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An efficient preparation, crystal structures, and properties of monocarbenium-ion compounds stabilized by 3-guaiazulenyl and anisyl groups

Shin-ichi Takekuma,[a,*] Masayuki Tamura,[a] Toshie Minematsu[b] and Hideko Takekuma[a]

[a] *Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, 3-4-1 Kowakae, Higashi-Osaka-shi, Osaka 577-8502, Japan*
[b] *School of Pharmaceutical Sciences, Kinki University, 3-4-1 Kowakae, Higashi-Osaka-shi, Osaka 577-8502, Japan*

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Abstract—Reaction of guaiazulene (**1**) with 2-methoxybenzaldehyde (**2**) in methanol in the presence of hexafluorophosphoric acid at 25 °C for 2 h gives (3-guaiazulenyl)(2-methoxyphenyl)methylium hexafluorophosphate (**5a**) in 93% yield. Similarly, reaction of **1** with 3-methoxybenzaldehyde (**3**) or 4-methoxybenzaldehyde (**4**) under the same reaction conditions as for **2** affords (3-guaiazulenyl)(3-methoxyphenyl)methylium hexafluorophosphate (**6**) (91% yield) or (3-guaiazulenyl)(4-methoxyphenyl)methylium hexafluorophosphate (**7**) (97% yield). The crystal structures as well as the spectroscopic, electrochemical, and chemical properties of these monocarbenium-ion compounds, possessing interesting resonance forms, stabilized by the 3-guaiazulenyl and anisyl (i.e., 2-, 3-, or 4-methoxyphenyl) groups are reported.

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1. Introduction

In the previous papers,[1–15] we reported a facile preparation and the crystal structures as well as the spectroscopic, electrochemical, and chemical properties of the delocalized mono- and dicarbenium-ion compounds stabilized by the expanded π-electron systems possessing a 3-guaiazulenyl (or azulen-1-yl) group. During the course of our basic and systematic investigations, we recently found that the reaction of **1** with 2- or 4-hydroxybenzaldehyde in methanol in the presence of hexafluorophosphoric acid at 25 °C for 2 h gave the corresponding monocarbenium-ion compound, (3-guaiazulenyl)(2-hydroxyphenyl)methylium hexafluorophosphate (**11**) or (3-guaiazulenyl)-(4-hydroxyphenyl)methylium hexafluorophosphate (**12**), quantitatively, possessing the interesting resonance forms of the 3-guaiazulenylium-ion structure **11′** (or **12′**) and the protonated *o*- (or *p*-) benzoquinonemethide structure **11″** (or **12″**) in acetonitrile (see Chart 1);[9] however, each X-ray crystallographic analysis of **11** and **12** could not be achieved because of difficulty in obtaining a single crystal suitable for that purpose.[16] On the other hand, in 1997 Yamaguchi, Tamura, and Maeda reported the crystal structure of phenolsulfonphthalein possessing a partial structure of the protonated *p*-benzoquinonemethide.[17] Thus, our interest has quite recently been focused on a comparative study on the crystal structures of the (3-guaiazulenyl)(2-methoxyphenyl)methylium-, (3-guaiazulenyl)(3-methoxyphenyl)methylium- and (3-guaiazulenyl)-(4-methoxyphenyl)methylium-ion compounds possessing similar resonance forms (see Chart 2) to those of **11** and **12**. In relation to this study, in 1960 Kirby and Reid reported the preparation of (3-guaiazulenyl)(4-methoxyphenyl)methylium perchlorate;[18] however, nothing has really been documented regarding its accurate spectroscopic data, crystal structure, and other properties. Furthermore, the synthesis, stability, spectroscopic and chemical properties, crystal structures, electrochemical behavior, and theoretical studies (e.g., ab initio calculations, DFT, GIAO-NMR, and NICS) of the azulenium-[19–21] and azulenylium- (and azulenylmethylium-)[22–32] ion compounds and the azulen-1-yl-substituted cation compounds[33–35] have been studied to a considerable extent, and a large number of the results and discussion regarding those cations with delocalized π-electron systems have been well documented. Along with the above investigations including our studies,[1–35] we now wish to report the detailed studies on the title chemistry: namely, an efficient preparation and the crystal structures as well as the spectroscopic, electrochemical, and chemical properties of the target monocarbenium-ion compounds **5a**–**7** (see Chart 2) with a view to a comparative study.

Keywords: Efficient preparation; Electrochemical behavior; Guaiazulene; 2-, 3- and 4-Methoxybenzaldehydes; Monocarbenium-ions; $NaBH_4$-reduction; Spectroscopic properties; X-ray crystal structures.

* Corresponding author. Tel.: +81 6 6730 5880x5222; fax: +81 6 6727 2024; e-mail: takekuma@apch.kindai.ac.jp

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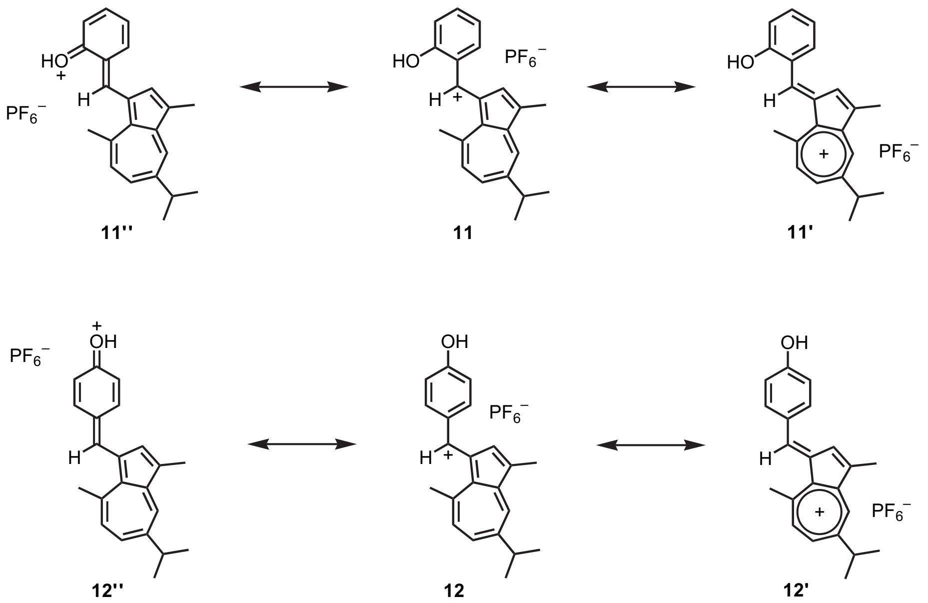

Chart 1.

2. Results and discussion

2.1. Preparation and spectroscopic properties of 5a, 6, and 7

The target compounds **5a**, **6**, and **7** ware prepared according to the procedures shown in Figure 1, Table 1, and Sections 4.1.1, 4.1.3, and 4.1.4. The structures of the products **5a**–**7** were established on the basis of the elemental analysis and the spectroscopic data [UV–vis, IR, exact FABMS, and ^{1}H and ^{13}C NMR including 2D NMR (i.e., H–H COSY, HMQC, and HMBC)].

Compound **5a** (93% yield) was obtained as dark-red blocks (decomp. >120 °C). The UV–vis spectrum showed that the spectral pattern of **5a** was close to that of **11**[9] and, further, the longest absorption wavelength of **5a** (λ_{max} 487 nm, log ε=4.44) (see Fig. 2) coincided with that of **11** (λ_{max}

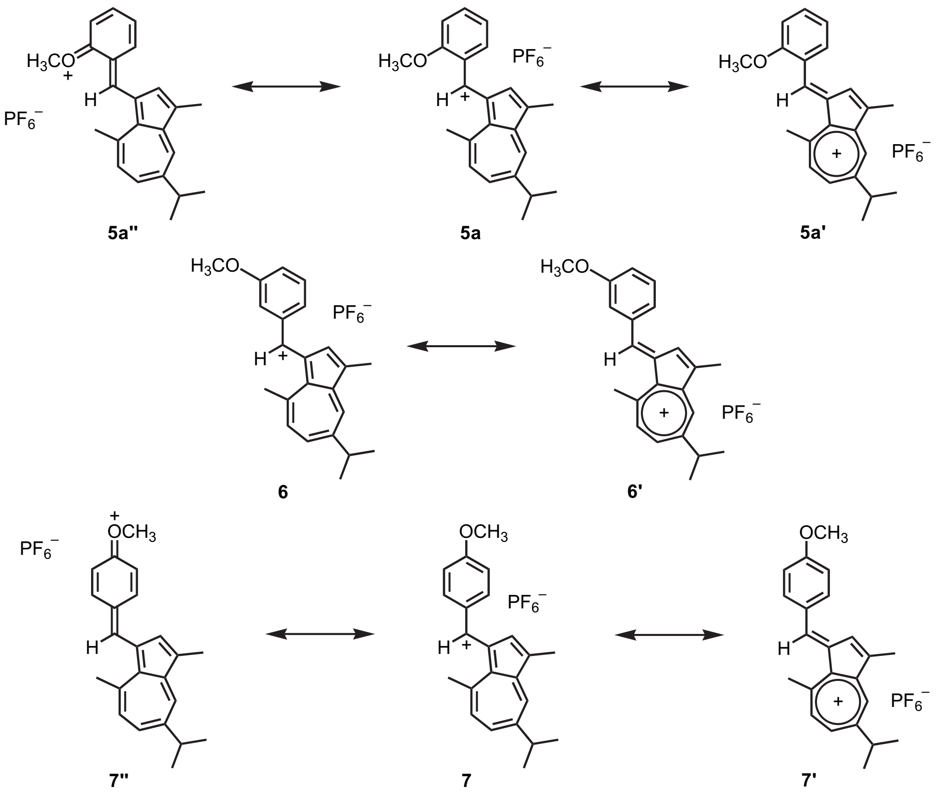

Chart 2.

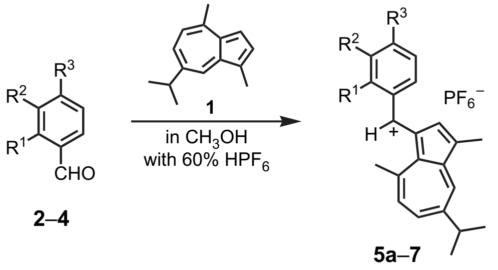

Figure 1. The reactions of **1** with **2–4** in methanol in the presence of hexafluorophosphoric acid at 25 °C for 2 h, affording the corresponding monocarbenium-ion compounds **5a**–**7**.

