Synthesis of 1-(2-Benzofurancarbonyl)azulenes Using 1-(Bromoacetyl)azulenes as New Building Blocks

Satoko Yamashiro

Department of Materials and Life Science, Graduate School of Science and Technology, Kumamoto University, Kurokami, Kumamoto 860-8555, Japan

Kimiaki Imafuku*

Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami, Kumamoto 860-8555, Japan

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1-Acetylazulene (**1**) was treated with trimethylphenylammonium tribromide in refluxing chloroform to afford 1-acetyl-3-bromoazulene (**3**) and 3-bromo-1-(bromoacetyl)azulene (**4**). In a similar manner, 3-methyl-, 3-ethyl-, 3-propyl-, and 3-methoxycarbonyl-substituted 1-acetylazulenes **2a-d** gave the corresponding 3-substituted 1-(bromoacetyl)azulenes **5a-d** as major products and 1-(dibromoacetyl)azulenes **6a-d** as minor ones. The 1-(bromoacetyl)azulenes **5a-d** are useful as new building blocks. Compounds **5a-d** reacted with salicylaldehydes **9a-g** to yield twenty-eight cyclized products, 1-(2-benzofurancarbonyl)azulenes **11aa-dg**, *via* 1-phenoxyacetylazulenes **10aa-dg**.

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It is well known that an acetyl group is a useful reactive functional group for the synthetic organic chemistry. In the chemistry of acetylazulenes, we found that self-cyclotrimerization of 1-acetylazulene gave 1,3,5-tri(1-azulenyl)benzene [1]. The condensation of 1-acetylazulenes with benzaldehydes gave 1-cinnamoylazulenes which reacted with malononitrile to afford 1-(4-aryl-2-pyridyl)-azulenes [2]. Furthermore, azulenes having a quinoline and related heterocyclic ring were prepared by the reactions of 1-acetylazulenes with 2-aminobenzaldehydes [3,4]. These reactions of the acetyl group are based on the electrophilicity of the carbonyl function and the nucleophilicity of the methyl carbon atom. In the mean while, the conversion of the acetyl group into a bromoacetyl group, α-haloketone, furnishes two electrophilic carbon atoms. This means umpolung of the methyl carbon atom and provides a new building block.

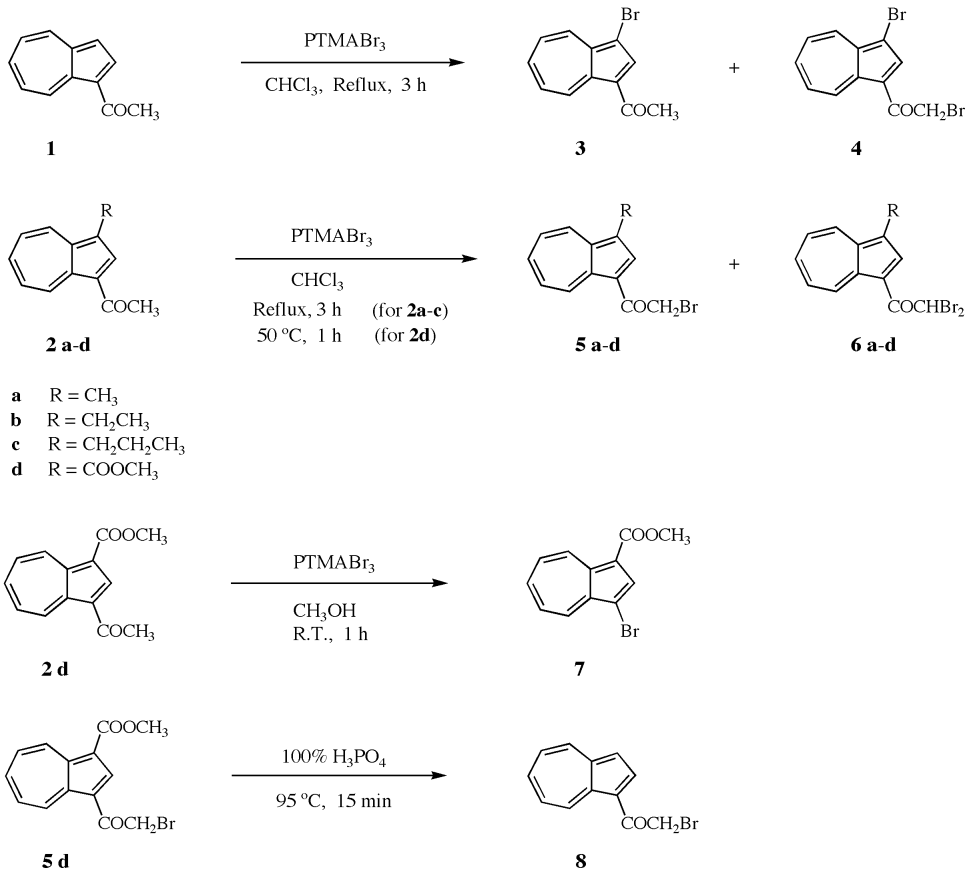
This paper deals with the construction of 1-(bromoacetyl)azulenes as new building blocks and the synthesis of 1-(2-benzofurancarbonyl)azulenes by their reactions with salicylaldehydes. Recently, 2-(arylmethyl)benzofurans and related functions are worth notice as one of components of insulin sensitive enhancers for non-insulin-dependent mellitius patients [5-7], and non-nucleoside reverse transcriptase [8].

Preparation of 1-(Bromoacetyl)azulenes **5a-d**.

It was reported that 1-acetylazulene was treated with *N*-bromosuccunimide to afford 1-acetyl-3-bromoazulene in 84% yield [9]. On the other hand, it is well-known that tropolones are very susceptible to bromination to yield 3-, 5-, and 7-brominated products [10,11]. Although 3-acetyltropolone gave 3-acetyl-5,7-dibromotropolone in a similar manner [12], we found that the reaction with quaternary ammonium tribromides in aprotic tetrahydrofuran afforded 3-(bromoacetyl)tropolone as a sole product [13]. In this communication, the bromination of 1-acetylazulenes was carried out in order to obtain 1-(bromoacetyl)azulenes as new building blocks.

When a solution of 1-acetylazulene (**1**) [14] in chloroform was refuxed for 3 hours in the presence of trimethylphenylammonium tribromide ($PTMABr_3$) (1.5 equivalents), 1-acetyl-3-bromoazulene (**3**) [9] and 3-bromo-1-(bromoacetyl)azulene (**4**) were isolated in 16 and 28% yield, respectively. In a similar manner, the bromination of 1-acetyl-3-methylazulene (**2a**) [3] gave 1-(bromoacetyl)- (**5a**) (58%) and 1-(dibromoacetyl)-3-methylazulene (**6a**) (26%) as monobrominated and dibrominated product of the acetyl group, respectively. The starting material **2a** (14%) was also recovered. 3-Ethyl- and 3-propyl-substituted azulenes **2b**,**c** [3] were also treated with $PTMABr_3$ to give **5b** (52%) and **6b** (8%) from the former and **5c** (56%) and **6c** (6%) from the latter, respectively. The bromination of 1-acetyl-3-methoxycarbonylazulene (**2d**) [15] was carried out in more mild condition, heating at 50 °C for 1 hour, to yield 1-(bromoacetyl)- (**5d**) (80%) and 1-(dibromoacetyl)-3-methoxycarbonyl-azulene (**6d**) (10%). When this reaction was performed in methanol at room temperature for 1 hour, the acetyl group was removed and 1-bromo-3-methoxycarbonylazulene (**7**) [16] was obtained in 80% yield. In methanol, the brominating agent might react with methanol to produce methyl hypobromite as a more active brominating species, which brominates the azulene **2d**. Thus, we found that 1-(bromoacetyl)azulenes were readily obtained by the bromination of 1-acetylazulenes with $PTMABr_3$ in chloroform and are new building blocks for synthesis of azulenes having a heterocyclic ring. In addition, 1-(bromoacetyl)-3-methoxycarbonylazulene (**5d**) was heated in 100% phosphoric acid to afford 1-(bromoacetyl)azulene (**8**) by deesterification.

Scheme 1



Synthesis of 1-(2-Benzofurancarbonyl)azulenes **11aa-dg**.

Construction of the benzofuran structure was accomplished by useful ring-closure reaction of *o*-hydroxybenzaldehydes with α–haloketones [17,18]. In this work, the reactions of 1-(bromoacetyl)azulenes having an alkyl or ester group at the 3-position with various aldehydes were carried out. A solution of 1-(bromoacetyl)-3-methylazulene (**5a**) and salicylaldehyde (**9a**) in acetonitrile was stirred for 30 minutes at room temperature followed by heating under refluxing temperature for 1 hour. Purification by silica gel column chromatography afforded 1-(2-benzofurancarbonyl)-3-methylazulene (**11aa**) in an excellent yield (92%). In a similar manner, the reactions with 3-methyl-, 4-methoxy-, 5-methoxy-, and 5-formyl-substituted salicylaldehydes **9b**,**e**,**f** gave the corresponding 1-(2-benzofurancarbonyl)azulenes **11ab**,**ae**,**af** in good yields (Table 1). Salicylaldehyde **9c** reacted with 1-(bromoacetyl)-3-methylazulene (**5a**) to give 1-[(2-formyl-4-methylphenoxy)acetyl]-3-methylazulene (**10ac**) (58%) and 3-methyl-1-(5-methylbenzofuran-2-carbonyl)azulene (**11ac**) (26%). On the other hand, the reaction of salicylaldehyde **9d** gave 1-[(2-formy-6-methoxylphenoxy)acetyl]-3-methylazulene (**10ad**) (84%) as a sole product. Results of the reactions of other 3-substituted 1-(bromoacetyl)azulenes **5b-d** with salicylaldehydes **9a-g** are summarized in Table 1. These reactions gave the substituted **10** and/or the cyclized products **11**.

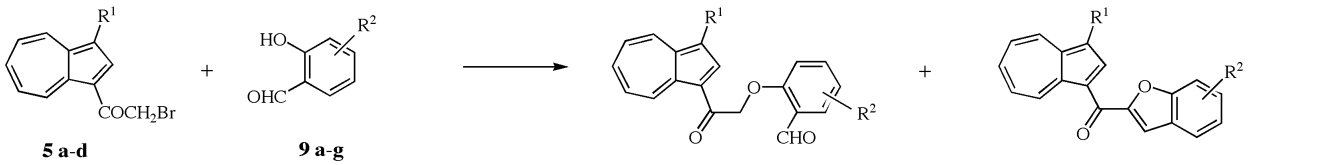
When the reactions were performed under refluxing temperature, all of the reactions gave the cyclized 1-(2-benzofurancarbonyl)azulenes **11aa-dg** in high yields.

These reactions provide a simple synthetic method for preparation of 1-(2-benzofurancarbonyl)azulenes. The products **11ag**,**bg**,**cg**,**dg** are expected to be useful precursors to insulin sensitive enhancers.

EXPERIMENTAL

All melting points were determined with a Yanaco MP JP-3 apparatus and are uncorrected. The ir spectra were taken on a JASCO IRA-1 spectrophotometer. The ^{1}H and ^{13}C nmr spectra were recorded with a JEOL JNM-EX 300 spectrometer (300 MHz for ^{1}H and 75.5 MHz for ^{13}C). The ms spectra were obtained under electron impact with a JEOL JMS-01-SG spectrometer. The high-resolution ms of compounds **10da**,**dg** were obtained using *p*-nitrobenzyl alcohol matrix containing sodium iodide. The elemental analyses were performed at the Center for Instrumental Analysis, Kumamoto University.

Scheme 2



5 a-d

a $R^1 = CH_3$
b $R^1 = CH_2CH_3$
c $R^1 = CH_2CH_2CH_3$
d $R^1 = COOCH_3$

9 a-g

a $R^2 = H$
b $R^2 = 3\text{-}CH_3$
c $R^2 = 5\text{-}CH_3$
d $R^2 = 3\text{-}OCH_3$
e $R^2 = 4\text{-}OCH_3$
f $R^2 = 5\text{-}OCH_3$
g $R^2 = 5\text{-}CHO$

10 ac-dg

ac $R^1 = CH_3$, $R^2 = 4'\text{-}CH_3$
ad $R^1 = CH_3$, $R^2 = 6'\text{-}OCH_3$
bb $R^1 = CH_2CH_3$, $R^2 = 6'\text{-}CH_3$
bc $R^1 = CH_2CH_3$, $R^2 = 4'\text{-}CH_3$
bd $R^1 = CH_2CH_3$, $R^2 = 6'\text{-}OCH_3$
be $R^1 = CH_2CH_3$, $R^2 = 5'\text{-}OCH_3$
bf $R^1 = CH_2CH_3$, $R^2 = 4'\text{-}OCH_3$
cb $R^1 = CH_2CH_2CH_3$, $R^2 = 6'\text{-}CH_3$
cc $R^1 = CH_2CH_2CH_3$, $R^2 = 4'\text{-}CH_3$
cd $R^1 = CH_2CH_2CH_3$, $R^2 = 6'\text{-}OCH_3$
ce $R^1 = CH_2CH_2CH_3$, $R^2 = 5'\text{-}OCH_3$
cf $R^1 = CH_2CH_2CH_3$, $R^2 = 4'\text{-}OCH_3$
da $R^1 = COOCH_3$, $R^2 = H$
db $R^1 = COOCH_3$, $R^2 = 6'\text{-}CH_3$
dc $R^1 = COOCH_3$, $R^2 = 4'\text{-}CH_3$
dd $R^1 = COOCH_3$, $R^2 = 6'\text{-}OCH_3$
dg $R^1 = COOCH_3$, $R^2 = 4'\text{-}CHO$

11 aa-dg

aa $R^1 = CH_3$, $R^2 = H$
ab $R^1 = CH_3$, $R^2 = 7'\text{-}CH_3$
ac $R^1 = CH_3$, $R^2 = 5'\text{-}CH_3$
ad $R^1 = CH_3$, $R^2 = 7'\text{-}OCH_3$
ae $R^1 = CH_3$, $R^2 = 6'\text{-}OCH_3$
af $R^1 = CH_3$, $R^2 = 5'\text{-}OCH_3$
ag $R^1 = CH_3$, $R^2 = 5'\text{-}CHO$
ba $R^1 = CH_2CH_3$, $R^2 = H$
bb $R^1 = CH_2CH_3$, $R^2 = 7'\text{-}CH_3$
bc $R^1 = CH_2CH_3$, $R^2 = 5'\text{-}CH_3$
bd $R^1 = CH_2CH_3$, $R^2 = 7'\text{-}OCH_3$
be $R^1 = CH_2CH_3$, $R^2 = 6'\text{-}OCH_3$
bf $R^1 = CH_2CH_3$, $R^2 = 5'\text{-}OCH_3$
bg $R^1 = CH_2CH_3$, $R^2 = 5'\text{-}CHO$
ca $R^1 = CH_2CH_2CH_3$, $R^2 = H$
cb $R^1 = CH_2CH_2CH_3$, $R^2 = 7'\text{-}CH_3$
cc $R^1 = CH_2CH_2CH_3$, $R^2 = 5'\text{-}CH_3$
cd $R^1 = CH_2CH_2CH_3$, $R^2 = 7'\text{-}OCH_3$
ce $R^1 = CH_2CH_2CH_3$, $R^2 = 6'\text{-}OCH_3$
cf $R^1 = CH_2CH_2CH_3$, $R^2 = 5'\text{-}OCH_3$
cg $R^1 = CH_2CH_2CH_3$, $R^2 = 5'\text{-}CHO$
da $R^1 = COOCH_3$, $R^2 = H$
db $R^1 = COOCH_3$, $R^2 = 7'\text{-}CH_3$
dc $R^1 = COOCH_3$, $R^2 = 5'\text{-}CH_3$
dd $R^1 = COOCH_3$, $R^2 = 7'\text{-}OCH_3$
de $R^1 = COOCH_3$, $R^2 = 6'\text{-}OCH_3$
df $R^1 = COOCH_3$, $R^2 = 5'\text{-}OCH_3$
dg $R^1 = COOCH_3$, $R^2 = 5'\text{-}CHO$

Bromination of 1-Acetylazulene (**1**).

