Reactions of 1-(3-Aryl-3-oxopropenyl)azulenes and 1-Cinnamoylazulenes with Malononitrile: Synthesis of 1-(2-Aryl-4-pyridyl)azulenes and 1-(4-Aryl-2-pyridyl)azulenes

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Dedicated to the memory of Professor Raymond N. Castle

The reactions of 1-formyl-3-methoxycarbonylazulene (**1**) with acetophenones **3a-e** gave 1-(3-aryl-3-oxopropenyl)-3-methoxycarbonylazulenes **4a-e** which reacted with malononitrile in the presence of sodium methoxide to afford 1-(2-aryl-4-pyridyl)-3-methoxycarbonylazulenes **9a-d**, except for 4'-nitro-substituted compounds. Heating of the compounds **9a-d** in 100% phosphoric acid yielded 1-(2-aryl-4-pyridyl)azulenes **10a-d**. In a similar manner, 1-(4-aryl-2-pyridyl)azulenes **12a-l** and 1-[4-(2-furyl)- and 4-(2-thienyl)-2-pyridyl)]azulenes **14a,b** were obtained.

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Introduction.

The pyridine nucleus is found in a large number of commonly used drugs which have diverse pharmacological activities. Interest in the synthesis of multicyclic pyridine containing compounds has increased in recent years because of their biological and pharmacological activities [1,2]. The synthesis of phenyl-substituted pyridines has been widely investigated [3].

Recently, several synthetic methods *via* condensation and cyclization were reported such as the reaction of α, β-unsaturated ketones with *N*-(1-phenylvinyl)iminophosphorane [4], the reaction of aromatic aldehydes and alkyl ketones with malononitrile in the presence of ammonium acetate [5], and the reaction of chalcones with malononitrile in the presence of sodium hydroxide [6]. We also reported the synthesis of 3-(4-aryl-2-pyridyl)tropolones in a similar manner [7]. On the other hand, little is known about azulenes possessing a heterocyclic ring as the side-chain, except for some compounds, such as pyridylazulenes [8-10], quinolylazulenes [11,12], and (1,3-benzothiazolyl)thioazulenes [13], have been reported in the field of azulenoid chemistry.

In our continuing interest in the chemistry of non-benzenoid aromatic compounds having a heterocyclic ring, the present paper deals with syntheses of 1-(2-aryl-4-pyridyl)azulenes and 1-(4-aryl-2-pyridyl)azulenes *via* 1-(3-aryl-3-oxopropenyl)azulenes and 1-cinnamoylazulenes.

Results and Discussion.

Preparation of 1-(3-Aryl-3-oxopropenyl)-3-methoxycarbonylazulenes **4a-e** and 1-Cinnamoyl-3-methoxycarboylazulenes **6a-m**.

It is well known that the condensation of acetophenones and benzaldehydes is a prototype reaction and leads to 1,3-diarylprop-2-en-1-ones [14,15]. The scope of this reaction is exceedingly broad. When a solution of 1-formyl-3-methoxycarbonylazulene (**1**) and 1.5 molar equivalents of acetophenone **3a-e** in methanol was heated for 24 hours under refluxing in the presence of sodium methoxide, the corresponding 1-(3-aryl-3-oxopropenyl)azulenes **4a-e** were obtained as red crystals in good yields, except for that of the 4'-nitro-substituted compound **4e** which was obtained in 44% yield. In a similar manner, 1-cinnamoyl-3-methoxycarbonylazulenes **6a-m** were obtained from 1-acetyl-3-methoxycarbonylazulene (**2**) and benzaldehydes **5a-m** in moderate to good yields. The reactions of 1-acetyl-3-methoxycarbonylazulene (**2**) with 2-furancarbaldehyde (**7a**) and 2-thiophenecarbaldehyde (**7b**) also gave 1-[3-(2-furyl)- and 3-(2-thienyl)-3-oxopropenyl]azulene **8a,b**, respectively. The structures of these products were confirmed by spectral data and elemental analyses (Experimental Part). The yields are summarized in Table 1.

Synthesis of 1-(6-Aryl-3-cyano-2-methoxy-4-pyridyl)-azulenes **10a-d** and 1-(4-Aryl-3-cyano-2-methoxy-6-pyridyl)azulenes **12a-l**.

The compounds, **4a-d**, **6a-l**, and **8a,b**, are α,β-unsaturated ketones which undergo Michael addition. To a solution of 1-(3-aryl-3-oxopropenyl)-3-methoxycarbonylazulenes **4a-d** and malononitrile in absolute methanol was added sodium methoxide solution. The mixture was stirred for 2-20 hours at 50 °C and gave the corresponding 1-(6-aryl-3-cyano-2-methoxy-4-pyridyl)-3-methoxycarbonylazulenes **9a-d** in 26-48% yields (Table 2). However, in the reactions of 1-[3-(4-nitrophenyl)-3-oxopropenyl]-3-methoxyazulene (**4e**) under the same conditions, the starting material **4e** was recovered.

When the products **9a-d** were heated in 100% phosphoric acid for 15 minutes at 90-100 °C, the ester group at

the 3-position was removed to afford 1-(6-aryl-3-cyano-2-methoxy-4-pyridyl)azulenes **10a-d** in moderate yields.

The reactions of isomeric 1-cinnamoyl-3-methoxycarbonylazulenes **6a-l** with malononitrile under similar conditions gave 1-(4-aryl-3-cyano-2-methoxy-6-pyridyl)-3-methoxycarbonylazulenes **11a-d** in 23-62% yields (Table 2), which were deesterified by heating in 100% phosphoric acid to give 1-(4-aryl-3-cyano-2-methoxy-6-pyridyl)azulenes **11a-d** in moderate yields. Similary, the reactions with 2-furancarbaldehyde (**7a**) and 2-thiophenecarbaldehyde (**7b**) gave 1-[4-(2-furyl)-3-cyano-2-methoxy-6-pyridyl]azulene (**14a**) and 1-[4-(2-thienyl)-3-cyano-2-methoxy-6-pyridyl]azulene (**14b**) in moderate yields *via* their 3-methoxycarbonyl substituted compounds **13a,b**, respectively.

The reactions might proceed *via* Michael addition of malononitrile to the α,β-unsaturated carbonyl functional group in compounds, **4a-d**, **6a-l**, and **8a,b**, leading to formation of 4,6-disubstituted 2-amino-4*H*-pyran-3-carbonitriles, followed by opening of the 4*H*-pyran ring, and subsequent pyridine-ring formation. No remarkable effects of the substituents in the benzene ring were observed.

In conclusion, it was found that pyridine heterocycles having two different aromatic rings, azulene and either benzene or a heterocyclic ring, were readily prepared.

