A Versatile Synthetic Method of 1-Alkylazulenes and Azulene by the Reactions of 3-Methoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one with *in situ* Generated Enamines[1)]

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Methyl 3-alkylazulene-1-carboxylates were synthesized in high yields by the reaction of 3-methoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one with *in situ* generated morpholine enamines of aldehydes. Treatment of the esters with 100% phosphoric acid gave 1-alkylazulenes in excellent yields. Azulene was also synthesized in a good yield via methyl azulene-1-carboxylate with a modification of this method.

The development of a facile synthetic method for alkylazulenes under mild conditions is of current interest not only because of their physical and chemical properties but also their physiological activities.[2)] Many alkylazulene synthetic methods have been developed.[3)] In general, 1-alkylazulenes have been synthesized by ring expansion reactions of alkylindenes,[4)] Friedel–Crafts-type alkylation,[5)] or reduction of corresponding carbonyl groups,[6)] such as 1-formyl-, 1-acetylazulene, and so on.

We have developed a method for synthesizing azulene derivatives by the reaction of 2*H*-cyclohepta[*b*]furan-2-one (**1**) with enamines via intermediates **A** and **B** as shown in Scheme 1 (the so-called enamine method).[7)] After discovering this reaction, several similar reactions with 2*H*-cyclohepta[*b*]furan-2-ones have been reported.[8)] In the enamine method, the yields of the azulene derivatives are good on the reaction of **1a** with pyrrolidine enamines derived from cycloalkanones or acyclic carbonyl compounds having long chains, but fairly low on the reactions with pyrrolidine enamines derived from carbonyl compounds having short alkyl chains, especially propanal or acetaldehyde, owing to the difficult isolation of the corresponding enamines. On the other hand, 3-methoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one (**1b**) that is the primary product on the preparation of 2*H*-cyclohepta[*b*]furan-2-ones from troponoids gave azulene derivatives in fairly low yields on the reactions with isolated pyrrolidine enamines.

From this point of view, finding the reaction conditions in which **1b** can be used as a substrate and establishing a method that is applicable for the syntheses of azulenes having a short alkyl side chains are very important for further extension of the enamine method as a versatile alkylazulene synthetic method.

It is well-known that the enamines of carbonyl compounds having short alkyl chains, such as propanal, are difficult to isolate because of their high reactivities.[9)] Therefore, we studied the reaction of **1b** with *in situ* generated enamines.

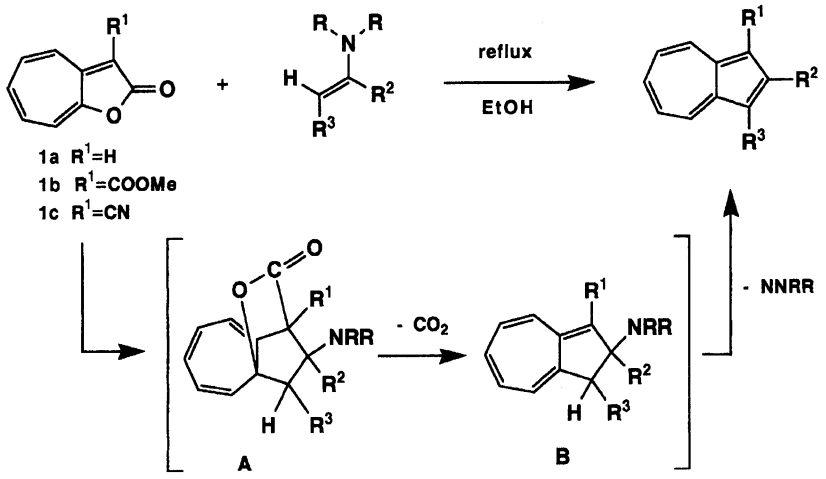
Results and Discussion

Synthesis of Methyl 3-Alkylazulene-1-carboxylate (2). The reactions of **1b** with *in situ* generated propanal enamines (**C**) were carried out as follows. A mixture of **1b** and propanal in ethanol was heated under refluxing in the presence of a specific amine (Scheme 2). The results of the reactions with various amines are summarized in Table 1. The yield of methyl 3-methylazulene-1-carboxylate (**2a**) was very low in the reaction with pyrrolidine that was known to give the most reactive enamine.[9)] In this case, it seems that a side reaction occurred to form a heptafulvene derivative by an attack of the amine on the 8a position of **1b**. Such products **3a** and **3b** were isolated on the reaction of **1b** or the 3-cyano derivative **1c** with pyrrolidine.[10)] The reactions using piperidine, hexahydroazepine, or diethylamine also gave the azulene derivative **2a** only in low yield.

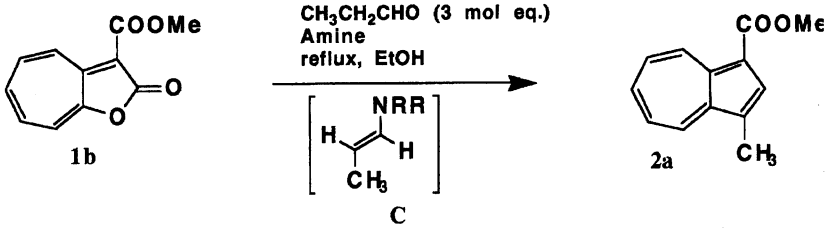
On the other hand, the reaction of **1b** with propanal in the presence of morpholine gave methyl 3-methylazulene-1-carboxylate (**2a**) in a good yield. Thus, a mixture of **1b**, propanal, and morpholine in ethanol was refluxed for 4 h. After the usual work, the product was isolated by column chromatography to give **2a** in a 97.7% yield as violet crystals. The structure of **2a** was confirmed by spectral inspection and by conversion to 1-methylazulene as described later.

These reaction conditions were successfully applied to the reactions of **1b** with *in situ* generated morpholine enamines (**D**) of other aldehydes to give methyl 3-alkylazulene-1-carboxylates (**2**) (Scheme 3) and these results are summarized in Table 2. In all the reactions with aldehydes, methyl 3-alkylazulene-1-carboxylates (**2**) were obtained in high yields. Although a fairly long reaction time was required for the reaction with 3-methylbutanal, the yield of azulene **2d** was good.

Synthesis of 1-Alkylazulenes (4). It is well-known that the alkoxycarbonyl group on the 1(3)-position of the azulene ring is easily removed by treatment with 100% phosphoric acid.[11)] The demethoxycarbonylation of methyl 3-methylazulene-1-carboxylate (**2a**) with this reagent at 95 °C under the usual manner gave 1-methylazulene (**4a**) in a only 75% yield as a blue oil together with unidentified green materials. On the other hand, the hydrolysis of **2a** with potassium hydroxide to give 3-methylazulene-1-carboxylic acid, and subsequent decarboxylation of the carboxylic acid by treatment with trichloroacetic acid in benzene under refluxing[12)] gave **4a** as blue prisms in a 95% overall



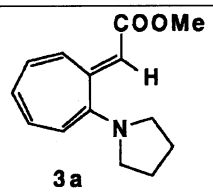
Scheme 1.



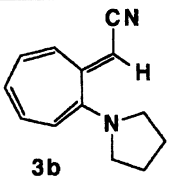
Scheme 2.