A solution of 1-acetylazulene (**1**) (340 mg, 2.0 mmoles) and $PTMABr_3$ (900 mg, 2.4 mmoles) in chloroform (65 ml) was refluxed for 3 hours. After removal of the solvent, the residue was chromatographed on a silica gel column [Merck's Kieselgel 60 (50 g)] with chloroform as eluent to give 1-acetyl-3-bromoazulene (**3**) (80 mg, 16%) and 3-bromo-1-(bromoacetyl)azulene (**4**) (190 mg, 28%).

1-Acetyl-3-bromoazulene (**3**).

This compound was obtained as bluish violet needles (from ethanol); mp 83-84 °C (lit. [9], 99-100 °C); ^{1}H nmr (deuteriochloroform): δ 2.55 (3H, s, $COCH_3$), 7.38 (1H, dd, *J* = 9.6, 9.6 Hz, 7-H), 7.45 (1H, dd, *J* = 9.9, 9.9 Hz, 5-H), 7.69 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.06 (1H, s, 2-H), 8.30 (1H, d, *J* = 9.9 Hz, 4-H), 9.65 (1H, d, *J* = 9.6 Hz, 8-H).

3-Bromo-1-(bromoacetyl)azulene (**4**).

This compound was obtained as reddish violet needles (from ethanol); mp 117-118 °C; ir (potassium bromide): ν 1623 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 4.35 (2H, s, CH_2Br), 7.41 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.46 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.71 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.06 (1H, s, 2-H), 8.25 (1H, d, *J* = 9.6 Hz, 4-H), 9.55 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 33.0 (CH_2Br), 105.2 (=C<), 120.3 (=C<), 128.8 (=CH-), 130.8 (=CH-), 138.0 (=CH-), 140.1 (=CH-), 140.6 (=CH-), 140.7 (=C<), 141.1 (=C<), 141.2 (=CH-), 187.1 (C=O); ms: *m/z* (%) 330/328/326 (M^+, 17/31/15), 233 (100), 126 (67), 63 (22).

Anal. Calcd. for $C_{12}H_8Br_2O$: M, 325.8941; C, 43.94; H, 2.46. Found: M^+, 325.9000; C, 43.69; H, 2.75.

Bromination of 3-Alkyl-Substituted 1-Acetylazulenes **2a-d**.

A Typical Procedure.

A solution of 1-acetyl-3-methylazulene (**2a**) (1.00 g, 5.4 mmoles) and $PTMABr_3$ (3.05 g, 8.1 mmoles) in chloroform (180 ml) was refluxed for 3 hours. After removal of the solvent, the residue was chromatographed on a silica gel column [Merck's Kieselgel 60 (70 g)] with chloroform as eluent to give 1-(bromoacetyl)-3-methylazulene (**5a**) (824 mg, 58%) and 1-(dibromoacetyl)-3-methylazulene (**6a**) (480 mg, 26%). The starting material **2a** (140 mg, 15%) was recovered.

Table 1

Reactions of 1-(Bromoacetyl)azulenes with Salicylaldehydes

Substrate	Reagent	Condition [a] Time h	Product **10**	Yield %	**11**	Yield %	Recovery **5**	Yield %
5a	**9a**	A		---	**11aa**	92		---
5a	**9a**	B 1.5		---	**11aa**	92		---
5a	**9b**	A		---	**11ab**	33		---
5a	**9b**	B 9		---	**11ab**	93		---
5a	**9c**	A	**10ac**	58	**11ac**	26		---
5a	**9c**	B 7		---	**11ac**	94		---
5a	**9d**	A	**10ad**	84		---		---
5a	**9d**	B 12		---	**11ad**	96		---
5a	**9e**	A		---	**11ae**	95		---
5a	**9e**	B 1.5		---	**11ae**	95		---
5a	**9f**	A		---	**11af**	95		---
5a	**9f**	B 1.5		---	**11af**	95		---
5a	**9g**	A		---	**11ag**	68		---
5a	**9g**	B 1.5		---	**11ag**	83		---
5b	**9a**	A		---	**11ba**	97		---
5b	**9a**	B 1.5		---	**11ba**	97		---
5b	**9b**	A	**10bb**	23		---		81
5b	**9b**	B 16		---	**11bb**	93		---
5b	**9c**	A	**10bc**	39		---		56
5b	**9c**	B 9		---	**11bc**	94		---
5b	**9d**	A	**10bd**	25		---		72
5b	**9d**	B 21		---	**11bd**	95		---
5b	**9e**	A	**10be**	33	**11be**	6		61
5b	**9e**	B 18		---	**11be**	93		---
5b	**9f**	A	**10bf**	17		---		79
5b	**9f**	B 20		---	**11bf**	90		---
5b	**9g**	A		---	**11bg**	83		---
5b	**9g**	B 1.5		---	**11bg**	83		---
5c	**9a**	A		---	**11ca**	77		---
5c	**9a**	B 1.5		---	**11ca**	77		---
5c	**9b**	A	**10cb**	74		---		---
5c	**9b**	B 12		---	**11cb**	93		---
5c	**9c**	A	**10cc**	41		---		59
5c	**9c**	B 14		---	**11cc**	91		---
5c	**9d**	A	**10cd**	82		---		---
5c	**9d**	B 6.5		---	**11cd**	98		---
5c	**9e**	A	**10ce**	62		---		---
5c	**9e**	B 9.5		---	**11ce**	99		---
5c	**9f**	A	**10cf**	35		---		59
5c	**9f**	B 17.5		---	**11cf**	98		---
5c	**9g**	A		---	**11cg**	62		---
5c	**9g**	B 1.5		---	**11cg**	62		---
5d	**9a**	A	**10da**	12	**11da**	13		58
5d	**9a**	B 3.5		---	**11da**	94		---
5d	**9b**	A	**10db**	30		---		67
5d	**9b**	B 4		---	**11db**	94		---
5d	**9c**	A	**10dc**	39		---		42
5d	**9c**	B 4		---	**11dc**	91		---
5d	**9d**	A	**10dd**	91		---		---
5d	**9d**	B 4.5		---	**11dd**	85		---
5d	**9e**	A		---	**11de**	88		---
5d	**9e**	B 1.5		---	**11de**	88		---
5d	**9f**	A		---	**11df**	73		---
5d	**9f**	B 1.5		---	**11df**	73		---
5d	**9g**	A	**10dg**	42		---		4.5
5d	**9g**	B 3.5		---	**11dg**	35		---

[a] Condition A: 0.5 hour at room temperature and 1.5 hours at refluxing; Condition B: Refluxing.

1-(Bromoacetyl)-3-methylazulene (**5a**).

This compound was obtained as deep violet needles (from ethanol); mp 95-96 °C; ir (potassium bromide): ν 1613 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.60 (3H, s, CH_3), 4.49 (2H, s, CH_2Br), 7.50 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.58 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.79 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.09 (1H, s, 2-H), 8.32 (1H, d, *J* = 9.6 Hz, 4-H), 9.75 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 12.6 (CH_3), 33.5 (CH_2Br), 119.7 (=C<), 126.3 (=C<), 127.2 (=CH-), 129.7 (=CH-), 135.7 (=CH-), 139.2 (=CH-), 139.8 (=CH-), 140.6 (=CH-), 142.1 (=C<), 142.9 (=C<), 187.6 (C=O); ms: *m/z* (%) 264/262 (M^+, 41/42), 170 (40), 169 (100), 155 (42), 139 (39), 115 (50).

Anal. Calcd. for $C_{13}H_{11}BrO$: M, 261.9993; C, 59.34; H, 4.21. Found: M^+, 261.9998; C, 59.57; H, 4.24.

1-(Dibromoacetyl)-3-methylazulene (**6a**).

This compound was obtained as deep violet needles (from ethanol); mp 144-145 °C; ir (potassium bromide): ν 1627 cm^{-1} (C=O); ^{1}H (deuteriochloroform): δ 2.60 (3H, s, CH_3), 6.89 (1H, s, $CHBr_2$), 7.47 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.54 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.78 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.14 (1H, s, 2-H), 8.27 (1H, d, *J* = 9.6 Hz, 4-H), 9.68 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 12.6 (CH_3), 43.0 ($CHBr_2$), 115.3 (=C<), 126.6 (=CH-), 128.1 (=CH-), 130.3 (=CH-), 135.7 (=C<), 139.3 (=CH-), 139.9 (=CH-), 140.0 (=CH-), 143.5 (=C<), 143.7 (=C<), 181.9 (C=O); ms: *m/z* (%) 344/342/340 (M^+, 6/13/7), 325 (9), 233 (10), 170 (19), 169 (100), 153 (18), 152 (13), 139 (15), 115 (18).

Anal. Calcd. for $C_{13}H_{10}Br_2O$: M, 339.9098. Found: M^+, 339.9127.

1-(Bromoacetyl)-3-ethylazulene (**5b**).

This compound was obtained from 1-acetyl-3-ethylazulene (**2b**) in the same manner in a yield of 52% as deep violet needles (from ethanol); mp 59-60 °C; ir (potassium bromide): ν 1619 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 1.28 (3H, t, *J* = 7.7 Hz, CH_2CH_3), 2.88 (2H, q, *J* = 7.7 Hz, CH_2CH_3), 4.41 (2H, s, CH_2Br), 7.33 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.41 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.64 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 7.80 (1H, s, 2-H), 8.25 (1H, d, *J* = 9.6 Hz, 4-H), 9.63 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 14.8 (CH_2CH_3), 20.0 (CH_2CH_3), 33.6 (CH_2Br), 119.6 (=C<), 127.2 (=CH-), 129.5 (=CH-), 132.8 (=C<), 135.1 (=CH-), 138.6 (=CH-), 139.1 (=CH-), 139.7 (=CH-), 141.9 (=C<), 142.0 (=C<), 187.4 (C=O); ms: *m/z* (%) 278/276 (M^+, 70/70), 183 (100), 139 (68), 115 (31), 84 (52).

Anal. Calcd. for $C_{14}H_{13}BrO$: M, 276.0149; C, 60.67; H, 4.73. Found: M^+, 276.0134; C, 61.01; H, 4.87.

1-(Dibromoacetyl)-3-ethylazulene (**6b**).

This compound was obtained from **2b** in a yield of 8% as deep violet needles (from ethanol); mp 117-118 °C; ir (potassium bromide): ν 1629 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 1.33 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 2.95 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 6.79 (1H, s, $CHBr_2$), 7.45 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.54 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.76 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.15 (1H, s, 2-H), 8.34 (1H, d, *J* = 9.6 Hz, 4-H), 9.72 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 14.9 (CH_2CH_3), 20.1 (CH_2CH_3), 43.0 ($CHBr_2$), 115.6 (=C<), 128.2 (=CH-), 130.3 (=CH-), 133.2 (=C<), 135.4 (=CH-), 138.2 (=CH-), 139.6 (=CH-), 140.1 (=CH-), 142.9 (=C<), 143.8 (=C<), 182.0 (C=O); ms: *m/z* (%) 356/354/352 (M^+, 26/51/26), 340 (26), 247 (24), 183 (100), 139 (43), 76 (32).

Anal. Calcd. for $C_{14}H_{12}Br_2O$: M, 353.9254; C, 47.23; H, 3.40. Found: M^+, 353.9277; C, 47.00; H, 3.53.

1-(Bromoacetyl)-3-propylazulene (**5c**).

This compound was obtained from 1-acetyl-3-propylazulene (**2c**) in the same manner in a yield of 56% as deep violet needles (from ethanol); mp 56-58 °C; ir (potassium bromide): ν 1620 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 0.99 (3H, t, *J* = 7.2 Hz, $CH_2CH_2CH_3$), 1.74 (2H, tq, *J* = 7.5, 7.2 Hz, $CH_2CH_2CH_3$), 2.92 (2H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 4.45 (2H, s, CH_2Br), 7.40 (1H, dd, *J* = 9.6, 9.6 Hz, 7-H), 7.48 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.72 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.08 (1H, s, 2-H), 8.34 (1H, d, *J* = 9.6 Hz, 4-H), 9.72 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 14.1 ($CH_2CH_2CH_3$), 23.9 ($CH_2CH_2CH_3$), 29.0 ($CH_2CH_2CH_3$), 33.5 (CH_2Br), 119.7 (=C<), 127.1 (=CH-), 129.5 (=CH-), 131.2 (=C<), 135.2 (=CH-), 139.0 (=CH-), 139.5 (=CH-), 139.6 (=CH-), 141.9 (=C<), 142.2 (=C<), 187.4 (C=O); ms: *m/z* (%) 292/290 (M^+, 26/26), 261 (38), 197 (100), 154 (18), 140 (20).

Anal. Calcd. for $C_{15}H_{15}BrO$: M, 290.0306; C, 61.87; H, 5.19. Found: M^+, 290.0326; C, 62.03; H, 5.17.

