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Synthesis and Properties of Extremely Stable Tris(6-methoxy-1-azulenyl)-methyl Cation and a Series of Di(1-azulenyl)phenylmethyl and (1-Azulenyl)diphenylmethyl Cations Stabilized by Methoxy Substituents[1)]

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Extremely stable carbocations, tris(6-methoxy-1-azulenyl)methyl (**8**), bis(6-methoxy-1-azulenyl)(4-methoxyphenyl)-methyl (**9a**), and (6-methoxy-1-azulenyl)bis(4-methoxyphenyl)methyl (**10a**) cations and a series of di(1-azulenyl)phenyl-methyl and (1-azulenyl)diphenylmethyl cations having methoxy substituents on each phenyl group, i.e., di(1-azulenyl)(4-methoxyphenyl)methyl (**9b**) and (1-azulenyl)bis(4-methoxyphenyl)methyl (**10b**) cations and 3-methyl-1-azulenyl (**9c** and **10c**) and 3,6-di-*t*-butyl-1-azulenyl (**9d** and **10d**) analogues, were synthesized by hydride abstraction from the corresponding methane derivatives and their properties were fully characterized. The pK_{R^+} values of **8** and **9a** were well beyond 14.0. The value of **10a** was determined as 13.2, which is higher by 10.2 pK units than that of (1-azulenyl)diphenylmethyl cation. The value also considerably increased by the methoxy substitution on each phenyl group. The values of **9b—d** (pK_{R^+} 11.7—13.4) and **10b—d** (pK_{R^+} 5.2—7.0) are higher by 1.0—1.4 and 2.2—2.4 pK units than those of the corresponding analogous benzyl and diphenylmethyl cations. The electrochemical reduction of **8**, **9a—d**, and **10a—d** showed a wave at −0.88, −0.71——0.83, and −0.56——0.71 V (V vs. Ag/Ag$^+$), respectively, upon cyclic voltammetry (CV). The relatively high reduction potentials also exhibited the stabilization of the methyl cations by the methoxy substituents. The oxidation of **8** in acetonitrile exhibited barely separated two-step, one-electron oxidation waves at a potential range of +0.90—+0.98 V upon CV, although **9a—d** and **10a—d** did not show two similar waves at a narrow potential range. The wave is ascribed to the oxidation of two azulene rings to generate a trication species.

We have recently reported the synthesis of a series of azulene analogues of triphenylmethyl cation (**1**), i.e., tri-(1-azulenyl)methyl (**2a**), di(1-azulenyl)phenylmethyl (**3a**), and (1-azulenyl)diphenylmethyl (**4a**) hexafluorophosphates (Chart 1).[2,3)] These cations (**2a—4a**) showed extreme stabilities with extraordinary high pK_{R^+} values (**2a**; 11.3, **3a**; 10.5, and **4a**; 3.0). The high stabilities of these cations can be explained by the large π-conjugative effect of 1-azulenyl groups with cationic carbon (e.g., **2′**). Although the methyl substituent on their azulene rings slightly stabilized these cations by its inductive electronic effect, *t*-butyl substituents on their azulene rings effectively stabilized these cations by their steric and also by their inductive electronic effects induced by the contribution of C–C hyperconjugation with the π systems.[2—4)] The pK_{R^+} value (14.3) of **2c** was the highest value ever reported for a methyl cation substituted with only hydrocarbon groups, and was 3.0 pK units higher than that of **2a** and 20.7 pK units higher than that of **1** (pK_{R^+} −6.4).[5)]

In our continuing efforts to prepare extremely stable carbocations, we have investigated the effect of the introduction of an electron-donating group into each phenyl ring of cations **3a—c** and **4a—c**, e.g., di(1-azulenyl)[4-(dimethylamino)-phenyl]methyl (**5a**) and (1-azulenyl)bis[4-(dimethylamino)-phenyl]methyl (**6a**) hexafluorophosphates and their 3-methyl-1-azulenyl and 3,6-di-*t*-butyl-1-azulenyl derivatives (**5b**, **c** and **6b**, **c**) (Chart 2).[6)] As expected, the stabilities of **3a—c** and **4a—c** were considerably increased by the introduction of the dimethylamino substituents on each phenyl ring. For further stabilization of these cations, introduction of an electron-donating group into both azulenyl and phenyl rings would be required. Although the ability of the methoxy substituent

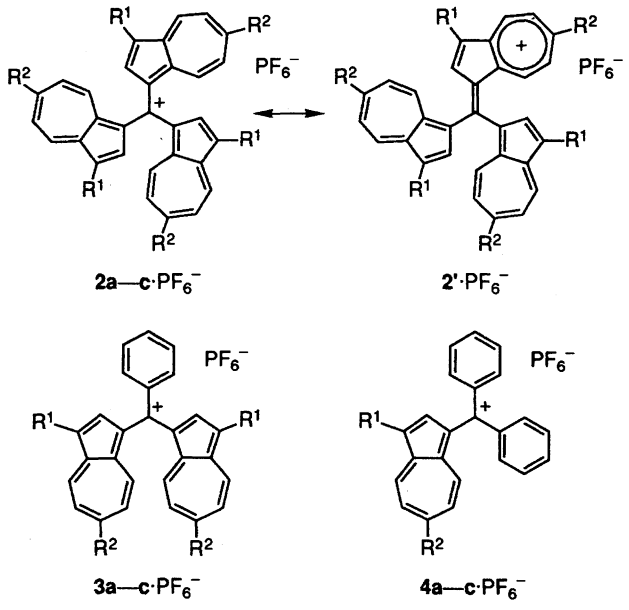
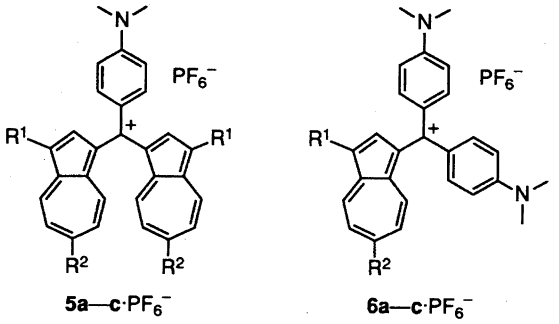


Chart 1.



5a—c·PF_6^- **6a—c**·PF_6^-

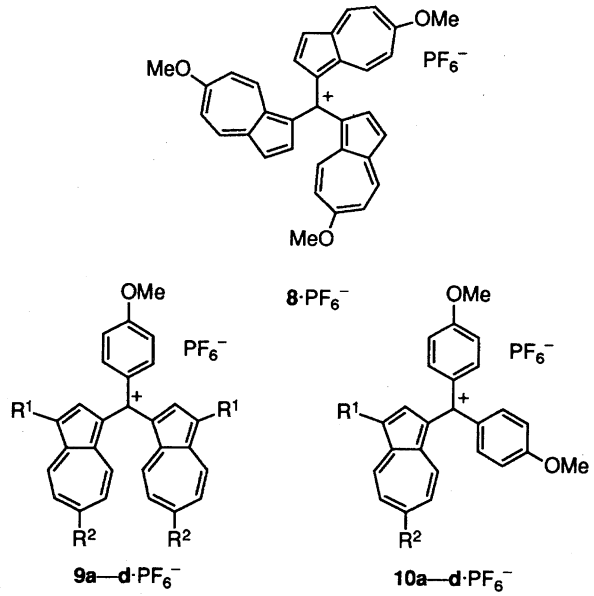
a:R^1=R^2=H, **b**:R^1=Me, R^2=H, **c**:R^1=R^2=*t*-Bu

Chart 2.

to stabilize the methyl cations is a little bit lower than that of dimethylamino group, the substituent on both azulenyl and phenyl rings should stabilize these cations effectively. This is because the three methoxy substituents on tri(4-methoxyphenyl)methyl cation (**7**) (pK_{R^+} +0.82)[5] stabilized the parent triphenylmethyl cation (**1**) by over 7.2 p*K* units. In the present paper we will report the synthesis and properties of tris(6-methoxy-1-azulenyl)methyl (**8**), bis(6-methoxy-1-azulenyl)(4-methoxyphenyl)methyl (**9a**), and (6-methoxy-1-azulenyl)bis(4-methoxyphenyl)methyl (**10a**) hexafluorophosphates, particularly, their high stabilities; a series of **3a—c**·PF_6^- and **4a—c**·PF_6^- having methoxy substituents on each phenyl group (**9b—d**·PF_6^- and **10b—d**·PF_6^-) are studied for comparison with 4-(dimethylamino)phenyl derivatives (**5a—c**·PF_6^- and **6a—c**·PF_6^-) (Chart 3).

Results and Discussion

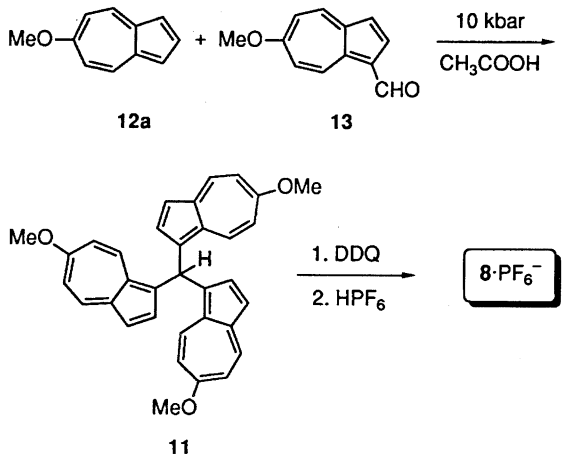
Synthesis. Synthesis of the cation **8** was accomplished by hydride abstraction from the corresponding methane derivative (**11**) (Scheme 1). The reaction of two molar amounts of 6-methoxyazulene (**12a**)[7] with 6-methoxy-



9a—d·PF_6^- **8**·PF_6^- **10a—d**·PF_6^-

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

Chart 3.

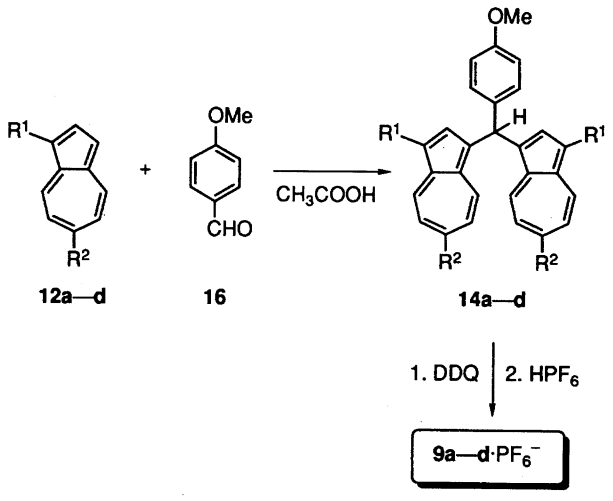


12a **13** **11**

Scheme 1.

1-azulenecarbaldehyde (**13**)[8] in acetic acid at room temperature, which were under similar conditions to those for the formation of tri(1-azulenyl)methane,[2,3] the precursor of **2a**·PF_6^-, did not afford satisfactory results because of the low reactivities of **12a** with the aldehyde **13** and instabilities of the product **11** under the reaction conditions. However, we found that the high-pressure reaction (10 kbar) of **12a** with **13** in a 50% acetic acid solution of dichloromethane at 30 °C for 2 d, afforded the desired **11** in 6.1% yield. Hydride abstraction reaction of **11** with DDQ in dichloromethane at room temperature proceeded under conditions similar to those employed for the formation of **2a**.[2—4] Addition of a 60% aqueous HPF_6 solution to the reaction mixture yielded **8** as a PF_6^- salt in 91% yield.