Table 1. Results of the Reactions of 3-Methoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one (**1b**) with Propanal in the Presence of Various Amines

Amine	Mol equiv	Solv.	React. time h	Yield of **2a** %
Pyrrolidine	3.0	EtOH	4.0	19.6
Pyrrolidine	1.0	EtOH	24	41.4
Piperidine	3.0	EtOH	14	72.1
Hexahydroazepine	5.0	*i*-PrOH	9.3	36.7
Morpholine	3.0	EtOH	4.0	97.7
Diethylamine	3.0	EtOH	53	52.8



3a



3b

yield. Demethoxycarbonylation of 3-ethyl derivative **2b** with 100% phosphoric acid gave 1-ethylazulene (**4b**) in a 92.5% yield (Scheme 4). The methoxycarbonyl group of other 3-alkyl derivatives (**2c**—**2j**) could be also removed in good yields to give 1-alkylazulenes **4c**—**4j**, respectively, as summarized in Table 3.

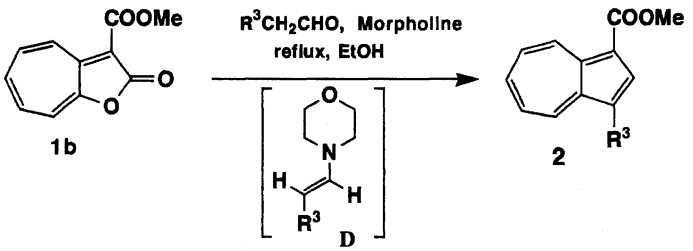
Thus, 1-alkylazulenes were easily synthesized by the reaction of 3-methoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one (**1b**) with *in situ* generated enamines followed by demethoxycarbonylation. This procedure provides a useful method of the synthesizing azulenes having an R^3 group at the 1-position by the use of aldehydes having a general formula R^3–CH_2–CHO because of its mild reaction conditions, simple procedures, and high yields in each step.

Synthesis of Azulene (6). For the synthesis of azulene by the enamine method, an acetaldehyde enamine is absolutely necessary. Attempted syntheses of piperidino[15] or diethylamino enamines[16] of acetaldehyde have been unsuccessful because of their high reactivities. The reactions of **1b** with *in situ* generated enamines which was successfully applied for the synthesis of 1-alkylazulenes as described above is most suitable for the reactions with highly reactive enamines.

The application of the above reaction conditions for the synthesis of azulene itself by the use of acetaldehyde did not give the desired products. After several attempts, the following method was established (Scheme 5). Thus, a suspension of **1b** in diethylamine was heated to reflux in the presence of acetaldehyde gave methyl azulene-1-carboxylate (**5**)[17] in an 85% yield.

Demethoxycarbonylation of **5** by treatment with 100% phosphoric acid in the usual manner gave azulene (**6**) in only a 45% yield. Decarboxylation of azulene-1-carboxylic acid (**8**)[18] that was obtained by alkaline hydrolysis of **5** gave azulene (**6**) in a 90% yield by treatment with trichloroacetic acid in benzene.[12] Azulene (**6**) was also obtained in a 60% yield by the reaction of **1a** with acetaldehyde in a similar manner.

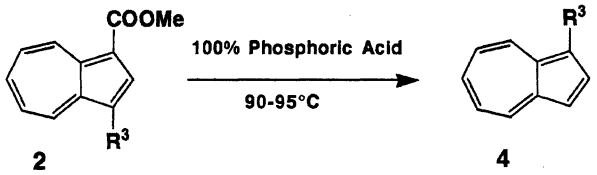
^{13}C NMR Chemical Shifts of Methyl 3-Alkylazulene-1-carboxylates. Braun and Kendeldei



Scheme 3.

Table 2. Yields of Methyl 3-Alkylazulene-1-carboxylates (**2**) on the Reactions of **1b** with *in situ* Generated Enamines

Aldehyde	Reaction time (h)	Azulene (2)		
		R^3	Compd	Yield (%)
Propanal	4	CH_3	**2a**	97.7
Butanal	4	CH_3CH_2	**2b**	96.8
Pentanal	4	$CH_3(CH_2)_2$	**2c**	98.8
3-Methylbutanal	30	$(CH_3)_2CH$	**2d**	83.2
Hexanal	4	$CH_3(CH_2)_3$	**2e**	99.4
Heptanal	4	$CH_3(CH_2)_4$	**2f**	95.0
Octanal	4	$CH_3(CH_2)_5$	**2g**	95.7
Nonanal	4	$CH_3(CH_2)_6$	**2h**	99.0
Decanal	4	$CH_3(CH_2)_7$	**2i**	96.4
3-Phenylpropanal	6	$PhCH_2$	**2j**	95.4



Scheme 4.

have investigated the ^{13}C NMR chemical shifts of various methyl azulenes.[19] The chemical shifts of the alkyl side chains of methyl 3-alkylazulene-1-carboxylates (**2a**—**2e**) were assigned by $^1H/^{13}C$ HETCOR data and the chemical shifts of the other esters **2f**—**2i** were assigned on the basis of T_1 values.[20] Assigned chemical shifts and typical data for the T_1 value of ester **2i** are shown in Table 4. The methyl signal of the 3-position of **2a** shifts to a higher field by 0.5 ppm in comparison with that of 1-methylazulene (**4a**), and by 9.2 ppm in comparison with the methyl group of toluene. The azulene ring shifts the α-carbon by 9.2—10.1 ppm and the β-carbon by 0.6—2.2 ppm in comparison with the benzene ring of alkylbenzenes.[21] It is readily apparent that the effect of the azulene ring is gradually decreased as the distance between the azulene ring and a specific carbon increases (Fig. 1).

The ^{13}C chemical shifts of the ring carbons of **2** are tabulated in Table 5. The values are almost equal among the compounds having longer side chains than a propyl group. As basic data of the ^{13}C chemical shifts of azulene derivatives, the substituent chemical shifts [SCS] of the methoxycarbonyl group of methyl azulene-1-carboxylate (**5**) were estimated in comparison of the ring carbon chemical shifts with those of azulene[22] as shown in Table 6.

Table 3. Yields of 1-Alkylazulenes (**4**) by Demethoxycarbonylation of **2** with 100% Phosphoric Acid

Substrate	Reaction time (min)	1-Alkylazulene			
		Compd	Yield (%)	R^3	Ref.
2a	15	**4a**	95.0[a]	CH_3	4)
2b	10	**4b**	92.5	CH_3CH_2	6b,7b)
2c	20	**4c**	98.8	$CH_3(CH_2)_2$	
2d	20	**4d**	96.6	$(CH_3)_2CH$	13)
2e	20	**4e**	86.3	$CH_3(CH_2)_3$	
2f	10	**4f**	95.4	$CH_3(CH_2)_4$	6b)
2g	15	**4g**	96.1	$CH_3(CH_2)_5$	
2h	20	**4h**	97.6	$CH_3(CH_2)_6$	
2i	6	**4i**	95.8	$CH_3(CH_2)_7$	
2j	30	**4j**	99.3	$PhCH_2$	14)