1-(Dibromoacetyl)-3-propylazulene (**6c**).

This compound was obtained from **2c** in a yield of 6% as deep violet needles (from ethanol); mp 106-107 °C; ir (potassium bromide): ν 1621 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 0.96 (3H, t, *J* = 7.2 Hz, $CH_2CH_2CH_3$), 1.73 (2H, tq, *J* = 7.5, 7.2 Hz, $CH_2CH_2CH_3$), 2.93 (2H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 7.18 (1H, s, $CHBr_2$), 7.42 (1H, dd, *J* = 9.6, 9.6 Hz, 7-H), 7.52 (1H, dd, *J* = 9.9, 9.9 Hz, 5-H), 7.74 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.08 (1H, s, 2-H), 8.36 (1H, d, *J* = 9.9 Hz, 4-H), 9.72 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 14.1 ($CH_2CH_2CH_3$), 23.9 ($CH_2CH_2CH_3$), 29.0 ($CH_2CH_2CH_3$), 43.1 ($CHBr_2$), 115.5 (=C<), 128.1 (=CH-), 130,2 (=CH-), 131.6 (=C<), 135.4 (=CH-), 139.0 (=CH-), 139.4 (=CH-), 140.0 (=CH-), 143.2 (=C<), 143.6 (=C<), 181.9 (C=O).

Anal. Cacld. for $C_{15}H_{14}Br_2O$: C, 48.88; H, 3.81. Found: C, 49.10; H, 3.83.

Bromination of 1-Acetyl-3-methoxycarbonylazulene (**2d**).

a) In aprotic chloroform: To a solution of 1-acetyl-3-methoxycarbonylazulene (**2d**) (114 mg, 0.5 mmole) in chloroform (20 ml) was added $PTMABr_3$ (206 mg, 0.55 mmole). After stirring for 1 hour at 50 °C, cold water (20 ml) was poured into the reaction mixture. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic extract was washed with water and dried over sodium sulfate. The evaporation residue was chromatographed on silica gel column [Merck's Kieselgel 60 (20 g)] with benzene to give 1-(bromoacetyl)-3-methoxycarbonylazulene (**5d**) (123 mg, 80%) and 1-(dibromoacetyl)-3-methoxycarbonylazulene (**6d**) (19 mg, 10%).

b) In protic methanol: A solution of 1-acetyl-3-methoxycarbonylazulene (**2d**) (114 mg, 0.5 mmole) in methanol (20 ml) was stirred for 1 hour at room temperature in the presence of $PTMABr_3$ (282 mg, 0.75 mmole). The reaction mixture was diluted with water and worked up, as described above, to afford 1-bromo-3-methoxycarbonylazulene (**7**) (99 mg, 80%).

1-(Bromoacetyl)-3-methoxycarbonylazulene (**5d**).

This compound was obtained as red needles (from ethanol); mp 125-126 °C; ir (potassium bromide): ν 1692 (C=O), 1647 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.97 (3H, s, $COOCH_3$), 4.54 (2H, s, CH_2Br), 7.80 (1H, dd, *J* = 9.9, 9.9 Hz, 7-H), 7.83 (1H, dd, *J* = 9.9, 9.9 Hz, 5-H), 8.02 (1H, dd, *J* = 9.9, 9.9 Hz, 6-H), 8.76 (1H, s, 2-H), 9.77 (1H, d, *J* = 9.9 Hz, 8-H), 9.93 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 33.1 (CH_2Br), 51.4 ($COOCH_3$), 116.4 (=C<), 120.2 (=C<), 132.0 (=CH-), 132.8 (=CH-), 139.7 (=CH-), 141.0 (=CH-), 141.7 (=CH-), 143.3 (=CH-), 144.5 (=C<), 144.8 (=C<), 164.9 ($COOCH_3$), 188.1 ($COCH_2Br$).

Anal. Calcd. for $C_{14}H_{11}BrO_3$: C, 54.74; H, 3.61. Found: C, 54.82; H, 3.76.

1-(Dibromoacetyl)-3-methoxycarbonylazulene (**6d**).

This compound **6d** was obtained as orange needles (from ethanol); mp 172-173 °C; ir (potassium bromide): ν 1697 (C=O), 1615 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.99 (3H, s, $COOCH_3$), 6.85 (1H, s, $CHBr_2$), 7.90 (1H, dd, *J* = 9.9, 9.9 Hz, 7-H), 7.92 (1H, dd, *J* = 9.9, 9.9 Hz, 5-H), 8.09 (1H, dd, *J* = 9.9, 9.9 Hz, 6-H), 8.92 (1H, s, 2-H), 9.86 (1H, d, *J* = 9.9 Hz, 8-H), 10.10 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 42.0 ($CHBr_2$), 51.5 ($COOCH_3$), 116.1 (=C<), 116.8 (=C<), 132.7 (=CH-), 133.3 (=CH-), 139.9 (=CH-), 141.1 (=CH-), 141.4 (=CH-), 143.1 (=CH-), 145.5 (=C<), 145.9 (=C<), 164.9 ($COOCH_3$), 182.9 ($COCHBr_2$).

Anal. Calcd. for $C_{14}H_{10}Br_2O_3$: C, 43.56; H, 2.61. Found: C, 43.72; H, 2.69.

1-Bromo-3-methoxycarbonylazulene (**7**).

This compound **7** was obtained as blue needles (from benzene); mp 88-89 °C (lit. [11], 87-88 °C); ir (potassium bromide): ν 1645 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.93 (3H, s, $COOCH_3$), 7.43 (1H, dd, *J* = 9.9, 9.9 Hz, 5-H), 7.50 (1H, dd, *J* = 9.9, 9.9 Hz, 7-H), 7.78 (1H, dd, *J* = 9.9, 9.9 Hz, 6-H), 8.27 (1H, s, 2-H), 8.41 (1H, d, *J* = 9.9 Hz, 8-H), 9.54 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.2 ($COOCH_3$), 104.3 (=C<), 115.7 (=C<), 127.1 (=CH-), 128.2 (=CH-), 137.4 (=CH-), 138.1 (=CH-), 139.8 (=C<), 140.1 (=C<), 140.7 (=CH-), 142.1 (=CH-), 164.7 (C=O).

Preparation of 1-(Bromoacetyl)azulene (**8**).

A mixture of 1-(bromoacetyl)-3-methoxycarbonylazulene (**5d**) (120 mg, 0.39 mmole) and 100% phosphoric acid (15 ml) was heated at 95-98 °C in an oil bath. The reaction mixture was triturated with water (6.5 ml) and extracted with benzene. The extract was dried over. The evaporation residue was purified by a preparative thin layer chromatography on Wakogel B-10 plate (20 x 20 cm) with chloroform to afford 1-(bromoacetyl)azulene (**8**).

1-(Bromoacetyl)azulene (**8**).

This compound was obtained as bluish violet crystals (from ethanol) in a yield of 64 mg (67%), mp 86-87 °C; ^1H nmr (deuteriochloroform): δ 4.45 (2H, s, CH_2Br), 7.20 (1H, d, *J* = 4.3 Hz, 3-H), 7.46 (1H, dd, *J* = 9.6, 9.6 Hz, 5-H), 7.57 (1H, dd, *J* = 9.9, 9.9 Hz, 7-H), 7.78 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.21 (1H, d, *J* = 4.3 Hz, 2-H), 8.40 (1H, d, *J* = 9.6 Hz, 4-H), 9.77 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 33.4 (CH_2Br), 118.3 (=CH-), 121.5 (=C<), 128.4 (=CH-), 130.2 (=CH-), 138.8 (=CH-), 139.8 (=CH-), 140.0 (=CH-), 140.1 (=CH-), 141.6 (=C<), 145.9 (=C<), 188.0 (C=O); ms: *m/z* (%) 250/248 (M^+, 37/37), 155 (100), 141 (30), 127 (53), 77 (21), 40 (32).

Anal. Calcd. for $C_{12}H_9BrO$: M, 247.9836; C, 57.86; H, 3.64. Found: M^+, 247.9868; C, 57.76; H, 3.65.

Reactions of 1-(Bromoacetyl)-3-methylazulene (**5a**) with Salicylaldehydes **9a-g**.

General Procedure.

a) A solution of 1-(bromoacetyl)-3-methylazulene (**5a**) (50 mg, 0.19 mmole) and salicylaldehyde **9a-g** (0.19 mmole) in acetonitrile (5 ml) was stirred for 30 minutes at room temperature in the presence of potassium carbonate (26 mg, 0.19 mmole) followed by refluxing for 1.5 hours. The reaction mixture was diluted with water (5 ml) and extracted with chloroform. The extract was dried over sodium sulfate. The evaporation residue was chromatographed on a preparative silica gel plate (Wakogel B-10, 20 x 20 cm) with chloroform to give 1-[(2-formylphenoxy)acetyl]-3-methylazulenes **10ac**,**ad** and 1-(2-benzofurancarbonyl)-3-methylazulenes **11aa-ac**,**ae-ag**. The yields are summarized in Table 1.

b) The same reaction using **5a** (50 mg, 0.19 mmole) was carried out under refluxing for the appropriate reaction time (see Table 1) and worked up, as described above, to give the products **11aa-ag**. The yields are summarized in Table 1.

1-(2-Benzofurancarbonyl)-3-methylazulene (**11aa**).

This compound was obtained by using salicylaldehyde (**9a**) as brown oil; ir (chloroform): ν 1604 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.54 (3H, s, CH_3), 7.22-7.47 (5H, m, 5-,5'-,6-, 6'-,7-H), 7.59-7.67 (3H, m, 3'-,4'-,7'-H), 8.19 (1H, d, *J* = 9.6 Hz, 4-H), 8.39 (1H, s, 2-H), 9.67 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 12.6 (CH_3), 112.0 (=CH-), 113.2 (=CH-), 121.9 (=C<), 122.6 (=CH-), 123.3 (=CH-), 126.0 (=C<), 126.5 (=C<), 126.9 (=CH-), 127.2 (=CH-), 128.7 (=CH-), 135.1 (=CH-), 138.2 (=CH-), 139.2 (=CH-), 141.5 (=CH-), 142.1 (=C<), 142.2 (=C<), 154.8 (=C<), 155.2 (=C<), 178.7 (C=O); ms: *m/z* (%) 286 (M^+, 100), 271 (26), 251 (60), 169 (94), 141 (34), 129 (31), 115 (40).

Anal. Calcd. for $C_{20}H_{14}O_2$: M, 286.0994. Found: M^+, 286.1062.

3-Methyl-1-(7-methylbenzofuran-2-carbonyl)azulene (**11ab**).

This compound was obtained by using 2-hydroxy-3-methylbenzaldehyde (**9b**) as brown crystals (from benzene); mp 117-118 °C; ir (potassium bromide): ν 1602 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.66 (3H, s, 3-CH_3), 2.67 (3H, s, 7'-CH_3), 7.19-7.27 (2H, m, 5'-,6'-H), 7.41-7.56 (4H, m, 3'-,4'-,5-,7-H), 7.78 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.37 (1H, d, *J* = 9.6 Hz, 4-H), 8.56 (1H, s, 2-H), 9.77 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 12.7 (3-CH_3), 15.2 (7'-CH_3), 113.7 (=CH-), 120.2 (=CH-), 122.3 (=C<), 122.4 (=C<), 123.6 (=CH-), 126.2 (=C<), 126.6 (=CH-), 126.9 (=C<), 127.8 (=CH-), 128.9 (=CH-), 135.4 (=CH-), 138.5 (=CH-), 139.4 (=CH-), 141.8 (=CH-), 142.3 (=C<), 142.6 (=C<), 154.7 (=C<), 154.9 (=C<), 179.1 (C=O); ms: *m/z* (%) 300 (M^+, 100), 285 (35), 271 (22), 169 (95), 115 (47).

Anal. Calcd. for $C_{21}H_{16}O_2$: M, 300.1150; C, 83.98; H, 5.37. Found: M^+, 300.1179; C, 83.91; H, 5.34.

1-[(2-Formyl-4-methylphenoxy)acetyl]-3-methylazulene (**10ac**).

This compound was obtained by using 2-hydroxy-3-methylbenzaldehyde (**9c**) as violet crystals (from benzene); mp 196-197 °C; ir (potassium bromide): ν 1676 (CHO), 1643 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.21 (3H, s, 3-CH_3), 2.56 (3H, s, 4'-CH_3), 5.34 (2H, s, CH_2), 6.80 (1H, d, *J* = 8.1 Hz, 6'-H), 7.20 (1H, dd, *J* = 8.1, 2.0 Hz, 5'-H), 7.43 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.49 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.59 (1H, d, *J* = 2.0 Hz, 3'-H), 7.75 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.11 (1H, s, 2-H), 8.33 (1H, d, *J* = 9.9 Hz, 4-H), 9.72 (1H, d, *J* = 9.6 Hz, 8-H) 10.54 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 12.6 (3-CH_3), 20.2 (4'-CH_3), 72.0 (CH_2), 100.5 (=C<), 112.9 (=CH-), 119.5 (=C<), 124.8 (=C<), 126.4 (=C<), 127.1 (=CH-), 128.5 (=CH-), 129.7 (=CH-), 130.7 (=C<), 135.8 (=CH-), 136.4 (=CH-), 139.0 (=CH-), 139.1 (=CH-), 139.8 (=CH-), 142.5 (=C<), 159.0 (=C<), 189.9 (C=O), 190.0 (CHO); ms: *m/z* (%) 318 (M^+, 29), 184 (21), 170 (20), 169 (100), 115 (24).

Anal. Calcd. for $C_{21}H_{18}O_3$: M, 318.1256; C, 79.22; H, 5.70. Found: M^+, 318.1346; C, 79.06; H, 5.67.

3-Methyl-1-(5-methylbenzofuran-2-carbonyl)azulene (**11ac**).

This compound was obtained by using **9c** as brown oil; ir (chloroform): ν 1603 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.41 (3H, s, 3-CH_3), 2.63 (3H, s, 5'-CH_3), 7.24 (1H, d, *J* = 6.9 Hz, 6'-H), 7.38-7.53 (5H, m, 3'-,4'-,5-,7-,7'-H), 7.74 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.35 (1H, d, *J* = 9.6 Hz, 4-H), 8.47 (1H, s, 2-H), 9.66 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 12.6 (3-CH_3), 21.2 (5'-CH_3), 111.7 (=CH-), 113.2 (=CH-), 122.2 (=CH-), 122.3 (=C<), 126.1 (=C<), 126.5 (=CH-), 127.4 (=C<), 128.6 (=CH-), 128.8 (=CH-), 133.0 (=C<), 135.3 (=CH-), 138.4 (=CH-), 139.3 (=CH-), 141.6 (=CH-), 142.2 (=C<), 142.4 (=C<), 153.9 (=C<), 155.1 (=C<), 179.0 (C=O); ms: *m/z* (%) 300 (100), 285 (27), 271 (18), 169 (63), 141 (23), 136 (22), 115 (29).

