Decarbonylation Reaction of 1-Azulenecarbaldehydes under Mild Conditions. A Strategy for the Protection of 1- and/or 3-Position of Azulene Rings

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The reaction of 1-azulenecarbaldehydes **9a** and **b** with pyrrole (**8**) in acetic acid resulted in decarbonylation to afford azulenes even at room temperature in 49 and 78% yields, respectively. 1,3-Azulenedicarbaldehydes also reacted with **8** to give azulenes in 36 and 52% yields, respectively. This decarbonylation reaction was adopted to the selective synthesis of 3,3′-unsubstituted di(1-azulenyl)methane derivatives **7a**—**d**. Acid-catalyzed condensation of **9a** and **b** with paraformaldehyde or benzaldehyde afforded 3,3′-methylenedi(1-azulenecarbaldehyde)s, following this decarbonylation reaction gave the desired **7a**—**d** as a sole product in 33—59% yields starting from **9a** and **b**. Such decarbonylation is because of the ability of protonation of azulene ring in acidic condition and because of electron-donating properties of pyrrole ring. This reaction would serve as a new strategy for the protection of 1- and/or 3-positions of azulene ring.

We have recently reported the synthesis of a series of (1-azulenyl)methyl cations, i.e., tri(1-azulenyl)methyl, di(1-azulenyl)phenylmethyl, and (1-azulenyl)diphenylmethyl hexafluorophosphates (**1a**·PF_6^-, **2a**·PF_6^-, and **3a**·PF_6^-) and their derivatives (e.g., **1b**, **c**·PF_6^-, **2b**, **c**·PF_6^-, and **3b**, **c**·PF_6^-) (Chart 1). These cations exhibited extreme stabilities with extraordinarily high pK_{R^+} values (e.g., **1a**; 11.3, **2a**; 10.8, and **3a**; 3.6, respectively).[1] They were readily prepared by the acid-catalyzed condensation of azulenes with aldehydes or diphenylmethanols and the subsequent hydride abstraction of the condensation products with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone.[1] However, we often encountered difficulties when 1,3-unsubstituted azulenes **4** were adapted to this acid-catalyzed condensation, because the condensation takes place at both 1- and 3-positions of **4**. Thus, the condensation of **4** with aldehydes such as paraformaldehyde (**5**) or benzaldehyde (**6**) in acetic acid gave a mixture of oligomeric products, e.g., 1,3-bis[(1-azulenyl)methyl]-azulene derivatives, including the desired di(1-azulenyl)-methane derivatives **7**.[1,3—5] Separation of these oligomeric mixture components is particularly troublesome. In most cases it is necessary to use a gel permeation chromatography (GPC) for the separation and the yield of the desired products **7** often becomes fairly low.[1] To avoid this undesired oligomerization, we need some protection method for one of the reactive 1,3-positions of **4**. Alkoxycarbonyl groups might be available for this purpose. However, removal of the alkoxycarbonyl groups requires strong conditions such as heating in high acidic or basic conditions.[2] Here we will report that the formyl substituents can serve as a protecting group of these reactive positions of **4**.

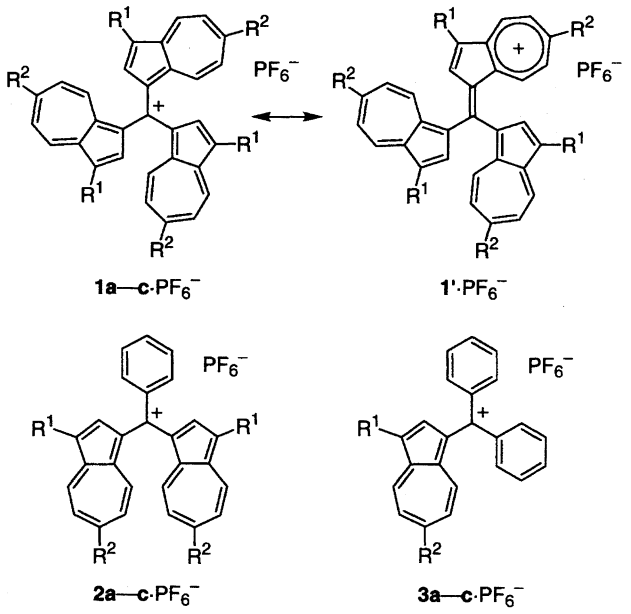
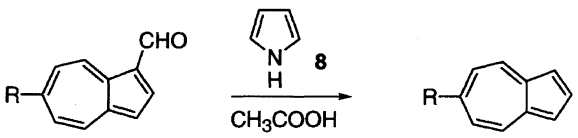


Chart 1.

Results and Discussion

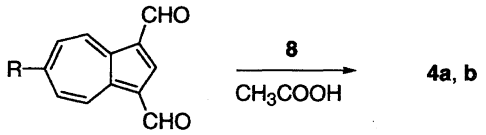
The reaction of pyrrole (**8**) with aldehydes in acidic conditions is a key reaction for the synthesis of porphyrin derivatives. However, we found that the reaction of 1-azulenecarbaldehydes **9a** and **b**[1a] with an excess amount of **8** in acetic acid resulted in decarbonylation to yield azulenes **4a** and **b**[1a] even at room temperature (Scheme 1). Representative results of this decarbonylation reaction are summarized in Table 1. 6-*t*-Butyl-1,3-azulenedicarbaldehyde (**10b**) was prepared by Vilsmeier formylation of **4b** in 90% yield (Scheme 2). The reaction of 1-azulenecarbaldehydes with **8** in acetic acid



Scheme 1.

Table 1. Decarbonylation Reaction of 1-Azulenecarbaldehydes **9a**, **b** and **10a**, **b**

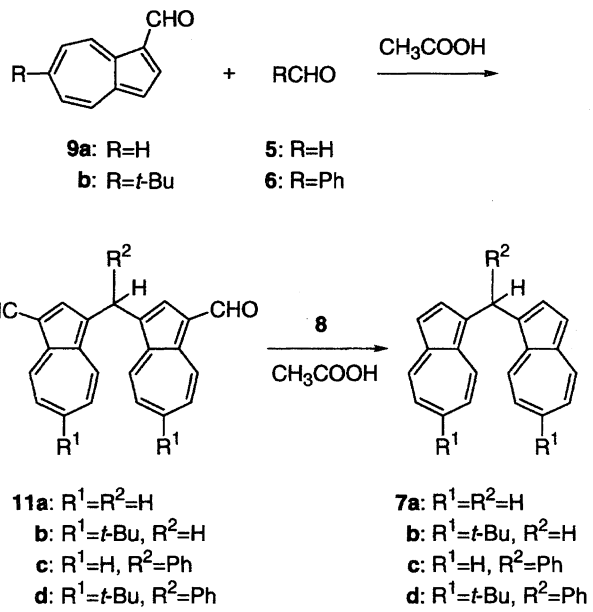
Entry	Substrate	R	Conditions	Product (Yield/%)
1	**9a**	H	R.T. 3 d	**4a** (49)
2	**9b**	*t*-Bu	R.T. 3 d	**4b** (78)
3	**10a**	H	R.T. 3 d	**4a** (36)
4	**10b**	*t*-Bu	R.T. 3 d	**4b** (52)



Scheme 2.

at room temperature for 3 d is a typical condition for this decarbonylation reaction. *t*-Butyl substituent at 6-position increased the yield of the decarbonylation (Entries 2 and 4). These results are suggesting that the formyl substituents might open a new protecting method of the reactive 1- and/or 3-positions of azulene ring.