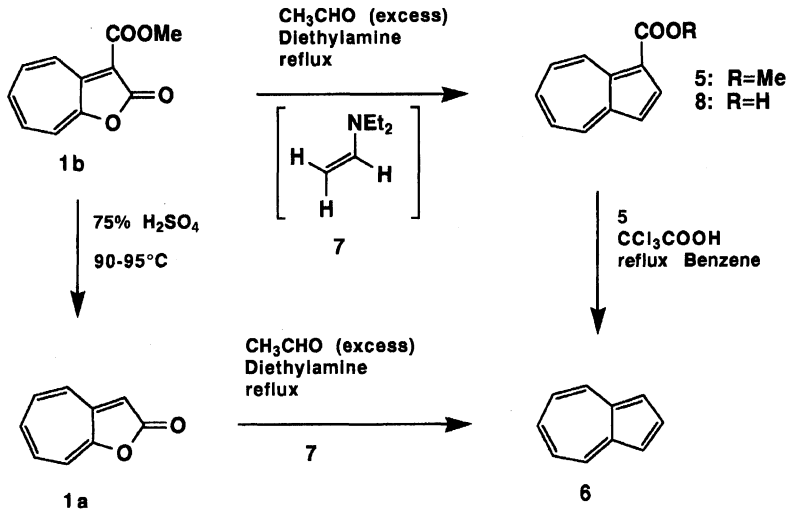
a) Yield obtained by method B via 3-methylazulene-1-carboxylic acid.

Experimental

Melting points were determined with a Yamato Model-MP21 melting point apparatus. Microanalyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University. NMR spectra were recorded on a R-24B (^1H), R-26 (^{13}C), EM-390 (^1H), FX-90Q (^1H, ^{13}C), Varian XL-200 (^1H, ^{13}C), or AM-600 and chemical shift values are given in δ (ppm) relative to internal tetramethylsilane. Infrared, ultraviolet, and mass spectra were recorded on a Hitachi Model 260-30, a Hitachi Model 323, and a Hitachi M-50 spectrometers, respectively.

The Reactions of 2*H*-Cyclohepta[*b*]furan-2-one (1b) with *in situ* Generated Enamines. A General Procedure: Morpholine (3 molar amounts) was added to a suspension of **1b** in ethanol containing an aldehyde (3 molar amounts), and the mixture was heated under reluxing. After being cooled to room temperature, the solvent was removed under reduced pressure, and the residue was dissolved in benzene. The benzene solution was washed with water, dried over Na_2SO_4, and the solvent was removed. The violet residual oil was purified by column chromatography with a silica-gel column to give a crude product. The crude product was purified by re-chromatography or by recrystallization. The reaction time and yields are shown in Table 2.

Synthesis of Methyl 3-Methylazulene-1-carboxylate (2a): Morpholine (13.0 g, 150 mmol) was added to a mixture of **1b** (10.2 g, 50 mmol) and propanal (8.7 g



Scheme 5.

Table 4. ^{13}C NMR Chemical Shifts (δ) of the Alkyl Side Chain of Methyl 3-Alkylazulene-1-carboxylate (**2**) and Relaxation Time (T_1/s) of the Octyl Side Chain of **2i**

Compd	α	β	γ	δ	ε	ζ	η	θ
2a	12.50	—						
2b	20.11	15.04	—					
2c	27.10	24.10	14.16	—				
2e	26.72	33.12	23.70	13.97	—			
2f	26.96	30.62	31.82	22.55	14.02	—		
2g	26.92	30.78	29.60	29.20	22.50	14.02	—	
2h	26.95	30.85	29.63	29.44	29.21	22.63	14.05	—
2i	26.99	30.92	29.64	29.46	29.22	31.84	22.61	14.04
2i (T_1)	0.869	1.014	1.159	1.449	1.739	2.463	2.898	3.188

Note: Signals of **2a**—**2e** were assigned on the basis of ^{1}H/^{13}C HETCOR, and signals of **2f**—**2i** were assigned on the basis of relaxation time (T_1).

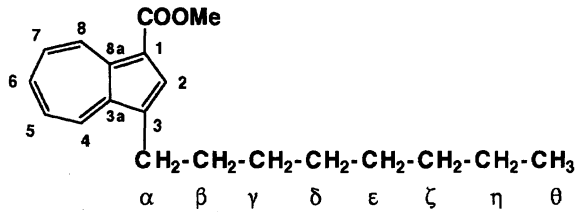


Fig. 1.

150 mmol) in ethanol (160 ml), and the mixture was heated under refluxing for 4 h. After being worked up under the general procedure, the crude product was purified by recrystallization from hexane to give **2a** (8.61 g, 97.7%).

2a: Dark violet prisms (hexane), mp 69—70.5 °C; UV (MeOH) 237 (log ε 4.34), 290 (4.58), 295.5 (4.58), 302 (4.67), 366 (sh, 3.87), 383 (3.94), 564 (2.61), and 610 (2.50) nm; IR (KBr) 2950, 1690, 1450, 1440, 1421, 1202, 1027, 774, and 746 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ=2.64 (s, CH_3), 3.96 (s, COOMe), 7.38 (ddd, J=10.0, 10.0, and 1.0 Hz, H-5), 7.45 (ddd, J=10.0, 10.0, and 1.0 Hz, H-7), 7.74 (ddd, J=10.0, 10.0, and 1.0 Hz, H-6), 8.19 (s, H-2), 8.34 (dd, J=10.0 and 1.0 Hz, H-4), and 9.56 (dd, J=10.0 and 1.0 Hz, H-8). Anal. ($C_{13}H_{12}O_2$), C, H.

Methyl 3-Ethylazulene-1-carboxylate (2b): The reaction of **1b** (5.0 g, 24.5 mmol) with butanal (5.30 g, 73.4 mmol) in the presence of morpholine (6.4 g, 73.4 mmol) gave **2b** (5.08 g, 96.8%).

2b: Violet oil; UV (MeOH): 237.5 (log ε 4.45), 265 (sh, 4.05), 291 (4.68), 296 (4.68), 302.5 (4.77), 366 (sh, 3.96), 382 (4.05), 562 (2.70), and 612 (2.58) nm; IR ($CHCl_3$) 3016, 2978, 2960, 1690, 1580, 1541, 1456, 1443, 1423, 1314, 1228, 1200, 1144, 1048, and 822 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.39 (t, J=7.0 Hz, $CH_2C\underline{H}_3$), 3.30 (q, J=7.0 Hz, $C\underline{H}_2CH_3$), 3.95 (s, COOMe), 7.35 (ddd, J=10.0, 10.0, and 1.0 Hz, H-5), 7.44 (ddd, J=10.0, 10.0, and 1.0 Hz, H-7), 7.72 (ddd, J=10.0, 10.0, and 1.0 Hz, H-6), 8.28 (s, H-2), 8.37 (dd, J=10.0 and 1.0 Hz, H-4), and 9.55 (dd, J=10.0 and 1.0 Hz, H-8). Anal. ($C_{14}H_{14}O_2$), C, H.

Methyl 3-Propylazulene-1-carboxylate (2c): The reaction of **1b** (5.0 g, 24.5 mmol) with pentanal (6.32 g, 73.4 mmol) in the presence of morpholine (6.3 g, 73.4 mmol) gave **2c** (5.53 g, 98.9%).