Anal. Calcd. for $C_{21}H_{16}O_2$: M, 300.1150. Found: M^+, 300.1179.

1-[(2-Formyl-6-methoxyphenoxy)acetyl]-3-methylazulene (**10ad**).

This compound was obtained by using 2-hydroxy-3-methoxybenzaldehyde (**9d**) as violet crystals (from benzene); mp 151-152 °C; ir (potassium bromide): ν 1692 (CHO), 1657 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.57 (3H, s, CH_3), 3.84 (3H, s, OCH_3), 5.49 (2H, s, CH_2), 7.05-7.13 (2H, m, 4'-,5'-H), 7.37-7.51 (3H, m, 3'-,5-,7-H), 7.74 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.04 (1H, s, 2-H), 8.31 (1H, d, *J* = 9.9 Hz, 4-H), 9.73 (1H, d, *J* = 9.9 Hz, 8-H), 10.71 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 12.5 (CH_3), 56.1 (OCH_3), 75.8 (CH_2), 117.9 (=CH-), 119.1 (=CH-), 119.6 (=C<), 123.8 (=CH-), 126.0 (=C<), 126.6 (=CH-), 129.2 (=CH-), 129.8 (=C<), 135.5 (=CH-), 138.8 (=CH-), 138.9 (=CH-), 139.6 (=CH-), 141.2 (=C<), 142.0 (=C<), 151.0 (=C<), 152.1 (=C<), 190.6 (CHO), 190.9 (C=O); ms: *m/z* (%) 334 (M^+, 23), 184 (22), 169 (100), 115 (15).

Anal. Calcd. for $C_{21}H_{18}O_4$: M, 334.1205; C, 75.43; H, 5.43. Found: M^+, 334.1187; C, 75.49; H, 5.53.

1-(7-Methoxybenzofuran-2-carbonyl)-3-methylazulene (**11ad**).

This compound was obtained by using **9d** as brown crystals (from benzene); mp 169-171 °C; ir (chloroform): ν 1615 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.69 (3H, s, CH_3), 4.07 (3H, s, OCH_3), 6.94 (1H, d, *J* = 7.8 Hz, 6'-H), 7.23 (1H, dd, *J* = 7.8, 7.8 Hz, 5'-H), 7.31 (1H, d, *J* = 7.8 Hz, 4'-H), 7.47 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.56 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.57 (1H, s, 3'-H), 7.80 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.40 (1H, d, *J* = 9.9 Hz, 4-H), 8.62 (1H, s, 2-H), 9.77 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 12.8 (CH_3), 56.1 (OCH_3), 108.8 (=CH-), 113.3 (=CH-), 114.7 (=CH-), 117.9 (=C<), 122.2 (=C<), 124.4 (=CH-), 126.4 (=C<), 126.7 (=CH-), 129.1 (=CH-), 135.4

(=CH-), 138.6 (=CH-), 139.4 (=CH-), 142.1 (=CH-), 142.5 (=C<), 142.7 (=C<), 145.2 (=C<), 146.0 (=C<), 155.5 (=C<), 178.9 (C=O); ms: *m/z* (%) 316 (M^+, 100), 169 (23).

Anal. Calcd. for $C_{21}H_{16}O_3$: M, 316.1099; C, 79.73; H, 5.10. Found: M^+, 316.1089; C, 79.40; H, 5.12.

1-(6-Methoxybenzofuran-2-carbonyl)-3-methylazulene (**11ae**).

This compound was obtained by using **9e** as brown crystals (from benzene); mp 99-100 °C; ir (chloroform): ν 1620 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.56 (3H, s, CH_3), 3.76 (3H, s, OCH_3), 6.97 (1H, dd, *J* = 7.2, 2.5 Hz, 5'-H), 7.02 (1H, d, *J* = 2.5 Hz, 7'-H), 7.34 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.40 (1H, d, *J* = 7.2 Hz, 4'-H), 7.43 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.46 (1H, s, 3'-H), 7.67 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.26 (1H, d, *J* = 9.6 Hz, 4-H), 8.41 (1H, s, 2-H), 9.63 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 12.6 (CH_3), 55.8 (OCH_3), 103.8 (=CH-), 112.9 (=CH-), 113.4 (=CH-), 117.0 (=CH-), 122.2 (=C<), 126.2 (=C<), 126.6 (=CH-), 127.9 (=C<), 128.9 (=CH-), 135.4 (=CH-), 138.5 (=CH-), 139.4 (=CH-), 141.8 (=CH-), 142.4 (=C<), 142.5 (=C<), 150.6 (=C<), 155.8 (=C<), 156.4 (=C<), 178.9 (C=O); ms: *m/z* (%) 316 (M^+, 100), 169 (30), 115 (10).

Anal. Calcd. for $C_{21}H_{16}O_3$: M, 316.1099; C, 79.73; H, 5.10. Found: M^+, 316.1076; C, 79.65; H, 5.09.

1-(5-Methoxybenzofuran-2-carbonyl)-3-methylazulene (**11af**).

This compound was obtained by using **9f** as brown crystals (from benzene); mp 120-122 °C; ir (chloroform): ν 1619 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.56 (3H, s, CH_3), 3.78 (3H, s, OCH_3), 6.84 (1H, dd, *J* = 8.6, 2.1 Hz, 6'-H), 7.03 (1H, d, *J* = 2.1 Hz, 4'-H), 7.31 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.38 (1H, d, *J* = 8.6 Hz, 7'-H), 7.41 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.47 (1H, s, 3'-H), 7.65 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.25 (1H, d, *J* = 9.6 Hz, 4-H), 8.37 (1H, s, 2-H), 9.59 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 12.6 (CH_3), 55.6 (OCH_3), 95.7 (=CH-), 113.7 (=CH-), 114.0 (=CH-), 120.7 (=C<), 122.5 (=C<), 123.1 (=CH-), 126.0 (=C<), 126.3 (=CH-), 128.6 (=CH-), 135.3 (=CH-), 138.4 (=CH-), 139.3 (=CH-), 141.5 (=CH-), 142.1 (=C<), 142.2 (=C<), 154.6 (=C<), 156.9 (=C<), 160.3 (=C<), 178.8 (C=O); ms: *m/z* (%) 316 (M^+, 100), 169 (20).

Anal. Calcd. for $C_{21}H_{16}O_3$: M, 316.1099; C, 79.73; H, 5.10. Found: M^+, 316.1111; C, 79.45; H, 5.10.

1-(5-Formylbenzofuran-2-carbonyl)-3-methylazulene (**11ag**).

This compound was obtained by using **9g** as brown crystals (from benzene); mp 144-145 °C; ir (potassium bromide): ν 1694 (CHO), 1604 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.58 (3H, s, CH_3), 7.40 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.49 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.52 (1H, s, 3'-H), 7.67 (1H, d, *J* = 8.6 Hz, 7'-H), 7.73 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 7.91 (1H, dd, *J* = 8.6, 1.8 Hz, 6'-H), 8.15 (1H, d, *J* = 1.8 Hz, 4'-H), 8.30 (1H, d, *J* = 9.6 Hz, 4-H), 8.40 (1H, s, 2-H), 9.66 (1H, d, *J* = 9.9 Hz, 8-H), 9.98 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 12.7 (CH_3), 113.0 (=CH-), 113.1 (=CH-), 121.8 (=C<), 126.4 (=CH-), 126.5 (=C<), 127.2 (=CH-), 127.7 (=CH-), 127.8 (=C<), 129.5 (=CH-), 132.8 (=C<), 135.6 (=CH-), 138.7 (=CH-), 139.7 (=CH-), 141.6 (=CH-), 142.3 (=C<), 142.8 (=C<), 156.7 (=C<), 158.5 (=C<), 178.2 (C=O), 191.3 (CHO); ms: *m/z* (%) 314 (M^+, 100), 169 (96), 115 (49).

Anal. Calcd. for $C_{21}H_{14}O_3$: M, 314.0943; C, 80.24; H, 4.49. Found: M^+, 314.0934; C, 80.09; H, 4.50.

Reactions of 1-(Bromoacetyl)-3-ethylazulene (**5b**) with Salicylaldehydes **9a-g**.

General Procedure.

a) A solution of 1-(bromoacetyl)-3-ethylazulene (**5b**) (100 mg, 0.36 mmole) and salicylaldehyde **9a-g** (0.36 mmole) in acetonitrile (10 ml) was stirred for 30 minutes at room temperature in the presence of potassium carbonate (50 mg, 0.36 mmole) followed by refluxing for 1.5 hours. The reaction mixture was worked up, as described above, and chromatographed on a preparative silica gel plate (30 x 30 cm) to give 3-ethyl-1-[(2-formylphenoxy)acetyl]azulenes **10bb-bf** and 1-(2-benzofurancarbonyl)-3-ethylazulenes **11ba**,**be**,**bg**. The compound **5b** was recovered from the reaction with **9b-f**. The yields are summarized in Table 1.

b) The same reaction using **5b** (100 mg, 0.36 mmole) was carried out under refluxing and worked up, as described above, to give the products **11ba-bg**. The yields are also summarized in Table 1.

1-(2-Benzofurancarbonyl)-3-ethylazulene (**11ba**).

This compound was obtained by using **9a** as brown oil; ir (chloroform): ν 1604 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 1.40 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 3.04 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 7.24-7.52 (5H, m, 5-,5'-,6'-,7-,7'-H), 7.63-7.75 (3H, m, 3'-,4'-,6-H), 8.37 (1H, d, *J* = 9.9 Hz, 4-H), 8.52 (1H, s, 2-H), 9.72 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 15.0 (CH_2CH_3), 20.1 (CH_2CH_3), 112.2 (=CH-), 113.3 (=CH-), 122.4 (=C<), 122.7 (=CH-), 123.5 (=CH-), 126.7 (=CH-), 127.1 (=CH-), 127.3 (=C<), 128.9 (=CH-), 132.9 (=C<), 135.0 (=CH-), 138.5 (=CH-), 139.4 (=CH-), 140.0 (=CH-), 141.5 (=C<), 142.5 (=C<), 155.0 (=C<), 155.4 (=C<), 179.1 (C=O); ms: *m/z* (%) 300 (M^+, 84), 286 (90), 285 (100), 169 (33), 83 (63).

Anal. Calcd. for $C_{21}H_{16}O_2$: M, 300.1150. Found: M^+, 300.1163.

3-Ethyl-1-[(2-formyl-6-methylphenoxy)acetyl]azulene (**10bb**).

This compound was obtained by using **9b** as violet crystals (from benzene); mp 157-158 °C; ir (potassium bromide): ν 1681 (CHO), 1649 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 1.38 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 2.43 (3H, s, CH_3), 3.02 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 5.32 (2H, s, CH_2), 7.17 (1H, dd, *J* = 7.5, 7.5 Hz, 4'-H), 7.47 (1H, d, *J* = 7.5 Hz, 5'-H), 7.49 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.60 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.72 (1H, d, *J* = 7.5 Hz, 3'-H), 7.83 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.06 (1H, s, 2-H), 8.44 (1H, d, *J* = 9.9 Hz, 4-H), 8.87 (1H, d, *J* = 9.6 Hz, 8-H), 10.52 (CHO); ^{13}C nmr (deuteriochloroform): δ 15.0 (CH_2CH_3), 16.0 (CH_3), 20.1 (CH_2CH_3), 77.8 (CH_2), 119.6 (=C<), 124.6 (=CH-), 126.7 (=CH-), 127.0 (=CH-), 129.4 (=C<), 129.6 (=CH-), 132.2 (=C<), 132.9 (=C<), 135.3 (=CH-), 137.0 (=CH-), 137.6 (=CH-), 139.2 (=CH-), 139.9 (=CH-), 141.5 (=C<), 141.6 (=C<), 160.4 (=C<), 189.3 (C=O), 190.7 (CHO); ms: *m/z* (%) 332 (M^+, 26), 198 (26), 183 (100).

Anal. Calcd. for $C_{22}H_{20}O_3$: M, 332.1412. Found: M^+, 332.1436.

3-Ethyl-1-(7-methylbenzofuran-2-carbonyl)azulene (**11bb**).

This compound was obtained by using **9b** as brown crystals (from benzene); mp 104-105 °C; ir (potassium bromide): ν 1594 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 1.47 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 2.66 (3H, s, 7'-CH_3), 3.12 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 7.20-7.28 (2H, m, 5'-,6'-H), 7.48 (1H, dd, *J* = 9.9, 9.6

Hz, 5-H), 7.56-7.61 (3H, m, 3'-,4'-,7-H), 7.82 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.47 (1H, d, *J* = 9.9 Hz, 4-H), 8.68 (1H, s, 2-H), 9.79 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 14.9 (CH_2CH_3), 15.2 (CH_3), 20.2 (CH_2CH_3), 113.6 (=CH-), 120.3 (=CH-), 122.5 (=C<), 122.6 (=C<), 123.6 (=CH-), 126.7 (=CH-), 126.9 (=C<), 127.9 (=CH-), 129.0 (=CH-), 132.9 (=C<), 135.0 (=CH-), 138.8 (=CH-), 139.5 (=CH-), 140.3 (=CH-), 141.6 (=C<), 142.8 (=C<), 154.8 (=C<), 155.1 (=C<), 179.3 (C=O); ms: *m/z* (%) 314 (M^+, 100), 299 (99).

Anal. Calcd. for $C_{22}H_{18}O_2$: M, 314.1307; C, 84.05; H, 5.77. Found: M^+, 314.1276; C, 84.05; H, 5.91.

1-Ethyl-3-[(2-formyl-4-methylphenoxy)acetyl]azulene (**10bc**).

