Lead(IV) Oxide-Mediated Oxidation of Azulen-2-ols to Form 1,1-Coupled Dimers and Hexacyclic Cage-Dimers.

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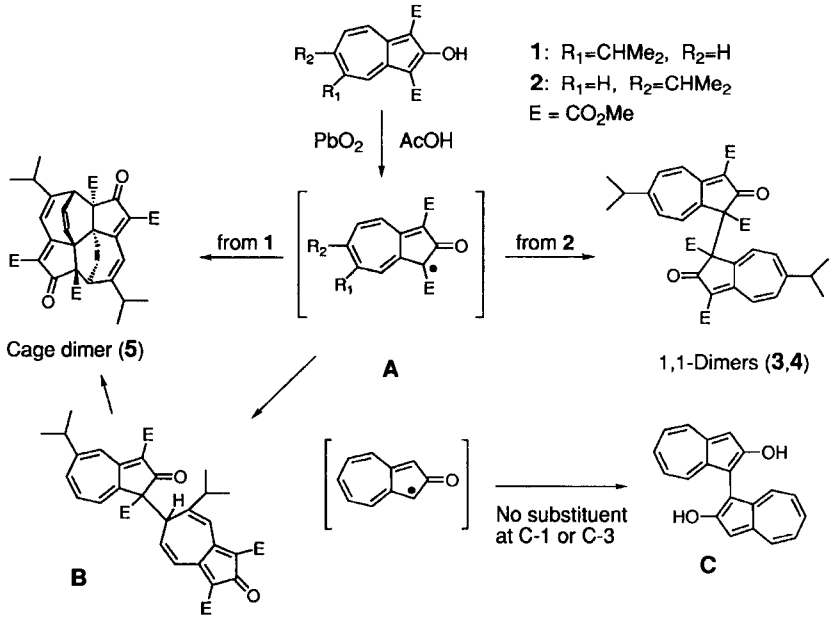
The lead(IV) oxide oxidation of various azulen-2-ol derivatives in acetic acid generates azulenoxy radicals via one-electron oxidation. The intermediates end up yielding recombined dimers, [1,1′-biazulene]-2,2′(1*H*,1′*H*)-dimers, as common type of products. In addition to these, hexacyclic cage dimers were obtained from 5-substituted azulen-2-ol derivatives. From dimethyl 2-hydroxyazulene-1,3-dicarboxylate, a hydroxyazulene having no substituent on the seven-membered ring was isolated a pair of dimethyl 2-hydroxy-4-[1,3-di(methoxycarbonyl)-2-oxo-1,2-dihydroazulenyl]azulene-1,3-dicarboxylate, but neither a cage dimer nor a 1,6-coupled dimer. The full structures of the dimers have been firmly established by an extensive X-ray crystallographic analysis and ^{13}C NMR spectral comparisons of the key derivatives. Concerning the mechanism of the formation of the cage dimers, a [5+5] π cycloaddition followed by recombination of the resultant biallyl system is suggested.

For the past few decades, we have been investigating the oxidation reactions of azulene derivatives with various oxidizing agents,[1] by which various modes of product formations have been recognized. In general, the oxidations of azulenes suffered a limitation regarding particular product selectivity. A notable exception was oxidation with aqueous bromine to form the azulenequinones in good yields.[2] In addition, we have already reported on the preliminary form of the lead(IV) oxide oxidation[3,4] of dimethyl 2-hydroxy-(5- and 6-isopropyl)azulene-1,3-dicarboxylates (**1** and **2**),[5] which showed a good material balance to give dimeric condensates. The obtained results therefrom were contrasted depending on the position of the isopropyl group; i.e., **2** gave dimers (**3** and **4**, 1,1-dimers) condensed at the C-1 position of the azulenoxy radical **A** in 80% yields, while **1** gave a hexacyclic dimer (**5**, cage dimer) along with 1,1-dimers. Dimer **5** was previously interpreted to be formed by an intramolecular Diels–Alder reaction of a hypothetical 1,6-coupled dimer **B**, which has, however, never been detected.[6] Therefore, it is urgent to carry out a study with several other azulenols to investigate the controlling factor of different reaction modes, 1,1- or 1,6-couplings. Herein, we have extended this one-electron oxidation to several other azulenol derivatives to find the mechanism of the oxidative dimerization of azulen-2-ols.

In general, the lead(IV) oxide oxidation of azulen-2-ol derivatives in acetic acid might generate azulenoxy radicals **A** via one-electron oxidation, and the intermediates might end up yielding recombined dimers, [1,1′-biazulene]-2,2′-diol **C**, after aromatization; indeed, this has been the case.[7] Therefore, the occurrence of hexacyclic cage dimers, such as **5**, which are equivalent to the [5+5] π cycloadducts of **A** from 1,3-disubstituted azulen-2-ol derivatives, might involve reversibly generated, thermodynamically stable azulenoxy radicals. In other words, the hexacyclic cage dimers are thermodynamically controlled products, which can be derived from the prevention of aromatization to **C**. At the same time, one might notice that hypothetical 1,6-coupled intermediates **B** possess a thermodynamically disfavored cyclopentadienone moiety in the molecules.[8] Thus, an intermediacy of such compounds should not be considered (Scheme 1).

The one-electron transfer oxidation of phenols is called



Scheme 1. PbO_2-oxidation of 5- and 6-isopropylazulenols, previous results.

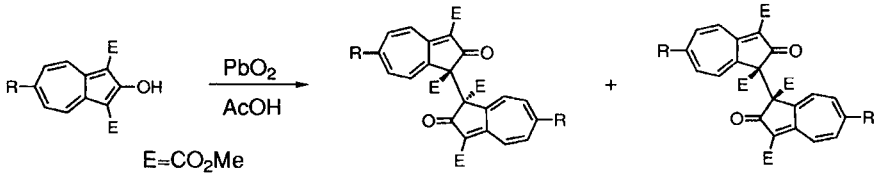
"phenol oxidation", and its importance in the biogenesis of natural products has been well established.[9] Since azulenols can be classified as phenolic compounds, their behaviors towards such oxidizing agents are worth investigating.

Results and Discussion

Lead(IV) Oxide-Oxidation Products from Dimethyl 2-Hydroxyazulene-1,3-Dicarboxylate (6). At first, we studied the reaction of an azulenol carrying no substituent on the seven-membered ring, dimethyl 2-hydroxyazulene-1,3-dicarboxylate (**6**); when **6** was treated with lead(IV) oxide in acetic acid at room temperature,[6] a very rapid reaction took place within only 40 min to form two products (**7** and **8**) in 31 and 40% yields, respectively. Their mass spectra confirmed that both products are dimers. Their ^1H and ^{13}C NMR spectra[6] closely resembled each other, and they are stereoisomers. In their ^1H NMR spectra, five consecutive aromatic proton signals were observed to indicate that they are symmetrical. The ^{13}C NMR chemical shifts of the sp^3 carbon atoms at C-1 and C-1 of the 1,1-coupling products were characteristic; a *dl* isomer **7** has a signal at a lower field (δ = 69.3) and a *meso* isomer **8** has a signal at a higher field (δ = 65.8). The UV spectra of both yellow needles, **7** and **8**, showed an absorption band around the 400 nm region, and retention of the seven-membered rings as a heptafulvene chromophore was ascertained.[10] From an X-ray crystallographic analysis,[11] **7** was determined to be a *dl* isomer and **8** was a *meso* isomer.

Lead(IV) Oxide-Oxidation Products from 6-Substituted 2-Azulenol Derivatives. As already described in a preliminary paper,[6] the treatment of dimethyl 2-hydroxy-6-isopropylazulene-1,3-dicarboxylate (**2**) with lead(IV) oxide in acetic acid afforded two dimeric products (**3** and **4**) in 80 and 15% yields, respectively. A ^{13}C NMR spectral comparison with the above criteria differentiated the stereostructures; i.e., **3** is a *dl* isomer (δ = 69.1) and **4** is a *meso* isomer (δ = 65.8). Both structures of **3** and **4** were confirmed by an X-ray diffraction analysis.[11]

Beside the 6-isopropyl derivative **2**, oxidation was extended to dimethyl 6-bromo-2-hydroxyazulene-1,3-dicarboxylate (**9**); when **9** was similarly treated with lead(IV) oxide, a pair of dimeric products (**10** and **11**) was obtained in 37 and 39% yields, respectively. The NMR spectra of **10** and **11** were consistent with the structures depicted in Scheme 2, and comparisons with those of **7** and **8** deduced the full structures; the C-1 carbon (juncture) signal of **10** appeared at δ = 69.3, whereas that of **11** appeared at δ = 66.1, respectively. These data led to the assignment of a *dl*-structure for **10** and a *meso*-structure for **11**, which were also confimed



6: R=H
2: R=CHMe$_2$
9: R=Br

7: R=H (31)
3: R=CHMe$_2$ (80)
10: R=Br (37)

8: R=H (40)
4: R=CHMe$_2$ (15)
11: R=Br (39)

Scheme 2. PbO_2-oxidation products (yield, %) of dimethyl 2-hydroxyazulene-1,3-dicarboxylate and its 6-isopropyl and 6-bromo derivatives.

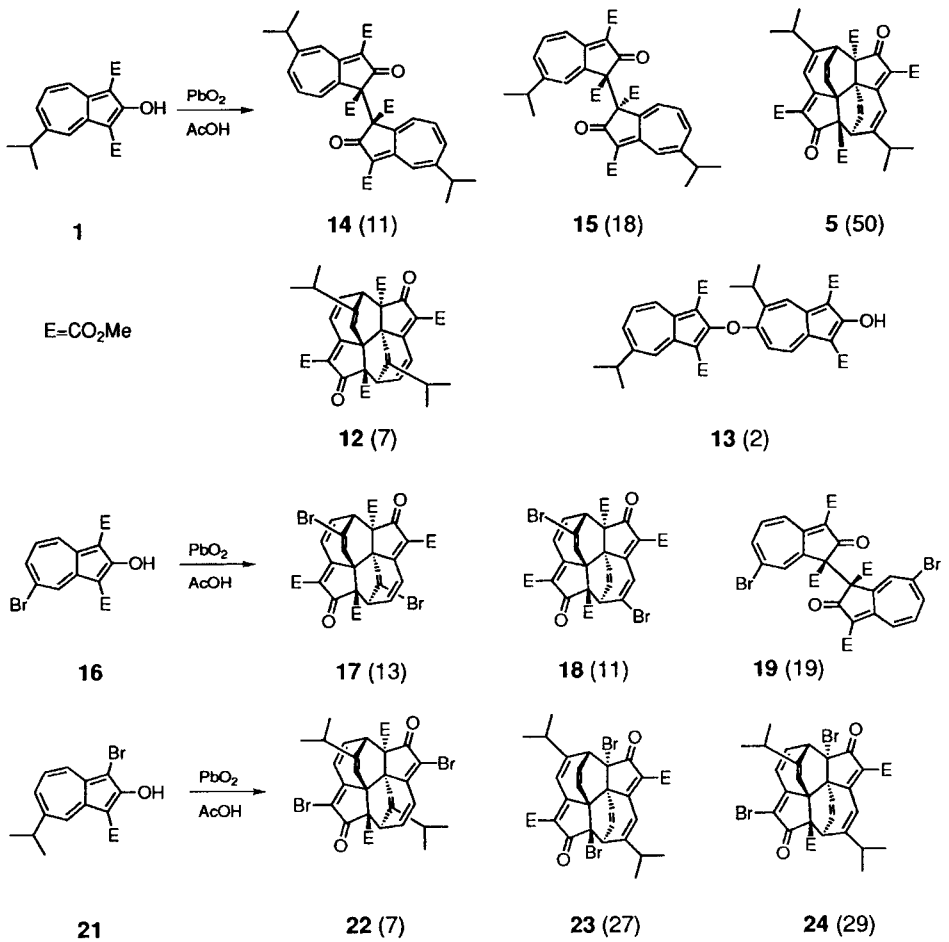
by X-ray crystallographic analyses.[11] This seems to have a diagnostic value for determination of stereochemistries of 1,1-dimers in general. Table 1 summarizes the assignments of stereochemistries.

