

Synthesis and Dynamic Stereochemistry of Azulene-Substituted 9-Fluorenyl, 9,10-Dihydro-10,10-dimethyl-9-anthryl, 10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl, and 5*H*-Dibenzo[*a*,*d*]cyclohepten-5-yl Cations. Correlations of Stabilities of the Carbocations and Rotational Barrier of Azulene Ring

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The carbocations in the title: 9-(1-Azulenyl)-9-fluorenyl, 9-(1-azulenyl)-9,10-dihydro-10,10-dimethyl-9-anthryl, 5-(1-azulenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl, and 5-(1-azulenyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl cations (**4c**, **5a–c**, **6a–c**, and **7a–c**) were prepared by hydride abstraction of the corresponding hydrocarbon derivatives and their properties were fully characterized. The p$K_R{}^+$ values of **4c**, **5a–c**, **6a–c**, and **7a–c** were determined as −2.7, 0.5–2.7, 8.4–9.1, and 7.4–8.5, respectively, which were higher by 8.1, 6.0–8.2, 15.1–16.1, and 13.1–14.3 pK units, respectively, than those of the corresponding phenyl derivatives. Conformations and energy barriers for **4c**, **5a–c**, **6a–c**, and **7a–c** were studied by means of dynamic nuclear magnetic resonance spectroscopy (DNMR) techniques. The thermodynamic stability of the cations and the barrier to the rotation of the 1-azulenyl group were significantly affected by not only the electron density effect but also the dynamic stereochemistry of the connected-ring systems.

The ground state of azulene ($C_{10}H_8$) significantly stabilizes carbocations through the contribution of a dipolar canonical structure.[1] We have previously reported the synthesis of a series of (1-azulenyl)methyl cations, i.e., tri(1-azulenyl)methylium, di(1-azulenyl)phenylmethylium, (1-azulenyl)diphenylmethylium hexafluorophosphates (**1a**·$PF_6{}^-$, **2a**·$PF_6{}^-$, and **3a**·$PF_6{}^-$) and their derivatives (e.g., **1b**, **c**·$PF_6{}^-$, **2b**, **c**·$PF_6{}^-$, and **3b**, **c**·$PF_6{}^-$) by hydride abstraction of the corresponding hydrocarbon derivatives (Chart 1).[2] These cations show high stability with large p$K_R{}^+$ values (e.g., **1a**, 11.3; **2a**, 10.5; and **3a**, 3.0, respectively).[2a] The high stability of these cations can be explained by the large π-conjugative effect of 1-azulenyl groups with cationic carbon (e.g., **1′**). The conjugative interaction between the cationic carbon and the azulene rings also largely contributes to the transition state of the rotation of the azulene rings as well as to the ground state. An analysis of the dynamic stereochemistry of tris(3-methyl-1-azulenyl)methyl cation (**1b**) confirms that the conformational change of the system is accomplished by a one-ring flip as the lowest energy (threshold) rotation mechanism.[2a]

In order to investigate the relationship between the barrier to the rotation of 1-azulenyl groups and the thermodynamic stability of carbocations, we have performed a systematic synthesis and an analysis of dynamic stereochemistry of 9-(1-azulenyl)-9-fluorenyl, 9-(1-azulenyl)-9,10-dihydro-10,10-dimethyl-9-anthryl, 5-(1-azulenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl, and 5-(1-azulenyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl cations (**4a–c**, **5a–c**, **6a–c**, and **7a–c**) using DNMR techniques. The stabilizing ability of carbocation exhibited by the 1-azulenyl group allowed the synthesis and the analysis of

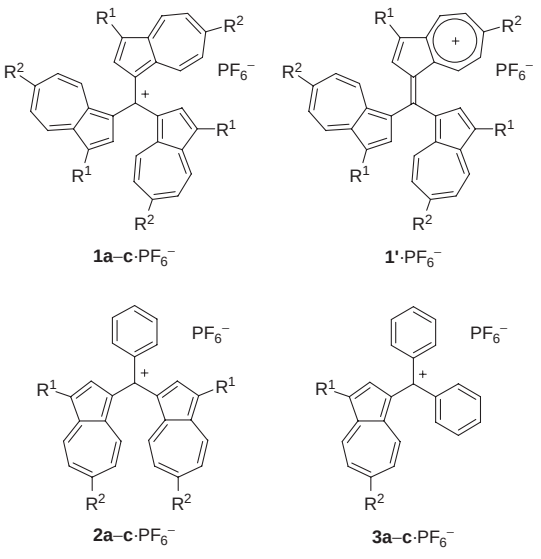

Chart 1.

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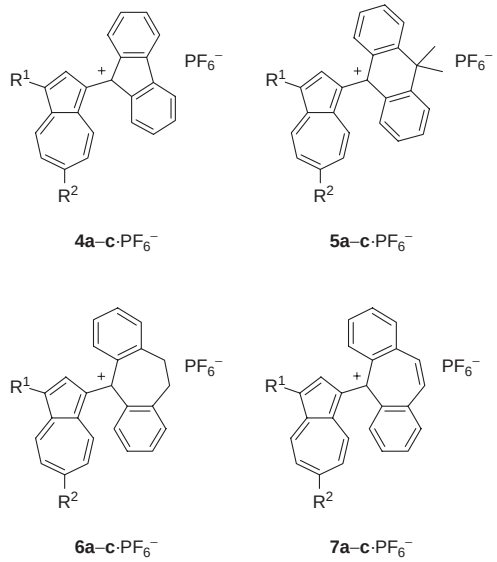


4a–c·PF_6^- **5a–c**·PF_6^-

6a–c·PF_6^- **7a–c**·PF_6^-

a: $R^1 = R^2 = H$, **b**: $R^1 = Me$, $R^2 = H$, **c**: $R^1 = R^2 = t$-Bu

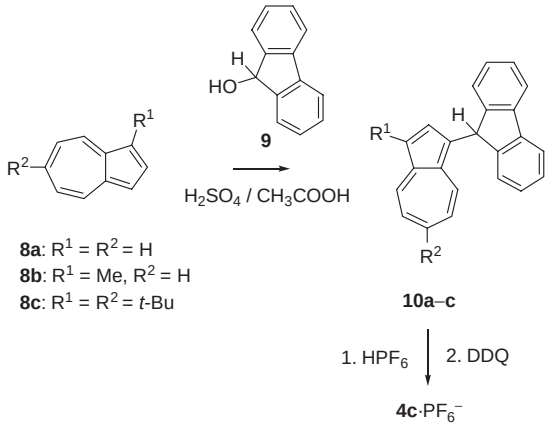
Chart 2.

dynamic stereochemistry of these cations, including "antiaromatic" fluorenyl cation **4c** (Chart 2).

Results and Discussion

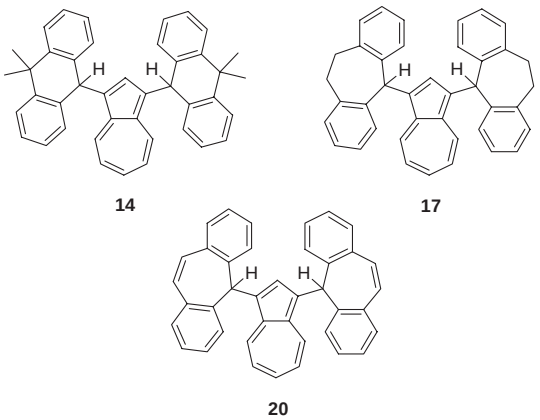
Synthesis. Synthesis of the series of carbocations is outlined in Schemes 1–4. The key step of the synthesis is a hydride abstraction reaction of the corresponding hydrocarbon derivatives. 9-(1-Azulenyl)fluorene (**10a**) was prepared by the reaction of azulene (**8a**) with 9-fluorenol (**9**) in acetic acid in the presence of H_2SO_4 at reflux temperature, according to the procedure reported by Mühlstädt et al.[3] 9-(3-Methyl- and 3,6-di-*t*-butyl-1-azulenyl)fluorenes (**10b** and **10c**) were synthesized by the similar reactions of 1-methyl- and 1,6-di-*t*-butylazulenes (**8b** and **8c**) with **9** in 28 and 35% yields, respectively. Oxidative hydride abstractions of **10a** and **10b** with DDQ in dichloromethane at room temperature, followed by an addition of a 60% HPF_6 solution, did not afford the corresponding 9-(1-azulenyl)fluorenyl cations **4a** and **4b**, because of the instability of these cations. In the case of the reaction of **10b** with DDQ, 3-(9-fluorenyl)-1-azulenecarbaldehyde (**11**) was obtained in low yield (18%). The product was identified by the synthesis utilizing the Vilsmeier reaction of **10a**. In contrast, during the reaction of **10c** with DDQ under the similar reaction conditions, 9-(3,6-di-*t*-butyl-1-azulenyl)fluorenyl cation (**4c**) was obtained as a hexafluorophosphate in 29% yield in the form of a deep-colored powder (Scheme 1). The yield of the cations **4c** was much improved in quantitative yield by the reaction with DDQ in dichloromethane in the presence of an aqueous HPF_6 solution. Hexafluorophosphate **4c**·PF_6^- was stable and storable in the crystalline state, although **4c** includes an "antiaromatic" fluorenyl cation moiety.[4] However, the reactions of **10a** and **10b** with DDQ in the presence of HPF_6 also did not afford the desired cations **4a** and **4b**.

The reaction of **8a** with 9,10-dihydro-10,10-dimethyl-9-anthrol (**12**)[5] in acetic acid at room temperature afforded 9-(1-azulenyl)-9,10-dihydro-10,10-dimethylanthracene (**13a**) in 84% yield, together with 1,3-bis(9,10-dihydro-10,10-dimethyl-9-anthryl)azulene (**14**) in 7% yield (Chart 3). Similarly, the reactions of **8b** and **8c** with **12** in acetic acid afforded **13b** and **13c** in 100 and 91% yields, respectively. Oxidative hydride abstractions of **13b** and **13c** with DDQ in dichloromethane at room temperature, followed by an addition of a 60% HPF_6 solution, afforded the corresponding cations **5b** and **5c** as hexafluorophosphates in 88 and 50% yields, respectively. The oxidative hydride abstraction of **13a** with DDQ in dichloromethane in the presence of an aqueous HPF_6 solution yielded the corresponding cation **5a** as a hexafluorophosphate in 82% yield (Scheme 2).



8a: $R^1 = R^2 = H$
8b: $R^1 = Me$, $R^2 = H$
8c: $R^1 = R^2 = t$-Bu

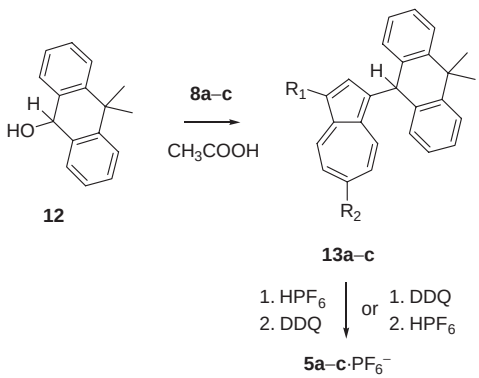
Scheme 1.



14 **17**

20

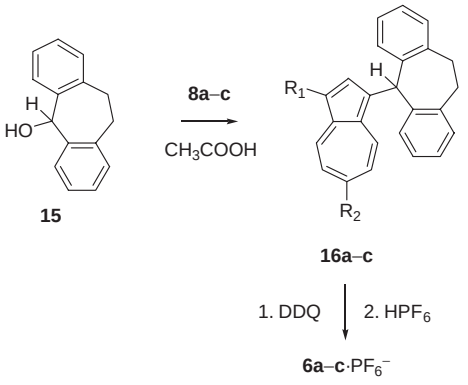
Chart 3.



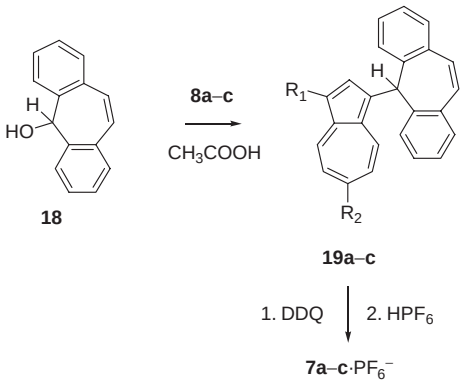
12 **13a–c**

5a–c·PF_6^-

Scheme 2.



Scheme 3.



Scheme 4.

Table 1. Longest Wavelength Absorption Maxima (nm) and Their Coefficients of Cations **3a–c**, **4c**, **5a–c**, **6a–c**, and **7a–c** in Acetonitrile

Sample	λ_{max} (log ε)	Sample	λ_{max} (log ε)
3a	487 (4.16)[a)]	**6a**	444 (4.26)
3b	495 (4.21)[a)]	**6b**	460 (4.09)
3c	489 (4.11)[a)]	**6c**	455 (4.09)
4c	553 (4.11)	**7a**	351 (4.07), 414 sh (3.94), 500 sh (3.77)
5a	471 (4.21)	**7b**	457 (3.85), 497 sh (3.83)
5b	484 (4.20)	**7c**	463 (3.91), 493 sh (3.88)
5c	479 (4.22)		

a) Data from Ref. 2a.

The reactions of **8a–c** with 10,11-dihydro-5*H*-dibenzo[*a*,*d*]-cyclohepten-5-ol (**15**) in acetic acid at room temperature afforded 5-(1-azulenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptenes (**16a–c**) in 49–94% yields, along with 1,3-bis-(10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)azulene (**17**) (Chart 3) in 35% yield in the case of the reaction of **8a**. Oxidative hydride abstractions of **16a–c** with DDQ, followed by treatment with an aqueous HPF_6 solution, afforded the presumed 5-(1-azulenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylium hexafluorophosphates (**6a–c**$\cdot PF_6^-$) in quantitative yields (Scheme 3).

Similarly, the reactions of **8a–c** with 5*H*-dibenzo[*a*,*d*]-cyclohepten-5-ol (**18**) in acetic acid at room temperature afforded 5-(1-azulenyl)-5*H*-dibenzo[*a*,*d*]cycloheptenes (**19a–c**) in 40–87% yields, together with 1,3-bis(5*H*-dibenzo[*a*,*d*]-cyclohepten-5-yl)azulene (**20**) (Chart 3) in 46% yield in the case of the reaction of **8a**. Oxidative hydride abstractions of **19a–c** with DDQ, followed by treatment with an aqueous HPF_6 solution, yielded the desired 5-(1-azulenyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylium hexafluorophosphates (**7a–c**$\cdot PF_6^-$) in quantitative yields (Scheme 4).

The oxidative hydride abstraction of (3-methyl-1-azulenyl)-diphenylmethane (**21**) with DDQ in dichloromethane in the presence of an aqueous HPF_6 solution was also found to yield (3-methyl-1-azulenyl)diphenylmethyl cation **3b** as a hexafluorophosphate in 91% yield, because cation **3b** was not prepared in pure form by the former reaction conditions.[2a] This allowed us to compare the properties of these cations with those of the series of cations **3a–c**.

Spectroscopic Properties. These cations: **4c**, **5a–c**, **6a–c**, and **7a–c**, were fully characterized by the spectral data as shown in the Experimental Section. Mass spectra of **4c**$\cdot PF_6^-$, **5a–c**$\cdot PF_6^-$, **6a–c**$\cdot PF_6^-$, and **7a–c**$\cdot PF_6^-$ ionized by FAB showed correct $M^+ - PF_6$ ion peaks, which indicated the cationic structure of these products. The characteristic bands of these hexafluorophosphates were observed at 836–842 (strong) and 558 (medium) cm^{-1} in their IR spectra, which also supported their cationic structures. In their electronic spectra, **4c**, **5a–c**, **6a–c**, and **7a–c** showed strong absorptions in the visible region, in analogy with the diphenylmethyl cations **3a–c**. The absorption maxima (nm) and their coefficients (log ε) of **4c**, **5a–c**, **6a–c**, and **7a–c** along with those of **3a–c** in the visible region are summarized in Table 1. UV–vis spectra of **4c**, **5c**, **6c**, and **7c** in acetonitrile along with that of **3c** are shown in Figs. 1 and 2. The longest wavelength absorption of **4c** showed an appreciable bathochromic shift by 64 nm compared with that of **3c**. The bathochromic shift may be attributed to the extra positive charge at the azulene ring due to the

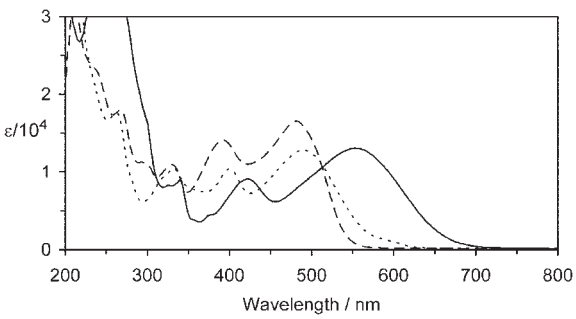


Fig. 1. UV–vis spectra of cations **4c** (solid line), **5c** (broken line), and **3c** (dotted line) in acetonitrile.