Table 1

Condensation of 1-Formyl-3-methoxycarbonylazulene (**1**) and 1-Acetyl-3-methoxycarbonyazulene (**2**)

Substrate	Reagent	R (X)	Time (hours)	Product	Yield/%
1	**3a**	H	6	**4a**	80
1	**3b**	CH_3	6	**4b**	73
1	**3c**	OCH_3	8	**4c**	65
1	**3d**	Cl	6	**4d**	90
1	**3e**	NO_2	12	**4e**	44
2	**5a**	H	24	**6a**	78
2	**5b**	2-CH_3	24	**6b**	67
2	**5c**	3-CH_3	24	**6c**	63
2	**5d**	4-CH_3	17	**6d**	81
2	**5e**	2-OCH_3	12	**6e**	80
2	**5f**	3-OCH_3	12	**6f**	91
2	**5g**	4-OCH_3	12	**6g**	78
2	**5h**	2,4-$(OCH_3)_2$	24	**6h**	48
2	**5i**	2,5-$(OCH_3)_2$	12	**6i**	56
2	**5j**	2-Cl	12	**6j**	71
2	**5k**	4-Cl	12	**6k**	90
2	**5l**	3,4-Cl_2	12	**6l**	59
2	**5m**	4-NO_2	12	**6m**	48
2	**7a**	O	8	**8a**	92
2	**7b**	S	24	**8b**	68

EXPERIMENTAL

Measurements.

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 nmr spectra were recorded with a JEOL JNM-EX 300 spectrometer (300 MHz for ^1H and 75.5 MHz for ^{13}C). The mass spectra were measured on a

Scheme 1

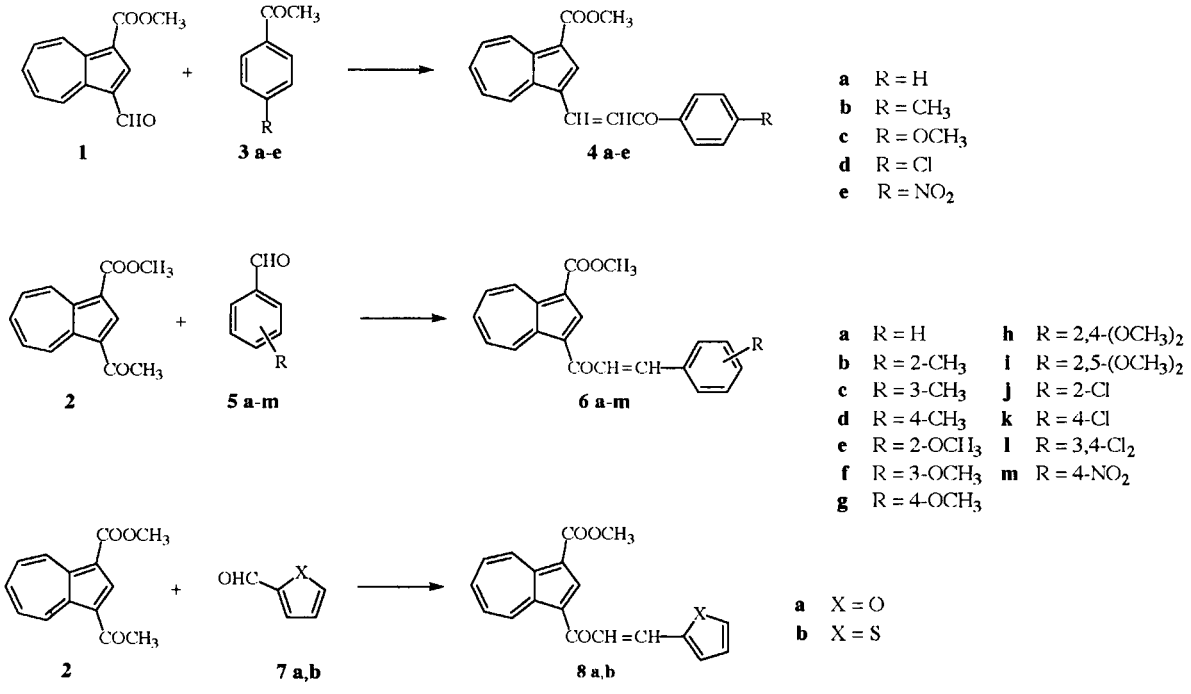


Table 2

Preparation and Deesterification of 1-(2-Aryl-4-pyridyl)azulenes **9a-d**,1-(4-Aryl-2-pyridyl)-3-methoxycarbonylazulenes **11a-e**, and Heterocyclic Analogs **13a,b**

Starting Material	R (X)	Time (hours)	Preparation	Yield/%	Deesterification	Yield/%
4a	H	12	**9a**	48	**10a**	69
4b	CH_3	24	**9b**	26	**10b**	56
4c	OCH_3	24	**9c**	44	**10c**	60
4d	Cl	12	**9d**	45	**10d**	47
6a	H	3	**11a**	50	**12a**	54
6b	2-CH_3	2	**11b**	40	**12b**	87
6c	3-CH_3	2	**11c**	36	**12c**	53
6d	4-CH_3	12	**11d**	42	**12d**	76
6e	2-OCH_3	2	**11e**	47	**12e**	71
6f	3-OCH_3	20	**11f**	23	**12f**	50
6g	4-OCH_3	20	**11g**	26	**12g**	52
6h	2,4-$(OCH_3)_2$	2	**11h**	43	**12h**	75
6i	2,5-$(OCH_3)_2$	3	**11i**	62	**12i**	85
6j	2-Cl	4	**11j**	51	**12j**	91
6k	4-Cl	6	**11k**	45	**12k**	61
6l	3,4-Cl_2	5	**11l**	55	**12l**	75
8a	O	5	**13a**	43	**14a**	57
8b	S	3	**13b**	46	**14b**	62

JEOL JMS-01-SG spectrometer. Elemental analyses were performed at the Center for Instrumental Analysis, Kumamoto University.

Materials.

Unless otherwise stated, chemicals were purchased and used without further purification. The following materials were prepared according to literature procedures: 1-formyl-3-methoxycarbonylazulene (**1**) [16] and 1-acetyl-3-methoxycarbonylazulene (**2**) [17].

Synthesis of 1-(3-Aryl-3-oxopropenyl)-3-methoxycarbonyl-azulenes (**4a-e**).