This decarbonylation reaction of 1-azulenecarbaldehydes under mild conditions was applied to the selective synthesis of di(1-azulenyl)methane derivatives **7a**—**d**, which demonstrated the utility of this reaction. Results of the selective synthesis of di(1-azulenyl)methane derivatives **7a**—**d** are summarized in Table 2. Condensation reaction of 1-azulenecarbaldehydes **9a** and **b** with paraformaldehyde (**5**) and benzaldehyde (**6**) in refluxing acetic acid afforded 3,3′-methylenedi(1-azulenecarbaldehyde)s **11a**—**d** selectively and in good yield (Table 2), because the reactivities of the aldehydes **5** and **6** are much higher than those of **9a** and **b** in this condensation condition. Decarbonylation of the di(1-azulenecarbaldehyde)s **11a**—**c** with **8** in acetic acid at room temperature afforded the desired **7a**—**c**[3–6] in 43—61% yields, as a sole product (Scheme 3). However, the decarbonylation reaction of **11d** with **8** in acetic acid at room temperature for 3 d gave a mixture of desired **7d**[1a] and monodecarbonylated product, i.e., 6-*t*-butyl-3-[6-*t*-butyl-1-azulenyl(phenyl)methyl]-1-azulenecarbaldehyde (**12**), in 8 and 10% yields, respectively, and 66% of starting **11d** was recovered, due to the low solubilities of **11d** in this decarbonylation condition. Using a 50% acetic acid/dichloromethane solution was effective for the decarbonylation using pyrrole (**8**) in the case of low soluble materials in acetic acid. The reaction of **11d** with **8** in this condition afforded the desired **7d** in 41% yield.

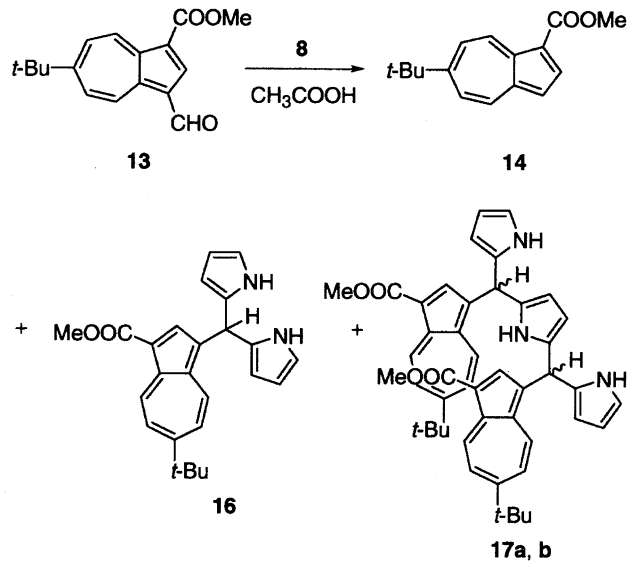


Scheme 3.

Methyl 6-*t*-butyl-3-formyl-1-azulenecarboxylate (**13**) was synthesized by the Vilsmeier formylation of methyl 6-*t*-butyl-1-azulenecarboxylate (**14**), which was prepared starting from **4b** by trifluoromethylcarbonylation with trifluoroacetic anhydride at 1-position,[7] followed by base catalyzed hydrolysis, and methylation with diazomethane in 77% yield. In contrast to the decarbonylation of carbaldehydes **9**—**11**, the reaction of **13** with pyrrole (**8**) in acetic acid afforded methyl 6-*t*-butyl-3-[di(2-pyrrolyl)methyl]-1-azulenecarboxylate (**16**) and a diastereomeric mixture of dimethyl 6,6′-di-*t*-butyl-3,3′-[pyrrole-2,5-diylbis(2-pyrrolylmethylene)]di(1-azulenecarboxylate) (**17a** and **b**) in 40 and 7% yields, respectively, together with the decarbonylated product **14** in 5% yield (Scheme 4). The ratio of **17a** and **b** was almost 1 : 1 and the mixture was inseparable both by silica gel and by GPC. The structure of the products **16** and **17a**, **b** was established on the basis of spectroscopic data (see Experimental section). The di(2-pyrrolyl)methane derivative **16** did not show any elimination of the di(2-pyrrolyl)methyl group in either acetic

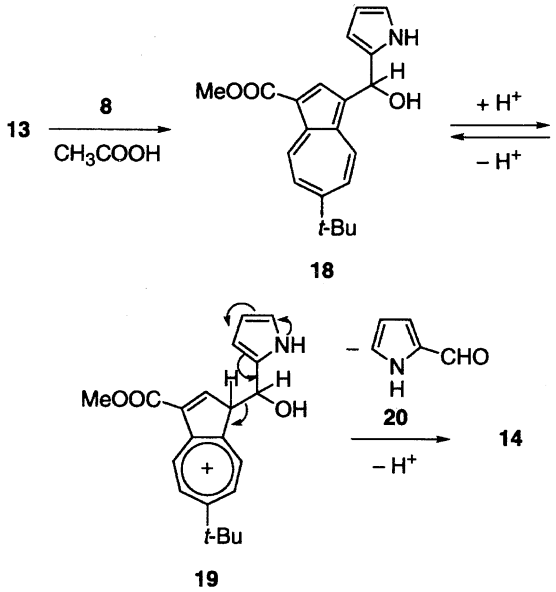
Table 2. Selective Synthesis of Di(1-azulenyl)methane Derivatives **7a**—**d**

