica gel with 30% ethyl acetate–hexane afforded **1b** (3.86 g, 69%) as a red oil (Found: C, 59.7; H, 7.45. Calc. for $C_{28}H_{42}O_4Sn$: C, 59.9; H, 7.5%); λ_{max} (CH_2Cl_2)/nm 235 (log ε 4.52), 275 (4.44), 311 (4.65), 377 (4.06) and 502 (2.88); ν_{max} (neat)/cm^{-1} 2957, 2928, 1694 (C=O), 1431, 1202 and 1048; δ_H (400 MHz, $CDCl_3$) 9.63 (d, *J* 10.0, 2H, 4,8-H), 8.83 (s, 1H, 2-H), 7.96 (d, *J* 10.0, 2H, 5,7-H), 4.44 (q, *J* 7.1, 4H, 1,3-COOEt), 1.58 (m, 6H, 2′-H), 1.46 (t, *J* 7.1, 6H, 1,3-COOEt), 1.35 (tq, *J* 7.3 and 7.3, 6H, 3′-H), 1.21 (m, 6H, 1′-H) and 0.90 (t, *J* 7.3, 9H, 4′-H); δ_C (100 MHz, $CDCl_3$) 166.6 (C-6), 165.1 (s, 1,3-COOEt), 143.6 (C-3a,8a), 143.5 (C-2), 138.6 (C-5,7), 136.6 (C-4,8), 115.7 (C-1,3), 59.9 (t, 1,3-COOEt), 28.9 (C-2′), 27.3 (C-3′), 14.6 (q, 1,3-COOEt), 13.6 (C-4′) and 10.6 (C-1′); *m*/*z* (EI) 562 (M^+, 40%) and 505 ($M^+ - Bu$, 100).

General procedure for the Stille cross-coupling reaction of 1a and 1b

To a degassed solution of **1a** or **1b** and aryl, acyl or azulenyl halides in dry solvent was added Pd(0)-catalyst, ligand and CsF. After the resulting mixture was refluxed under an Ar atmosphere, the solvent was removed under reduced pressure. The products were isolated by column chromatography on silica gel with CH_2Cl_2 and/or 5–10% ethyl acetate–CH_2Cl_2, medium-pressure column chromatography on silica gel with 30% ethyl acetate–hexane and/or gel permeation chromatography (GPC) with $CHCl_3$.

Diethyl 6-tolylazulene-1,3-dicarboxylate 5. The general procedure was followed by using **1b** (116 mg, 0.207 mmol), **4a** (104 mg, 0.608 mmol), $Pd_2(dba)_3$ (18.3 mg, 0.0200 mmol), P(*t*-Bu)$_3$ (20.1 mg, 0.0993 mmol), CsF (66.5 mg, 0.438 mmol) and dioxane (20 cm^3). Chromatographic purification afforded **5** (55.4 mg, 74%) as deep red needles, **7b** (4.4 mg, 8%) as red crystals and **8b** (2.7 mg, 5%) as a purple powder.

For ***5***. Mp 171.5–175 °C (Found: C, 75.8; H, 6.15. Calc. for $C_{23}H_{22}O_4$: C, 76.2; H, 6.1%); λ_{max} (CH_2Cl_2)/nm 235 (log ε 4.57), 271 (4.24), 335 (4.71) and 508 (2.92); ν_{max} (KBr disk)/cm^{-1} 1684 (C=O), 1580, 1432, 1426, 1392, 1210, 1194, 1086, 1050 and 814; δ_H (500 MHz, $CDCl_3$) 9.79 (d, *J* 10.2, 2H, 4,8-H), 8.80 (s, 1H, 2-H), 7.94 (d, *J* 10.2, 2H, 5,7-H), 7.58 (d, *J* 8.2, 2H, 2′,6′-H), 7.34 (d, *J* 8.2, 2H, 3′,5′-H), 4.44 (q, *J* 7.1, 4H, 1,3-COOEt), 2.45 (s, 3H, 4′-Me) and 1.46 (t, *J* 7.1, 6H, 1,3-COOEt); δ_C (125 MHz, $CDCl_3$) 165.1 (s, 1,3-COOEt), 154.6 (C-6), 142.9 (C-2), 142.6 (C-3a,8a), 140.6 (C-1′), 139.2 (C-4′), 138.4 (C-4,8), 130.7 (C-5,7), 129.8 (C-3′,5′), 128.7 (C-2′,6′), 116.3 (C-1,3), 60.0 (t, 1,3-COOEt), 21.2 (4′-Me) and 14.6 (q, 1,3-COOEt); *m*/*z* (EI) 362 (M^+, 100%), 317 ($M^+ - OEt$, 41) and 289 ($M^+ - COOEt$, 38).

For ***7b***. Mp 121.5–122.5 °C (lit.[18] mp 120–121 °C).

For ***8b***. Mp 227.5–230 °C (Found: C, 70.8; H, 5.6. Calc. for $C_{32}H_{30}O_8$: C, 70.8; H, 5.6%); λ_{max} (CH_2Cl_2)/nm 240 (log ε 4.72), 271 (4.51), 341 (4.79) and 519 (3.17); ν_{max} (KBr disk)/cm^{-1} 1705 (C=O), 1435, 1213 and 1200; δ_H (400 MHz, $CDCl_3$) 9.87 (d, *J* 11.0, 4H, 4,8-H), 8.90 (s, 2H, 2-H), 7.95 (d, *J* 11.0, 4H, 5,7-H), 4.47 (q, *J* 7.2, 8H, 1,3-COOEt) and 1.48 (t, *J* 7.2, 12H, 1,3-COOEt); δ_C (100 MHz, $CDCl_3$) 164.8 (s, 1,3-COOEt), 155.8 (C-6), 144.4 (C-2), 142.9 (C-3a,8a), 138.3 (C-4,8), 131.2 (C-5,7), 117.3 (C-1,3), 60.3 (t, 1,3-COOEt) and 14.5 (q, 1,3-COOEt); *m*/*z* (EI) 542 (M^+, 100%) and 497 ($M^+ - OEt$, 21).