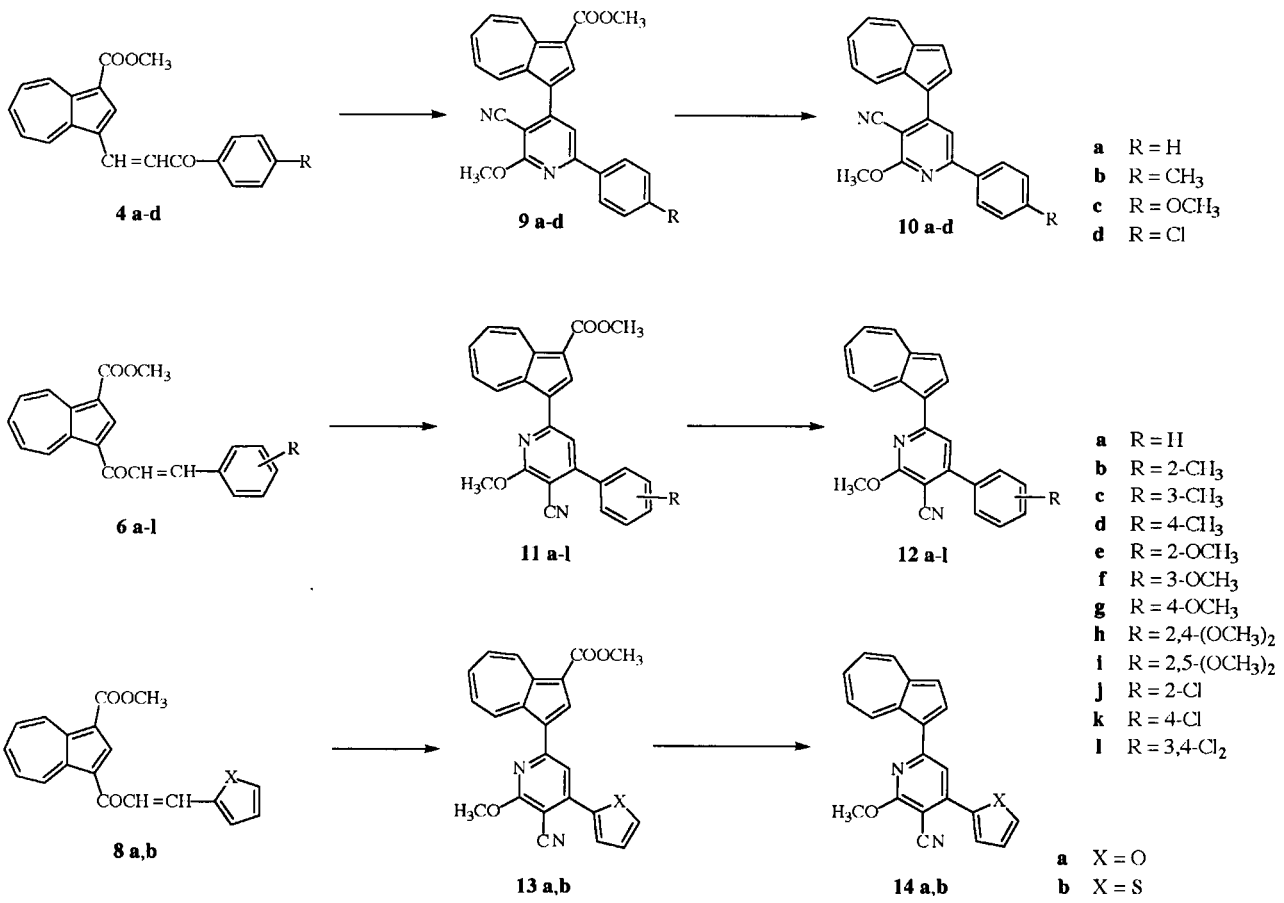
General Procedure.

A solution of 1-formyl-3-methoxycarbonylazulene (**1**) (107 mg, 0.5 mmole) and acetophenone **3a-e** (0.75 mmole) in absolute methanol (30 ml) was refluxed for 24 hours in the presence of sodium methoxide, prepared from sodium (92 mg, 4.0 mmoles) and absolute methanol (5 ml). The reaction mixture was diluted with water (95 ml), acidified with 2m hydrochloric acid, and extracted with chloroform (3x20 ml). The extract was dried over sodium sulfate. The evaporation residue was chromatographed on a column (Merck, Kieselgel 60, 10 g) with benzene as eluent to give 1-(3-aryl-3-oxopropenyl)-3-methoxycarbonylazulenes **4a-e**.

1-(3-Phenyl-3-oxopropenyl)-3-methoxycarbonylazulene (**4a**).

This compound was obtained as greenish needles (from benzene) in a yield of 126 mg (80%), mp 172-173 °C; ir

Scheme 2



(potassium bromide): ν max 1699 (C=O), 1642 cm-1 (C=O); ^{1}H nmr (deuteriochloroform): δ 3.97 (3H, s, $COOCH_3$), 7.48-7.60 (5H, m), 7.64 (1H, d, J = 15.2 Hz, =CHCO), 7.83 (1H, t, J = 9.9 Hz, 6-H), 8.08 (2H, d, J = 7.5 Hz, 2'-,6'-H), 8.40 (1H, d, J = 15.2 Hz, 1-CH=), 8.70 (1H, dd, J = 9.9 Hz, 8-H), 8.76 (1H, s, 2-H), 9.59 (1H, d, J = 9.6 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.3 ($COOCH_3$), 117.9 (=C<), 119.5 (=CH-), 123.6 (=C<), 128.2 (=C<), 128.3 (=CH-), 128.4 (=CH-), 128.5 (=CH-), 129.7 (=CH-), 132.5 (=CH- x 2), 135.3 (=CH-), 138.1 (=CH-), 138.6 (=CH-), 140.4 (=CH-), 142.9 (=C<), 143.4 (=C<), 165.1 (*C*OOCH3), 189.8 (*C*OCH=CH).

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.68; H, 5.13.

3-Methoxycarbonyl-1-[3-(4-methylphenyl)-3-oxopropenyl]-azulene (**4b**).

This compound was obtained as greenish needles (from benzene) in a yield of 129 mg (78%), mp 121-122 °C; ir (potassium bromide): ν max 1694 (C=O), 1646 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.44 (3H, s, CH_3), 3.99 (3H, s, $COOCH_3$), 7.31 (2H, d, J = 7.5 Hz, 3'-,5'-H), 7.52 (1H, dd, J = 15.2 Hz, =CHCO), 7.56 (1H, t, J = 9.9 Hz, 5-H), 7.59 (1H, dd, J = 10.2, 9.4 Hz, 7-H), 7.82 (1H, dd, J = 10.2, 9.9 Hz, 6-H), 8.00 (2H, d, J = 7.5 Hz, 2'-,6'-H), 8.43 (1H, d, J = 15.2 Hz, 1-CH=), 8.76 (1H, d, J = 9.9 Hz, 8-H), 8.80 (1H, s, 2-H), 9.62 (1H, d, J = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 21.6 (CH3), 51.4 ($COOCH_3$), 117.8 (=C<), 119.7 (=CH-), 123.8 (=C<), 128.4 (=CH-), 128.5 (=CH-), 129.3 (=CH-), 129.7 (=CH-), 135.0 (=CH-), 135.5 (=CH-), 136.1 (=C<), 138.1 (=CH-), 138.7 (=CH-), 140.5 (=CH-), 142.9 (=C<), 143.3 (=C<), 143.4 (=C<), 165.3 ($COOCH_3$), 189.5 (*C*OCH=CH).

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.81; H, 5.48.