Entry	Azulene	Aldehyde	Condensation (Yield/%)	R^1	R^2	Solvent	Decarbonylation (Yield/%)
1	**9a**	**5**	**11a** (76)	H	H	AcOH	**7a** (43)
2	**9b**	**5**	**11b** (96)	*t*-Bu	H	AcOH	**7b** (61)
3	**9a**	**6**	**11c** (84)	H	Ph	AcOH	**7c** (57)
4	**9b**	**6**	**11d** (94)	*t*-Bu	Ph	$AcOH/CH_2Cl_2$	**7d** (41)

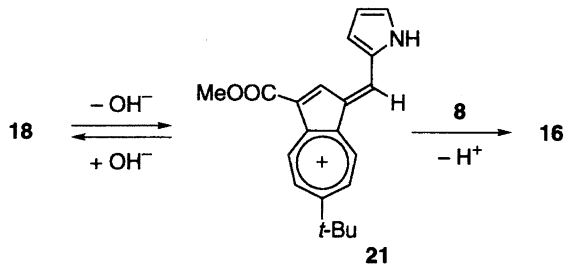


Scheme 4.

acid or acetic acid/dichloromethane solution in the presence of **8**, but exhibited some decomposition in this reaction condition. Thus, the di(2-pyrrolyl)methane derivative **16** is not an intermediate for this decarbonylation reaction. These results provided the suggestion for the reaction course of this decarbonylation reaction. The decarbonylation course of the carboxylate **13** could be illustrated as shown in Scheme 5. The carboxylate **13** would react with pyrrole (**8**) in acidic condition to afford an intermediate **18**. Protonation of **18** could be considered in this medium to form an azulenium ion intermediate **19**. Elimination of 2-pyrrolecarbaldehyde (**20**) from **19** results in the decarbonylation to produce **14**. We could not separate **20** from the reaction mixture owing to the reactivity of **20** in this decarbonylation condition. An electron-withdrawing group such as alkoxycarbonyl group on azulene ring disadvantages this protonation step to form **19**. Therefore, the intermediate **18** bearing methoxycarbonyl



Scheme 5.



Scheme 6.

substituent would promote the further reaction with pyrrole (**8**) to give **16** via **21** (Scheme 6). The formation of the product **17a** and **b** is caused by the second reaction of **16** with the intermediate **21**. Therefore, the decarbonylation is considered owing to the ability of protonation of azulene ring and the electron-donating properties of pyrrole ring. The formation of di(2-pyrrolyl)methane derivatives **16** in the case of **13**, which has an electron-withdrawing substituent, would represent a limitation of this strategy for the protection of 1- and/or 3-position of azulene ring.

In conclusion, removal of formyl groups at 1- and/or 3-positions of azulene ring could be achieved under mild conditions. Since the formylation at 1- and/or 3-positions of azulenes are easily carried out by Vilsmeier formylation reaction using phosphoryl chloride in dimethylformamide (DMF),[2] this decarbonylation reaction of 1-azulenecarbaldehydes would be a useful reaction to afford a new protecting strategy in azulene chemistry.

Experimental

General Procedures. Melting points were determined on a Yanagimoto micro melting point apparatus MP-S3 and are uncorrected. Mass spectra were obtained with a JEOL HX-110 or a Hitachi M-2500 instrument usually at 70 eV. IR and UV spectra were measured on a Shimadzu FTIR-8100M and a Hitachi U-3410 spectrophotometer, respectively. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded on a JEOL GSX 400 at 400 MHz (100 MHz) or a Bruker AM 600 spectrometer at 600 MHz (150 MHz). GPC were performed on a TSKgel G2000H$_6$. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

6-*t*-Butyl-1,3-azulenedicarbaldehyde (10b). Phosphoryl chloride (5.6 ml, 60 mmol) was added slowly at room temperature to a solution of 6-*t*-butylazulene (**4b**) (1.85 g, 10.0 mmol) in DMF (40 ml). The blue solution became brown and was heated at 90 °C for 5 h. After the resulting mixture was poured into ice water, the mixture was alkalified with 2 M (1 M = 1 mol dm^{-3}) NaOH and extracted with benzene. The organic layer was washed with water, dried with MgSO$_4$, and concentrated in vacuo. Purification of the residue by column chromatography on silica gel with ethyl acetate/CH_2Cl_2 gave the 1,3-azulenedicarbaldehyde **10b** (2.17 g, 90%). Red prisms; mp 130.0—131.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 240 (M^+; 100), 239 (57), 225 (22), 183 (20), and 152 (20); IR (KBr disk) ν_{max} 1663, 1649, 1509, 1449, 1418, 1399, 1391, 1364, and 1150 cm^{-1}; UV (CH_2Cl_2) λ_{max}, nm (log ε) 241 (4.50), 293 (4.71), 317 (4.57), 387 (4.04), and 481 (2.99); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.31 (s, 2H, 1,3-CHO), 9.79 (d, J = 11.0 Hz, 2H, $H_{4,8}$), 8.54 (s, 1H, H_2), 8.13 (d, J = 11.0 Hz, 2H, $H_{5,7}$), and 1.54 (s, 9H, 6-*t*-Bu); ^{13}C NMR (100

MHz, $CDCl_3$) δ = 187.01 (d, 1,3-CHO), 168.19 (s, C_6), 147.59 (d, C_2), 143.06 (s, $C_{3a,8a}$), 139.48 (d, $C_{4,8}$), 132.18 (d, $C_{5,7}$), 125.64 (s, $C_{1,3}$), 39.41 (s, 6-*t*-Bu), and 31.77 (q, 6-*t*-Bu). Found: C, 79.85; H, 6.73%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

3,3′-Methylenedi(1-azulenecarbaldehyde) (11a). A solution of 1-azulenecarbaldehyde (**9a**) (782 mg, 5.01 mmol) and paraformaldehyde (**5**) (154 mg, 5.13 mmol) in acetic acid (30 ml) was refluxed under an Ar atmosphere for 8 h. The solvent was rotary-evaporated, and the residue was diluted with CH_2Cl_2. The organic solution was washed with 5% aqueous $NaHCO_3$ and water. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with ethyl acetate/CH_2Cl_2 to afford the di(1-azulenecarbaldehyde) **11a** (621 mg, 76%). Brown crystals; mp 163.5—165.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 324 (M^+; 65), 296 (25), 295 (100), 265 (49), and 252 (20); IR (KBr disk) ν_{max} 1636, 1441, 1429, 1399, and 745 cm^{-1}; UV (CH_2Cl_2) λ_{max}, nm (log ε) 238 (4.61), 276 (4.59), 314 (4.84), 391 (4.29), and 552 (3.00); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.28 (s, 2H, 3-CHO), 9.54 (d, *J* = 9.8 Hz, 2H, H_4), 8.52 (d, *J* = 9.8 Hz, 2H, H_8), 7.96 (s, 2H, H_2), 7.86 (dd, *J* = 9.8, 9.8 Hz, 2H, H_6), 7.61 (dd, *J* = 9.8, 9.8 Hz, 2H, H_5), 7.50 (dd, *J* = 9.8, 9.8 Hz, 2H, H_7), and 4.79 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.04 (d, 3-CHO), 142.16 (s, C_{8a}), 141.82 (d, C_2), 141.31 (s, C_{3a}), 139.95 (d, C_6), 137.28 (d, C_4), 135.87 (d, C_8), 129.55 (s, C_1), 129.41 (d, C_5), 127.64 (d, C_7), 124.48 (s, C_3), and 25.37 (t, CH_2). Found: C, 85.03; H, 5.00%. Calcd for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97%.