489 nm, log ε=4.50).[9] The IR spectrum showed that two specific bands (ν_{max} 841 and 559 cm^{-1}) based on the counter anion (PF_6^-) of **5a** coincided with those of **11** (ν_{max} 845 and 559 cm^{-1}).[9] The formula $C_{23}H_{25}O$ for the monocarbenium-ion part ($[M-PF_6]^+$) was determined by the exact FABMS spectrum. An elemental analysis confirmed the formula $C_{138}H_{150}F_{30}O_6P_5$ (i.e., $6C_{23}H_{25}O+5PF_6$). The ^1H NMR spectrum showed signals based on the 3-guaiazulenylmethylium-ion part with a resonance form **5a′** (see Chart 2), and revealed signals based on the 2-methoxyphenyl group with a resonance form **5a″** (see Chart 2), whose signals (δ and J values) were carefully assigned using the H–H COSY technique and the computer-assisted simulation analysis (see Tables 3 and 4 and Sections 4.1 and 4.1.1). The ^{13}C NMR spectrum exhibited 22 carbon signals (δ) assigned by the HMQC and HMBC techniques (see Tables 5 and 6 and Section 4.1.1). Thus, the elemental analysis and the spectroscopic data for **5a** led to the structure, (3-guaiazulenyl)-(2-methoxyphenyl)methylium hexafluorophosphate.

Compound **6** (91% yield) was obtained as red plates (decomp. >130 °C). The UV–vis spectrum showed that, although the spectral pattern of **6** resembled that of **5a**, the longest absorption wavelength of **6** (λ_{max} 466 nm, log ε=4.34) revealed a hypsochromic shift (Δ 21 nm) and a hypochromic effect in comparison with that of **5a** (see Fig. 2). The IR spectrum showed that two specific bands (ν_{max} 841 and 559 cm^{-1}) based on PF_6^- of **6** coincided with those of **5a**. The formula $C_{23}H_{25}O$ for $[M-PF_6]^+$ was determined by the exact FABMS spectrum. An elemental analysis confirmed the formula $C_{230}H_{250}F_{66}O_{10}P_{11}$ (i.e., $10C_{23}H_{25}O+11PF_6$). The ^1H NMR spectrum showed signals based on the 3-guaiazulenylmethylium-ion part with a resonance form **6′** (see Chart 2), and revealed signals based on the 3-methoxyphenylium-ion part, whose signals were carefully assigned using similar techniques to those of **5a** (see Tables 3 and 4 and Section 4.1.3). The ^{13}C NMR spectrum exhibited 22 carbon signals assigned using similar techniques to those of **5a** (see Tables 5 and 6 and Section 4.1.3). Thus, the elemental analysis and the spectroscopic data for **6** led to the structure (3-guaiazulenyl)(3-methoxyphenyl)methylium hexafluorophosphate.

Table 1. The yield (%) of the products **5a**–**7** obtained from the reactions of **1** with **2**–**4** in CH_3OH in the presence of hexafluorophosphoric acid

Entry	Substituent			Temp/°C	Time/h	Product	Yield[a]/%
	R^1	R^2	R^3				
1	OCH_3	H	H	25	2	**5a**	93
2	H	OCH_3	H	25	2	**6**	91
3	H	H	OCH_3	25	2	**7**	97

[a] Isolated yield.

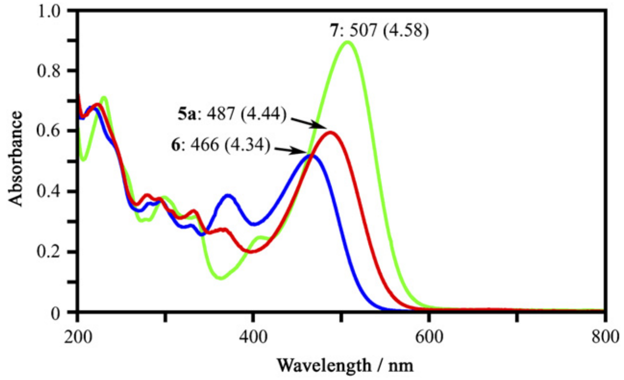

Figure 2. The UV–vis spectra of **5a**, **6**, and **7** in CH_3CN. Concentrations, **5a**: 0.10 g/L (216 μmol/L), **6**: 0.11 g/L (238 μmol/L), and **7**: 0.11 g/L (238 μmol/L). Length of the cell: 0.1 cm each. The log ε values are given in parenthesis.

Compound **7** (97% yield) was obtained as dark-red plates (decomp. >162 °C). The UV–vis spectrum showed that the characteristic spectral pattern of **7** was close to that of **12** and, further, the longest absorption wavelength of **7** (λ_{max} 507 nm, log ε=4.58) coincided with that of **12** (λ_{max} 510 nm, log ε=4.67)[9] (see Fig. 2). The IR spectrum showed that two specific bands (ν_{max} 841 and 556 cm^{-1}) based on PF_6^- of **7** coincided with those of **12** (ν_{max} 837 and 556 cm^{-1}).[9] The formula $C_{23}H_{25}O$ for $[M-PF_6]^+$ was determined by the exact FABMS spectrum. An elemental analysis confirmed the formula $C_{23}H_{25}F_6OP$. The ^1H NMR spectrum showed signals based on the 3-guaiazulenylmethylium-ion part with a resonance form **7′** (see Chart 2), and revealed signals based on the 4-methoxyphenyl group with a resonance form **7″** (see Chart 2), whose signals were carefully assigned using similar techniques to those of **5a** (see Tables 3 and 4 and Section 4.1.4). The ^{13}C NMR spectrum exhibited 20 carbon signals assigned using similar techniques to those of **5a** (see Tables 5 and 6 and Section 4.1.4). Thus, the elemental analysis and the spectroscopic data for **7** led to the structure (3-guaiazulenyl)(4-methoxyphenyl)methylium hexafluorophosphate.

2.2. X-ray crystal structures of 5b, 6, and 7

Although it was very difficult to obtain a single crystal of **5a** suitable for the X-ray crystallographic analysis, each recrystallization of (3-guaiazulenyl)(2-methoxyphenyl)methylium tetrafluoroborate (**5b**) (see Section 4.1.2), **6**, and **7** from a mixed solvent of acetonitrile (or acetone) and diethyl ether provided a single crystal suitable for that purpose. Thus, the crystal structures of **5b**–**7** could be determined by means of X-ray diffraction, producing accurate structural parameters (see Section 4.1.8 for **5b**, Section 4.1.9 for **6**, and Section 4.1.10 for **7**). The ORTEP drawings of **5b**–**7** with the numbering scheme, indicating the structures illustrated in Chart 2, compared with that of **13**[4,5] (see Chart 3) are shown in Figure 3 along with the selected bond lengths (see Tables 7 and 8). As the results, it was found that (i) from the dihedral angles between the least-squares planes, the plane of the

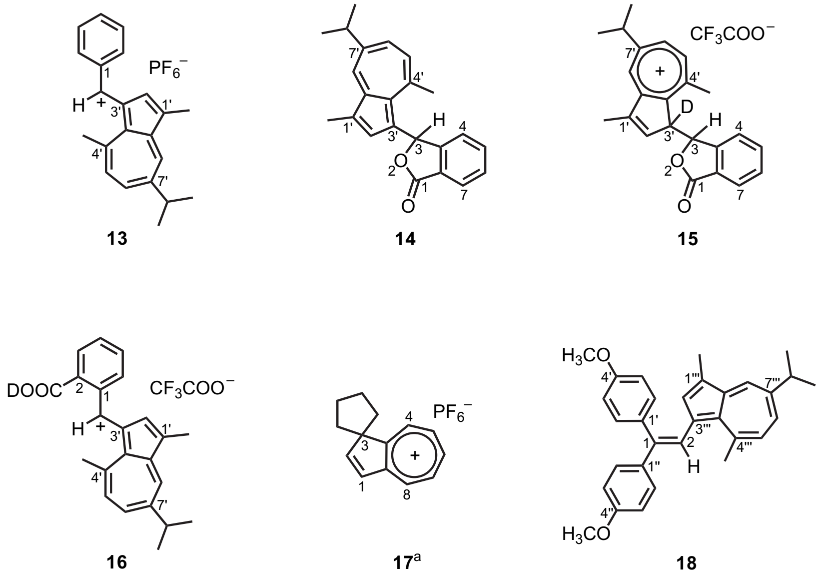

Chart 3. a. For a comparative purpose, the numbering scheme of the 1-azulenium-ion structure of **17**[20] was changed to that of the 3-azulenium-ion structure.

2-methoxyphenyl group of **5b** twisted by 35.4° from that of the 3-guaiazulenyl group, owing to the influence of steric hindrance and repulsion between the hydrogen atoms of the C-6 and C-2′ positions. This result coincided with the dihedral angle between the planes of the 3-methoxyphenyl and 3-guaiazulenyl groups of **6** (35.0°), however, whose angle was larger than those of **7** (22.7°) and **13** (21.3°); (ii) similarly as in the case of **13**, each 3-guaiazulenylmethylium-ion part of **5b–7** clearly underwent bond alternation between the single and double bonds in comparison with those of **8** (see Fig. 7), **18**[8] (see Chart 3), and **19**[9] (see Chart 4), as shown in Table 7; (iii) each methoxyphenyl group of **5b–7**