This compound was obtained also by using **9c** as violet crystals (from benzene); mp 158-159 °C; ir (potassium bromide): ν 1670 (CHO), 1651 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 1.33 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 2.20 (3H, s, CH_3), 2.97 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 5.35 (s, CH_2), 6.80 (1H, d, *J* = 8.4 Hz, 6'-H), 7.19 (1H, d, *J* = 8.4 Hz, 5'-H), 7.41 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.48 (1H, dd, *J* = 9.9, 9.9 Hz, 7-H), 7.57 (1H, s, 3'-H), 7.73 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.14 (1H, s, 2H), 8.36 (1H, d, *J* = 9.9 Hz, 4-H), 9.72 (1H, d, *J* = 9.9 Hz, 8-H), 10.54 (1H, s, CHO); ^{13}C nmr (deuteriochloroforom): δ 15.0 (CH_2CH_3), 20.1 (CH_2CH_3), 20.2 (4'-CH_3), 72.0 (CH_2), 112.9 (=CH-), 119.6 (=C<), 124.7 (=C<), 127.2 (=CH-), 128.5 (=CH-), 129.7 (=CH-), 130.6 (=C<), 133.1 (=C<), 135.4 (=CH-), 136.4 (=CH-), 137.3 (=CH-), 138.5 (=C<), 139.1 (=CH-), 139.9 (=CH-), 141,6 (=C<), 141.8 (=C<), 159.0 (C=O), 190.0 (CHO); ms: *m/z* (%) 332 (M^+, 33), 198 (16), 183 (100).

Anal. Calcd. for $C_{22}H_{20}O_3$: M, 332.1412; C, 79.50; H, 6.06. Found: M^+, 332.1422; C, 79.33; H, 6.10.

3-Ethyl-1-(5-methylbenzofuran-2-carbonyl)azulene (**11bc**).

This compound was obtained by using **9c** as brown crystals (from benzene); mp 53-54 °C; ir (potassium bromide): ν 1592 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 1.44 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 2.47 (3H, s, CH_3), 3.10 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 7.26 (1H, d, *J* = 8.4 Hz, 6'-H), 7.42-7.58 (5H, m, 3'-,4'-,5-,7-,7'-H), 7.79 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.44 (1H, d, *J* = 9.6 Hz, 4-H), 8.56 (1H, s, 2-H), 9.73 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 15.2 (CH_2CH_3), 20.2 (CH_2CH_3), 21.3 (CH_3), 111.8 (=CH-), 113.3 (=CH-), 122.4 (=C<), 122.6 (=CH-), 126.6 (=CH-), 127.5 (=C<), 128.7 (=CH-), 128.9 (=CH-), 132.9 (=C<), 133.1 (=C<), 135.1 (=CH-), 138.7 (=CH-), 139.5 (=CH-), 140.1 (=CH-), 141.5 (=C<), 142.6 (=C<), 154.0 (=C<), 155.2 (=C<), 179.3 (C=O); ms: *m/z* (%) 314 (M^+, 100), 299 (85), 149 (67).

Anal. Calcd. for $C_{22}H_{18}O_2$: M, 314.1307; C, 84.05; H, 5.77. Found: M^+, 314.1355; C, 83.76; H, 5.93.

3-Ethyl-1-[(2-formyl-6-methoxyphenoxy)acetyl]azulene (**10bd**).

This compound was obtained by using **9d** as violet crystals (from benzene); mp 104-105 °C; ir (potassium bromide): ν 1686 (CHO), 1658 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 1.39 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 3.03 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 3.89 (3H, s, OCH_3), 5.54 (2H, s, CH_2), 7.09-7.16 (2H, m, 4'-,5'-H), 7.42-7.48 (2H, m, 3'-,5-H), 7.54 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.79 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.13 (1H, s, 2-H), 8.42 (1H, d, *J* = 9.6 Hz, 4-H), 9.79 (1H, d, *J* = 9.6 Hz, 8-H), 10.71 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 15.0 (CH_2CH_3), 20.1 (CH_2CH_3), 56.1 (OCH_3), 75.9 (CH_2), 118.0 (=CH-), 119.2 (=CH-), 119.9 (=C<), 123.9 (=CH-), 126.7 (=CH-), 129.3 (=CH-), 129.9 (=C<), 132.7 (=C<), 135.2 (=CH-), 137.2 (=CH-), 139.0 (=CH-), 139.7 (=CH-), 141.3 (=C<), 141.4 (=C<), 151.1 (=C<), 152.2 (=C<), 190.7 (C=O), 190.9 (CHO); ms: *m/z* (%) 348 (M^+, 30), 198 (26), 183 (100).

Anal. Calcd. for $C_{22}H_{20}O_4$: M, 348.1362; C, 75.84; H, 5.79. Found: M^+, 348.1370; C, 75.69; H, 5.93.

3-Ethyl-1-(7-methoxybenzofuran-2-carbonyl)azulene (**11bd**).

This compound was obtained by using **9d** as brown crystals (from benzene); mp 115-116 °C; ir (potassium bromide): ν 1594 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 1.33 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 2.99 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 3.96 (3H, s, OCH_3), 6.82 (1H, d, *J* = 7.5 Hz, 6'-H), 7.09-7.22 (2H, m, 4'-,5'-H), 7.33 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.40-7.68 (2H, m, 3'-,7-H), 7.66 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.31 (1H, d, *J* = 9.9 Hz, 4-H), 8.55 (1H, s, 2-H), 9.57 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 15.0 (CH_2CH_3), 20.1 (CH_2CH_3), 56.2 (6'-OCH_3), 108.9 (=CH-), 113.2 (=CH-), 114.7 (=CH-), 122.3 (=C<), 124.2 (=CH-), 126.7 (=CH-), 128.9 (=C<), 129.0 (=CH-), 133.0 (=C<), 134.9 (=CH-), 138.6 (=CH-), 139.4 (=CH-), 140.4 (=CH-), 141.6 (=C<), 142.8 (=C<), 154.1 (=C<), 146.0 (=C<), 155.4 (=C<), 178.9 (C=O); ms: *m/z* (%) 330 (M^+, 100), 315 (91), 300 (10), 215 (11), 158 (17).

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.99; H, 5.60.

3-Ethyl-1-[(2-formyl-5-methoxyphenoxy)acetyl]azulene (**10be**).

This compound was obtained by using **9e** as violet crystals (from benzene); mp 125-127 °C; ir (potassium bromide): ν 1669 (CHO), 1602 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 1.40 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 3.04 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 3.79 (3H, s, OCH_3), 5.40 (s, CH_2), 6.46 (1H, d, *J* = 2.1 Hz, 6'-H), 6.53 (1H, dd, *J* = 8.7, 2.1 Hz, 4'-H), 7.49 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.56 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.81 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 7.83 (1H, d, *J* = 8.7 Hz, 3'-H), 8.22 (1H, s, 2-H), 8.44 (1H, d, *J* = 9.9 Hz, 4-H), 9.80 (1H, d, *J* = 9.6 Hz, 8-H), 10.46 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 14.9 (CH_2CH_3), 20.1 (CH_2CH_3), 55.5 (OCH_3), 71.9 (CH_2), 99.2 (=CH-), 106.4 (=CH-), 119.2 (=C<), 119.6 (=C<), 127.2 (=CH-), 129.7 (=CH-), 130.5 (=CH-), 133.1 (=C<), 135.4 (=CH-), 137.3 (=CH-), 139.1 (=CH-), 139.9 (=CH-), 141.7 (=C<), 141.8 (=C<), 162.5 (=C<), 165.9 (=C<), 188.3 (CHO), 189.5 (C=O); ms: *m/z* (%) 348 (M^+, 32), 198 (25), 183 (100).

Anal. Calcd. for $C_{22}H_{20}O_4$: M, 348.1362; C, 75.84; H, 5.79. Found: M^+, 348.1324; C, 75.66; H, 5.92.

3-Ethyl-1-(6-methoxybenzofuran-2-carbonyl)azulene (**11be**).

This compound was obtained by using **9e** as brown crystals (from benzene); mp 69-70 °C; ir (potassium bromide): ν 1623 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 1.45 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 3.12 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 3.91 (3H, s, OCH_3), 6.96 (1H, dd, *J* = 8.6, 1.8 Hz, 5'-H), 7.15 (1H, d, *J* = 1.8 Hz, 7'-H), 7.43-7.61 (4H, m, 3'-,4'-,5-,7-H), 7.81 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.46 (1H, d, *J* = 9.9 Hz, 4-H), 8.53 (1H, s, 2-H), 9.71 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 15.2 (CH_2CH_3), 20.2 (CH_2CH_3), 55.7 (OCH_3), 95.7 (=CH-), 113.8 (=CH-), 114.2 (=CH-), 120.8 (=C<), 122.8 (=C<), 123.1 (=CH-), 126.4 (=CH-), 128.7 (=CH-), 132.8 (=C<), 135.0 (=CH-), 138.6 (=CH-), 139.5 (=CH-), 139.8 (=CH-), 141.3 (=C<), 142.4 (=C<), 154.6 (=C<), 157.0 (=C<), 160.3 (=C<),

179.0 (C=O); ms: *m/z* (%) 330 (M^+, 100), 315 (64), 183 (16).

Anal. Calcd. for $C_{22}H_{18}O_4$: M, 330.1256; C, 79.98; H, 5.49. Found: M^+, 330.1263; C, 79.74; H, 5.68.

1-Ethyl-3-[(2-formyl-4-methoxyphenoxy)acetyl]azulene (**10bf**).

This compound was obtained also by using **9f** as violet crystals (from benzene); mp 127-128 °C; ir (potassium bromide): ν 1682 (CHO), 1643 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 1.41 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 3.05 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 3.78 (3H, s, OCH_3), 5.42 (s, CH_2), 6.95 (1H, d, *J* = 9.0 Hz, 6'-H), 7.06 (1H, d, *J* = 9.0 Hz, 5'-H), 7.35 (1H, s, 3'-H), 7.50 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.57 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.82 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.20 (1H, s, 2-H), 8.45 (1H, d, *J* = 9.9 Hz, 4-H), 9.80 (1H, d, *J* = 9.6 Hz, 8-H), 10.62 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 15.0 (CH_2CH_3), 20.1 (CH_2CH_3), 55.8 (OCH_3), 72.6 (CH_2), 110.3 (=CH-), 114.9 (=CH-), 119.6 (=C<), 123.4 (=CH-), 125.4 (=C<), 127.2 (=CH-), 129.7 (=CH-), 133.1 (=C<), 135.4 (=CH-), 137.2 (=CH-), 139.1 (=CH-), 139.9 (=CH-), 141.6 (=C<), 141.8 (=C<), 153.9 (=C<), 155.7 (=C<), 189.6 (CHO), 190.1 (C=O); ms: *m/z* (%) 348 (M^+, 29), 198 (14), 183 (100), 44 (23).

Anal. Calcd. for $C_{22}H_{20}O_4$: M, 348.1362; C, 75.84; H, 5.79. Found: M^+, 348.1407; C, 75.58; H, 6.06.

3-Ethyl-1-(5-methoxybenzofuran-2-carbonyl)azulene (**11bf**).

This compound was obtained by using **9f** as violet crystals (from benzene); mp 98-99 °C; ir (potassium bromide): ν 1610 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 1.44 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 3.10 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 3.87 (3H, s, OCH_3), 7.06-7.14 (2H, m, 4'-,6'-H), 7.42-7.59 (4H, m, 3'-,5-,7-, 7'-H), 7.79 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.44 (1H, d, *J* = 9.9 Hz, 4-H), 8.56 (1H, s, 2-H), 9.74 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 15.2 (CH_2CH_3), 20.2 (CH_2CH_3), 55.8 (OCH_3), 103.8 (=CH-), 112.9 (=CH-), 113.5 (=CH-), 117.0 (=CH-), 122.5 (=C<), 126.7 (=CH-), 127.9 (=C<), 129.0 (=CH-), 132.9 (=C<), 135.1 (=CH-), 138.7 (=CH-), 139.5 (=CH-), 140.1 (=CH-), 141.5 (=C<), 142.6 (=C<), 150.7 (=C<), 155.8 (=C<), 156.4 (=C<), 179.1 (C=O); ms: *m/z* (%) 330 (M^+, 100), 315 (71), 183 (74), 152 (80).

Anal. Calcd. for $C_{22}H_{18}O_3$: M, 330.1256; C, 79.98; H, 5.49. Found: M^+, 330.1207; C, 80.03; H, 5.41.

3-Ethyl-1-(5-formylbenzofuran-2-carbonyl)azulene (**11bg**).

This compound was obtained by using **9g** as brown crystals (from benzene); mp 137-138 °C; ir (potassium bromide): ν 1694 (CHO), 1598 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 1.35 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 3.00 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 7.40 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.45 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.52 (1H, s, 3'-H), 7.67 (1H, d, *J* = 8.4 Hz, 7'-H), 7.73 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 7.91 (1H, d, *J* = 8.4 Hz, 6'-H), 8.16 (1H, s, 4'-H), 8.36 (1H, d, *J* = 9.9 Hz, 4-H), 8.44 (1H, s, 2-H), 9.67 (1H, d, *J* = 9.6 Hz, 8-H), 9.98 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 15.1 (CH_2CH_3), 20.2 (CH_2CH_3), 113.1 (=CH-), 113.2 (=CH-), 122.0 (=C<), 126.5 (=CH-), 127.3 (=CH-), 127.7 (=CH-), 127.9 (=C<), 129.5 (=CH-), 132.8 (=C<), 133.3 (=C<), 135.3 (=CH-), 138.9 (=CH-), 139.8 (=CH-), 140.0 (=CH-), 142.0 (=C<), 143.0 (=C<), 156.7 (=C<), 158.5 (=C<), 178.3 (C=O), 191.3 (CHO); ms: *m/z* (%) 328 (M^+, 56), 313 (54), 252 (15), 149 (31), 148 (19), 44 (100).

Anal. Calcd. for $C_{22}H_{16}O_3$: M, 328.1099; C, 80.47; H, 4.91. Found: M^+, 328.1104; C, 80.36; H, 4.88.

Reactions of 1-(Bromoacetyl)-3-propylazulene (**5c**) with Salicylaldehydes **9a-g**.

General Procedure.

A solution of 1-(bromoacetyl)-3-propylazulene (**5c**) (100 mg, 0.34 mmole) and salicylaldehyde **9a-g** (0.34 mmole) in acetonitrile (10 ml) was stirred for 30 minutes at room temperature in the presence of potassium carbonate (47 mg, 0.34 mmole) followed by refluxing for 1.5 hours. The reaction mixture was worked up, as described above, to give 1-[(2-formylphenoxy)acetyl]-3-propylazulenes **10cb-cf** and 1-(2-benzofurancarbonyl)-3-propylazulenes **11ca**,**cg**. The compound **5c** was recovered from the reaction with **9c**,**f**. The yields are summarized in Table 1.

b) The same reaction using **5c** (100 mg, 0.34 mmol) was carried out under refluxing and worked up, as described above, to give the products **11ca-cg**. The yields are also summarized in Table 1.