6,6′-Di-*t*-butyl-3,3′-methylenedi(1-azulenecarbaldehyde) (11b). The same procedure as for the preparation of **11a** was adopted here. The reaction of 6-*t*-butyl-1-azulenecarbaldehyde (**9b**) (1.11 g, 5.23 mmol) with paraformaldehyde (**5**) (152 mg, 5.06 mmol) in refluxing acetic acid (30 ml) for 6 h afforded the di-(1-azulenecarbaldehyde) **11b** (1.10 g, 96%). Brown crystals; mp 191.0—193.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 436 (M^+; 75), 408 (35), 407 (100), and 57 (30); IR (KBr disk) ν_{max} 1647, 1634, 1580, 1449, 1404, 1393, and 1370 cm^{-1}; UV (CH_2Cl_2) λ_{max}, nm (log ε) 242 (4.58), 278 (4.61), 320 (4.91), 393 (4.31), and 539 (3.11); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.26 (s, 2H, 3-CHO), 9.44 (d, *J* = 10.5 Hz, 2H, H_4), 8.47 (d, *J* = 10.8 Hz, 2H, H_8), 7.91 (s, 2H, H_2), 7.78 (dd, *J* = 10.5, 2.0 Hz, 2H, H_5), 7.68 (dd, *J* = 10.8, 2.0 Hz, 2H, H_7), 4.73 (s, 2H, CH_2), and 1.48 (s, 18H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.78 (s, 3-CHO), 164.58 (s, C_6), 141.05 (s, C_{8a}), 140.66 (d, C_2), 140.29 (s, C_{3a}), 136.21 (d, C_4), 134.95 (d, C_8), 129.36 (s, C_1), 127.36 (d, C_5), 126.15 (d, C_7), 124.23 (s, C_3), 38.94 (s, 6-*t*-Bu), 31.81 (q, 6-*t*-Bu), and 25.25 (t, CH_2). Found: C, 83.62; H, 7.45%. Calcd for $C_{31}H_{32}O_2 \cdot 1/2H_2O$: C, 83.56; H, 7.46%.

3,3′-Benzylidenedi(1-azulenecarbaldehyde) (11c). The same procedure as for the preparation of **11a** was adopted here. The reaction of 1-azulenecarbaldehyde (**9a**) (1.64 g, 10.5 mmol) with benzaldehyde (**6**) (2.66 g, 25.1 mmol) in refluxing acetic acid (30 ml) for 24 h afforded the di(1-azulenecarbaldehyde) **11c** (1.76 g, 84%). Brown crystals; mp 130.5—134.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 400 (M^+; 100), 372 (29), 371 (95), 323 (36), 265 (25), and 215 (30); IR (KBr disk) ν_{max} 1647, 1435, 1406, and 1399 cm^{-1}; UV (CH_2Cl_2) λ_{max}, nm (log ε) 238 (4.64), 277 (4.58), 315 (4.77), 391 (4.25), and 551 (2.95); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.23 (s, 2H, 3-CHO), 9.60 (d, *J* = 9.5 Hz, 2H, H_4), 8.39 (d, *J* = 9.8 Hz, 2H, H_8), 7.84 (dd, *J* = 9.8, 9.8 Hz, 2H, H_6), 7.74 (s, 2H, H_2), 7.63 (dd, *J* = 9.8, 9.5 Hz, 2H, H_5), 7.42 (dd, *J* = 9.8, 9.8 Hz, 2H, H_7), 7.33 (dd, *J* = 7.1, 6.8 Hz, 2H, $H_{3',5'}$), 7.27 (t, *J* = 7.1 Hz, 1H, $H_{4'}$), 7.20 (d, *J* = 6.8 Hz, 2H, $H_{2',6'}$), and 6.57 (s, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.26 (d, 3-CHO), 143.27 (s, $C_{1'}$), 142.48 (d, C_2), 141.62 (s, C_{3a}), 141.47 (s, C_{8a}), 140.03 (d, C_6), 137.75 (d, C_4), 136.22 (d, C_8), 133.21 (s, C_1), 129.78 (d, C_5), 128.81 (d, $C_{3',5'}$), 128.74 (d, $C_{2',6'}$), 127.97 (d, C_7), 126.83 (d, $C_{4'}$), 124.31 (s, C_3), and 42.61 (d, CH). Found: C, 87.10; H, 5.19%. Calcd for $C_{29}H_{20}O_2$: C, 86.98; H, 5.03%.

6,6′-Di-*t*-butyl-3,3′-benzylidenedi(1-azulenecarbaldehyde) (11d). The same procedure as for the preparation of **11a** was adopted here. The reaction of 6-*t*-butyl-1-azulenecarbaldehyde (**9b**) (2.13 g, 10.0 mmol) with benzaldehyde (**6**) (2.66 g, 25.1 mmol) in refluxing acetic acid (30 ml) for 24 h afforded the di(1-azulenecarbaldehyde) **11d** (2.43 g, 94%). Brown crystals; mp 287.0—289.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 512 (M^+; 100), 484 (34), 483 (84), 455 (29), and 435 (32); IR (KBr disk) ν_{max} 1651, 1582, 1443, 1406, and 1391 cm^{-1}; UV (CH_2Cl_2) λ_{max}, nm (log ε) 279 (4.61), 321 (4.88), 394 (4.29), and 536 (3.08); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.20 (s, 2H, 3-CHO), 9.50 (d, *J* = 10.5 Hz, 2H, H_4), 8.33 (d, *J* = 10.8 Hz, 2H, H_8), 7.79 (dd, *J* = 10.5, 1.8 Hz, 2H, H_5), 7.66 (s, 2H, H_2), 7.59 (dd, *J* = 10.8, 1.8 Hz, 2H, H_7), 7.32 (dd, *J* = 7.5, 6.9 Hz, 2H, $H_{3',5'}$), 7.26 (t, *J* = 7.5 Hz, 1H, $H_{4'}$), 7.21 (d, *J* = 6.9 Hz, 2H, $H_{2',6'}$), 6.51 (s, 1H, CH), and 1.45 (s, 18H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.02 (d, 3-CHO), 164.69 (s, C_6), 143.52 (s, $C_{1'}$), 141.36 (d, C_2), 140.52 (s, C_{3a}), 140.36 (s, C_{8a}), 136.66 (d, C_4), 135.21 (d, C_8), 132.95 (s, C_1), 128.78 (d, $C_{2',6'}$), 128.72 (d, $C_{3',5'}$), 127.78 (d, C_5), 126.70 (d, $C_{4'}$), 126.45 (d, C_7), 124.07 (s, C_3), 42.46 (d, CH), 38.94 (s, 6-*t*-Bu), and 31.79 (q, 6-*t*-Bu). Found: C, 84.19; H, 7.28%. Calcd for $C_{37}H_{36}O_2 \cdot H_2O$: C, 83.74; H, 7.22%.