2c: Dark violet prisms (pentane), mp 39.5—40 °C; UV (MeOH) 238 (log ε 4.44), 259 (sh, 4.07), 291.5 (4.38), 296.5 (4.38), 303 (4.79), 348 (sh, 3.66), 366 (sh, 3.95), 381 (4.40), 562 (2.66), and 606 (2.55) nm; IR (KBr) 2949, 1686, 1442, 1422, 1199, 1130, 1041, 1029, and 774 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.00 (t, J=7.0 Hz, CH_3), 1.79 (sext, J=7.0 Hz, $CH_2C\underline{H}_2CH_3$), 2.99 (t, J=7.0 Hz, $C\underline{H}_2CH_2CH_3$),

Table 5. ^{13}C NMR Spectral Data of Methyl 3-Alkylazulene-1-carboxylate (**2**). Azulene Ring Carbons and Methyoxycarbonyl Group

Compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-3a	C-8a	COOMe	
2a	114.82	140.68	125.40	135.00	125.32	138.69	126.92	137.08	141.48	140.94	50.99	165.75
2b	115.00	138.68	130.54	134.71	125.36	138.68	126.89	136.13	141.02	139.77	50.97	165.79
2c	115.00	139.77	130.54	134.71	125.36	138.68	125.89	137.12	141.02	139.77	50.89	165.76
2e	114.99	139.73	130.76	134.72	125.36	138.71	126.91	137.15	141.03	140.94	51.00	165.81
2f	114.88	139.65	130.78	134.70	125.36	138.70	126.89	137.11	140.98	140.90	50.99	165.80
2g	115.00	139.64	130.75	134.70	125.39	138.71	127.00	137.00	141.00	140.87	51.02	165.82
2h	114.98	139.69	130.79	134.71	125.36	138.70	126.98	137.12	141.02	140.86	50.98	165.80
2i	114.99	139.70	130.78	134.71	125.35	138.69	126.99	137.20	141.10	140.85	51.01	165.79
2j	114.90	139.64	130.76	134.66	125.31	138.65	126.85	137.08	140.97	140.88	50.94	165.75

Note: Assignments of signals are based on the results of $^1H/^{13}C$ HECTOR and $^1H/^{13}C$ COLOC on 50 or 150 MHz spectrometers.

Table 6. Substituent Chemical Shifts [SCS] of the Methoxycarbonyl Group at the 1-Position of Methyl Azulene-1-carboxylate (**5**)

	C-1	C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-8	C-8a	COOMe	
5	116.71	140.09	117.57	144.69	138.12	126.63	138.89	127.56	137.69	140.68	51.03	165.7
Azulene	118.03	137.14	118.03	140.28	136.98	122.72	136.52	122.72	136.98	140.28		
[SCS]	−1.32	2.95	−0.46	4.41	1.14	3.91	2.37	4.84	0.71	0.40		

3.95 (s, COOMe), 7.36 (ddd, J=10.0, 10.0, and 1.0 Hz, H-5), 7.44 (ddd, J=10.0, 10.0, and 1.0 Hz, H-7), 7.73 (ddd, J=10.0, 10.0, and 1.0 Hz, H-6), 8.24 (s, H-2), 8.38 (dd, J=10.0 and 1.0 Hz, H-4), and 9.56 (dd, J=10.0 and 1.0 Hz, H-8); Picrate, mp 99 °C. Anal. ($C_{21}H_{19}N_3O_9$) C, H, N.

Methyl 3-Isopropylazulene-1-carboxylate (2d): The reaction of **1b** (5.0 g, 24.5 mmol) with 3-methylbutanal (6.32 g, 73.4 mmol) in the presence of morpholine (6.4 g, 73.4 mmol) gave **2d** (4.6 g, 83.2%).

2d: Violet oil; UV (MeOH), 237.5 (log ε 4.55), 260 (sh, 4.15), 291.5 (4.79), 296 (4.79), 302.5 (4.88), 364 (sh, 4.04), 382 (4.15), 564 (2.76), and 610 (2.64) nm; IR ($CHCl_3$) 2964, 1686, 1577, 1537, 1455, 1442, 1421, 1387, 1231, 1202, 1147, and 1038 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ=1.37 (d, J=6.8 Hz, $CH(CH_3)_2$), 3.48 (sept, J=6.8 Hz, $CH(CH_3)_2$), 3.91 (s, COOMe), 7.1—7.8 (3H, m, H-5,6, and 7), 8.28 (s, H-2), 8.35 (dd, J=9.8 and 1.6 Hz, H-4), and 9.56 (dd, J=9.8 and 2.0 Hz, H-8); Picrate, mp 109 °C. Anal. ($C_{21}H_{19}N_3O_9$), C, H, N.

Methyl 3-Butylazulene-1-carboxylate (2e): The reaction of **1b** (8.0 g, 39.2 mmol) with hexanal (11.78 g, 117.6 mmol) in the presence of morpholine (10.2 g, 117.6 mmol) gave **2e** (9.44 g, 99.4%).

2e: Violet oil; UV (MeOH) 238 (log ε 4.49), 260 (sh, 4.09), 291 (4.72), 296 (4.72), 303 (4.81), 347 (sh, 3.66), 365 (sh, 3.98), 382 (4.00), 565 (2.66), and 610 (2.55) nm; IR ($CHCl_3$) 2956, 2932, 1686, 1455, 1442, 1420, 1231—1208 (br), 1200, 1121, and 1045 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ=0.95 (t, J=7.0 Hz, CH_3), 1.47 (sext, J=7.0 Hz, $CH_2CH_2CH_2CH_3$), 1.74 (quint, J=7.0 Hz, $CH_2CH_2CH_2CH_3$), 3.02 (t, $CH_2CH_2CH_2CH_3$), 3.98 (s, COOMe), 7.36 (ddd, J=10.0, 10.0, and 1.0 Hz, H-5), 7.44 (ddd, J=10.0, 10.0, and 1.0 Hz, H-7), 7.73 (ddd, J=10.0, 10.0, and 1.0 Hz, H-6), 8.23 (s, H-2), 8.38 (dd, J=10.0 and 1.0 Hz, H-4), and 9.56 (dd, J=10.0 and 1.0 Hz, H-8); Picrate, mp 75 °C. Anal. ($C_{22}H_{21}O_9N_3$), C, H, N.

Methyl 3-Pentylazulene-1-carboxylate (2f); The reaction of **1b** (3.0 g, 14.7 mmol) with heptanal (5.04 g, 44.1 mmol) in the presence of morpholine (3.87 g, 44.1 mmol) gave **2f** (3.58 g, 95%).

2f: Violet oil; UV (MeOH) 238 (log ε 4.43), 260 (4.05), 291.5 (4.66), 296.5 (4.65), 303 (4.75), 364 (sh, 3.89), 382 (4.00), 565 (2.61), and 610 (2.49) nm; IR ($CHCl_3$) 2958, 2934, 1688, 1580, 1537, 1456, 1443, 1422, 1231—1209 (br), 1199, 1142, and 1045 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ= 0.90 (t, J=7.0 Hz, CH_3), 1.1—2.0 (6H, m, CH_2), 3.94 (s, COOMe), 7.2—7.9 (3H, m, H-5,6, and 7), 8.26 (s, H-2), 8.39 (dd, J=9.8 and 1.4 Hz, H-4), and 9.59 (dd, J=9.8 and 1.4 Hz, H-8); Picrate, mp 81°C. Anal. ($C_{23}H_{23}O_9N_3$), C, H, N.

Methyl 3-Hexylazulene-1-carboxylate (2g); The reaction of **1b** (3 g, 14.7 mmol) with octanal (5.65 g, 44.1 mmol) in the presence of morpholine (3.87 g, 44.1 mmol) gave **2g** (3.80 g, 95.7%).