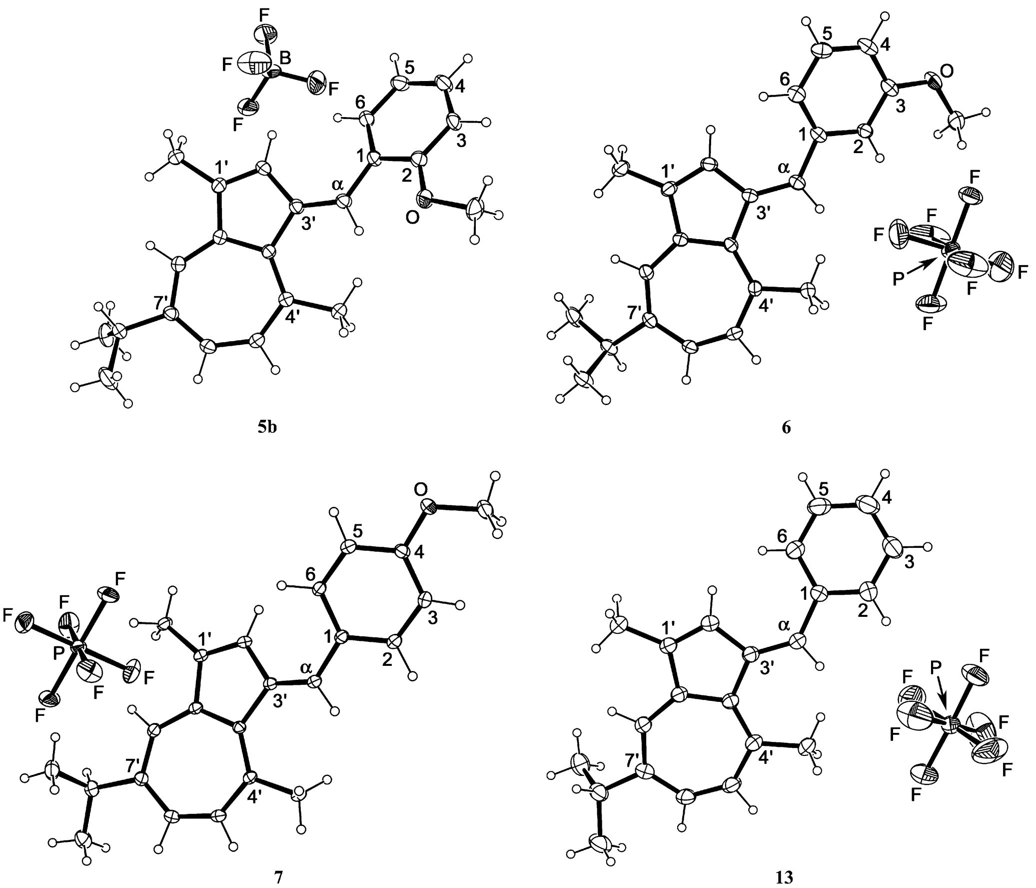

Figure 3. The ORTEP drawings with the numbering scheme (30% probability thermal ellipsoids) of **5b–7** and **13**.

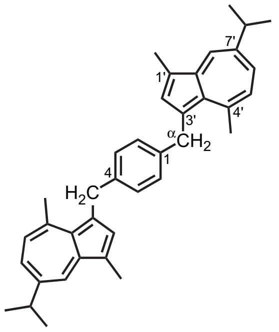

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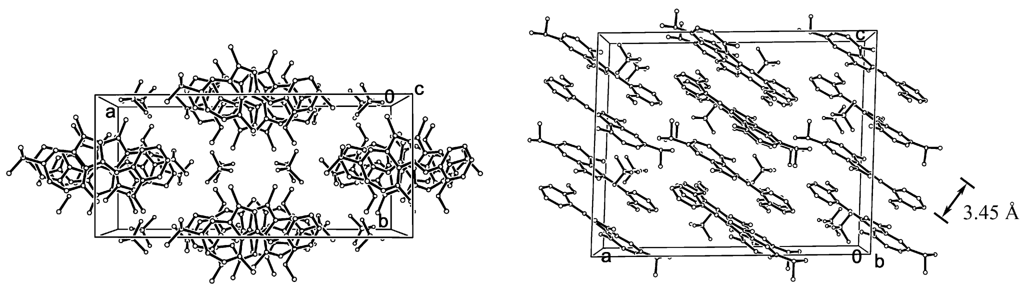
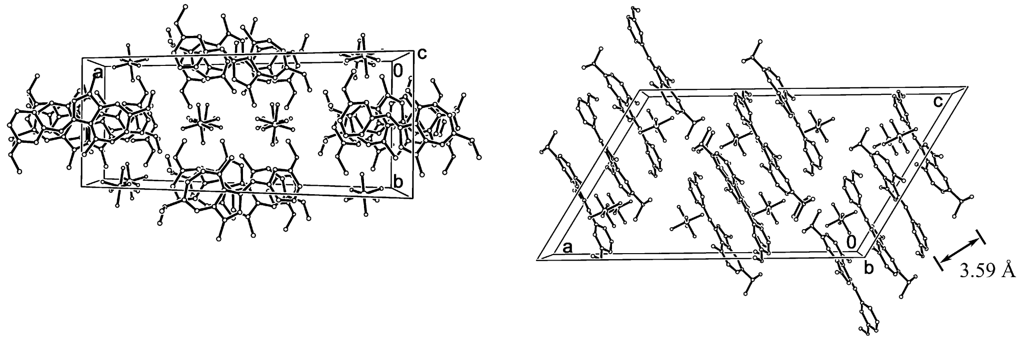
Chart 4.

also clearly underwent bond alternation between the single and double bonds in comparison with those of **8** and **18**, as shown in Table 8 and, further, the bond alternation pattern of the 4-methoxyphenylmethylium-ion part of **7** coincided with that of the protonated *p*-benzoquinonemethide part of phenolsulfonphthalein;[17] (iv) the average bond length for each seven-membered ring of the 3-guaiazulenyl groups of **5b** (1.401 Å), **6** (1.400 Å), and **7** (1.403 Å) coincided with that of **13** (1.401 Å), however, whose average bond lengths were longer than that of azulenium-ion structure **17** (1.379 Å)[20] (see Chart 3); (v) the bond lengths for the five-membered ring of the 3-guaiazulenyl group of **5b** appreciably varied between 1.353 and 1.472 Å; in particular, the C1′–C2′ bond length (1.353 Å) was characteristically



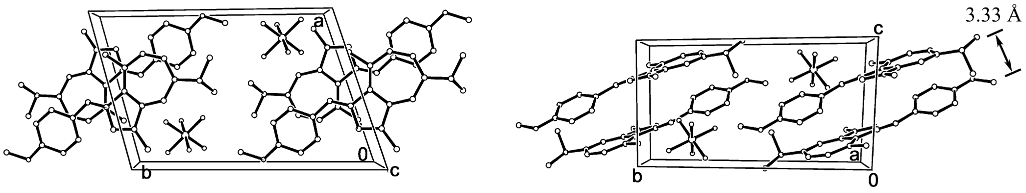
5b: Top view

5b: Side view



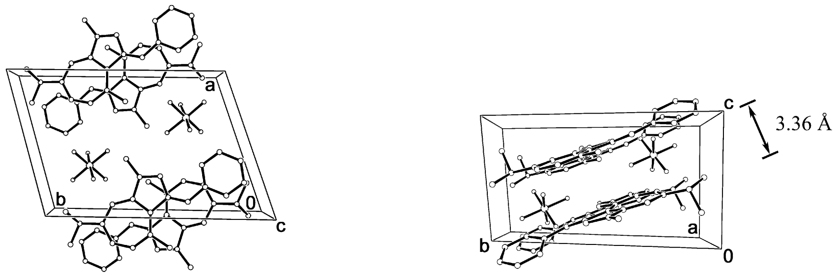
6: Top view

6: Side view



7: Top view

7: Side view



13: Top view

13: Side view

Figure 4. Two different (top and side) views for the packing (molecular) structures of **5b**–**7** and **13**; hydrogen atoms are omitted for reasons of clarity.

shorter than the average bond length for the five-membered ring (1.435 Å), whose bond alternation pattern coincided with those of **6**, **7**, and **13**; (vi) the C3′–Cα bond lengths of **5b** (1.370 Å), **6** (1.371 Å), and **7** (1.364 Å) were also characteristically shorter than the C1–Cα bond lengths of **5b** (1.443 Å), **6** (1.468 Å), and **7** (1.448 Å); (vii) although the C3′–Cα bond lengths of **5b**, **6**, and **7** coincided with that of **13** (1.361 Å), these bond lengths were characteristically shorter than those of **8** (1.507 Å) and **19** (1.503 Å) and the C2–C3‴ bond length of **18** (1.464 Å); (viii) the C1–Cα bond lengths of **5b** (1.443 Å) and **7** (1.448 Å) were shorter than those of **6** (1.468 Å), **13** (1.461 Å), **19** (1.533 Å), and the C1–C1′ (1.487 Å) and C1–C1″ (1.486 Å) bond lengths of **18**; (ix) although the C2–C3 (1.397 Å) and C6–C1 (1.419 Å) bond lengths of **5b** were longer than those of **8** [C2–C3 (1.382 Å) and C6–C1 (1.381 Å)], the C5–C6 bond length (1.376 Å) of **5b** was shorter than that of **8** (1.395 Å); (x) the C2–O bond length (1.353 Å) of **5b** was shorter than that of **8** (1.374 Å) and the C4–O bond length (1.351 Å) of **7** was also shorter than those of **18** (1.373 and 1.375 Å) and, further, the C2–O and C4–O bond lengths of **5b** and **7** were slightly shorter than the C3–O bond length (1.357 Å) of **6**. In conclusion, it can be inferred that the structural parameters based on the X-ray crystallographic analyses of **5b**–**7**, compared with those of **8**, **13**, **17**–**19**, and phenolsulfonphthalein, lead to the crystal structures with the interesting resonance forms illustrated in Chart 2.

Along with the ORTEP drawings of **5b**–**7**, the top and side views for the packing structures of **5b**–**7** revealed that, similarly as in the case of **13**, these molecules formed π-stacking structures in their single crystals, and showed that each average inter-plane distance between the overlapping molecules [i.e., the 3-guaiazulenylmethylium plane of a molecule and the 2-methoxyphenyl (or 3-methoxyphenyl or 4-methoxyphenyl) plane of another molecule], which were overlapped so that those dipole moments might be negated mutually, was 3.45 Å for **5b**, 3.59 Å for **6**, or 3.33 Å for **7** (see Fig. 4).

2.3. Electrochemical behavior of 5a–7

We have been interested further in the electrochemical properties of **5a**–**7** with a view to a comparative study. The electrochemical behavior of **5a**–**7** was, therefore, measured by means of the CV and DPV [potential (in volt) vs SCE] in CH_3CN containing 0.1 M $[n\text{-}Bu_4N]PF_6$ as a supporting electrolyte. As the results, it was found that **5a**–**7** underwent one-electron reduction, respectively, at the potentials of −0.28 V (E_{pc}, irreversible) by CV [−0.25 V (E_p) by DPV] for **5a**, −0.28 V (E_{pc}, irreversible) by CV [−0.22 V (E_p) by DPV] for **6**, and −0.35 V (E_{pc} irreversible) by CV [−0.29 V (E_p) by DPV] for **7**, as shown in Figure 5, generating the corresponding radical species [i.e., (3-guaiazulenyl)(2-methoxyphenyl)methyl, (3-guaiazulenyl)(3-methoxyphenyl)methyl, and (3-guaiazulenyl)(4-methoxyphenyl)methyl radical species]. Thus, **5a** and **6** are slightly susceptible to reduction as compared with **7**, owing to a difference in electron affinity based on each delocalized π-electron system and, further, although **5a** is slightly susceptible to reduction than **11** [−0.34 V (E_{pc}, irreversible) by CV (−0.28 V by DPV)],[9] the reduction potential of **7** coincided with that of **12** [−0.36 V (E_{pc}, irreversible) by CV (−0.31 V by DPV)].[9] In conclusion, the facility of one-electron reduction is in the order of **6**>**5a**>**7**, whose result coincides with the order of the following longest absorption wavelengths (**6**: 466 nm<**5a**: 487 nm<**7**: 507 nm) (see Fig. 2).