Diethyl 6-(4-nitrophenyl)azulene-1,3-dicarboxylate 9a. The general procedure was followed by using **1b** (111 mg, 0.198 mmol), 4-bromonitrobenzene (120 mg, 0.594 mmol), $Pd_2(dba)_3$ (17.6 mg, 0.0192 mmol), P(*t*-Bu)$_3$ (21.8 mg, 0.108 mmol), CsF (66.7 mg, 0.439 mmol) and dioxane (20 cm^3). Chromatographic purification afforded **9a** (65.7 mg, 84%) as purple crystals, **7b** (2.6 mg, 5%) and **8b** (5.4 mg, 10%).

For ***9a***. Mp 175–175.5 °C (Found: C, 67.0; H, 5.0; N, 3.7. Calc. for $C_{22}H_{19}NO_6$: C, 67.2; H, 4.9; N, 3.6%); λ_{max} (CH_2Cl_2)/nm 236 (log ε 4.44), 272 (4.26), 327 (4.72) and 525 (2.78); ν_{max} (KBr disk)/cm^{-1} 1694 (C=O), 1522, 1437, 1347, 1206 and 1048; δ_H (500 MHz, $CDCl_3$) 9.85 (d, *J* 11.1, 2H, 4,8-H), 8.87 (s, 1H, 2-H), 8.38 (d, *J* 8.9, 2H, 3′,5′-H), 7.89 (d, *J* 11.1, 2H, 5,7-H), 7.83 (d, *J* 8.9, 2H, 2′,6′-H), 4.46 (q, *J* 7.1, 4H, 1,3-COOEt) and 1.47 (t, *J* 7.1, 6H, 1,3-COOEt); δ_C (125 MHz, $CDCl_3$) 164.8 (s, 1,3-COOEt), 151.4 (C-6), 149.7 (C-1′), 148.0 (C-4′), 144.2 (C-2), 142.9 (C-3a,8a), 138.4 (C-4,8), 130.3 (C-5,7), 129.6 (C-2′,6′), 124.2 (C-3′,5′), 117.2 (C-1,3), 60.2 (t, 1,3-COOEt) and 14.5 (q, 1,3-COOEt); *m*/*z* (EI) 393 (M^+, 100%), 348 ($M^+ - OEt$, 41) and 320 ($M^+ - COOEt$, 17).

Diethyl 6-(4-acetylphenyl)azulene-1,3-dicarboxylate 9b. The general procedure was followed by using **1b** (118 mg, 0.210 mmol), 4-bromoacetophenone (123 mg, 0.618 mmol), $Pd_2(dba)_3$ (21.6 mg, 0.0236 mmol), P(*t*-Bu)$_3$ (19.6 mg, 0.0969 mmol), CsF (75.8 mg, 0.499 mmol) and dioxane (20 cm^3). Chromatographic purification afforded **9b** (53.1 mg, 65%) as purple crystals, **7b** (2.3 mg, 4%) and **8b** (2.6 mg, 5%).

For ***9b***. Mp 125–126.5 °C (Found: C, 73.65; H, 5.7. Calc. for $C_{24}H_{22}O_5$: C, 73.8; H, 5.7%); λ_{max} (CH_2Cl_2)/nm 235 (log ε 4.46), 270 (4.22), 328 (4.79) and 521 (2.86); ν_{max} (KBr disk)/cm^{-1} 1686 (C=O), 1437, 1393, 1248, 1208 and 1048; δ_H (500 MHz, $CDCl_3$) 9.83 (d, *J* 11.1, 2H, 4,8-H), 8.85 (s, 1H, 2-H), 8.11 (d, *J* 8.5, 2H, 3′,5′-H), 7.93 (d, *J* 11.1, 2H, 5,7-H), 7.77 (d, *J* 8.5, 2H, 2′,6′-H), 4.45 (q, *J* 7.1, 4H, 1,3-COOEt), 2.68 (s, 3H, 4′-COMe) and 1.47 (t, *J* 7.1, 6H, 1,3-COOEt); δ_C (125 MHz, $CDCl_3$) 197.4 (s, 4′-COMe), 164.9 (s, 1,3-COOEt), 152.9 (C-6), 147.9 (C-1′), 143.8 (C-2), 142.9 (C-3a,8a), 138.4 (C-4,8), 137.0 (C-4′), 130.5 (C-5,7), 129.0 (C-2′,6′ and C-5′,6′), 116.8 (C-1,3), 60.1 (t, 1,3-COOEt), 20.8 (q, 4′-COMe) and 14.6 (q, 1,3-COOEt); *m*/*z* (EI) 390 (M^+, 100%), 345 ($M^+ - OEt$, 36) and 317 ($M^+ - COOEt$, 25).

Diethyl 6-(4-methoxyphenyl)azulene-1,3-dicarboxylate 9c. The general procedure was followed by using **1b** (114 mg, 0.203 mmol), 4-bromoanisole (128 mg, 0.684 mmol), $Pd_2(dba)_3$ (19.6 mg, 0.0214 mmol), P(*t*-Bu)$_3$ (21.5 mg, 0.106 mmol), CsF (68.4 mg, 0.450 mmol) and dioxane (20 cm^3). Chromatographic purification afforded **9c** (49.5 mg, 64%) as red crystals, **7b** (2.5 mg, 5%) and **8b** (1.4 mg, 3%).

For ***9c***. Mp 149–150 °C (Found: C, 72.8; H, 6.0. Calc. for $C_{23}H_{22}O_5$: C, 73.0; H, 5.9%); λ_{max} (CH_2Cl_2)/nm 269 (log ε 4.25), 300 (4.21), 349 (4.59) and 505 (2.94); ν_{max} (KBr disk)/cm^{-1} 1686 (C=O), 1678 (C=O), 1578, 1510, 1429, 1389, 1200, 1183, 1049 and 1036; δ_H (500 MHz, $CDCl_3$) 9.77 (d, *J* 11.1, 2H, 4,8-H), 8.78 (s, 1H, 2-H), 7.93 (d, *J* 11.1, 2H, 5,7-H), 7.65 (d, *J* 8.9, 2H, 2′,6′-H), 7.06 (d, *J* 8.9, 2H, 3′,5′-H), 4.44 (q, *J* 7.1, 4H, 1,3-COOEt), 3.90 (s, 3H, 4′-OMe) and 1.46 (t, *J* 7.1, 6H, 1,3-COOEt); δ_C (125 MHz, $CDCl_3$) 165.1 (s, 1,3-COOEt), 160.6 (C-4′), 154.3 (C-6), 142.7 (C-2), 142.4 (C-3a,8a), 138.4 (C-4,8), 135.8 (C-1′), 130.4 (C-5,7), 130.1 (C-2′,6′), 116.3 (C-1,3), 114.6 (C-3′,5′), 60.0 (t, 1,3-COOEt), 55.5 (4′-OMe) and 14.6 (q, 1,3-COOEt); *m*/*z* (EI) 378 (M^+, 100%), 333 ($M^+ - OEt$, 32) and 305 ($M^+ - COOEt$, 20).