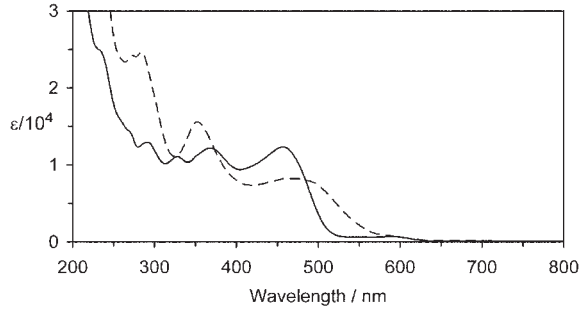


Fig. 2. UV–vis spectra of cations **6c** (solid line) and **7c** (broken line) in acetonitrile.

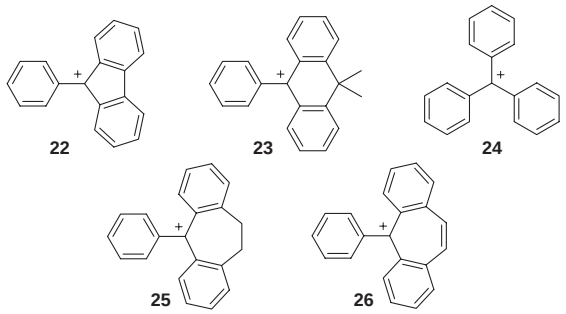


Chart 4.

Table 2. pK_R^+ Values[a] and Redox Potentials[b] of **3a–c**, **4c**, **5a–c**, **6a–c**, and **7a–c**

Sample	pK_R^+[c]	E_1^{red}	E_1^{ox}
3a	3.0[d]	(−0.43)	(+1.73)
3b	3.7[d]	(−0.51)	(+1.57)
3c	4.6[d]	(−0.55)	(+1.57)
4c	-2.7 ± 0.1[e]	−0.22	(+1.54)
5a	0.5 ± 0.1	(−0.29)	(+1.33)
5b	1.9 ± 0.1 (97%)	(−0.37)	(+1.23)
5c	2.7 ± 0.1 (88%)	−0.40	(+1.26)
6a	8.4 ± 0.1 (62%)	(−0.48)	(+1.90)
6b	8.5 ± 0.1 (45%)	(−0.51)	(+1.85)
6c	9.1 ± 0.1 (67%)	(−0.58)	(+1.88)
7a	7.4 ± 0.1 (54%)	(−0.46)	(+1.48)
7b	7.8 ± 0.1 (58%)	(−0.49)	(+1.41)
7c	8.5 ± 0.1 (35%)	−0.57	(+1.49)

a) The pK_R^+ values were determined spectrophotometrically at 25 °C in a buffered solution prepared in 50% aqueous MeCN. b) The redox potetials were measured by cyclic voltammetry (V vs $Ag/AgNO_3$, 0.1 M Et_4NClO_4 in benzonitrile, Pt electrode, scan rate 100 mV s^{-1}, and $Fc/Fc^+ = +0.15$ V). Irreversible processes are shown in parentheses. c) Regenerated absorption maxima (%) of the cations in the visible region by immediate acidification of the alkaline solution with HCl are shown in parentheses. d) Data from Ref. 2a. e) The value was measured in an aqueous H_2SO_4 solution.

destabilization by the substituted-antiaromatic 9-fluorenyl group. Absorption maxima of cations **5a–c** and **6a–c** showed hypsochromic shifts by 10–16 and 34–43 nm, respectively, compared with those of **3a–c**. Cations **7a–c** exhibited several absorptions in this region, and the longest wavelength absorption of **7a–c** exhibited bathochromic shifts compared with those of **6a–c**.

Thermodynamic Stability. As a measure of the thermodynamic stability, the pK_R^+ values of these cations were determined spectrophotometrically at 25 °C in a buffer solution prepared in 50% aqueous acetonitrile,[6] except for the value of **4c** which was determined in an aqueous H_2SO_4 solution due to its low thermodynamic stability. The pK_R^+ scales stand for the carbocation in aqueous solution ($pK_R^+ = -\log K_R^+$). The K_R^+ scale is defined by the equilibrium constant for the reaction of a carbocation with a water molecule ($K_R^+ = [ROH][H_3O^+]/[R^+]$). Therefore, a larger pK_R^+ index value indicates a higher stability of the carbocation.

The values are summarized in Table 2 along with those of **3a–c**.[2a] Although the cation **4c** is potentially destabilized by its antiaromatic 9-fluorenyl character, the high pK_R^+ value of **4c** ($pK_R^+ = -2.7$) relative to that of 9-phenyl-9-fluorenyl cation (**22**) ($pK_R^+ = -10.82$)[7] (Chart 4) indicates the stabilization of the cyclopentadienyl-type cation by 1-azulenyl group.

9,10-Dihydro-9-anthryl cations **5a–c** are expected to show higher stability than those of **3a–c**, since a pK_R^+ value of 9,10-dihydro-10,10-dimethyl-9-phenyl-9-anthryl cation (**23**) ($pK_R^+ = -5.49$) larger than that of triphenylmethyl cation (**24**) ($pK_R^+ = -6.63$) is reported in the literature.[8] However, contrary to such expectation, cation **5a** ($pK_R^+ = 0.5$) was less stable than the corresponding diphenylmethyl cation **3a**. The 3-methyl derivative **5b** increased the stability ($pK_R^+ = 1.9$) compared with that of **5a**. The *t*-butyl derivative **5c** exhibited the highest stability among these series members ($pK_R^+ = 2.7$). The effective stabilization of the 3,6-di-*t*-butyl substituents should be attributed to their steric effect, in addition to the inductive electronic effect induced by the C–C hyperconjugation.

The stability values of **6a–c** and **7a–c** ($pK_R^+ = 8.4$–9.1 and 7.4–8.5, respectively) are much higher than those of diphenylmethyl cations **3a–c**, although the pK_R^+ values of the corresponding 5-phenyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl and 5-phenyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl cations

(**25** and **26**) ($pK_R^+ = -6.7$–-7.0 and -5.7–-5.8, respectively) are almost equal to that of triphenylmethyl cation (**24**).[9] The neutralization of these cations was not completely reversible. This is attributed to the instability of the neutralized products under the conditions of the pK_R^+ measurement. After the measurement, acidification of the alkaline solutions of **5b**, **5c**, **6a–c**, and **7a–c** with HCl regenerated the characteristic absorption in the visible region in 35–97% (Table 2).

Redox Properties. The redox potentials (V vs $Ag/AgNO_3$) of **4c**, **5a–c**, **6a–c**, and **7a–c** were measured by cyclic voltammetry (CV) in benzonitrile. The results are summarized in Table 2 together with those of **3a–c**. The reduction of **4c** in acetonitrile showed an reversible wave at -0.22 V upon the CV. This wave is ascribed to the formation of a neutral radical. The least negative reduction potential among these cations indicates the lowest electrochemical stability of **4c**. The reduction potentials of **5a–c** (-0.29–-0.40 V) are less negative than those of **3a–c**, comparable with the results of their lower pK_R^+ values. In contrast to the high pK_R^+ values, the reduction potentials of **6a–c** and **7a–c** (-0.48–-0.58 and -0.46–-0.57 V, respectively) are almost equal to those of **3a–c**. This indicates that there is poor linear correlation between the pK_R^+ values and the electrochemical stabilities within these series of carbocations. The most negative reduction potentials of the *t*-butyl derivatives within the series of substituents on the 1-azulenyl group correspond to the electrochemical stabilization by the *t*-butyl groups, as was true for the thermodynamic stability values.

The oxidations of **4c**, **5a–c**, **6a–c**, and **7a–c** exhibited voltammograms that were characterized by an irreversible wave at +1.54, +1.23–+1.33, +1.85–+1.90, and +1.41–+1.49 V, respectively, probably due to the generation of radical dications. The oxidation potentials depend on the structure of the carbocations. The oxidation potential shows some correlation to the barrier to the rotation of 1-azulenyl group, as described later, except for cation **4c**. The cations with more positive oxidation potential exhibit the higher barriers to the rotation.

^{13}C Chemical Shifts. The ^{13}C NMR chemical shifts and their assignments for these cations are shown in the Experimental Section. The electron densities at the cationic carbons should be evaluated by the chemical shifts (^{13}C NMR) of the cationic carbons. The electron densities at the cationic carbons would reflect the thermodynamic stability of the carbocations and the rotational barrier of the 1-azulenyl groups. Indeed, it is reported that the chemical shift of cationic carbon in **22** ($\delta = 224.2$ ppm)[4a] is more deshielded compared with those of **24**, **25**, and **26** (**24**; $\delta = 211.9$, **25**; 205.2, and **26**; 183.7 ppm).[10] However, we found that the ^{13}C NMR chemical shift is significantly affected by the structural features of the carbocations in the case of highly stable carbocations. Among the series, the least stable 9-fluorenyl cation **4c** ($\delta = 157.7$ ppm) exhibits the most shielded chemical shift. The ^{13}C NMR chemical shifts completely reverse the situation, which is suggested by the thermodynamic stability (e.g., **5c**; $\delta = 159.9$, **6c**; $\delta = 169.2$, and **7c**; $\delta = 163.9$ ppm). However, with respect to the substituent effects on the 1-azulenyl group, the stable carbocations exhibit the reduction in the chemical shift of the central cationic carbon (e.g., **5a**, $\delta = 164.4$; **5b**, $\delta = 160.7$; and **5c**, $\delta = 159.9$ ppm).

Dynamic Stereochemistry. The frozen ^{1}H NMR spectrum for the rotation of the 1-azulenyl group about the 9-fluorenyl bond was observed at room temperature for **4c** in 0.01 M (1 M = 1 mol dm^{-3}) $(CDCl_2)_2$ solvent. The destabilization of the cation by the 9-fluorenyl ring should induce the significant contribution of the canonical forms in which the double bond character exists between the 9-fluorenyl and the 1-azulenyl groups. ^{1}H NMR spectrum of **4c** is composed of unsymmetrical 9-fluorenyl signals together with a set of 3,6-di-*t*-butyl-1-azulenyl ones at that temperature. These signals showed some line broadening upon heating the solution at 80 °C, but further warming resulted in the decomposition of **4c**, which hampered the determination of the barrier to the rotation of the 1-azulenyl group by the temperature-dependent NMR spectra. The rotational barrier of the 1-azulenyl group is estimated by the coalescence method to be far above $\Delta G^{\ddagger}_{70} \gg 70.4$ kJ mol^{-1}.

We have previously reported the analysis of the dynamic stereochemistry of **3a** and **3c** using temperature-dependent ^{1}H NMR spectra in $CDCl_3$.[2a] However, recently, we found that the activation energy for the rotation of 1-azulenyl group in **3a** exhibited some concentration dependence. For the cation **3a**, the aromatic protons in the two phenyl groups were observed as magnetically equivalents at room temperature. When the temperature was lowered, the signals became two sets of 1-phenyl signals. The temperature dependence corresponds to the restricted rotation of 1-azulenyl group around the diphenylmethylium bond. The barrier to the rotation ($\Delta G^{\ddagger}_{20}$) of the 1-azulenyl group in **3a** was calculated to be 61.5 ± 1.7 kJ mol^{-1} in a 0.01 M $CDCl_3$ solution by the line-shape analysis.[11] However, cation **3a** in a 0.1 M $CDCl_3$ solution exhibited a frozen ^{1}H NMR spectrum for the rotation of the 1-azulenyl group even at room temperature. The ^{1}H NMR experiments of **3a** in 0.01 M and 0.1 M $CDCl_3$ solutions indicate that the barrier to the rotation of the 1-azulenyl group is clearly increased when the concentration becomes high. This behavior is indicative of cation–anion interactions which may form contact ion pairs in $CDCl_3$ solvent. Indeed, cation **3a** showed a frozen conformation up to 60 °C in a 0.01 M 10% $CF_3CO_2D/CDCl_3$ solution upon the ^{1}H NMR measurement. Therefore, the temperature-dependent NMR study of the other cations was examined by using constant concentration to compare the activation energy for the rotation of 1-azulenyl group within the series of these cations. The 3-methyl derivative **3b** showed a similar rotational barrier of the 1-azulenyl group to that of **3a** in a 0.01 M $CDCl_3$ solution ($\Delta G^{\ddagger}_{20} = 61.6 \pm 0.9$ kJ mol^{-1}). The rotational barriers ($\Delta G^{\ddagger}_{20}$) for **3c** in a 0.01 M $(CDCl_2)_2$ solution was calculated to be 88.4 ± 3.2 kJ mol^{-1}. Clearly, the barrier to the rotation in this case is higher than the corresponding rotational barrier for **3a** and **3b**.

The central six-membered ring in the 9,10-dihydroanthryl cations **5a–c** is assumed to be a boat conformation in the ground state. Therefore, in principle, two dynamic motions are expected in the structure of **5a–c**. One is the ring-inversion of the central six-membered ring and the other is the rotation of 1-azulenyl group, as illustrated in Fig. 3. The ring-inversion of the central six-membered ring reflects the temperature dependence of the signals on the 10,10-dimethyl substituents and that of the aromatic signals on the two benzene ring pro-

tons corresponds to the rotation of the 1-azulenyl group. ^{1}H NMR (400 MHz) of **5c** in a CD_2Cl_2 solvent (0.01 M) at various temperatures are shown in Fig. 4 ((a) aromatic region, (b) calculated spectra in 9,10-dihydro-9-anthryl signals, and (c) methyl region). At −80 °C the NMR consists of two methyl signals with same intensity along with two *t*-butyl signals in aliphatic region and eight aromatic signals together with a set of signals of 3,6-disubstituted 1-azulenyl group in the aromatic region. The spectrum exhibited that both the dynamic motions of **5c** are frozen on the NMR time scale at that temperature. When the sample was warmed to −40 °C, noticeable line broadening occurred; further warming resulted in the coalescence of the two methyl signals and the eight aromatic signals to a singlet and four signals, respectively, which became sharp at 40 °C. The signals on the 1-azulenyl group did not show any temperature dependence on the NMR spectra, except for the slight downfield shift of all the signals during the warming. ^{1}H NMR spectra of **5a** and **5b** also exhibited similar temperature dependency.

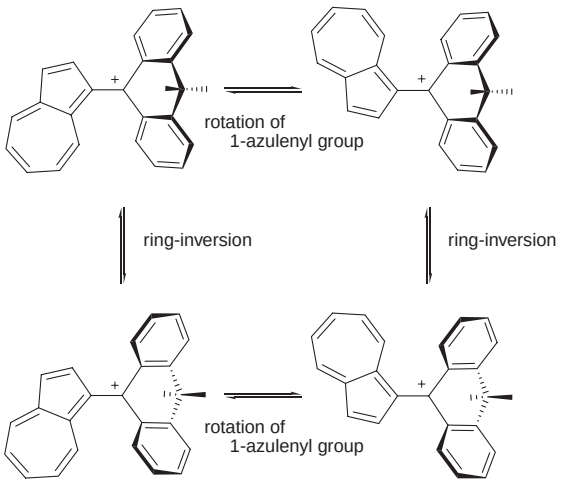


Fig. 3. Two dynamic motions in 9,10-dihydro-9-anthryl cation **5a**.