1-(2-Benzofurancarbonyl)-3-propylazulene (**11ca**).

This compound was obtained by using **9a** as brown oil; ir (chloroform): ν 1604 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 0.93 (3H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 1.71 (2H, tq, *J* = 7.5, 7.2 Hz, $CH_2CH_2CH_3$), 2.92 (2H, t, *J* = 7.2 Hz, $CH_2CH_2CH_3$), 7.14-7.68 (8H, m, 3'-,4'-,5-,5'-,6-,6'-,7-,7'-H), 8.31 (1H, d, *J* = 9.9 Hz, 4-H), 8.42 (1H, s, 2-H), 9.62 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 14.1 ($CH_2CH_2CH_3$), 24.1 ($CH_2CH_2CH_3$), 29.1 ($CH_2CH_2CH_3$), 112.3 (=CH-), 113.4 (=CH-), 122.5 (=C<), 122.8 (=CH-), 123.5 (=CH-), 126.6 (=CH-), 127.1 (=CH-), 127.4 (=C<), 128.9 (=CH-), 131.3 (=C<), 135.1 (=CH-), 138.5 (=CH-), 139.4 (=CH-), 140.9 (=CH-), 141.9 (=C<), 142.5 (=C<), 155.0 (=C<), 155.5 (=C<), 179.2 (C=O); ms: *m/z* (%) 314 (M^+, 93), 286 (48), 285 (100), 255 (22), 228 (23), 140 (20), 139 (39).

Anal. Calcd. for $C_{22}H_{18}O_2$: M, 314.1307. Found: M^+, 314.1382.

1-[(2-Formyl-6-methylphenoxy)acetyl]-3-propylazulene (**10cb**).

This compound was obtained by using **9b** as violet crystals (from benzene); mp 113-114 °C; ir (potassium bromide): ν 1683 (CHO), 1649 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 1.00 (3H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 1.77 (2H, tq, *J* = 7.5, 7.5 Hz, $CH_2CH_2CH_3$), 2.43 (3H, s, CH_3), 2.87 (2H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 5.32 (s, CH_2), 7.18 (1H, t, *J* = 7.6 Hz, 4'-H), 7.46-7.52 (2H, m, 5-,5'-H), 7.59 (1H, dd, *J* = 9.9, 9.9 Hz, 7-H), 7.73 (1H, dd, *J* = 7.6, 1.8 Hz, 3'-H), 7.83 (1H, dd, *J* = 9.9, 9.9 Hz, 6-H), 8.05 (1H, s, 2-H), 8.44 (1H, d, *J* = 9.9 Hz, 4-H), 9.87 (1H, d, *J* = 9.9 Hz, 8-H), 10.53 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 14.2 ($CH_2CH_2CH_3$), 16.0 (6'-CH_3), 24.1 ($CH_2CH_2CH_3$), 29.1 ($CH_2CH_2CH_3$), 77.8 (CH_2), 119.6 (=C<), 124.6 (=CH-), 126.7 (=CH-), 127.0 (=CH-), 129.4 (=CH-), 129.5 (=C<), 131.4 (=C<), 132.2 (=C<), 135.5 (=CH-), 137.6 (=CH-), 137.8 (=CH-), 139.1 (=CH-), 139.8 (=CH-), 141.6 (=C<), 141.9 (=C<), 160.4 (=C<), 189.4 (C=O), 190.7 (CHO); ms: *m/z* (%) 346 (M^+, 41), 212 (32), 198 (20), 197 (100), 183 (28), 140 (13), 44 (52).

Anal. Calcd. for $C_{23}H_{22}O_3$: M, 346.1569; C, 79.74; H, 6.40. Found: M^+, 346.1576; C, 79.72; H, 6.52.

1-(7-Methylbenzofuran-2-carbonyl)-3-propylazulene (**11cb**).

This compound was obtained by using **9b** as brown crystals (from benzene); mp 69-70 °C; ir (potassium bromide): ν 1591 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 0.95 (3H, t, *J* = 7.2

Hz, $CH_2CH_2CH_3$), 1.73 (2H, tq, *J* = 7.5, 7.2 Hz, $CH_2CH_2CH_3$), 2.53 (3H, s, CH_3), 2.92 (2H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 7.07-7.15 (2H, m, 5'-,6'-H), 7.31 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.39-7.45 (3H, m, 3'-,4'-,7-H), 7.65 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.31 (1H, d, *J* = 9.9 Hz, 4-H), 8.51 (1H, s, 2-H), 9.66 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 14.2 ($CH_2CH_2CH_3$), 15.1 (CH_3), 23.9 ($CH_2CH_2CH_3$), 29.1 ($CH_2CH_2CH_3$), 113.6 (=CH-), 120.2 (=CH-), 122.3 (=C<), 122.4 (=C<), 123.6 (=CH-), 126.6 (=CH-), 126.8 (=C<), 127.8 (=CH-), 128.9 (=CH-), 131.2 (=C<), 135.0 (=CH-), 138.5 (=CH-), 139.4 (=CH-), 141.0 (=CH-), 141.8 (=C<), 142.6 (=C<), 154.6 (=C<), 154.9 (=C<), 179.2 (C=O); ms: *m/z* (%) 328 (M^+, 93), 299 (100), 255 (11), 149 (16).

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.88; H, 5.96.

1-[(2-Formyl-4-methylphenoxy)acetyl]-3-propylazulene (**10cc**).

This compound was obtained by using **9c** as violet crystals (from benzene); mp 129-130 °C; ir (potassium bromide): ν 1676 (CHO), 1613 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 0.94 (3H, t, *J* = 7.2 Hz, $CH_2CH_2CH_3$), 1.71 (2H, tq, *J* = 7.5, 7.2 Hz, $CH_2CH_2CH_3$), 2.20 (3H, s, CH_3), 2.91 (2H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 5.34 (2H, s, CH_2), 6.79 (1H, d, *J* = 8.5 Hz, 6'-H), 7.19 (1H, dd, *J* = 8.5, 1.8 Hz, 5'-H), 7.42 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.47 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.57 (1H, d, *J* = 1.8 Hz, 3'-H), 7.73 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.12 (1H, s, 2-H), 8.36 (1H, d, *J* = 9.6 Hz, 4-H), 9.72 (1H, d, *J* = 9.9 Hz, 8-H), 10.53 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 14.2 ($CH_2CH_2CH_3$), 20.2 (CH_3), 24.1 ($CH_2CH_2CH_3$), 29.1 ($CH_2CH_2CH_3$), 72.0 (CH_2), 112.9 (=CH-), 119.6 (=C<), 124.7 (=C<), 127.2 (=CH-), 128.4 (=CH-), 129.6 (=CH-), 130.6 (=C<), 131.5 (=C<), 135.5 (=CH-), 136.4 (=CH-), 138.1 (=CH-), 139.0 (=CH-), 139.9 (=CH-), 141.7 (=C<), 142.0 (=C<), 158.9 (=C<), 178.5 (C=O), 190.0 (CHO); ms: *m/z* (%) 346 (M^+, 53), 328 (27), 299 (61), 212 (28), 185 (69), 132 (50).

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 79.53; H, 6.41.

1-(5-Methylbenzofuran-2-carbonyl)-3-propylazulene (**11cc**).

This compound was obtained by the reaction with **9c** as a brown oil; ir (chloroform): ν 1603 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 0.91 (3H, t, *J* = 7.4 Hz, $CH_2CH_2CH_3$), 1.69 (2H, tq, *J* = 7.5, 7.4 Hz, $CH_2CH_2CH_3$), 2.32 (3H, s, CH_3), 2.89 (2H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 7.12 (1H, d, *J* = 7.4 Hz, 6'-H), 7.27 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.33-7.42 (4H, m, 3'-,4'-,7-,7'-H), 7.61 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.27 (1H, d, *J* = 9.9 Hz, 4-H), 8.39 (1H, s, 2-H), 9.59 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 14.1 ($CH_2CH_2CH_3$), 21.2 (CH_3), 24.1 ($CH_2CH_2CH_3$), 29.1 ($CH_2CH_2CH_3$), 111.7 (=CH-), 113.3 (=CH-), 122.3 (=CH-), 122.5 (=C<), 126.5 (=CH-), 127.4 (=C<), 128.6 (=CH-), 128.7 (=CH-), 131.2 (=C<), 133.0 (=CH-), 135.1 (=C<), 138.4 (=CH-), 139.4 (=CH-), 140.8 (=CH-), 141.7 (=C<), 142.4 (=C<), 153.9 (=C<), 155.1 (=C<), 179.2 (C=O); ms: *m/z* (%) 328 (M^+, 50), 300 (24), 299 (100).

Anal. Calcd. for $C_{23}H_{20}O_2$: M, 328.1463. Found: M^+, 328.1425.

1-[(2-Formyl-6-methoxyphenoxy)acetyl]-3-propylazulene (**10cd**).

This compound was obtained also by using **9d** as violet crystals (from benzene); mp 106-107 °C; ir (potassium bromide): ν 1675 (CHO), 1651 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 0.91 (3H, t, *J* = 7.2 Hz, $CH_2CH_2CH_3$), 1.68 (2H, tq, *J* = 7.5, 7.2 Hz, $CH_2CH_2CH_3$), 2.87 (2H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 3.78 (3H, s, OCH_3), 5.44 (2H, s, CH_2), 6.98-7.05 (2H, m, 4'-,5'-H), 7.31-7.45 (3H, m, 3'-,5-,7-H), 7.67 (1H, dd, *J* = 9.9,9.6 Hz, 6-H), 8.01 (1H, s, 2-H), 8.31 (1H, d, *J* = 9.9 Hz, 4-H), 9.68 (1H, d, *J* = 9.6 Hz, 8-H), 10.63 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 14.1 ($CH_2CH_2CH_3$), 24.1 ($CH_2CH_2CH_3$), 29.1 ($CH_2CH_2CH_3$), 56.1 (OCH_3), 75.8 (CH_2), 117.9 (=CH-), 119.1 (=CH-), 119.8 (=C<), 123.9 (=CH-), 126.7 (=CH-), 129.2 (=CH-), 129.8 (=C<), 131.2 (=C<), 135.2 (=CH-), 137.9 (=CH-), 138.9 (=CH-), 139.6 (=CH-), 141.3 (=C<), 141.6 (=C<), 151.0 (=C<), 152.1 (=C<), 190.7 (C=O), 190.9 (CHO); ms: *m/z* (%) 362 (M^+, 31), 212 (27), 197 (100), 183 (17), 44 (17).

Anal. Calcd. for $C_{23}H_{22}O_4$: M, 362.1518; C, 76.22; H, 6.12. Found: M^+, 362.1501; C, 75.91; H, 6.18.

1-(7-Methoxybenzofuran-2-carbonyl)-3-propylazulene (**11cd**).

This compound was obtained by using **9d** as brown oil; ir (chloroform): ν 1591 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 0.90 (3H, t, *J* = 7.4 Hz, $CH_2CH_2CH_3$), 1.68 (2H, tq, *J* = 7.5, 7.4 Hz, $CH_2CH_2CH_3$), 2.87 (2H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 3.90 (3H, s, OCH_3), 6.78 (1H, d, *J* = 7.8 Hz, 6'-H), 7.07 (1H, dd, *J* = 7.8, 7.5 Hz, 5'-H), 7.15 (1H, d, *J* = 7.5 Hz, 4'-H), 7.26 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.37 (1H, dd, *J* = 9.9, 9.9 Hz, 7-H), 7.41 (1H, s, 3'-H), 7.60 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.25 (1H, d, *J* = 9.9 Hz, 4-H), 8.48 (1H, s, 2-H), 9.62 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 14.2 ($CH_2CH_2CH_3$), 23.9 ($CH_2CH_2CH_3$), 29.1 ($CH_2CH_2CH_3$), 56.0 (OCH_3), 108.8 (=CH-), 113.2 (=CH-), 114.6 (=CH-), 122.2 (=C<), 124.1 (=CH-), 126.6 (=CH-), 128.8 (=CH-), 128.9 (=C<), 131.3 (=C<), 135.0 (=CH-), 138.4 (=CH-), 139.3 (=CH-), 141.0 (=CH-), 141.8 (=C<), 142.6 (=C<), 145.0 (=C<), 145.9 (=C<), 155.2 (=C<), 178.8 (C=O); ms: *m/z* (%) 344 (M^+, 47), 316 (23), 315 (100).

Anal. Calcd. for $C_{23}H_{20}O_3$: M, 344.1412. Found: M^+, 344.1431.

1-[(2-Formyl-5-methoxyphenoxy)acetyl]-3-propylazulene (**10ce**).

This compound was obtained by using **9e** as violet crystals (from benzene); mp 125-126 °C; ir (potassium bromide): ν 1682 (CHO), 1605 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 0.90 (3H, t, *J* = 7.2 Hz, $CH_2CH_2CH_3$), 1.69 (2H, tq, *J* = 7.5, 7.2 Hz, $CH_2CH_2CH_3$), 2.89 (2H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 3.69 (3H, s, OCH_3), 5.30 (2H, s, CH_2), 6.37 (1H, d, *J* = 2.1 Hz, 6'-H), 6.44 (1H, dd, *J* = 8.6, 2.1 Hz, 4'-H), 7.39 (1H, dd, *J* = 9.9, 9.9 Hz, 5-H), 7.45 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.67-7.75 (2H, m, 3'-,6-H), 8.11 (1H, s, 2-H), 8.34 (1H, d, *J* = 9.9 Hz, 4-H), 9.70 (1H, d, *J* = 9.6 Hz, 8-H), 10.37 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 14.1 ($CH_2CH_2CH_3$), 24.0 ($CH_2CH_2CH_3$), 29.1 ($CH_2CH_2CH_3$), 55.5 (OCH_3), 71.9 (CH_2), 99.1 (=CH-), 106.4 (=CH-), 119.2 (=C<), 119.6 (=C<), 127.2 (=CH-), 129.6 (=CH-), 130.4 (=CH-), 131.6 (=C<), 135.5 (=CH-), 138.2 (=CH-), 138.9 (=CH-), 139.8 (=CH-), 141.8 (=C<), 142.0 (=C<), 162.7 (=C<), 165.9 (=C<), 188.2 (C=O), 189.6 (CHO); ms: *m/z* (%) 362 (M^+, 26), 212 (28), 197 (100), 140 (13).