6-(4-Tolyl)azulene 9d. The general procedure was followed by using **1a** (134 mg, 0.321 mmol), 4-bromotoluene (176 mg, 1.029 mmol), $Pd_2(dba)_3$ (27.4 mg, 0.0299 mmol), P(*t*-Bu)$_3$ (34.5 mg, 0.171 mmol), CsF (98.4 mg, 0.648 mmol) and dioxane (30 cm^3). Chromatographic purification afforded **9d** (42.1 mg, 60%) as blue plates, **7a** (2.0 mg, 5%) and **8a** (4.8 mg, 12%) as green crystals.

*For **9d**.* Mp 202–203 °C (lit.[3b] mp 199–200 °C, lit.[21] mp 203–205 °C).

*For **8a**.* Mp >300 °C (lit.[24b] mp >315 °C).

6-(4-Nitrophenyl)azulene 9e. The general procedure was followed by using **1a** (130 mg, 0.312 mmol), 4-bromonitrobenzene (183 mg, 0.906 mmol), $Pd_2(dba)_3$ (28.2 mg, 0.0308 mmol), P(*t*-Bu)$_3$ (24.1 mg, 0.119 mmol), CsF (106 mg, 0.698 mmol) and dioxane (30 cm^3). Chromatographic purification afforded **9e** (64.4 mg, 83%) as a deep green powder, **7a** (1.8 mg, 5%) and the recovered **1a** (5.9 mg, 5%).

*For **9e**.* Mp 205–206 °C (Found: C, 76.9; H, 4.7; N, 5.6. Calc. for $C_{16}H_{11}NO_2$: C, 77.1; H, 4.45; N, 5.6%); λ_{max} (CH_2Cl_2)/nm 236 (log ε 4.17), 307 (4.66), 351 (4.01), 373 (4.08) and 604 (2.55); ν_{max} (KBr disk)/cm^{-1} 1593, 1574, 1512, 1395, 1339, 839 and 770; δ_H (500 MHz, $CDCl_3$) 8.43 (d, *J* 10.5, 2H, 4,8-H), 8.33 (d, *J* 9.0, 2H, 3′,5′-H), 7.98 (t, *J* 3.7, 1H, 2-H), 7.78 (d, *J* 9.0, 2H, 2′,6′-H), 7.47 (d, *J* 3.7, 2H, 1,3-H) and 7.34 (d, *J* 10.5, 2H, 5,7-H); δ_C (125 MHz, $CDCl_3$) 151.7 (C-1′), 147.9 (C-6), 147.4 (C-4′), 139.3 (C-3a,8a), 138.3 (C-2), 135.7 (C-4,8), 129.4 (C-2′,6′), 123.9 (C-3′,5′), 122.9 (C-5,7) and 119.2 (C-1,3); *m*/*z* (EI) 249 (M^+, 100%) and 202 ($M^+ - NO_2$, 55).

6-(4-Acetylphenyl)azulene 9f. The general procedure was followed by using **1a** (125 mg, 0.300 mmol), 4-bromoacetophenone (181.3 mg, 0.909 mmol), $Pd_2(dba)_3$ (30.2 mg, 0.0330 mmol), P(*t*-Bu)$_3$ (31.7 mg, 0.157 mmol), CsF (119 mg, 0.783 mmol) and dioxane (30 cm^3). Chromatographic purification afford **9f** (49.2 mg, 67%) as blue needles and the recovered **1a** (0.9 mg, 1%).

*For **9f**.* Mp 232.5–233.5 °C (Found: C, 87.4; H, 5.8. Calc. for $C_{18}H_{14}O$: C, 87.8; H, 5.7%); λ_{max} (CH_2Cl_2)/nm 238 (log ε 4.12), 305 (4.89), 353 (3.95), 371 (4.01) and 598 (2.58); ν_{max} (KBr disk)/cm^{-1} 1682 (C=O), 1578, 1402, 1270 and 822; δ_H (500 MHz, $CDCl_3$) 8.41 (d, *J* 10.5, 2H, 4,8-H), 8.06 (d, *J* 8.5, 2H, 3′,5′-H), 7.94 (t, *J* 3.7, 1H, 2-H), 7.72 (d, *J* 8.5, 2H, 2′,6′-H), 7.44 (d, *J* 3.7, 2H, 1,3-H), 7.37 (d, *J* 10.5, 2H, 5,7-H) and 2.66 (s, 3H, 4′-COMe); δ_C (125 MHz, $CDCl_3$) 197.7 (s, 4′-COMe), 149.9 (C-1′), 149.3 (C-6), 139.2 (C-3a,8a), 137.7 (C-2), 136.2 (C-4′), 135.8 (C-4,8), 128.8 (C-2′,6′), 128.7 (C-3′,5′), 123.1 (C-5,7), 118.8 (C-1,3) and 26.7 (q, 4′-COMe); *m*/*z* (EI) 246 (M^+, 100%), 203 ($M^+ -$ COMe, 28) and 202 ($M^+ -$ COMe − H, 30).

6-(4-Methoxyphenyl)azulene 9g. The general procedure was followed by using **1a** (129 mg, 0.309 mmol), 4-bromoanisole (179 mg, 0.957 mmol), $Pd_2(dba)_3$ (31.7 mg, 0.0346 mmol), P(*t*-Bu)$_3$ (33.0 mg, 0.163 mmol), CsF (112 mg, 0.737 mmol) and dioxane (30 cm^3). Chromatographic purification afforded **9g** (45.4 mg, 63%) as violet crystals, **7a** (2.3 mg, 6%) and the recovered **1a** (10.6 mg, 8%).