Simulations of the variable temperature ^{1}H NMR of the methyl region and the aromatic region were accomplished independently. The rate data determined by the line-shape analysis were used to calculate the free energies of activation for each process. Consequently, the barrier ($\Delta G^{\ddagger}_{20}$) to the ring-inversion of the six-membered ring was calculated to be 44.4 ± 0.4 kJ mol^{-1} for **5c** in 0.01 M CD_2Cl_2 solution. The rotational barrier ($\Delta G^{\ddagger}_{20}$) of the 1-azulenyl group for **5c** was also calculated to be 46.4 ± 0.7 kJ mol^{-1} in the same concentration. Similarly, the barrier ($\Delta G^{\ddagger}_{20}$) to the ring-inversion of the six-membered ring for **5b** in 0.01 M CD_2Cl_2 solution was calculated to be 42.5 ± 3.1 kJ mol^{-1}. However, the barrier to the rotation of 1-azulenyl group of **5b** could not be determined because the frozen NMR on the aromatic region was not obtained on even cooling the solution to −90 °C. The concentration dependency of the ^{1}H NMR spectra of cation **5b** was rather small compared with that of **3a**. However, increasing the concentration of **5b** in CD_2Cl_2 from 0.01 to 0.05 M allowed the calculation of the barrier ($\Delta G^{\ddagger}_{20}$) to the rotation of 1-azulenyl group of **5b** to 40.1 ± 1.3 kJ mol^{-1}. Thus, the dynamic stereochemistry of **5a** was also examined in 0.05 M CD_2Cl_2 solution. The barrier ($\Delta G^{\ddagger}_{20}$) to the ring-inversion of the six-membered ring for **5a** was calculated to be 40.9 ± 0.6 kJ mol^{-1} in 0.05 M CD_2Cl_2 solution. However, the barrier to the rotation of 1-azulenyl group of **5a** could not be determined under these conditions because the frozen NMR on the aromatic region was not obtained even on cooling the solution at −90 °C.

The seven-membered rings in **6a–c** and **7a–c** should adopt a

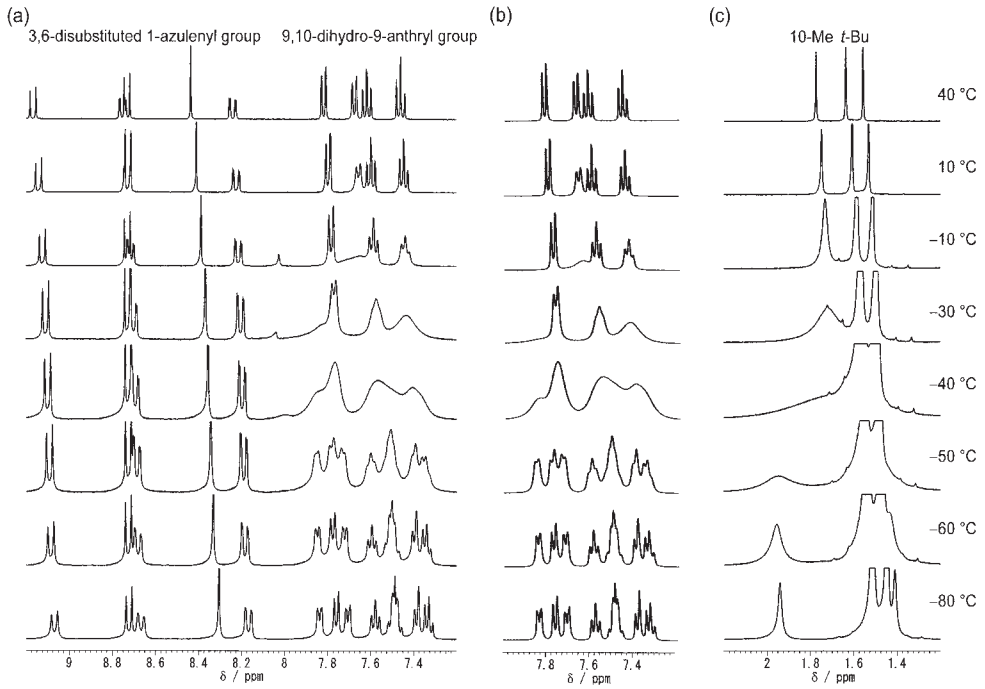


Fig. 4. ^{1}H NMR of **5c** (400 MHz, (a) aromatic region, (b) calculated spectra in 9,10-dihydro-9-anthryl signals, and (c) methyl region) in CD_2Cl_2 at various temperatures.

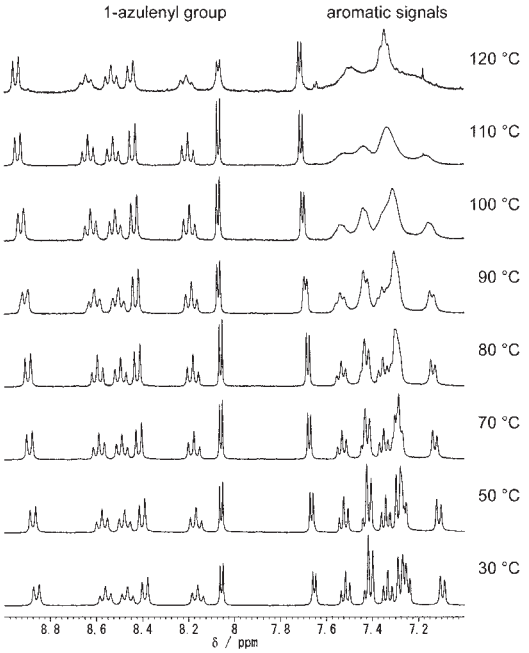


Fig. 5. ^{1}H NMR of **6a** (400 MHz, aromatic region) in $(CDCl_2)_2$ at various temperatures.

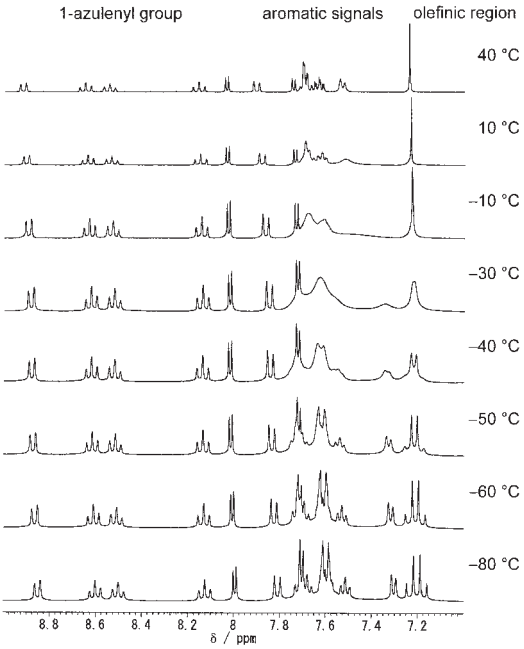


Fig. 6. ^{1}H NMR of **7a** (400 MHz, olefinic region) in CD_2Cl_2 at various temperatures.

boat conformation. Therefore, in principle these cations also should exhibit two dynamic motions: the ring-inversion of the central seven-membered ring and the rotation of the 1-azulenyl group. In the case of **6a–c**, the dynamic motions of the central seven-membered ring should include the flip of $-CH_2CH_2-$ bridge. The ring-inversion process should appear in the spectral changes of the $-CH_2CH_2-$ bridge signals. However, the complexity of the signals hampered the analysis of the dynamic motion of the ring-inversion processes. The ^{1}H NMR (400 MHz) results of **6a** in a $(CDCl_2)_2$ solvent (0.01 M) in the aromatic region at various temperatures are shown in Fig. 5. The NMR consists of eight aromatic signals with the same intensity, along with a set of signals of 1-azulenyl group at room temperature. The spectrum exhibits the frozen conformation of **6a** in terms of the rotation of the 1-azulenyl group at that temperature. When the sample was warmed to 100 °C, noticeable line broadening occurred, but **6a** exhibited decomposition during further warming up to 120 °C. ^{1}H NMR of **6b** and **6c** also exhibited similar temperature dependency. The spectral changes of the aromatic region were employed for the analysis of the rotational barriers of the 1-azulenyl groups. The calculation yielded the rotational barriers of the 1-azulenyl groups for **6a–c** ($\Delta G^{\ddagger}_{20} = 80.8 \pm 3.1$, 89.2 ± 5.6, and 94.3 ± 1.1 kJ mol^{-1}, respectively) in a 0.01 M $(CDCl_2)_2$ solution.

At −80 °C the ^{1}H NMR (400 MHz) results of **7a** in 0.01 M CD_2Cl_2 solution consist of two olefin signals with the same intensity and unsymmetrical aromatic signals along with a set of signals of the 1-azulenyl group in the olefinic region (Fig. 6). When the sample was warmed to −30 °C, noticeable line broadening occurred; further warming resulted in the coalescence of the two olefin signals to a singlet, which became sharp at 40 °C. ^{1}H NMR results of **7b** and **7c** also exhibited similar temperature dependency. The spectral changes in the ^{1}H NMR data of **7a–c** are caused by the rotation of 1-azulenyl groups, because, in these cases, the ring-inversion of the central seven-membered ring does not affect the temperature dependency of the NMR spectra. The calculation using the temperature dependency of the olefin protons yielded the rotational barriers of the 1-azulenyl groups for **7a–c** ($\Delta G^{\ddagger}_{20} = 50.3 \pm 2.2$, 56.7 ± 2.4, and 61.2 ± 1.6 kJ mol^{-1}, respectively) in a 0.01 M CD_2Cl_2 solution.

Correlation of Stability and Rotational Barrier of Azulene Ring. The rotational barriers of the 1-azulenyl group of cations **4c**, **5a–c**, **6a–c**, and **7a–c** along with those of **3a–c** are summarized in Table 3. The lower stability of the carbocation should be assumed to induce the contribution of the canonical form in which the double bond character exists between the cationic carbon and 1-azulenyl group. Indeed, the slow rotation about the 1-azulenyl group to the 9-fluorenyl bond was observed from the ^{1}H NMR spectra of **4c**. However, on the basis of the consideration of the stability of the carbocations alone, the lower barrier to the rotation for the 1-azulenyl group of **5a–c** compared with those of **6a–c** and **7a–c** could not be explained, because the stability of **5a–c** is lower than those of **6a–c** and **7a–c**.

We supposed that the lower barrier to the rotation of the 1-azulenyl group for **5a–c** is due to some disadvantage of the delocalization of positive charge by the dynamic stereochemistry. The ring inversion of these cations could not maintain the conformation of the 1-azulenyl group because the severe steric interaction between the azulene and the fused ring systems could be arisen by the planar transition state for the ring inversion process. Indeed, the ring inversion of the six-membered ring of **5a–c** is observed under the conditions in which the dynamics of the 1-azulenyl group is observed.

Although we could not analyze the barrier to the ring inversion of **6a–c** and **7a–c**, the barrier to the ring inversion of the six-membered ring in **5a–c** is expected to be lower than those of the seven-membered rings in **6a–c** and **7a–c** because diben-

Table 3. $\Delta G^{\ddagger}$ Values (kJ mol^{-1}) of the Rotation of Azulene Ring and the Ring Inversion

Sample	$\Delta G^{\ddagger}_{20}$ for 1-azulenyl group	$\Delta G^{\ddagger}_{20}$ for ring inversion	Solvent	Concentration
3a	61.5 ± 1.7		$CDCl_3$	0.01 M
3b	61.6 ± 0.9		$CDCl_3$	0.01 M
3c	88.4 ± 3.2		$(CDCl_2)_2$	0.01 M
4c	$\gg 70.4$[a)]		$(CDCl_2)_2$	0.01 M
5a	b)	40.9 ± 0.6	CD_2Cl_2	0.05 M
5b	b)	42.5 ± 3.1	CD_2Cl_2	0.01 M
	40.1 ± 1.3	43.6 ± 1.0	CD_2Cl_2	0.05 M
5c	46.4 ± 0.7	44.4 ± 0.4	CD_2Cl_2	0.01 M
6a	80.8 ± 3.1	c)	$(CDCl_2)_2$	0.01 M
6b	89.2 ± 5.6	c)	$(CDCl_2)_2$	0.01 M
6c	94.3 ± 1.1	c)	$(CDCl_2)_2$	0.01 M
7a	50.3 ± 2.2	d)	CD_2Cl_2	0.01 M
7b	56.7 ± 2.4	d)	CD_2Cl_2	0.01 M
7c	61.2 ± 1.6	d)	CD_2Cl_2	0.01 M

a) Estimated $\Delta G^{\ddagger}_{70}$ value. b) The frozen spectra could not be observed even at -90 °C. c) The complexity of the $-CH_2CH_2-$ bridge signals hampered the determination of these values. d) In principal the dynamic motion could not be observed by NMR spectra.

zocycloheptatriene is reported to exhibit a barrier to the ring inversion of $\Delta G^{\ddagger} = 38$ kJ mol^{-1} in a CS_2 solvent,[12] in contrast to the facile ring-inversion of 9,10-dihydroanthracene at -60 °C in a same solvent.[13] Thus, it is assumed that the ground state energy levels of the cations **5a–c** are increased by the ring-inversion process; consequently, such increases lower the energy requirement for the rotation of the 1-azulenyl group.

This assumption is in accord with the lower pK_R^+ values of **5a–c** compared with those of **3a–c** against the prediction from the higher stability of **23** compared with that of **24**. The lower pK_R^+ values of **5a–c** could be explained by the disadvantage of the delocalization of positive charge to the 1-azulenyl group by the dynamic stereochemistry. The higher rotational barriers for **6a–c** and **7a–c** relative to those of **5a–c** would increase the delocalization of positive charge that would be reflected by the higher thermodynamic stability of **6a–c** and **7a–c**, although we could not overlook the electron density effects as in the cases of **7a–c** with "aromatic" dibenzotropylium ion.

Substituent effects on the 1-azulenyl groups to the rotational barriers for the cations **5a–c**, **6a–c**, and **7a–c** are rather small (relative to those of **3a–c**), but, in general, the barriers to the rotation of 3,6-di-*t*-butyl derivatives are higher than those of the corresponding unsubstituted cations. The *t*-butyl groups stabilize the carbocations to a considerable extent, as demonstrated by the pK_R^+ measurement. Thus, the higher rotational barrier for the *t*-butyl derivatives is undoubtedly a result of the high electron-donating ability of the 3,6-di-*t*-butyl-1-azulenyl group.

Conclusion

We have synthesized a series of azulene-substituted 9-fluorenyl, 9,10-dihydro-10,10-dimethyl-9-anthryl, 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl, and 5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl cations (**4c**, **5a–c**, **6a–c**, and **7a–c**), which permit the comparison of the thermodynamic stability with the dynamic stereochemistry of the cations in these series. We found that the thermodynamic stability of the cations and the barrier to the rotation of 1-azulenyl group were significantly affected by not only the electron density but also the dynamic stereochemistry of the connected-ring systems. The dynamic process of the six membered-ring for **5a–c** decreases the delocalization of the positive charge to the 1-azulenyl group. As a result, the ground state energy level of the cations **5a–c** is increased to exhibit the lower thermodynamic stability and the lower rotational barriers relative to those of **6a–c** and **7a–c**. The change of the 1-azulenyl groups to 3-methyl- and 3,6-di-*t*-butyl-1-azulenyl groups increased the barrier to the rotation and the thermodynamic stability. The highest barriers to the rotation and thermodynamic stability of 3,6-di-*t*-butyl derivatives are ascribed to the stabilization of the ground state due to the two electronegative *t*-butyl groups. The high stability of these cations is attributed to the large conjugative effect of the 1-azulenyl group with the central cationic carbon. Therefore, the steric inhibition of conjugation by the connected-ring systems is important to determine the stability of these cations.

Experimental

General. Melting points 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 Hitachi 270-30 or a Shimadzu FTIR-8100M and on 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 A 500 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 in a tetraethylammonium perchlorate (0.1 M) benzonitrile solution with a BAS100B/W electrochemical workstation equipped with Pt working (i.d. = 1.6 mm) and auxiliary electrodes and a reference electrode formed from $Ag/AgNO_3$ (0.01 M) in a tetrabutylammonium perchlorate (0.1 M) acetonitrile solution. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Graduate School of Science, Tohoku University.

9-(1-Azulenyl)fluorene (10a). Concentrated H_2SO_4 (0.1 mL) was added to a solution of **8a** (1.28 g, 10.0 mmol) and **9** (3.65 g, 20.0 mmol) in acetic acid (60 mL). After the mixture was stirred at reflux temperature for 1 h, the reaction mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with 5% $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with 5% ethyl acetate/hexane to afford **10a** (514 mg, 18%) and 1,3-di(9-fluorenyl)azulene (**27**) (939 mg, 21%).