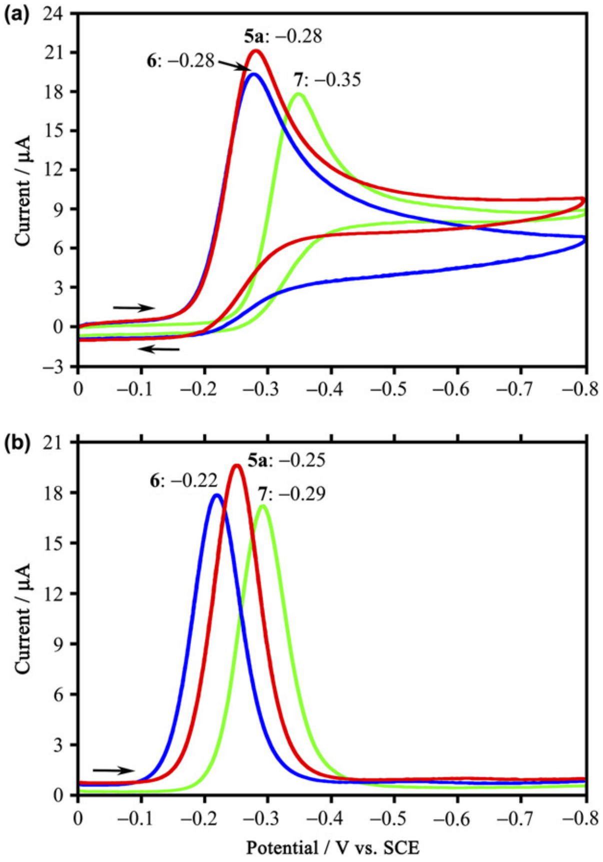


Figure 5. (a) Cyclic and (b) differential pulse voltammograms of **5a** (3.0 mg, 6.5 μmol), **6** (3.0 mg, 6.5 μmol), and **7** (3.0 mg, 6.5 μmol) in 0.1 M $[n\text{-}Bu_4N]PF_6$, CH_3CN (10 mL) at a glassy carbon (ID: 3 mm) and a platinum wire served as the working and auxiliary electrodes; scan rates 100 mV s^{-1} at 25 °C under argon. For comparative purposes, the oxidation potential using ferrocene as a standard material showed +0.42 V (E_p) by DPV and +0.40 V ($E_{1/2}$) by CV under the same electrochemical measurement conditions as for **5a**, **6**, and **7**.

2.4. Reductions of 5a–7 with NaBH₄

The reduction of **5a** with $NaBH_4$ in a mixed solvent of ethanol and acetonitrile at 25 °C for 30 min gave as high as 95% yield of **8** (see Fig. 6 and Table 2), whose product was obtained as blue blocks (mp 108 °C). The molecular formula $C_{23}H_{26}O$ was determined by the exact EIMS spectrum. The

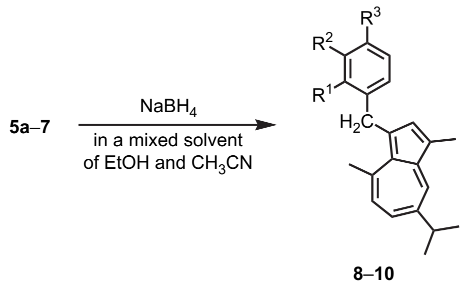


Figure 6. The reactions of **5a**–**7** with $NaBH_4$ in a mixed solvent of ethanol and acetonitrile at 25 °C for 30 min, providing **8**, **9**, and **10**, respectively.

Table 2. The yield (%) of the products **8**–**10** obtained from the reactions of **5a**–**7** with NaBH$_4$ in a mixed solvent of ethanol and acetonitrile

Entry	Substituent			Temp/°C	Time/min	Product	Yield[a]/%
	R^1	R^2	R^3				
1	OCH$_3$	H	H	25	30	**8**	95
2	H	OCH$_3$	H	25	30	**9**	93
3	H	H	OCH$_3$	25	30	**10**	95

[a] Isolated yield.

^{1}H NMR spectrum showed signals based on the 3-guaiazulenylmethyl and 2-methoxyphenyl groups, whose signals were carefully assigned using similar techniques to those of **5a** (see Tables 3 and 4 and Section 4.1.5). The ^{13}C NMR spectrum exhibited 22 carbon signals assigned using similar techniques to those of **5a** (see Tables 5 and 6 and Section 4.1.5). Thus, the spectroscopic data for **8** led to the molecular structure 1-(3-guaiazulenylmethyl)-2-methoxybenzene, in which a hydride-ion attached to the C$^+$-α position of **5a**, selectively. In the previous paper,[13] we submitted that, from comparative studies on the ^{1}H and ^{13}C NMR spectral properties of **16** with those of 1-(3-guaiazulenylmethyl)-2-(methoxycarbonyl)benzene, **14**, and **15**, the positive charge of the 3-guaiazulenylmethylium-ion part of **16** apparently was transferred to the seven-membered ring or the benzene ring, generating a resonance form of the 3-guaiazulenylium- or phenylium-ion structure and, further, the same result could be inferred for **13** (see Chart 3). The chemical shifts for the ^{1}H and ^{13}C NMR signals of **5a** compared with those of **8**, **11**,[9] and **13**–**16**[13] are shown in Tables 3–6, leading to the formation of **5a** with the interesting resonance forms **5a**′ and **5a**″ illustrated in Chart 2.

The reduction of **6** with NaBH$_4$ under the same reaction conditions as for **5a** afforded as high as 93% yield of **9** (see Fig. 6 and Table 2), whose product was a blue paste. The molecular formula $C_{23}H_{26}O$ was determined by the exact EIMS spectrum. The ^{1}H NMR spectrum showed signals based on the 3-guaiazulenylmethyl and 3-methoxyphenyl groups, whose signals were carefully assigned using similar techniques to those of **8** (see Tables 3 and 4 and Section 4.1.6). The ^{13}C NMR spectrum exhibited 22 carbon signals assigned using similar techniques to those of **8** (see Tables 5 and 6 and Section 4.1.6). Thus, the spectroscopic data for **9** led to the molecular structure 1-(3-guaiazulenylmethyl)-3-methoxybenzene, in which a hydride-ion attached to the C$^+$-α position of **6**, selectively. The chemical shifts for the ^{1}H and ^{13}C NMR signals of **6** compared with those of **9** and **13**–**16** are shown in Tables 3–6, leading to the formation of **6** with a resonance form **6**′ illustrated in Chart 2.

Table 4. The ^{1}H NMR chemical shifts (δ, ppm) for the phenyl groups of **5a**–**13** and **16**

Compound	H-2	H-3	H-4	H-5	H-6	CH$_3$O-2	CH$_3$O-3	CH$_3$O-4
5a[a]	—	7.17	7.62	7.18	7.71	3.95	—	—
11[a]	—	7.01	7.46	7.08	7.69	—	—	—
6[a]	7.33	—	7.17	7.52	7.40	—	3.88	—
7[a]	7.90	7.16	—	7.16	7.90	—	—	3.93
12[a]	7.83	7.04	—	7.04	7.83	—	—	—
13[a]	7.82	7.610	7.616	7.610	7.82	—	—	—
16[b]	—	8.40	7.73	7.85	7.54	—	—	—
8[c]	—	6.91	7.16	6.75	6.59	3.88	—	—
9[c]	6.59	—	6.69	7.15	6.62	—	3.72	—
10[c]	6.94	6.78	—	6.78	6.94	—	—	3.74

[a] Measurement solvent: CD$_3$CN.
[b] Measurement solvent: CF$_3$COOD.
[c] Measurement solvent: CD$_2$Cl$_2$.

The reduction of **7** with NaBH$_4$ under the same reaction conditions as for **5a** provided as high as 95% yield of **10** (see Fig. 6 and Table 2), whose product was a blue solid (mp 56 °C). The molecular formula $C_{23}H_{26}O$ was determined by the exact EIMS spectrum. The ^{1}H NMR spectrum showed signals based on the 3-guaiazulenylmethyl and 4-methoxyphenyl groups, whose signals were carefully assigned using similar techniques to those of **8** (see Tables 3 and 4 and Section 4.1.7). The ^{13}C NMR spectrum exhibited 20 carbon signals assigned using similar techniques to those of **8** (see Tables 5 and 6 and Section 4.1.7). Thus, the spectroscopic data for **10** led to the molecular structure 1-(3-guaiazulenylmethyl)-4-methoxybenzene, in which a hydride-ion attached to the C$^+$-α position of **7**, selectively. The chemical shifts for the ^{1}H and ^{13}C NMR signals of **7** compared with those of **10**, **12**,[9] and **13**–**16** are shown in Tables 3–6, leading to the formation of **7** with the interesting resonance forms **7**′ and **7**″ illustrated in Chart 2.

Table 3. The ^{1}H NMR chemical shifts (δ, ppm) for the 3-guaiazulenylmethylium-ion structures of **5a**–**7**, **11**–**13**, and **16**, 3-guaiazulenylmethyl groups of **8**–**10** and **14**, and 3-guaiazulenium-ion structure of **15**

Compound	HC^+-α	Me-1′	H-2′	Me-4′	H-5′	H-6′	$Me_2C\mathit{H}$-7′	$(C\mathit{H}_3)_2CH$-7′	H-8′
5a[a]	9.04	2.51	7.96	3.34	8.51	8.41	3.49	1.45	8.59
11[a]	9.01	2.50	7.98	3.32	8.48	8.39	3.48	1.45	8.57
6[a]	8.74	2.51	7.99	3.36	8.54	8.43	3.50	1.46	8.59
7[a]	8.74	2.53	8.09	3.34	8.45	8.36	3.47	1.45	8.57
12[a]	8.72	2.53	8.08	3.33	8.43	8.37	3.46	1.44	8.56
13[a]	8.78	2.51	7.99	3.37	8.55	8.44	3.50	1.46	8.59
14[a]	7.56[d]	2.46	6.99	3.20	7.22	7.56	3.12	1.35	8.26
15[b]	6.58[d]	2.27	6.50	3.30	8.65	8.58	3.52	1.54	8.63
16[b]	9.47	2.48	7.61	3.45	8.57	8.43	3.49	1.53	8.66
8[c]	4.52[e]	2.60	7.34	2.79	6.80	7.27	3.03	1.35	8.09
9[c]	4.57[e]	2.60	7.39	2.84	6.81	7.27	3.03	1.35	8.09
10[c]	4.53[e]	2.60	7.37	2.84	6.80	7.26	3.02	1.34	8.08

[a] Measurement solvent: CD$_3$CN.
[b] Measurement solvent: CF$_3$COOD.
[c] Measurement solvent: CD$_2$Cl$_2$.
[d] H-3.
[e] 1-CH$_2$-3′.