General Procedure for the Decarbonylation Reaction of 9a, b, 10a, b and 11a—d. A solution of 1-azulenecarbaldehydes **9a**, **b** and **10a**, **b** or 3,3′-methylenedi(1-azulenecarbaldehyde)s **11a—d** and pyrrole (**8**) in acetic acid or a solution of 50% acetic acid in CH_2Cl_2 was stirred at room temperature under an Ar atmosphere for 3 d. During the time the color of the solution turned brown. The solvent was rotary-evaporated, and the residue was diluted with CH_2Cl_2. The organic solution was washed with 5% aqueous $NaHCO_3$ and water. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ to afford azulenes **4a** and **b** and di(1-azulenyl)methanes **7a—d**, respectively.

Decarbonylation of 1-Azulenecarbaldehyde (9a). The reaction of **9a** (163 mg, 1.04 mmol) with pyrrole (**8**) (682 mg, 10.2 mmol) in acetic acid (6 ml) afforded azulene (**4a**) (65 mg, 49%).

Decarbonylation of 6-*t*-Butyl-1-azulenecarbaldehyde (9b). The reaction of **9b** (217 mg, 1.02 mmol) with pyrrole (**8**) (687 mg, 10.2 mmol) in acetic acid (6 ml) afforded 6-*t*-butylazulene (**4b**) (146 mg, 78%).[1a]

Decarbonylation of 1,3-Azulenedicarbaldehyde (10a). The reaction of **10a** (186 mg, 1.01 mmol) with pyrrole (**8**) (1.35 g, 20.1 mmol) in acetic acid (6 ml) afforded azulene (**4a**) (46 mg, 36%).

Decarbonylation of 6-*t*-Butyl-1,3-azulenedicarbaldehyde (10b). The reaction of **10b** (242 mg, 1.01 mmol) with pyrrole (**8**) (1.34 g, 20.0 mmol) in acetic acid (6 ml) afforded 6-*t*-butylazulene (**4b**) (96 mg, 52%).[1a]

Decarbonylation of 3,3′-Methylenedi(1-azulenecarbaldehyde) (11a). The reaction of **11a** (326 mg, 1.00 mmol) with pyrrole (**8**) (1.35 g, 20.1 mmol) in acetic acid (12 ml) afforded di(1-azulenyl)methane (**7a**) (115 mg, 43%).[3—5]

Decarbonylation of 6,6′-Di-*t*-butyl-3,3′-methylenedi(1-azulenecarbaldehyde) (11b). The reaction of **11b** (438 mg, 1.00 mmol) with pyrrole (**8**) (1.35 g, 20.1 mmol) in acetic acid

(12 ml) afforded bis(6-*t*-butyl-1-azulenyl)methane (**7b**) (233 mg, 61%). Blue oil; MS (70 eV) *m/z* (rel intensity) 380 (M^+; 100), 323 (41), and 57 (23); IR (neat) ν_{max} 2955, 1576, 1401, and 839 cm^{-1}; UV (CH_2Cl_2) λ_{max}, nm (log ε) 239 (4.51), 297 (4.94), 351 (4.11), 366 (3.89), and 590 (2.84); ^1H NMR (400 MHz, $CDCl_3$) δ = 8.33 (d, J = 10.8 Hz, 2H, H_8), 8.11 (d, J = 10.3 Hz, 2H, H_4), 7.55 (d, J = 3.5 Hz, 2H, H_2), 7.24 (d, J = 10.8 Hz, 2H, H_7), 7.23 (d, J = 10.3 Hz, 2H, H_5), 7.20 (d, J = 3.5 Hz, 2H, H_3), 4.82 (s, 2H, CH_2), and 1.42 (s, 18H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.86 (s, C_6), 139.49 (s, C_{3a}), 137.00 (d, C_2), 135.42 (d, C_4), 134.25 (s, C_{8a}), 132.62 (d, C_8), 129.75 (s, C_1), 120.12 (d, C_5), 119.77 (d, C_7), 116.07 (d, C_3), 38.42 (s, 6-*t*-Bu), 31.90 (q, 6-*t*-Bu), and 25.55 (t, CH_2). HRMS Calcd for $C_{29}H_{32}$: M, 380.2504. Found: *m/z* 380.2500. Found: C, 91.08; H, 8.68%. Calcd for $C_{29}H_{32}$: C, 91.52; H, 8.48%.

Decarbonylation of 3,3′-Benzylidenedi(1-azulenecarbaldehyde) (11c). The reaction of **11c** (401 mg, 1.00 mmol) and pyrrole (**8**) (1.35 g, 20.1 mmol) in acetic acid (12 ml) afforded di(1-azulenyl)phenylmethane (**7c**) (197 mg, 57%).[1a,6]

Decarbonylation of 6,6′-Di-*t*-butyl-3,3′-benzylidenedi(1-azulenecarbaldehyde) (11d). The reaction of **11d** (516 mg, 1.01 mmol), and pyrrole (**8**) (1.36 g, 20.3 mmol) in acetic acid (6 ml) and CH_2Cl_2 (6 ml) afforded bis(6-*t*-butyl-1-azulenyl)phenylmethane (**7d**) (188 mg, 41%).[1a] The reaction of **11d** (514 mg, 1.00 mmol) and **8** (1.35 g, 20.1 mmol) in acetic acid (12 ml) afforded the di(1-azulenyl)methane **7d** (35 mg, 8%), 6-*t*-butyl-3-[6-*t*-butyl-1-azulenyl(phenyl)methyl]-1-azulenecarbaldehyde (**12**) (49 mg, 10%), and the recovered **11d** (340 mg, 66%).