10a: Blue needles; mp 92.2–94.9 °C (EtOAc/hexane); [lit.[3] mp 86–89 °C]; ^{1}H NMR (400 MHz, $(CDCl_2)_2$, 80 °C) δ 8.33 (d, $J = 9.8$ Hz, 1H, $H_{8'}$), 8.23 (d, $J = 9.5$ Hz, 1H, $H_{4'}$), 7.81 (dd, $J = 7.7$, 0.6 Hz, 2H, $H_{4,5}$), 7.53 (dd, $J = 9.8$, 9.8 Hz, 1H, $H_{6'}$), 7.36 (d, $J = 4.0$ Hz, 1H, $H_{2'}$), 7.35 (ddd, $J = 7.7$, 7.3, 0.7 Hz, 2H, $H_{3,6}$), 7.25 (d, $J = 7.7$ Hz, 2H, $H_{1,8}$), 7.23 (d, $J = 4.0$ Hz, 1H, $H_{3'}$), 7.17 (ddd, $J = 7.7$, 7.3, 0.6 Hz, 2H, $H_{2,7}$), 7.09 (dd, $J = 9.8$, 9.5 Hz, 1H, $H_{5'}$), 7.07 (dd, $J = 9.8$, 9.8 Hz, 1H, $H_{7'}$), and 5.75 (s, 1H, H_9); ^{13}C NMR (100 MHz, $(CDCl_2)_2$, 80 °C) δ 148.9 ($C_{8a,9a}$), 141.7 ($C_{3'a}$), 141.0 ($C_{4a,4b}$), 137.7 ($C_{6'}$), 137.0 ($C_{2'}$), 136.7 ($C_{4'}$ and $C_{8'a}$), 133.8 ($C_{8'}$), 129.3 ($C_{1'}$), 127.5 ($C_{2,7}$ and $C_{3,6}$), 125.4 ($C_{1,8}$), 122.9 ($C_{5'}$), 122.3 ($C_{7'}$), 120.2 ($C_{4,5}$), 115.6 ($C_{3'}$), and 47.8 (C_9).

27: Blue needles; mp 211.0–213.1 °C (EtOAc/hexane); [lit.[3] mp 210–215 °C]; ^{1}H NMR (400 MHz, $(CDCl_2)_2$, 80 °C) δ 8.09 (d, $J = 9.8$ Hz, 2H, $H_{4,8}$), 7.77 (d, $J = 7.6$ Hz, 4H, $H_{4',5'}$), 7.45 (t, $J = 9.8$ Hz, 1H, H_6), 7.32 (dd, $J = 7.6$, 7.1 Hz, 4H, $H_{3',6'}$), 7.20 (d, $J = 7.6$ Hz, 4H, $H_{1',8'}$), 7.15 (dd, $J = 7.6$, 7.1 Hz, 4H, $H_{2',7'}$), 7.13 (s, 1H, H_2), 6.94 (dd, $J = 9.8$, 9.8 Hz, 2H, $H_{5,7}$), and 5.64 (s, 2H, $H_{9'}$); ^{13}C NMR (100 MHz, $(CDCl_2)_2$, 80 °C) δ 148.7 ($C_{8'a,9'a}$), 140.9 ($C_{4'a,4'b}$), 138.8 (C_6), 137.8 ($C_{3a,8a}$), 137.6 (C_2), 133.8 ($C_{4,8}$), 127.9 ($C_{1,3}$), 127.4 ($C_{2',7'}$ and $C_{3',6'}$), 125.4 ($C_{1',8'}$), 122.1 ($C_{5,7}$), 120.1 ($C_{4',5'}$), and 48.0 ($C_{9'}$).

9-(3-Methyl-1-azulenyl)fluorene (10b). The same procedure as for the preparation of **10a** was adopted here. The reaction of **8b** (714 mg, 5.02 mmol) with **9** (1.82 g, 10.0 mmol) in acetic acid (25 mL) in the presence of H_2SO_4 (0.05 mL) at reflux temperature for 15 min, followed by column chromatography on silica gel with 3% ethyl acetate/hexane, afforded **10b** (427 mg, 28%). Blue needles; mp 144.0–145.0 °C (EtOAc/hexane); MS (70 eV) m/z 306 (M^+; 100), 305 (22), 291 (51), and 289 (44); IR (KBr disk) ν_{max} 1576, 1450, and 740 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$) 246 (4.36), 255 sh (4.41), 266 sh (4.50), 277 sh (4.61), 287 (4.68), 296 sh (4.53), 341 sh (3.51), 354 (3.71), 371 (3.58), 574 sh (2.33), 600 sh (2.41), 624 (2.47), 653 sh (2.40), 678 (2.39), 725 sh (2.05), and 755 sh (1.96); ^{1}H NMR (600 MHz, $(CDCl_2)_2$, 80 °C) δ 8.27 (d, $J = 9.7$ Hz, 1H, $H_{8'}$), 8.10 (d, $J = 9.5$ Hz, 1H, $H_{4'}$), 7.81 (d, $J = 7.5$ Hz, 2H, $H_{4,5}$), 7.46 (dd, $J = 9.8$, 9.8 Hz, 1H, $H_{6'}$), 7.35 (ddd, $J = 7.5$, 7.4, 0.6 Hz, 2H, $H_{3,6}$), 7.26 (d, $J = 7.5$ Hz, 2H, $H_{1,8}$), 7.18 (dd, $J = 7.5$, 7.4 Hz, 2H, $H_{2,7}$), 7.17 (s, 1H, $H_{2'}$), 6.99 (dd, $J = 9.8$, 9.5 Hz, 1H, $H_{5'}$), 6.96 (dd, $J = 9.8$, 9.7 Hz, 1H, $H_{7'}$), 5.72 (s, 1H, H_9), and 2.51 (s, 3H, 3′-Me); ^{13}C NMR (150 MHz, $(CDCl_2)_2$, 80 °C) δ 149.0 ($C_{8a,9a}$), 141.0 ($C_{4a,4b}$), 137.9 ($C_{3'a}$), 137.8 ($C_{2'}$), 137.6 ($C_{6'}$), 137.0 ($C_{8'a}$), 133.5 ($C_{4'}$), 133.2 ($C_{8'}$), 127.7 ($C_{1'}$), 127.4 ($C_{2,7}$ and $C_{3,6}$), 125.5 ($C_{1,8}$ and $C_{3'}$), 121.4 ($C_{7'}$), 121.3 ($C_{5'}$), 120.2 ($C_{4,5}$), 47.5 (C_9), and 12.7 (3′-Me); HRMS calcd for $C_{24}H_{18}$ 306.1408, found 306.1407. Anal. calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%. Found: C, 93.92; H, 6.22%.

9-(3,6-Di-*t*-butyl-1-azulenyl)fluorene (10c). The same procedure as for the preparation of **10a** was adopted here. The reaction of **8c** (432 mg, 1.80 mmol) with **9** (736 mg, 4.04 mmol) in acetic acid (12 mL) in the presence of H_2SO_4 (0.2 mL) at reflux temperature for 30 min, followed by column chromatography on silica gel with hexane, afforded **10c** (256 mg, 35%). Blue prisms; mp 169.8–171.1 °C (CH_2Cl_2/MeOH); MS (70 eV) m/z 404 (M^+; 97), 390 (33), 389 (100), and 165 (25); IR (KBr disk) ν_{max} 2968, 1580, 1450, 1366, and 738 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$) 244 sh (4.36), 252 sh (4.39), 278 (4.55), 291 (4.73), 300 sh (4.70), 329 sh (3.52), 340 sh (3.59), 357 (3.76), 373 (3.54), 556 sh (2.33), 609 (2.47), 663 sh (2.38), and 738 sh (1.90); ^{1}H NMR (400 MHz, $(CDCl_2)_2$, 80 °C) δ 8.50 (d, $J = 10.5$ Hz, 1H, $H_{4'}$), 8.14 (d, $J = 10.5$ Hz, 1H, $H_{8'}$), 7.81 (dd, $J = 7.6$, 0.7 Hz, 2H, $H_{4,5}$), 7.35 (ddd, $J = 7.6$, 7.3, 0.9 Hz, 2H, $H_{3,6}$), 7.29 (d, $J = 7.6$ Hz, 2H, $H_{1,8}$), 7.22 (s, 1H, $H_{2'}$), 7.19 (ddd, $J = 7.6$, 7.3, 0.7 Hz, 2H, $H_{2,7}$), 7.16 (dd, $J = 10.5$, 1.7 Hz, 1H, $H_{5'}$), 7.09 (dd, $J = 10.5$, 1.7 Hz, 1H, $H_{7'}$), 5.69 (s, 1H, H_9), 1.47 (s, 9H, 3′-*t*-Bu), and 1.43 (s, 9H, 6′-*t*-Bu); ^{13}C NMR (100 MHz, $(CDCl_2)_2$, 80 °C) δ 160.9 ($C_{6'}$), 149.0 ($C_{8a,9a}$), 141.0 ($C_{4a,4b}$), 138.4 ($C_{3'}$), 136.6 ($C_{3'a}$), 135.0 ($C_{2'}$ and $C_{8'a}$), 134.7 ($C_{4'}$), 132.4 ($C_{8'}$), 127.4 ($C_{2,7}$), 127.3 ($C_{3,6}$), 126.1 ($C_{1'}$), 125.5 ($C_{1,8}$), 120.1 ($C_{4,5}$), 119.6 ($C_{7'}$), 118.8 ($C_{5'}$), 47.9 (C_9), 38.4 (s, 6′-*t*-Bu), 33.5 (s, 3′-*t*-Bu), 32.6 (q, 3′-*t*-Bu), and 32.1 (q, 6′-*t*-Bu); HRMS calcd for $C_{31}H_{32}$ 404.2504, found 404.2487. Anal. calcd for $C_{31}H_{32}$: C, 92.03; H, 7.97%. Found: C, 92.20; H, 7.99%.

3-(9-Fluorenyl)-1-azulenecarbaldehyde (11). Phosphoryl chloride (0.030 mL, 0.32 mmol) was added slowly at room temperature to a solution of **10a** (32 mg, 0.11 mmol) in DMF (2 mL). The mixture was stirred at the same temperature for 30 min. The resulting solution was poured into water, alkalified with 2 M NaOH, and extracted with toluene. The organic layer was washed with water, dried with $MgSO_4$, and concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel with 10% ethyl acetate/CH_2Cl_2 gave **11** (28 mg, 80%). Brown prisms; mp 223.0–225.3 °C; MS (70 eV) m/z 320 (M^+; 100), 292 (22), 291 (70), 290 (23), and 289 (58); IR (KBr disk) ν_{max} 1648 (s, C=O), 1436, 1406, and 742 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$) 241 sh (4.51), 268 (4.52), 295 sh (4.44), 307 (4.53), 313 (4.54), 371 sh (3.80), 389 (3.97), 405 sh (3.88), 511 sh (2.59), 548 (2.69), 594 sh (2.57), and 655 sh (2.04); ^{1}H NMR (500 MHz, $(CDCl_2)_2$, 80 °C) δ 10.21 (s, 1H, 1-CHO), 9.45 (d, $J = 9.7$ Hz, 1H, H_8), 8.37 (brd, $J = 9.8$ Hz, 1H, H_4), 7.84 (s, 1H, H_2), 7.83 (d, $J = 7.3$ Hz, 2H, $H_{4',5'}$), 7.78 (dd, $J = 9.9$, 9.8 Hz, 1H, H_6), 7.54 (dd, $J = 9.9$, 9.7 Hz, 1H, H_7), 7.40 (dd, $J = 9.8$, 9.8 Hz, 1H, H_5), 7.37 (dd, $J = 7.5$, 7.3 Hz, 2H, $H_{3',6'}$), 7.23 (d, $J = 7.2$ Hz, 2H, $H_{1',8'}$), 7.19 (ddd, $J = 7.5$, 7.2, 1.0 Hz, 2H, $H_{2',7'}$), and 5.68 (s, 1H, $H_{9'}$); ^{13}C NMR (125 MHz, $(CDCl_2)_2$, 80 °C) δ 186.1 (1-CHO), 147.9 ($C_{8'a,9'a}$), 142.8 (C_{3a}), 141.7 (C_{8a}), 141.6 (C_2), 141.1 ($C_{4'a,4'b}$), 140.1 (C_6), 137.3 (C_8), 136.3 (C_4), 130.6 (C_3), 129.5 (C_7), 127.9 (C_5), 127.8 ($C_{3',6'}$), 127.7 ($C_{2',7'}$), 125.2 (C_1 and $C_{1',8'}$), 120.4 ($C_{4',5'}$), and 47.5 ($C_{9'}$); HRMS calcd for $C_{24}H_{16}O$ 320.1201, found 320.1195. Anal. calcd for $C_{24}H_{16}O \cdot 1/4H_2O$: C, 88.73; H, 5.12%. Found: C, 88.78; H, 5.15%.

9-(3,6-Di-*t*-butyl-1-azulenyl)fluoren-9-ylium Hexafluorophosphate (4c·PF$_6^-$). DDQ (138 mg, 0.608 mmol) was added at room temperature to a mixture of **10c** (203 mg, 0.502 mmol), CH_2Cl_2 (50 mL), 60% HPF_6 (5 mL), and water (50 mL). After the mixture was stirred at the same temperature for 10 min, the resulting suspension was filtered with suction. The organic layer was separated, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in a small amount of CH_2Cl_2 and then Et_2O was added to the solution. The precipitated crystals were collected by filtration, washed with Et_2O, and dried in vacuo

to give **4c**·PF_6^- (275 mg, 100%). Violet powder; mp 154.9–157.9 °C (CH_2Cl_2/ether); MS (FAB) m/z 403 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1556, 1448, 1432, 1334, 838, 734, and 558 cm^{-1}; UV–vis (MeCN) λ_{max}, nm ($\log \varepsilon$) 233 sh (4.52), 242 sh (4.58), 247 (4.62), 257 (4.69), 275 sh (4.48), 301 sh (4.22), 327 (3.91), 341 (3.95), 374 sh (3.62), 424 (3.95), and 553 (4.11); ^{1}H NMR (600 MHz, CD_3CN) δ 9.49 (d, $J = 10.5$ Hz, 1H, $H_{8'}$), 9.18 (d, $J = 10.8$ Hz, 1H, $H_{4'}$), 8.78 (dd, $J = 10.8$, 2.2 Hz, 1H, $H_{5'}$), 8.61 (dd, $J = 10.5$, 2.2 Hz, 1H, $H_{7'}$), 8.16 (s, 1H, $H_{2'}$), 7.91 (dd, $J = 7.7$, 0.8 Hz, 1H, H_8), 7.76 (dd, $J = 7.7$, 0.8 Hz, 1H, H_1), 7.62 (dd, $J = 7.5$, 0.8 Hz, 1H, H_5), 7.61 (dd, $J = 7.5$, 0.8 Hz, 1H, H_4), 7.46 (ddd, $J = 7.7$, 7.5, 0.8 Hz, 2H, H_3 and H_6), 7.33 (ddd, $J = 7.7$, 7.7, 0.8 Hz, 1H, H_7), 7.21 (ddd, $J = 7.7$, 7.7, 0.8 Hz, 1H, H_2), 1.62 (s, 9H, 3′-*t*-Bu), and 1.56 (s, 9H, 6′-*t*-Bu); ^{13}C NMR (150 MHz, CD_3CN) δ 174.1 ($C_{6'}$), 158.5 ($C_{3'a}$), 157.7 (C_9), 156.7 ($C_{3'}$), 154.0 ($C_{8'a}$), 144.8 (C_{4a}), 143.8 (C_{4b}), 143.4 ($C_{5'}$), 143.1 ($C_{8'}$), 141.0 ($C_{4'}$ and $C_{7'}$), 138.9 ($C_{2'}$), 138.3 (C_{8a}), 137.6 ($C_{1'}$), 136.2 (C_{9a}), 135.0 (C_3), 134.3 (C_6), 132.3 (C_1), 131.4 (C_8), 129.3 (C_7), 128.9 (C_2), 121.9 (C_5), 121.7 (C_4), 40.0 (s, 6′-*t*-Bu), 33.5 (s, 3′-*t*-Bu), 30.4 (q, 6′-*t*-Bu), and 29.0 (q, 3′-*t*-Bu); HRMS calcd for $C_{31}H_{31}$ 403.2426, found 403.2408. Anal. calcd for $C_{31}H_{31}F_6P$: C, 67.88; H, 5.70%. Found: C, 67.67; H, 5.73%.

9-(1-Azulenyl)-9,10-dihydro-10,10-dimethylanthracene (13a). A solution of **8a** (644 mg, 5.02 mmol) and **12** (1.17 g, 5.22 mmol) in acetic acid (25 mL) was stirred at room temperature for 5 h. The reaction mixture was concentrated under reduced pressure and the residue was diluted with CH_2Cl_2. The organic solution was washed with 5% $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ to afford **13a** (1.42 g, 84%) and **14** (100 mg, 7.1%).