2g: Violet oil; UV (MeOH) 238 (log ε 4.43), 260 (sh, 4.06), 292.5 (4.64), 296.5 (4.64), 303 (4.74), 364 (sh, 3.90), 384 (4.01), 565 (2.60), and 610 (2.49) nm; IR ($CHCl_3$) 2958, 2936, 2860, 1687, 1454, 1442, 1418, 1230—1208 (br), 1200, 1140, and 1044 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ=0.87 (t, J=7.0 Hz, CH_3), 1.04—1.92 (8H, m, CH_2), 2.91 (2H, bt, J=7.0 Hz, CH_2), 3.88 (s, COOMe), 6.99—7.82 (3H, m, H-5,6, and 7), 8.16 (s, H-2), 8.22 (dd, J=9.6 and 1.4 Hz, H-4), and 9.52 (dd, J=9.6 and 1.4 Hz, H-8); Picrate, mp 71°C. Anal. ($C_{24}H_{25}O_9N_3$), C, H, N.

Methyl 3-Heptylazulene-1-carboxylate (2h): The reaction of **1b** (1.0 g, 4.89 mmol) with nonanal (2.08 g, 14.7 mmol) in the presence of morpholine (1.278 g, 14.7 mmol) gave **2h** (1.376 g, 99%).

2h: Violet oil; UV (MeOH) 237.5 (log ε 4.42), 259 (4.04), 286 (sh, 4.58), 291 (4.64), 296 (4.64), 302.5 (4.73), 364 (sh, 3.90), 382 (4.00), 562 (2.64), and 608 (2.54) nm; IR ($CHCl_3$) 2957, 2934, 2860, 1688, 1455, 1443, 1420, 1231—1210 (br), 1201, and 1045 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$)

δ=0.87 (brt, J=7.2 Hz, CH_3), 1.07—2.0 (10H, m, CH_2), 2.98 (t, J=7.2 Hz, CH_2), 3.91 (s, COOMe), 7.1—7.8 (3H, m, H-5,6, and 7), 8.18 (s, H-2), 8.31 (dd, J=9.8 and 1.4 Hz, H-4), and 9.51 (dd, J=9.6 and 1.4 Hz, H-8). Anal. ($C_{19}H_{24}O_2$), C, H.

Methyl 3-Octylazulene-1-carboxylate (2i): The reaction of **1b** (1.0 g, 4.89 mmol) with decanal (2.29 g, 14.7 mmol) in the presence of morpholine (1.278 g, 14.7 mmol) gave **2i** (1.407 g, 96.4%).

2i: Violet oil; UV (MeOH) 237.5 (log ε 4.44), 259 (sh, 4.06), 291.5 (4.67), 296 (4.67), 303 (4.76), 365 (sh, 3.92), 382 (4.01), 564 (2.06), and 610 (2.48) nm; IR ($CHCl_3$) 3018, 2965, 2943, 2867, 1690, 1458, 1447, 1424, 1228, 1200, and 1046 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ=0.87 (CH_3), 1.03—2.00 (12H, m, CH_2), 3.01 (brt, J=7.4 Hz, CH_2), 3.92 (s, COOMe), 7.1—7.9 (3H, m, H-5,6, and 7), 8.22 (s, H-2), 8.36 (dd, J=10.0 and 1.2 Hz, H-4), and 9.55 (dd, J=9.8 and 1.2 Hz, H-8); Picrate, mp 55.5 °C. Anal. ($C_{26}H_{29}O_9N_3$), C, H, N.

Methyl 3-Benzylazulene-1-carboxylate (2j): The reaction of **1b** (1.0 g, 4.89 mmol) with 3-phenylpropanal (1.97 g, 14.7 mmol) in the presence of morpholine (1.278 g, 14.7 mmol) gave **2j** (1.289 g, 95.4%).

2j: Violet micro-prisms (cyclohexane), mp 92—92.5 °C; UV (MeOH) 237 (log ε 4.41), 259 (sh, 4.13), 292.5 (4.57), 297.5 (4.57), 303.5 (4.66), 362 (sh, 3.83), 381 (3.94), and 560 (2.67) nm; IR (KBr) 1694, 1456, 1440, 1416, 1203, 1029, 773, and 740 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ=3.91 (s, COOMe), 4.38 (brs, CH_2), 7.19 (5H, brs, Ph), 7.41 (2H, ddd, J=9.8, 9.8, and 1.2 Hz, H-5 and 7), 7.70 (dd, J=9.8 and 9.8 Hz, H-6), 8.13 (s, H-2), 8.34 (dd, J=9.8 and 1.6 Hz, H-4), and 9.55 (dd, J=9.8 and 1.6 Hz, H-8). Anal. ($C_{19}H_{16}O_2$), C, H.

Demethoxycarbonylation of Methyl 3-Alkylazulene-1-carboxylate (2). Synthesis of 1-Alkylazulenes (4). Method A: Freshly prepared 100% phosphoric acid was added to ester compound **2** in a flask, and the mixture was heated in a water bath with occasional stirring with a glass rod. Vigorous evolution of CO_2 gas was observed. After confirmation of the absence of the substrate by TLC, the reaction mixture was poured into water, and the mixture was extracted with benzene. The benzene solution was washed with water, dried over Na_2SO_4, and the solvent was removed under reduced pressure to give crude 1-alkylazulene (**4**). The crude product was purified with an alumina column eluted with hexane to give **4**.

Method B: An ester compound was hydrolyzed to a 3-alkylazulene-1-carboxylic acid, and the carboxylic acid was treated with trichloroacetic acid in benzene under refluxing. The product was purified by alumina column chromatography eluted with hexane. This method was successfully applied for the synthesis of 1-methylazulene (**4a**) and azulene (**6**).

Synthesis of 1-Methylazulene (4a). Method A: Ester **2a** (2.28 g, 11.4 mmol) was treated with 100% phosphoric acid (40 ml) for 15 min. After being worked up under the general procedure described above, the crude product was purified with an alumina column to give **4a** (1.22 g, 75%) as a blue oil.

Method B: A solution of potassium hydroxide (30 g) in water (60 ml) was added to a solution of **2a** (10.8 g, 54 mmol) in ethanol (300 ml), and the mixture was refluxed for 2h. After being cooled to room temperature, the reaction mixture was poured into water (100 ml), and acidified with hydrochloric acid to pH 3. The precipitates of the carboxylic acid were collected by suction filtration, washed with water, and dried in a vacuum desiccator until a constant weight was shown to give 3-methylazulene-1-carboxylic acid (10.05 g, 100%).

Trichloroacetic acid (300 mg) was added to a suspension of the carboxylic acid (5.0 g, 21.8 mmol) in benzene (300 ml), and the mixture was refluxed for 2 h. During the reaction, the color of the reaction mixture changed from violet to blue. After being cooled to room temperature, a large portion of the solvent was removed under reduced pressure. The residue was dissolved in benzene and the solution was passed through a short alumina column eluted with benzene. The crude product obtained from the first fraction was purified by re-chromatography with an alumina column eluted with hexane to give **4a** (3.62 g, 95%) as crystals.