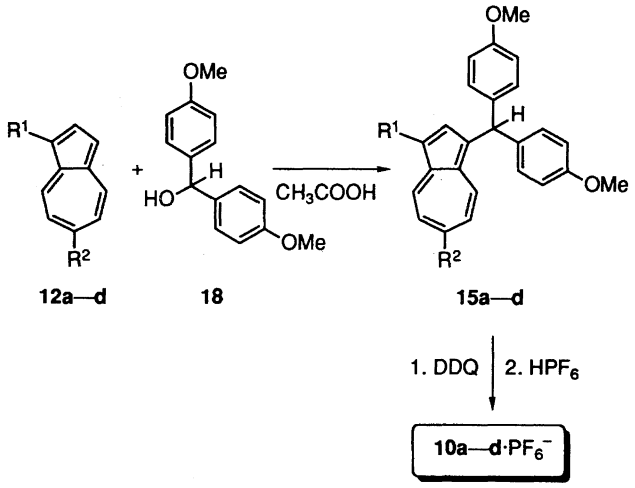
Similarly, **9a—d** and **10a—d** were synthesized by the hydride abstraction from the corresponding methane derivatives (**14a—d** and **15a—d**) (Schemes 2 and 3). The high-pressure (10 kbar) reaction was also required for the synthesis of bis(6-methoxy-1-azulenyl)(4-methoxyphenyl)methane (**14a**). The high-pressure reaction of two molar amounts of **12a** with 4-methoxybenzaldehyde (**16**) in a 50% acetic acid



12a—d **16** **14a—d** **9a—d**·PF_6^-

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

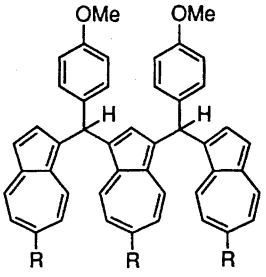
Scheme 2.



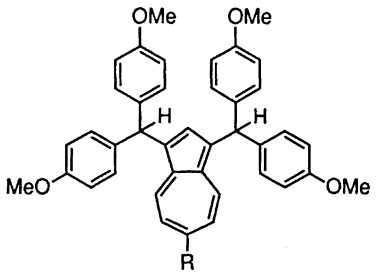
a: R^1=H, R^2=OMe, **b**: R^1=R^2=H, **c**: R^1=Me, R^2=H, **d**: R^1=R^2=*t*-Bu

Scheme 3.

solution of dichloromethane at 30 °C for 1 d afforded the desired **14a** in 13% yield, together with 1,3-bis[(6-methoxy-1-azulenyl)(4-methoxyphenyl)methyl]azulene (**17a**) in 7.5% yield. The reactions of azulene (**12b**), its 1-methyl (**12c**), and 1,6-di-*t*-butyl derivatives (**12d**)[3,4] with **16** proceeded in atmospheric pressure in acetic acid at room temperature to afford **14b—d** in 11—82% yields, together with 1,3-bis[(1-azulenyl)(4-methoxyphenyl)methyl]azulene (**17b**) in 7.6% yield, in the case of **12b** (Chart 4). Hydride abstraction of **14a—d** with DDQ in dichloromethane at room temperature, followed by addition of a 60% aqueous HPF_6 solution, afforded **9a—d**·PF_6^- in 46—94% yields.



17a: R=OMe
17b: R=H



19a: R=OMe
19b: R=H

Chart 4.

The reaction of azulenes **12a—d** with bis(4-methoxyphenyl)methanol (**18**) in acetic acid at room temperature for 21 h afforded desired **15a—d** in 53—94% yields, respectively, together with 1,3-bis[bis(4-methoxyphenyl)methyl]-6-methoxyazulene (**19a**) and 1,3-bis[bis(4-methoxyphenyl)-methyl]azulene (**19b**) in 52 and 54% yields, respectively, in the case of **12a** and **12b**. Hydride abstraction of **15a—d** with DDQ in dichloromethane at room temperature, followed by the addition of a 60% aqueous HPF_6 solution, yielded **10a—d**·PF_6^- in 84—93% yields.

Spectroscopic Properties. Mass spectra of **8**·PF_6^-, **9a—d**·PF_6^-, and **10a—d**·PF_6^- ionized by FAB showed the correct $M^+ - PF_6$ ion peaks, which were indicative of the cationic structure of these compounds. The characteristic bands of hexafluorophosphate were observed at 837—841 (strong) and 558 (medium) cm^{-1} in the IR spectra of **8**·PF_6^-, **9a—d**·PF_6^-, and **10a—d**·PF_6^-, which also supported the cationic structure of these compounds. These hexafluorophosphates **8**·PF_6^-, **9a—d**·PF_6^-, and **10a—d**·PF_6^- also showed strong absorption in the visible region in analogy with the hexafluorophosphates **2a—c**·PF_6^-, **3a—c**·PF_6^-, **4a—c**·PF_6^-, and so on. The absorption maxima (nm) and the coefficients (log ϵ) of these hexafluorophosphates in visible region are summarized in Table 1. UV-vis spectra of **8** and **2a** in acetonitrile along with those of related 4-methoxyphenyl analogs (**9a**, **9b**, **3a**, **10a**, **10b**, and **4a**) are shown in Figs. 1, 2, and 3. The absorption maxima of these hexafluorophosphates were not strongly influenced by the methoxy substituents on azulenyl groups. The maxima of cations **8**, **9a**, and **10a** were almost the same as those of **2a**, **9b**, and **10b**. The substituents on phenyl groups affected the absorption maxima in a striking manner. There was a difference between the directionality of the shifts of **9b—d** and those of **10b—d**. Cations **9b—d** exhibited a hypsochromic shift by 13 nm, compared with cations **3a—c**. Cations **10b—d** showed an appreciable bathochromic shift by 57, 49, and 60 nm, respectively, compared with cations **4a—c**. As expected, the shifts caused by the methoxy substituents was

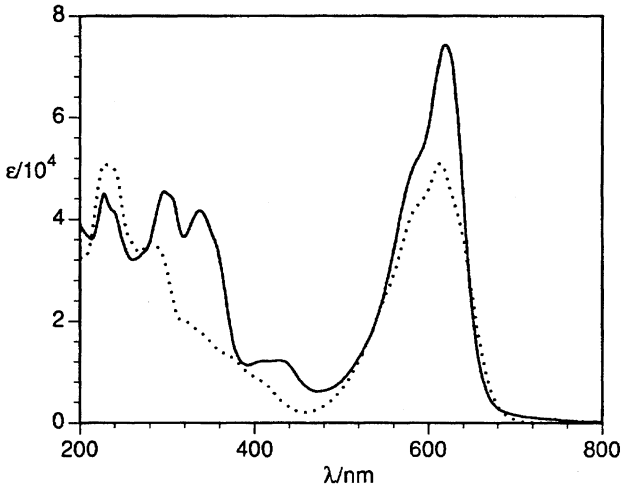


Fig. 1. UV-vis spectra of cations **8** (solid line) and **2a** (dotted line) in acetonitrile.

Table 1. The Longest Wavelength Absorption and Their Coefficients of **8**, **9a—d**, and **10a—d** and Those of **2a—c**, **3a—c**, and **4a—c** for Comparison[3)]

Sample	λ_{max}, nm (log ϵ)	Sample	λ_{max}, nm (log ϵ)	Sample	λ_{max}, nm (log ϵ)
8	620 (4.87)	**9a**	624 (4.83)	**10a**	535 (4.34)
2a	614 (4.70)	**9b**	626 (4.52)	**10b**	544 (4.56)
2b	652 (4.57)	**9c**	663 (4.52)	**10c**	544 (4.41)
2c	650 (4.62)	**9d**	668 (4.64)	**10d**	549 (4.50)
		3a	639 (4.57)	**4a**	487 (4.16)
		3b	676 (4.53)	**4b**	495 (4.21)
		3c	681 (4.61)	**4c**	489 (4.11)

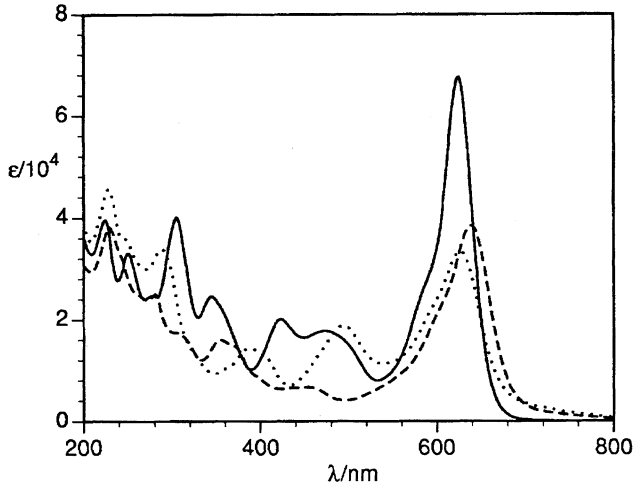


Fig. 2. UV-vis spectra of cations **9a** (solid line), **9b** (dotted line), and **3a** (broken line) in acetonitrile.

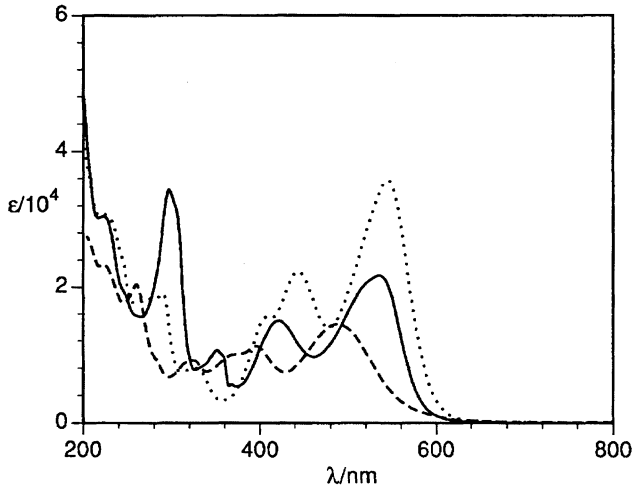


Fig. 3. UV-vis spectra of cations **10a** (solid line), **10b** (dotted line), and **4a** (broken line) in acetonitrile.

much less than those by the dimethylamino substituents.[6)] These results are in agreement with those among substituted triphenylmethyl cations.[9)]

The ^{1}H NMR chemical shifts of the methine protons of **11**, **14a**, and **15a** were slightly upfield compared with those of tri(1-azulenyl)methane and their related phenyl derivatives.[3)] Those of **14b—d** and **15b—d** also showed similar slight upfield shift in the methine protons, compared with those of the corresponding analogous phenyl derivatives. These signals disappeared on the ^{1}H NMR spectra of cations **8**, **9a—d**, and **10a—d**. Thus the ^{1}H NMR spectra also indicated an ionic structure of these compounds. In contrast to the high stabilities, the chemical shifts (^{13}C NMR) of cationic carbons for **8**, **9a**, and **10a** (δ = 156.31, 164.25, and 172.17, respectively) are comparable with those for the stable carbocations **2a**, **3a**, and **4d** (δ = 157.40, 165.54, and 168.58), respectively.[3)] The cationic carbons for **9b—d** (**9b**; δ = 165.43, **9c**; δ = 161.95, and **9d**; δ = 161.67) and **10b—d** (**10b**; δ = 174.34, **10c**; δ = 171.06, and **10d**; δ = 170.31) were also comparable with those for the stable carbocations **3a—c** (**3b**; δ = 161.58 and **3c**; δ = 161.11) and **4d**, respectively.

Thermodynamic Stability. As a criterion of the thermodynamic stability, the pK_{R^+} values of the cations **8**, **9a—d**, and **10a—d** were measured spectrophotometrically at 25 °C in a buffer solution prepared in 50% aqueous MeCN.[3,6,10)] The exact pK_{R^+} values of the cations **8** and **9a** could not be determined by this method because of their extreme stabilities. The pK_{R^+} values of the cations **9b—d** and **10a—d** are summarized in Table 2 along with those of the corresponding parent cations (**2a—c**, **3a—c**, and **4a—c**).[2—4)] The neutralizations of these cations (**9b—d** and **10a—d**) are not completely reversible due to the instability of the neutralized products in the basic conditions. Immediate acidification of the alkaline solutions of **9b—d** and **10a—d** with HCl regenerated the absorption maxima of the cations in the visible region in 37—98%, which are also summarized in Table 2.