Lead(IV) Oxide-Oxidation Products from 5-Substituted 2-Azulenol Derivatives. The lead(IV) oxide oxidation of dimethyl 2-hydroxy-5-isopropylazulene-1,3-dicarboxylate (**1**) in acetic acid afforded five products (**5**, **12**—**15**) with complicated product distributions, of which product **5** and a regioisomeric pair of 1,1-dimers (**14** and **15**) were mentioned in a preliminary paper.[6] The major product **5** showed an element of symmetry in the ^{1}H and ^{13}C NMR spectra, and there were only eighteen sp^2-carbons. Therefore, two additional C–C bonds must have been formed. According to the IR spectrum, its C=O groups are those cyclopentenone derivatives in nature, indicating a sort of cage structure formed. The lowest proton signal appearing at δ = 7.20 (2H, ddd, J = 10.5, 8.4, 1.2 Hz) was assigned for the proton at the 7-position, and the signal observed at δ = 5.75 as a doublet was assigned for a proton at the 4-position; therefore, there are isopropyl groups on the conjugated C=C system.[7] Product **12** also revealed an element of symmetry with both isopropyl groups on the the isolated etheno bridges; also, the lowest proton signal appearing at δ = 6.99 (2H, d, J = 1.3 Hz) was assigned for the proton at the 8-position. An X-ray crystallographic analysis determined the full structures of **5**[6] and **12**,[11] as shown in Scheme 3.

A yellow crystalline compound **13**, obtained only in 2% yield, was determined to be a diazulenyl ether, dimethyl 2-hydroxy-5-isopropyl-6-[5-isopropyl-1,3-bis(methoxycarbonyl)-2-azulenyloxy]azulene-1,3-dicarboxylate, according to a determination of the molecular weight from the mass spectrum. The NMR spectral data showed no sp^3 carbon signal, except for the signals of the subsituents. The structures of a regioisomeric pair of 1,1-dimers (**14** and **15**) were differentiated by NMR spectroscopy; while **14** showed the presence

Table 1. Stereochemistries of the 1,1-Coupled Dimers

Compounds	**7**	**8**	**3**	**4**	**10**	**11**	**14**	**15**	**19**	**29**	**30**	**31**	**32**
(SP^3-carbons)	69.3	65.8	69.1	65.8	69.3	66.1	69.3	65.1 65.9	68.5	68.5 69.0	68.0	60.3 63.8	68.0
Assignment	*d,l*	*meso*	*d,l*	*meso*	*d,l*	*meso*	*d,l*	*meso*	*d,l*	*d,l*	*d,l*	*meso*	*d,l*



Scheme 3. PbO_2-dimerization products (yield, %) from various 5-substituted azulen-2-ol derivatives.

of a symmetry element in the ^1H and ^{13}C NMR spectra; **15** did not. Since the lowest signals of **14** appeared at δ = 8.21 (2H) as a singlet, it must be a 1,1-dimer of **1**. Unsymmetrical **15**, having signals at δ = 8.12 (1H, d, J = 12.0 Hz) and 8.28 (1H, s), is a 1,3-dimer. The ^{13}C NMR spectra again identified the stereochemistry; i.e., **14** (δ = 69.3) and **15** (δ = 65.1 and 65.9) showed the sp^3-carbon signals appropriate for *dl*- and *meso*-types, respectively. An X-ray crystallographic analysis of **15**[11] verified this assignment, as illustrated in Scheme 3.

Also, the oxidation of dimethyl 5-bromo-2-hydroxyazulene-1,3-dicarboxylate (**16**)[13] in acetic acid gave four products (**17**—**20**); two major products (**17** and **18**) were hexacyclic cage compounds. Taking the overlapping signals into account, **17** was a symmetrical molecule with two bromine atoms on the isolated C=C bond, and **18** was an unsymmetrical molecule. Product **19** was a *dl* 1,1-dimer, since its diagnostic ^{13}C NMR chemical shift (δ = 68.5) is close to 69.3 of **7**, 69.1 of **3**, and 69.3 of **10**. The remaining product, **20**, was obtained in less than 5% yield only as a mixture with **19**; at present, its spectral similarity with the cage dimers suggested it to be the remaining symmetrical isomer with two bromine atoms on the conjugated C=C systems, but no further study could be carried out.

Moreover, the oxidation of methyl 1-bromo-2-hydroxy-5-isopropylazulene-3-carboxylate (**21**) in acetic acid afforded three cage products (**22**—**24**); **22** and **23** were symmetrical molecules and **24** was unsymmetrical as depicted. The structures of **22**—**24** were confirmed by an X-ray crystallographic analysis;[11] an ORTEP[12] drawing of **23** is shown in Fig. 1.

The oxidation of methyl 1-cyano-2-hydroxy-5-isopropylazulene-3-carboxylate (**25**) in acetic acid was complicated to give seven products (**26**—**32**). Among them, **26**, **27**, and **28** were hexacyclic cage dimers, whilst **29**, **30**, **31**, and **32** were 1,1-dimers. The symmetry elements in the NMR spectra and the chemical shifts criteria of key signals deduced the structures of all of these products. Namely, a symmetrical cage dimer **26** showed the lowest proton signal at δ = 7.13 (s), indicating that the the ester group and the C-5 proton remained in a conjugated system. However, the other symmetrical cage dimer **28** showed the lowest signal at δ = 7.35 (dd, J = 10.0 and 8.6 Hz), the cyano group and the C-7 proton of the starting material remained in a conjugated C=C system. These observations provided the full stereostructures of both products. The remaining cage dimer **27** was thus a mixed type and the NMR spectral features are fully in accord with this. All four 1,1-dimers (**29**, **30**, **31**, and **32**) revealed very weak molecular ion peaks in the mass spectra, and the next intense peaks in mass numbers are the dissociated fragments, corresponding to the azulenoxy radical ions at *m/z* 269. Because two of them, **30** and **32**, showed overlapped single signals for ester methyl protons, they are symmetrical. Their lowest proton signals were at δ = 7.52 (d, J = 1.6 Hz) in **30** and δ = 7.93 (d, J = 1.7 Hz) in **32**, indicating that the former was a 1,1-condensate and the later was a 3,3-condensate from the azulenoxy radical generated from **25**. Since both compounds had a signal ascribable to the quaternary carbons at δ = 68.0 (2C, each), **30** and **32** are *dl* isomers. The remaining products (**29** and **31**) were unsymmetrical [δ = 3.75 and 3.77 (3H, s, each) for **29** and 3.87 and 3.89 (3H, s, each) for **31**], and the chemical shift difference of the quaternary carbons appearing at δ = 68.5 and 69.0 for **29** and at δ = 60.3 and 63.8 for **31** clarified the stereostructures. Since the carbon atom bearing a cyano group is as reactive as that bearing an ester group, the product distributions are complicated. The structures of **26**—**28**, **30**, and **32** were confirmed by the X-ray method.[11]

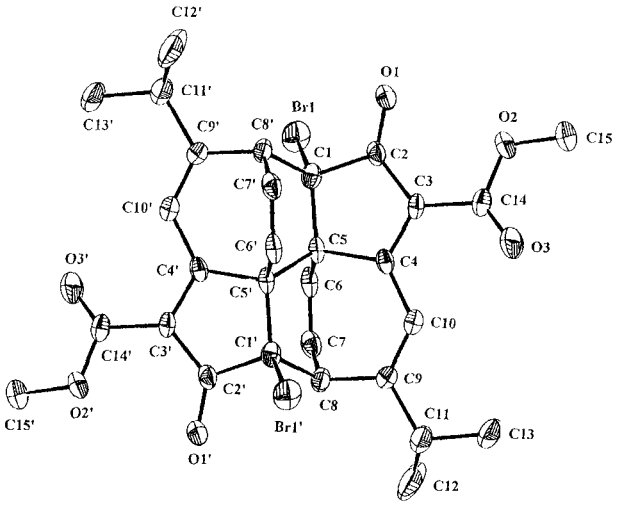
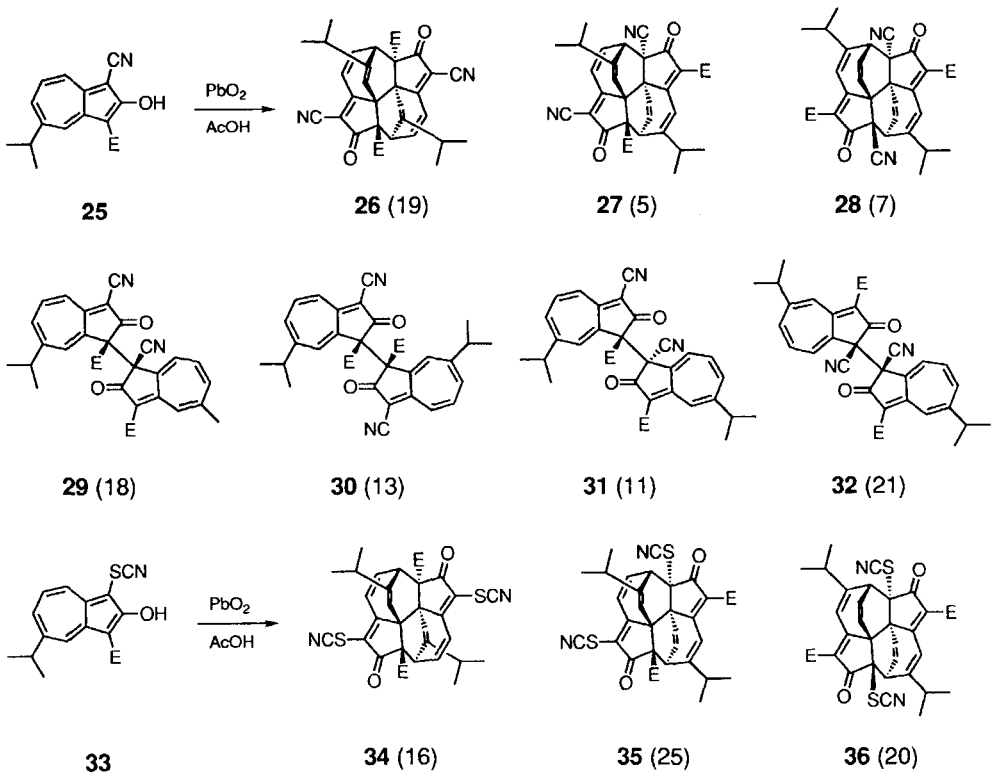


Fig. 1. ORTEP drawing of **23** with the numbering of atoms.