4a: Blue prisms (Pentane), mp 26—27 °C; Picrate, mp 124—125 °C (lit,[4] 135 °C), TNB 161 °C (lit,[4] 161 °C); IR ($CHCl_3$) 3012, 2930, 1577, 1510, 1455, 1396, 947, and 880 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ=2.67 (s, CH_3), 7.03 (dd, J=11.0 and 11.0 Hz, H-5), 7.06 (dd, J=11.0 and 11.0 Hz, H-7), 7.31 (d, J=4.0 Hz, H-3), 7.51 (dd, J=11.0 and 11.0 Hz, H-6), 7.74 (d, J=4.0 Hz, H-2), and 8.22 (d, J=11.0 Hz, H-4 and 8); ^{13}C NMR (50 MHz, $CDCl_3$) δ=12.68 (q, CH_3), 116.52 (d, C-3), 121.05 (d, C-5), 121.85 (d, C-7), 126.11 (d, C-1), 133.53 (d, C-8), 136.08 (d, C-4), 136.34 (s, C-8a), 137.13 (d, C-6), 137.99 (d, C-2), and 140.59 (s, C-3a). Anal. ($C_{11}H_{10}$), C, H.

Synthesis of 1-Ethylazulene (4b): Demethoxycarbonylation of **2b** (4.0 g, 18.7 mmol) with 100% phosphoric acid (80 ml) gave **4b** (2.70 g, 92.5%).

4b: Blue oil, Picrate, mp 96 °C, IR ($CHCl_3$) 3017, 2982, 2945, 1582, 1460, 1437, 1402, 1300, 947, and 877 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ=1.36 (t, J=7.4 Hz, CH_3), 3.08 (q, J=7.4 Hz, CH_2), 7.00 (2H, dd, J=9.8 and 9.8 Hz, H-5 and 7), 7.31 (d, J=3.6 Hz, H-3), 7.50 (dd, J=9.8 and 9.8 Hz, H-6), 7.79 (d, J=3.6 Hz, H-2), and 8.22 (2H, brd, J=9.8 Hz, H-4 and 8). Anal. ($C_{12}H_{12}$), C, H.

Synthesis of 1-Propylazulene (4c): Demethoxycarbonylation of **2c** (2.0 g, 8.76 mmol) with 100% phosphoric acid (40 ml) gave **4c** (1.44 g, 96.8%).

4c: Blue oil; UV (MeOH): 239 (log ε 4.30), 268 (sh, 4.68), 273.5 (4.80), 277.5 (4.85), 282 (4.80), 288 (sh, 4.56), 297 (sh, 3.73), 329 (sh, 3.42), 345 (3.71), 360 (3.42), 610 (2.50), and 666 (2.39) nm; IR ($CHCl_3$) 3012, 2968, 2937, 2878, 1577, 1458, 1445, 1397, and 949 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) 0.98 (t, J=7.2 Hz, CH_3), 2.59 (sext, J=7.4 Hz, $CH_2C\underline{H}_2CH_3$), 3.03 (t, J=7.4 Hz, $C\underline{H}_2CH_2CH_3$), 6.97 (2H, dd, J=9.8 and 9.8 Hz, H-5 and 7), 7.27 (d, J=3.4 Hz, H-3), 7.46 (dd, J=9.8 and 9.8 Hz, H-6), 7.73 (d, J=3.4 Hz H-2), and 8.20 (2H, dd, J=9.8 and 9.8 Hz, H-4 and 8); ^{13}C NMR (25 MHz, $CDCl_3$) δ=14.2 (q, CH_3), 24.7 (t, CH_2), 29.4 (t, CH_2), 116.7 (d, C-3), 121.0 (d, C-7 or 5), 121.7 (d, C-5 or 7) 131.3 (s, C-1), 133.2 (d, C-2), 135.8 (s, C-8a or 3a), 136.0 (d, C-6), 136.9 (d, C-4 and 8), and 140.5 (s, C-3a or 8a). Picrate, mp 89.5 °C. Anal. ($C_{17}H_{17}N_3O_7$), C, H, N.

Synthesis of 1-Isopropylazulene (4d): Demethoxycarbonylation of **2d** (1.0 g, 4.38 mmol) with 100% phosphoric acid (20 ml) gave **4d** (720 mg, 96.6%).

4d: Blue oil, IR ($CHCl_3$) 3008, 2966, 2934, 2876, 1575, 1503, 1456, 1430, 1413, 1393, 1383, 1366, 1063, 1048, 983, and 947 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ=1.33 (d, J=7.0 Hz, $CH(C\underline{H}_3)_2$), 3.88 (sept, J=7.0 Hz, $C\underline{H}(CH_3)_2$), 6.89 (2H, dd, J=9.8 and 9.8 Hz, H-5 and 7), 7.26 (d, J=4.0 Hz, H-3), 7.39 (dd, J=9.8 and 9.8 Hz, H-6), 7.79 (d, J=4.0 Hz, H-2), 8.12 (d, J=9.8 Hz, H-8 or 4), and 8.20 (d, J=9.8 Hz, H-4 or 8); Picrate, mp 93.5 °C. Anal. ($C_{19}H_{17}O_7N_3$), C, H, N.

Synthesis of 1-Butylazulene (4e): Demethoxycarbonylation of **2e** (2.0 g, 8.25 mmol) with 100% phosphoric acid (40 ml) gave **4e** (1.282 g, 84.3%).

4e: Blue oil; UV (MeOH) 239 (log ε 4.29), 268 (sh, 4.66), 273.5 (4.78), 278 (4.83), 288.5 (sh, 4.54), 297 (sh, 3.76), 330 (3.43), 345.5 (3.70), 360 (3.43), 610 (2.49), and 666 (2.40) nm; IR ($CHCl_3$) 3008, 2958, 2932, 2960, 1574, 1466, 1453, 1446, 1393, 1300, and 945 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) 0.95 (t, J=7.0 Hz, CH_3), 1.1—2.0 (4H, m, CH_2), 3.00 (2H, brt, J=7.4 Hz, CH_2), 6.98 (2H, dd, J=9.8 and 9.8 Hz, H-5 and 7), 7.28 (d, J=3.8 Hz, H-2), 7.47 (dd, J=9.8 and 9.8 Hz, H-6), 7.74 (d, J=3.8 Hz, H-3), and 8.13 (2H, brd, J=9.6 Hz, H-4 and 8); ^{13}C NMR (25 MHz, $CDCl_3$) δ=14.0 (q, CH_3), 22.8 (t, CH_2), 27.1 (t, CH_2), 33.7 (t, CH_2), 116.7 (d, C-3), 121.0 (d, C-7 or 5), 121.7 (d, C-5 or 7), 131.5 (s, C-1), 133.1 (d, C-6), 135.6 (s, C-3a or 8a), 136.0 (d, C-2), 137.0 (d, C-4 and 8), and 140.5 (s, C-8a or 3a); TNB, mp 91.5 °C. Anal. ($C_{20}H_{19}O_6N_3$), C, H, N.

Synthesis of 1-Pentylazulene (4f): Demethoxycarbonylation of **2f** (2.0 g, 7.80 mmol) with 100% phosphoric acid (40 ml) gave **4f** (1.476 g, 95.4%).