As expected, the methoxy substituents effectively stabilized the cations. The pK_{R^+} values of **8** and **9a** were well beyond 14.0. The values of **8** and **9a** are extremely high for a methyl cation. The pK_{R^+} value of **10a** was determined as 13.2, which is higher by 10.2 pK units than that of **4a**. Di(1-azulenyl)phenylmethyl (**3a**) and (1-azulenyl)diphenylmethyl (**4a**) cations also considerably stabilized with the methoxy substituents on each phenyl group. The pK_{R^+} values of the cations **9b—d** (11.7—13.4) and **10b—d** (5.2—7.0) are higher by 1.0—1.4 and 2.2—2.4 pK units than those of the corresponding analogous benzyl and diphenylmethyl cations. Relatively high stabilization effect of the cations **10b—d** compared with that of **9b—d** is attributable to the difference of the number of the methoxy substituents contributing to the stabilization. The pK_{R^+} values of **9b** (11.7) and **10b** (5.2) are high for a methyl cation. The methyl substituents on the azulene rings slightly increase the pK_{R^+} values (**9c**; 12.2 and **10c**; 6.0). Introduction of bulky *t*-butyl groups at the 3,6-positions rather efficiently stabilized these

Table 2. pK_{R^+} Values and Redox Potentials[a] of **8**, **9a—d**, and **10a—d** and Those of **2a—c**, **3a—c**, and **4a—c** for Comparison[3]

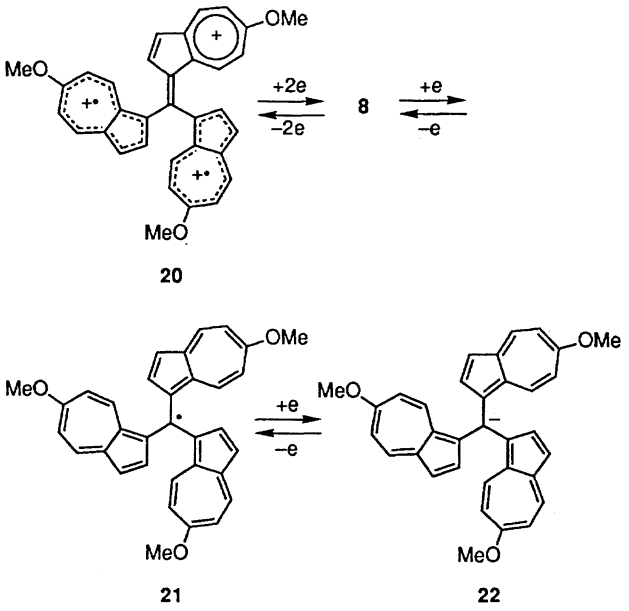
Sample	pK_{R^+}[b]	E_1^{red}	E_2^{red}	E_1^{ox}	E_2^{ox}
8	>14.0	−0.88	(−1.64)	(+0.90)	(+0.98)
2a	11.3	−0.78	(−1.56)	(+0.98)	(+1.07)
2b	11.4	−0.82	(−1.59)	(+0.85)	(+0.94)
2c	14.3	−0.91	(−1.72)	+0.84	+0.95
9a	>14.0	−0.80	(−1.63)	(+0.94)	—
9b	11.7±0.1 (83%)	−0.71	(−1.55)	(+1.04)	—
9c	12.2±0.1 (83%)	−0.75	(−1.60)	(+0.91)	—
9d	13.4±0.1 (37%)	−0.83	(−1.67)	+0.88	(+1.36)
3a	10.5	−0.66	(−1.52)	(+1.04)	—
3b	10.8	−0.70	(−1.57)	(+0.90)	—
3c	12.4	−0.78	(−1.64)	+0.88	(+1.38)
10a	13.2±0.1 (98%)	−0.69	(−1.62)	(+1.33)	—
10b	5.2±0.1 (95%)	(−0.56)	—	(+1.37)	—
10c	6.0±0.2 (96%)	(−0.65)	—	(+1.27)	—
10d	7.0±0.1 (73%)	−0.71	(−1.66)	+1.28	(+1.68)
4a	3.0	−0.48	—	(+1.41)	—
4b	3.7	—	—	—	—
4c	4.6	−0.59	(−1.54)	(+1.53)	—

a) The redox potentials were measured by cyclic voltammetry (V vs. Ag/Ag^+, 0.1 M Et_4NClO_4 in MeCN, Pt electrode, and scan rate 100 mV s^{-1}) (1 M = 1 mol dm^{-3}). Irreversible processes were shown in parentheses. b) Regenerated absorption maxima (%) of the cations in visible region by immediate acidification of the alkaline solution with HCl after the pK_{R^+} measurement were shown in parentheses.

cations (**9b** and **10b**). The values of the *t*-butyl derivatives (**9d**; 13.4 and **10d**; 7.0) are higher by 1.7 and 1.8 p*K* units than those of **9b** and **10b**, respectively. Consequently, the combination of 1-azulenyl groups with 4-methoxyphenyl groups also stabilized the methyl cations effectively. However, the stabilities of these cations **9b—d** and **10b—d** were a little bit lower than those of dimethylamino derivatives (**5a—c** and **6a—c**). The pK_{R^+} values of dimethylamino derivatives **5a—c** and **6a—c** were higher by 0.4—1.5 and 3.6—7.4 p*K* units than those of **9b—d** and **10b—d**.[6]

Redox Potentials. The redox potentials (V vs. Ag/Ag^+) of **8**, **9a—d**, and **10a—d** measured by cyclic voltammetry (CV) in acetonitrile are also summarized in Table 2 together with those of the corresponding parent cations (**2a—c**, **3a—c**, and **4a—c**).[3] Redox behaviors of these cations were little affected by the substitution with methoxy groups on both azulenyl and phenyl rings. The oxidation of **8** exhibited voltammograms that were characterized by barely separated irreversible waves at +0.90—+0.98 V. The oxidation process is due to generating a trication species (**20**) by the oxidation of two azulene rings. The oxidation potentials are in the potential range comparable with those of **2a—c**. The reduction of **8** showed a reversible wave at −0.88 V and an irreversible wave at −1.64 V upon the CV. These two waves are ascribed to the formation of a radical and an anion species such as **21** and **22**, respectively (Scheme 4). In spite of the high pK_{R^+} value, reduction potentials of **8** were also in the potential range comparable with those of **2a—c** (−0.78——0.91 V).

Although the dimethylamino derivatives **5a—c** and **6a—c** exhibited a barely separated two-step oxidation wave at around +0.75—+1.01 and +0.74—+0.92 V,[6] the oxidation of **9a—d** and **10a—d** showed a wave at +0.88—+1.04 and



Scheme 4.

+1.27—+1.37 V, respectively. The waves of **9a—c** and **10a—c** were irreversible under the conditions of the CV measurements. The *t*-butyl substituents on the azulene rings apparently stabilize the oxidation states, as indicated by the oxidation of **9d** and **10d**. Relatively low oxidation potentials of **9a—d**, compared with those of **10a—d**, are due to the oxidation of an azulene ring to give a dication radical.

The reduction of **9a—d** and **10a**, **d** showed a reversible wave at −0.69——0.83 V and an irreversible wave at −1.55——1.67 V upon the CV, although the reduction of the **10b**, **c** showed an irreversible wave at −0.56——0.65 V.

The reduction potentials of **9b—d** and **10b**, **d** are slightly more negative than those of **3a—c** and **4a**, **c** by 0.05—0.12 V; this indicates the stabilization of the methyl cations by the methoxy substituent on the phenyl groups. The more negative reduction potentials of the *t*-butyl derivatives **9d** and **10d** (−0.83 and −0.71 V) among **9a—d** and **10a—d** correspond to high electrochemical stability.

These cations showed high stabilities with high pK_{R^+} values compared with parent tri(1-azulenyl)methyl (**2**), di(1-azulenyl)phenylmethyl (**3**), and (1-azulenyl)diphenylmethyl (**4**) cations. These results clearly indicate that the methoxy substituents on both azulenyl and phenyl groups effectively stabilized the methyl cations. The tropylium ion substituted with bicyclo[2.2.2]octene units and cyclopropenium ion substituted with dialkylamino groups were reported as stable cyclic cations with high pK_{R^+} values around 13.[11,12] Very recently, 2,6,10-tris(diethylamino)-4,8,12-trioxa-4,8,12,*12c*-tetrahydrodibenzo[*cd*,*mn*]pyrenylium hexafluorophosphate was reported as extremely stable carbocation with the pK_{R^+} value of 19.7.[13] The cations **8**, **9a**, and **10a** are one of the exceptionally stable methyl cations, and have extraordinary high pK_{R^+} values. The unusual stability of **8**, **9a**, and **10a** is ascribed to dipolar structures of azulene rings in addition to the contribution of mesomeric effects of the three methoxy groups.

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 Shimadzu FTIR-8100M and a Hitachi U-3410 spectrophotometer, respectively. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded on a Hitachi R-90H at 90 MHz (22.5 MHz), a JEOL GSX 400 at 400 MHz (100 MHz), a JEOL JNM A500 at 500 MHz (125 MHz), or a Bruker AM 600 spectrometer at 600 MHz (150 MHz). Gel permeation chromatographies (GPC) were performed on Showadenko Shodex K2001 and K2002. Voltammetry measurements were carried out with a BAS100B/W electrochemical workstation equipped with Pt working and auxiliary electrodes, a reference electrode formed from Ag/$AgNO_3$ (0.01 M, 1 M = 1 mol dm^{-3}), and tetraethylammonium perchlorate (TEAP) as a supporting electrolyte, at the scan rate of 100 mV s^{-1}. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

6-Methoxy-1-azulenecarbaldehyde (13). $POCl_3$ (2.2 ml, 24 mmol) was slowly added at 0 °C to a solution of 6-methoxyazulene (**12a**) (3.16 g, 20.0 mmol) in DMF (80 ml). The mixture was stirred at room temperature for 10 min. The resulting solution was poured into ice-water, made alkaline with 2 M aqueous NaOH, and then extracted with CH_2Cl_2. The organic layer was washed with water, dried with $MgSO_4$, and concentrated in vacuo. Purification of the residue by column chromatography on silica gel with CH_2Cl_2 gave the azulene **13** (3.72 g, 100%). Reddish orange crystals; mp 73.0—75.0 °C (CH_2Cl_2/hexane); MS (70 eV) *m/z* (rel intensity) 186 (M^+; 81) and 185 (100); IR (KBr disk) ν_{max} 1636, 1580, 1458, 1404, 1391, 1273, 1254, 1204, and 841 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 266 (3.85), 327 (4.70), 393 (3.84), and 482 (2.93); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.25 (s, 1H, 1-CHO), 9.42 (d, J = 11.2 Hz, 1H, H_8), 8.30 (d, J = 11.3 Hz, 1H, H_4), 7.94 (d, J = 4.0 Hz, 1H, H_2), 7.17 (d, J = 4.0 Hz, 1H, H_3), 7.12 (dd, J = 11.3, 4.0 Hz, 1H, H_5), 7.10 (d, J = 11.2, 4.0 Hz, 1H, H_7), and 3.97 (s, 3H, 6-OMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.88 (d, 1-CHO), 169.13 (s), 141.47 (s), 138.33 (d, C_4), 138.04 (d, C_2), 137.42 (d, C_8), 135.53 (s), 126.71 (s), 119.48 (d, C_3), 116.66 (d, C_7), 114.87 (d, C_5), and 56.24 (q, 6-OMe). Found: C, 77.66; H, 5.46%. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41%.

General Procedure for the High Pressure Reaction of 6-Methoxyazulene (12a) with Aldehydes (13 and 16). A solution of 6-methoxyazulene (**12a**) and 6-methoxy-1-azulenecarbaldehyde (**13**) or 4-methoxybenzaldehyde (**16**) in a 1 : 1 mixture of acetic acid and CH_2Cl_2 (9.1 ml) was pressed up to 10 kbar at 30 °C for 24—48 h. The reaction mixture was concentrated under reduced pressure. The residue was diluted with CH_2Cl_2. The organic solution was washed with 5% aqueous $NaHCO_3$ 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 $CHCl_3$. The product was further purified by recrystallization.