13a: Blue needles; mp 181.9–183.4 °C (CH_2Cl_2/MeOH); MS (70 eV) m/z 334 (M^+; 100), 319 (46), 304 (33), 303 (32), and 302 (23); IR (KBr disk) ν_{max} 1576, 1396, 760, and 740 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$) 238 (4.27), 286 (4.67), 322 sh (3.33), 337 sh (3.56), 349 (3.71), 364 (3.44), 549 sh (2.36), 597 (2.49), 645 (2.41), and 713 (1.97); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, $J = 9.8$ Hz, 1H, $H_{8'}$), 8.30 (d, $J = 9.5$ Hz, 1H, $H_{4'}$), 7.61 (dd, $J = 8.1$, 1.1 Hz, 2H, $H_{4,5}$), 7.59 (d, $J = 3.9$ Hz, 1H, $H_{2'}$), 7.55 (dd, $J = 9.8$, 9.8 Hz, 1H, $H_{6'}$), 7.37 (d, $J = 3.9$ Hz, 1H, $H_{3'}$), 7.21 (dd, $J = 8.1$, 7.0 Hz, 2H, $H_{3,6}$), 7.13 (dd, $J = 9.8$, 9.5 Hz, 1H, $H_{5'}$), 7.06 (dd, $J = 9.8$, 9.8 Hz, 1H, $H_{7'}$), 6.96 (ddd, $J = 7.8$, 7.0, 1.1 Hz, 2H, $H_{2,7}$), 6.77 (d, $J = 7.8$ Hz, 2H, $H_{1,8}$), 6.01 (s, 1H, H_9), 1.98 (s, 3H, 10-Me), and 1.65 (s, 3H, 10-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2 ($C_{4a,10a}$), 141.2 ($C_{3'a}$), 139.0 ($C_{2'}$), 138.3 ($C_{8a,9a}$), 137.5 ($C_{6'}$), 136.6 ($C_{4'}$), 135.6 ($C_{8'a}$), 134.2 ($C_{1'}$), 133.7 ($C_{8'}$), 128.8 ($C_{1,8}$), 126.4 ($C_{3,6}$), 125.8 ($C_{2,7}$), 125.2 ($C_{4,5}$), 122.8 ($C_{5'}$), 122.2 ($C_{7'}$), 117.6 ($C_{3'}$), 41.1 (C_9), 38.4 (C_{10}), 33.2 (10-Me), and 30.8 (10-Me); HRMS calcd for $C_{26}H_{22}$ 334.1722, found 334.1719. Anal. calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63%. Found: C, 93.47; H, 6.74%.

14: Blue needles; mp 215.4–216.2 °C (CH_2Cl_2/MeOH); MS (70 eV) m/z 540 (M^+; 100); IR (KBr disk) ν_{max} 2968, 2932, 1574, 1490, 1472, 1454, 1430, 1370, 764, and 712 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$) 242 (4.33), 293 (4.60), 300 (4.60), 328 sh (3.33), 355 (3.70), 373 (3.54), 566 sh (2.37), 615 (2.51), 666 sh (2.44), and 742 (1.96); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, $J = 9.5$ Hz, 2H, $H_{4,8}$), 7.59 (d, $J = 7.8$ Hz, 4H, $H_{4',5'}$), 7.52 (s, 1H, H_2), 7.47 (t, $J = 9.8$ Hz, 1H, H_6), 7.21 (dd, $J = 7.6$, 7.1 Hz, 4H, $H_{3',6'}$), 6.99 (dd, $J = 7.8$, 7.1 Hz, 4H, $H_{2',7'}$), 6.95 (dd, $J = 9.8$, 9.5 Hz, 2H, $H_{5,7}$), 6.78 (d, $J = 7.6$ Hz, 4H, $H_{1',8'}$), 5.94 (s, 2H, $H_{9'}$), 1.94 (s, 6H, 10′-Me), and 1.57 (s, 6H, 10′-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5 ($C_{4'a,10'a}$), 142.3 (C_2), 138.6 ($C_{8'a,9'a}$), 137.7 (C_6), 136.9 ($C_{3a,8a}$), 134.1 ($C_{4,8}$), 132.3 ($C_{1,3}$), 128.6 ($C_{1',8'}$), 126.4 ($C_{3',6'}$), 125.7 ($C_{2',7'}$), 124.8 ($C_{4',5'}$), 122.2 ($C_{5,7}$), 41.6 ($C_{9'}$), 38.5 ($C_{10'}$), 32.8 (10′-Me), and 29.6 (10′-Me); HRMS calcd for $C_{42}H_{36}$ 540.2817, found 540.2817. Anal. calcd for $C_{42}H_{36}$: C, 93.29; H, 6.71%. Found: C, 93.32; H, 6.75%.

9,10-Dihydro-10,10-dimethyl-9-(3-methyl-1-azulenyl)anthracene (13b). The same procedure as for the preparation of **13a** was adopted here. The reaction of **8b** (754 mg, 5.30 mmol) with **12** (1.21 g, 5.39 mmol) in acetic acid (25 mL) at room temperature for 4.5 h, followed by recrystallization from CH_2Cl_2/MeOH, afforded **13b** (1.84 g, 100%). Blue plates; mp 192.8–194.9 °C (CH_2Cl_2/MeOH); MS (70 eV) m/z 348 (M^+; 100), 333 (29), 318 (32), 303 (23), and 302 (22); IR (KBr disk) ν_{max} 1574, 1490, 1450, 1364, 762, 750, 732, 708, and 568 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$) 241 (4.26), 290 (4.67), 296 sh (4.63), 327 sh (3.27), 339 sh (3.51), 354 (3.73), 372 (3.60), 575 sh (2.34), 603 sh (2.43), 624 (2.48), 652 sh (2.42), 681 (2.39), 726 sh (2.05), and 755 sh (1.96); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.36 (d, $J = 9.7$ Hz, 1H, $H_{8'}$), 8.17 (d, $J = 9.5$ Hz, 1H, $H_{4'}$), 7.61 (dd, $J = 8.1$, 1.2 Hz, 2H, $H_{4,5}$), 7.51 (dd, $J = 9.8$, 9.8 Hz, 1H, $H_{6'}$), 7.30 (s, 1H, $H_{2'}$), 7.21 (ddd, $J = 8.1$, 7.1, 1.3 Hz, 2H, $H_{3,6}$), 7.05 (dd, $J = 9.8$, 9.5 Hz, 1H, $H_{5'}$), 6.99 (dd, $J = 9.8$, 9.7 Hz, 1H, $H_{7'}$), 6.96 (ddd, $J = 7.8$, 7.1, 1.2 Hz, 2H, $H_{2,7}$), 6.82 (d, $J = 7.8$ Hz, 2H, $H_{1,8}$), 5.99 (s, 1H, H_9), 2.55 (s, 3H, 3′-Me), 1.95 (s, 3H, 10-Me), and 1.67 (s, 3H, 10-Me); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 143.8 ($C_{4a,10a}$), 139.9 ($C_{2'}$), 138.7 ($C_{8a,9a}$), 137.4 ($C_{6'}$), 137.3 ($C_{3'a}$), 136.0 ($C_{8'a}$), 134.6 ($C_{1'}$), 134.4 ($C_{4'}$), 133.9 ($C_{8'}$), 129.8 ($C_{1,8}$), 127.2 ($C_{3,6}$), 126.7 ($C_{4,5}$), 126.6 ($C_{2,7}$ and $C_{3'}$), 122.2 ($C_{7'}$), 122.1 ($C_{5'}$), 41.4 (C_9), 38.9 (C_{10}), 34.3 (10-Me), 32.9 (10-Me), and 13.2 (3′-Me); HRMS calcd for $C_{27}H_{24}$ 348.1878, found 348.1877. Anal. calcd for $C_{27}H_{24}$: C, 93.06; H, 6.94%. Found: C, 92.85; H, 7.22%.

9-(3,6-Di-*t*-butyl-1-azulenyl)-9,10-dihydro-10,10-dimethylanthracene (13c). The same procedure as for the preparation of **13a** was adopted here. The reaction of **8c** (725 mg, 3.02 mmol) with **12** (690 g, 3.08 mmol) in acetic acid (15 mL) at room temperature for 5 h, followed by column chromatography on silica gel with CH_2Cl_2, afforded **13c** (1.23 g, 91%). Blue needles; mp 224.0–225.0 °C (CH_2Cl_2/MeOH); MS (70 eV) m/z 446 (M^+; 100), 432 (27), and 431 (69); IR (KBr disk) ν_{max} 2968, 1580, 1364, and 760 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$) 242 (4.23), 293 (4.72), 302 (4.74), 330 sh (3.40), 341 sh (3.59), 347 sh (3.62), 357 (3.76), 374 (3.51), 560 sh (2.36), 608 (2.49), 660 sh (2.40), and 735 sh (1.94); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, $J = 10.5$ Hz, 1H, $H_{4'}$), 8.12 (d, $J = 10.8$ Hz, 1H, $H_{8'}$), 7.61 (dd, $J = 7.8$, 1.2 Hz, 2H, $H_{4,5}$), 7.43 (s, 1H, $H_{2'}$), 7.22 (dd, $J = 7.8$, 7.1 Hz, 2H, $H_{3,6}$), 7.21 (dd, $J = 10.5$, 1.8 Hz, 1H, $H_{5'}$), 7.08 (dd, $J = 10.8$, 1.8 Hz, 1H, $H_{7'}$), 6.98 (ddd, $J = 7.9$, 7.1, 1.2 Hz, 2H, $H_{2,7}$), 6.78 (d, $J = 7.9$ Hz, 2H, $H_{1,8}$), 5.92 (s, 1H, H_9), 1.98 (s, 3H, 10-Me), 1.62 (s, 3H, 10-Me), 1.53 (s, 9H, 3′-*t*-Bu), and 1.43 (s, 9H, 6′-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5 ($C_{6'}$), 143.4 ($C_{4a,10a}$), 138.7 ($C_{8a,9a}$), 138.6 ($C_{3'}$), 137.0 ($C_{2'}$), 135.4 ($C_{8'a}$), 134.7 ($C_{3'a}$), 134.4 ($C_{4'}$), 132.3 ($C_{8'}$), 130.5 ($C_{1'}$), 128.8 ($C_{1,8}$), 126.2 ($C_{3,6}$), 125.7 ($C_{2,7}$), 124.8 ($C_{4,5}$), 119.7 ($C_{7'}$), 118.5 ($C_{5'}$), 41.2 (C_9), 38.5 (C_{10}), 38.2 (s, 6′-*t*-Bu), 33.3 (s, 3′-*t*-Bu), 32.8 (10-Me), 32.3 (q, 3′-*t*-Bu), 31.8 (q, 6′-*t*-Bu), and 30.1 (10-Me); HRMS calcd for $C_{34}H_{38}$ 446.2973, found 446.2974. Anal. calcd for $C_{34}H_{38}$: C, 91.43; H, 8.57%. Found: C, 91.47; H, 8.58%.

9-(1-Azulenyl)-9,10-dihydro-10,10-dimethyl-9-anthrylium

Hexafluorophosphate (5a·PF_6^-). The same procedure as for the preparation of **4c**·PF_6^- was followed using DDQ (137 mg, 0.604 mmol), **13a** (167 mg, 0.499 mmol), and 60% HPF_6 (5 mL) in CH_2Cl_2 (50 mL). Recrystallization from CH_2Cl_2/Et_2O gave **5a**·PF_6^- (197 mg, 82%). Brown powder; mp 118.8–121.9 °C (CH_2Cl_2/ether); MS (FAB) m/z 333 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1545, 1424, 1372, 841, 774, and 558 cm^{-1}; UV–vis (MeCN) λ_{max}, nm ($\log \varepsilon$) 236 sh (4.35), 261 (4.24), 287 (4.20), 292 sh (4.18), 318 (3.88), 348 sh (3.77), 363 sh (3.93), 386 (4.04), and 471 (4.21); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98–8.96 (m, 1H, $H_{4'}$), 8.81 (d, $J = 10.0$ Hz, 1H, $H_{8'}$), 8.68 (d, $J = 5.4$ Hz, 1H, $H_{2'}$), 8.59–8.51 (m, 2H, $H_{5',6'}$), 8.28–8.20 (m, 1H, $H_{7'}$), 7.87 (d, $J = 5.4$ Hz, 1H, $H_{3'}$), 7.77 (d, $J = 7.3$ Hz, 2H, $H_{4,5}$), 7.69 (dd, $J = 7.6$, 1.2 Hz, 2H, $H_{1,8}$), 7.59 (ddd, $J = 7.8$, 7.3, 1.2 Hz, 2H, $H_{3,6}$), 7.44 (ddd, $J = 7.8$, 7.6, 1.0 Hz, 2H, $H_{2,7}$), and 1.74 (s, 6H, 10-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (C_9), 162.3 ($C_{3'a}$), 154.8 ($C_{8'a}$), 148.0 ($C_{4a,10a}$), 147.6 ($C_{6'}$), 145.5 ($C_{5'}$), 145.4 ($C_{2'}$), 143.3 ($C_{4'}$), 143.2 ($C_{8'}$), 142.2 ($C_{7'}$), 135.7 ($C_{8a,9a}$), 134.8 ($C_{3'}$), 132.9 ($C_{1'}$), 133.1 ($C_{3,6}$), 131.0 ($C_{1,8}$), 126.8 ($C_{2,7}$), 124.8 ($C_{4,5}$), 41.3 (C_{10}), and 29.6 (10-Me); HRMS calcd for $C_{26}H_{21}$ 333.1643, found 333.1588. Anal. calcd for $C_{26}H_{21}F_6P \cdot 1/2H_2O$: C, 64.07; H, 4.55%. Found: C, 64.13; H, 4.52%.

9,10-Dihydro-10,10-dimethyl-9-(3-methyl-1-azulenyl)-9-anthrylium Hexafluorophosphate (5b·PF_6^-). DDQ (320 mg, 1.41 mmol) was added at room temperature to a solution of **13b** (348 mg, 1.00 mmol) in CH_2Cl_2 (100 mL). After the solution was stirred at the same temperature for 1 h, 60% HPF_6 (5 mL) was added to the mixture. After stirring for an additional 15 min, water (20 mL) was added to the mixture. The resulting suspension was filtered with suction. The organic layer was separated, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in a small amount of CH_2Cl_2 and then Et_2O was added to the solution. The precipitated crystals were collected by filtration, washed with Et_2O, and dried in vacuo to give **5b**·PF_6^- (434 mg, 88%). Brown powder; mp 168.9–172.9 °C (CH_2Cl_2/ether); MS (FAB) m/z 347 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1586, 1570, 1550, 1450, 1436, 1358, 1068, 880, 842, 776, 750, and 558 cm^{-1}; UV–vis (MeCN) λ_{max}, nm ($\log \varepsilon$) 214 sh (4.50), 238 sh (4.31), 263 (4.19), 289 (4.03), 296 sh (4.00), 319 (3.94), 390 (4.09), and 484 (4.20); ^{1}H NMR (400 MHz, CD_3CN) δ 8.84 (d, $J = 9.9$ Hz, 1H, $H_{4'}$), 8.72 (d, $J = 9.9$ Hz, 1H, $H_{8'}$), 8.59 (dd, $J = 9.9$, 9.4 Hz, 1H, $H_{5'}$), 8.54 (s, 1H, $H_{2'}$), 8.49 (dd, $J = 10.0$, 9.4 Hz, 1H, $H_{6'}$), 8.20 (dd, $J = 10.0$, 9.9 Hz, 1H, $H_{7'}$), 7.81 (dd, $J = 7.8$, 0.9 Hz, 2H, $H_{4,5}$), 7.70 (dd, $J = 7.6$, 1.1 Hz, 2H, $H_{1,8}$), 7.59 (ddd, $J = 7.8$, 7.4, 1.1 Hz, 2H, $H_{3,6}$), 7.41 (ddd, $J = 7.6$, 7.4, 0.9 Hz, 2H, $H_{2,7}$), 2.60 (s, 3H, 3′-Me), and 1.71 (s, 6H, 10-Me); ^{13}C NMR (100 MHz, CD_3CN) δ 162.9 ($C_{3'a}$), 160.7 (C_9), 157.5 ($C_{8'a}$), 148.7 ($C_{4a,10a}$), 148.0 ($C_{6'}$), 146.4 ($C_{5'}$), 145.2 ($C_{3'}$), 144.2 ($C_{8'}$), 144.0 ($C_{2'}$), 143.9 ($C_{7'}$), 141.2 ($C_{4'}$), 137.2 ($C_{8a,9a}$), 133.3 ($C_{1'}$), 132.3 ($C_{3,6}$), 132.0 ($C_{1,8}$), 127.5 ($C_{2,7}$), 125.6 ($C_{4,5}$), 42.0 (C_{10}), 29.5 (10-Me), and 13.5 (3′-Me); HRMS calcd for $C_{27}H_{23}$ 347.1799, found 347.1797. Anal. calcd for $C_{27}H_{23}F_6P$: C, 65.85; H, 4.71%. Found: C, 66.02; H, 4.70%.