3-Methoxycarbonyl-1-[3-(4-methoxylphenyl)-3-oxopropenyl]-azulene (**4c**).

This compound was obtained as greenish needles (from benzene) in a yield of 113 mg (65%), mp 156-157 °C; ir (potassium bromide): ν max 1693 (C=O), 1654 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.88 (3H, s, OCH3), 3.97 (3H, s, $COOCH_3$), 6.98 (2H, d, J = 7.1 Hz, 3'-,5'-H), 7.52 (1H, dd, J = 10.2, 9.0 Hz, 5-H), 7.55 (1H, d, J = 9.9 Hz, 7-H), 7.64 (1H, dd, J = 15.2 Hz, =CHCO), 7.82 (1H, dd, J = 10.2, 9.9 Hz, 6-H), 8.09 (2H, d, J = 7.1 Hz, 2'-,6'-H), 8.37 (1H, d, J = 15.2 Hz, 1-CH=), 8.69 (1H, d, J = 9.9 Hz, 8-H), 8.75 (1H, s, 2-H), 9.57 (1H, d, J = 9.0 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.3 ($COOCH_3$), 55.4 (OCH_3), 113.7 (=CH-), 117.7 (=C<), 119.4 (=CH-), 123.8 (=C<), 128.2 (=CH-), 129.5 (=CH-), 130.5 (=CH-), 131.5 (=C<), 134.5 (=CH-), 135.3 (=CH-), 138.0 (=CH-), 138.5 (=CH-), 140.4 (=CH-), 142.7 (=C<), 143.3 (=C<), 163.2 (=C<), 165.2 ($COOCH_3$), 188.1 (*C*OCH=CH).

Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.36; H, 5.50.

1-[3-(4-Chlorophenyl)-3-oxopropenyl]-3-methoxycarbonyl-azulene (**4d**).

This compound was obtained as greenish needles (from benzene) in a yield of 158 mg (90%), mp 118-119 °C; ir (potassium bromide): ν max 1703 (C=O), 1654 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.99 (3H, s, $COOCH_3$), 7.45 (2H, d, J = 8.6 Hz, 3'-,5'-H), 7.56 (1H, dd, J = 9.9, 9.6 Hz, 5-H), 7.59 (1H, d, J = 15.0 Hz, =CHCO), 7.61 (1H, dd, J = 9.6, 9.3 Hz, 7-H), 7.86 (1H, dd, J = 9.9, 9.6 Hz, 6-H), 8.01 (2H, d, J = 8.6 Hz, 2'-,6'-H), 8.42 (1H, d, J = 15.0 Hz, 1-CH=), 8.72 (1H, d, J = 9.3 Hz, 8-H), 8.78 (1H, s, 2-H), 9.62 (1H, d, J = 9.6 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.4 ($COOCH_3$), 118.9 (=CH-), 123.5 (=C<), 128.6 (=CH-), 128.8 (=CH-), 129.5 (=C<), 129.7 (=CH-), 129.9 (=CH-), 135.4 (=CH-), 135.8 (=CH-), 137.0 (=CH-), 138.1 (=CH-), 138.8 (=CH-), 140.6 (=CH-), 143.1 (=C<), 143.6 (=C<), 165.2 ($COOCH_3$), 188.5 (*C*OCH=CH).

Anal. Calcd. for $C_{21}H_{15}ClO_3$: C, 71.90; H, 4.31. Found: C, 71.99; H, 4.33.

3-Methoxycarbonyl-1-[3-(4-nitrophenyl)-3-oxopropenyl]azulene (**4e**).

This compound was obtained as yellowish green needles (from benzene) in a yield of 79 mg (44%), mp 231-232 °C; ir (potassium bromide): ν max 1700 (C=O), 1651 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 4.01 (3H, s, $COOCH_3$), 7.62 (1H, d, J = 15.3 Hz, =CHCO), 7.66 (1H, dd, J = 10.2, 9.9 Hz, 5-H), 7.69 (1H, dd, J = 9.9, 9.6 Hz, 7-H), 7.94 (1H, t, J = 9.9 Hz, 6-H), 8.21 (2H, d, J = 6.6 Hz, 2'-,6'-H), 8.36 (2H, d, J = 6.6 Hz, 3'-,5'-H), 8.52 (1H, d, J = 15.3 Hz, 1-CH=), 8.80 (1H, d, J = 9.6 Hz, 8-H), 8.85 (1H, s, 2-H), 9.69 (1H, d, J = 10.2 Hz, 4-H).

Anal. Calcd. for $C_{21}H_{15}NO_5$: C, 69.80; H, 4.18; N, 3.88. Found: C, 70.03; H, 4.14; N, 3.59.

Preparation of 1-Cinnamoyl-3-methoxycarbonylazulenes (**6a-m**).

General Procedure.

To a solution of 1-acetyl-3-methoxycarbonylazulene (**2**) (114 mg, 0.5 mmole) and benzaldehyde **5a-m** (0.75 mmole) in absolute methanol (30 ml) was added a sodium methoxide solution, prepared from sodium (92 mg, 4.0 mmoles) and absolute methanol (5 ml). The mixture was refluxed for 12-24 hours. Work up of the reaction mixture was carried out, as described above. The product was chromatographed on a column (Merck, Kieselgel 60, 10 g) with benzene as eluent to give 1-cinnamoyl-3-methoxycarbonylazulenes **6a-m**.

1-Cinnamoyl-3-methoxycarbonylazulene (**6a**).

This compound was obtained as red needles (from ethanol) in a yield of 123 mg (78%), mp 172-173 °C; ir (potassium bromide): ν max 1696 (C=O), 1646 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.97 (3H, s, $COOCH_3$), 7.36-7.68 (2H, m), 7.67 (1H, d, J = 15.2 Hz, =CHCO), 7.74 (1H, t, J = 9.8 Hz, 5-H), 7.78 (1H, dd, J = 10.3, 9.8 Hz, 7-H), 7.82 (1H, d, J = 15.2 Hz, COCH=C*H*), 7.96 (1H, t, J = 9.8 Hz, 6-H), 8.85 (1H, s, 2-H), 9.74 (1H, d, J = 10.3 Hz, 8-H), 10.08 (1H, d, J = 9.7 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.4 ($COOCH_3$), 116.1 (=C<), 124.7 (=CH-), 125.0 (=C<), 128.4 (=CH-), 128.9 (=CH-), 130.4 (=CH-), 131.4 (=CH-), 132.2 (=CH-), 135.3 (=C<), 139.4 (=CH-), 141.1 (=CH-), 141.3 (=CH-), 142.3 (=CH-), 142.9 (=CH-), 144.3 (=C<), 144.6 (=C<), 165.2 ($COOCH_3$), 186.3 (*C*OCH=CH).

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.72; H, 5.10. Found: C, 79.93; H, 5.20.

3-Methoxycarbonyl-1-(2-methylcinnamoyl)azulene (**6b**).