Tris(6-methoxy-1-azulenyl)methane (11). The general procedure was followed using 6-methoxyazulene (**12a**) (1.58 g, 10.0 mmol) and 6-methoxy-1-azulenecarbaldehyde (**13**) (935 mg, 5.02 mmol) at 10 kbar (30 °C) for 48 h. Column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ afforded the methane **11** (61 mg, 6.1%) and the recovered **12a** (922 mg, 58%). Purple crystals; mp 254.0—257.0 °C decomp (CH_2Cl_2/hexane); MS (70 eV) *m/z* (rel intensity) 484 (M^+; 100), 470 (30), 328 (66), 158 (88), 128 (20), and 115 (47); IR (KBr disk) ν_{max} 1580, 1402, 1196, 1167, and 835 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 232 (4.52), 280 (4.92), 309 (5.02), 348 (4.25), 365 (4.28), and 552 (2.92); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.13 (d, J = 11.0 Hz, 3H, H_8), 8.11 (d, J = 10.5 Hz, 3H, H_4), 7.15 (s, 1H, CH), 7.14 (d, J = 4.4 Hz, 3H, H_2), 7.13 (d, J = 4.4 Hz, 3H, H_3), 6.68 (dd, J = 10.5, 2.7 Hz, 3H, H_5), 6.57 (dd, J = 11.0, 2.7 Hz, 3H, H_7), and 3.87 (s, 9H, 6-OMe); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.86 (s, C_6), 136.64 (s, C_{3a}), 135.74 (d, C_4), 135.68 (s, C_1), 134.10 (d, C_2), 133.01 (d, C_8), 130.69 (s, C_{8a}), 117.56 (d, C_3), 109.15 (d, C_5), 108.90 (d, C_7), 55.77 (q, 6-OMe), and 36.08 (d, CH). Found: C, 81.29; H, 5.97%. Calcd for $C_{34}H_{28}O_3 \cdot H_2O$: C, 81.25; H, 6.02%.

Bis(6-methoxy-1-azulenyl)(4-methoxyphenyl)methane (14a). The general procedure was followed using 6-methoxyazulene (**12a**) (1.58 g, 10.0 mmol) and 4-methoxybenzaldehyde (**16**) (682 mg, 5.01 mmol) at 10 kbar (30 °C) for 24 h. Column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ afforded the methane **14a** (197 mg, 13%), 1,3-bis[(6-methoxy-1-azulenyl)(4-methoxyphenyl)methyl]-6-methoxyazulene (**17a**) (124 mg, 7.5%), and the recovered **12a** (471 mg, 30%).

14a: Purple crystals; mp 173.5—174.0 °C (CH_2Cl_2/hexane); MS (70 eV) *m/z* (rel intensity) 434 (M^+; 100), 433 (25), and 327 (26); IR (KBr disk) ν_{max} 1582, 1508, 1404, 1266, 1248, 1232, 1198, 1166, and 836 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 228 (4.56), 290 (4.93), 310 (4.95), 347 (4.08), 364 (4.16), and 547 (2.76); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.11 (d, J = 10.7 Hz, 2H, H_4), 8.10 (d, J = 10.7 Hz, 2H, H_8), 7.16 (d, J = 4.4 Hz, 2H, H_2), 7.15 (d, J = 4.4 Hz, 2H, H_3), 7.08 (d, J = 8.7 Hz, 2H, $H_{2',6'}$), 6.78 (d, J = 8.7 Hz, 2H, $H_{3',5'}$), 6.68 (dd, J = 10.7, 2.7 Hz, 2H, H_5), 6.60 (dd, J = 10.7, 2.7 Hz, 2H, H_7), 6.56 (s, 1H, CH), 3.87 (s, 6H, 6-OMe), and 3.76 (s, 3H, 4′-OMe); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.96 (s, C_6), 157.65 (s, $C_{4'}$), 138.19 (s, $C_{1'}$), 136.58 (s, C_{3a}), 135.87 (d, C_4), 134.97 (s, C_1), 133.95 (d, C_2), 133.06 (d, C_8), 130.92 (s, C_{8a}), 129.69 (s, $C_{2',6'}$), 117.53 (d, C_3), 113.51 (d, $C_{3',5'}$), 109.33 (d, C_5), 109.00 (d, C_7), 55.76 (q, 6-OMe), 55.18 (q, 4′-OMe), and 42.07 (d,

CH). Found: C, 82.39; H, 6.36%. Calcd for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03%.

17a: Diastereomeric mixture (***A*** : ***B*** = 51 : 49); purple crystals; mp 126.5—130.0 °C (CH_2Cl_2/hexane); MS (70 eV) *m/z* (rel intensity) 710 (M^+; 100), 434 (33), 433 (87), 278 (55), and 277 (52); IR (KBr disk) ν_{max} 1582, 1508, 1402, 1250, 1196, 1166, and 832 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 228 (4.68), 294 (5.09), 363 (4.27), and 551 (2.92); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.068 (d, *J* = 10.6 Hz, 2H, ***B***-$H_{4'}$), 8.053 (d, *J* = 10.8 Hz, 2H, $H_{4,8}$), 8.045 (d, *J* = 10.6 Hz, 2H, ***A***-$H_{4'}$), 8.040 (d, *J* = 10.8 Hz, 2H, $H_{4,8}$), 7.997 (d and d, *J* = 10.9 Hz, 4H, ***A***-$H_{8'}$ and ***B***-$H_{8'}$), 7.086 (d, *J* = 3.8 Hz, 2H, ***B***-$H_{3'}$), 7.064 (d, *J* = 3.8 Hz, 2H, ***B***-$H_{2'}$), 7.052 (d, *J* = 3.8 Hz, 2H, ***A***-$H_{3'}$), 7.034 (d, *J* = 3.8 Hz, 2H, ***A***-$H_{2'}$), 7.003 (d, *J* = 8.7 Hz, 4H, ***A***-$H_{2'',6''}$), 6.977 (d, *J* = 8.7 Hz, 4H, ***B***-$H_{2'',6''}$), 6.913 (s, 1H, ***B***-H_2), 6.894 (s, 1H, ***A***-H_2), 6.721 (d, *J* = 8.7 Hz, 4H, ***A***-$H_{3'',5''}$), 6.684 (d, *J* = 8.7 Hz, 4H, ***B***-$H_{3'',5''}$), 6.660 (dd, *J* = 10.6, 2.7 Hz, 2H, ***B***-$H_{5'}$), 6.643 (dd, *J* = 10.6, 2.7 Hz, 2H, ***A***-$H_{5'}$), 6.542 (dd, *J* = 10.9, 2.7 Hz, 2H, ***B***-$H_{7'}$), 6.522 (dd, *J* = 10.9, 2.7 Hz, 2H, ***A***-$H_{7'}$), 6.488 (d and s, *J* = 10.8 Hz, 4H, $H_{5,7}$ and ***B***-CH), 6.483 (s, 2H, ***A***-CH), 6.480 (d, *J* = 10.8 Hz, 2H, $H_{5,7}$), 3.858 (s, 6H, ***B***-6′-OMe), 3.851 (s, 6H, ***A***-6′-OMe), 3.783 (s, 3H, ***B***-6-OMe), 3.779 (s, 3H, ***A***-6-OMe), 3.730 (s, 6H, ***A***-4″-OMe), and 3.719 (s, 6H, ***B***-4″-OMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 166.85 (s, $C_{6'}$), 166.83 (s, s, and s, C_6 and $C_{6'}$), 157.52 (s, $C_{4''}$), 157.49 (s, $C_{4''}$), 137.98 (s and s, $C_{1''}$), 136.62 (s, $C_{3'a}$), 136.56 (s, $C_{3'a}$), 135.79 (d, $C_{4'}$), 135.73 (d, $C_{4'}$), 135.71 (d, ***B***-C_2), 135.59 (d, ***A***-C_2), 134.80 (s, $C_{1'}$), 134.77 (s, $C_{1'}$), 133.93 (d and d, $C_{2'}$), 133.46 (s, $C_{1,3}$), 133.43 (s, $C_{1,3}$), 133.28 (d, $C_{8'}$), 133.19 (d, $C_{8'}$), 132.80 (d, $C_{4,8}$), 132.76 (d, $C_{4,8}$), 131.63 (s, $C_{3a,8a}$), 131.62 (s, $C_{3a,8a}$), 130.95 (s, $C_{8'a}$), 130.90 (s, $C_{8'a}$), 129.63 (d and d, $C_{2'',6''}$), 117.42 (d, ***B***-$C_{3'}$), 117.34 (d, ***A***-$C_{3'}$), 113.38 (d, $C_{3'',5''}$), 113.34 (d, $C_{3'',5''}$), 109.24 (d, $C_{5'}$), 109.20 (d, $C_{5'}$), 108.82 (d, $C_{7'}$), 108.79 (d, $C_{7'}$), 108.37 (d and d, $C_{5,7}$), 55.72 (q, 6′-OMe), 55.70 (q, 6′-OMe), 55.64 (q and q, 6-OMe), 55.15 (q, 4″-OMe), 55.12 (q, 4″-OMe), and 42.01 (d and d, CH). Found: C, 82.87; H, 6.19%. Calcd for $C_{49}H_{42}O_5$: C, 82.79; H, 5.96%.

General Procedure for the Synthesis of Di(1-azulenyl)-(6-methoxyphenyl)methanes (14b—d) and (1-Azulenyl)bis(6-methoxyphenyl)methanes (15a—d). A solution of azulenes (**12b—d**) and 4-methoxybenzaldehyde (**16**) or azulenes (**12a—d**) and bis(4-methoxyphenyl)methanol (**18**) in glacial acetic acid was stirred at room temperature under an Ar atmosphere until the reaction was completed. The solvent was removed under reduced pressure. The residue was diluted with CH_2Cl_2. The organic layer was washed with 5% aqueous $NaHCO_3$ 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/or GPC with $CHCl_3$. The product was further purified by recrystallization.

Di(1-azulenyl)(4-methoxyphenyl)methane (14b). The general procedure was followed using azulene (**12b**) (1.34 g, 10.5 mmol) and 4-methoxybenzaldehyde (**16**) (697 mg, 5.12 mmol) in glacial acetic acid (60 ml). The reaction mixture was stirred at room temperature for 5 d. Column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ afforded the methane **14b** (143 mg, 11%), 1,3-bis[(1-azulenyl)(4-methoxyphenyl)methyl]azulene (**17b**) (110 mg, 7.6%), and the recovered **12b** (443 mg, 33%).

14b: Blue crystals; mp 153.0—155.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 374 (M^+; 100), 373 (28), 267 (20), and 265 (21); IR (KBr disk) ν_{max} 1574, 1509, 1393, 1250, and 772 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 238 (4.59), 279 (4.87), 350 (4.01), 366 (3.91), 601 (2.82), and 651 (2.73); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.27 (d, *J* = 9.5 Hz, 2H, H_4), 8.25 (d, *J* = 9.8 Hz, 2H, H_8), 7.50 (dd, *J* = 10.0, 9.8 Hz, 2H, H_6), 7.45 (d, *J* = 3.8 Hz, 2H, H_2), 7.27 (d, *J* = 3.8 Hz, 2H, H_3), 7.07 (dd, *J* = 9.8, 9.5 Hz, 2H, H_5), 7.07 (d, *J* = 8.6 Hz, 2H, $H_{2',6'}$), 6.98 (dd, *J* = 10.0, 9.8 Hz, 2H, H_7), 6.79 (d, *J* = 8.6 Hz, 2H, $H_{3',5'}$), 6.70 (s, 1H, CH), and 3.75 (s, 3H, 4′-OMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.78 (s, $C_{4'}$), 141.06 (s, C_{3a}), 138.28 (d, C_2), 137.93 (s, $C_{1'}$), 137.30 (d, C_6), 136.69 (d, C_4), 134.95 (s, C_{8a}), 133.69 (d, C_8), 133.66 (s, C_1), 129.70 (d, $C_{2',6'}$), 122.46 (d, C_5), 121.91 (d, C_7), 116.55 (d, C_3), 113.61 (d, $C_{3',5'}$), 55.20 (q, 4′-OMe), and 41.98 (d, CH). Found: C, 89.20; H, 5.96%. Calcd for $C_{28}H_{22}O$: C, 89.81; H, 5.92%.