12: Brown crystals; mp 141.0—142.5 °C (methanol); MS (70 eV) *m/z* (rel intensity) 484 (M^+; 100), 455 (24), 427 (38), and 407 (26); IR (KBr disk) ν_{max} 2963, 1657, 1580, 1443, 1406, 1389, and 841 cm^{-1}; UV (CH_2Cl_2) λ_{max}, nm (log ε) 238 (4.54), 298 (4.87), 321 (4.60), 351 (4.01), 368 (3.86), 395 (3.98), and 543 (2.98); ^1H NMR (400 MHz, $CDCl_3$) δ = 10.19 (s, 1H, 3-CHO), 9.47 (d, J = 10.5 Hz, 1H, H_4), 8.33 (d, J = 10.8 Hz, 1H, H_8), 8.25 (d, J = 10.5 Hz, 1H, $H_{4'}$), 8.21 (d, J = 10.5 Hz, 1H, $H_{8'}$), 7.75 (dd, J = 10.5, 1.9 Hz, 1H, H_5), 7.69 (s, 1H, H_2), 7.55 (dd, J = 10.8, 1.9 Hz, 1H, H_7), 7.43 (d, J = 3.7 Hz, 1H, $H_{2'}$), 7.30 (dd, J = 10.5, 1.7 Hz, 1H, $H_{5'}$), 7.28 (dd, J = 7.6, 6.8 Hz, 2H, $H_{3'',5''}$), 7.22 (dd, J = 10.5, 1.7 Hz, 1H, $H_{7'}$), 7.21 (t, J = 7.6 Hz, 1H, $H_{4''}$), 7.21 (d, J = 3.9 Hz, 1H, $H_{3'}$), 7.20 (d, J = 6.8 Hz, 2H, $H_{2'',6''}$), 6.60 (s, 1H, CH), 1.43 (s, 9H, 6-*t*-Bu), and 1.41 (s, 9H, 6′-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.14 (d, 3-CHO), 164.30 (s, C_6), 161.27 (s, $C_{6'}$), 144.72 (s, $C_{1''}$), 141.69 (d, C_2), 140.50 (s, C_{3a} and C_{8a}), 139.74 (s, $C_{3'a}$), 137.21 (d, $C_{2'}$), 136.48 (d, C_4), 135.93 (d, $C_{4'}$), 135.39 (d, C_8), 134.35 (s, C_1), 133.85 (s, $C_{8'a}$), 132.58 (d, $C_{8'}$), 131.58 (s, $C_{1'}$), 128.81 (d, $C_{2'',6''}$), 128.45 (d, $C_{3'',5''}$), 127.50 (d, C_5), 126.32 (d, C_7), 126.25 (d, $C_{4''}$), 123.96 (s, C_3), 120.88 (d, $C_{5'}$), 120.36 (d, $C_{7'}$), 116.12 (d, $C_{3'}$), 42.57 (d, CH), 38.86 (s, 6-*t*-Bu), 38.50 (s, 6′-*t*-Bu), 31.87 (q, 6′-*t*-Bu), and 31.80 (q, 6-*t*-Bu). Found: C, 88.42; H, 7.47%. Calcd for $C_{36}H_{36}O$: C, 89.21; H, 7.49%.

1-(6-*t*-Butyl-1-azulenyl)-2,2,2-trifluoroethanone (15). Trifluoroacetic anhydride (14 ml, 100 mmol) was added at room temperature to a solution of 6-*t*-butylazulene (**4b**) (18.4 g, 100 mmol) in CCl_4 (300 ml). The blue solution turned purple. After the solution was stirred at the same temperature for 10 min, the reaction mixture was poured into water. The organic layer was separated, washed with water, dried with $MgSO_4$, and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford the 1-azulenyl ketone **15** (28.0 g, 100%). Red needles; mp 97.5—99.0 °C; MS (70 eV) *m/z* (rel intensity) 280 (M^+; 47) and 211 (100); IR (KBr disk) ν_{max} 1663, 1632, 1406, 1269, 1242, 1211, 1190, 1183, 1150, 1132, 1046, and 855 cm^{-1}; UV (CH_2Cl_2) λ_{max}, nm (log ε) 273 (4.09), 322 (4.52), 383 (4.06), 402 (4.11), and 498 (3.04); ^1H NMR (400 MHz, $CDCl_3$) δ = 9.81 (d, J = 10.8 Hz, 1H, H_8), 8.48 (d, J = 10.8 Hz, 1H, H_4), 8.26 (dq, J = 4.4 Hz and J_{HF} = 2.4 Hz, 1H, H_2), 7.97 (dd, J = 10.8, 2.0 Hz, 1H, H_7), 7.86 (dd, J = 10.8, 2.0 Hz, 1H, H_5), 7.23 (d, J = 4.4 Hz, 1H, H_3), and 1.51 (s, 9H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.67 (s, J_{CF} = 33.5 Hz, 1-$COCF_3$), 165.68 (s, C_6), 146.10 (s, C_{3a}), 142.85 (s, C_{8a}), 140.11 (d, J_{CF} = 3.6 Hz, C_2), 138.77 (d, C_8), 138.02 (d, C_4), 129.62 (d, C_7), 128.68 (d, C_5), 119.02 (d, C_3), 117.48 (s, J_{CF} = 291.6 Hz, 1-$COCF_3$), 117.00 (s, C_1), 39.12 (s, 6-*t*-Bu), and 31.82 (q, 6-*t*-Bu). Found: C, 68.77; H, 5.35%. Calcd for $C_{16}H_{15}OF_3$: C, 68.56; H, 5.39%.