This compound was obtained as red needles (from ethanol) in a yield of 111 mg (67%), mp 165-167 °C; ir (potassium bromide):

ν max 1693 (C=O), 1646 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.48 (3H, s, CH_3), 3.95 (3H, s, $COOCH_3$), 7.19 (1H, d, *J* = 7.3 Hz, 3'-H), 7.23-7.27 (2H, m), 7.71-7.74 (3H, m), 7.91 (1H, t, *J* = 9.8 Hz, 6-H), 8.09 (1H, d, *J* = 15.3 Hz, COCH=C*H*), 8.81 (1H, s, 2-H), 9.70 (1H, d, *J* = 10.4 Hz, 8-H), 10.06 (1H, d, *J* = 9.8 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 19.8 (CH_3), 51.2 ($COOCH_3$), 116.0 (=C<), 124.9 (=CH-), 125.6 (=CH-), 126.2 (=CH-), 126.3 (=CH-), 129.8 (=CH-), 130.8 (=CH-), 131.3 (=CH-), 132.0 (=C<), 134.2 (=C<), 138.0 (=C<), 139.3 (=CH-), 139.8 (=CH-), 141.1 (=CH-), 141.2 (=CH-), 142.9 (=CH-), 144.2 (=C<), 144.6 (=C<), 165.1 ($COOCH_3$), 186.2 (*C*OCH=CH).

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.24; H, 5.70.

3-Methoxycarbonyl-1-(3-methylcinnamoyl)azulene (**6c**).

This compound was obtained as red needles (from ethanol) in a yield of 104 mg (63%), mp 137-138 °C; ir (potassium bromide): ν max 1692 (C=O), 1645 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.39 (3H, s, CH_3), 3.97 (3H, s, $COOCH_3$), 7.19-7.20 (2H, m, 4'-,5'-H), 7.47 (1H, d, *J* = 7.6 Hz, 6'-H), 7.48 (1H, s, 2'-H), 7.65 (1H, d, *J* = 15.3 Hz, COCH=), 7.72 (1H, dd, *J* = 9.8, 9.7 Hz, 5-H), 7.78 (1H, dd, *J* = 9.8, 7.2 Hz, 7-H), 7.79 (1H, d, *J* = 15.3 Hz, COCH=C*H*), 7.94 (1H, t, *J* = 9.7 Hz, 6-H), 8.85 (1H, s, 2-H), 9.73 (1H, d, *J* = 9.8 Hz, 8-H), 10.08 (1H, d, *J* = 9.8 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 21.3 (CH_3), 51.3 ($COOCH_3$), 116.0 (=C<), 124.4 (=CH-), 125.0 (=CH-), 125.6 (=CH-), 128.7 (=CH-), 128.9 (=CH-), 130.9 (=CH-), 131.3 (=CH-), 132.1 (=C<), 135.2 (=C<), 138.4 (=C<), 139.3 (=CH-), 141.1 (=CH-), 141.3 (=CH-), 142.5 (=CH-), 142.9 (=CH-), 144.3 (=C<), 144.6 (=C<), 165.2 ($COOCH_3$), 186.3 (*C*OCH=CH).

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 80.17; H, 5.35.

3-Methoxycarbonyl-1-(4-methylcinnamoyl)azulene (**6d**).

This compound was obtained as red needles (from ethanol) in a yield of 134 mg (81%), mp 141-142 °C; ir (potassium bromide): ν max 1693 (C=O), 1646 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.36 (3H, s, CH_3), 3.97 (3H, s, $COOCH_3$), 7.19 (2H, d, *J* = 7.9 Hz, 3'-,5'-H), 7.56 (2H, d, *J* = 7.9 Hz, 2'-,6'-H), 7.63 (1H, d, *J* = 15.5 Hz, COCH=), 7.71 (1H, dd, *J* = 10.4, 9.7 Hz, 5-H), 7.72 (1H, dd, *J* = 9.8, 9.7 Hz, 7-H), 7.79 (1H, d, *J* = 15.5 Hz, COCH=C*H*), 7.93 (1H, t, *J* = 9.7 Hz, 6-H), 8.84 (1H, s, 2-H), 9.72 (1H, d, *J* = 10.4 Hz, 8-H), 10.07 (1H, d, *J* = 9.8 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 21.5 (CH_3), 51.3 ($COOCH_3$), 116.0 (=C<), 123.6 (=CH-), 125.0 (=CH-), 128.3 (=CH-), 128.7 (=CH-), 130.8 (=CH-), 131.2 (=CH-), 132.0 (=C<), 132.4 (=C<), 132.5 (=C<), 139.3 (=CH-), 141.1 (=CH-), 142.4 (=CH-), 142.8 (=CH-), 144.2 (=C<), 144.6 (=C<), 165.2 ($COOCH_3$), 186.4 (*C*OCH=CH).

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.69; H, 5.61.

3-Methoxycarbonyl-1-(2-methoxycinnamoyl)azulene (**6e**).

This compound was obtained as red needles (from ethanol) in a yield of 139 mg (80%), mp 142-143 °C; ir (potassium bromide): ν max 1698 (C=O), 1637 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.94 (3H, s, OCH_3), 3.98 (3H, s, $COOCH_3$), 6.96 (1H, d, *J* = 8.4 Hz, 3'-H), 7.02 (1H, t, *J* = 8.4, 7.6 Hz, 4''-H), 7.38 (1H, dd, *J* = 7.6, 7.5 Hz, 5'-H), 7.73 (1H, d, *J* = 7.5 Hz, 6'-H), 7.78 (1H, d, *J* = 15.6 Hz, COCH=), 7.81 (1H, dd, *J* = 10.2, 9.6 Hz, 5-H), 7.88 (1H, dd, *J* = 10.2, 9.0 Hz, 7-H), 8.03 (1H, dd, *J* = 10.2, 9.6 Hz, 6-H), 8.18 (1H, d, *J* = 15.6 Hz, COCH=C*H*), 8.93 (1H, s, 2-H), 9.82 (1H, d, *J* = 10.2 Hz, 8-H), 10.15 (1H, d, *J* = 10.2 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.3 ($COOCH_3$), 55.2 (OCH_3), 111.2 (=CH-), 116.0 (=C<), 120.6 (=CH-), 124.3 (=C<), 125.3 (=C<), 125.4 (=CH-), 128.7 (=CH-), 131.2 (=CH-), 131.3 (=CH-), 132.0 (=CH-), 137.9 (=CH-), 139.3 (=CH-), 141.1 (=CH-), 141.3 (=CH-), 143.1 (=CH-), 144.4 (=C<), 144.7 (=C<), 158.6 (=C<), 165.4 ($COOCH_3$), 187.2 (*C*OCH=CH).

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.12; H, 5.17.

3-Methoxycarbonyl-1-(3-methoxycinnamoyl)azulene (**6f**).