9-(3,6-Di-*t*-butyl-1-azulenyl)-9,10-dihydro-10,10-dimethyl-9-anthrylium Hexafluorophosphate (5c·PF_6^-). The same procedure as for the preparation of **5b**·PF_6^- was followed using DDQ (155 mg, 0.683 mmol), **13c** (224 mg, 0.501 mmol), and 60% HPF_6 (5 mL) in CH_2Cl_2 (100 mL). Recrystallization from CH_2Cl_2/Et_2O gave **5c**·PF_6^- (148 mg, 50%). Brown powder; mp 169.3–172.5 °C (CH_2Cl_2/ether); MS (FAB) m/z 445 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 2976, 1554, 1436, 1342, 842, 834, and 558 cm^{-1}; UV–vis (MeCN) λ_{max}, nm ($\log \varepsilon$) 238 sh (4.36), 266 (4.25), 293 (4.05), 329 (4.04), 391 (4.15), and 479 (4.22); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.26 (d, $J = 11.0$ Hz, 1H, $H_{4'}$), 8.90 (dd, $J = 11.0$, 2.0 Hz, 1H, $H_{5'}$), 8.75 (d, $J = 10.8$ Hz, 1H, $H_{8'}$), 8.33 (s, 1H, $H_{2'}$), 8.26 (dd, $J = 11.0$, 2.0 Hz, 1H, $H_{7'}$), 7.76 (dd, $J = 7.8$, 1.2 Hz, 2H, $H_{4,5}$), 7.67 (dd, $J = 7.8$, 1.2 Hz, 2H, $H_{1,8}$), 7.57 (ddd, $J = 7.8$, 7.8, 1.2 Hz, 2H, $H_{3,6}$), 7.44 (ddd, $J = 7.8$, 7.8, 1.2 Hz, 2H, $H_{2,7}$), 1.75 (s, 6H, 10-Me), 1.61 (s, 9H, 3′-*t*-Bu), and 1.53 (s, 9H, 6′-*t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.5 ($C_{6'}$), 159.9 (C_9), 159.6 ($C_{3'a}$), 155.7 ($C_{8'a}$), 155.6 ($C_{3'}$), 147.7 ($C_{4a,10a}$), 144.2 ($C_{5'}$), 141.7 ($C_{8'}$), 141.1 ($C_{4'}$), 139.7 ($C_{7'}$), 139.5 ($C_{2'}$), 136.3 ($C_{8a,9a}$), 131.5 ($C_{3,6}$), 131.3 ($C_{1'}$), 130.6 ($C_{1,8}$), 126.6 ($C_{2,7}$), 124.7 ($C_{4,5}$), 41.3 (C_{10}), 40.3 (s, 6′-*t*-Bu), 33.6 (s, 3′-*t*-Bu), 31.3 (q, 6′-*t*-Bu), 29.8 (q, 3′-*t*-Bu), and 29.3 (10-Me); HRMS calcd for $C_{34}H_{37}$ 445.2895, found 445.2881. Anal. calcd for $C_{34}H_{37}F_6P$: C, 69.14; H, 6.31%. Found: C, 68.85; H, 6.14%.

5-(1-Azulenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (16a). A solution of **8a** (642 mg, 5.01 mmol) and **15** (1.05 g, 4.99 mmol) in acetic acid (30 mL) was stirred at room temperature for 6 h. The reaction mixture was concentrated under reduced pressure and the residue was diluted with CH_2Cl_2. The organic solution was washed with 5% $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ to afford **16a** (790 mg, 49%) and **17** (451 mg, 35%).

16a: Blue prisms; mp 148.0–149.0 °C (CH_2Cl_2/hexane); MS (70 eV) m/z 320 (M^+; 44), 192 (100), and 191 (28); IR (KBr disk) ν_{max} 1576, 1496, 1456, 1396, 770, and 748 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$) 236 (4.31), 275 sh (4.49), 286 (4.69), 289 sh (4.69), 295 (4.67), 325 sh (3.41), 334 sh (3.56), 340 sh (3.62), 350 (3.77), 366 (3.66), 553 sh (2.38), 575 sh (2.46), 601 (2.52), 625 sh (2.46), 651 (2.43), 692 sh (2.10), and 719 (1.99); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, $J = 9.5$ Hz, 1H, $H_{4'}$), 8.17 (d, $J = 9.8$ Hz, 1H, $H_{8'}$), 7.48 (m, 2H, $H_{4,6}$), 7.44 (dd, $J = 10.0$, 9.8 Hz, 1H, $H_{6'}$), 7.36 (d, $J = 3.9$ Hz, 1H, $H_{2'}$), 7.22–7.15 (m, 4H, $H_{2,3,7,8}$), 7.21 (d, $J = 3.9$ Hz, 1H, $H_{3'}$), 7.12–7.08 (m, 2H, $H_{1,9}$), 7.01 (dd, $J = 9.8$, 9.5 Hz, 1H, $H_{5'}$), 6.89 (dd, $J = 10.0$, 9.8 Hz, 1H, $H_{7'}$), 5.79 (s, 1H, H_5), 3.25–3.16 (m, 2H, $H_{10,11}$), and 2.74–2.65 (m, 2H, $H_{10,11}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7 ($C_{4a,5a}$), 141.4 ($C_{3'a}$), 139.8 ($C_{9a,11a}$), 138.9 ($C_{2'}$), 137.3 ($C_{6'}$), 136.8 ($C_{4'}$), 134.9 ($C_{8'}$), 134.4 ($C_{8'a}$), 132.5 ($C_{1'}$), 130.8 ($C_{1,9}$), 130.5 ($C_{4,6}$), 127.0 ($C_{2,8}$), 126.2 ($C_{3,7}$), 122.5 ($C_{5'}$), 121.8 ($C_{7'}$), 116.1 ($C_{3'}$), 54.2 (C_5), and 32.0 ($C_{10,11}$); HRMS calcd for $C_{25}H_{20}$ 320.1565, found 320.1566. Anal. calcd for $C_{25}H_{20}$: C, 93.71; H, 6.29%. Found: C, 93.87; H, 6.39%.

17: Blue plates; mp 203.6–205.0 °C (CH_2Cl_2/hexane); MS (70 eV) m/z 512 (M^+; 58), 193 (20), 192 (100), and 191 (32); IR (KBr disk) ν_{max} 754 and 732 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$) 240 (4.37), 276 sh (4.37), 295 (4.65), 299 sh (4.64), 304 (4.66), 333 sh (3.38), 343 sh (3.56), 350 sh (3.64), 360 (3.79), 370 sh (3.62), 378 (3.84), 573 sh (2.38), 621 (2.51), 680 sh (2.41), and 753 sh (1.94); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, $J = 9.8$ Hz, 2H, $H_{4,8}$), 7.36–7.32 (m, 4H, $H_{4',6'}$), 7.28 (t, $J = 10.0$ Hz, 1H, H_6), 7.12–7.08 (m, 8H, $H_{2',3',7',8'}$), 7.02–6.98 (m, 4H, $H_{1',9'}$), 6.77 (dd, $J = 10.0$, 9.8 Hz, 2H, $H_{5,7}$), 6.75 (s, 1H, H_2), 5.68 (s, 2H, $H_{5'}$), 3.04–2.95 (m, 4H, $H_{10',11'}$), and 2.69–2.60 (m, 4H, $H_{10',11'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6 (C_2 and $C_{4'a,5'a}$), 139.5 ($C_{9'a,11'a}$), 137.3 (C_6), 135.5 ($C_{3a,8a}$), 134.8 ($C_{4,8}$), 130.5 ($C_{1',9'}$), 130.2 ($C_{1,3}$ and $C_{4',6'}$), 126.8 ($C_{2',8'}$), 126.1 ($C_{3',7'}$), 121.6 ($C_{5,7}$), 53.7 ($C_{5'}$), and 31.9 ($C_{10',11'}$);

HRMS calcd for $C_{40}H_{32}$ 512.2504, found 512.2506. Anal. calcd for $C_{40}H_{32}$: C, 93.71; H, 6.29%. Found: C, 93.87; H, 6.39%.

10,11-Dihydro-5-(3-methyl-1-azulenyl)-5*H*-dibenzo[*a*,*d*]cycloheptene (16b). The same procedure as for the preparation of **16a** was adopted here. The reaction of **8b** (718 mg, 5.05 mmol) with **15** (1.06 g, 5.04 mmol) in acetic acid (30 mL) at room temperature for 6 h, followed by column chromatography on silica gel with CH_2Cl_2, afforded **16b** (1.59 g, 94%). Blue plates; mp 166.5–169.5 °C (CH_2Cl_2/MeOH); MS (70 eV) m/z 334 (M^+; 73), 192 (100), 191 (24), and 142 (31); IR (KBr disk) ν_{max} 770, 752, 736, and 726 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 239 (4.27), 276 sh (4.46), 291 (4.68), 299 sh (4.64), 329 sh (3.27), 341 sh (3.51), 357 (3.74), 375 (3.73), 577 sh (2.39), 606 sh (2.47), 630 (2.53), 661 sh (2.45), 689 (2.43), 735 sh (2.06), and 767 sh (1.95); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.11 (d, $J = 9.6$ Hz, 1H, $H_{4'}$), 8.10 (d, $J = 9.7$ Hz, 1H, $H_{8'}$), 7.46–7.45 (m, 2H, $H_{4,6}$), 7.39 (dd, $J = 9.9$, 9.7 Hz, 1H, $H_{6'}$), 7.22–7.18 (m, 4H, $H_{2,3,7,8}$), 7.21 (s, 1H, $H_{2'}$), 7.13–7.12 (m, 2H, $H_{1,9}$), 6.94 (dd, $J = 9.7$, 9.6 Hz, 1H, $H_{5'}$), 6.79 (dd, $J = 9.9$, 9.7 Hz, 1H, $H_{7'}$), 5.78 (s, 1H, H_5), 3.27–3.21 (m, 2H, $H_{10,11}$), 2.72–2.66 (m, 2H, $H_{10,11}$), and 2.53 (s, 3H, 3′-Me); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 142.6 ($C_{4a,5a}$), 140.6 ($C_{9a,11a}$ and $C_{2'}$), 138.1 ($C_{3'a}$ and $C_{6'}$), 135.2 ($C_{8'a}$), 134.9 ($C_{8'}$), 134.4 ($C_{4'}$), 131.5 ($C_{1,9}$ and $C_{1'}$), 131.2 ($C_{4,6}$), 127.7 ($C_{2,8}$), 126.9 ($C_{3,7}$), 124.8 ($C_{3'}$), 121.6 ($C_{5'}$), 121.5 ($C_{7'}$), 54.6 (C_5), 32.7 ($C_{10,11}$), and 13.1 (3′-Me); HRMS calcd for $C_{26}H_{22}$ 334.1722, found 334.1721. Anal. calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63%. Found: C, 93.50; H, 6.76%.

5-(3,6-Di-*t*-butyl-1-azulenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (16c). The same procedure as for the preparation of **16a** was adopted here. The reaction of **8c** (489 mg, 2.03 mmol) with **15** (427 mg, 2.03 mmol) in acetic acid (12 mL) at room temperature for 6 h, followed by column chromatography on silica gel with CH_2Cl_2, afforded **16c** (697 mg, 79%). Blue needles; mp 198.2–198.8 °C (CH_2Cl_2/MeOH); MS (70 eV) m/z 432 (M^+; 67), 417 (25), 241 (23), 240 (100), 226 (20), 225 (97), 192 (29), and 191 (51); IR (KBr disk) ν_{max} 2976 and 1580 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 241 (4.25), 294 (4.73), 305 (4.79), 332 sh (3.44), 342 sh (3.59), 350 sh (3.67), 359 (3.79), 377 (3.70), 565 sh (2.40), 613 (2.52), 668 sh (2.43), and 744 sh (1.94); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, $J = 10.8$ Hz, 1H, $H_{4'}$), 8.09 (d, $J = 10.8$ Hz, 1H, $H_{8'}$), 7.45–7.41 (m, 2H, $H_{4,6}$), 7.20 (s, 1H, $H_{2'}$), 7.20–7.13 (m, 4H, $H_{2,3,7,8}$), 7.11–7.07 (m, 2H, $H_{1,9}$), 7.10 (dd, $J = 10.8$, 2.0 Hz, 1H, $H_{5'}$), 6.96 (dd, $J = 10.8$, 2.0 Hz, 1H, $H_{7'}$), 5.74 (s, 1H, H_5), 3.31–3.22 (m, 2H, $H_{10,11}$), 2.75–2.66 (m, 2H, $H_{10,11}$), 1.46 (s, 9H, 3′-*t*-Bu), and 1.36 (s, 9H, 6′-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 ($C_{6'}$), 141.9 ($C_{4a,5a}$), 139.7 ($C_{9a,11a}$), 136.8 ($C_{2'}$ and $C_{3'}$), 134.6 ($C_{4'}$), 134.3 ($C_{3'a}$), 134.1 ($C_{8'a}$), 133.5 ($C_{8'}$), 130.7 ($C_{1,9}$), 130.5 ($C_{4,6}$), 129.5 ($C_{1'}$), 126.8 ($C_{2,8}$), 126.1 ($C_{3,7}$), 119.1 ($C_{7'}$), 118.5 ($C_{5'}$), 53.9 (C_5), 38.1 (s, 6′-*t*-Bu), 33.1 (s, 3′-*t*-Bu), 32.2 (q, 3′-*t*-Bu), 32.0 ($C_{10,11}$), and 31.8 (q, 6′-*t*-Bu); HRMS calcd for $C_{33}H_{36}$ 432.2817, found 432.2815. Anal. calcd for $C_{33}H_{36}$: C, 91.61; H, 8.39%. Found: C, 91.46; H, 8.53%.

5-(1-Azulenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylium Hexafluorophosphate (6a·PF_6^-). The same procedure as for the preparation of **5b**·PF_6^- was followed using DDQ (306 mg, 1.35 mmol), **16a** (321 mg, 1.00 mmol), and 60% HPF_6 (10 mL) in CH_2Cl_2 (100 mL). Recrystallization from CH_2Cl_2/hexane gave **6a**·PF_6^- (465 mg, 100%). Yellow powder; mp 121.5–123.0 °C (CH_2Cl_2/hexane); MS (FAB) m/z 319 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1586, 1558, 1432, 1372, 838, and 558 cm^{-1}; UV–vis (MeCN) λ_{max}, nm (log ε) 213 sh (4.63), 233 sh (4.45), 259 sh (4.18), 288 (4.29), 319 sh (4.02), and 444 (4.26); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.98 (dd, $J = 9.8$, 1.1 Hz, 1H, $H_{4'}$), 8.65 (ddd, $J = 9.9$, 9.8, 1.0 Hz, 1H, $H_{5'}$), 8.57 (dddd, $J = 9.9$, 9.6, 1.1, 1.0 Hz, 1H, $H_{6'}$), 8.50 (dd, $J = 9.8$, 1.0 Hz, 1H, $H_{8'}$), 8.24 (ddd, $J = 9.8$, 9.6, 1.0 Hz, 1H, $H_{7'}$), 8.03 (d, $J = 5.4$ Hz, 1H, $H_{2'}$), 7.74 (d, $J = 5.4$ Hz, 1H, $H_{3'}$), 7.53 (ddd, $J = 7.6$, 7.5, 1.0 Hz, 1H, H_2), 7.44 (dd, $J = 7.6$, 0.5 Hz, 1H, H_1), 7.43 (ddd, $J = 7.6$, 7.5, 1.5 Hz, 1H, H_8), 7.36 (ddd, $J = 7.9$, 7.5, 1.0 Hz, 1H, H_7), 7.32 (dd, $J = 7.9$, 1.5 Hz, 1H, H_6 and dd, $J = 7.6$, 1.0 Hz, 1H, H_9), 7.31 (ddd, $J = 7.6$, 7.5, 0.5 Hz, 1H, H_3), 7.18 (dd, $J = 7.6$, 1.0 Hz, 1H, H_4), 3.52 (ddd, $J = 16.4$, 8.0, 4.3 Hz, 1H, H_{11}), 3.41 (ddd, $J = 15.8$, 9.0, 4.3 Hz, 1H, H_{10}), 3.10 (ddd, $J = 16.4$, 9.0, 4.4 Hz, 1H, H_{11}), and 3.04 (ddd, $J = 15.8$, 8.0, 4.4 Hz, 1H, H_{10}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.1 (C_5), 164.7 ($C_{3'a}$), 154.2 ($C_{8'a}$), 147.9 ($C_{6'}$), 147.4 ($C_{5'}$), 146.2 ($C_{2'}$), 144.2 ($C_{7'}$), 144.0 ($C_{4'}$), 143.9 ($C_{8'}$), 139.7 (C_{5a}), 138.1 (C_{11a}), 137.7 (C_{9a}), 137.5 ($C_{1'}$), 137.1 (C_{4a}), 135.0 ($C_{3'}$), 131.9 (C_2), 131.3 (C_1), 130.6 (C_8), 130.1 (C_9), 129.7 (C_4), 128.9 (C_6), 126.9 (C_3), 126.2 (C_7), 32.6 (C_{11}), and 32.1 (C_{10}); HRMS calcd for $C_{25}H_{19}$ 319.1487, found 319.1458. Anal. calcd for $C_{25}H_{19}F_6P$: C, 64.66; H, 4.12%. Found: C, 64.50; H, 4.38%.