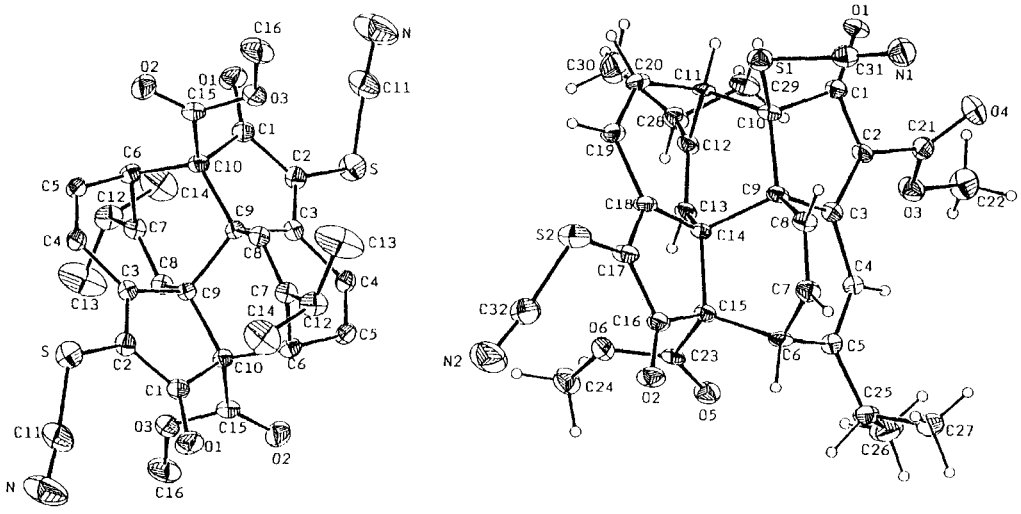
Finally, the oxidation of methyl 2-hydroxy-5-isopropyl-1-thiocyanatoazulene-3-carboxylate (**33**) in acetic acid gave three cage dimers (**34**, **35**, and **36**); **34** was a symmetrical molecule having an isopropyl group on the isolated C=C bond, whilst **35** was an unsymmetrical cage dimer. The third product **36** was detected and its spectral behaviors suggested a symmetrical cage dimer; also, it seems to be certain that the isopropyl groups are on the isolated C=C due to a difficulty in separating from **35**. No further characterization was, however, attempted. All structures of these cage dimers are shown as depicted in Scheme 4. Both **34** and **35** were also confirmed by the X-ray method,[11] and these ORTEP drawing are shown in Fig. 2. The selected interatomic distances for **23**, **34**, and **35** are listed in Table 2.

In the cage dimers, the positions of the isopropyl groups could be determined from the ^1H NMR chemical shifts of the heptet methine protons; as Table 3 shows, the heptet methines of the isopropyl groups on the conjugated terminal appear at ca. δ = 2.3, whilst those on the etheno bridge are at ca. δ = 2.6, or lower. In addition, the splitting patterns and the positions of the lowest signals, one for δ-protons (dd, with large coupling constants) and the others for γ-protons (with only a long range coupling, if any), are informative, indeed.

Mechanistic Considerations. Taking the above-mentioned fact into account, there might be two explanations that should be provided concerning the mechanism of cage-dimer formation. Namely, the first mechanism, a 1,6-coupling process following an intramolecular Diels–Alder re-



Scheme 4. PbO_2-dimerization products (yield, %) from various 5-substituted azulen-2-ol derivatives.



34 35

Fig. 2. ORTEP drawings of **34** and **35** with the numbering of atoms.

action, and the second mechanism, [5+5] π cycloaddition followed by a recombination of the resultant biallyl system (Scheme 5). Although the former was tentatively described in a preliminary paper,[6] at that time no positive evidence was available.

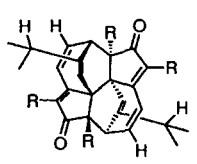
It should also be noted that the observed product distributions of cage-dimers are not consistent with the steric energy of the molecules calclulated by the MM3[14] method; i.e., **5** (50% yield, 308.4 kJ mol^{-1}) > **12** (7%, 296.6), **17** (13%, 280.3) > **18** (11%, 281.6) > **20** (< 5%, 290.0), **24** (29%, 270.3) > **23** (27%, 297.9) > **22** (7%, 254.8), **26** (19%, 253.1) > **28** (7%, 289.1) > **27** (5%, 264.4), and **35** (25%, 262.3) > **34** (16%, 253.1), which are difficult to explain on the basis of the 1,6-coupling process followed by the Diels–Alder reaction.

Other than these, although it might not be equally plausible, one must consider the sigmatropic generation of formal 1,6-dimers from 1,1-dimers as a third mechanism. However, a twice-[3,3] sigmatropic process of a 1,1-dimer should generate the cyclopentadienone moiety in the intermediates. Consequently, the disfavored cyclopentadienones[8] therefrom should be stabilized via protonation, but not via an in-

Table 2. Selected Bond Lengths (Å) of **23**, **34**, and **35**

23				**34**				**35**			
Molecule A		Molecule B		Molecule A		Molecule B					
Br1–C1	1.95(1)	Br1–C1	2.00(1)	S–C2	1.76(3)	S–C2	1.76(3)	S1–C10	1.84(5)	C17–C18	1.36(8)
C1–C2	1.53(2)	C1–C2	1.50(2)	S–C11	1.69(4)	S–C11	1.67(4)	S1–C31	1.58(2)	C18–C19	1.45(8)
O1–C2	1.24(1)	O1–C2	1.21(1)	C1–C2	1.44(4)	C1–C2	1.45(4)	S2–C17	1.75(6)	C19–C20	1.34(8)
C1–C5	1.58(2)	C1–C5	1.57(1)	C1–C10	1.55(4)	C1–C10	1.54(4)	S2–C32	1.70(7)		
C1–C8′	1.56(2)	C1–C8′	1.53(2)	C1–O1	1.21(4)	C1–O1	1.21(4)	N1–C31	1.15(8)		
C2–C3	1.43(2)	C2–C3	1.45(2)	C2–C3	1.35(4)	C2–C3	1.35(4)	N2–C32	1.12(9)		
C3–C4	1.37(2)	C3–C4	1.37(2)	C3–C4	1.45(4)	C3–C4	1.45(4)	O1–C1	1.20(6)		
C4–C10	1.44(2)	C4–C10	1.43(2)	C3–C9	1.54(2)	C3–C9	1.54(2)	O2–C16	1.20(7)		
C4–C5	1.55(2)	C4–C5	1.54(2)	C4–C5	1.33(2)	C4–C5	1.33(2)	C1–C2	1.44(8)		
C5–C6	1.51(2)	C5–C6	1.51(2)	C5–C6	1.51(2)	C5–C6	1.50(2)	C1–C10	1.55(8)		
C5–C5′	1.60(2)	C5–C5′	1.59(2)	C6–C7	1.52(4)	C6–C7	1.52(4)	C2–C3	1.35(7)		
C6–C7	1.32(2)	C6–C7	1.32(2)	C6–C10	1.55(4)	C6–C10	1.56(4)	C3–C4	1.47(8)		
C7–C8	1.51(2)	C7–C8	1.53(2)	C7–C8	1.32(4)	C7–C8	1.32(4)	C3–C9	1.52(7)		
C8–C9	1.49(2)	C8–C9	1.53(2)	C7–C12	1.52(4)	C7–C12	1.51(4)	C4–C5	1.36(8)		
C8–C1′	1.56(2)	C8–C1′	1.53(2)	C8–C9	1.51(4)	C8–C9	1.51(4)	C5–C6	1.50(8)		
C9–C10	1.34(2)	C9–C10	1.35(2)	C9–C9	1.61(4)	C9–C9	1.61(4)	C6–C7	1.52(8)		
Br1–C1′	1.95(1)	Br1–C1′	1.98(1)	C9–C10	1.58(4)	C9–C10	1.58(4)	C6–C15	1.55(8)		
C1′–C2′	1.53(2)	C1′–C2′	1.51(2)	C10–C15	1.53(4)	C10–C15	1.53(4)	C7–C8	1.31(8)		
C1′–C5′	1.60(2)	C1′–C5′	1.57(1)	C11–N	1.13(6)	C11–N	1.13(6)	C8–C9	1.51(7)		
C2′–C3′	1.45(2)	C2′–C3′	1.45(2)	C12–C13	1.52(6)	C12–C13	1.49(6)	C9–C10	1.55(7)		
O1′–C2′	1.23(1)	O1′–C2′	1.22(1)	C12–C14	1.51(6)	C12–C14	1.48(6)	C9–C14	1.61(7)		
C3′–C4′	1.35(2)	C3′–C4′	1.38(1)	C15–O2	1.19(4)	C15–O2	1.20(4)	C10–C11	1.57(7)		
C4′–C5′	1.55(1)	C4′–C5′	1.54(2)	C15–O3	1.33(4)	C15–O3	1.33(4)	C11–C12	1.54(7)		
C4′–C10′	1.45(2)	C4′–C10′	1.42(2)	C16–O3	1.45(4)	C16–O3	1.45(4)	C11–C20	1.49(8)		
C5′–C6′	1.50(1)	C5′–C6′	1.50(1)					C12–C13	1.32(8)		
C6′–C7′	1.33(2)	C6′–C7′	1.30(2)					C13–C14	1.51(7)		
C7′–C8′	1.51(2)	C7′–C8′	1.55(2)					C14–C15	1.58(7)		
C8′–C9′	1.49(2)	C8′–C9′	1.48(2)					C15–C16	1.55(7)		
C9′–C10′	1.34(2)	C9′–C10′	1.35(2)					C16–C17	1.45(8)		

Table 3. ^{1}H NMR Spectral Characteristics of the Isopropylated Cage Dimers



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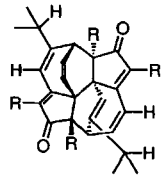

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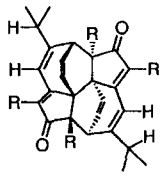