Table 5. The selected ^{13}C NMR chemical shifts (δ, ppm) for the 3-guaiazulenylmethylium-ion structures of **5a**–**7**, **11**–**13**, and **16**, 3-guaiazulenylmethyl groups of **8**–**10** and **14**, and 3-guaiazulenium-ion structure of **15**

Compound	HC$^+$-α	C-1′	C-2′	C-3′	C-3a′	C-4′	C-5′	C-6′	C-7′	C-8′	C-8a′
5a[a]	146.4	145.6	141.8	139.7	153.6	157.7	150.5	144.9	171.3	139.9	161.4
11[a]	146.2	145.4	141.8	139.2	153.6	157.5	150.3	144.8	170.9	139.8	161.1
6[a]	150.3	146.4	141.5	140.7	153.8	158.2	151.0	145.2	172.2	140.0	161.8
7[a]	151.3	144.9	141.7	137.8	153.4	157.3	149.4	144.5	169.7	139.7	159.9
12[a]	151.7	144.6	141.8	137.3	153.3	157.1	149.1	144.3	169.3	139.6	159.6
13[a]	149.6	145.5	140.6	139.6	152.9	157.3	150.1	144.3	171.2	139.1	160.9
14[a]	80.2[d]	125.8	138.0	121.5	135.6	146.5	129.8	136.6	143.1	135.7	140.1
15[b]	79.5[d]	149.9	145.5	57.4	166.2	159.8	152.2	147.4	179.7	140.7	170.1
16[b]	151.8	146.3	142.1	141.1	154.1	158.4	151.4	145.4	174.5	139.4	164.1
8[c]	30.7[e]	123.9	140.6	125.0	132.8	145.2	125.6	134.3	138.4	132.8	137.5
9[c]	36.7[e]	123.9	140.7	125.1	132.6	145.0	125.8	134.3	138.6	133.0	137.5
10[c]	35.8[e]	123.8	140.6	125.8	132.5	145.0	125.7	134.3	138.5	133.0	137.5

[a] Measurement solvent: CD_3CN.
[b] Measurement solvent: CF_3COOD.
[c] Measurement solvent: CD_2Cl_2.
[d] C-3.
[e] 1-CH_2-3′.

2.5. X-ray crystal structure of 8

Although each X-ray crystallographic analysis of **9** and **10** has not yet been achieved because of difficulty in obtaining a single crystal suitable for that purpose,[36] the crystal structure of **8** has been determined by means of X-ray diffraction, producing accurate structural parameters (see Section 4.1.11), which enabled us to compare with that of **5b** (see Section 2.2). An ORTEP drawing of **8** with the numbering scheme, indicating the molecular structure, 1-(3-guaiazulenylmethyl)-2-methoxybenzene (see Fig. 7a), is shown in Figure 7b. The selected bond lengths of **8** compared with those of **18**[8] and **19**[9] are shown in Tables 7 and 8. As the results, it was found that (i) from the dihedral angles between the least-squares planes, the plane of the 2-methoxyphenyl group of **8** twisted by 89.2° from that of the 3-guaiazulenyl group; (ii) the average bond length for the seven-membered ring of the 3-guaiazulenyl group of **8** (1.409 Å) coincided with those of **18** (1.405 Å) and **19** (1.406 Å); (iii) the bond lengths for the five-membered ring of the 3-guaiazulenyl group of **8** appreciably varied between 1.390 and 1.509 Å; in particular, the C1′–C2′ bond length (1.390 Å) was characteristically shorter than the average bond length (1.427 Å) for the five-membered ring, whose bond alternation pattern coindided with those of **18** and **19**; (iv) the average bond length for the five-membered ring of the 3-guaiazulenyl group of **8** (1.427 Å) coincided with that of **18** (1.427 Å), and was slightly longer than that of **19** (1.419 Å); (v) the average bond length for the benzene ring of the 2-methoxyphenyl group of **8** (1.389 Å) was slightly longer than those of the benzene rings of **18** (1.382 and 1.380 Å) and **19** (1.376 Å); (vi) the C3′–Cα bond length (1.507 Å) of **8** coincided with that of **19** (1.503 Å), however, whose bond length was longer than the C2–C3‴ bond length (1.464 Å) of **18**; (vii) the C1–Cα bond length (1.523 Å) of **8** was longer than the C1–C1′ (1.487 Å) and C1–C1″ (1.486 Å) bond lengths of **18**, however, whose bond length was shorter than that of **19** (1.533 Å); (viii) an apparent difference between the bond lengths of the carbenium-ion compound **5b** and those of **8** was observed (see Tables 7 and 8).

Along with the ORTEP drawing of **8**, the top and side views for the packing structure of **8** are shown in Figure 7c and d.

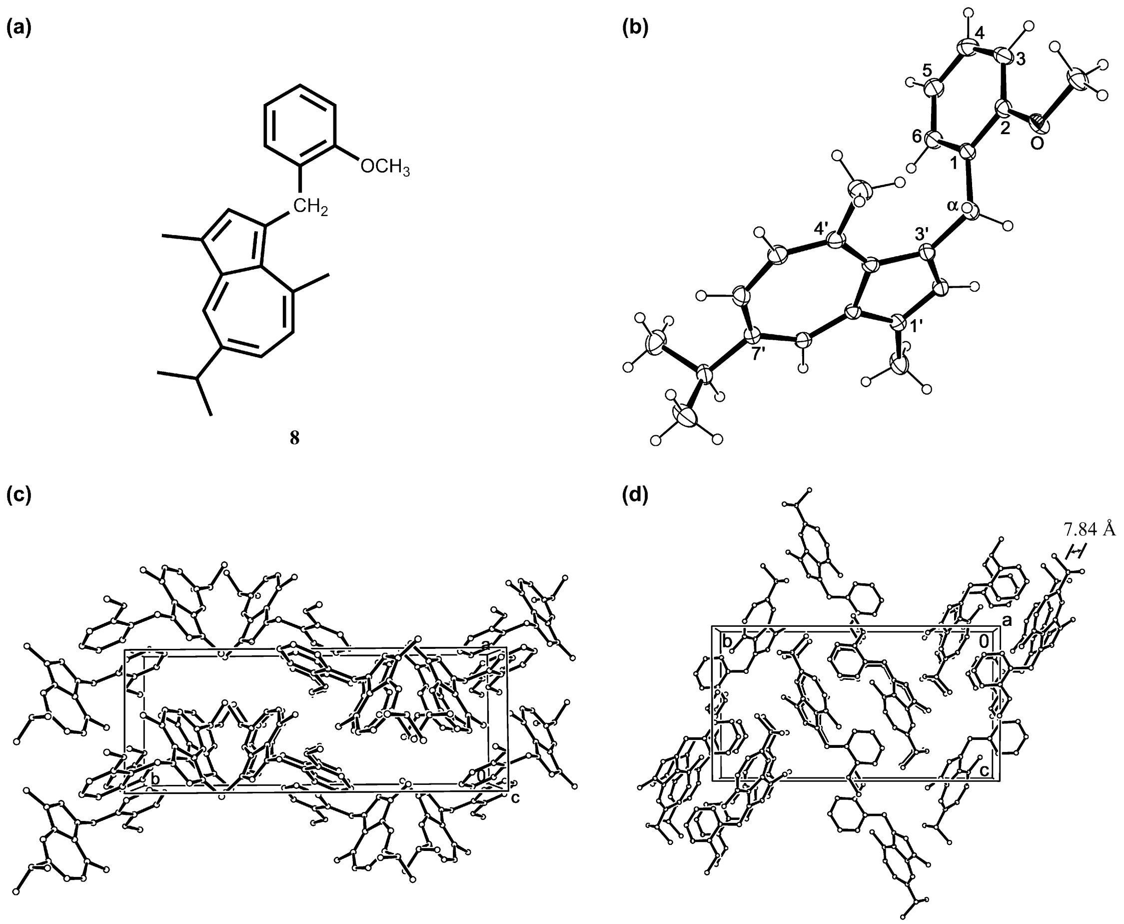
3. Conclusion

We have reported the following seven points in this paper: (i) the reaction of guaiazulene (**1**) with 2-methoxybenzaldehyde (**2**) in methanol in the presence of hexafluorophosphoric acid at 25 °C for 2 h gave as high as 93% yield of (3-guaiazulenyl)(2-methoxyphenyl)methylium hexafluorophosphate (**5a**). Similarly, the reactions of **1** with 3-methoxybenzaldehyde (**3**) and 4-methoxybenzaldehyde (**4**) under the same conditions as the above reaction afforded (3-guaiazulenyl)(3-methoxyphenyl)methylium hexafluorophosphate

Table 6. The ^{13}C NMR chemical shifts (δ, ppm) for the phenyl groups of **5a**–**13** and **16**

Compound	C-1	C-2	C-3	C-4	C-5	C-6	CH_3O-2	CH_3O-3	CH_3O-4
5a[a]	125.5	161.3	112.8	135.6	122.4	134.9	57.0	—	—
11[a]	124.0	159.5	117.2	135.7	122.2	134.7	—	—	—
6[a]	137.8	118.2	161.1	118.9	131.5	126.1	—	56.3	—
7[a]	129.2	137.1	116.4	165.1	116.4	137.1	—	—	56.7
12[a]	128.6	137.6	118.3	163.3	118.3	137.6	—	—	—
13[a]	135.6	132.8	129.5	132.1	129.5	132.8	—	—	—
16[b]	138.8	128.9	133.9	132.3	135.5	134.2	—	—	—
8[c]	131.5	156.4	109.4	126.4	120.0	129.5	55.0	—	—
9[c]	144.8	114.2	159.5	110.2	128.8	120.5	—	54.7	—
10[c]	135.2	128.9	113.3	157.4	113.3	128.9	—	—	54.8

[a] Measurement solvent: CD_3CN.
[b] Measurement solvent: CF_3COOD.
[c] Measurement solvent: CD_2Cl_2.