*For **9g**.* Mp 212.5–214 °C (Found: C, 86.85; H, 5.8. Calc. for $C_{17}H_{14}O$: C, 87.15; H, 6.0%); λ_{max} (CH_2Cl_2)/nm 234 (log ε 4.19), 286 (4.49), 315 (4.61), 377 (4.11) and 581 (2.58); ν_{max} (KBr disk)/cm^{-1} 1582, 1404, 1296, 1252, 1178, 826, 816 and 752; δ_H (500 MHz, $CDCl_3$) 8.38 (d, *J* 10.4, 2H, 4,8-H), 7.87 (br, 1H, 2-H), 7.61 (d, *J* 8.8, 2H, 2′,6′-H), 7.40 (br, 2H, 1,3-H), 7.39 (d, *J* 10.4, 2H, 5,7-H), 7.02 (d, *J* 8.8, 2H, 3′,5′-H) and 3.89 (s, 3H, 4′-OMe); δ_C (125 MHz, $CDCl_3$) 159.8 (C-4′), 150.6 (C-6), 138.7 (C-3a,8a), 137.8 (C-1′), 136.4 (C-2), 135.8 (C-4,8), 129.7 (C-2′,6′), 123.1 (C-5,7), 118.2 (C-1,3), 114.2 (C-3′,5′) and 55.4 (4′-OMe); *m*/*z* (EI) 234 (M^+, 100%) and 219 ($M^+ -$ Me, 12).

Diethyl 6-benzoylazulene-1,3-dicarboxylate 10a. The general procedure was followed by using **1b** (131 mg, 0.233 mmol), benzoyl chloride (84.3 mg, 0.600 mmol), $Pd_2(dba)_3$ (20.4 mg, 0.0223 mmol), P(*t*-Bu)$_3$ (29.9 mg, 0.148 mmol), CsF (69.8 mg, 0.460 mmol) and dioxane (20 cm^3). Chromatographic purification afforded **10a** (80.3 mg, 91%) as deep green needles, mp 153–155 °C (Found: C, 73.2; H, 5.5. Calc. for $C_{23}H_{20}O_5$: C, 73.4; H, 5.4%); λ_{max} (CH_2Cl_2)/nm 242 (log ε 4.53), 269 (4.34), 313 (4.77), 349 (3.97), 378 (3.95) and 548 (2.73); ν_{max} (KBr disk)/cm^{-1} 1701 (C=O), 1663 (C=O), 1439, 1235, 1196 and 1042; δ_H (500 MHz, $CDCl_3$) 9.82 (d, *J* 10.9, 2H, 4,8-H), 8.96 (s, 1H, 2-H), 8.02 (d, *J* 10.9, 2H, 5,7-H), 7.83 (dd, *J* 8.2 and 1.1, 2H, 2′,6′-H), 7.66 (tt, *J* 7.4 and 1.1, 1H, 4′-H), 7.52 (dd, *J* 8.2 and 7.4, 2H, 3′,5′-H), 4.46 (q, *J* 7.1, 4H, 1,3-COOEt) and 1.47 (t, *J* 7.1, 6H, 1,3-COOEt); δ_C (100 MHz, $CDCl_3$) 197.5 (CO), 164.7 (s, 1,3-COOEt), 148.2 (C-6), 145.6 (C-2), 144.4 (C-3a,8a), 138.2 (C-4,8), 136.2 (C-1′), 133.6 (C-4′), 130.6 (C-2′,6′), 130.1 (C-5,7), 128.6 (C-3′,5′), 117.4 (C-1,3), 60.3 (t, 1,3-COOEt) and 14.5 (q, 1,3-COOEt); *m*/*z* (EI) 376 (M^+, 100%), 331 ($M^+ -$ OEt, 37) and 303 ($M^+ -$ COOEt, 14).

Diethyl 6-(*n*-heptanoyl)azulene-1,3-dicarboxylate 10b. The general procedure was followed by using **1b** (112 mg, 0.200 mmol), *n*-heptanoyl chloride (88.6 mg, 0.596 mmol), $Pd_2(dba)_3$ (18.7 mg, 0.0204 mmol), P(*t*-Bu)$_3$ (35.4 mg, 0.175 mmol), CsF (88.1 mg, 0.580 mmol) and dioxane (20 cm^3). Chromatographic purification afforded **10b** (56.3 mg, 73%) as purple needles and **7b** (12.0 mg, 22%).

*For **10b**.* Mp 65–66 °C (Found: C, 71.7; H, 7.5. Calc. for $C_{23}H_{28}O_5$: C, 71.85; H, 7.3%); λ_{max} (CH_2Cl_2)/nm 245 (log ε 4.50), 272 (4.22), 314 (4.75), 349 (3.90), 377 (3.83) and 559 (2.69); ν_{max} (KBr disk)/cm^{-1} 1698 (C=O), 1686 (C=O), 1429, 1233, 1210 and 1032; δ_H (400 MHz, $CDCl_3$) 9.84 (d, *J* 11.0, 2H, 4,8-H), 8.91 (s, 1H, 2-H), 8.28 (d, *J* 11.0, 2H, 5,7-H), 4.45 (q, *J* 7.1, 4H, 1,3-COOEt), 3.14 (t, *J* 7.3, 2H, 2′-H), 1.80 (tt, *J* 7.5 and 7.3, 2H, 3′-H), 1.47 (t, *J* 7.1, 6H, 1,3-COOEt), 1.42 (m, 2H, 4′-H), 1.38–1.32 (m, 4H, 5′,6′-H) and 0.91 (m, 3H, 7′-H); δ_C (100 MHz, $CDCl_3$) 202.1 (C-1′), 164.6 (s, 1,3-COOEt), 145.8 (C-2 and C-6), 144.6 (C-3a,8a), 138.1 (C-4,8), 128.7 (C-5,7), 117.2 (C-1,3), 60.3 (t, 1,3-COOEt), 39.6 (C-2′), 31.6 (C-5′ or C-6′), 28.9 (C-4′), 24.5 (C-3′), 22.5 (C-5′ or C-6′), 14.5 (q, 1,3-COOEt) and 14.0 (C-7′); *m*/*z* (EI) 384 (M^+, 100%), 339 ($M^+ -$ OEt, 21), 299 ($M^+ - C_6H_{13}$, 7) and 271 ($M^+ - COC_6H_{13}$, 6).