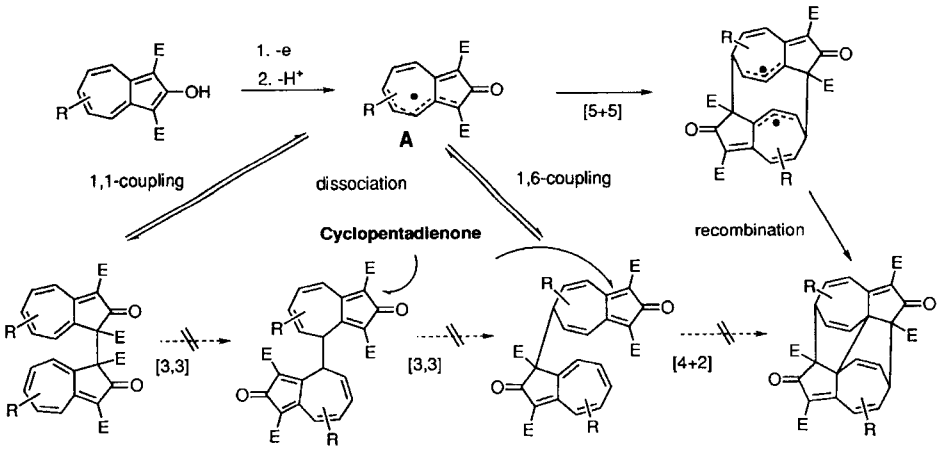
B-type

Lowest proton signals		Heptet signals	
5 7.20 (2H, ddd, J = 10.5, 8.4, 1.2 Hz)	B	2.21 (2H)	B
12 6.99 (2H, d, J = 1.3 Hz)	A	2.94 (2H)	A
22 6.99 (2H, d, J = 1.3 Hz)	A	2.66 (2H)	A
23 7.06 (2H, dd, J = 8.6, 8.5 Hz)	B	2.20 (2H)	B
24 6.60—6.79 (4H, m)	AB	2.27, 2.92 (2H)	AB
26 7.13 (2H, s)	A	2.76 (2H)	A
27 7.20 (1H, dd, J = 10.0, 8.5 Hz)	AB	2.32, 2.92 (2H)	AB
28 7.35 (2H, dd, J = 10.0, 8.6 Hz)	B	2.25 (2H)	B
34 6.99 (2H, d, J = 1.3 Hz)	A	2.66 (2H)	A
35 6.98 (1H,s)	AB	2.33, 3.01 (2H)	AB

tramolecular Diels–Alder process. In other words, the 1, 1-dimers dissociate to the azulenoxy radicals **A**, which may also reversibly recombine to the alternative 1,4- or 1,6-, (as well as 4,4-, 4,6-, and 6,6-)-dimers, depending on the substitution patterns of azulenols.

In a preliminary paper, we carried out a PM3[15] calculation to evaluate the large spin densities at the C-1 and C-3, C-4, C-6, and C-8 positions for both 5- and 6-isopropyl derivatives (**1** and **2**), so as to justify the C-1–C-1 coupling or the C-1–C-6 coupling for both **1** and **2**. An attractive possibility to overcome the points seemed to be only the [5+5] π cycloaddition process. Indeed, the HOMO and the LUMO levels of the azulenoxy radical **A** for **1** showed consistent results; namely, the largest C-6 (−0.48) and C-1 (−0.38) of the HOMO level fit to the largest C-1 (−0.45) and C-6 (−0.29) of the LUMO level to give the intermediate diradical. The HOMO and the LUMO levels of the azulenoxy radical **A** for **2** also showed consistent results; namely, the largest C-6 (−0.50) of the HOMO level fits to the largest C-1(−0.45) of the LUMO level to give the intermediate diradical. It is known that bond formation between the carbon atoms with the larger coefficient is more favored;[16] the bond formations between each C-1 and C-6 positions of the HOMO and LUMO levels occurred to give the [5+5] π cycloaddition intermediate. This explanation for the cage dimer formation, involving no cyclopentadienone system, is reasonable and does not contradict the concerted cycloaddition mechanism.

In order to judge the mechanistic pathway for dimerizations, the electronic states of the radicals and 1,1-, 4,4-, and 1,6-dimers as well as the [5+5] π cycloaddition intermediate were calculated with the RHF/PM3 method and/or the



Scheme 5. [5+5] π Mechanism for cage dimers.

UHF/PM3 method[15] to obtain the optimized structures. Figure 3 shows the optimized structures of the 1,1- and 1,6-dimers and the [5+5] π cycloaddition intermediate.

The heats of formation of the 1,1-, 1,6-dimers, and the [5+5] π cycloaddition intermediate were calculated to be −1093.28, −1094.06, and −1100.70 kJ mol^{-1}, respectively. From the values of the calculated heat of formation, the [5+5] π cycloaddition intermediate is more stable than the 1,1-dimer. In the case of the 1,1-dimer, the atomic distances of the C-1–C-1′ and C-4–C-4′ were calculated to be 1.57 Å and 5.09 Å. The twist angle of two azulenone skeletons was calculated to be ca. 75°. Therefore, a [3,3] sigmatropic reaction of a formal 4,4-dimer from 1,1-dimer is stereochemically disfavorable.

Conclusion.

It is noteworthy that the combined yields of each reaction were fairly good, and extensions to a halogenoazulenol and an alkylazulenol assured the generality of the oxidation. The oxidation products belong to a group of azulene-2(1*H*)-ones, and since the substituent on C-1 is easily removed or apt to further transformations, the compounds have synthetic potentials.

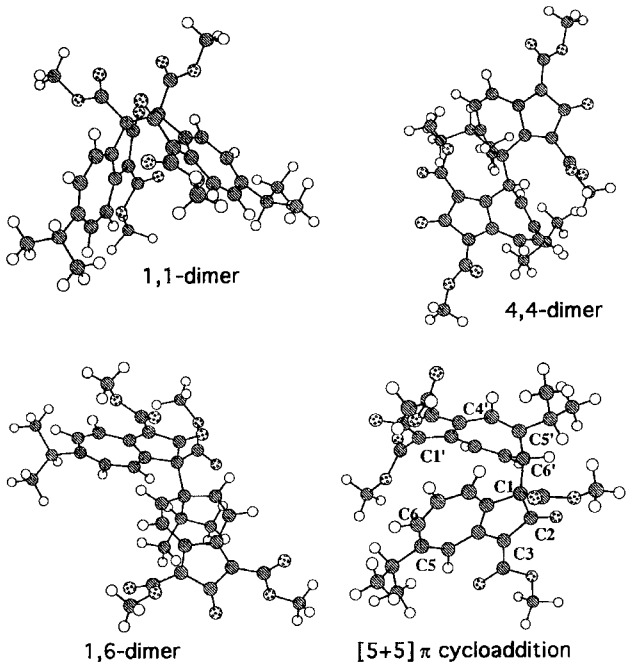


Fig. 3. Optimized structures of 1,1-, 1,6-dimers, and [5+5] π cycloaddition intermediate.

Experimental

The NMR spectra were measured by means of Brucker an AC 300 Model spectrometer in $CDCl_3$ at 300 MHz for protons and 75 MHz for carbons; the chemical shifts are expressed in δ units. The mass spectra were measured with a Finnigan TSQ-46-C spectrometer. The IR spectra were taken as KBr disks, using a Perkin-Elmer 983 G spectrometer. The UV-vis spectra were taken with a Shimadzu UV-3101 PC MODEL spectrophotometer in a methanol solution. The stationary phase for column chromatography was a Merck 7734 (70-230 mesh).

General Procedure for PbO_2-Oxidation Products from Azulenols. An AcOH solution (20 cm^3) of azulenol (ca. 1 mmol) was treated with PbO_2 (240 mg) for 7 h by occasional monitoring the reaction with a thin-layer chromatogram. To the mixture was then added 3% H_2O_2 to quench an excess amount of PbO_2, and the solution was diluted with water and extracted with CH_2Cl_2. After washing with water (to pH 7) and drying over $MgSO_4$, silica-gel column chromatography of the organic extract afforded the products.

PbO_2-Oxidation Products from Dimethyl 2-Hydroxyazulene-1,3-dicarboxylate (6) to 7 and 8. **7:** Yellow needles; mp 189—190 °C, 31%. Found: 518.4781. Calcd for $C_{28}H_{22}O_{10}$: 518.4767. ^{1}H NMR δ = 3.61 (6H, s), 3.66 (6H, s), 6.85 (2H, ddd, J = 10.8, 8.7, 1.1 Hz), 6.69 (2H, ddd, J = 10.8, 9.1, 1.4 Hz), 7.13 (2H, ddd, J = 11.8, 8.7, 1.4 Hz), 7.69 (2H, dd, J = 9.1, 1.1 Hz), and 8.35 (2H, dd, J = 11.8, 1.1 Hz); ^{13}C NMR δ = 51.3 (2C), 53.1 (2C), 69.3 (2C), 114.1 (2C), 132.3 (2C), 135.9 (2C), 136.07 (2C), 136.13 (2C), 140.5 (2C), 148.9 (2C), 164.2 (2C), 168.3 (2C), 170.7 (2C), and 188.8 (2C); MS *m/z*, 518 (M$^+$, 100), 487 (4.8), 459 (5.0), 415 (11), 260 (40), 232 (7.7), and 197 (84); UV ($CHCl_3$) 250 (ε 4.10), 277 (4.51), 312 (3.40), and 399 nm (4.60); IR (KBr) ν 1739, 1705, 1695, and 1682 cm^{-1}.

8: Yellow needles, mp 204—205 °C, 40%. Found: 518.4776. Calcd for $C_{28}H_{22}O_{10}$: 518.4767. ^{1}H NMR δ = 3.70 (6H, s), 3.83 (6H, s), 6.80—6.85 (4H, m), 7.03 (2H, ddd, J = 11.8, 8.2, 1.0 Hz), 7.33 (2H, dd, J = 8.2, 1.0 Hz), and 8.41 (2H, dd, J = 11.8, 1.0 Hz); ^{13}C NMR δ = 51.6 (2C), 53.7 (2C), 65.8 (2C), 116.6 (2C), 132.9

(2C), 135.4 (2C), 136.0 (2C), 140.1 (2C), 146.9 (2C), 164.6 (2C), 168.3 (2C), 169.8 (2C), 190.5 (2C), and 193.8 (2C); MS *m/z*, 518 (M^+, 31), 487 (3), 415 (13), 260 (19), 231 (80), 197 (92), 170 (57), and 113 (100); UV ($CHCl_3$) 254 (ε 4.12), 279 (4.53), 310 (3.42), and 398 nm (4.63); IR (KBr) 1740, 1699, and 1686 cm^{-1}.