4f: Blue oil, UV (MeOH) 239 (log ε 4.28), 268 (sh, 4.64), 273 (4.75), 278 (4.81), 282 (4.76), 288 (sh, 4.58), 297 (sh, 3.78), 329 (sh, 3.50), 345.5 (3.70), 360 (3.50), 610 (2.47), and 664 (2.42) nm; IR ($CHCl_3$) 3016, 2966, 2940, 2872, 1577, 1470, 1456, 1440, 1397, 1301, and 950 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ=0.88 (CH_3), 1.0—1.7 (6H, m, CH_2), 3.04 (brt, rJ=7.6 Hz, CH_2), 6.95 (2H, dd, J=9.6 and 9.6 Hz, H-5 and 7), 7.29 (d, J=4.0 Hz, H-3), 7.44 (dd, J=9.6 and 9.6 Hz, H-6), 7.77 (d, J=4.0 Hz, H-2), 8.16 (d, J=9.6 Hz, H-8 or 4), and 8.20 (d, J=9.6 Hz, H-4 or 8); ^{13}C NMR (25 MHz, $CDCl_3$) δ=14.1 (q, CH_3), 22.7 (t, CH_2), 27.4 (t, CH_2), 31.3 (t, CH_2), 32.0 (t, CH_2), 116.7 (d, C-3), 121.1 (d, C-7 or 5), 121.8 (d, C-5 or 7), 131.6 (s, C-1), 133.2 (d, C-2), 135.7 (s, C-8a or 3a), 136.1 (d, C-6), 136.9 (d, C-8 or 4), 137.1 (C-4 or 8), and 140.5 (s, C-3a or 8a); TNB, mp 80.5—81 °C. Anal. ($C_{21}H_{21}O_6N_3$), C, H, N.

Synthesis of 1-Hexylazulene (4g): Demethoxycarbonylation of **2g** (2.0 g, 7.39 mmol) with 100% phosphoric acid (40 ml) gave **4g** (1.51 g, 96.1%).

4g: Blue oil, UV (MeOH) 239 (log ε 4.30), 268 (sh, 4.67), 273 (4.79), 275.5 (4.85), 282 (4.79), 288 (sh, 4.56), 297 (3.75), 330 (sh, 3.47), 345 (3.73), 360.5 (3.46), 608 (2.49), and 664 (2.41) nm; IR ($CHCl_3$) 3005, 2958, 2934, 2857, 1574, 1505, 1468, 1454, 1440, 1393, 1298, and 946 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ=0.88 (t, J=7.0 Hz, CH_3), 1.03—2.06 (8H, m, CH_2), 3.05 (2H, brt, J=7.6 Hz, CH_2), 6.95 (dd, J=9.6 and 9.6 Hz, H-5 and 7), 6.93 (d, J=4.0 Hz, H-3), 7.45 (dd, J=9.6 and 9.6 Hz, H-6), 7.71 (d, J=4.0 Hz, H-2), and 8.16 (2H, brd, J=9.6 Hz, H-4 and 8); ^{13}C NMR (50 MHz, $CDCl_3$) δ=14.1 (q, CH_3), 22.7 (t, CH_2), 27.4 (t, CH_2), 29.5 (t, CH_2) 31.6 (t, CH_2), 31.8 (t, CH_2), 116.6 (d, C-3), 121.1 (d, C-7 or 5), 121.9 (d, C-5 or 7), 131.7 (s, C-1), 133.3 (d, C-2), 135.7 (s, C-8a or 3a), 136.2 (d, C-6), 136.9 (d, C-4 or 8), 137.2 (d, C-8 or 4), and 140.5 (s, C-3a and 8a); Picrate, mp 65.5 °C. Anal. ($C_{22}H_{23}O_7N_3$) C, H, N.

Synthesis of 1-Heptylazulene (4h): Demethoxycarbonylation of **2h** (1.0 g, 3.51 mmol) with 100% phosphoric acid (20 ml) gave **4h** (770 mg, 97.6%).

4h: Blue oil, UV (MeOH) 240 (log ε 4.24), 268 (sh, 4.60), 273.5 (4.72), 278 (4.77), 283 (4.72), 288 (sh, 4.51), 298 (sh, 3.87), 346 (3.67), 360.5 (3.47), 608 (2.48), and 666 (2.32) nm; ^1H NMR (60 MHz, $CDCl_3$) δ=0.88 (CH_3), 1.04—2.06 (10H, m, CH_2), 3.06 (brt, CH_2), 6.99 (dd, J=9.6 and 9.6 Hz, H-5 and 7), 7.33 (d, J=3.8 Hz, H-3), 7.47 (dd, J=9.6 and 9.6 Hz, H-6), 7.78 (d, J=3.8 Hz, H-2), 8.21 (d, J=9.6 Hz, H-8 or 4), and 8.23 (d, J=9.6 Hz, H-4 or 8); ^{13}C NMR (25 MHz, $CDCl_3$) δ=14.1 (q, CH_3), 22.7 (t, CH_2), 27.4 (t, CH_2), 29.3 (t, CH_2), 29.8 (t, CH_2), 31.6 (t, CH_2), 31.9 (t, CH_2), 116.6 (d, C-3), 121.0 (d, C-7 or 5), 121.7 (d, C-5 or 7), 131.6 (s, C-1), 133.2 (d, C-2), 135.6 (s, C-8a or 3a), 136.0 (d, C-6), 136.9 (d, C-8 or 4), 137.0 (d, C-4 or 8), and 140.5 (s, C-3a and 8a). Anal. ($C_{17}H_{22}$), C, H.

Synthesis of 1-Octylazulene (4i): Demethoxycarbonylation of **2i** (2.0 g, 6.70 mmol) with 100% phosphoric acid (40 ml) gave **4i** (1.5 g, 95.8%).

4i: Blue oil; UV (MeOH) 240 (log ε 4.17), 268 (sh, 4.54), 273 (4.66), 278 (4.71), 282.5 (4.66), 288 (sh, 4.44), 297 (3.66), 330 (sh, 3.40), 345.5 (3.62), 360 (3.39), 610 (2.40), and 663 (2.34) nm; IR ($CHCl_3$) 3006, 2962, 2935, 2860, 1575, 1506, 1468, 1458, 1442, 1394, 1300, and 947 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ=0.87 (CH_3), 1.04—1.99 (12H, m, CH_2), 3.03 (2H, brt, J=7.4 Hz, CH_2), 6.91 (2H, dd, J=9.6 and 9.6 Hz, H-5 and 7), 7.25 (d, J=3.8 Hz, H-3), 7.41 (dd, J=9.6 and 9.6 Hz, H-6), 7.70 (d, J=3.8 Hz, H-2), 8.11 (d, J=9.6 Hz, H-8 or 4), and 8.15 (d, J=9.6 Hz, H-4 or 8); ^{13}C NMR (25 MHz, $CDCl_3$) δ=14.1 (q, CH_3), 22.7 (t, CH_2), 27.4 (t, CH_2), 29.4 (t, CH_2), 29.6 (t, CH_2), 29.8 (t, CH_2), 31.6 (t, CH_2), 31.9 (t, CH_2), 116.6 (d, C-3), 121.0 (d, C-7 or 5), 121.7 (d, C-5 or 7), 131.6 (s, C-1), 133.2 (d, C-2), 135.6 (s, C-8a or 3a), 136.0 (d, C-6), 136.8 (d, C-8 or 4), 137.0 (d, C-4 or 8), and 140.5 (s, C-3a and 8a); TNB, mp 57.5 °C. Anal. ($C_{24}H_{27}O_6N_3$), C, H, N.