Diethyl 6-acetylazulene-1,3-dicarboxylate 10c. The general procedure was followed by using **1b** (122 mg, 0.217 mmol), acetyl chloride (57.9 mg, 0.738 mmol), $Pd_2(dba)_3$ (20.1 mg, 0.0219 mmol), P(*t*-Bu)$_3$ (27.0 mg, 0.133 mmol), CsF (79.0 mg, 0.520 mmol) and dioxane (20 cm^3). Chromatographic purification afforded **10c** (17.7 mg, 26%) as purple plates and **7b** (29.5 mg, 50%).

*For **10c**.* Mp 120.5–123 °C (lit.[22] mp 129–130 °C).

Tetraethyl 6,6′-biazulene-1,1′,3,3′-tetracarboxylate 8b. Following the general procedure, the reaction of **1b** (113 mg, 0.201 mmol) with **2b** (79.8 mg, 0.227 mmol) in refluxing dioxane (20 cm^3) for 2 h in the presence of $Pd_2(dba)_3$ (19.5 mg, 0.0213 mmol), P(*t*-Bu)$_3$ (26.7 mg, 0.132 mmol) and CsF (75.5 mg, 0.497 mmol) afforded **8b** (73.9 mg, 68%).

Diethyl 6,6′-biazulene-1,3-dicarboxylate 11. Following the general procedure, the reaction of **1b** (113 mg, 0.201 mmol) with **2a** (50.0 mg, 0.241 mmol) in refluxing dioxane (20 cm^3) for 2 h in the presence of $Pd_2(dba)_3$ (18.8 mg, 0.0205 mmol), P(*t*-Bu)$_3$ (24.3 mg, 0.120 mmol) and CsF (69.8 mg, 0.460 mmol) afforded **11** (36.7 mg, 46%) as deep purple crystals, mp 190–191 °C (Found: C, 78.2; H, 5.7. Calc. for $C_{26}H_{22}O_4$: C, 78.4; H, 5.6%); λ_{max} (CH_2Cl_2)/nm 241 (log ε 4.61), 273 (4.54), 328 (4.88), 376 (4.53), 448 (3.06) and 520 (3.03); ν_{max} (KBr disk)/cm^{-1} 1686

(C=O), 1678 (C=O), 1433, 1391, 1198 and 1044; δ_H (500 MHz, $CDCl_3$) 9.84 (d, *J* 11.1, 2H, 4,8-H), 8.86 (s, 1H, 2-H), 8.45 (d, *J* 10.5, 2H, 4′,8′-H), 8.00 (t, *J* 3.8, 1H, 2′-H), 7.98 (d, *J* 11.1, 2H, 5,7-H), 7.50 (d, *J* 3.8, 2H, 1′,3′-H), 7.39 (d, *J* 10.5, 2H, 5′,7′-H), 4.46 (q, *J* 7.1, 4H, 1,3-COOEt) and 1.47 (t, *J* 7.1, 6H, 1,3-COOEt); δ_C (125 MHz, $CDCl_3$) 165.0 (s, 1,3-COOEt), 158.1 (C-6), 152.4 (C-6′), 143.7 (C-2), 142.9 (C-3a,8a), 139.3 (C-3′a,8′a), 138.5 (C-2′), 138.3 (C-4,8), 135.6 (C-4′,8′), 131.6 (C-5,7), 124.0 (C-5′,7′), 119.4 (C-1′,3′), 116.8 (C-1,3), 60.1 (t, 1,3-COOEt) and 14.6 (q, 1,3-COOEt); *m*/*z* (EI) 398 (M^+, 100%), 353 ($M^+ - OEt$, 18) and 325 ($M^+ - COOEt$, 12).

Diethyl 2,6′-biazulene-1′,3′-dicarboxylate 12. Following the general procedure, the reaction of **1b** (113 mg, 0.201 mmol) with **13** (50.7 mg, 0.245 mmol) in refluxing dioxane (20 cm^3) in the presence of $Pd_2(dba)_3$ (18.4 mg, 0.0201 mmol), P(*t*-Bu)$_3$ (22.5 mg, 0.111 mmol) and CsF (73.7 mg, 0.485 mmol) afforded **12** (41.3 mg, 51%) as green needles, mp 193–195 °C (Found: C, 78.2; H, 5.7. Calc. for $C_{26}H_{22}O_4$: C, 78.4; H, 5.6%); λ_{max} (CH_2Cl_2)/nm 244 (log ε 4.63), 279 (4.25), 326 (4.69), 336 (4.71), 364 (4.62), 380 (4.64), 415 (4.61) and 540 (3.20); ν_{max} (KBr disk)/cm^{-1} 1692 (C=O), 1440, 1394, 1208, 1184 and 800; δ_H (500 MHz, $CDCl_3$) 9.78 (d, *J* 11.1, 2H, 4′,8′-H), 8.76 (s, 1H, 2′-H), 8.37 (d, *J* 11.1, 2H, 5′,7′-H), 8.36 (d, *J* 9.8, 2H, 4,8-H), 7.77 (s, 2H, 1,3-H), 7.60 (t, *J* 9.9, 1H, 6-H), 7.21 (dd, *J* 9.9 and 9.8, 2H, 5,7-H), 4.45 (q, *J* 7.1, 4H, 1′,3′-COOEt) and 1.47 (t, *J* 7.1, 6H, 1′,3′-COOEt); δ_C (125 MHz, $CDCl_3$) 165.1 (s, 1′,3′-COOEt), 150.7 (C-2), 149.2 (C-6′), 143.2 (C-2′), 142.9 (C-3′a,8′a), 141.4 (C-3a,8a), 138.7 (C-6), 138.3 (C-4,8), 138.2 (C-4′,8′), 130.6 (C-5′,7′), 124.5 (C-5,7), 116.5 (C-1,3), 116.4 (C-1′,3′), 60.0 (t, 1′,3′-COOEt) and 14.6 (q, 1′,3′-COOEt); *m*/*z* (EI) 398 (M^+, 100%), 353 ($M^+ - OEt$, 27) and 325 ($M^+ - COOEt$, 17).