PbO_2-Oxidation Products from Dimethyl 2-Hydroxy-6-isopropylazulene-1,3-dicarboxylate (2) to 3 and 4. **3:** Yellow needles; mp 201—202 °C, 80%. Found: 602.6368. Calcd for $C_{34}H_{34}O_{10}$: 602.6380. ^{1}H NMR δ = 1.24 (12H, d, J = 6.8 Hz), 2.70 (2H, hept, J = 6.8 Hz), 3.67 (6H, s), 3.73 (6H, s), 6.92 (2H, dd, J = 9.4, 1.9 Hz), 7.13 (2H, dd, J = 12.2, 1.9 Hz), 7.71 (2H, d, J = 9.4 Hz), and 8.38 (2H, d, J = 12.2 Hz); ^{13}C NMR δ = 22.7 (2C), 22.9 (2C), 37.9 (2C), 51.2 (2C), 53.0 (2C), 69.1 (2C), 113.0 (2C), 131.7 (2C), 132.0 (2C), 136.0 (2C), 142.0 (2C), 146.5 (2C), 157.1 (2C), 164.4 (2C), 168.6 (2C), 170.1 (2C), and 188.8 (2C); MS *m/z*, 602 (M^+, 0.5), 302 (27), 270 (100), 239 (64), and 212 (36); UV ($CHCl_3$) 248 (ε 4.06), 253 (4.13), 259 (4.20), 274 (4.47), 318 (3.42), and 394 nm (4.54); IR (KBr) 1724 and 1688 cm^{-1}.

4: Yellow needles, mp 208—210 °C, 15%. Found: 602.6371. Calcd for $C_{34}H_{34}O_{10}$: 602.6380. ^{1}H NMR δ = 1.20 (12H, d, J = 6.8 Hz), 2.72 (2H, hept, J = 6.8 Hz), 3.69 (6H, s), 3.82 (6H, s), 6.74 (2H, dd, J = 9.3, 1.9 Hz), 7.03 (2H, dd, J = 12.3, 1.9 Hz), 7.30 (2H, d, J = 9.3 Hz), and 8.44 (2H, d, J = 12.3 Hz); ^{13}C NMR δ = 22.6 (2C), 22.7 (2C), 37.9 (2C), 51.5 (2C), 53.6 (2C), 65.8 (2C), 115.4 (2C), 131.3 (2C), 132.4 (2C), 135.7 (2C), 141.7 (2C), 144.6 (2C), 157.3 (2C), 164.9 (2C), 168.6 (2C), 169.3 (2C), and 190.8 (2C); MS *m/z*, 602 (M^+, 6), 302 (24), 270 (100), 239 (40), and 212 (24); UV ($CHCl_3$) 236 (ε 4.15), 250 (4.31), 258 (4.25), 276 (4.55), 322 (3.48), and 397 nm (4.61); IR (KBr) 1724 and 1688 cm^{-1}.

PbO_2-Oxidation Products from Dimethyl 6-Bromo-2-hydroxyazulene-1,3-dicarboxylate (9) to 10 and 11. **10:** Yellow needles, mp 186—188 °C, 37%. Found: 676.2701. Calcd for $C_{28}H_{20}Br_2O_{10}$: 676.2688. ^{1}H NMR δ = 3.65 (6H, s), 3.71 (6H, s), 7.25 (2H, dd, J = 9.7, 2.0 Hz), 7.36 (2H, dd, J = 12.5, 2.0 Hz), 7.46 (2H, d, J = 9.7 Hz), and 8.07 (2H, d, J = 12.5 Hz); ^{13}C NMR δ = 51.5 (2C), 53.2 (2C), 69.3 (2C), 115.4 (2C), 130.7 (2C), 132.0 (2C), 134.0 (2C), 137.7 (2C), 144.1 (2C), 147.4 (2C), 163.7 (2C), 168.0 (2C), 168.8 (2C), and 188.5 (2C); MS *m/z*, 340 ($M^{+/2}$, 23), 338 (21), 308 (100), 306 (84), 277 (81), 275 (71), and 248 (43); UV ($CHCl_3$) 255 (ε 4.22), 275 (4.44), 318 (3.44), and 394 nm (4.56); IR (KBr) 1733, 1715, and 1689 cm^{-1}.

11: Yellow needles, mp 210—212 °C, 39%. Found: 676.2697. Calcd for $C_{28}H_{20}Br_2O_{10}$: 676.2688. ^{1}H NMR δ = 3.68 (6H, s), 3.84 (6H, s), 7.02 (2H, dd, J = 10.4, 2.1 Hz), 7.14 (2H, dd, J = 12.7, 2.1 Hz), 7.20 (2H, d, J = 10.4 Hz), and 8.19 (2H, d, J = 12.7 Hz); ^{13}C NMR δ = 51.9 (2C), 53.9 (2C), 66.1 (2C), 118.1 (2C), 131.5 (2C), 132.2 (2C), 133.2 (2C), 136.9 (2C), 143.7 (2C), 145.4 (2C), 164.2 (2C), 167.7 (2C), 169.5 (2C), and 188.7 (2C). MS *m/z*, 340 ($M^{+/2}$, 34), 338 (30), 308 (94), 306 (75), 277 (100), 275 (79), and 250 (76); UV ($CHCl_3$) 257 (ε 4.22), 274 (4.44), 317 (3.44), and 394 nm (4.55); IR (KBr) 1734, 1719, and 1686 cm^{-1}.

PbO_2-Oxidation Products from Dimethyl 2-Hydroxy-5-isopropylazulene-1,3-dicarboxylate (1) to 5, 12, 13, 14, and 15. **5:** Colorless needles, mp 203—204 °C, 50%. Found: 602.6392. Calcd for $C_{34}H_{34}O_{10}$: 602.6380. ^{1}H NMR δ = 0.93 (12H, d, J = 6.9 Hz), 2.21 (2H, hept, J = 6.9 Hz), 3.68 (2H, dd, J = 8.4, 0.8 Hz), 3.71 (6H, s), 3.81 (6H, s), 5.75 (2H, d, J = 1.2 Hz), 6.95 (2H, dd, J = 10.5, 0.8 Hz), and 7.20 (2H, ddd, J = 10.5, 8.4, 1.2 Hz); ^{13}C NMR δ = 20.0 (2C), 20.5 (2C), 34.3 (2C), 45.1 (2C), 52.2 (2C), 52.8 (2C), 64.0 (2C), 72.8 (2C), 119.5 (2C), 121.7 (2C), 128.7 (2C), 149.5 (2C), 154.4 (2C), 162.8 (2C), 169.4 (2C), 174.0 (2C), and 196.5 (2C); MS *m/z*, 602 (M^+, 38), 302 (88), 270 (100), 239 (66), and 212 (25); UV ($CHCl_3$) 282 (ε 4.83) and 303 nm (4.48); IR (KBr) 1744, 1711, and 1688 cm^{-1}.

12: Colorless needles, mp 216—218 °C, 7%. Found: 602.6397. Calcd for $C_{34}H_{34}O_{10}$: 602.6380. ^{1}H NMR δ = 1.18 (12H, d, J = 6.9 Hz), 2.94 (2H, hept, J = 6.9 Hz), 3.66 (6H, s), 3.68 (2H, dd, J = 8.1, 1.5 Hz), 3.85 (6H, s), 5.96 (2H, ddd, J = 8.6, 8.1, 1.3 Hz), 6.33 (2H, dd, J = 8.6, 1.5 Hz), and 6.99 (2H, d, J = 1.3 Hz); ^{13}C NMR δ = 19.4 (2C), 20.9 (2C), 38.6 (2C), 48.1 (2C), 52.1 (2C), 52.7 (2C), 64.1 (2C), 71.8 (2C), 115.0 (2C), 127.6 (2C), 129.9 (2C), 134.4 (2C), 163.1 (2C), 169.3 (2C), 173.0 (2C), 175.2 (2C), and 197.4 (2C); MS *m/z*, 602 (M^+, 17), 302 (79), 270 (100), 239 (57), and 212 (22); UV ($CHCl_3$) 289 (ε 4.91) and 313 nm (4.40); IR (KBr) 1751, 1720, and 1678 cm^{-1}.

13: Yellow needles, mp 93—96 °C, 2%. Found: 602.6378. Calcd for $C_{34}H_{34}O_{10}$: 602.6380. ^{1}H NMR δ = 1.41 (6H, d, J = 6.9 Hz), 1.54 (6H, d, J = 6.9 Hz), 3.30 (1H, hept, J = 6.9 Hz), 3.55 (6H, s), 3.81 (3H, s), 3.96 (3H, s), 4.02 (1H, hept, J = 6.9 Hz), 7.05 (1H, d, J = 11.5 Hz), 7.88 (1H, dd, J = 10.2, 9.5 Hz), 8.09 (1H, dd, J = 9.5, 1.9 Hz), 8.88 (1H, d, J = 11.5 Hz), 9.60 (1H, dd, J = 10.2, 1.1 Hz), 9.72 (1H, s), 9.82 (1H, d, J = 1.9 Hz), and 11.2 (1H, s, OH); ^{13}C NMR δ = 23.0 (2C), 24.6 (2C), 30.8, 39.3, 51.0, 51.2, 51.4, 51.5, 99.7, 100.8, 106.2, 106.2, 118.1, 131.9, 132.5, 133.3, 137.2, 138.3, 138.4, 139.6, 140.0, 142.6, 142.7, 143.7, 154.3, 161.5, 163.4, 164.0, 164.2, 167.1, 167.6, and 170.3; MS *m/z*, 603 (M^++1, 23), 570 (23), 538 (23), 464 (21), 300 (100), 269 (84), 239 (81), and 154 (71); UV ($CHCl_3$) 237 (ε 3.76), 265 (3.45), 314 (4.54), 385 (3.11), and 453 nm (2.75); IR (KBr) 3450, 1693, and 1647 cm^{-1}.

14: Yellow needles, mp 171—173 °C, 11%. Found: 602.6388. Calcd for $C_{34}H_{34}O_{10}$: 602.6380. ^{1}H NMR δ = 1.19 (12H, d, J = 6.8 Hz), 2.78 (2H, hept, J = 6.8 Hz), 3.64 (6H, s), 3.71 (6H, s), 6.85—6.88 (4H, m), 7.14 (2H, d, J = 10.9 Hz), and 8.21 (2H, s); ^{13}C NMR δ = 22.7 (2C), 23.0 (2C), 38.0 (2C), 51.3 (2C), 53.0 (2C), 69.3 (2C), 113.2 (2C), 131.8 (2C), 132.1 (2C), 134.8 (2C), 136.0 (2C), 142.1 (2C), 157.1 (2C), 159.0 (2C), 168.6 (2C), 170.2 (2C), and 188.6 (2C); MS *m/z*, 602 (M^+, 2), 302 (38), 270 (100), 239 (82), and 212 (43); UV ($CHCl_3$) 247 (ε 4.08), 253 (4.15), 259 (4.23), 274 (4.49), 318 (3.45), and 394 nm (4.56); IR (KBr) 1742, 1685, and 1673 cm^{-1}.