10,11-Dihydro-5-(3-methyl-1-azulenyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylium Hexafluorophosphate (6b·PF_6^-). The same procedure as for the preparation of **5b**·PF_6^- was followed using DDQ (303 mg, 1.33 mmol), **16b** (335 mg, 1.00 mmol), and 60% HPF_6 (10 mL) in CH_2Cl_2 (100 mL). Recrystallization from CH_2Cl_2/hexane gave **6b**·PF_6^- (479 mg, 100%). Yellow powder; mp 117.0–119.0 °C (CH_2Cl_2/hexane); MS (FAB) m/z 333 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1586, 1574, 1556, 1436, 1356, 842, 758, and 558 cm^{-1}; UV–vis (MeCN) λ_{max}, nm (log ε) 214 sh (4.52), 234 sh (4.36), 259 sh (4.12), 288 (4.13), 318 sh (3.93), 369 (4.03), and 460 (4.09); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.86 (d, $J = 9.9$ Hz, 1H, $H_{4'}$), 8.70 (dd, $J = 9.9$, 9.6 Hz, 1H, $H_{5'}$), 8.53 (dd, $J = 9.9$, 9.6 Hz, 1H, $H_{6'}$), 8.44 (d, $J = 9.7$ Hz, 1H, $H_{8'}$), 8.21 (dd, $J = 9.9$, 9.7 Hz, 1H, $H_{7'}$), 7.80 (s, 1H, $H_{2'}$), 7.49 (ddd, $J = 7.4$, 7.3, 1.1 Hz, 1H, H_2), 7.42 (d, $J = 7.3$ Hz, 1H, H_1), 7.41 (ddd, $J = 7.6$, 7.4, 1.7 Hz, 1H, H_8), 7.36 (dd, $J = 7.5$, 7.4 Hz, 1H, H_7), 7.34 (dd, $J = 7.5$, 1.7 Hz, 1H, H_6), 7.31 (d, $J = 7.6$ Hz, 1H, H_9), 7.27 (dd, $J = 7.6$, 7.4 Hz, 1H, H_3), 7.15 (dd, $J = 7.6$, 1.1 Hz, 1H, H_4), 3.50 (ddd, $J = 16.4$, 8.0, 4.3 Hz, 1H, H_{11}), 3.39 (ddd, $J = 15.8$, 9.1, 4.3 Hz, 1H, H_{10}), 3.08 (ddd, $J = 16.4$, 9.1, 4.4 Hz, 1H, H_{11}), 3.02 (ddd, $J = 15.8$, 8.0, 4.4 Hz, 1H, H_{10}), and 2.55 (s, 3H, 3′-Me); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1 (C_5), 163.9 ($C_{3'a}$), 155.3 ($C_{8'a}$), 147.4 ($C_{6'}$), 147.3 ($C_{5'}$), 144.4 ($C_{7'}$), 143.9 ($C_{3'}$), 143.7 ($C_{2'}$), 143.0 ($C_{8'}$), 140.9 ($C_{4'}$), 139.9 (C_{5a}), 138.0 (C_{11a}), 137.6 (C_{9a}), 137.2 (C_{4a}), 135.9 ($C_{1'}$), 131.6 (C_2), 131.1 (C_1), 130.2 (C_8), 130.0 (C_9), 129.9 (C_4), 128.7 (C_6), 126.8 (C_3), 126.2 (C_7), 32.6 (C_{11}), 32.0 (C_{10}), and 13.4 (3′-Me); HRMS calcd for $C_{26}H_{21}$ 333.1643, found 333.1604. Anal. calcd for $C_{26}H_{21}F_6P$: C, 65.27; H, 4.42%. Found: C, 64.96; H, 4.64%.

5-(3,6-Di-*t*-butyl-1-azulenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylium Hexafluorophosphate (6c·PF_6^-). The same procedure as for the preparation of **5b**·PF_6^- was followed using DDQ (301 mg, 1.33 mmol), **16c** (433 mg, 1.00 mmol), and 60% HPF_6 (10 mL) in CH_2Cl_2 (100 mL). Recrystallization from CH_2Cl_2/hexane gave **6c**·PF_6^- (577 mg, 100%). Yellow powder; mp 161.0–162.8 °C (CH_2Cl_2/hexane); MS (FAB) m/z 431 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 2976, 1590, 1570, 1438, 1334, 836, and 558 cm^{-1}; UV–vis (MeCN) λ_{max}, nm (log ε) 235 sh (4.39), 257 sh (4.20), 268 sh (4.16), 291 (4.11), 327 (4.04), 367 (4.08), and 455 (4.09); ^{1}H NMR (600 MHz, $CDCl_3$)

δ 9.25 (d, $J = 11.1$ Hz, 1H, $H_{4'}$), 8.94 (dd, $J = 11.1$, 2.2 Hz, 1H, $H_{5'}$), 8.40 (d, $J = 10.7$ Hz, 1H, $H_{8'}$), 8.20 (dd, $J = 10.7$, 2.2 Hz, 1H, $H_{7'}$), 7.64 (s, 1H, $H_{2'}$), 7.47 (ddd, $J = 7.6$, 7.6, 1.2 Hz, 1H, H_2), 7.39 (dd, $J = 7.6$, 0.8 Hz, 1H, H_1), 7.37 (ddd, $J = 7.5$, 7.4, 1.6 Hz, 1H, H_8), 7.31 (ddd, $J = 7.6$, 7.4, 1.0 Hz, 1H, H_7), 7.28 (dd, $J = 7.6$, 1.6 Hz, 1H, H_6 and dd, $J = 7.5$, 1.0 Hz, 1H, H_9), 7.25 (ddd, $J = 7.6$, 7.6, 0.8 Hz, 1H, H_3), 7.12 (dd, $J = 7.6$, 1.2 Hz, 1H, H_4), 3.48 (ddd, $J = 16.3$, 7.9, 4.5 Hz, 1H, H_{11}), 3.37 (ddd, $J = 15.7$, 9.0, 4.5 Hz, 1H, H_{10}), 3.04 (ddd, $J = 16.3$, 9.0, 4.5 Hz, 1H, H_{11}), 2.99 (ddd, $J = 15.7$, 7.9, 4.5 Hz, 1H, H_{10}), 1.48 (s, 9H, 3′-*t*-Bu), and 1.46 (s, 9H, 6′-*t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.6 ($C_{6'}$), 169.2 (C_5), 161.4 ($C_{3'a}$), 155.4 ($C_{3'}$), 154.9 ($C_{8'a}$), 145.3 ($C_{5'}$), 142.1 ($C_{8'}$), 141.4 ($C_{4'}$), 141.3 ($C_{7'}$), 140.1 ($C_{2'}$), 139.9 (C_{5a}), 137.9 (C_{11a}), 137.7 (C_{9a}), 137.4 (C_{4a}), 135.5 ($C_{1'}$), 131.5 (C_2), 131.2 (C_1), 130.1 (C_8 and C_9), 129.8 (C_4), 128.4 (C_6), 126.7 (C_3), 126.0 (C_7), 40.3 (s, 6′-*t*-Bu), 33.3 (s, 3′-*t*-Bu), 32.5 (C_{11}), 32.0 (C_{10}), 31.2 (q, 6′-*t*-Bu), and 29.5 (q, 3′-*t*-Bu); HRMS calcd for $C_{33}H_{35}$ 431.2739, found 431.2722. Anal. calcd for $C_{33}H_{35}F_6P \cdot 1/2H_2O$: C, 67.68; H, 6.20%. Found: C, 67.98; H, 6.23%.

5-(1-Azulenyl)-5*H*-dibenzo[*a*,*d*]cycloheptene (19a). A solution **8a** (642 mg, 5.01 mmol) and **18** (1.05 g, 5.04 mmol) in acetic acid (30 mL) was stirred at reflux temperature for 15 min. The reaction mixture was concentrated under reduced pressure and the residue was diluted with benzene. The organic solution was washed with 5% $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ to afford **19a** (636 mg, 40%) and **20** (590 mg, 46%).

19a: Blue plates; mp 193.2–195.0 °C (CH_2Cl_2/hexane); MS (70 eV) m/z 318 (M^+; 100) and 317 (56); IR (KBr disk) ν_{max} 1394, 794, and 768 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$) 228 (4.57), 240 sh (4.44), 283 (4.78), 287 sh (4.77), 333 sh (3.69), 340 sh (3.68), 350 (3.74), 366 (3.51), 551 sh (2.35), 575 sh (2.44), 598 (2.50), 620 sh (2.44), 648 (2.41), 683 sh (2.11), and 715 (1.95); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, $J = 9.3$ Hz, 1H, $H_{4'}$), 7.99 (d, $J = 9.8$ Hz, 1H, $H_{8'}$), 7.64 (d, $J = 7.6$ Hz, 2H, $H_{4,6}$), 7.41 (ddd, $J = 7.6$, 7.3, 1.7 Hz, 2H, $H_{3,7}$), 7.39 (dd, $J = 10.0$, 9.8 Hz, 1H, $H_{6'}$), 7.32 (dd, $J = 7.7$, 1.7 Hz, 2H, $H_{1,9}$), 7.27 (ddd, $J = 7.7$, 7.3, 1.3 Hz, 2H, $H_{2,8}$), 7.22 (d, $J = 3.9$ Hz, 1H, $H_{2'}$), 7.10 (d, $J = 3.9$ Hz, 1H, $H_{3'}$), 6.96 (dd, $J = 9.8$, 9.3 Hz, 1H, $H_{5'}$), 6.84 (dd, $J = 10.0$, 9.8 Hz, 1H, $H_{7'}$), 6.78 (s, 2H, $H_{10,11}$), and 5.97 (s, 1H, H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3 ($C_{4a,5a}$ and $C_{3'a}$), 138.5 ($C_{2'}$), 137.0 ($C_{6'}$), 136.2 ($C_{4'}$), 135.4 ($C_{8'a}$), 135.0 ($C_{9a,11a}$), 134.5 ($C_{8'}$), 131.1 ($C_{10,11}$), 129.7 ($C_{1,9}$), 129.4 ($C_{4,6}$), 128.7 ($C_{3,7}$), 128.3 ($C_{1'}$), 126.4 ($C_{2,8}$), 122.3 ($C_{5'}$), 121.6 ($C_{7'}$), 115.7 ($C_{3'}$), and 53.3 (C_5); HRMS calcd for $C_{25}H_{18}$ 318.1409, found 318.1413. Anal. calcd for $C_{25}H_{18}$: C, 94.30; H, 5.70%. Found: C, 94.40; H, 5.87%.

20: Green needles; mp 117.2–120.0 °C (CH_2Cl_2/hexane); MS (70 eV) m/z 508 (M^+; 100), 317 (37), 315 (22), and 191 (21); IR (KBr disk) ν_{max} 794, 776, and 722 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$) 228 (4.72), 288 (4.76), 343 sh (3.66), 352 sh (3.67), 361 (3.73), 379 (3.64), 568 sh (2.31), 617 (2.43), 671 sh (2.33), and 741 sh (1.89); ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.87 (d, $J = 9.5$ Hz, 2H, $H_{4,8}$), 7.49 (d, $J = 7.6$ Hz, 4H, $H_{4',6'}$), 7.30 (ddd, $J = 7.6$, 6.8, 1.8 Hz, 4H, $H_{3',7'}$), 7.23 (dd, $J = 7.7$, 1.8 Hz, 4H, $H_{1',9'}$), 7.20 (t, $J = 10.0$ Hz, 1H, H_6), 7.19 (ddd, $J = 7.7$, 6.8, 1.2 Hz, 4H, $H_{2',8'}$), 6.68 (s, 1H, H_2), 6.67 (dd, $J = 10.0$, 9.5 Hz, 2H, $H_{5,7}$), 6.63 (s, 4H, $H_{10',11'}$), and 5.77 (s, 2H, $H_{5'}$); ^{13}C NMR (100 MHz, $CDCl_3$, 50 °C) δ 141.3 (C_2 and $C_{4'a,5'a}$), 136.5 (C_6), 136.4 ($C_{3a,8a}$), 135.1 ($C_{9'a,11'a}$), 133.6 ($C_{4,8}$), 131.2 ($C_{10',11'}$), 129.5 ($C_{1',9'}$), 129.3 ($C_{4',6'}$), 128.5 ($C_{3',7'}$), 126.3 ($C_{2',8'}$), 125.7 ($C_{1,3}$), 121.1 ($C_{5,7}$), and 52.6 ($C_{5'}$); HRMS calcd for $C_{40}H_{28}$ 508.2191, found 508.2191. Anal. calcd for $C_{40}H_{28}$: C, 94.45; H, 5.55%. Found: C, 94.72; H, 5.71%.

5-(3-Methyl-1-azulenyl)-5*H*-dibenzo[*a*,*d*]cycloheptene (19b). The same procedure as for the preparation of **19a** was adopted here. The reaction of **8b** (714 mg, 5.02 mmol) with **18** (1.06 g, 5.09 mmol) in acetic acid (30 mL) at room temperature for 6 h, followed by column chromatography on silica gel with CH_2Cl_2, afforded **19b** (1.45 g, 87%). Blue needles; mp 178.0–179.5 °C (CH_2Cl_2/hexane); MS (70 eV) m/z 332 (M^+; 100), 317 (39), and 315 (24); IR (KBr disk) ν_{max} 802, 778, 744, and 724 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$) 230 sh (4.53), 240 sh (4.41), 286 (4.75), 342 sh (3.60), 348 sh (3.62), 375 (3.64), 576 sh (2.36), 601 sh (2.44), 626 (2.50), 657 sh (2.43), 682 (2.41), 726 sh (2.06), and 759 sh (1.93); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.02 (d, $J = 9.6$ Hz, 1H, $H_{4'}$), 7.96 (d, $J = 9.7$ Hz, 1H, $H_{8'}$), 7.64 (dd, $J = 7.6$, 1.3 Hz, 2H, $H_{4,6}$), 7.43 (ddd, $J = 7.6$, 7.3, 1.5 Hz, 2H, $H_{3,7}$), 7.35 (dd, $J = 7.7$, 1.5 Hz, 2H, $H_{1,9}$ and dd, $J = 9.9$, 9.8 Hz, 1H, $H_{6'}$), 7.30 (ddd, $J = 7.7$, 7.3, 1.3 Hz, 2H, $H_{2,8}$), 7.08 (s, 1H, $H_{2'}$), 6.89 (dd, $J = 9.8$, 9.6 Hz, 1H, $H_{5'}$), 6.82 (s, 2H, $H_{10,11}$), 6.76 (dd, $J = 9.9$, 9.7 Hz, 1H, $H_{7'}$), 5.97 (s, 1H, H_5), and 2.46 (s, 3H, 3′-Me); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 142.1 ($C_{4a,5a}$), 140.4 ($C_{2'}$), 137.8 ($C_{3'a}$ and $C_{6'}$), 136.1 ($C_{8'a}$), 135.7 ($C_{9a,11a}$), 134.5 ($C_{8'}$), 133.9 ($C_{4'}$), 131.9 ($C_{10,11}$), 130.5 ($C_{1,9}$), 130.2 ($C_{4,6}$), 129.5 ($C_{3,7}$), 127.4 ($C_{1'}$), 127.2 ($C_{2,8}$), 124.4 ($C_{3'}$), 121.4 ($C_{5'}$ and $C_{7'}$), 53.7 (C_5), and 13.0 (3′-Me); HRMS calcd for $C_{26}H_{20}$ 332.1566, found 332.1564. Anal. calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06%. Found: C, 93.88; H, 6.23%.