1,4-Bis[1,3-bis(ethoxycarbonyl)azulen-6-yl]benzene 18. Following the general procedure, the reaction of **1b** (283 mg, 0.504 mmol) with **14** (46.1 mg, 0.195 mmol) in refluxing dioxane (20 cm^3) for 18 h in the presence of $Pd_2(dba)_3$ (36.3 mg, 0.0396 mmol), P(*t*-Bu)$_3$ (56.1 mg, 0.277 mmol) and CsF (177 mg, 1.17 mmol) afforded **18** (38.3 mg, 32%) as a pink powder, **19** (8.6 mg, 11%) as reddish purple prisms and the recovered **1b** (80.1 mg, 28%).

*For **18**.* Mp >300 °C (Found: C, 72.8; H, 5.7. Calc. for $C_{38}H_{34}O_8 \cdot ½H_2O$: C, 72.7; H, 5.6%); λ_{max} (CH_2Cl_2)/nm 237 (log ε 4.78), 269 (4.51), 358 (4.88), 376 (4.89) and 515 (3.26); ν_{max} (KBr disk)/cm^{-1} 1690 (C=O), 1431, 1391, 1204 and 1046; δ_H (500 MHz, $CDCl_3$) 9.87 (d, *J* 11.1, 4H, 4′,8′-H), 8.86 (s, 2H, 2′-H), 8.02 (d, *J* 11.1, 4H, 5′,7′-H), 7.87 (s, 4H, 2,3,5,6-H), 4.47 (q, *J* 7.1, 8H, 1′,3′-COOEt) and 1.48 (t, *J* 7.1, 12H, 1′,3′-COOEt); δ_C (125 MHz, $CDCl_3$) 165.0 (s, 1′,3′-COOEt), 153.3 (C-6′), 144.1 (C-1,4), 143.6 (C-2′), 142.9 (C-3′a,8′a), 138.5 (C-4′,8′), 130.6 (C-5′,7′), 129.5 (C-2,3,5,6), 116.8 (C-1′,3′), 60.1 (t, 1′,3′-COOEt) and 14.6 (q, 1′,3′-COOEt); *m*/*z* (EI) 618 (M^+, 100%) and 573 ($M^+ - OEt$, 15).

*For **19**.* Mp 111–113 °C (Found: C, 75.5; H, 6.9. Calc. for $C_{26}H_{28}O_4 \cdot ½H_2O$: C, 75.5; H, 7.1%); λ_{max} (CH_2Cl_2)/nm 236 (log ε 4.54), 271 (4.20), 336 (4.70) and 507 (2.92); ν_{max} (KBr disk)/cm^{-1} 1688 (C=O), 1431, 1391, 1204 and 1046; δ_H (500 MHz, $CDCl_3$) 9.80 (d, *J* 11.1, 2H, 4′,8′-H), 8.80 (s, 1H, 2′-H), 7.96 (d, *J* 11.1, 2H, 5′,7′-H), 7.61 (d, *J* 8.3, 2H, 2,6-H), 7.35 (d, *J* 8.3, 2H, 3,5-H), 4.44 (q, *J* 7.1, 4H, 1′,3′-COOEt), 2.71 (t, *J* 7.7, 2H, 1″-H), 1.67 (tt, *J* 7.7 and 7.6, 2H, 2″-H), 1.46 (t, *J* 7.1, 6H, 1′,3′-COOEt), 1.41 (qt, *J* 7.6 and 7.3, 2H, 3″-H) and 0.97 (t, *J* 7.3, 3H, 4″-H); δ_C (125 MHz, $CDCl_3$) 165.1 (s, 1′,3′-COOEt), 154.7 (C-6′), 144.3 (C-3′a,8′a), 142.9 (C-2′), 142.7 (C-4), 140.9 (C-1), 138.5 (C-4′,8′), 130.8 (C-5′,7′), 129.2 (C-3,5), 128.7 (C-2,6), 116.3 (C-1′,3′), 60.0 (t, 1′,3′-COOEt), 35.3 (C-1″), 33.5 (C-2″), 22.4 (C-3″), 14.6 (q, 1′,3′-COOEt) and 13.9 (C-4″); *m*/*z* (EI) 404 (M^+, 100%), 359 ($M^+ - OEt$, 24) and 331 ($M^+ - COOEt$, 12).

1,3,5-Tris[1,3-bis(ethoxycarbonyl)azulen-6-yl]benzene 20. Following the general procedure, the reaction of **1b** (391 mg, 0.697 mmol) with **15** (61.3 mg, 0.195 mmol) in refluxing dioxane (20 cm^3) for 18 h in the presence of $Pd_2(dba)_3$ (53.8 mg, 0.0588 mmol), P(*t*-Bu)$_3$ (48.2 mg, 0.238 mmol) and CsF (235 mg, 1.55 mmol) afforded **20** (47.9 mg, 28%) as a purple powder, **21** (16.5 mg, 13%) as red needles and the recovered **1b** (76.3 mg, 20%).

*For **20**.* Mp >300 °C. (lit.[12] mp >300 °C).

*For **21**.* Mp 240–241 °C (Found: C, 73.8; H, 6.4. Calc. for $C_{42}H_{42}O_8 \cdot ½H_2O$: C, 73.8; H, 6.3%); λ_{max} (CH_2Cl_2)/nm 236 (log ε 4.76), 272 (4.49), 336 (4.91) and 513 (3.18); ν_{max} (KBr disk)/cm^{-1} 1694 (C=O), 1435, 1393, 1202 and 1040; δ_H (500 MHz, $CDCl_3$) 9.85 (d, *J* 11.1, 4H, 4′,8′-H), 8.85 (s, 2H, 2′-H), 8.01 (d, *J* 11.1, 4H, 5′,7′-H), 7.78 (t, *J* 1.7, 1H, 2-H), 7.61 (d, *J* 1.7, 2H, 4,6-H), 4.46 (q, *J* 7.1, 8H, 1′,3′-COOEt), 2.85 (t, *J* 7.8, 2H, 1″-H), 1.77 (tt, *J* 7.8 and 7.5, 2H, 2″-H), 1.48 (qt, *J* 7.5 and 7.3, 2H, 3″-H), 1.47 (t, *J* 7.1, 12H, 1′,3′-COOEt) and 1.00 (t, *J* 7.3, 3H, 4″-H); δ_C (125 MHz, $CDCl_3$) 165.0 (s, 1′,3′-COOEt), 154.0 (C-6′), 144.9 (C-5), 144.6 (C-1,3), 143.5 (C-2′), 142.8 (C-3′a,8′a), 138.5 (C-4′,8′), 130.8 (C-5′,7′), 129.4 (C-4,6), 126.6 (C-2), 116.7 (C-1′,3′), 60.1 (t, 1′,3′-COOEt), 35.8 (C-1″), 33.7 (C-2″), 22.5 (C-3″), 14.6 (q, 1′,3′-COOEt) and 13.9 (C-4″); *m*/*z* (FAB) 675 ($M^+ + H$), 674 (M^+) and 629 ($M^+ - OEt$).