Top view Side view

Figure 7. (a) The molecular structure of **8**. (b) The ORTEP drawing of **8** (30% probability thermal ellipsoids). Two different [top (c) and side (d)] views for the packing (molecular) structure of **8**; hydrogen atoms are omitted for reasons of clarity.

(**6**) and (3-guaiazulenyl)(4-methoxyphenyl)methylium hexafluorophosphate (**7**) in 91 and 97% yields; (ii) although it was very difficult to obtain a single crystal of **5a** suitable for the X-ray crystallographic analysis, each recrystallization of (3-guaiazulenyl)(2-methoxyphenyl)methylium tetrafluoroborate (**5b**), **6**, and **7** from a mixed solvent of acetonitrile (or acetone) and diethyl ether provided a stable single crystal suitable for that purpose; (iii) the structural parameters based on the X-ray crystallographic analyses of **5b**–**7**, compared with those of **8**, **13**, **17**–**19**, and phenolsulfonphthalein, led to the crystal structures with the interesting resonance forms illustrated in Chart 2; (iv) the reduction potentials of **5a**–**7** based on the CV and DPV data indicated that the facility of one-electron reduction was in the order of

Table 7. The selected C–C bond distances (Å) for the 3-guaiazulenylmethylium-ion structures of **5b**–**7** and **13**, 3-guaiazulenylmethyl groups of **8** and **19**, 3-azulenium-ion structure of **17**, and 3-guaiazulenyl group of **18**

Atom	**5b**	**8**	**6**	**7**	**13**	**17**[a]	**18**	**19**
C1′–C2′	1.353	1.390	1.340	1.353	1.345	1.314	1.382	1.391
C2′–C3′	1.450	1.405	1.443	1.450	1.449	1.496	1.407	1.390
C3′–C3a′	1.472	1.416	1.488	1.485	1.481	1.497	1.416	1.413
C3a′–C4′	1.406	1.394	1.394	1.400	1.398	1.370	1.393	1.391
C4′–C5′	1.415	1.405	1.411	1.415	1.408	1.402	1.390	1.401
C5′–C6′	1.370	1.393	1.380	1.383	1.375	1.372	1.388	1.417
C6′–C7′	1.389	1.388	1.398	1.402	1.393	1.340	1.383	1.394
C7′–C8′	1.388	1.388	1.379	1.391	1.394	1.359	1.384	1.358
C8′–C8a′	1.387	1.387	1.391	1.388	1.389	1.400	1.382	1.375
C8a′–C1′	1.449	1.415	1.457	1.458	1.459	1.432	1.413	1.394
C3a′–C8a′	1.451	1.509	1.445	1.443	1.450	1.412	1.515	1.508
C3′–Cα	1.370	1.507	1.371	1.364	1.361	—	1.464[b]	1.503

[a] For a comparative purpose, the numbering scheme of the 1-azulenium-ion structure of **17**[20] was changed to that of the 3-azulenium-ion structure (see Chart 3).

[b] C2–C3‴.

Table 8. The C–C bond distances (Å) for the 2-methoxyphenyl groups of **5b** and **8**, 3-methoxyphenyl group of **6**, 4-methoxyphenyl groups of **7** and **18**, and phenyl groups of **13** and **19**

Atom	**5b**	**8**	**6**	**7**	**13**	**18**	**19**
C1–C2	1.402	1.405	1.400	1.400	1.393	1.390[a] (1.394)[b]	1.372
C2–C3	1.397	1.382	1.397	1.385	1.384	1.377[a] (1.373)[b]	1.388
C3–C4	1.388	1.389	1.400	1.397	1.380	1.377[a] (1.374)[b]	—
C4–C5	1.383	1.380	1.375	1.398	1.379	1.377[a] (1.376)[b]	—
C5–C6	1.376	1.395	1.392	1.374	1.376	1.382[a] (1.380)[b]	—
C6–C1	1.419	1.381	1.388	1.417	1.407	1.390[a] (1.382)[b]	1.368
C1–Cα	1.443	1.523	1.468	1.448	1.461	1.487[c] (1.486)[d]	1.533
C2–O	1.353	1.374	—	—	—	—	—
C3–O	—	—	1.357	—	—	—	—
C4–O	—	—	—	1.351	—	1.373[a] (1.375)[b]	—
O–CH_3	1.425	1.429	1.427	1.438	—	1.397[a] (1.415)[b]	—

[a] (*Z*)-*p*-$CH_3OC_6H_4$–.

[b] (*E*)-*p*-$CH_3OC_6H_4$–.

[c] C1–C1′.

[d] C1–C1″.

6>**5a**>**7**, whose result coincided with the order of the following longest absorption wavelengths (**6**: 466 nm<**5a**: 487 nm<**7**: 507 nm); (v) the reduction of **5a** with $NaBH_4$ in a mixed solvent of ethanol and acetonitrile at 25 °C for 30 min gave as high as 95% yield of **8**. Similarly, the reductions of **6** and **7** with $NaBH_4$ under the same reaction conditions as for **5a** afforded **9** (93% yield) and **10** (95% yield). Thus, a hydride-ion attached to each C^+-α position of **5a**–**7**, selectively; (vi) the chemical shifts for the ^1H and ^{13}C NMR signals of **5a**–**7** compared with those of **8**–**16** are shown in Tables 3–6, apparently leading to the formation of **5a**–**7** with the interesting resonance forms illustrated in Chart 2; (vii) although each X-ray crystallographic analysis of **9** and **10** could not be achieved because of difficulty in obtaining a single crystal suitable for that purpose, the crystal structure of **8** could be determined by means of X-ray diffraction, producing accurate structural parameters, which enabled us to compare with that of **5b**.

4. Experimental

4.1. General

Thermal (TGA/DTA) and elemental analyses were taken on a Shimadzu DTG-50H thermal analyzer and a Yanaco MT-3 CHN corder, respectively. MS spectra were taken on a JEOL The Tandem Mstation JMS–700 TKM data system. UV–vis and IR spectra were taken on a Beckman DU640 spectrophotometer and a Shimadzu FTIR-4200 Grating spectrometer, respectively. NMR spectra were recorded with JEOL GX-500 (500 MHz for ^1H and 125 MHz for ^{13}C) and JNM-ECA600 (600 MHz for ^1H and 150 MHz for ^{13}C) cryospectrometers at 25 °C. The ^1H NMR spectra were assigned using the computer-assisted simulation analysis (the software: gNMR developed by Adept Scientific plc) on a DELL Dimension XPS T500 personal computer with a Pentium III processor. Cyclic and differential pulse voltammograms were measured by an ALS Model 600 electrochemical analyzer.

4.1.1. Preparation of (3-guaiazulenyl)(2-methoxyphenyl)methylium hexafluorophosphate (5a). To a solution of commercially available guaiazulene (**1**) (70 mg, 0.35 mmol) in methanol (1.0 mL) was added a solution of commercially available 2-methoxybenzaldehyde (**2**) (48 μL, 0.40 mmol) in methanol (1.0 mL) containing hexafluorophosphoric acid (60% aqueous solution, 0.2 mL). The mixture was stirred at 25 °C for 2 h, precipitating a dark-red solid of **5a**, and then was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (1:5, v/v) (several times) to provide pure **5a** as stable single crystals (151 mg, 0.33 mmol, 93% yield).

Compound **5a**: dark-red blocks, mp >120 °C (decomp.) [determined by thermal analysis (TGA and DTA)]. Found: C, 63.11; H, 5.80%. Calcd for $C_{138}H_{150}F_{30}O_6P_5$ ($6C_{23}H_{25}O+5PF_6$): C, 63.03; H, 5.75%; UV–vis λ_{max} (CH_3CN) nm (log ε) 222 (4.50), 279 (4.25), 293sh (4.24), 332 (4.19), 367 (4.10), and 487 (4.44); IR ν_{max} (KBr) cm^{-1}: 841 and 559 (PF_6^-); exact FABMS (3-nitrobenzyl alcohol matrix): found: *m/z* 317.1928; calcd for $C_{23}H_{25}O$: $[M-PF_6]^+$, *m/z* 317.1905; 500 MHz ^1H NMR (CD_3CN): signals based on the 3-guaiazulenylmethylium-ion structure: δ 1.45 (6H, d, J=7.0 Hz, $(CH_3)_2CH$-7′), 2.51 (3H, d, J=0.7 Hz, Me-1′), 3.34 (3H, s, Me-4′), 3.49 (1H, sept, J=7.0 Hz, $(CH_3)_2CH$-7′), 7.96 (1H, br q, J=0.7 Hz, H-2′), 8.41 (1H, dd, J=11.2, 2.3 Hz, H-6′), 8.51 (1H, d, J=11.2 Hz, H-5′), 8.59 (1H, d, J=2.3 Hz, H-8′), and 9.04 (1H, s, HC^+-α); signals based on the 2-methoxyphenyl group: δ 3.95 (3H, s, MeO-2), 7.17 (1H, d, J=8.5 Hz, H-3), 7.18 (1H, dd, J=7.6, 7.5 Hz, H-5), 7.62 (1H, ddd, J=8.5, 7.5, 1.6 Hz, H-4), and 7.71 (1H, dd, J=7.6, 1.6 Hz, H-6); 125 MHz ^{13}C NMR (CD_3CN): δ 171.3 (C-7′), 161.4 (C-8a′), 161.3 (C-2), 157.7 (C-4′), 153.6 (C-3a′), 150.5 (C-5′), 146.4 (HC^+-α), 145.6 (C-1′), 144.9 (C-6′), 141.8 (C-2′), 139.9 (C-8′), 139.7 (C-3′), 135.6 (C-4), 134.9 (C-6), 125.5 (C-1), 122.4 (C-5), 112.8 (C-3), 57.0 (MeO-2), 40.2 ($(CH_3)_2CH$-7′), 29.7 (Me-4′), 23.8 ($(CH_3)_2CH$-7′), and 13.8 (Me-1′).

4.1.2. Preparation of (3-guaiazulenyl)(2-methoxyphenyl)methylium tetrafluoroborate (5b). To a solution of guaiazulene (**1**) (70 mg, 0.35 mmol) in methanol (1.0 mL) was added a solution of 2-methoxybenzaldehyde (**2**) (48 μL, 0.40 mmol) in methanol (1.0 mL) containing tetrafluoroboric acid (42% aqueous solution, 0.2 mL). The mixture was stirred at 25 °C for 2 h, precipitating a dark-red solid of **5b**, and then was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (1:5, v/v) (several times) to provide pure **5b** as stable single crystals (135 mg, 0.34 mmol, 96% yield).