Methyl 6-*t*-Butyl-1-azulenecarboxylate (14). A solution of 1-(6-*t*-butyl-1-azulenyl)-2,2,2-trifluroethanone (**15**) (28.0 g, 100 mmol) and sodium hydroxide (12.0 g, 299 mmol) in ethanol (300 ml) and water (150 ml) was refluxed for 12 h. The red color of the solution turned purple. The reaction mixture was poured into CH_2Cl_2 (200 ml) and water (200 ml). The aqueous layer was separated, washed with CH_2Cl_2, acidified with 2 M HCl, and then extracted with CH_2Cl_2. The organic layer was washed with water, dried with $MgSO_4$, and concentrated in vacuo to give purple crystals. To the ether (100 ml) suspension of the crystals, an ethereal solution of CH_2N_2, which was prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (43.2 g, 202 mmol), potassium hydroxide (10.0 g, 178 mmol), water (16 ml), ethanol (50 ml), and ether (400 ml), was added dropwise for 30 min at 0 °C. After the solution was stirred at the same temperature for 3 h, acetic acid was added until no evolution of N_2 gas occurred. The reaction mixture was evaporated in vacuo. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford the carboxylate **14** (18.7 g, 77%). Purple oil; MS (70 eV) *m/z* (rel intensity) 242 (M^+; 100) and 211 (38); IR (neat) ν_{max} 2965, 1694, 1586, 1449, 1408, 1244, 1217, 1150, and 849 cm^{-1}; UV (CH_2Cl_2) λ_{max}, nm (log ε) 235 (4.21), 295 (4.59), 307(4.70), 343 (3.77), 371 (3.86), and 525 (2.73); ^1H NMR (400 MHz, $CDCl_3$) δ = 9.55 (d, J = 10.8 Hz, 1H, H_8), 8.38 (d, J = 10.3 Hz, 1H, H_4), 8.27 (d, J = 4.2 Hz, 1H, H_2), 7.73 (dd, J = 10.8, 1.9 Hz, 1H, H_7), 7.61 (dd, J = 10.3, 1.9 Hz, 1H, H_5), 7.19 (d, J = 4.2 Hz, 1H, H_3), 3.95 (s, 3H, 1-COOMe), and 1.47 (s, 9H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.92 (s, 1-COOMe), 163.35 (s, C_6), 143.46 (s, C_{3a}), 139.54 (s, C_{8a}), 139.16 (d, C_2), 137.19 (d, C_4), 136.75 (d, C_8), 125.82 (d, C_7), 124.91 (d, C_5), 116.95 (d, C_3), 116.17 (s, C_1), 50.96 (q, 1-COOMe), 38.76 (s, 6-*t*-Bu), and 31.87 (q, 6-*t*-Bu). Found: C, 79.61; H, 7.75%. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

Methyl 6-*t*-Butyl-3-formyl-1-azulenecarboxylate (13). The same procedure as for the preparation of **10b** was adopted here. The reaction of methyl 6-*t*-butyl-1-azulenecarboxylate (**14**) (18.7 g, 77.3 mmol) with phosphoryl chloride (43.3 ml, 465 mmol) in DMF (310 ml) gave the carboxylate **13** (19.5 g, 93%). Orange needles; mp 112.5—114.0 °C (CH_2Cl_2/hexane); MS (70 eV) *m/z* (rel intensity) 386 (M^+; 100), 385 (21), 329 (27), 327 (44), 269 (12), 242 (55), 144 (40), and 67 (39); IR (KBr disk) ν_{max} 1701, 1640, 1455, 1362, 1208, and 1194 cm^{-1}; UV (CH_2Cl_2) λ_{max}, nm (log ε) 238 (4.53), 284 (4.63), 314 (4.62), 376 (4.05), and 486 (2.97); ^1H NMR (400 MHz, $CDCl_3$) δ = 10.28 (s, 1H, 3-CHO), 9.74 (d, J = 10.8 Hz, 1H, H_4), 9.73 (d, J = 11.3 Hz, 1H, H_8), 8.65 (s, 1H, H_2), 8.05 (dd, J = 11.3, 2.0 Hz, 1H, H_7), 8.03 (d, J = 10.8, 2.0 Hz, 1H, H_5), 3.97 (s, 3H, 1-COOMe), and 1.52 (s, 9H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 187.17 (d, 3-CHO), 166.93 (s, 1-COOMe), 165.22 (s, C_6), 145.44 (d, C_2), 144.20 (s, C_{8a}), 141.75 (s, C_{3a}), 139.01 (d, C_8), 138.73 (d, C_4), 130.61 (d, C_5 and C_7), 124.42 (s, C_3), 116.85 (s,

C_1), 51.31 (q, 1-COOMe), 39.21 (s, 6-*t*-Bu), and 31.79 (q, 6-*t*-Bu). Found: C, 75.33; H, 6.66%. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%.

Reaction of Methyl 6-*t*-Butyl-3-formyl-1-azulenecarboxylate (13) with Pyrrole (8) in Acetic Acid. The same procedure as for the general procedure of the decarbonylation reaction was adopted here. The reaction of **13** (2.70 g, 10.0 mmol) with **8** (6.17 g, 92.0 mmol) in acetic acid (60 ml) afforded methyl 6-*t*-butyl-1-azulenecarboxylate (**14**) (129 mg, 5%), methyl 6-*t*-butyl-3-[di(2-pyrrolyl)methyl]-1-azulenecarboxylate (**16**) (1.54 g, 40%), and a diastereomeric mixture of dimethyl 6,6′-di-*t*-butyl-3,3′-[pyrrole-2,5-diylbis(2-pyrrolylmethylene)]di(1-azulenecarboxylate) (**17a** and **b**) (244 mg, 7%).

16: Purple crystals; mp 202.0—205.0 °C decomp (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 386 (M^+; 100), 385 (22), 329 (33), 327 (53), 242 (56), 144 (44), and 67 (30); IR (KBr disk) ν_{max} 3443, 3283, 1663, 1456, 1428, 1221, and 1210 cm^{-1}; UV (CH_2Cl_2) λ_{max}, nm (log ε) 231 (4.52), 310 (4.65), 383 (3.94), and 540 (2.75); ^1H NMR (400 MHz, $CDCl_3$) δ = 9.53 (d, J = 10.8 Hz, 1H, H_4), 8.35 (d, J = 10.8 Hz, 1H, H_8), 8.03 (s, H, H_2), 7.96 (br, 2H, NH), 7.70 (dd, J = 10.8, 2.0 Hz, 1H, H_5), 7.54 (dd, J = 10.8, 2.0 Hz, 1H, H_7), 6.66 (ddd, J = 2.7, 2.7, 1.5 Hz, 2H, $H_{5'}$), 6.16 (ddd, J = 4.4, 2.7, 1.7 Hz, 2H, $H_{4'}$), 6.07 (s, 1H, CH), 5.97 (dddd, J = 4.4, 1.5, 0.7, 0.7 Hz, 2H, $H_{3'}$), 3.85 (s, 3H, 3-COOMe), and 1.45 (s, 9H, 6-*t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.91 (s, 3-COOMe), 163.91 (s, C_6), 140.37 (s, C_{3a}), 139.05 (s, C_{8a}), 138.82 (d, C_2), 137.04 (d, C_4), 134.31 (d, C_8), 132.50 (s, $C_{2'}$), 128.58 (s, C_1), 126.11 (d, C_5), 124.83 (d, C_7), 114.59 (s, C_3), 108.38 (d, $C_{4'}$), 106.80 (d, $C_{3'}$), 50.92 (q, 3-COOMe), 38.92 (s, 6-*t*-Bu), 36.49 (d, CH), and 31.80 (q, 6-*t*-Bu). Found: C, 75.47; H, 6.74; N, 6.89%. Calcd for $C_{25}H_{26}N_2O_2 \cdot 1/2H_2O$: C, 75.92; H, 6.88; N, 7.08%.