17b: Diastereomeric mixture (***A*** : ***B*** = 48 : 52); blue crystals; mp 127.0—137.5 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 620 (M^+; 26), 457 (44), 437 (46), 422 (35), 421 (100), 417 (67), 401 (31), 377 (50), and 328 (72); IR (KBr disk) ν_{max} 1574, 1509, 1393, 1248, 1175, 1034, 768, and 735 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 239 (4.63), 281 (4.88), 350 (4.05), 366 (4.02), 609 (3.00), and 649 (2.98); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.237 (d, *J* = 9.6 Hz, 2H, ***B***-$H_{4'}$), 8.218 (d, *J* = 9.9 Hz, 2H, $H_{4,8}$), 8.208 (d and d, *J* = 9.9 and 9.7 Hz, 2H and 2H, $H_{4,8}$ and ***A***-$H_{4'}$), 8.161 (d, *J* = 9.7 Hz, 2H, ***B***-$H_{8'}$), 8.136 (d, *J* = 9.7 Hz, 2H, ***A***-$H_{8'}$), 7.502 (dd, *J* = 9.8, 9.8 Hz, 2H, ***B***-$H_{6'}$), 7.468 (dd, *J* = 9.8, 9.8 Hz, 2H, ***A***-$H_{6'}$), 7.409 (t and t, *J* = 9.8 and 9.8 Hz, 1H and 1H, ***A***-H_6 and ***B***-H_6), 7.334 (d, *J* = 3.8 Hz, 2H, ***B***-$H_{2'}$), 7.286 (d, *J* = 3.8 Hz, 2H, ***A***-$H_{2'}$), 7.206 (d, *J* = 3.8 Hz, 2H, ***B***-$H_{3'}$), 7.159 (d, *J* = 3.8 Hz, 2H, ***A***-$H_{3'}$), 7.132 (s, 1H, ***A***-H_2), 7.122 (s, 1H, ***B***-H_2), 7.065 (dd, *J* = 9.8, 9.6 Hz, 2H, ***B***-$H_{5'}$), 7.044 (dd, *J* = 9.8, 9.6 Hz, 2H, ***A***-$H_{5'}$), 6.982 (d, *J* = 8.6 Hz, 4H, ***A***-$H_{2'',6''}$), 6.947 (dd, *J* = 9.8, 9.7 Hz, 2H, ***B***-$H_{7'}$), 6.936 (d, *J* = 8.6 Hz, 4H, ***B***-$H_{2'',6''}$), 6.899 (dd, *J* = 9.8, 9.7 Hz, 2H, ***A***-$H_{7'}$), 6.895 (t, *J* = 9.9, 9.8 Hz, 2H, $H_{5,7}$), 6.890 (t, *J* = 9.9, 9.8 Hz, 2H, $H_{5,7}$), 6.731 (d, *J* = 8.6 Hz, 4H, ***A***-$H_{3'',5''}$), 6.677 (d, *J* = 8.6 Hz, 4H, ***B***-$H_{3'',5''}$), 6.626 (s and s, 2H and 2H, CH and CH), 3.740 (s, 6H, ***A***-4″-OMe), and 3.724 (s, 6H, ***B***-4″-OMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 157.65 (s, ***A***-$C_{4''}$), 157.60 (s, ***B***-$C_{4''}$), 141.06 (s, ***B***-$C_{3a'}$), 141.01 (s, ***A***-$C_{3a'}$), 139.79 (d, ***A***-C_2), 139.71 (d, ***B***-C_2), 138.25 (d, ***B***-$C_{2'}$), 138.21 (d, ***A***-$C_{2'}$), 137.70 (s, ***AB***-$C_{1''}$), 137.69 (d, ***AB***-C_6), 137.34 (d, ***AB***-$C_{6'}$), 137.20 (d, $C_{4'}$), 136.64 (d, $C_{4'}$), 136.59 (s, ***AB***-$C_{3a,8a}$), 135.78 (s, ***B***-$C_{8a'}$), 134.96 (s, ***A***-$C_{8a'}$), 133.86 (d, ***B***-$C_{8'}$), 133.77 (d, ***A***-$C_{8'}$), 133.62 (d, C_8), 133.58 (d, C_8), 133.45 (s, $C_{1'}$), 133.42 (s, $C_{1'}$), 132.12 (s, $C_{1,3}$), 129.61 (d, ***A***-$C_{2'',6''}$), 129.59 (d, ***B***-$C_{2'',6''}$), 122.39 (d, $C_{5'}$), 122.36 (d, $C_{5'}$), 121.78 (d, ***AB***-$C_{7'}$), 121.60 (d, $C_{5,7}$), 116.47 (d, ***B***-$C_{3'}$), 116.39 (d, ***A***-$C_{3'}$), 113.50 (d, ***A***-$C_{3'',5''}$), 113.44 (d, ***B***-$C_{3'',5''}$), 55.18 (q, 4″-OMe), 55.17 (q, 4″-OMe), 41.91 (d, CH), and 41.88 (d, CH). Found: C, 88.75; H, 6.02%. Calcd for $C_{46}H_{36}O_2$: C, 89.00; H, 5.85%.

Bis(3-methyl-1-azulenyl)(4-methoxyphenyl)methane (14c). The general procedure was followed using 1-methylazulene (**12c**) (710 mg, 4.99 mmol) and 4-methoxybenzaldehyde (**16**) (341 mg, 2.50 mmol) in glacial acetic acid (30 ml). The mixture was stirred at room temperature for 4 d. Column chromatography on silica gel with CH_2Cl_2/CCl_4 afforded the methane **14c** (658 mg, 65%). Blue crystals; mp 161.0—162.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 402 (M^+; 100) and 387 (33); IR (KBr disk) ν_{max} 1572, 1509, 1248, and 733 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 241 (4.58), 281 (4.92), 357 (4.05), 374 (4.02), and 632 (2.91); ^{1}H NMR (90 MHz, $CDCl_3$) δ = 8.13 (d and d, *J* = 9.5 and 9.5 Hz, 4H, H_4 and H_8), 7.42 (dd, *J* = 9.8 Hz, 2H, H_6), 7.29 (s, 2H, H_2), 7.05 (d, *J* = 8.6 Hz, 2H, $H_{2',6'}$), 6.94 (dd, *J* = 9.8, 9.5 Hz, 2H, H_5), 6.84 (dd, *J* = 9.8, 9.5 Hz, 2H, H_7), 6.77 (d, *J* = 8.6 Hz, 2H, $H_{3',5'}$), 6.62 (s, 1H, CH), 3.76 (s, 3H, 4′-OMe), and 2.56 (s, 6H, 3-Me); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 157.62 (s), 139.29 (d, C_2), 138.07 (s), 137.10 (d, C_6), 136.97 (s), 135.02 (s), 133.44 (d, C_4), 132.98 (d,

C_8), 132.00 (s), 129.59 (d, $C_{2',6'}$), 124.47 (s), 120.94 (d, C_7), 120.66 (d, C_5), 113.56 (d, $C_{3',5'}$), 55.17 (q, 4′-OMe), 41.57 (d, CH), and 12.73 (q, 3-Me). Found: C, 88.80; 6.63%. Calcd for $C_{30}H_{26}O$: C, 89.52; H, 6.51%.

Bis(3, 6- di- *t*- butyl- 1- azulenyl)(4- methoxyphenyl)methane (14d). The general procedure was followed using 1,6-di-*t*-butylazulene (**12d**) (1.20 g, 4.99 mmol) and 4-methoxybenzaldehyde (**16**) (341 mg, 2.50 mmol) in glacial acetic acid (50 ml). The mixture was stirred at room temperature for 4 d. Column chromatography on silica gel with benzene/hexane afforded the methane **14d** (1.22 g, 82%). Blue crystals; mp 215.0—217.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 598 (M^+; 100), 542 (43), 541 (99), 284 (24), and 57 (27); IR (KBr disk) ν_{max} 2963, 1574, 1509, 1460, 1364, 1248, 1227, 1175, and 835 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 243 (4.52), 287 (4.93), 304 (4.87), 357 (4.05), 376 (3.96), and 616 (2.82); ^1H NMR (90 MHz, $CDCl_3$) δ = 8.53 (d, J = 10.8 Hz, 2H, H_4), 8.15 (d, J = 11.0 Hz, 2H, H_8), 7.37 (s, 2H, H_2), 7.14 (dd, J = 10.8, 1.8 Hz, 2H, H_5), 7.03 (d, J = 11.0, 1.8 Hz, 2H, H_7), 7.03 (dd, J = 8.7 Hz, 2H, $H_{2',6'}$), 6.75 (d, J = 8.7 Hz, 2H, $H_{3',5'}$), 6.58 (s, 1H, CH), 3.76 (s, 3H, 4′-OMe), 1.49 (s, 9H, 3-*t*-Bu), and 1.40 (s, 9H, 6-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 160.12 (s), 157.43 (s), 138.50 (s), 137.52 (s), 136.21 (d, C_2), 134.56 (s), 134.32 (d, C_4), 134.14 (s), 132.10 (d, C_8), 130.88 (s), 129.63 (d, $C_{2',6'}$), 119.08 (d, C_7), 118.13 (d, C_5), 113.40 (d, $C_{3',5'}$), 55.20 (q, 4′-OMe), 41.24 (d, CH), 38.22 (s, 6-*t*-Bu), 33.31 (s, 3-*t*-Bu), 32.33 (q, 3-*t*-Bu), and 31.91 (q, 6-*t*-Bu). Found: C, 87.33; H, 9.03%. Calcd for $C_{44}H_{54}O \cdot 1/2H_2O$: C, 86.93; H, 9.12%.

(6-Methoxy-1-azulenyl)bis(4-methoxyphenyl)methane (15a). The general procedure was followed using 6-methoxyazulene (**12a**) (318 mg, 2.01 mmol) and bis(4-methoxyphenyl)methanol (**18**) (490 mg, 2.01 mmol) in acetic acid (12 ml) and CH_2Cl_2 (4.5 ml). The mixture was stirred at room temperature for 24 h. Column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ afforded the methane **15a** (305 mg, 57%), 1,3-bis[bis(4-methoxyphenyl)methyl]-6-methoxyazulene (**19a**) (346 mg, 28%), and the recovered **12a** (97 mg, 31%).

15a: Purple crystals; mp 94.0—95.5 °C (hexane); MS (70 eV) *m/z* (rel intensity) 384 (M^+; 100), 383 (20), and 277 (58); IR (KBr disk) ν_{max} 1582, 1509, 1254, 1200, and 1175 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 230 (4.49), 308 (4.82), 347 (3.71), 362 (3.84), 448 (2.06), and 544 (2.47); ^1H NMR (500 MHz, $CDCl_3$) δ = 8.12 (d, J = 10.7 Hz, 1H, H_4), 8.06 (d, J = 11.0 Hz, 1H, H_8), 7.17 (d, J = 3.9 Hz, 1H, H_3), 7.16 (d, J = 3.9 Hz, 1H, H_2), 7.05 (d, J = 8.8 Hz, 4H, $H_{2',6'}$), 6.80 (d, J = 8.8 Hz, 4H, $H_{3',5'}$), 6.70 (dd, J = 10.7, 2.7 Hz, 1H, H_5), 6.64 (dd, J = 11.0, 2.7 Hz, 1H, H_7), 5.97 (s, 1H, CH), 3.88 (s, 3H, 6-OMe), and 3.77 (s, 6H, 4′-OMe); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.12 (s, C_6), 157.79 (s, $C_{4'}$), 137.60 (s, $C_{1'}$), 136.61 (s, C_{3a}), 136.05 (d, C_4), 134.14 (s, C_1), 133.80 (d, C_2), 133.16 (d, C_8), 131.21 (s, C_{8a}), 129.97 (d, $C_{2',6'}$), 117.55 (d, C_3), 113.58 (d, $C_{3',5'}$), 109.60 (d, C_5), 109.12 (d, C_7), 55.80 (q, 6-OMe), 55.22 (q, 4′-OMe), and 48.20 (d, CH). Found: C, 79.38; H, 6.33%. Calcd for $C_{26}H_{24}O_3 \cdot 1/2H_2O$: C, 79.37; H, 6.40%.