5-(3,6-Di-*t*-butyl-1-azulenyl)-5*H*-dibenzo[*a*,*d*]cycloheptene (19c). The same procedure as for the preparation of **19a** was adopted here. The reaction of **8c** (516 mg, 2.15 mmol) with **18** (457 mg, 2.19 mmol) in acetic acid (12 mL) at room temperature for 6 h, followed by column chromatography on silica gel with CH_2Cl_2, afforded **19c** (763 mg, 83%). Blue needles; mp 132.8–134.0 °C (CH_2Cl_2/hexane); MS (70 eV) m/z 430 (M^+; 100), 416 (28), 415 (78), and 373 (25); IR (KBr disk) ν_{max} 2972, 1576, and 800 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm ($\log \varepsilon$) 230 sh (4.53), 242 sh (4.38), 293 (4.79), 300 sh (4.74), 342 sh (3.67), 350 sh (3.70), 359 (3.78), 377 (3.61), 557 sh (2.36), 608 (2.50), 662 sh (2.41), and 740 sh (1.92); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, $J = 10.5$ Hz, 1H, $H_{4'}$), 7.99 (d, $J = 10.8$ Hz, 1H, $H_{8'}$), 7.61 (d, $J = 7.6$ Hz, 2H, $H_{4,6}$), 7.38 (ddd, $J = 7.6$, 7.3, 1.5 Hz, 2H, $H_{3,7}$), 7.32 (dd, $J = 7.8$, 1.5 Hz, 2H, $H_{1,9}$), 7.24 (ddd, $J = 7.8$, 7.3, 1.2 Hz, 2H, $H_{2,8}$), 7.14 (s, 1H, $H_{2'}$), 7.06 (dd, $J = 10.5$, 1.8 Hz, 1H, $H_{5'}$), 6.94 (dd, $J = 10.8$, 1.8 Hz, 1H, $H_{7'}$), 6.82 (s, 2H, $H_{10,11}$), 5.91 (s, 1H, H_5), 1.43 (s, 9H, 3′-*t*-Bu), and 1.36 (s, 9H, 6′-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1 ($C_{6'}$), 141.5 ($C_{4a,5a}$), 136.9 ($C_{2'}$), 136.3 ($C_{3'}$), 135.1 ($C_{9a,11a}$), 135.0 ($C_{8'a}$), 134.2 ($C_{3'a}$), 133.9 ($C_{4'}$), 132.9 ($C_{8'}$), 131.2 ($C_{10,11}$), 129.6 ($C_{1,9}$), 129.4 ($C_{4,6}$), 128.6 ($C_{3,7}$), 126.2 ($C_{2,8}$), 125.2 ($C_{1'}$), 118.9 ($C_{7'}$), 118.3 ($C_{5'}$), 52.8 (C_5), 38.0 (s, 6′-*t*-Bu), 33.0 (s, 3′-*t*-Bu), 32.1 (q, 3′-*t*-Bu), and 31.8 (q, 6′-*t*-Bu); HRMS calcd for $C_{33}H_{34}$ 430.2661, found 430.2664. Anal. calcd for $C_{33}H_{34}$: C, 92.04; H, 7.96%. Found: C, 91.99; H, 8.14%.

5-(1-Azulenyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylium Hexafluorophosphate (7a·PF_6^-). The same procedure as for the preparation of **5b**·PF_6^- was followed using DDQ (304 mg, 1.34 mmol), **19a** (319 mg, 1.00 mmol), and 60% HPF_6 (10 mL) in CH_2Cl_2 (100 mL). Recrystallization from CH_2Cl_2/hexane gave **7a**·PF_6^- (463 mg, 100%). Red powder; mp 177.2–179.5 °C (CH_2Cl_2/hexane); MS (FAB) m/z 317 ($M^+ - PF_6$); IR (KBr disk)

ν_{max} 1584, 1568, 1432, 1372, 840, 806, and 558 cm^{-1}; UV–vis (MeCN) λ_{max}, nm ($\log \varepsilon$) 223 (4.56), 233 sh (4.51), 286 (4.38), 351 (4.07), 414 sh (3.94), and 500 sh (3.77); ^{1}H NMR (400 MHz, $(CDCl_2)_2$, 80 °C) δ 8.83 (dd, $J = 9.8$, 1.2 Hz, 1H, $H_{4'}$), 8.64 (ddd, $J = 9.8$, 9.6, 1.0 Hz, 1H, $H_{5'}$), 8.45 (dddd, $J = 9.8$, 9.6, 1.2, 1.1 Hz, 1H, $H_{6'}$), 8.09 (ddd, $J = 10.0$, 9.8, 1.0 Hz, 1H, $H_{7'}$), 7.93 (d, $J = 5.5$ Hz, 1H, $H_{2'}$), 7.79 (d, $J = 10.0$ Hz, 1H, $H_{8'}$), 7.65 (d, $J = 5.5$ Hz, 1H, $H_{3'}$), 7.64–7.54 (m, 6H, $H_{1,2,3,7,8,9}$), 7.46 (d, $J = 7.3$ Hz, 2H, $H_{4,6}$), and 7.14 (s, 2H, $H_{10,11}$); ^{13}C NMR (100 MHz, $(CDCl_2)_2$, 80 °C) δ 168.3 (C_5), 164.7 ($C_{3'a}$), 154.4 ($C_{8'a}$), 147.7 ($C_{6'}$), 147.3 ($C_{5'}$), 146.5 ($C_{2'}$), 143.8 ($C_{4'}$, $C_{7'}$, or $C_{8'}$), 143.7 (2C, $C_{4'}$, $C_{7'}$, or $C_{8'}$), 138.3 ($C_{1'}$), 135.6 ($C_{3'}$), 134.7 ($C_{4a,5a}$ or $C_{9a,11a}$), 133.8 ($C_{4a,5a}$ or $C_{9a,11a}$), 131.3 ($C_{10,11}$), 130.9 ($C_{1,9}$, $C_{2,8}$, or $C_{3,7}$), 129.4 ($C_{1,9}$, $C_{2,8}$, or $C_{3,7}$), 129.3 ($C_{1,9}$, $C_{2,8}$, or $C_{3,7}$), and 128.6 ($C_{4,6}$); HRMS calcd for $C_{25}H_{17}$ 317.1305, found 317.1330. Anal. calcd for $C_{25}H_{17}F_6P \cdot 1/3H_2O$: C, 64.11; H, 3.80%. Found: C, 64.06; H, 4.03%.

5-(3-Methyl-1-azulenyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylium Hexafluorophosphate (7b·PF_6^-). The same procedure as for the preparation of **5b**·PF_6^- was followed using DDQ (304 mg, 1.34 mmol), **19b** (333 mg, 1.00 mmol), and 60% HPF_6 (10 mL) in CH_2Cl_2 (100 mL). Recrystallization from CH_2Cl_2/hexane gave **7b**·PF_6^- (477 mg, 100%). Red powder; mp 129.0–132.0 °C (CH_2Cl_2/hexane); MS (FAB) m/z 331 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1578, 1436, 1354, 840, 806, and 558 cm^{-1}; UV–vis (MeCN) λ_{max}, nm ($\log \varepsilon$) 222 sh (4.55), 234 sh (4.52), 256 sh (4.30), 287 (4.32), 354 (4.07), 457 (3.85), and 497 sh (3.83); ^{1}H NMR (400 MHz, $(CDCl_2)_2$, 80 °C) δ 8.70 (d, $J = 9.8$ Hz, 1H, $H_{4'}$), 8.61 (dd, $J = 9.8$, 9.3 Hz, 1H, $H_{5'}$), 8.45 (dd, $J = 9.8$, 9.3 Hz, 1H, $H_{6'}$), 8.07 (dd, $J = 10.3$, 9.8 Hz, 1H, $H_{7'}$), 7.72 (d, $J = 10.3$ Hz, 1H, $H_{8'}$), 7.69 (s, 1H, $H_{2'}$), 7.60–7.53 (m, 6H, $H_{1,2,3,7,8,9}$), 7.42 (d, $J = 7.3$ Hz, 2H, $H_{4,6}$), 7.14 (s, 2H, $H_{10,11}$), and 2.48 (s, 3H, 3′-Me); ^{13}C NMR (100 MHz, $(CDCl_2)_2$, 80 °C) δ 165.0 (C_5), 163.9 ($C_{3'a}$), 155.6 ($C_{8'a}$), 147.2 ($C_{5'}$ and $C_{6'}$), 144.7 ($C_{3'}$), 144.2 ($C_{2'}$), 144.0 ($C_{7'}$), 142.9 ($C_{8'}$), 140.6 ($C_{4'}$), 136.7 ($C_{1'}$), 135.0 ($C_{4a,5a}$ or $C_{9a,11a}$), 133.9 ($C_{4a,5a}$ or $C_{9a,11a}$), 131.3 ($C_{10,11}$), 130.6 ($C_{1,9}$, $C_{2,8}$, or $C_{3,7}$), 129.3 (2C, $C_{1,9}$, $C_{2,8}$, or $C_{3,7}$), 128.6 ($C_{4,6}$), and 13.5 (3′-Me); HRMS calcd for $C_{26}H_{19}$ 331.1486, found 331.1469. Anal. calcd for $C_{26}H_{19}F_6P$: C, 65.55; H, 4.02%. Found: C, 65.73; H, 4.19%.

5-(3,6-Di-*t*-butyl-1-azulenyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylium Hexafluorophosphate (7c·PF_6^-). The same procedure as for the preparation of **5b**·PF_6^- was followed using DDQ (344 mg, 1.52 mmol), **19c** (431 mg, 1.00 mmol), and 60% HPF_6 (10 mL) in CH_2Cl_2 (100 mL). Recrystallization from CH_2Cl_2/hexane gave **7c**·PF_6^- (575 mg, 100%). Orange powder; mp 218.2–220.5 °C (CH_2Cl_2/hexane); MS (FAB) m/z 429 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1576, 1440, 1334, 1176, 838, 804, and 558 cm^{-1}; UV–vis (MeCN) λ_{max}, nm ($\log \varepsilon$) 222 (4.63), 235 sh (4.60), 272 (4.38), 283 (4.39), 351 (4.19), 463 (3.91), and 493 sh (3.88); ^{1}H NMR (400 MHz, $(CDCl_2)_2$, 100 °C) δ 9.08 (d, $J = 11.0$ Hz, 1H, $H_{4'}$), 8.76 (dd, $J = 11.0$, 2.2 Hz, 1H, $H_{5'}$), 8.07 (dd, $J = 10.8$, 2.2 Hz, 1H, $H_{7'}$), 7.76 (d, $J = 10.8$ Hz, 1H, $H_{8'}$), 7.62–7.53 (m, 6H, $H_{1,2,3,7,8,9}$), 7.61 (s, 1H, $H_{2'}$), 7.45 (d, $J = 7.3$ Hz, 2H, $H_{4,6}$), 7.15 (s, 2H, $H_{10,11}$), 1.48 (s, 9H, 3′-*t*-Bu), and 1.47 (s, 9H, 6′-*t*-Bu); ^{13}C NMR (100 MHz, $(CDCl_2)_2$, 100 °C) δ 175.2 ($C_{6'}$), 163.9 (C_5), 161.6 ($C_{3'a}$), 156.5 ($C_{3'}$), 155.3 ($C_{8'a}$), 144.8 ($C_{5'}$), 142.0 ($C_{8'}$), 141.2 ($C_{4'}$), 140.9 ($C_{7'}$), 140.5 ($C_{2'}$), 136.4 ($C_{1'}$), 135.2 ($C_{4a,5a}$ or $C_{9a,11a}$), 133.9 ($C_{4a,5a}$ or $C_{9a,11a}$), 131.3 ($C_{10,11}$), 130.4 ($C_{1,9}$, $C_{2,8}$, or $C_{3,7}$), 129.2 ($C_{1,9}$, $C_{2,8}$, or $C_{3,7}$), 129.1 ($C_{1,9}$, $C_{2,8}$, or $C_{3,7}$), 128.6 ($C_{4,6}$), 40.5 (s, 6′-*t*-Bu), 33.6 (s, 3′-*t*-Bu), 31.5 (q, 6′-*t*-Bu), and 29.9 (q, 3′-*t*-Bu); HRMS calcd for $C_{33}H_{33}$ 429.2583, found 429.2569. Anal. calcd for $C_{33}H_{33}F_6P \cdot 2/3H_2O$: C, 67.57; H, 5.90%. Found: C, 67.40; H, 5.85%.

(3-Methyl-1-azulenyl)diphenylmethylium Hexafluorophosphate (3b·PF_6^-). The same procedure as for the preparation of **4c**·PF_6^- was followed using DDQ (275 mg, 1.21 mmol), (3-methyl-1-azulenyl)diphenylmethane (**21**) (315 mg, 1.02 mmol), and 60% HPF_6 (10 mL) in CH_2Cl_2 (100 mL). Recrystallization from CH_2Cl_2/Et_2O gave **3b**·PF_6^- (419 mg, 91%). Red powder; mp 188.8–190.4 °C (CH_2Cl_2/ether); MS (FAB) m/z 307 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1522, 1434, 1360, 1072, 836, 756, 704, and 558 cm^{-1}; UV–vis (MeCN) λ_{max}, nm ($\log \varepsilon$) 222 (4.41), 237 sh (4.32), 262 (4.24), 313 (4.08), 326 sh (4.00), 367 sh (3.99), 397 (4.07), and 495 (4.21); ^{1}H NMR (400 MHz, CD_3CN) δ 8.88 (dd, $J = 9.9$, 1.3 Hz, 1H, H_4), 8.55 (ddd, $J = 9.9$, 9.4, 1.2 Hz, 1H, H_5), 8.47 (dddd, $J = 9.7$, 9.4, 1.3, 1.3 Hz, 1H, H_6), 8.18 (dd, $J = 9.9$, 1.3 Hz, 1H, H_8), 8.10 (ddd, $J = 9.9$, 9.7, 1.2 Hz, 1H, H_7), 7.80 (s, 1H, H_2 and tt, $J = 7.5$, 1.2 Hz, 1H, $H_{4'}$ or $H_{4''}$), 7.74 (tt, $J = 7.5$, 1.2 Hz, 1H, $H_{4'}$ or $H_{4''}$), 7.61 (dd, $J = 8.3$, 7.5 Hz, 2H, $H_{3',5'}$ or $H_{3'',5''}$), 7.59 (dd, $J = 8.3$, 7.5 Hz, 2H, $H_{3',5'}$ or $H_{3'',5''}$), 7.42 (dd, $J = 8.3$, 1.2 Hz, 2H, $H_{2',6'}$ or $H_{2'',6''}$), 7.35 (dd, $J = 8.3$, 1.2 Hz, 2H, $H_{2',6'}$ or $H_{2'',6''}$), and 2.57 (s, 3H, 3-Me); ^{13}C NMR (100 MHz, CD_3CN) δ 170.1 (C^+), 162.4 (C_{3a}), 156.4 (C_{8a}), 147.7 (C_6), 147.2 (C_2), 145.1 (C_5), 143.7 (C_3 and C_8), 143.1 (C_7), 141.9 ($C_{1'}$ or $C_{1''}$), 141.6 (C_4), 140.8 ($C_{1'}$ or $C_{1''}$), 138.4 (C_1), 136.0 ($C_{2',6'}$ or $C_{2'',6''}$), 135.0 ($C_{2',6'}$ or $C_{2'',6''}$), 134.5 ($C_{4'}$ or $C_{4''}$), 134.0 ($C_{4'}$ or $C_{4''}$), 130.2 ($C_{3',5'}$ or $C_{3'',5''}$), 129.8 ($C_{3',5'}$ or $C_{3'',5''}$), and 13.3 (3-Me); HRMS calcd for $C_{24}H_{19}$ 307.1487, found 307.1423. Anal. calcd for $C_{24}H_{19}F_6P$: C, 63.72; H, 4.23%. Found: C, 63.75; H, 4.53%.

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Supporting Information

Kinetic data of the dynamic processes and rate constants of site-exchanges of the reported carbocations. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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