Anal. Calcd. for $C_{23}H_{22}O_4$: M, 362.1518; C, 76.22; .H, 6.12. Found: M^+, 362.1511; C, 76.45; H, 6.42.

1-(6-Methoxybenzofuran-2-carbonyl)-3-propylazulene (**11ce**).

This compound was obtained by using **9e** as brown oil; ir (chloroform): ν 1623 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform):

δ 0.90 (3H, t, *J* = 7.4 Hz, $CH_2CH_2CH_3$), 1.68 (2H, tq, *J* = 7.5, 7.4 Hz, $CH_2CH_2CH_3$), 2.88 (2H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 3.73 (3H, s, OCH_3), 6.80 (1H, d, *J* = 8.7 Hz, 5'-H), 6.99 (1H, s, 7'-H), 7.25 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.32-7.44 (3H, m, 3'-,4'-,7-H), 7.59 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.25 (1H, d, *J* = 9.6 Hz, 4-H), 8.35 (1H, s, 2-H), 9.56 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 14.1 ($CH_2CH_2CH_3$), 24.1 ($CH_2CH_2CH_3$), 29.0 ($CH_2CH_2CH_3$), 55.6 (OCH_3), 95.6 (=CH-), 113.6 (=CH-), 114.0 (=CH-), 120.6 (=C<), 122.5 (=C<), 123.0 (=CH-), 126.3 (=CH-), 128.4 (=CH-), 131.1 (=C<), 135.0 (=CH-), 138.3 (=CH-), 139.3 (=CH-), 140.4 (=CH-), 141.5 (=C<), 142.2 (=C<), 154.4 (=C<), 156.8 (=C<), 160.2 (=C<), 178.8 (C=O); ms: *m/z* (%) 344 (M^+, 44), 316 (24), 315 (100).

Anal. Calcd. for $C_{23}H_{20}O_3$: M, 344.1412. Found: M^+, 344.1428.

1-[(2-Formyl-4-methoxyphenoxy)acetyl]-3-propylazulene (**10cf**).

This compound was obtained also by using **9f** as violet crystals (from benzene); mp 132-134 °C; ir (potassium bromide): ν 1678 (CHO), 1659 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 0.90 (3H, t, *J* = 7.2 Hz, $CH_2CH_2CH_3$), 1.71 (2H, tq, *J* = 7.5, 7.2 Hz, $CH_2CH_2CH_3$), 2.91 (2H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 3.69 (3H, s, OCH_3), 5.33 (2H, s, CH_2), 6.86 (1H, d, *J* = 9.0 Hz, 6'-H), 6.97 (1H, dd, *J* = 9.0, 3.0 Hz, 5'-H), 7.26 (1H, d, *J* = 3.0 Hz, 3'-H), 7.40 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.48 (1H, dd, 9.9, 9.6 Hz, 7-H), 7.72 (1H, dd, J = 9.9, 9.6 Hz, 6-H), 8.11 (1H, s, 2-H), 8.36 (1H, d, *J* = 9.9 Hz, 4-H), 9.71 (1H, d, *J* = 9.6 Hz, 8-H), 10.53 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 14.2 ($CH_2CH_2CH_3$), 24.1 ($CH_2CH_2CH_3$), 29.1 ($CH_2CH_2CH_3$), 55.7 (OCH_3), 72.6 (CH_2), 110.3 (=CH-), 114.9 (=CH-), 119.6 (=C<), 123.3 (=CH-), 125.4 (=C<), 127.1 (=CH-), 129.6 (=CH-), 131.5 (=C<), 135.5 (=CH-), 138.1 (=CH-), 139.0 (=CH-), 139.9 (=CH-), 141.8 (=C<), 142.0 (=C<), 153.9 (=C<), 155.6 (=C<), 189.6 (CHO), 190.1 (CHO); ms: *m/z* (%) 362 (M^+, 25), 212 (16), 197 (100), 44 (58).

Anal. Calcd. for $C_{23}H_{22}O_4$: M, 362.1518; C, 76.22; H, 6.12. Found: M^+, 362.1513; C, 76.05; H, 6.33.

1-(5-Methoxybenzofuran-2-carbonyl)-3-propylazulene (**11cf**).

This compound was obtained by using **9f** as brown crystals (from benzene); mp 79-80 °C; ir (potassium bromide): ν 1609 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 0.91 (3H, t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 1.69 (2H, tq, *J* = 7.6, 7.5 Hz, $CH_2CH_2CH_3$), 2.89 (2H, t, *J* = 7.6 Hz, $CH_2CH_2CH_3$), 3.72 (3H, s, OCH_3), 6.94 (1H, dd, *J* = 8.9, 2.1 Hz, 6'-H), 6.99 (1H, d, *J* = 2.1 Hz, 4'-H), 7.28 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.35-7.43 (3H, m, 3'-, 7-,7'-H), 7.62 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.27 (1H, d, *J* = 9.6 Hz, 4-H), 8.40 (1H, s, 2-H), 9.60 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 14.1 ($CH_2CH_2CH_3$), 24.1 ($CH_2CH_2CH_3$), 29.1 ($CH_2CH_2CH_3$), 55.7 (OCH_3), 103.7 (=CH-), 112.8 (=CH-), 113.5 (=CH-), 116.9 (=CH-), 122.4 (=C<), 126.6 (=CH-), 127.8 (=C<), 128.8 (=CH-), 131.3 (=C<), 135.1 (=CH-), 138.4 (=CH-), 139.4 (=CH-), 140.8 (=CH-), 141.8 (=C<), 142.5 (=C<), 150.5 (=C<), 155.7 (=C<), 156.3 (=C<), 179.0 (C=O); ms: *m/z* (%) 344 (M^+, 10), 329 (14), 299 (100).

Anal. Calcd. for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 79.96; H, 5.75.

1-(5-Formylbenzofuran-2-carbonyl)-3-propylazulene (**11cg**).

This compound was obtained by using **9g** as brown needles (from benzene); mp 122-124 °C; ir (potassium bromide): ν 1691 (CHO), 1603 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 0.97 (3H, t, *J* = 7.4 Hz, $CH_2CH_2CH_3$), 1.75 (2H, tq, *J* = 7.7, 7.4 Hz, $CH_2CH_2CH_3$), 2.97 (2H, t, *J* = 7.7 Hz, $CH_2CH_2CH_3$), 7.42 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.51 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.53 (1H, s, 3'-H), 7.69 (1H, d, *J* = 7.2 Hz, 7'-H), 7.75 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 7.93 (1H, dd, *J* = 7.2, 1.2 Hz, 6'-H), 8.19 (1H, d, *J* = 1.2 Hz, 4'-H), 8.39 (1H, d, *J* = 9.9 Hz, 4-H), 8.40 (1H, s, 2-H), 9.68 (1H, d, *J* = 9.6 Hz, 8-H) 10.00 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 14.2 ($CH_2CH_2CH_3$), 24.1 ($CH_2CH_2CH_3$), 29.2 ($CH_2CH_2CH_3$), 113.1 (=CH-), 113.2 (=CH-), 122.0 (=C<), 126.5 (=CH-), 127.2 (=CH-), 127.7 (=CH-), 127.8 (=C<), 129.4 (=CH-), 131.7 (=C<), 132.8 (=C<), 135.4 (=CH-), 138.7 (=CH-), 139.8 (=CH-), 140.7 (=CH-), 142.3 (=C<), 142.9 (=C<), 156.6 (=C<), 158.5 (=C<), 178.3 (C=O), 191.3 (CHO); ms: *m/z* (%) 342 (M^+, 51), 313 (100), 156 (13).

Anal. Calcd. for $C_{23}H_{18}O_3$: M, 342.1256. Found: M^+, 342.1246.

Reactions of 1-(Bromoacetyl)-3-methoxycarbonylazulene (**5d**) with Salicylaldehydes **9a-g**.

General Procedure.

a) A solution of 1-(bromoacetyl)-3-methoxycarbonylazulene (**5d**) (100 mg, 0.33 mmole) and salicylaldehyde **9a-g** (0.33 mmole) in acetonitrile (5 ml) was stirred for 30 minutes at room temperature in the presence of potassium carbonate (46 mg, 0.19 mmole) followed by refluxing for 1.5 hours. The reaction mixture was worked up, as described above, to give 1-(2-formylphenoxyacetyl)-3-methoxycarbonylazulenes **10da-dd**,**dg** and 1-(2-benzofurancarbonyl)-3-methoxycarbonylazulenes **11da**,**de**,**df**. The compound **5d** was recovered from the reaction with **9a-c**,**g**. The yields are summarized in Table 1.

b) The same reaction using **5d** (100 mg, 0.33 mmole) was carried out under refluxing and worked up, as described above, to give the products **11da-dg**. The yields are also summarized in Table 1.

1-[(2-Formylphenoxy)acetyl]-3-methoxycarbonylazulene (**10da**).

This compound was obtained by using **9a** as red needless (from benzene); mp 191-192 °C; ir (potassium bromide): ν 1694 ($COOCH_3$), 1667 (CHO), 1598 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.99 (3H, s, $COOCH_3$), 5.48 (2H, s, CH_2), 6.98 (1H, d, *J* = 8.4 Hz, 6'-H), 7.05 (1H, dd, *J* = 7.5, 7.5 Hz, 4'-H), 7.50 (1H, dd, *J* = 8.4, 7.5 Hz, 5'-H), 7.83-7.90 (3H, m, 3'-,5-,7-H), 8.07 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.88 (1H, s, 2-H), 9.85 (1H, d, *J* = 9.9 Hz, 8-H), 10.01 (1H, d, *J* = 9.9 Hz, 4-H), 10.66 (1H, s, CHO); ^{13}C nmr (deuteriochloform): δ 55.6 ($COOCH_3$), 71.7 (CH_2), 112.9 (=CH-), 116.7 (=C<), 120.1 (=C<), 121.5 (=CH-), 125.3 (=C<), 128.6 (=CH-), 132.2 (=CH-), 133.0 (=CH-), 135.8 (=CH-), 140.0 (=CH-), 141.0 (=CH-), 142.0 (=CH-), 142.1 (=CH-), 144.4 (=C<), 144.7 (=C<), 160.7 (=C<), 165.0 ($COOCH_3$), 189.7 (CHO), 190.4 (C=O); ms ($C_{21}H_{16}O_5$): *m/z* (%) 348 (M^+, 8), 330 (29), 271 (13), 230 (18), 213 (100).

Anal. Calcd. for $C_{21}H_{16}O_5Na$: M, 371.0896. Found: M^+, 371.0970.

1-(2-Benzofurancarbonyl)-3-methoxycarbonylazulene (**11da**).

This compound was obtained by using **9a** as orange crystals (from benzene); mp 142-143 °C; ir (potassium bromide): ν 1703 ($COOCH_3$), 1622 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 4.01 (3H, s, $COOCH_3$), 7.34 (1H, dd, *J* = 7.5, 7.2 Hz, 5'-H), 7.50

(1H, dd, *J* = 7.5, 7.2 Hz, 6'-H), 7.61 (1H, s, 3'-H), 7.70 (1H, d, *J* = 7.5 Hz, 4'-H), 7.76 (1H, d, *J* = 7.5 Hz, 7'-H), 7.85 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.87 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 8.06 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 9.15 (1H, s, 2-H), 9.87 (1H, d, *J* = 9.6 Hz, 8-H), 9.91 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.5 (COO*C*H$_3$), 112.5 (=CH-), 114.4 (=CH-), 116.5 (=C<), 123.0 (=CH-), 123.8 (=CH-), 127.2 (=C<), 127.7 (=CH-), 131.7 (=CH-), 132.2 (=CH-), 139.6 (=CH-), 140.5 (=CH-), 141.5 (=CH-), 144.4 (=CH-), 144.7 (=C<), 145.1 (=C<), 154.2 (=C<), 155.7 (=C<), 165.4 (=C<), 179.7 (*C*OOCH$_3$), 200.5 (C=O) ; ms: *m/z* (%) 330 (M$^+$, 100), 315 (15), 299 (21), 271 (39), 213 (59).

Anal. Calcd. for $C_{21}H_{14}O_4$: C, 76.35; H, 4.27. Found: C, 76.29; H, 4.39.

1-[(2-Formyl-6-methylphenoxy)acetyl]-3-methoxycarbonylazulene (**10db**).

This compound was obtained by using **9b** as red crystals (from benzene); mp 184-185 °C; ir (potassium bromide): ν 1702 (COOCH$_3$), 1691 (CHO), 1659 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.40 (3H, s, CH$_3$), 3.96 (3H, s, COOCH$_3$), 5.35 (2H, s, CH$_2$), 7.20 (1H, dd, *J* = 7.5, 7.0 Hz, 4'-H), 7.49 (1H, d, *J* = 7.0 Hz, 5'-H), 7.73 (1H, d, *J* = 7.5 Hz, 3'-H), 7.88 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.91 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 8.09 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.73 (1H, s, 2-H), 9.86 (1H, d, *J* = 9.6 Hz, 8-H), 10.10 (1H, d, *J* = 9.9 Hz, 4-H), 10.53 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 16.1 (CH$_3$), 51.4 (COO*C*H$_3$), 77.3 (CH$_2$), 116.4 (=C<), 120.1 (=C<), 124.7 (=CH-), 127.1 (=CH-), 129.3 (=C<), 131.9 (=CH-), 132.1 (=C<), 132.8 (=CH-), 137.6 (=CH-), 139.8 (=CH-), 141.1 (=CH-), 141.7 (=CH-), 141.8 (=CH-), 144.2 (=C<), 144.6 (=C<), 160.0 (=C<), 165.0 (*C*OOCH$_3$), 190.2 (C=O), 190.6 (CHO); ms: *m/z* (%) 362 (M$^+$, 13), 344 (42), 285 (15), 228 (22), 213 (100).

Anal. Calcd. for $C_{22}H_{18}O_5$: M, 362.1154; C, 72.92; H, 5.01. Found: M$^+$, 362.1153; C, 72.98; H, 4.99.

3-Methoxycarbonyl-1-(7-methylbenzofuran-2-carbonyl)azulene (**11db**).