Synthesis of 1-Benylazulene (4j): Demethoxycarbonylation of **2j** (1.0 g, 3.60 mmol) with 100% phosphoric acid (20 ml) gave **4j** (730 mg, 99.3%).

4j: Bluish-violet prisms, mp 74.5—75 °C; IR (KBr); 3036, 2905, 1578, 1500, 1457, 785, 778, 737, and 704 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) 4.43 (2H, s, CH_2), 7.03 (2H, dd, J=9.8 and 9.8 Hz, H-5 and 7), 7.16 (5H, s, C_6H_5), 7.32 (d, J=3.8 Hz, H-3), 7.52 (dd, J=9.8 and 9.8 Hz, H-6), 7.71 (d, J=3.8 Hz, H-2), and 8.28 (2H, brd, J=9.8 Hz, H-4 and 8). Anal. ($C_{17}H_{14}$), C, H.

Preparation of Methyl Azulene-1-carboxylate (5). Acetaldehyde (Merck Cat. No 800004, 20 ml) was added to a mixture of **1b** (10.0 g, 48.9 mmol) in diethylamine (250 ml), and the mixture was refluxed for 3 h in an oil bath. After being cooled to room temperature, diethylamine was removed under reduced pressure. The residual oil was dissolved in benzene, washed three times with water, dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residual red oil was dissolved in benzene and passed through a short silica-gel column to give **5** (7.73 g, 85%).

5: Violet oil; ^1H NMR (200 MHz, $CDCl_3$) δ=3.96 (s,

COOMe), 7.29 (d, J=4 Hz, H-3), 7.45 (ddd, J=10, 10, and 1 Hz, H-5), 7.55 (ddd, J=10, 10, and 1 Hz, H-7), 7.82 (ddd, J=10, 10, and 1 Hz, H-6), 8.37 (d, J=4 Hz, H-2), 8.45 (dd, J=10 and 1 Hz, H-4), and 9.64 (dd, J=10 and 1 Hz, H-8); ^{13}C NMR (50 MHz, $CDCl_3$) δ=51.03 (q, $COO\underline{C}H_3$), 116.71 (s, C-1), 117.57 (d, C-3), 126.63 (d, C-5), 127.56 (d, C-7), 137.69 (d, C-8), 138.12 (d, C-4), 138.89 (d, C-6), 140.09 (d, C-2), 140.68 (d, C-8a), 144.69 (d, C-3a), and 165.77 (d, $\underline{C}OOCH_3$).

Hydrolysis of Methyl Azulene-1-carboxylate (5). A potassium hydroxide (40 g) solution in water (60 ml) was added to a solution of **5** (10.0 g, 53.7 mmol) in ethanol (300 ml), and the mixture was refluxed in an oil bath for 2 h. After being cooled to room temperature, a large portion of the solvent was removed under reduced pressure, and the residue was diluted with water. After acidification with 6 M (mol dm^{-3}) hydrochloric acid, the precipitates of the carboxylic acid (**8**) were collected by suction filtration, washed with water, and dried in a vacuum desiccator until a constant weight was shown to give **8** (6.01 g, 100%).

Decarboxylation of 8. Preparation of Azulene (6). Trichloroacetic acid (400 mg) was added to a suspension of azulene-1-carboxylic acid (**8**, 10 g, 62.4 mmol) in benzene (200 ml) and the mixture was refluxed in an oil bath for 6 h. After being cooled to room temperature, the reaction mixture was washed with water, dried over anhydrous magnesium sulfate, and a half portion of the solvent was removed under reduced pressure. The resulting solution was passed through a short alumina column eluted with benzene, and crude azulene eluted in the first fraction was purified by re-chromatography with an alumina column eluted with hexane to give azulene (**6**) (7.20 g, 90%).

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References

1) A part of this study was presented at the "43rd National Meeting of the Chemical Society of Japan," Tokyo, March 30, 1981, Abstr., No. 1H44.

2) T. Yanagisawa, S. Wakabayashi, T. Tomiyama, M. Yasunami, and K. Takase, *Chem. Pharm. Bull.*, **36**, 6412 (1988).

3) K. -P. Zeller, "Methoden der Organischen Chemie," ed by Heinz Kropf, Georg, Thieme Verlag, Stuttgart (1985), Vol. 5/2c, pp. 127—418.

4) P. A. Plattner and J. Wyss, *Helv. Chim. Acta*, **24**, 483 (1941).

5) K. Hafner, A. Stephan, and C. Bernhard, *Justus Liebigs Ann. Chem.*, **650**, 42 (1961).

6) a) K. Hafner and C. Bernhard, *Justus Liebigs Ann. Chem.*, **625**, 108 (1959); b) A. G. Anderson and R. D. Breageale, *J. Org. Chem.*, **34**, 2375 (1969).

7) a) P. W. Yang, M. Yasunami, and K. Takase, *Tetrahedron Lett.*, **1971**, 4275; b) M. Yasunami, Alice Chen, P. W. Yang, and K. Takase, *Chem. Lett.*, **1980**, 579; c) K. Takase and M. Yasunami, *Yuki Gosei Kagaku Kyokai Shi*, **39**, 1172 (1981).

8) a) T. Nozoe, P. W. Yang, C. P. Wu, T. S. Huang, T. H. Lee, H. Okai, H. Wakabayashi, and S. Ishikawa, *Heterocycles*, **29**, 1225 (1989); T. Nozoe, H. Wakabayashi, S. Ishikawa, C. P. Wu, and P. W. Yang, *Heterocycles*, **31**, 17 (1990); T. Nozoe, H. Wakabayashi, K. Shindo, S. Ishikawa, C. P. Wu, and P. W. Yang, *Heterocycles*, **32**, 213 (1991); b) G. R. Tian, S. Sugiyama, A. Mori, H. Takeshita, M. Higashi, and H. Yamaguchi, *Chem. Lett.*, **1988**, 941.

9) "Enamines," ed by A. G. Cook, Marcel Dekker, New York and London (1969).

10) M. Yasunami, A. Chen, Y. Noro, and K. Takase, *Chem. Lett.*, **1981**, 555.

11) T. Nozoe, K. Takase, T. Nakazawa, and S. Fukuda, *Tetrahedron*, **27**, 3357 (1971).

12) M. Yasunami, M. Sato, and K. Takase, to be published.

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

14) A. G. Anderson and E. J. Cowles, *J. Am. Chem. Soc.*, **77**, 4617 (1955).

15) C. Mannichi and H. Davidsen, *Chem. Ber.*, **69B**, 2106 (1936).

16) G. Laban and R. Mayer, *Z. Chem.*, **7**, 12 (1967).

17) A. G. Anderson, Jr., J. J. Tazuma, and J. A. Nelson, *J. Am. Chem. Soc.*, **75**, 4980 (1953).

18) W. Treibs, H. -J. Neupert, and J. Heebsch, *Chem. Ber.*, **92**, 1216 (1959).

19) S. Braun and J. Kendeldei, *Tetrahedron*, **33**, 1827 (1977).

20) It is well known that the T_1 value increases on the carbon nearer to the end of the alkyl side chain: K. Nakanishi, "Superconducted FT-NMR," Kohdansha, Tokyo (1986), pp. 54—57.

21) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York and London (1972) p. 98.

22) a) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, **1961**, 468; b) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).