15: Yellow needles, mp 176—178 °C, 18%. Found: 602.6390. Calcd for $C_{34}H_{34}O_{10}$: 602.6380. ^{1}H NMR δ = 1.09 (6H, d, J = 6.8 Hz), 1.20 (6H, d, J = 6.8 Hz), 2.57 (1H, hept, J = 6.8 Hz), 2.80 (1H, hept, J = 6.8 Hz), 3.64 (3H, s), 3.65 (3H, s), 3.69 (3H, s), 3.74 (3H, s), 6.77 (1H, d, J = 7.6 Hz), 6.93—7.12 (3H, m), 7.14 (1H, s), 7.34 (1H, d, J = 10.6 Hz), 8.12 (1H, d, J = 12.0 Hz), and 8.28 (1H, s); ^{13}C NMR δ = 21.7, 22.0, 22.9, 23.1, 37.1, 37.5, 51.1, 52.0, 52.9, 53.3, 65.1, 65.9, 112.4, 113.5, 131.0, 131.4, 131.9, 132.2, 134.1, 134.9, 135.9, 136.2, 142.2, 142.8, 157.1, 157.5, 158.7, 158.9, 167.9, 168.4, 169.3, 171.1, 185.9, and 187.8; MS *m/z*, 602 (M^+, 1), 302 (42), 270 (100), 239 (80), and 212 (35); UV ($CHCl_3$) 247 (ε 3.39), 252 (4.44), 259 (4.50), 273 (4.64), 318 (3.30), and 393 nm (4.59); IR (KBr) 1735, 1724, 1702, 1691, and 1682 cm^{-1}.

PbO_2-Oxidation Products from Dimethyl 5-Bromo-2-hydroxyazulene-1,3-dicarboxylate (16) to 17, 18, and 19. **17:** Colorless needles, mp 205—206 °C, 13%. Found: 676.2694. Calcd for $C_{28}H_{20}Br_2O_{10}$: 676.2688. ^{1}H NMR δ = 3.83 (2H, ddd, J = 7.7, 2.1, 0.7 Hz), 3.85 (6H, s), 3.88 (6H, s), 6.20 (2H, dd, J = 8.8, 0.7 Hz), 6.49 (2H, ddd, J = 8.8, 7.7, 2.1 Hz), and 7.52 (2H, d, J = 2.1 Hz); ^{13}C NMR δ = 52.5 (2C), 53.2 (2C), 63.1 (2C), 71.8 (2C), 125.1 (2C), 125.9 (2C), 128.7 (2C), 130.4 (2C), 133.0 (2C), 146.4 (2C), 162.2 (2C), 168.2 (2C), 171.5 (2C), and 195.2 (2C); MS *m/z*, 678 (M^+, 5), 676 (M^+, 9), 674 (M^+, 5),, 672 (M^+, 8), 597 (86), 595 (83), 340 (25), 338 (29), 311 (98), 309 (100), 277 (50), 275 (51),

250 (29), and 248 (30); UV ($CHCl_3$) 228 (ε 4.27), 255 (4.09), 318 (4.56), and 370 nm (3.93); IR (KBr) 1730 and 1725 cm^{-1}.

18: Colorless needles, mp 192—194 °C, 11%. Found: 676.2697. Calcd for $C_{28}H_{20}O_{10}Br_2$: 676.2688. ^1H NMR δ = 3.71 (3H, s), 3.80 (3H, s), 3.85 (3H, s), 3.88 (3H, s), 4.06 (1H, dd, J = 7.6, 0.8 Hz), 4.15 (1H, d, J = 8.4, 1.1 Hz), 6.04 (1H, dd, J = 10.5, 0.8 Hz), 6.47 (1H, dd, J = 10.5, 7.6 Hz), 6.64 (1H, d, J = 1.7 Hz), 7.07 (1H, dd, J = 10.6, 1.1 Hz), 7.20 (1H, dd, J = 10.6, 8.4 Hz), and 7.55 (1H, s); ^{13}C NMR δ = 51.4, 51.8, 53.0, 53.7, 62.8, 63.4, 72.0, 72.9, 122.6, 124.8, 127.5, 129.4, 130.1, 131.4, 132.0, 133.2, 133.9, 134.5, 145.9, 146.1, 161.9, 162.7, 168.1, 168.8, 172.5, 172.9, 193.6, and 194.5; MS *m/z*, 678 (M^+, 5), 676 (M^+, 9), 674 (M^+, 5), 672 (M^+, 9), 597 (84), 595 (81), 340 (27), 338 (29), 311 (92), 309 (100), 277 (49), 275 (50), 250 (27), and 248 (28); UV ($CHCl_3$) 261 (ε 4.44) and 308 nm (4.51); IR (KBr) 1745, 1705, and 1680 cm^{-1}.

19: Yellow needles, mp 227—229 °C, 19%. Found: 676.2690. Calcd for $C_{28}H_{20}O_{10}Br_2$: 676.2688. ^1H NMR δ = 3.72 (6H, s), 3.73 (6H, s), 6.88—6.92 (4H, m), 7.83 (2H, d, J = 2.3 Hz), and 8.20 (2H, dd, J = 11.5, 0.7 Hz); ^{13}C NMR δ = 50.9 (2C), 53.1 (2C), 68.5 (2C), 115.2 (2C), 132.7 (2C), 135.0 (2C), 135.5 (2C), 136.9 (2C), 138.8 (2C), 142.0 (2C), 148.0 (2C), 148.9 (2C), 165.6 (2C), and 177.4 (2C); MS *m/z*, 678 (M^+, 6), 676 (M^+, 9), 674 (M^+, 6), 672 (M^+, 9), 340 (27), 338 (29), 311 (91), 309 (100), 277 (49), 175 (50), 250 (27), and 248 (28); UV ($CHCl_3$) 236 (ε 4.58), 322 (4.02), and 422 nm (4.55); IR (KBr) 1755, 1710, and 1693 cm^{-1}.

PbO_2-Oxidation Products from Methyl 1-Bromo-2-hydroxy-5-isopropylazulene-3-carboxylate (21) to 22, 23, and 24. 22: Colorless needles, mp 194—195 °C, 7%. Found: 644.3572. Calcd for $C_{30}H_{28}Br_2O_6$: 644.3567. ^1H NMR δ = 1.18 (12H, d, J = 6.9 Hz), 2.66 (2H, hept, J = 6.9 Hz), 3.72 (2H, dd, J = 7.9, 1.3 Hz), 3.88 (6H, s), 6.29 (2H, ddd, J = 8.8, 7.9, 1.3 Hz), 6.66 (2H, dd, J = 8.8, 1.3 Hz), and 6.99 (2H, d, J = 1.3 Hz); ^{13}C NMR δ = 19.1 (2C), 20.5 (2C), 38.9 (2C), 50.8 (2C), 52.3 (2C), 62.3 (2C), 73.1 (2C), 117.2 (2C), 126.8 (2C), 133.1 (2C), 147.4 (2C), 162.7 (2C), 170.0 (2C), 170.3 (2C), and 195.4 (2C); MS *m/z*, 646 (M^+, 3), 644 (M^+, 5), 642 (M^+, 3), 565 (32), 563 (32), 484 (100), 428 (45), 324 (42), 323 (50), 322 (66), 321 (57), 295 (64), and 293 (64); UV ($CHCl_3$) 231 (ε 4.33), 240 (3.98), and 313 nm (4.52); IR (KBr) 1755 and 1743 cm^{-1}.

23: Colorless needles, mp 222—224 °C, 27%. Found: 644.3581. Calcd for $C_{30}H_{28}Br_2O_6$: 644.3567. ^1H NMR δ = 0.91 (12H, d, J = 6.9 Hz), 2.20 (2H, hept, J = 6.9 Hz), 3.67 (2H, dd, J = 8.5, 1.2 Hz), 3.73 (6H, s), 5.69 (2H, d, J = 1.2 Hz), 6.47 (2H, dd, J = 8.6, 1.1 Hz), and 7.06 (2H, dd, J = 8.6, 8.5 Hz); ^{13}C NMR δ = 20.1 (2C), 21.4 (2C), 37.7 (2C), 51.7 (2C), 52.4 (2C), 63.2 (2C), 74.5 (2C), 118.0 (2C), 127.1 (2C), 134.2 (2C), 148.3 (2C), 165.1 (2C), 169.0 (2C), 171.0 (2C), and 189.6 (2C); MS *m/z*, 646 (M^+, 2), 644 (M^+, 4), 642 (M^+, 2), 565 (33), 563 (33), 484 (100), 428 (44), 324 (40), 232 (51), 322 (67), 321 (57), 295 (65), and 293 (68); UV ($CHCl_3$) 233 (ε 4.31), 238 (4.00), and 308 nm (4.55); IR (KBr) 1749, 1726, and 1680 cm^{-1}.

24: Colorless needles, mp 198—199 °C, 29%. Found: 644.3579. Calcd for $C_{30}H_{28}Br_2O_6$: 644.3567. ^1H NMR δ = 1.10 (6H, d, J = 7.1 Hz), 1.24 (6H, d, J = 6.5 Hz), 2.27 (1H, hept, J = 6.5 Hz), 2.92 (1H, hept, J = 7.1 Hz), 3.66 (1H, d, J = 6.7 Hz), 3.68 (3H, s), 3.76 (1H, d, J = 7.5 Hz), 3.83 (3H, s), 5.37 (1H, d, J = 0.9 Hz), 6.28 (1H, dd, J = 8.7, 7.5 Hz), and 6.60—6.79 (4H, m); ^{13}C NMR δ = 19.3, 20.4 (2C), 21.0, 34.1, 38.7, 46.6, 48.6, 52.2, 52.8, 62.5, 63.1, 70.3, 75.0, 114.1, 120.0, 123.8, 125.5, 126.4, 133.2, 133.4, 146.6, 153.9, 162.8, 163.0, 169.1, 171.7, 172.9, 195.1, and 196.0; MS *m/z*, 646 (M^+, 3), 644 (M^+, 5), 642 (M^+, 3), 565 (31), 563 (34), 484 (100), 428 (44), 324 (42), 323 (51), 322 (66), 321 (56), 295 (63), and 293 (67); UV ($CHCl_3$) 229 (ε 4.31), 242 (3.94), and 312 nm (4.58); IR (KBr) 1775, 1755, 1703, and 1692 cm^{-1}.

PbO_2-Oxidation Products from Methyl 1-Cyano-2-hydroxy-5-isopropylazulene-1-carboxylate (25) to 26, 27, 28, 29, 30, 31, and 32. 26: Colorless needles, mp 210—212 °C, 19%. Found: 536.5850. Calcd for $C_{32}H_{28}N_2O_6$: 536.5841. ^1H NMR δ = 1.24 (12H, d, J = 7.1 Hz), 2.76 (2H, hept, J = 7.1 Hz), 3.73 (2H, dd, J = 7.3, 1.3 Hz), 3.87 (6H, s), 6.40 (2H, ddd, J = 8.8, 7.3, 1.3 Hz), 6.51 (2H, dd, J = 8.8, 1.3 Hz), and 7.13 (2H, s); ^{13}C NMR δ = 19.7 (2C), 20.0 (2C), 34.2 (2C), 45.0 (2C), 53.3 (2C), 60.3 (2C), 64.8 (2C), 73.0 (2C), 110.7 (2C), 118.8 (2C), 121.5 (2C), 152.5 (2C), 155.3 (2C), 168.3 (2C), 171.0 (2C), and 194.7 (2C) ; MS *m/z*, 536 (M^+, 2), 433 (18), 269 (81), 240 (100), and 222 (27); UV ($CHCl_3$) 241 (ε 3.70) and 313 nm (4.54); IR (KBr) 2202, 1773, 1739, and 1683 cm^{-1}.