This compound was obtained as red needles (from ethanol) in a yield of 158 mg (91%), mp 105-106 °C; ir (potassium bromide): ν max 1697 (C=O), 1648 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.87 (3H, s, OCH_3), 4.00 (3H, s, $COOCH_3$), 6.95 (1H, d, *J* = 7.8 Hz, 6'-H), 7.20 (1H, s, 2-H), 7.29-7.36 (2H, m, 4'-,5'-H), 7.68 (1H, d, *J* = 15.6 Hz, COCH=), 7.70 (1H, dd, *J* = 10.2, 9.9 Hz, 5-H), 7.77 (1H, t, *J* = 9.9 Hz, 7-H), 7.79 (1H, t, *J* = 9.9 Hz, 6-H), 8.88 (1H, s, 2-H), 9.77 (1H, dd, *J* = 9.9 Hz, 8-H), 10.10 (1H, d, *J* = 10.2 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.3 ($COOCH_3$), 55.3 (OCH_3), 113.4 (=CH-), 115.7 (=CH-), 116.0 (=C<), 121.0 (=CH-), 124.8 (=C<), 129.8 (=CH-), 131.4 (=CH-), 132.2 (=CH-), 136.6 (=C<), 139.4 (=CH-), 141.2 (=CH-), 141.3 (=CH-), 142.2 (=CH-), 142.9 (=CH-), 144.3 (=C<), 144.7 (=C<), 159.8 (=C<), 165.2 ($COOCH_3$), 186.3 (*C*OCH=CH).

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 75.98; H, 5.35.

3-Methoxycarbonyl-1-(4-methoxycinnamoyl)azulene (**6g**).

This compound was obtained as red needles (from ethanol) in a yield of 135 mg (78%), mp 182-183 °C; ir (potassium bromide): ν max 1704 (C=O), 1648 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.86 (3H, s, OCH_3), 4.00 (3H, s, $COOCH_3$), 6.95 (1H, d, *J* = 8.7 Hz, 3''-,5''-H), 7.60 (1H, d, *J* = 15.6 Hz, COCH=), 7.66 (1H, d, *J* = 15.6 Hz, COCH=C*H*), 7.76-7.86 (2H, m, 5-,7-H), 8.01 (1H, dd, *J* = 10.2, 9.9 Hz, 6-H), 8.92 (1H, s, 2-H), 9.81 (1H, d, *J* = 9.9 Hz, 8-H), 10.14 (1H, d, *J* = 10.2 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.4 ($COOCH_3$), 55.4 (OCH_3), 114.4 (=CH-), 116.0 (=C<), 122.5 (=CH-), 125.3 (=C<), 128.0 (=C<), 130.1 (=CH-), 131.3 (=CH-), 132.0 (=CH-), 139.4 (=CH-), 141.2 (=CH-), 141.3 (=CH-), 142.3 (=CH-), 142.9 (=CH-), 144.4 (=C<), 144.7 (=C<), 161.4 (=C<), 165.3 ($COOCH_3$), 186.2 (*C*OCH=CH).

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.02; H, 5.23.

1-(2,4-Dimethoxycinnamoyl)-3-methoxycarbonylazulene (**6h**).

This compound was obtained as red needles (from ethanol) in a yield of 90 mg (48%), mp 208-209 °C; ir (potassium bromide): ν max 1709 (C=O), 1641 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.87 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 4.00 (3H, s, $COOCH_3$), 6.49 (1H, d, *J* = 2.4 Hz, 3'-H), 6.55 (1H, dd, *J* = 8.7, 2.4 Hz, 5'-H), 7.66 (1H, d, *J* = 8.7 Hz, 6'-H), 7.70 (1H, d, *J* = 15.6 Hz, COCH=), 7.78 (1H, dd, *J* = 9.9, 9.8 Hz, 5-H), 7.82 (1H, dd, *J* = 9.9, 9.8 Hz, 7-H), 8.01 (1H, t, *J* = 9.8 Hz, 6-H), 8.12 (1H, d, *J* = 15.6 Hz, COCH=C*H*), 8.91 (1H, s, 2-H), 9.80 (1H, d, *J* = 9.9 Hz, 8-H), 10.14 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C nmr

(deuteriochloroform): δ 51.4 ($COOCH_3$), 55.5 (OCH_3), 55.6 (OCH_3), 98.4 (=CH-), 105.4 (=CH-), 115.9 (=C<), 117.5 (=C<), 123.0 (=CH-), 125.7 (=C<), 130.3 (=CH-), 131.1 (=CH-), 131.9 (=CH-), 138.0 (=CH-), 139.3 (=CH-), 141.1 (=CH-), 141.2 (=CH-), 142.9 (=CH-), 144.3 (=C<), 144.5 (=C<), 160.2 (=C<), 162.7 (=C<), 165.5 ($COOCH_3$), 187.3 (COCH=CH).

Anal. Calcd. for $C_{23}H_{20}O_5$: C, 73.39; H, 5.36. Found: C, 73.10; H, 5.17.

1-(2,5-Dimethoxycinnamoyl)-3-methoxycarbonylazulene (**6i**).

This compound was obtained as red needles (from ethanol) in a yield of 105 mg (56%), mp 133-134°C; ir (potassium bromide): ν max 1698 (C=O), 1643 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.85 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 4.00 (3H, s, $COOCH_3$), 6.87 (1H, d, *J* = 9.0 Hz, 3'-H), 6.93 (1H, dd, *J* = 9.0, 2.7 Hz, 4'-H), 7.26 (1H, d, *J* = 2.7 Hz, 6'-H), 7.73 (1H, d, *J* = 15.6 Hz, COCH=), 7.79 (1H, dd, *J* = 9.8, 9.6 Hz, 5-H), 7.82 (2H, dd, *J* = 10.2, 9.6 Hz, 7-H), 8.00 (1H, t, *J* = 9.6 Hz, 6-H), 8.14 (1H, d, *J* = 15.6 Hz, COCH=C*H*), 8.91 (1H, s, 2-H), 9.80 (1H, d, *J* = 10.2 Hz, 8-H), 10.13 (1H, d, *J* = 9.8 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.3 ($COOCH_3$), 55.9 (OCH_3), 56.2 (OCH_3), 112.4 (=CH-), 113.5 (=CH-), 115.9 (=C<), 116.6 (=C<), 125.0 (=CH-), 125.2 (=C<), 125.6 (=CH-), 131.1 (=CH-), 132.0 (=CH-), 137.6 (=CH-), 139.8 (=CH-), 141.2 (=CH-), 141.3 (=CH-), 143.0 (=CH-), 144.3 (=C<), 144.6 (=C<), 153.2 (=C<), 153.5 (=C<), 165.3 ($COOCH_3$), 186.9 (COCH=CH).

Anal. Calcd. for $C_{23}H_{20}O_5$: C, 73.39; H, 5.36. Found: C, 73.60; H, 5.32.

1-(2-Chlorocinnamoyl)-3-methoxycarbonylazulene (**6j**).