19a: Purple crystals; mp 148.0—149.0 °C (hexane); MS (70 eV) *m/z* (rel intensity) 610 (M^+; 100), 384 (26), 383 (74), 227 (35), and 121 (65); IR (KBr disk) ν_{max} 1578, 1509, 1258, 1244, 1202, 1177, 1169, and 1032 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 230 (4.66), 316 (4.84), 369 (3.86), 453 (2.29), 564 (2.48), and 678 (1.76); ^1H NMR (500 MHz, $CDCl_3$) δ = 8.00 (d, J = 11.2 Hz, 2H, $H_{4,8}$), 6.99 (d, J = 8.8 Hz, 8H, $H_{2',6'}$), 6.86 (s, 1H, H_2), 6.75 (d, J = 8.8 Hz, 8H, $H_{3',5'}$), 6.54 (d, J = 11.2 Hz, 2H, $H_{5,7}$), 5.91 (s, 2H, CH), 3.83 (s, 3H, 6-OMe), and 3.75 (s, 12H, 4′-OMe); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.06 (s, C_6), 157.71 (s, $C_{4'}$), 137.48 (d, C_2), 135.21 (s, $C_{1'}$), 132.98 (d, $C_{4,8}$), 132.61 (s, $C_{1,3}$), 131.91 (s, $C_{3a,8a}$), 129.90 (d, $C_{2',6'}$), 113.49 (d, $C_{3',5'}$), 108.71 (d, $C_{5,7}$), 55.73 (q, 6-OMe), 55.22 (q, 4′-OMe), and 48.05 (d, CH). Found: C, 79.36; H, 6.28%. Calcd for $C_{41}H_{38}O_5 \cdot 1/2H_2O$: C, 79.46; H, 6.34%.

(1-Azulenyl)bis(4-methoxyphenyl)methane (15b). The general procedure was followed using azulene (**12b**) (641 mg, 5.00 mmol) and bis(4-methoxyphenyl)methanol (**18**) (1.22 g, 4.99 mmol) in glacial acetic acid (30 ml). The mixture was stirred at room temperature for 21 h. Column chromatography on silica gel with CH_2Cl_2 afforded the methane **15b** (770 mg, 53%), 1,3-bis[bis(4-methoxyphenyl)methyl]azulene (**19b**) (785 mg, 54%), and the recovered **12b** (119 mg, 19%).

15b: Blue crystals; mp 141.0—142.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 354 (M^+; 100), 353 (30), and 247 (48); IR (KBr disk) ν_{max} 1509, 1260, 1246, 1173, and 1036 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 233 (4.53), 284 (4.71), 349 (3.77), 365 (3.60), 600 (2.51), and 651 (2.43); ^1H NMR (400 MHz, $CDCl_3$) δ = 8.27 (d, J = 9.5 Hz, 1H, H_4), 8.21 (d, J = 9.5 Hz, 1H, H_8), 7.51 (dd, J = 9.8, 9.8 Hz, 1H, H_6), 7.48 (d, J = 3.8 Hz, 1H, H_2), 7.29 (d, J = 3.8 Hz, 1H, H_3), 7.08 (dd, J = 9.8, 9.5 Hz, 1H, H_5), 7.04 (d, J = 8.6 Hz, 4H, $H_{2',6'}$), 7.02 (dd, J = 9.8, 9.5 Hz, 1H, H_7), 6.80 (d, J = 8.6 Hz, 4H, $H_{3',5'}$), 6.04 (s, 1H, CH), and 3.76 (s, 6H, 4′-OMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.83 (s, $C_{4'}$), 141.03 (s, C_{3a}), 138.15 (d, C_2), 137.42 (d, C_6), 137.39 (s, $C_{1'}$), 136.74 (d, C_4), 135.23 (s, C_{8a}), 133.72 (d, C_8), 132.99 (s, C_1), 129.95 (d, $C_{2',6'}$), 122.56 (d, C_5), 122.01 (d, C_7), 116.54 (d, C_3), 113.60 (d, $C_{3',5'}$), 55.19 (q, 4′-OMe), and 48.11 (d, CH). Found: C, 84.39; H, 6.24%. Calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26%.

19b: Blue crystals; mp 71.0—73.5 °C (MeOH/H_2O); MS (70 eV) *m/z* (rel intensity) 580 (M^+; 80), 353 (22), 243 (32), 228 (40), 227 (100), and 149 (30); IR (KBr disk) ν_{max} 1509, 1248, 1175, and 1036 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 231 (4.67), 291 (4.63), 359 (3.78), 376 (3.75), and 621 (2.54); ^1H NMR (400 MHz, $CDCl_3$) δ = 8.17 (d, J = 9.5 Hz, 2H, $H_{4,8}$), 7.44 (t, J = 9.9 Hz, 1H, H_6), 7.17 (s, 1H, H_2), 6.99 (d, J = 8.6 Hz, 8H, $H_{2',6'}$), 6.94 (dd, J = 9.9, 9.5 Hz, 2H, $H_{5,7}$), 6.77 (d, J = 8.6 Hz, 8H, $H_{3',5'}$), 5.99 (s, 2H, CH), and 3.77 (s, 12H, 4′-OMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.75 (s, $C_{4'}$), 139.42 (d, C_2), 137.47 (d, C_6), 137.32 (s, $C_{1'}$), 136.05 (s, $C_{3a,8a}$), 133.65 (d, $C_{4,8}$), 131.43 (s, $C_{1,3}$), 129.88 (d, $C_{2',6'}$), 121.78 (d, $C_{5,7}$), 113.52 (d, $C_{3',5'}$), 55.20 (q, 4′-OMe), and 47.98 (d, CH). Found: C, 82.77; H, 6.51%. Calcd for $C_{40}H_{36}O_4$: C, 82.73; H, 6.25%.

(3-Methyl-1-azulenyl)bis(4-methoxyphenyl)methane (15c). The general procedure was followed using 1-methylazulene (**12c**) (712 mg, 5.01 mmol) and bis(4-methoxyphenyl)methanol (**18**) (1.22 g, 4.99 mmol) in glacial acetic acid (30 ml). The mixture was stirred at room temperature for 21 h. Column chromatography on silica gel with CH_2Cl_2 afforded the methane **15c** (1.73 g, 94%). Blue crystals; mp 36.5—38.0 °C; MS (70 eV) *m/z* 368 (M^+; 100), 353 (43), and 261 (48); IR (KBr disk) ν_{max} 1610, 1576, 1510, 1464, 1442, 1302, 1250, 1176, 1034, 832, and 734 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 233 (4.43), 289 (4.63), 356 (3.62), 374 (3.55), and 628 (2.38); ^1H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, J = 9.5 Hz, 1H, H_4), 8.09 (d, J = 9.5 Hz, 1H, H_8), 7.42 (dd, J = 9.8, 9.8 Hz, 1H, H_6), 7.40 (s, 1H, H_2), 7.03 (d, J = 8.7 Hz, 4H, $H_{2',6'}$), 7.00 (dd, J = 9.8, 9.5 Hz, 1H, H_5), 6.88 (dd, J = 9.8, 9.5 Hz, 1H, H_7), 6.79 (d, J = 8.7 Hz, 4H, $H_{3',5'}$), 6.00 (s, 1H, CH), 3.76 (s, 6H, 4′-OMe), and 2.58 (s, 3H, 3-OMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.80 (s, $C_{4'}$), 139.23 (d, C_2), 137.50 (s, $C_{1'}$), 137.32 (d, C_6), 137.00 (s, C_{3a}), 135.39 (s, C_{8a}), 133.63 (d, C_4), 133.11 (d, C_8), 131.31 (s, C_1), 129.94 (d, $C_{2',6'}$), 124.55 (s, C_3), 121.10 (d, C_7), 120.85 (d, C_5),

113.57 (d, $C_{3',5'}$), 55.18 (q, 4′-OMe), 47.90 (d, CH), and 12.65 (q, 3-Me). Found: C, 85.19; H, 6.72%. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57%.

(3, 6- Di-*t*- butyl- 1- azulenyl)bis(4- methoxyphenyl)methane (15d). The general procedure was followed using 1,6-di-*t*-butylazulene (**12d**) (1.20 g, 4.99 mmol) and bis(4-methoxyphenyl)-methanol (**18**) (1.22 g, 4.99 mmol) in glacial acetic acid (30 ml). The mixture was stirred at room temperature for 21 h. Column chromatography on silica gel with CH_2Cl_2 afforded the methane **15d** (1.50 g, 64%). Blue crystals; mp 166.0—168.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 466 (M^+; 100), 452 (32), 451 (93), and 409 (27); IR (KBr disk) ν_{max} 2953, 1576, 1509, 1246, 1177, and 1034 cm^{-1}; ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 233 (4.46), 293 (4.74), 303 (4.77), 358 (3.79), 376 (3.64), and 614 (2.53); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.55 (d, J = 10.4 Hz, 1H, H_4), 8.07 (d, J = 10.4 Hz, 1H, H_8), 7.30 (s, 1H, H_2), 7.16 (dd, J = 10.4, 1.6 Hz, 1H, H_5), 7.07 (dd, J = 10.4, 1.6 Hz, 1H, H_7), 7.03 (d, J = 8.8 Hz, 4H, $H_{2',6'}$), 6.79 (d, J = 8.8 Hz, 4H, $H_{3',5'}$), 5.97 (s, 1H, CH), 3.77 (s, 6H, 4′-OMe), 1.51 (s, 9H, 3-*t*-Bu), and 1.40 (s, 9H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.52 (s, C_6), 157.70 (s, $C_{4'}$), 137.67 (s, $C_{1'}$), 137.57 (s, C_3), 135.97 (d, C_2), 134.91 (s, C_{8a}), 134.61 (d, C_4), 134.07 (s, C_{3a}), 132.29 (d, C_8), 130.04 (s, C_1), 129.99 (d, $C_{2',6'}$), 119.27 (d, C_7), 118.48 (d, C_5), 113.51 (d, $C_{3',5'}$), 55.18 (q, 4′-OMe), 47.98 (d, CH), 38.18 (s, 6-*t*-Bu), 33.22 (s, 3-*t*-Bu), 32.23 (q, 3-*t*-Bu), and 31.80 (q, 6-*t*-Bu). Found: C, 84.18; H, 8.17%. Calcd for $C_{33}H_{38}O_2$: C, 84.94; H, 8.21%.

General Procedure for the Preparation of the Hexafluorophosphates (8·PF_6^-, 9a—d·PF_6^-, and 10a—d·PF_6^-). DDQ was added at room temperature to a solution of tris(6-methoxy-1-azulenyl)methane (**11**), di(1-azulenyl)(4-methoxyphenyl)methanes (**14a—d**), and (1-azulenyl)bis(4-methoxyphenyl)methanes (**15a—d**) in CH_2Cl_2. The solution was stirred at room temperature for 10 min—7 h until the reaction was completed. A 60% aqueous HPF_6 solution was added to the reaction mixture. After stirring at room temperature for an additional 5 min, water was added to the mixture. The resulting suspension was filtered with suction. The organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (3—5 ml) and then ether (50—100 ml) was added to the solution. The precipitated crystals were collected by filtration, washed with ether, and dried in vacuo to give the hexafluorophosphates **8**·PF_6^-, **9a—d**·PF_6^-, and **10a—c**·PF_6^-. The product was further purified by recrystallization from CH_2Cl_2/ether.