Compound **5b**: dark-red blocks, mp >120 °C (decomp.) [determined by thermal analysis (TGA and DTA)]. Found: C, 68.24; H, 6.26%. Calcd for $C_{23}H_{25}BF_4O$: C, 68.34; H, 6.23%.

4.1.3. Preparation of (3-guaiazulenyl)(3-methoxyphenyl)methylium hexafluorophosphate (6). To a solution of guaiazulene (**1**) (70 mg, 0.35 mmol) in methanol (1.0 mL) was added a solution of commercially available 3-methoxybenzaldehyde (**3**) (49 μL, 0.40 mmol) in methanol (1.0 mL) containing hexafluorophosphoric acid (60% aqueous solution, 0.2 mL). The mixture was stirred at 25 °C for 2 h, precipitating a red solid of **6**, and then was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether, and was recrystallized from acetone–diethyl ether (1:5, v/v) (several times) to provide pure **6** as stable single crystals (147 mg, 0.32 mmol, 91% yield).

Compound **6**: red plates, mp >130 °C (decomp.) [determined by thermal analysis (TGA and DTA)]. Found: C, 58.19; H, 5.08%. Calcd for $C_{230}H_{250}F_{66}O_{10}P_{11}$ ($10C_{23}H_{25}O+11PF_6$): C, 57.92; H, 5.28%; UV–vis λ_{max} (CH_3CN) nm (log ε) 215 (4.46), 283 (4.18), 294 (4.19), 328 (4.08), 370 (4.21), and 466 (4.34); IR ν_{max} (KBr) cm^{-1}: 841 and 559 (PF_6^-); exact FABMS (3-nitrobenzyl alcohol matrix): found: *m/z* 317.1918; calcd for $C_{23}H_{25}O$: $[M-PF_6]^+$, *m/z* 317.1905; 500 MHz ^1H NMR (CD_3CN): signals based on the 3-guaiazulenylmethylium-ion structure: δ 1.46 (6H, d, J=6.9 Hz, $(CH_3)_2CH$-7′), 2.51 (3H, d, J=0.6 Hz, Me-1′), 3.36 (3H, s, Me-4′), 3.50 (1H, sept,

J=6.9 Hz, (CH$_3$)$_2$CH-7′), 7.99 (1H, br q, J=0.6 Hz, H-2′), 8.43 (1H, dd, J=11.2, 2.3 Hz, H-6′), 8.54 (1H, d, J=11.2 Hz, H-5′), 8.59 (1H, d, J=2.3 Hz, H-8′), and 8.74 (1H, s, HC$^+$-α); signals based on the 3-methoxyphenyl group: δ 3.88 (3H, s, MeO-3), 7.17 (1H, ddd, J=8.1, 2.0, 0.7 Hz, H-4), 7.33 (1H, dd, J=2.0, 1.7 Hz, H-2), 7.40 (1H, ddd, J=7.8, 1.7, 0.7 Hz, H-6), and 7.52 (1H, dd, J=8.1, 7.8 Hz, H-5); 125 MHz ^{13}C NMR (CD$_3$CN): δ 172.2 (C-7′), 161.8 (C-8a′), 161.1 (C-3), 158.2 (C-4′), 153.8 (C-3a′), 151.0 (C-5′), 150.3 (HC$^+$-α), 146.4 (C-1′), 145.2 (C-6′), 141.5 (C-2′), 140.7 (C-3′), 140.0 (C-8′), 137.8 (C-1), 131.5 (C-5), 126.1 (C-6), 118.9 (C-4), 118.2 (C-2), 56.3 (MeO-3), 40.3 ((CH$_3$)$_2$$C$H-7′), 29.8 (Me-4′), 23.8 ((CH$_3$)$_2$CH-7′), and 13.8 (Me-1′).

4.1.4. Preparation of (3-guaiazulenyl)(4-methoxyphenyl)methylium hexafluorophosphate (7). To a solution of guaiazulene (**1**) (70 mg, 0.35 mmol) in methanol (1.0 mL) was added a solution of commercially available 4-methoxybenzaldehyde (**4**) (49 μL, 0.40 mmol) in methanol (1.0 mL) containing hexafluorophosphoric acid (60% aqueous solution, 0.2 mL). The mixture was stirred at 25 °C for 2 h, precipitating a dark-red solid of **7**, and then was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (1:5, v/v) (several times) to provide pure **7** as stable single crystals (157 mg, 0.34 mmol, 97% yield).

Compound **7**: dark-red plates, mp >162 °C (decomp.) [determined by thermal analysis (TGA and DTA)]. Found: C, 59.98; H, 5.43%. Calcd for C$_{23}$H$_{25}$F$_6$OP: C, 59.74; H, 5.45%; UV–vis $\lambda_{\max}$ (CH$_3$CN) nm (log ε) 230 (4.48), 277sh (4.11), 298 (4.20), 334 (4.12), 408 (4.02), and 507 (4.58); IR $\nu_{\max}$ (KBr) cm^{-1}: 841 and 556 (PF$_6^-$); exact FABMS (3-nitrobenzyl alcohol matrix): found: m/z 317.1928; calcd for C$_{23}$H$_{25}$O: [M−PF$_6$]$^+$, m/z 317.1905; 500 MHz ^{1}H NMR (CD$_3$CN): signals based on the 3-guaiazulenylmethylium-ion structure: δ 1.45 (6H, d, J=6.9 Hz, (CH_3)$_2$CH-7′), 2.53 (3H, d, J=0.9 Hz, Me-1′), 3.34 (3H, s, Me-4′), 3.47 (1H, sept, J=6.9 Hz, (CH$_3$)$_2$CH-7′), 8.09 (1H, br q, J=0.9 Hz, H-2′), 8.36 (1H, dd, J=11.2, 2.1 Hz, H-6′), 8.45 (1H, d, J=11.2 Hz, H-5′), 8.57 (1H, d, J=2.1 Hz, H-8′), and 8.74 (1H, s, HC$^+$-α); signals based on the 4-methoxyphenyl group: δ 3.93 (3H, s, MeO-4), 7.16 (2H, ddd, J=8.6, 2.5, 1.0 Hz, H-3,5), and 7.90 (2H, ddd, J=8.6, 2.5, 1.0 Hz, H-2,6); 125 MHz ^{13}C NMR (CD$_3$CN): δ 169.7 (C-7′), 165.1 (C-4), 159.9 (C-8a′), 157.3 (C-4′), 153.4 (C-3a′), 151.3 (HC$^+$-α), 149.4 (C-5′), 144.9 (C-1′), 144.5 (C-6′), 141.7 (C-2′), 139.7 (C-8′), 137.8 (C-3′), 137.1 (C-2,6), 129.2 (C-1), 116.4 (C-3,5), 56.7 (MeO-4), 40.1 ((CH$_3$)$_2$$C$H-7′), 29.9 (Me-4′), 23.8 ((CH$_3$)$_2$CH-7′), and 13.8 (Me-1′).

4.1.5. Reduction of (3-guaiazulenyl)(2-methoxyphenyl)methylium hexafluorophosphate (5a) with NaBH$_4$. To a solution of NaBH$_4$ (6 mg, 162 μmol) in ethanol (1.5 mL) was added a solution of **5a** (50 mg, 108 μmol) in acetonitrile (1.0 mL). The mixture was stirred at 25 °C for 30 min, and then evaporated in vacuo. The residue thus obtained was dissolved in hexane and filtered. The hexane filtrate was evaporated in vacuo, giving a blue pasty residue, which was carefully separated by silica-gel column chromatography with hexane–ethyl acetate (9:1, v/v) as an eluant, and was recrystallized from hexane to provide pure 1-(3-guaiazulenylmethyl)-2-methoxybenzene (**8**) as blue blocks (33 mg, 104 μmol, 95% yield).

Compound **8**: blue blocks [R_f=0.45 on silica-gel TLC (hexane–AcOEt=9:1, v/v)], mp 108 °C [determined by thermal analysis (TGA and DTA)]; exact EIMS (70 eV): found: m/z 318.1995; calcd for C$_{23}$H$_{26}$O: M$^+$, m/z 318.1984; 600 MHz ^{1}H NMR (CD$_2$Cl$_2$): signals based on the 3-guaiazulenylmethyl group: δ 1.35 (6H, d, J=6.9 Hz, (CH_3)$_2$CH-7′), 2.60 (3H, s, Me-1′), 2.79 (3H, s, Me-4′), 3.03 (1H, sept, J=6.9 Hz, (CH$_3$)$_2$CH-7′), 4.52 (2H, s, 1-CH$_2$-3′), 6.80 (1H, d, J=10.7 Hz, H-5′), 7.27 (1H, dd, J=10.7, 2.1 Hz, H-6′), 7.34 (1H, s, H-2′), and 8.09 (1H, d, J=2.1 Hz, H-8′); signals based on the 2-methoxyphenyl group: δ 3.88 (3H, s, MeO-2), 6.59 (1H, dd, J=7.5, 1.6 Hz, H-6), 6.75 (1H, ddd, J=7.7, 7.5, 1.0 Hz, H-5), 6.91 (1H, dd, J=8.0, 1.0 Hz, H-3), and 7.16 (1H, ddd, J=8.0, 7.7, 1.6 Hz, H-4); 150 MHz ^{13}C NMR (CD$_2$Cl$_2$): δ 156.4 (C-2), 145.2 (C-4′), 140.6 (C-2′), 138.4 (C-7′), 137.5 (C-8a′), 134.3 (C-6′), 132.8 (C-3a′), 132.8 (C-8′), 131.5 (C-1), 129.5 (C-6), 126.4 (C-4), 125.6 (C-5′), 125.0 (C-3′), 123.9 (C-1′), 120.0 (C-5), 109.4 (C-3), 55.0 (MeO-2), 37.3 ((CH$_3$)$_2$$C$H-7′), 30.7 (1-CH$_2$-3′), 25.6 (Me-4′), 24.0 ((CH$_3$)$_2$CH-7′), and 12.3 (Me-1′).