This compound was obtained as red needles (from ethanol) in a yield of 125 mg (71%), mp 151-152 °C; ir (potassium bromide): ν max 1706 (C=O), 1648 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.95 (3H, s, $COOCH_3$), 7.28-7.34 (2H, m), 7.52-7.56 (2H, m), 7.57 (1H, d, *J* = 15.2 Hz, COCH=), 7.68 (1H, d, *J* = 15.2 Hz, COCH=C*H*), 7.70 (1H, t, *J* = 9.7 Hz, 5-H), 7.74 (1H, t, *J* = 9.7 Hz, 7-H), 7.93 (1H, t, *J* = 9.7 Hz, 6-H), 8.76 (1H, s, 2-H), 9.68 (1H, d, *J* = 9.7 Hz, 8-H), 10.02 (1H, d, *J* = 9.7 Hz, 4-H).

Anal. Calcd. for $C_{21}H_{15}ClO_3$: C, 71.90; H, 4.31. Found: C, 72.18; H, 4.24.

1-(4-Chlorocinnamoyl)-3-methoxycarbonylazulene (**6k**).

This compound was obtained as red needles (from ethanol) in a yield of 158 mg (90%), mp 178-179 °C; ir (potassium bromide): ν max 1701 (C=O), 1648 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.98 (3H, s, $COOCH_3$), 7.29-7.32 (2H, m), 7.42-7.44 (2H, m), 7.65 (1H, d, *J* = 15.8 Hz, COCH=), 7.79 (1H, dd, *J* = 10.1, 9.7 Hz, 5-H), 7.80 (1H, d, *J* = 15.8 Hz, COCH=C*H*), 7.83 (1H, dd, *J* = 9.7, 9.2 Hz, 7-H), 8.01 (1H, t, *J* = 10.1 Hz, 6-H), 8.87 (1H, s, 2-H), 9.78 (1H, d, *J* = 9.2 Hz, 8-H), 10.12 (1H, d, *J* = 9.7 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.4 ($COOCH_3$), 116.1 (=C<), 124.7 (=C<), 127.0 (=CH-), 127.3 (=C<), 130.2 (=CH-), 130.7 (=CH-), 131.6 (=CH-), 132.3 (=CH-), 133.6 (=C<), 135.4 (=C<), 138.2 (=CH-), 139.5 (=CH-), 141.3 (=CH-), 141.5 (=CH-), 143.0 (=CH-), 144.4 (=C<), 165.2 ($COOCH_3$), 186.0 (COCH=CH).

Anal. Calcd. for $C_{21}H_{15}ClO_3$: C, 71.90; H, 4.31. Found: C, 72.04; H, 4.32.

1-(3,4-Dichlorocinnamoyl)-3-methoxycarbonylazulene (**6l**).

This compound was obtained as red needles (from ethanol) in a yield of 114 mg (59%), mp 181-182 °C; ir (potassium bromide): ν max 1709 (C=O), 1651 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 4.00 (3H, s, $COOCH_3$), 7.43 (1H, d, *J* = 8.7 Hz, 6'-H), 7.46 (1H, d, *J* = 8.7 Hz, 5'-H), 7.62 (1H, d, *J* = 15.3 Hz, COCH=), 7.68 (1H, d, *J* = 15.3 Hz, COCH=C<u>H</u>), 7.72 (1H, s, 2'-H), 7.80 (1H, dd, *J* = 9.3, 8.7 Hz, 5-H), 7.83 (1H, dd, *J* = 9.0, 8.7 Hz, 7-H), 8.02 (1H, t, *J* = 9.9 Hz, 6-H), 8.85 (1H, s, 2-H), 9.78 (1H, d, *J* = 9.3 Hz, 8-H), 10.09 (1H, d, *J* = 10.2 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.4 ($COOCH_3$), 116.2 (=CH-), 124.5 (=C<), 126.0 (=CH-), 127.4 (=CH-), 129.4 (=CH-), 130.8 (=CH-), 131.7 (=CH-), 132.4 (=CH-), 133.1 (=C<), 133.8 (=C<), 135.3 (=C<), 139.4 (=CH-), 139.5 (=CH-), 141.2 (=CH-), 141.5 (=CH-), 142.9 (=C<), 144.4 (=C<), 144.9 (=C<), 165.1 ($COOCH_3$), 185.4 (COCH=CH).

Anal. Calcd. for $C_{21}H_{14}Cl_2O_3$: C, 65.47; H, 3.66. Found: C, 65.92; H, 3.79.

3-Methoxycarbonyl-1-(4-nitrocinnamoyl)azulene (**6m**).

This compound was obtained as red needles (from ethanol) in a yield of 87 mg (48%), mp 255-256 °C; ir (potassium bromide): ν max 1700 (C=O), 1651 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 4.02 (3H, s, $COOCH_3$), 7.80-7.85 (3H, m), 7.84 (2H, d, *J* = 8.4 Hz, 2'-,6'-H), 7.92 (1H, dd, *J* = 10.2, 9.6 Hz, 7-H), 8.09 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 8.30 (2H, d, *J* = 8.4 Hz, 3'-,5'-H), 8.92 (1H, s, 2-H), 9.87 (1H, d, *J* = 10.2 Hz, 8-H), 10.18 (1H, d, *J* = 9.9 Hz, 4-H).

Anal. Calcd. for $C_{21}H_{15}NO_5$: C, 69.80; H, 4.18; N, 3.88. Found: C, 69.82; H, 4.21; N, 3.85.

Preparation of 1-(3-Heterocycle-substituted 2-Propenoyl)-3-methoxycarbonylazulenes (**8a,b**).

General Procedure.

A solution of 1-acetyl-3-methoxycarbonylazulene (**2**) (114 mg, 0.5 mmole) and 2-furancarbaldehyde (**7a**) or 2-thiophenecarbaldehyde (**7b**) (0.75 mmole) in absolute methanol (30 ml) was refluxed for 8-24 hours in the presence of sodium methoxide, prepared from sodium (92 mg, 4.0 mmoles) and absolute methanol (5 ml). The mixture was worked up, as described above, and chromatographed on a column (Merck, Kieselgel 60, 10 g) with benzene as eluent to give 1-(3-heterocycle-substituted 2-propenoyl)-3-methoxycarbonylazulenes **8a,b**.

1-[3-(2-Furyl)-2-propenoyl]-3-methoxycarbonylazulene (**8a**).