Tris(6- methoxy- 1- azulenyl)methyl Hexafluorophosphate (8·PF_6^-). The general procedure was followed using DDQ (29 mg, 0.13 mmol), tris(6-methoxy-1-azulenyl)methane (**11**) (49 mg, 0.10 mmol), and 60% HPF_6 (2 ml) in CH_2Cl_2 (20 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **8**·PF_6^- (58 mg, 91%). Brown powder; mp 206.0—208.0 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 682 (M^+) and 483 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1582, 1460, 1372, 1277, 1204, 1173, 839, 710, and 558 cm^{-1}; ES (MeCN) λ_{max}, nm (log ϵ) 228 (4.65), 297 (4.66), 337 (4.62), 430 (4.09), and 620 (4.87); ^{1}H NMR (600 MHz, DMSO-d_6, 80 °C) δ = 8.83 (d, J = 11.1 Hz, 3H, H_4), 7.75 (d, J = 11.2 Hz, 3H, H_8), 7.73 (d, J = 4.3 Hz, 3H, H_3), 7.67 (d, J = 4.3 Hz, 3H, H_2), 7.62 (dd, J = 11.1, 4.3 Hz, 3H, H_5), 7.18 (dd, J = 11.2, 4.3 Hz, 3H, H_7), and 4.10 (s, 9H, 6-OMe); ^{13}C NMR (150 MHz, DMSO-d_6, 80 °C) δ = 170.60 (s, C_6), 156.31 (s, C^+), 145.28 (s, C_{3a}), 140.53 (d, C_2), 139.93 (d, C_4), 139.85 (s, C_{8a}), 137.40 (d, C_8), 133.00 (s, C_1), 123.66 (d, C_3), 119.20 (d, C_5), 117.52 (d, C_7), and 56.78 (q, 6-OMe). Found: C, 64.55; H, 4.64%. Calcd for $C_{34}H_{28}O_3$·PF_6: C, 64.97; H, 4.33%.

Bis(6-methoxy-1-azulenyl)(4-methoxyphenyl)methyl Hexafluorophosphate (9a·PF_6^-). The general procedure was followed using DDQ (55 mg, 0.24 mmol), bis(6-methoxy-1-azulenyl)(4-methoxyphenyl)methane (**14a**) (87 mg, 0.20 mmol), and 60% HPF_6 (2 ml) in CH_2Cl_2 (20 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **9a**·PF_6^- (109 mg, 94%). Brown powder; mp 204.0—205.5 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 578 (M^+) and 433 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1599, 1466, 1375, 1264, 1208, 841, and 558 cm^{-1}; ES (MeCN) λ_{max}, nm (log ϵ) 224 (4.60), 250 (4.52), 278 (4.40), 304 (4.60), 345 (4.39), 423 (4.30), 472 (4.25), and 624 (4.83); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.57 (d, J = 11.2 Hz, 2H, H_4), 7.74 (d, J = 11.2 Hz, 2H, H_8), 7.55 (d, J = 4.6 Hz, 2H, H_2), 7.51 (dd, J = 11.2, 2.9 Hz, 2H, H_5), 7.49 (d, J = 4.6 Hz, 2H, H_3), 7.36 (d, J = 8.6 Hz, 2H, $H_{2',6'}$), 7.09 (d, J = 8.6 Hz, 2H, $H_{3',5'}$), 7.05 (dd, J = 11.2, 2.9 Hz, 2H, H_7), 4.04 (s, 6H, 6-OMe), and 4.00 (s, 3H, 4′-OMe); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.11 (s, C_6), 164.80 (s, $C_{4'}$), 164.25 (s, C^+), 148.23 (s, C_{3a}), 142.27 (s, C_{8a}), 141.90 (d, C_2), 140.74 (d, C_4), 139.14 (d, C_8), 137.80 (d, $C_{2',6'}$), 133.92 (s, C_1), 125.85 (d, C_3), 122.18 (d, C_5), 119.08 (d, C_7), 114.87 (d, $C_{3',5'}$), 57.31 (q, 6-OMe), and 55.98 (q, 4′-OMe). Found: C, 62.59; H, 4.59%. Calcd for $C_{30}H_{25}O_3$·PF_6: C, 62.29; H, 4.36%.

Di(1- azulenyl)(4- methoxyphenyl)methyl Hexafluorophosphate (9b·PF_6^-). The general procedure was followed using DDQ (136 mg, 0.599 mmol), di(1-azulenyl)(4-methoxyphenyl)-methane (**14b**) (187 mg, 0.499 mmol), and 60% HPF_6 (5 ml) in CH_2Cl_2 (50 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **9b**·PF_6^- (169 mg, 65%). Brown powder; mp 139.0—141.5 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 518 (M^+) and 373 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1597, 1468, 1377, 1312, 1277, 1169, 841, and 558 cm^{-1}; ES (MeCN) λ_{max}, nm (log ϵ) 228 (4.66), 287 (4.53), 385 (4.15), 494 (4.27), and 626 (4.52); ^{1}H NMR (600 MHz, $CDCl_3$, 50 °C) δ = 8.76 (d, J = 9.8 Hz, 2H, H_4), 8.07 (dd, J = 9.8, 9.8 Hz, 2H, H_6), 7.94 (dd, J = 9.8, 9.8 Hz, 2H, H_5), 7.93 (d, J = 9.9 Hz, 2H, H_8), 7.88 (d, J = 4.5 Hz, 2H, H_2), 7.69 (d, J = 4.5 Hz, 2H, H_3), 7.55 (dd, J = 9.9, 9.8 Hz, 2H, H_7), 7.36 (d, J = 8.6 Hz, 2H, $H_{2',6'}$), 7.12 (d, J = 8.6 Hz, 2H, $H_{3',5'}$), and 3.99 (s, 3H, 4′-OMe); ^{13}C NMR (150 MHz, $CDCl_3$, 50 °C) δ = 165.57 (s, $C_{4'}$), 165.43 (s, C^+), 153.42 (s, C_{3a}), 147.74 (s, C_{8a}), 146.44 (d, C_2), 143.45 (d, C_6), 141.42 (d, C_4), 139.47 (d, C_8), 138.13 (d, $C_{2',6'}$), 134.82 (d, C_5), 133.96 (d, C_7), 133.66 (s, $C_{1'}$), 133.05 (s, C_1), 125.96 (d, C_3), 115.35 (d, $C_{3',5'}$), and 56.09 (q, 4′-OMe). Found: C, 64.69; H, 3.96%. Calcd for $C_{28}H_{21}O$·PF_6: C, 64.87; H, 4.08%.

Bis(3- methyl- 1- azulenyl)(4- methoxyphenyl)methyl Hexafluorophosphate (9c·PF_6^-). The general procedure was followed using DDQ (136 mg, 0.599 mmol), bis(3-methyl-1-azulenyl)(4-methoxyphenyl)methane (**14c**) (201 mg, 0.499 mmol), and 60% HPF_6 (5 ml) in CH_2Cl_2 (50 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **9c**·PF_6^- (253 mg, 93%). Purple powder; mp 185.5—188.0 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 546 (M^+) and 401 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1480, 1433, 1406, 1341, 1314, 1266, 839, and 558 cm^{-1}; ES (MeCN) λ_{max}, nm (log ϵ) 234 (4.64), 293 (4.51), 400 (4.27), 511 (4.19), and 663 (4.52); ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ = 8.64 (d, J = 9.3 Hz, 2H, H_4), 8.02 (dd, J = 9.8, 9.8 Hz, 2H, H_6), 7.92 (dd, J = 9.8, 9.3 Hz, 2H, H_5), 7.82 (d, J = 9.9 Hz, 2H, H_8), 7.73 (s, 2H, H_2), 7.46 (dd, J = 9.9, 9.8 Hz, 2H, H_7), 7.34 (d, J = 8.7 Hz, 2H, $H_{2',6'}$), 7.11 (d, J = 8.7 Hz, 2H, $H_{3',5'}$), 4.00 (s, 3H, 4′-OMe), and 2.69 (s, 6H, 3-Me); ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ = 164.92 (s, $C_{4'}$), 161.95 (s, C^+), 151.21 (s, C_{3a}), 148.44 (s, C_{8a}), 145.75 (d, C_2), 143.07 (d, C_6), 138.90 (d, C_8), 138.25 (d, C_4), 137.69 (d,

$C_{2',6'}$), 134.68 (s, C_3), 134.09 (s, C1′), 133.86 (d, C_5), 133.71 (d, C_7), 131.91 (s, C_1), 115.12 (d, $C_{3',5'}$), 56.01 (q, 4′-OMe), and 12.84 (q, 3-Me). Found: C, 66.38; H, 4.85%. Calcd for $C_{30}H_{25}O{\cdot}PF_6$: C, 65.94; H, 4.61%.

Bis(3, 6- di- *t*- butyl- 1- azulenyl)(4- methoxyphenyl)methyl Hexafluorophosphate (9d·PF$_6^-$). The general procedure was followed using DDQ (136 mg, 0.599 mmol), bis(3,6-di-*t*-butyl-1-azulenyl)(4-methoxyphenyl)methane (**14d**) (300 mg, 0.501 mmol), and 60% HPF_6 (5 ml) in CH_2Cl_2 (50 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **9d**·PF_6^- (172 mg, 46%). Purple powder; mp 184.0—186.5 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 742 (M^+) and 597 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 2963, 1597, 1474, 1439, 1418, 1368, 1337, 1310, 1262, 1240, 1175, 841, and 558 cm^{-1}; ES (MeCN) λ_{max}, nm (log ϵ) 234 (4.67), 253 (4.63), 302 (4.60), 398 (4.30), 502 (4.20), and 668 (4.64); ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ = 9.03 (d, *J* = 11.0 Hz, 2H, H_4), 8.11 (dd, *J* = 11.0, 1.9 Hz, 2H, H_5), 7.85 (d, *J* = 10.8 Hz, 2H, H_8), 7.61 (dd, *J* = 10.8, 1.9 Hz, 2H, H_7), 7.60 (s, 2H, H_2), 7.39 (d, *J* = 8.4 Hz, 2H, $H_{2',6'}$), 7.15 (d, *J* = 8.4 Hz, 2H, $H_{3',5'}$), 4.04 (s, 3H, 4′-OMe), 1.58 (s, 18H, 3-*t*-Bu), and 1.46 (s, 18H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$, 50 °C) δ = 168.67 (s, C_6), 164.81 (s, $C_{4'}$), 161.67 (s, C^+), 148.52 (s, C_{3a}), 148.26 (s, C_{8a}), 146.80 (s, C_3), 143.01 (d, C_2), 139.04 (d, C_4), 138.28 (d, C_8), 137.24 (d, $C_{2',6'}$), 133.67 (s, $C_{1'}$), 131.49 (d, C_5), 131.33 (s, C_1), 131.14 (d, C_7), 115.15 (d, $C_{3',5'}$), 56.06 (q, 4′-OMe), 39.36 (s, 6-*t*-Bu), 33.33 (s, 3-*t*-Bu), 31.57 (q, 6-*t*-Bu), and 31.26 (q, 3-*t*-Bu). Found: C, 73.07; H, 7.66%. Calcd for $C_{44}H_{53}O{\cdot}PF_6$: C, 71.14; H, 7.19%.