1,2,4,5-Tetrakis[1,3-bis(ethoxycarbonyl)azulen-6-yl]benzene 22. Following the general procedure, the reaction of **1b** (575 mg, 1.02 mmol) with **16** (78.0 mg, 0.198 mmol) in refluxing dioxane (20 cm^3) for 18 h in the presence of $Pd_2(dba)_3$ (73.2 mg, 0.0799 mmol), P(*t*-Bu)$_3$ (82.5 mg, 0.408 mmol) and CsF (329 mg, 2.17 mmol) afforded **22** (30.7 mg, 13%) as red crystals, **23** (9.8 mg, 5%) as a deep red powder, **24** (10.0 mg, 6%) as a brown powder and the recovered **1b** (70.1 mg, 12%).

*For **22**.* Mp 225 °C (decomp.) (Found: C, 71.95; H, 5.4. Calc. for $C_{70}H_{62}O_{16} \cdot ½H_2O$: C, 72.0; H, 5.4%); λ_{max} (CH_2Cl_2)/nm 238 (log ε 5.06), 271 (4.85), 331 (5.14) and 519 (3.44); ν_{max} (KBr disk)/cm^{-1} 1694 (C=O), 1433, 1210 and 1049; δ_H (500 MHz, $CDCl_3$) 9.61 (d, *J* 11.0, 8H, 4′,8′-H), 8.80 (s, 4H, 2′-H), 7.85 (s, 2H, 3,6-H), 7.74 (d, *J* 11.0, 8H, 5′,7′-H), 4.39 (q, *J* 7.1, 16H, 1′,3′-COOEt) and 1.42 (t, *J* 7.1, 24H, 1′,3′-COOEt); δ_C (125 MHz, $CDCl_3$) 164.8 (s, 1′,3′-COOEt), 151.8 (C-6′), 144.2 (C-2′), 143.2 (C-1,2,4,5), 142.8 (C-3′a,8′a), 138.0 (C-4′,8′), 134.0 (C-3,6), 132.4 (C-5′,7′), 117.2 (C-1′,3′), 60.1 (t, 1′,3′-COOEt) and 14.5 (q, 1′,3′-COOEt); *m*/*z* (FAB) 1159 ($M^+ + H$), 1158 (M^+), 1113 ($M^+ - OEt$) and 1085 ($M^+ - COOEt$).

*For **23**.* Mp 280–285 °C (Found: C, 72.8; H, 6.0. Calc. for $C_{58}H_{56}O_{12} \cdot ½H_2O$: C, 73.0; H, 6.0%); λ_{max} (CH_2Cl_2)/nm 237 (log ε 4.95), 271 (4.75), 326 (4.97) and 511 (3.32); ν_{max} (KBr disk)/cm^{-1} 1694 (C=O), 1433, 1206 and 1044; δ_H (500 MHz, $CDCl_3$) 9.86 (d, *J* 10.8, 2H, 4‴,8‴-H), 9.59 (d, *J* 11.1, 2H, 4″,8″-H), 9.54 (d, *J* 11.0, 2H, 4′,8′-H), 8.89 (s, 1H, 2‴-H), 8.79 (s, 1H, 2′-H or 2″-H), 8.76 (s, 1H, 2′-H or 2″-H), 7.85 (d, *J* 10.8, 2H, 5‴,7‴-H), 7.70 (d, *J* 11.1, 2H, 5″,7″-H), 7.67 (d, *J* 11.0, 2H, 5′,7′-H), 7.58 (s, 1H, 6-H), 7.52 (s, 1H, 3-H), 4.47 (q, *J* 7.1, 4H, COOEt), 4.40 (q, *J* 7.1, 4H, COOEt), 4.37 (q, *J* 7.2, 4H, COOEt), 2.73 (t, *J* 7.9, 2H, 1⁗-H), 1.57 (tt, *J* 7.9 and 7.5, 2H, 2⁗-H), 1.48 (t, *J* 7.1, 6H, COOEt), 1.42 (t, *J* 7.1, 6H, COOEt), 1.40 (t, *J* 7.2, 6H, COOEt), 1.26 (qt, *J* 7.5 and 7.3, 2H, 3⁗-H) and 0.80 (t, *J* 7.3, 3H, 4⁗-H); δ_C (125 MHz, $CDCl_3$) 165.0 (s, COOEt), 164.9 (s, COOEt), 164.8 (s, COOEt), 153.5 (C-6‴), 153.1 (C-6″), 152.8 (C-6′), 144.3 (C-4), 143.8 (C-2′, C-2″ and C-2‴), 143.1 (C-3‴a,8‴a), 142.8 (C-3′a,8′a or C-3″a,8″a), 142.7 (C-1 and C-3′a,8′a or C-3″a,8″a), 141.1 (C-5), 140.3 (C-2), 138.2 (C-4‴,8‴), 138.0 (C-4″,8″), 137.9 (C-4′,8′), 132.8 (C-5′,7′ or C-5″,7″), 132.7 (C-6 and C-5′,7′ or C-5″,7″), 132.3 (C-3), 131.9 (C-5‴,7‴), 116.9 (C-1′,3′, C-1″,3″ and C-1‴,3‴), 60.2 (t, COOEt), 60.1 (t, COOEt), 60.0 (t, COOEt), 33.3 (C-2⁗), 32.6 (C-1⁗), 22.5 (C-3⁗), 14.6 (q, COOEt), 14.5 (q, 2C, COOEt) and 13.8 (C-4⁗); *m*/*z* (FAB) 944 (M^+), 899 ($M^+ - OEt$) and 871 ($M^+ - COOEt$).