This compound was obtained by using **9b** as orange crystals (from benzene); mp 93-94 °C; ir (potassium bromide): ν 1704 (COOCH$_3$), 1620 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.56 (3H, s, CH$_3$), 3.89 (3H, s, COOCH$_3$), 7.10-7.19 (2H, m, 5'-,6'-H), 7.45-7.49 (2H, m, 3'-,4'-H), 7.70 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.72 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.91 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 9.10 (1H, s, 2-H), 9.72 (1H, d, *J* = 9.6 Hz, 8-H), 9.82 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 15.1 (CH$_3$), 51.4 (COO*C*H$_3$), 114.5 (=CH-), 116.4 (=C<), 120.4 (=CH-), 122.5 (=C<), 122.9 (=C<), 123.8 (=CH-), 126.7 (=C<), 128.3 (=CH-), 131.5 (=CH-), 132.1 (=CH-), 139.4 (=CH-), 140.4 (=CH-), 141.4 (=CH-), 144.5 (=CH-), 144.6 (=C<), 145.1 (=C<), 154.0 (=C<), 154.8 (=C<), 165.3 (*C*OOCH$_3$), 179.6 (C=O); ms: *m/z* (%) 344 (M$^+$, 100), 329 (20), 313 (16), 285 (46), 213 (53).

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.56; H, 4.68.

1-[(2-Formyl-4-methylphenoxy)acetyl]-3-methoxycarbonylazulene (**10dc**).

This compound was obtained by using **9c** as red crystals (from benzene); mp 185-186 °C; ir (potassium bromide): ν 1696 (COOCH$_3$), 1668 (CHO), 1612 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.20 (3H, s, CH$_3$), 3.90 (3H, s, COOCH$_3$), 5.36 (2H, s, CH$_2$), 6.79 (1H, d, *J* = 8.6 Hz, 6'-H), 7.20 (1H, d, *J* = 8.6 Hz, 5'-H), 7.58 (1H, s, 3'-H), 7.75 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.77 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.96 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.77 (1H, s, 2-H), 9.73 (1H, d, *J* = 9.9 Hz, 8-H), 9.89 (1H, d, *J* = 9.6 Hz, 4-H), 10.54 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 20.2 (CH$_3$), 51.5 (COO*C*H$_3$), 71.7 (CH$_2$), 112.8 (=CH-), 116.5 (=C<), 120.0 (=C<), 124.8 (=C<), 128.5 (=CH-), 130.9 (=C<), 132.0 (=CH-), 132.9 (=CH-), 136.4 (=CH-), 139.8 (=CH-), 140.9 (=CH-), 141.8 (=CH-), 142.0 (=CH-), 144.3 (=C<), 144.6 (=C<), 158.7 (=C<), 164.9 (*C*OOCH$_3$), 189.8 (CHO), 190.6 (C=O).

Anal. Calcd. for $C_{22}H_{18}O_5$: C, 72.92; H, 5.01. Found: C, 72.78; H, 4.95.

3-Methoxycarbonyl-1-(5-methylbenzofuran-2-carbonyl)azulene (**11dc**).

This compound was obtained by using **9c** as orange crystals (from benzene); mp 183-184 °C; ir (potassium bromide): ν 1703 (COOCH$_3$), 1619 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.39 (3H, s, CH$_3$), 3.92 (3H, s, COOCH$_3$), 7.21 (1H, dd, *J* = 8.4, 1.8 Hz, 6'-H), 7.43-7.49 (3H, m, 3'-,4'-7'-H), 7.71-7.79 (2H, m, 5-,7-H), 7.95 (1H, dd, *J* = 9.6, 9.6 Hz, 6-H), 9.05 (1H, s, 2-H), 9.76 (1H, d, *J* = 9.6 Hz, 8-H), 9.81 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 21.3 (CH$_3$), 51.4 (COO*C*H$_3$), 111.9 (=CH-), 114.2 (=CH-), 116.4 (=C<), 122.5 (=CH-), 123.1 (=C<), 127.3 (=C<), 129.2 (=CH-), 131.5 (=CH-), 132.1 (=CH-), 133.3 (=C<), 139.5 (=CH-), 140.5 (=CH-), 141.5 (=CH-), 144.3 (=CH-), 144.6 (=C<), 145.0 (=C<), 154.2 (=C<), 154.3 (=C<), 165.4 (*C*OOCH$_3$), 179.7 (C=O); ms: *m/z* (%) 344 (M$^+$, 100), 329 (21), 313 (16), 285 (48), 213 (55).

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.50; H, 4.83.

1-[(2-Formyl-6-methoxyphenoxy)acetyl]-3-methoxycarbonylazulene (**10dd**).

This compound was obtained by using **9d** as red crystals (from benzene); mp 186-187 °C; ir (potassium bromide): ν 1712 (COOCH$_3$), 1688 (CHO), 1671 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.90 (3H, s, OCH$_3$), 3.98 (3H, s, COOCH$_3$), 5.55 (2H, s, CH$_2$), 7.15 (2H, m, 4'-,5'-H), 7.48 (1H, dd, *J* = 6.0, 2.3 Hz, 3'-H), 7.83 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.84 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 8.04 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.79 (1H, s, 2-H), 9.80 (1H, d, *J* = 9.6 Hz, 8-H), 10.00 (1H, d, *J* = 9.9 Hz, 4-H), 10.74 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 51.4 (OCH$_3$), 56.1 (COO*C*H$_3$), 75.6 (CH$_2$), 116.3 (=C<), 118.0 (=CH-), 119.2 (=CH-), 120.3 (=C<), 123.4 (=CH-), 124.1 (=CH-), 129.9 (=C<), 131.7 (=CH-), 132.6 (=CH-), 140.9 (=CH-), 141.7 (=CH-), 141.9 (=C<), 144.1 (=C<), 144.4 (=C<), 150.3 (=CH-), 152.1 (=C<), 165.1 (*C*OOCH$_3$), 190.8 (CHO), 191.4 (C=O); ms: *m/z* (%) 378 (M$^+$, 10), 228 (23), 213 (100).

Anal. Calcd. for $C_{22}H_{18}O_6$: M, 378.1105; C, 69.83; H, 4.79. Found: M$^+$, 378.1103; C, 69.58; H, 4.84.

1-(7-Methoxybenzofuran-2-carbonyl)-3-methoxycarbonylazulene (**11dd**).

This compound was obtained by using **9d** as orange crystals (from benzene); mp 145-146 °C; ir (potassium bromide): ν 1703 (COOCH$_3$), 1625 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.89 (3H, s, OCH$_3$), 3.98 (3H, s, COOCH$_3$), 6.85 (1H, d, *J* = 7.8 Hz, 6'-H), 7.10-7.23 (2H, m, 4'-,5'-H), 7.49 (1H, s, 3'-H), 7.71 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.72 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.92 (1H, dd, *J* = 9.6, 9.6 Hz, 6-H), 9.07 (1H, s, 2-H), 9.72 (1H, d, *J* = 9.9 Hz, 8-H), 9.80 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.4 (OCH$_3$), 56.2 (COO*C*H$_3$), 109.3 (=CH-),

114.2 (=CH-), 114.8 (=CH-), 116.5 (=C<), 122.8 (=C<), 124.4 (=CH-), 128.8 (=C<), 131.5 (=CH-), 132.1 (=CH-), 139.4 (=CH-), 140.4 (=CH-), 141.4 (=CH-), 144.5 (=CH-), 145.0 (=C<), 145.9 (=C<), 154.3 (=C<), 145.9 (=C<), 154.3 (=C<), 165.3 (*C*OOCH$_3$), 179.3 (C=O); ms: *m/z* (%) 360 (M$^+$, 100), 345 (14), 301 (31), 213 (53).

Anal. Calcd. for $C_{22}H_{16}O_5$: C, 73.33; H, 4.48. Found: C, 72.95; H, 4.66.

1-(6-Methoxybenzofuran-2-carbonyl)-3-methoxycarbonylazulene (**11de**).

This compound was obtained by using **9e** as orange crystals (from benzene); mp 205-206 °C; ir (potassium bromide): ν 1693 (COOCH$_3$), 1618 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.91 (3H, s, OCH$_3$), 4.01 (3H, s, COOCH$_3$), 6.97 (1H, d, *J* = 8.5 Hz, 5'-H), 7.16 (1H, s, 7'-H), 7.55 (1H, s, 3'-H), 7.61 (1H, d, *J* = 8.5 Hz, 4'-H), 7.82 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.83 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 8.04 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 9.10 (1H, s, 2-H), 9.84 (1H, d, *J* = 9.6 Hz, 8-H), 9.87 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.4 (OCH$_3$), 55.7 (COO*C*H$_3$), 95.7 (=CH-), 114.1 (=CH-), 115.0 (=CH-), 116.3 (=C<), 120.6 (=C<), 123.2 (=CH-), 123.3 (=C<), 131.4 (=CH-), 131.9 (=CH-), 139.5 (=CH-), 140.4 (=CH-), 141.4 (=CH-), 144.0 (=CH-), 144.5 (=C<), 144.9 (=C<), 153.8 (=C<), 157.3 (=C<), 160.7 (=C<), 165.4 (*C*OOCH$_3$), 179.3 (C=O); ms: *m/z* (%) 360 (M$^+$, 100), 345 (22), 301 (33), 213 (39).

Anal. Calcd. for $C_{22}H_{16}O_5$: M, 360.0998; C, 73.33; H, 4.48. Found: M$^+$, 360.0991; C, 73.11; H, 4.64.

1-(5-Methoxybenzofuran-2-carbonyl)-3-methoxycarbonylazulene (**11df**).

This compound was obtained by using **9f** as orange crystals (from benzene); mp 211-213 °C; ir (potassium bromide): ν 1702 (COOCH$_3$), 1612 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.38 (3H, s, OCH$_3$), 4.01 (3H, s, COOCH$_3$), 7.11 (1H, dd, *J* = 8.8, 2.5 Hz, 6'-H), 7.16 (1H, d, *J* = 2.5 Hz, 4'-H), 7.58 (1H, d, *J* = 8.8 Hz, 7'-H), 7.60 (1H, s, 3'-H), 7.85 (1H, dd, *J* = 9.9, 9.9 Hz, 7-H), 7.87 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 8.06 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 9.16 (1H, s, 2-H), 9.88 (1H, d, *J* = 9.9 Hz, 8-H), 9.92 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.5 (OCH$_3$), 55.9 (COO*C*H$_3$), 103.8 (=CH-), 113.1 (=CH-), 114.4 (=CH-), 116.5 (=C<), 117.7 (=CH-), 123.0 (=C<), 127.8 (=C<), 131.6 (=CH-), 132.2 (=CH-), 139.6 (=CH-), 140.5 (=CH-), 141.5 (=CH-), 144.7 (=C<), 145.1 (=CH-), 150.9 (=C<), 155.0 (=C<), 156.5 (=C<), 165.4 (=C<), 179.6 (C=O); ms: *m/z* (%) 360 (M$^+$, 100), 314 (35), 313 (31), 301 (31), 213 (44), 169 (15).

Anal. Calcd. for $C_{22}H_{16}O_5$: M, 360.0998; C, 73.33; H, 4.48. Found: M$^+$, 360.1008; C, 73.30; H, 4.66.

1-[(2,4-Diformylphenoxy)acetyl]-3-methoxycarbonylazulene (**10dg**).

This compound was obtained by using **9g** as red needles (from benzene); mp 209-210 °C; ir (potassium bromide): ν 1693 (COOCH$_3$), 1657 (CHO), 1594 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 4.01 (3H, s, COOCH$_3$), 5.65 (2H, s, CH$_2$), 7.09 (1H, d, *J* = 8.7 Hz, 6'-H), 7.90 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.92 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 8.01-8.14 (2H, m, 5'-,6-H), 8.29 (1H, s, 3'-H), 8.87 (1H, s, 2-H), 9.88 (1H, d, *J* = 9.9 Hz, 8-H), 9.95 (1H, s, 4'-CHO), 10.01 (1H, d, *J* = 9.9 Hz, 4-H), 10.67 (1H, s, 2'-CHO); ^{13}C nmr (deuteriochloroform): δ 51.6 (COO*C*H$_3$), 71.4 (CH$_2$), 113.6 (=CH-), 116.9 (=C<), 119.6 (=C<), 125.2 (=C<), 130.2 (=C<), 132.2 (=CH-), 132.5 (=CH-), 133.3 (=CH-), 135.3 (=CH-), 140.2 (=CH-), 141.1 (=CH-), 14.7 (=CH-), 142.2 (=CH-), 144.5 (=C<), 144.9 (=C<), 164.7 (=C<), 164.9 (*C*OOCH$_3$), 188.5 (CHO), 188.9 (C=O), 190.1 (CHO); ms ($C_{22}H_{16}O_6$): *m/z* (%) 376 (M$^+$, 5), 214 (15), 213 (100).

Anal. Calcd. for $C_{22}H_{16}O_6Na$: M, 399.0845. Found: M$^+$, 399.0910.

1-(5-Formylbenzofuran-2-carbonyl)-3-methoxycarbonylazulene (**11dg**).

This compound was obtained by the reaction with **9g** as orange crystals (from benzene); mp 217-218 °C; ir (potassium bromide): ν 1704 (CHO), 1702 (COOCH$_3$), 1611 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 4.02 (3H, s, COOCH$_3$), 7.71 (1H, s, 3'-H), 7.81-7.94 (3H, m, 5-,7-,7'-H), 8.04-8.13 (2H, m, 6-,6'-H), 8.31 (1H, d, *J* = 1.5 Hz, 4'-H), 9.15 (1H, s, 2-H), 9.90 (1H, d, *J* = 9.9 Hz, 8-H), 9.95 (1H, d, *J* = 9.9 Hz, 4-H), 10.11 (1H, s, CHO); ^{13}C nmr (deuteriochloroform): δ 51.5 (COO*C*H$_3$), 113.3 (=CH-), 114.2 (=CH-), 116.8 (=C<), 122.5 (=C<), 126.7 (=CH-), 127.7 (=C<), 128.2 (=CH-), 132.0 (=CH-), 132.6 (=CH-), 133.0 (=C<), 139.8 (=CH-), 140.7 (=CH-), 141.8 (=CH-), 144.4 (=CH-), 144.9 (=C<), 145.2 (=C<), 155.9 (=C<), 158.7 (=C<), 165.3 (*C*OOCH$_3$), 179.0 (C=O) 191.2 (CHO); ms: *m/z* (%) 358 (M$^+$, 32), 343 (4), 327 (9), 299 (10), 213 (31).

Anal. Calcd. for $C_{22}H_{14}O_5$: C, 73.74; H, 3.94. Found: C, 73.48; H, 4.05.

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