27: Colorless needles, mp 141—142 °C, 5%. Found: 536.5847. Calcd for $C_{32}H_{28}N_2O_6$: 536.5841. ^1H NMR δ = 1.11 (6H, d, J = 7.0 Hz), 1.25 (6H, d, J = 7.5 Hz), 2.32 (1H, hept, J = 7.0 Hz), 2.92 (1H, hept, J = 7.5 Hz), 3.61 (1H, d, J = 6.2 Hz), 3.67 (1H, d, J = 7.6 Hz), 3.71 (3H, s), 3.84 (3H, s), 5.38 (1H, d, J = 0.9 Hz), 6.37—6.45 (2H, m), 6.87—6.93 (2H, m), and 7.20 (1H, dd, J = 10.0, 8.5 Hz); ^{13}C NMR δ = 19.1, 19.9, 20.3, 20.9, 33.9, 39.0, 45.8, 46.3, 52.4, 53.1, 61.0, 61.5, 62.0, 71.3, 110.5, 114.4, 116.4, 116.5, 119.9, 125.7, 126.2, 128.6, 135.6, 149.3, 154.0, 161.9, 168.1, 172.5, 174.3, 174.4, 190.9, and 195.5; MS *m/z*, 536 (M^+, 3), 433 (17), 269 (79), 240 (100), and 222 (26); UV ($CHCl_3$) 238 (ε 3.70) and 314 nm (4.58); IR (KBr) 2210, 1780, 1755, 1738, and 1691 cm^{-1}.

28: Colorless needles, mp 251—252 °C, 7%. Found: 536.5853. Calcd for $C_{32}H_{28}N_2O_6$: 536.5841. ^1H NMR δ = 0.96 (12H, d, J = 6.8 Hz), 2.25 (2H, hept, J = 6.8 Hz), 3.77 (6H, s), 3.78 (2H, ddd, J = 8.6, 1.3, 1.0 Hz), 5.70 (2H, d, J = 1.3 Hz), 6.59 (2H, dd, J = 10.0, 1.0 Hz), and 7.35 (2H, dd, J = 10.0, 8.6 Hz); ^{13}C NMR δ = 20.0 (2C), 20.5 (2C), 34.3 (2C), 45.1 (2C), 53.3 (2C), 64.9 (2C), 73.1 (2C), 110.8 (2C), 114.0 (2C), 118.8 (2C), 121.5 (2C), 152.5 (2C), 155.4 (2C), 168.4 (2C), 178.1 (2C), and 194.8 (2C); MS *m/z*, 536 (M^+, 3), 433 (16), 269 (79), 240 (100), and 222 (25); UV ($CHCl_3$) 239 (ε 3.66) and 311 nm (4.47); IR (KBr) 2204, 1768, 1749, and 1682 cm^{-1}.

29: Yellow needles, mp 222—223 °C, 18%. Found: 536.5846. Calcd for $C_{32}H_{28}O_6N_2$: 536.5841. ^1H NMR δ = 1.14 (6H, d, J = 6.0 Hz), 1.21 (6H, d, J = 6.7 Hz), 2.72 (1H, hept, J = 6.0 Hz), 2.84 (1H, hept, J = 6.7 Hz), 3.75 (3H, s), 3.77 (3H, s), 7.00—7.08 (3H, m), 7.21—7.30 (3H, m), 7.48 (1H, d, J = 1.6 Hz), and 8.35 (1H, d, J = 1.0 Hz); ^{13}C NMR δ = 21.6, 21.9, 22.1, 22.3, 38.9, 39.1, 52.0, 53.8, 68.5, 69.0, 98.1, 98.4, 111.6, 114.8, 128.9, 131.1, 131.7, 134.1, 134.5, 137.0, 138.9, 142.7, 144.0, 144.9, 156.4, 162.5, 165.9, 166.1, 168.7, 170.1, 183.5, and 187.1; MS *m/z*, 536 (M^+, 4), 269 (87), 240 (100), and 222 (21); UV ($CHCl_3$) 238 (ε 4.62), 314 (3.91), and 419 nm (4.52); IR (KBr) 2204, 1749, 1744, 1726, and 1680 cm^{-1}.

30: Yellow needles, mp 208—209 °C, 13%. Found: 536.5855. Calcd for $C_{32}H_{28}O_6N_2$: 536.5841. ^1H NMR δ = 1.21 (12H, d, J = 6.8 Hz), 2.75 (2H, hept, J = 6.8 Hz), 3.66 (6H, s), 6.81 (2H, ddd, J = 8.8, 2.6, 1.6 Hz), 7.11 (2H, dd, J = 11.3, 8.8 Hz), 7.30 (2H, dd, J = 11.3, 2.6 Hz), and 7.52 (2H, d, J = 1.6 Hz); ^{13}C NMR δ = 22.5 (2C), 22.8 (2C), 39.1 (2C), 53.6 (2C), 68.0 (2C), 98.3 (2C), 113.7 (2C), 128.9 (2C), 133.4 (2C), 139.7 (2C), 141.8 (2C), 148.0 (2C), 160.1 (2C), 166.6 (2C), 172.0 (2C), and 186.9 (2C); MS *m/z*, 536 (M^+, 2), 269 (79), 240 (100), and 222 (23); UV ($CHCl_3$) 236 (ε 4.56), 317 (3.94), and 418 nm (4.55); IR (KBr) 2205, 1755, and 1680 cm^{-1}.

31: Yellow needles, mp 178—180 °C, 11%. Found: 536.5848. Calcd for $C_{32}H_{28}N_2O_6$: 536.5841. ^{1}H NMR δ = 1.26 (6H, d, J = 6.4 Hz), 1.31 (6H, d, J = 6.7 Hz), 2.80 (2H, m), 3.87 (3H, s), 3.89 (3H, s), 6.60 (1H, dd, J = 8.5, 3.2 Hz), 6.70 (1H, dd, J = 9.3, 8.5 Hz), 6.82 (1H, ddd, J = 9.3, 3.2, 1.7 Hz), 6.91 (1H, ddd, J = 8.5, 1.3, 1.0 Hz), 7.17 (1H, dd, J = 11.3, 8.5 Hz), 7.25 (1H, dd, J = 11.3, 1.0 Hz), 8.05 (1H, d, J = 1.7 Hz), and 8.60 (1H, d, J = 1.3 Hz); ^{13}C NMR δ = 22.3, 22.5, 22.5, 22.8, 38.9, 39.5, 51.7, 54.1, 60.3, 63.8, 99.1, 99.3, 112.7, 115.5, 129.3, 130.7, 131.3, 133.0, 134.2, 137.5, 139.7, 142.4, 144.8, 145.2, 159.6, 163.6, 163.9, 165.8, 169.0, 169.8, 184.7, and 187.0; MS *m/z*, 536 (M^+, 7), 269 (78), 240 (100), and 222 (19); UV ($CHCl_3$) 239 (ε 4.66), 319 (3.99), and 422 nm (4.56); IR (KBr) 2205, 1779, 1757, 1736, and 1683 cm^{-1}.

32: Yellow needles, mp 227—229 °C, 21%. Found: 536.5845. Calcd for $C_{32}H_{28}N_2O_6$: 536.5841. ^{1}H NMR δ = 1.27 (12H, d, J = 6.7 Hz), 2.85 (2H, hept, J = 6.7 Hz), 3.69 (6H, s), 6.93 (2H, d, J = 8.6 Hz), 7.19—7.33 (4H, m), and 7.93 (2H, d, J = 1.7 Hz); ^{13}C NMR δ = 22.5 (2C), 22.6 (2C), 38.9 (2C), 53.5 (2C), 68.0 (2C), 97.0 (2C), 113.1 (2C), 129.2 (2C), 132.6 (2C), 139.2 (2C), 142.4 (2C), 148.0 (2C), 159.9 (2C), 167.5 (2C), 171.1 (2C), and 187.5 (2C); MS *m/z*, 536 (M^+, 3), 269 (84), 240 (100), and 222 (29); UV ($CHCl_3$) 237 (ε 4.61), 318 (3.87), and 417 nm (4.45); IR (KBr) 2205, 1771, and 1695 cm^{-1}.

PbO_2-Oxidation Products from Methyl 2-Hydroxy-5-isopropyl-1-thiocyanatoazulene-3-carboxylate (33) to 34 and 35. 34: Colorless needles, mp 164—165 °C, 16%. Found: 600.7047. Calcd for $C_{32}H_{28}N_2O_6S_2$: 600.7041. ^{1}H NMR δ = 1.18 (12H, d, J = 6.9 Hz), 2.66 (2H, hept, J = 6.9 Hz), 3.72 (2H, d, J = 7.8 Hz), 3.88 (6H, s), 6.29 (2H, d, J = 8.7 Hz), 6.66 (2H, d, J = 8.7 Hz), and 6.99 (2H, d, J = 1.3 Hz); ^{13}C NMR δ = 19.9 (2C), 21.3 (2C), 35.7 (2C), 46.7 (2C), 52.7 (2C), 63.8 (2C), 73.0 (2C), 113.5 (2C), 120.5 (2C), 129.6 (2C), 136.1 (2C), 147.2 (2C), 157.8 (2C), 168.0 (2C), 171.0 (2C), and 192.6 (2C) ; MS *m/z*, 600 (M^+, 2), 485 (6), 301 (10), 269 (100), and 171 (9); UV ($CHCl_3$) 239 (ε 3.99) and 313 nm (4.58); IR (KBr) 2159, 1749, and 1724 cm^{-1}.

35: Colorless needles, mp 232—234 °C, 25%. Found: 600.7050. Calcd for $C_{32}H_{28}N_2O_6S_2$: 600.7041. ^{1}H NMR δ = 0.92 (3H, d, J = 6.8 Hz), 0.96 (3H, d, J = 6.8 Hz), 1.14 (3H, d, J = 7.3 Hz), 1.27 (3H, d, J = 7.3 Hz), 2.33 (1H, hept, J = 7.3 Hz), 3.01 (1H, hept, J = 6.8 Hz), 3.62 (1H, d, J = 8.4 Hz), 3.70 (3H, s), 3.84 (3H, s), 3.92 (1H, d, J = 7.4 Hz), 5.36 (1H, s), 6.34 (1H, d, J = 8.6 Hz), 6.46 (1H, dd, J = 8.6, 7.4 Hz), 6.81 (1H, d, J = 9.7 Hz), 6.93 (1H, dd, J = 9.7, 8.4 Hz), and 6.98 (1H, s); ^{13}C NMR δ = 19.2, 20.2, 20.5, 21.1, 34.0, 39.0, 46.0, 47.6, 52.3, 53.1, 62.4, 64.3, 70.5, 73.1, 106.3, 110.4, 114.6, 119.2, 120.6, 126.7, 127.2, 134.9, 136.1, 144.4, 155.1, 162.2, 167.9, 168.5, 172.0, 175.0, 193.4, and 195.8; MS *m/z*, 600 (M^+, 2), 485 (7), 301 (10), 269 (100), and 171 (11); UV ($CHCl_3$) 238 (ε 4.02) and 313 nm (4.57); IR (KBr) 2163, 1750, and 1735 cm^{-1}.