*For **24**.* Mp 151.5–153 °C (lit.[12] mp 150–153 °C).

Reaction of 1b with 17. Following the general procedure, the reaction of **1b** (804 mg, 1.43 mmol) with **17** (104 mg, 0.189 mmol) in refluxing dioxane (20 cm^3) in the presence of $Pd_2(dba)_3$ (105 mg, 0.115 mmol), P(*t*-Bu)$_3$ (121 mg, 0.598 mmol) and CsF (497 mg, 3.27 mmol) afforded **20** (27.5 mg, 16%), a mixture (1.6 : 1) of **22** and **25** (16.8 mg, 8%) and the recovered **1b** (119.2 mg, 15%).

For ***25****.* δ_H (500 MHz, $CDCl_3$) 9.89 (d, *J* 11.1, 2H, 4‴″,8‴″-H), 9.55 (d, *J* 11.1, 4H, 4′,8′-H and 4‴,8‴-H), 9.31 (d, *J* 11.1, 2H, 4″,8″-H), 8.88 (s, 1H, 2‴″-H), 8.78 (s, 2H, 2′-H and 2‴-H), 8.68 (s, 1H, 2″-H), 8.08 (d, *J* 11.1, 2H, 5‴″,7‴″-H), 7.96 (s, 2H, 4,6-H), 7.68 (d, *J* 11.1, 4H, 5′,7′-H and 5‴,7‴-H), 7.50 (d, *J* 11.1, 2H, 5″,7″-H), 4.45 (q, *J* 7.1, 4H, 1″,3″- or 1‴″,3‴″-COOEt), 4.38 (q, *J* 7.1, 8H, 1′,3′- and 1‴,3‴-COOEt), 4.32 (q, *J* 7.1, 4H, 1″,3″- or 1‴″,3‴″-COOEt), 1.47 (t, *J* 7.1, 6H, 1″,3″- or 1‴″,3‴″-COOEt), 1.41 (t, *J* 7.1, 12H, 1′,3′- and 1‴,3‴-COOEt) and 1.36 (t, *J* 7.1, 6H, 1″,3″- or 1‴″,3‴″-COOEt); δ_C (125 MHz, $CDCl_3$) 164.9 (s, 1‴″,3‴″-COOEt), 164.7 (s, 1′,3′- and 1‴,3‴-COOEt), 164.6 (s, 1″,3″-COOEt), 152.4 (C-6′ and C-6‴), 151.8 (C-6‴″), 150.0 (C-6″), 144.9 (C-1,3), 144.4 (C-2‴″), 144.2 (C-5), 144.1 (C-2′, C-2″ and C-2‴), 142.9 (C-3″a,8″a), 142.8 (C-3′a,8′a and C-3‴a,8‴a), 142.6 (C-3‴″a,8‴″a), 140.8 (C-2), 138.6 (C-4‴″,8‴″), 137.8 (C-4′,8′ and C-4‴,8‴), 137.2 (C-4″,8″), 133.7 (C-5″,7″), 132.2 (C-5′,7′ and C-5‴,7‴), 131.0 (C-4,6), 130.4 (C-5‴″,7‴″), 117.4 (C-1″,3″), 117.2 (C-1′,3′, C-1‴,3‴ and C-1‴″,3‴″), 60.2 (t, 1″,3″- or 1‴″,3‴″-COOEt), 60.1 (t, 1′,3′-, 1‴,3‴- and 1″,3″- or 1‴″,3‴″-COOEt), 14.6 (q, 1″,3″- or 1‴″,3‴″-COOEt), 14.5 (q, 1′,3′- and 1‴,3‴-COOEt) and 14.5 (q, 1″,3″- or 1‴″,3‴″-COOEt).

2-(Tri-*n*-butylstannyl)azulene 27

The same procedure as was used for the preparation of **1a** was adopted. The reaction of **13** (106 mg, 0.512 mmol) with **3** (583 mg, 1.01 mmol) in dry toluene (20 cm^3) in the presence of $Pd(PPh_3)_4$ (28.7 mg, 0.0248 mmol) followed by chromatographic purification on silica gel with hexane and CH_2Cl_2 afforded **28** (31.1 mg, 48%) as a green powder. Further purification of the hexane eluate by medium-pressure column chromatography on silica gel with hexane afforded **27** (23.1 mg, 11%) as a blue oil.

For 27. (Found: C, 63.3; H, 8.2. Calc. for $C_{22}H_{34}Sn$: C, 63.3; H, 8.2%); λ_{max} (CH_2Cl_2)/nm 242 (log ε 4.25), 288 (4.74), 336 (3.78), 351 (3.82), 364 (3.48), 589 (2.52) and 632 (2.46); ν_{max} (neat)/cm^{-1} 2957, 2926, 2870, 2853, 1458, 1393, 803, 727 and 573; δ_H (500 MHz, $CDCl_3$) 8.27 (d, *J* 9.7, 2H, 4,8-H), 7.53 (t, *J* 9.9, 1H, 6-H), 7.53 (s, 2H, 1,3-H), 7.13 (dd, *J* 9.9 and 9.7, 2H, 5,7-H), 1.60 (m, 2H, 2′-H), 1.36 (qt, *J* 7.4 and 7.3, 2H, 3′-H), 1.14 (m, 2H, 1′-H) and 0.90 (t, *J* 7.4, 3H, 4′-H); δ_C (125 MHz, $CDCl_3$) 153.9 (C-2), 140.0 (C-3a,8a), 136.9 (C-6), 134.9 (C-4,8), 126.5 (C-1,3), 122.5 (C-5,7), 29.3 (C-2′), 27.4 (C-3′), 13.7 (C-4′) and 10.0 (C-1′); *m*/*z* (EI) 418 (M^+, 15%), 361 (100), 360 (50), 359 (77), 357 (40), 305 (45), 249 (72), 247 (92), 245 (62) and 129 (43).

For 28. Mp >300 °C (lit.[23a] mp >320 °C).

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