(6-Methoxy-1-azulenyl)bis(4-methoxyphenyl)methyl Hexafluorophosphate (10a·PF$_6^-$). The general procedure was followed using DDQ (137 mg, 0.604 mmol), (6-methoxy-1-azulenyl)-bis(4-methoxyphenyl)methane (**15a**) (193 mg, 0.502 mmol), and 60% HPF_6 (5 ml) in CH_2Cl_2 (50 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **10a**·PF_6^- (243 mg, 92%). Brown powder; mp 104.0—106.0 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 383 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1592, 1489, 1412, 1377, 1308, 1287, 1267, 1215, 1171, 1127, 839, and 558 cm^{-1}; ES (MeCN) λ_{max}, nm (log ϵ) 223 (4.49), 296 (4.54), 352 (4.02), 421 (4.18), and 535 (4.34); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.66 (d, *J* = 11.2 Hz, 1H, H_4), 7.97 (d, *J* = 11.2 Hz, 1H, H_8), 7.83 (dd, *J* = 11.2, 2.7 Hz, 1H, H_5), 7.57 (d, *J* = 4.9 Hz, 1H, H_2), 7.53 (d, *J* = 4.9 Hz, 1H, H_3), 7.46 (dd, *J* = 11.2, 2.7 Hz, 1H, H_7), 7.40 (d, *J* = 8.8 Hz, 2H, $H_{2',6'}$), 7.31 (d, *J* = 8.8 Hz, 2H, $H_{2'',6''}$), 7.13 (d, *J* = 8.8 Hz, 2H, $H_{3'',5''}$), 7.12 (d, *J* = 8.8 Hz, 2H, $H_{3',5'}$), 4.16 (s, 3H, 6-OMe), 4.02 (s, 3H, 4″-OMe), and 3.99 (s, 3H, 4′-OMe); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 174.16 (s, C_6), 172.17 (s, C^+), 166.06 (s, $C_{4''}$), 165.33 (s, $C_{4'}$), 153.43 (s, C_{3a}), 145.73 (s, C_{8a}), 143.20 (d, C_2), 141.63 (d, C_4), 141.52 (d, C_8), 138.80 (d, $C_{2',6'}$), 137.95 (d, $C_{2'',6''}$), 136.38 (s, C_1), 133.02 (s, $C_{1'}$), 131.71 (s, $C_{1''}$), 129.72 (s, C_3), 128.36 (s, C_5), 122.49 (s, C_7), 115.45 (d, $C_{3'',5''}$), 114.91 (d, $C_{3',6'}$), 58.10 (q, 6-OMe), 56.14 (q, 4″-OMe), and 56.02 (q, 4′-OMe). Found: C, 59.04; H, 4.73%. Calcd for $C_{26}H_{23}O_3{\cdot}PF_6$: C, 59.10; H, 4.39%.

(1-Azulenyl)bis(4-methoxyphenyl)methyl Hexafluorophosphate (10b·PF$_6^-$). The general procedure was followed using DDQ (273 mg, 1.20 mmol), (1-azulenyl)bis(4-methoxyphenyl)-methane (**15b**) (354 mg, 1.00 mmol), and 60% HPF_6 (10 ml) in CH_2Cl_2 (100 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **10b**·PF_6^- (420 mg, 84%). Reddish purple crystals; mp 170.0—171.0 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 498 (M^+) and 353 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1589, 1489, 1393, 1348, 1310, 1269, 1266, 1171, 837, and 558 cm^{-1}; ES (MeCN) λ_{max}, nm (log ϵ) 222 (4.49), 266 (4.26), 277 (4.26), 290 (4.28), 328 (3.90), 404 (4.19), 443 (4.35), and 544 (4.56); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.88 (d, *J* = 9.6 Hz, 1H, H_4), 8.34 (dd, *J* = 9.6, 9.6 Hz, 1H, H_6), 8.26 (dd, *J* = 9.6, 9.6 Hz, 1H, H_5), 8.16 (d, *J* = 9.8 Hz, 1H, H_8), 7.97 (dd, *J* = 9.8, 9.6 Hz, 1H, H_7), 7.95 (d, *J* = 4.7 Hz, 1H, H_2), 7.77 (d, *J* = 4.7 Hz, 1H, H_3), 7.45 (d, *J* = 8.6 Hz, 2H, $H_{2'',6''}$), 7.35 (d, *J* = 8.5 Hz, 2H, $H_{2',6'}$), 7.17 (d, 2H, *J* = 8.6 Hz, $H_{3'',5''}$), 7.14 (d, *J* = 8.5 Hz, 2H, $H_{3',5'}$), 4.03 (s, 3H, 4′-OMe), and 4.01 (s, 3H, 4″-OMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 174.34 (s, C^+), 166.67 (s, $C_{4'}$), 166.20 (s, $C_{4''}$), 157.80 (s, C_{3a}), 151.68 (s, C_{8a}), 147.73 (d, C_2), 145.41 (d, C_6), 142.46 (d, C_4), 141.47 (d, C_8), 139.57 (d, $C_{2'',6''}$), 139.37 (d, C_5), 138.58 (d, $C_{2',6'}$), 137.89 (d, C_7), 135.00 (s, C_1), 132.89 (s, $C_{1''}$), 131.75 (s, $C_{1'}$), 129.41 (s, C_3), 115.66 (d, $C_{3',5'}$), 115.35 (d, $C_{3'',5''}$), 56.28 (q, 4′-OMe), and 56.21 (q, 4″-OMe). Found: C, 60.07; H, 4.19%. Calcd for $C_{25}H_{21}O{\cdot}PF_6$: C, 60.25; H, 4.25%.

(3-Methyl-1-azulenyl)bis(4-methoxyphenyl)methyl Hexafluorophosphate (10c·PF$_6^-$). The general procedure was followed using DDQ (268 mg, 1.18 mmol), (3-methyl-1-azulenyl)-bis(4-methoxyphenyl)methane (**15c**) (362 mg, 0.982 mmol), and 60% HPF_6 (10 ml) in CH_2Cl_2 (100 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **10c**·PF_6^- (426 mg, 85%). Purple powder; mp 99.5—104.0 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 512 (M^+) and 367 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1590, 1489, 1422, 1358, 1267, 1171, 1067, 839, and 558 cm^{-1}; ES (MeCN) λ_{max}, nm (log ϵ) 229 (4.47), 270 (4.27), 337 (3.88), 413 (4.23), 437 (4.23), and 554 (4.41); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.78 (m, 1H, H_4), 8.32 (m, 2H, $H_{5,6}$), 8.09 (d, *J* = 9.9 Hz, 1H, H_8), 7.94 (m, 1H, H_7), 7.78 (s, 1H, H_2), 7.42 (d, *J* = 8.9 Hz, 2H, $H_{2'',6''}$), 7.29 (d, *J* = 8.9 Hz, 2H, $H_{2',6'}$), 7.15 (d, *J* = 8.9 Hz, 2H, $H_{3'',5''}$), 7.11 (d, *J* = 8.9 Hz, 2H, $H_{3',5'}$), 4.01 (s, 3H, 4′-OMe), 4.00 (s, 3H, 4″-OMe), and 2.66 (s, 3H, 3-Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.06 (s, C^+), 166.06 (s, $C_{4'}$), 165.54 (s, $C_{4''}$), 156.88 (s, C_{3a}), 153.12 (s, C_{8a}), 146.52 (d, C_2), 145.23 (d, C_6), 141.05 (d, C_8), 139.57 (d, C_5), 139.55 (d, C_4), 138.91 (d and s, $C_{2'',6''}$ and C_3), 138.35 (d, C_7), 138.07 (d, $C_{2',6'}$), 134.08 (s, C_1), 132.98 (s, $C_{1''}$), 131.93 (s, $C_{1'}$), 115.44 (d, $C_{3',5'}$), 115.19 (d, $C_{3'',5''}$), 56.16 (q, 4′-OMe), 56.10 (q, 4″-OMe), and 13.05 (q, 3-Me). Found: C, 61.51; H, 4.58%. Calcd for $C_{26}H_{23}O_2{\cdot}PF_6$: C, 60.94; H, 4.52%.

(3, 6- Di- *t*- butyl- 1- azulenyl)bis(4- methoxyphenyl)methyl Hexafluorophosphate (10d·PF$_6^-$). The general procedure was followed using DDQ (273 mg, 1.20 mmol), (3,6-di-*t*-butyl-1-azulenyl)bis(4-methoxyphenyl)methane (**15d**) (467 mg, 1.00 mmol), and 60% HPF_6 (10 ml) in CH_2Cl_2 (100 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **10d**·PF_6^- (571 mg, 93%). Reddish brown powder; mp 223.0—228.0 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 610 (M^+) and 465 ($M^+ - PF_6$); IR (KBr) ν_{max} 1593, 1497, 1352, 1310, 1269, 1262, 1173, 839, and 558 cm^{-1}; ES (MeCN) λ_{max}, nm (log ϵ) 230 (4.51), 273 (4.37), 302 (4.29), 339 (4.03), 417 (4.35), and 549 (4.50); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.15 (d, *J* = 11.0 Hz, 1H, H_4), 8.51 (dd, *J* = 11.0, 2.0 Hz, 1H, H_5), 8.13 (d, *J* = 10.8 Hz, 1H, H_8), 8.02 (dd, *J* = 10.8, 2.0 Hz, 1H, H_7), 7.66 (s, 1H, H_2), 7.39 (d, *J* = 8.8 Hz, 2H, $H_{2'',6''}$), 7.31 (d, *J* = 8.8 Hz, 2H, $H_{2',6'}$), 7.15 (d, *J* = 8.8 Hz, 2H, $H_{3'',5''}$), 7.13 (d, *J* = 8.8 Hz, 2H, $H_{3',5'}$), 4.02 (s, 3H, 4′-OMe), 4.00 (s, 3H, 4″-OMe), 1.58 (s, 9H, 3-*t*-Bu), and 1.51 (s, 9H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.87 (s, C_6), 170.31 (s, C^+), 165.80 (s, $C_{4'}$), 165.18 (s, $C_{4''}$), 154.77 (s, C_{3a}), 153.11 (s, C_{8a}), 151.01 (s, C_3), 143.24 (d, C_2), 140.40 (d, C_8), 140.24 (d, C_4), 138.52 (d, $C_{2'',6''}$), 137.88 (d, C_5), 137.81 (d, $C_{2',6'}$), 135.99 (d, C_7), 133.88 (s, C_1), 133.16 (s, $C_{1''}$), 132.08 (s, $C_{1'}$), 115.39 (d, $C_{3',5'}$), 115.02 (d, $C_{3'',5''}$), 56.17 (q, 4′-OMe), 56.03 (q, 4″-OMe), 39.90 (s, 6-*t*-Bu), 33.27 (s, 3-*t*-Bu), 31.42 (q, 6-*t*-Bu), and 30.37 (q, 3-*t*-Bu). Found: C, 64.98; H,

5.88%. Calcd for $C_{33}H_{37}O_2 \cdot PF_6$: C, 64.91; H, 6.11%.

The pK_{R^+} Value. The sample solutions of the hexafluorophosphates **8**·PF_6^-, **9a—d**·PF_6^-, and **10a**·PF_6^- were prepared by dissolving in a glycine (0.1 M) solution (50 ml) and made up to 100 ml by adding MeCN; the sample solution with lower acidity was made by further alkalification with 20% aqueous NaOH. For the preparation of a sample solution of the hexafluorophosphates **10b—d**·PF_6^-, buffer solutions of slightly different acidities were prepared by mixing CH_3COONa (1 M) and HCl (1M) for pH 1.0—2.0, CH_3COONa (0.1 M) and CH_3COOH (0.1 M) for pH 3.2—5.0, KH_2PO_4 (0.1 M) and $Na_2B_4O_7$ (0.05 M) for pH 6.0—9.0, $Na_2B_4O_7$ (0.05 M) and Na_2CO_3 (0.05 M) for pH 10.0, and $Na_2B_4O_7$ (0.05 M) and NaOH (0.1 M) for pH 11.0—11.4, in various portions. Each 1 ml portion of the stock solution, prepared by dissolving 2—3 mg of the hexafluorophosphates **10b—d**·PF_6^- in MeCN (20 ml), was pipetted out and made up to 10 ml by adding an appropriate buffer solution (5 ml) and MeCN. The pH of each sample was made on a Horiba pH meter F-13 calibrated with standard buffers before use. The observed absorbance at the specific absorption maxima in visible region of the cations **8**, **9a—d**, and **10a—d** were plotted against the pH, giving classical titration curves whose midpoints were taken as the pK_{R^+} values.

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