4.1.6. Reduction of (3-guaiazulenyl)(3-methoxyphenyl)methylium hexafluorophosphate (6) with NaBH$_4$. To a solution of NaBH$_4$ (6 mg, 162 μmol) in ethanol (1.5 mL) was added a solution of **6** (50 mg, 108 μmol) in acetonitrile (1.5 mL). The mixture was stirred at 25 °C for 30 min, and then evaporated in vacuo. The residue thus obtained was dissolved in hexane and filtered. The hexane filtrate was evaporated in vacuo, giving a blue pasty residue, which was carefully separated by silica-gel column chromatography with hexane–ethyl acetate (9:1, v/v) as an eluant, giving pure 1-(3-guaiazulenylmethyl)-3-methoxybenzene (**9**) as a blue paste (32 mg, 100 μmol, 93% yield).

Compound **9**: blue paste [R_f=0.43 on silica-gel TLC (hexane–AcOEt=9:1, v/v)]; exact EIMS (70 eV): found: m/z 318.1990; calcd for C$_{23}$H$_{26}$O: M$^+$, m/z 318.1984; 600 MHz ^{1}H NMR (CD$_2$Cl$_2$): signals based on the 3-guaiazulenylmethyl group: δ 1.35 (6H, d, J=6.9 Hz, (CH_3)$_2$CH-7′), 2.60 (3H, s, Me-1′), 2.84 (3H, s, Me-4′), 3.03 (1H, sept, J=6.9 Hz, (CH$_3$)$_2$CH-7′), 4.57 (2H, s, 1-CH$_2$-3′), 6.81 (1H, d, J=10.8 Hz, H-5′), 7.27 (1H, dd, J=10.8, 2.1 Hz, H-6′), 7.39 (1H, s, H-2′), and 8.09 (1H, d, J=2.1 Hz, H-8′); signals based on the 3-methoxyphenyl group: δ 3.72 (3H, s, MeO-3), 6.59 (1H, dd, J=1.2, 0.8 Hz, H-2), 6.62 (1H, ddd, J=7.7, 1.8, 1.2 Hz, H-6), 6.69 (1H, ddd, J=8.1, 1.8, 0.8 Hz, H-4), and 7.15 (1H, dd, J=8.1, 7.7 Hz, H-5); 150 MHz ^{13}C NMR (CD$_2$Cl$_2$): δ 159.5 (C-3), 145.0 (C-4′), 144.8 (C-1), 140.7 (C-2′), 138.6 (C-7′), 137.5 (C-8a′), 134.3 (C-6′), 133.0 (C-8′), 132.6 (C-3a′), 128.8 (C-5), 125.8 (C-5′), 125.1 (C-3′), 123.9 (C-1′), 120.5 (C-6), 114.2 (C-2), 110.2 (C-4), 54.7 (MeO-3), 37.3 ((CH$_3$)$_2$$C$H-7′), 36.7 (1-CH$_2$-3′), 26.1 (Me-4′), 24.0 ((CH$_3$)$_2$CH-7′), and 12.2 (Me-1′).

4.1.7. Reduction of (3-guaiazulenyl)(4-methoxyphenyl)methylium hexafluorophosphate (7) with NaBH$_4$. To a solution of NaBH$_4$ (6 mg, 162 μmol) in ethanol (1.5 mL) was added a solution of **7** (50 mg, 108 μmol) in acetonitrile

(1.5 mL). The mixture was stirred at 25 °C for 30 min, and then evaporated in vacuo. The residue thus obtained was dissolved in hexane and filtered. The hexane filtrate was evaporated in vacuo, giving a blue pasty residue, which was carefully separated by silica-gel column chromatography with hexane–ethyl acetate (9:1, v/v) as an eluant, and was recrystallized from chloroform–methanol (1:7, v/v) to provide pure 1-(3-guaiazulenylmethyl)-4-methoxybenzene (**10**) as a blue solid (33 mg, 104 μmol, 95% yield).

Compound **10**: blue solid [R_f=0.42 on silica-gel TLC (hexane–AcOEt=9:1, v/v)], mp 56 °C [determined by thermal analysis (TGA and DTA)]; exact EIMS (70 eV): found: m/z 318.1992; calcd for $C_{23}H_{26}O$: M$^+$, m/z 318.1984; 600 MHz ^{1}H NMR (CD_2Cl_2): signals based on the 3-guaiazulenylmethyl group: δ 1.34 (6H, d, J=6.9 Hz, $(CH_3)_2$CH-7′), 2.60 (3H, s, Me-1′), 2.84 (3H, s, Me-4′), 3.02 (1H, sept, J=6.9 Hz, $(CH_3)_2CH$-7′), 4.53 (2H, s, 1-CH_2-3′), 6.80 (1H, d, J=10.8 Hz, H-5′), 7.26 (1H, dd, J=10.8, 2.1 Hz, H-6′), 7.37 (1H, s, H-2′), and 8.08 (1H, d, J=2.1 Hz, H-8′); signals based on the 4-methoxyphenyl group: δ 3.74 (3H, s, MeO-4), 6.78 (2H, ddd, J=8.6, 2.6, 0.8 Hz, H-3,5), and 6.94 (2H, ddd, J=8.6, 2.6, 0.8 Hz, H-2,6); 150 MHz ^{13}C NMR (CD_2Cl_2): δ 157.4 (C-4), 145.0 (C-4′), 140.6 (C-2′), 138.5 (C-7′), 137.5 (C-8a′), 135.2 (C-1), 134.3 (C-6′), 133.0 (C-8′), 132.5 (C-3a′), 128.9 (C-2,6), 125.8 (C-3′), 125.7 (C-5′), 123.8 (C-1′), 113.3 (C-3,5), 54.8 (MeO-4), 37.3 ($(CH_3)_2CH$-7′), 35.8 (1-CH_2-3′), 26.1 (Me-4′), 24.0 ($(CH_3)_2$CH-7′), and 12.2 (Me-1′).

4.1.8. X-ray crystal structure of (3-guaiazulenyl)(2-methoxyphenyl)methylium tetrafluoroborate (5b). A total of 4995 reflections with $2\theta_{max}$=55.0° were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated Mo Kα radiation (λ=0.71069 Å, rotating anode: 50 kV, 180 mA) at 198 K. The structure was solved by direct methods (SIR97) and expanded using Fourier techniques (DIRDIF94). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2. All calculations were performed using the teXsan crystallographic software package. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 283199.

Crystallographic data for **5b**: $C_{23}H_{25}BF_4O$ (FW=404.25), dark-red block (crystal size: 0.20×0.30×0.30 mm^3), monoclinic, $C2/c$ (#15), a=22.476(6) Å, b=10.092(7) Å, c=17.775(5) Å, β=92.29(2)°, V=4028(3) Å^3, Z=8, D_{calcd}=1.333 g/cm^3, μ(Mo Kα)=1.04 cm^{-1}, scan width=(1.26+0.30 tan θ)°, scan mode=$\omega-2\theta$, scan rate=8.0°/min, measured reflections=4995, observed reflections=4609, no. of parameters=262, $R1$=0.067, $wR2$=0.205, and Goodness of Fit Indicator=1.40.

4.1.9. X-ray crystal structure of (3-guaiazulenyl)(3-methoxyphenyl)methylium hexafluorophosphate (6). A total of 5326 reflections with $2\theta_{max}$=55.0° were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated Mo Kα radiation (λ=0.71069 Å, rotating anode: 50 kV, 180 mA) at 198 K. The structure was solved by direct methods (SIR97) and expanded using Fourier techniques (DIRDIF94). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2. All calculations were performed using the teXsan crystallographic software package. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 289587.

Crystallographic data for **6**: $C_{23}H_{25}F_6OP$ (FW=462.41), red plate (crystal size: 0.30×0.20×0.30 mm^3), monoclinic, $C2/c$ (#15), a=28.699(4) Å, b=10.084(4) Å, c=17.445(4) Å, β=121.69(1)°, V=4295(2) Å^3, Z=8, D_{calcd}=1.430 g/cm^3, μ(Mo Kα)=1.92 cm^{-1}, scan width=(1.47+0.30 tan θ)°, scan mode=$\omega-2\theta$, scan rate=8.0°/min, measured reflections=5326, observed reflections=4939, no. of parameters=280, $R1$=0.083, $wR2$=0.249, and Goodness of Fit Indicator=1.96.

4.1.10. X-ray crystal structure of (3-guaiazulenyl)(4-methoxyphenyl)methylium hexafluorophosphate (7). A total of 5100 reflections with $2\theta_{max}$=55.0° were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated Mo Kα radiation (λ=0.71069 Å, rotating anode: 50 kV, 180 mA) at 163 K. The structure was solved by direct methods (SIR97) and expanded using Fourier techniques (DIRDIF94). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2. All calculations were performed using the teXsan crystallographic software package. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 271390.

Crystallographic data for **7**: $C_{23}H_{25}F_6OP$ (FW=462.41), dark-red plate (crystal size: 0.30×0.20×0.50 mm^3), triclinic, P-1 (#2), a=10.267(2) Å, b=14.453(2) Å, c=8.011(2) Å, α=97.97(2)°, β=111.40(2)°, γ=71.67(1)°, V=1050.3(4) Å^3, Z=2, D_{calcd}=1.462 g/cm^3, μ(Mo Kα)=1.96 cm^{-1}, scan width=(1.26+0.30 tan θ)°, scan mode=$\omega-2\theta$, scan rate=16.0°/min, measured reflections=5100, observed reflections=3541, no. of parameters=280, $R1$=0.045, $wR2$=0.134, and Goodness of Fit Indicator=1.81.

4.1.11. X-ray crystal structure of 1-(3-guaiazulenylmethyl)-2-methoxybenzene (8). A total of 4659 reflections with $2\theta_{max}$=55.0° were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite monochromated Mo Kα radiation (λ=0.71069 Å, rotating anode: 50 kV, 180 mA) at 198 K. The structure was solved by direct methods (SIR97) and expanded using Fourier techniques (DIRDIF94). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2. All calculations were performed using the teXsan crystallographic software package. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 609977.

Crystallographic data for **8**: $C_{23}H_{26}O$ (FW=318.46), blue block (crystal size: 0.30×0.30×0.50 mm^3), monoclinic, $P2_1/c$ (#14), a=7.845(3) Å, b=20.913(4) Å, c=11.249(3) Å, β=93.74(3)°, V=1841.5(8) Å^3, Z=4, D_{calcd}=1.149 g/cm^3, μ(Mo Kα)=0.68 cm^{-1}, scan width=(0.94+0.30 tan θ)°, scan mode=$\omega-2\theta$, scan rate=16.0°/min, measured reflections=4659, observed reflections=4227, no. of parameters=217, $R1$=0.055, $wR2$=0.170, and Goodness of Fit Indicator=1.28.

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