17a and b: Diastereomeric mixture; purple crystals; mp 180.5—182.5 °C decomp (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 705 (M^+; 0.1), 387 (40), 386 (100), 385 (30), 384 (25), 329 (22), and 327 (43); IR (KBr disk) ν_{max} 3436, 3380, 2965, 1690, 1584, 1449, 1424, 1412, 1246, and 1208 cm^{-1}; UV (CH_2Cl_2) λ_{max}, nm (log ε) 235 (4.78), 310 (4.92), 383 (4.21), and 534 (3.25); ^1H NMR (600 MHz, $CDCl_3$) δ = 9.505 (d, J = 10.8 Hz, 2H, $H_{4'}$), 9.503 (d, J = 10.8 Hz, 2H, $H_{4'}$), 8.330 (d, J = 10.6 Hz, 2H, $H_{8'}$), 8.326 (d, J = 10.6 Hz, 2H, $H_{8'}$), 7.992 (s, 2H, $H_{2'}$), 7.988 (s, 2H, $H_{2'}$), 7.947 (br, 2H, $H_{1''}$), 7.882 (br, 1H, H_1), 7.850 (br, 1H, H_1), 7.679 (dd, J = 10.8, 1.8 Hz, 2H, $H_{5'}$), 7.677 (dd, J = 10.8, 1.8 Hz, 2H, $H_{5'}$), 7.521 (dd, J = 10.6, 1.8 Hz, 2H, $H_{7'}$), 7.512 (dd, J = 10.6, 1.8 Hz, 2H, $H_{7'}$), 6.622 (ddd, J = 3.0, 2.6, 1.3 Hz, 2H, $H_{5''}$), 6.615 (ddd, J = 3.0, 2.6, 1.3 Hz, 2H, $H_{5''}$), 6.089 (ddd, J = 4.8, 3.0, 2.9 Hz, 2H, $H_{4''}$), 6.084 (ddd, J = 4.8, 3.0, 2.9 Hz, 2H, $H_{4''}$), 5.955 (s, 2H, CH), 5.901 (ddd, J = 4.8, 2.2, 1.3 Hz, 2H, $H_{3''}$), 5.895 (ddd, J = 4.8, 2.2, 1.3 Hz, 2H, $H_{3''}$), 5.809 (d, J = 2.6 Hz, 2H, $H_{3,4}$), 5.779 (d, J = 2.6 Hz, 2H, $H_{3,4}$), 3.855 (s, 6H, 3′-COOMe), 3.852 (s, 6H, 3′-COOMe), 1.441 (s, 18H, 6′-*t*-Bu), and 1.437 (s, 18H, 6′-*t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 165.688 (s, 3′-COOMe), 163.819 (s, $C_{6'}$), 163.802 (s, $C_{6'}$), 140.347 (s, $C_{3'a}$), 140.330 (s, $C_{3'a}$), 138.981 (s, $C_{8'a}$), 138.928 (d, $C_{2'}$), 138.890 (d, $C_{2'}$), 136.986 (d, $C_{4'}$), 134.332 (d, $C_{8'}$), 134.300 (d, $C_{8'}$), 132.524 (s, $C_{2''}$), 132.501 (s, $C_{2''}$), 132.257 (s, $C_{2,5}$), 132.223 (s, $C_{2,5}$), 128.647 (s, $C_{1'}$), 128.581 (s, $C_{1'}$), 126.029 (d, $C_{5'}$), 126.006 (d, $C_{5'}$), 124.761 (d, $C_{7'}$), 124.750 (d, $C_{7'}$), 117.009 (d, $C_{5''}$), 116.986 (d, $C_{5''}$), 114.581 (s, $C_{3'}$), 114.547 (s, $C_{3'}$), 108.259 (d, $C_{4''}$), 108.246 (d, $C_{4''}$), 107.046 (d, $C_{3,4}$), 107.038 (d, $C_{3,4}$), 106.677 (d, $C_{3''}$), 106.667 (d, $C_{3''}$), 50.919 (q, 3′-COOMe), 38.760 (s, 6′-*t*-Bu), 36.631 (d, CH), 36.614 (d, CH), and 31.798 (q, 6′-*t*-Bu). Found: C, 77.28; H, 6.90; N, 5.81%. Calcd for $C_{46}H_{47}N_3O_4 \cdot 1/2H_2O$: C, 77.28; H, 6.77; N, 5.88%.

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References

1 a) S. Ito, N. Morita, and T. Asao, *Bull. Chem. Soc. Jpn.*, **68**, 1409 (1995). b) S. Ito, N. Morita, and T. Asao, *Bull. Chem. Soc. Jpn.*, **68**, 2011 (1995). c) S. Ito, N. Morita, and T. Asao, *Bull. Chem. Soc. Jpn.*, **68**, 2639 (1995). d) S. Ito, M. Fujita, N. Morita, and T. Asao, *Bull. Chem. Soc. Jpn.*, **68**, 3611 (1995). e) S. Ito, N. Morita, and T. Asao, *J. Org. Chem.*, **61**, 5077 (1996). f) S. Ito, H. Kobayashi, S. Kikuchi, N. Morita, and T. Asao, *Bull. Chem. Soc. Jpn.*, **69**, 3225 (1996). g) S. Ito, S. Kikuchi, H. Kobayashi, N. Morita, and T. Asao, *J. Org. Chem.*, **62**, 2423 (1997). h) S. Ito, S. Kikuchi, N. Morita, and T. Asao, *Bull. Chem. Soc. Jpn.*, **72**, 839 (1999).

2 K. -P. Zeller, in Houben-Weyl, "Methoden der Organischen Chemie," ed by E. Müller, Georg Thieme Verlag, Stuttgart (1985), Vol. 5, Part 2c, p. 127.

3 K. Hafner, H. Pelster, and J. Schneider, *Liebigs Ann. Chem.*, **650**, 62 (1961).

4 W. Treibs, M. Mühlstädt, and K. -D. Köhler, *Naturwissenschaften*, **45**, 336 (1958).

5 S. Takekuma, Z. Zhao, Y. Matsubara, M. Makihara, H. Yamamoto, and T. Nozoe, *Nippon Kagaku Kaishi*, **1994**, 399.

6 H. Franke and M. Mühlstädt, *J. Prakt. Chem.*, **35**, 262 (1967).

7 A. G. Anderson and R. G. Anderson, *J. Org. Chem.*, **27**, 3578 (1962).