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11 X-ray structure determinations.

Crystal data for 7. Red prisms, $C_{28}H_{22}O_{10}$, MW = 518.48, triclinic, space group $P\bar{1}$, a = 8.266(5), b = 10.975(8), c = 15.01(1) Å, α = 110.30(6)°, β = 99.18(6)°, γ = 102.91(6)°, V = 1201(4) Å^3, D_{calcd} = 1.432 g cm^{-3}, and Z = 2. Data collection was performed with Mo$K\alpha$ radiation (λ = 0.71069 Å) on a Rigaku AFC6S diffractometer. The structures were solved by direct method and expanded using Fourier syntheses. Totals of 1662 reflections having intensities greater than 3.0 times their standard deviations were used to refine the structures in full-matrix least squares. The final R and R_w were 0.063 and 0.057.

Crystal data for 3. Red prisms, $C_{34}H_{34}O_{10}$, MW = 602.64, tetragonal, space group $I42d$, a = 22.917(4), c = 11.509(4) Å, V = 6044(2) Å^3, Z = 8, D_{calcd} = 1.324 g cm^{-3}. The final R and R_w were 0.071 and 0.047.

Crystal data for 4. Red prisms, $C_{34}H_{34}O_{10}$, MW = 602.64, triclinic, space group $P\bar{1}$, a = 10.590(3), b = 12.626(5), c = 12.864(4) Å, α = 110.22(3)°, β = 106.63(3)°, γ = 99.67(3)°, V = 1476.9(9) Å^3, Z = 2, D_{calcd} = 1.355 g cm^{-3}. The final R and R_w were 0.078 and 0.076.

Crystal data for 10·CH_2Cl_2. Single crystal of **10**·CH_2Cl_2 suitable for an X-ray structural analysis were obtained by recrystallization from dichlorometane. Red prisms, $C_{29}H_{22}Br_2Cl_2O_{10}$,

MW = 761.20, monoclinic, space group $C2/c$, $a = 32.900(4)$, $b = 10.519(3)$, $c = 20.964(5)$ Å, $\beta = 122.789(10)°$, $V = 6099(2)$ Å^3, $Z = 8$, $D_{calcd} = 1.658$ g cm^{-3}. The final R and R_w were 0.071 and 0.047.

Crystal data for 11. Yellow prisms, $C_{28}H_{20}Br_2O_{10}$, MW = 676.26, triclinic, space group $P\bar{1}$, $a = 7.159(18)$, $b = 9.216(10)$, $c = 10.736(16)$ Å, $\alpha = 78.180(10)°$, $\beta = 69.832(16)°$, $\gamma = 76.918(14)°$, $V = 641.3(20)$ Å^3, $Z = 1$, $D_{calcd} = 1.751$ g cm^{-3}. The final R and R_w values were 0.040 and 0.037.

Crystal data for 12. Colorless prisms, $C_{34}H_{34}O_{10}$, MW = 602.64, triclinic, space group $P\bar{1}$, $a = 9.102(3)$, $b = 9.583(5)$, $c = 10.358(10)$ Å, $\alpha = 77.26(6)°$, $\beta = 63.46(5)°$, $\gamma = 72.13(3)°$, $V = 765.6(9)$ Å^3, $Z = 1$, $D_{calcd} = 1.307$ g cm^{-3}. The final R and R_w values were 0.048 and 0.048.

Crystal data for 15. Red prisms, $C_{34}H_{34}O_{10}$, MW = 602.64, monoclinic, space group $P2_1/c$, $a = 8.954(2)$, $b = 24.169(2)$, $c = 14.719(2)$ Å, $\beta = 101.29(1)°$, $V = 3120.4(9)$ Å^3, $Z = 4$, $D_{calcd} = 1.283$ g cm^{-3}. The final R and R_w values were 0.048 and 0.048.

Crystal data for 22. Colorless prisms, $C_{30}H_{28}Br_2O_6$, MW = 644.35, monoclinic, space group $P2_1/c$, $a = 8.682(3)$, $b = 17.866(5)$, $c = 8.619(17)$ Å, $\beta = 96.08(3)°$, $V = 1329.4(6)$ Å^3, $Z = 2$, $D_{calcd} = 1.610$ g cm^{-3}. The final R and R_w values were 0.165 and 0.190.

Crystal data for 23. Colorless prisms, $C_{30}H_{26}Br_2O_6$, MW = 642.33, triclinic, space group $P\bar{1}$, $a = 8.7415(12)$, $b = 14.969(5)$, $c = 20.270(6)$ Å, $\alpha = 93.26(3)°$, $\beta = 99.817(19)°$, $\gamma = 91.155(19)°$, $V = 2608.1(12)$ Å^3, $Z = 4$, $D_{calcd} = 1.636$ g cm^{-3}. The final R and R_w values were 0.092 and 0.091.

Crystal data for 24. Colorless prisms, $C_{30}H_{28}Br_2O_6$, MW = 644.35, monoclinic, space group $P2_1/c$, $a = 9.774(3)$, $b = 43.848(10)$, $c = 13.528(6)$ Å, $\beta = 109.80(4)°$, $V = 5454.0(3)$ Å^3, $Z = 8$, $D_{calcd} = 1.569$ g cm^{-3}. The final R and R_w values were 0.089 and 0.104.

Crystal data for 26. Colorless prisms, $C_{32}H_{28}N_2O_6$, MW = 536.58, monoclinic, space group $P2_1/n$, $a = 9.5895(18)$, $b = 10.565(3)$, $c = 14.042(4)$ Å, $\beta = 106.615(22)°$, $V = 1363.3(6)$ Å^3, $Z = 2$, $D_{calcd} = 1.307$ g cm^{-3}. The final R and R_w values were 0.054 and 0.047.

Crystal data for 27. Colorless prisms, $C_{35}H_{35}N_3O_7$, MW = 609.67, monoclinic, space group $P2_1/n$, $a = 14.784(5)$, $b = 14.286(5)$, $c = 16.060(6)$ Å, $\beta = 92.95(3)°$, $V = 3387.3(20)$ Å^3, $Z = 4$, $D_{calcd} = 1.196$ g cm^{-3}. The final R and R_w were 0.160 and 0.182.

Crystal data for 28. Colorless prisms, $C_{32}H_{28}N_2O_6$, MW = 536.58, orthorhombic, space group $Pbca$, $a = 14.653(5)$, $b = 8.217(3)$, $c = 21.769(6)$ Å, $V = 2620.9(14)$ Å^3, $Z = 4$, $D_{calcd} = 1.360$ g cm^{-3}. The final R and R_w were 0.061 and 0.055.

Crystal data for 30. Yellow prisms, $C_{32}H_{28}N_2O_6$, MW = 536.58, triclinic, space group $P\bar{1}$, $a = 8.335(4)$, $b = 13.303(5)$, $c = 13.692(6)$ Å, $\alpha = 79.71(3)°$, $\beta = 72.09(3)°$, $\gamma = 87.55(3)°$, $V = 1421.3(11)$ Å^3, $Z = 2$, $D_{cacld} = 1.237$ g cm^{-3}. The final R and R_w values were 0.084 and 0.087.

Crystal data for 32. Yellow prisms, $C_{32}H_{28}N_2O_6$, MW = 536.58, triclinic, space group $P\bar{1}$, $a = 10.648(4)$, $b = 11.010(5)$, $c = 12.940(4)$ Å, $\alpha = 99.17(3)°$, $\beta = 95.81(3)°$, $\gamma = 101.52(3)°$, $V = 1453.5(10)$ Å^3, $Z = 2$, $D_{cacld} = 1.267$ g cm^{-3}. The final R and R_w values were 0.062 and 0.066.

Crystal data for 34. Colorless prisms, $C_{32}H_{28}N_2O_6S_2$, MW = 600.70, triclinic, space group $P\bar{1}$, $a = 9.271(3)$, $b = 11.531(4)$, $c = 13.707(4)$ Å, $\alpha = 88.06(3)°$, $\beta = 79.96(3)°$, $\gamma = 77.35(3)°$, $V = 1407.9(8)$ Å^3, $Z = 2$, $D_{cacld} = 1.417$ g cm^{-3}. The final R and R_w values were 0.053 and 0.054.

Crystal data for 35. Colorless prisms, $C_{32}H_{28}N_2O_6S_2$, MW = 600.70, monoclinic, space group $P2_1/n$, $a = 9.6665(20)$, $b = 12.575(5)$, $c = 26.248(11)$ Å, $\beta = 92.97(3)°$, $V = 3186.3(20)$ Å^3, $Z = 4$, $D_{calcd} = 1.342$ g cm^{-3}. The final R and R_w were 0.054 and 0.056.

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13 Preparation of Dimethyl 5-Bromo-2-hydroxyazulene-1,3-dicarboxylate (**16**). To a solution of dimethyl 6-amino-5-bromo-2-hydroxyazulene-1,3-dicarboxylate (355 mg, 1 mmol), prepared from bromine and dimethyl 6-amino-2-hydroxyazulene-1,3-dicarboxylate, in 50 mL of DME were added 1,4-benzoquinone (113 mg, 1 mmol) and concentrated sulfuric acid (1 mmol). A solution of isopentyl nitrite (20 mL) in DME (50 mL) and a solution of 1, 4-benzoquinone (113 mg) in DME (50 mL) were added dropwise over a period of 20 min., respectively. Stirring was continued for approximately four hours longer. The mixture was poured into a large amount of ice-water (1.2 L). The product precipitated from the solution. The precipitate was washed with hexane and recrystallized from acetone, the product (241 mg, 71%) was obtained as yellow needles, mp 154—155°C. ^{1}H NMR (300 MHz, $CDCl_3$), δ = 4.03 (3H, s), 4.05 (3H, s), 7.41 (1H, t, J = 10.4 Hz), 8.01 (1H, d, J = 10.4 Hz), 9.22 (1H, d, J = 9.8 Hz), 9.63 (1H, s), and 11.80 (1H, s); EIMS m/z (rel intensity) 340 (54), 338 (53), 308 (100), 306 (99), 277 (79), 275 (78), 250 (57), 248 (57), and 199 (23); UV ($CHCl_3$) 370 (ε 3.93), 318 (4.56), 255 (4.09), and 228 nm (4.27); IR (KBr) 3350—3550, and 1680 cm^{-1}.

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