This compound was obtained as red needles (from ethanol) in a yield of 141 mg (92%), mp 201-203 °C; ir (potassium bromide): ν max 1698 (C=O), 1649 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 4.00 (3H, s, $COOCH_3$), 6.52 (1H, dd, *J* = 3.3, 1.8 Hz, 4'-H), 6.72 (1H, d, *J* = 3.3 Hz, 5'-H), 7.55 (1H, d, *J* = 1.8 Hz, 3'-H), 7.60 (1H, d, *J* = 15.3 Hz, COCH=), 7.67 (2H, d, *J* = 15.3 Hz, COCH=C*H*), 7.81 (1H, dd, *J* = 9.9, 9.6 Hz, 5'-H), 7.84 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 8.03 (1H, t, *J* = 9.9 Hz, 6-H), 8.94 (1H, s, 2-H), 9.82 (1H, d, *J* = 9.9 Hz, 8-H), 10.16 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.4 ($COOCH_3$), 112.5 (=CH-), 115.3 (=CH-), 116.1 (=C<), 122.3 (=CH-), 125.1 (=C<), 128.6 (=C<), 131.4 (=CH-), 132.2 (=CH-), 139.4 (=CH-), 141.2 (=CH-), 141.4 (=CH-), 143.0 (=CH-), 144.5 (=C<), 144.8 (=C<), 152.0 (=CH-), 165.4 ($COOCH_3$), 186.1 (COCH=CH).

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.32; H, 4.65.

3-Methoxycarbonyl-1-[3-(2-thienyl)-2-propenoyl]azulene (**8b**).

This compound was obtained as redish needles (from ethaqnol) in a yield of 110 mg (68%), mp 177-178 °C; ir (potassium bromide): ν max 1699 (C=O), 1638 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 4.01 (3H, s, $COOCH_3$), 7.10 (1H, dd, *J* = 5.0, 3.8 Hz, 4'-H), 7.38 (1H, d, *J* = 3.8 Hz, 5'-H), 7.41 (1H, d, *J* = 5.0 Hz, 3'-H), 7.52 (1H, d, *J* = 15.3 Hz, 3'-H), 7.82 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.84 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.97 (1H, d, *J* = 15.3 Hz, COCH=C*H*), 8.03 (1H, t, *J* = 9.0 Hz, 6'-H), 8.90 (1H, s, 2-H), 9.82 (1H, d, *J* = 9.9 Hz, 8-H), 10.14 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.4 ($COOCH_3$), 116.1 (=C<), 123.6 (=CH-), 125.0 (=C<), 128.1 (=CH-), 128.2 (=CH-), 131.4 (=CH-), 131.5 (=CH-), 132.3 (=C<), 135.0 (=CH-), 139.5 (=CH-), 140.8 (=CH-), 141.3 (=CH-), 141.4 (=CH-), 142.9 (=CH-), 144.4 (=C<), 144.8 (=C<), 165.4 (*C*OCH_3), 185.9 (*C*OCH=CH).

Anal. Calcd. for $C_{19}H_{14}O_3S$: C, 70.79; H, 4.38. Found: C, 71.07; H, 4.39.

Synthesis of 1-(6-Aryl-3-cyano-2-methoxy-4-pyridyl)-3-methoxycarbonylazulenes (**9a-e**).

General Procedure.

A solution of 1-(3-aryl-3-oxopropenyl)-3-methoxycarbonylazulene **4a-e** (0.5 mmole) and malononitrile (46 mg, 0.75 mmole) in methanol (10 ml) was refluxed for 24 hours in the presence of sodium methoxide, prepared from sodium (46 mg, 2.0 mmoles) and aboslute methanol (5 ml). The reaction mixture was worked up, as described above, to give 1-(6-aryl-3-cyano-2-methoxy-4-pyridyl)-3-methoxy-carbonylazulenes **9a-e**.

3-Methoxycarbonyl-1-(6-phenyl-3-cyano-2-methoxy-4-pyridyl)azulene (**9a**).

This compound was obtained as violet needles (from methanol) in a yield of 95 mg (48%), mp 274-275 °C; ir (potassium bromide): ν max 2216 (CN), 1683 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.98 (3H, s, $COOCH_3$), 4.24 (3H, s, OCH_3), 7.49-7.51 (3H, m, 3"-,4"-,5"-H), 7.57 (1H, s, 2-H), 7.58 (1H, dd, *J* = 9.9, 9.6 Hz, 5H), 7.70 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.94 (1H, t, *J* = 9.6 Hz, 6-H), 8.09-8.13 (2H, m, 2"-,6"-H), 8.51 (1H, d, *J* = 9.9 Hz, 8'-H), 8.63 (1H, s, 5'-H), 9.81 (1H, d, *J* = 9.9 Hz, 4'-H); ^{13}C nmr (deuteriochloroform): δ 51.4 ($COOCH_3$), 54.6 (OCH_3), 94.5 (=C<), 115.1 (=CH-), 115.8 (=C<), 116.6 (=C<), 123.9 (=CH-), 127.3 (=CH-), 128.3 (=CH-), 128.4 (=CH-), 128.9 (=CH-), 129.4 (=CH-), 130.4 (=CH-), 137.1 (=CH-), 137.4 (=C<), 139.2 (=CH-), 140.5 (=C<), 140.7 (=CH-), 142.4 (=C<), 151.8 (=C<), 157.7 (=C<), 165.2 (CN), 165.4 (*C*$OOCH_3$).

Anal. Calcd. for $C_{25}H_{18}N_2O_3$: C, 76.13; H, 4.60; N, 7.10. Found: C, 76.21; H, 4.54; N, 7.28.

1-[3-Cyano-2-methoxy-6-(4-methylphenyl)-4-pyridyl]-3-methoxycarbonylazulene (**9b**).

This compound was obtained as violet needles (from methanol) in a yield of 53 mg (26%), mp 288-289 °C; ir (potassium bromide): ν max 2214 (CN), 1693 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.43 (3H, s, CH_3), 3.98 (3H, s, $COOCH_3$), 4.23 (3H, s, OCH_3), 7.30 (1H, d, *J* = 8.1 Hz, 3"-,5"-H), 7.53 (1H, s, 2-H), 7.58 (1H, t, *J* = 9.9 Hz, 5-H), 7.69 (1H, t, *J* = 9.9 Hz, 7-H), 7.93 (1H, t, *J* = 9.9 Hz, 6'-H), 8.01 (2H, d, *J* = 8.1 Hz, 2"-,6"-H), 8.51 (1H, d, *J* = 9.9 Hz, 8-H), 8.62 (1H, s, 5'-H), 9.81 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 21.4 (CH_3), 51.4 ($COOCH_3$), 54.5 (OCH_3), 114.7 (=CH-), 116.5 (=C<), 120.5 (=C<), 124.0 (=C<), 127.3 (=CH-), 128.3 (=CH-), 128.4 (=CH-), 129.3 (=CH-), 129.6 (=CH-), 134.6 (=C<), 137.0 (=CH-), 139.2 (=CH-), 140.5 (=C<), 140.6 (=CH-), 140.7 (=C<), 140.9 (=C<), 142.4 (=C<), 151.6 (=C<), 157.7 (=C<), 165.1 (CN), 165.4 (*C*$OOCH_3$).

Anal. Calcd. for $C_{26}H_{20}N_2O_3$: C, 76.45; H, 4.94; N, 6.86. Found: C, 76.25; H, 4.93; N, 6.93.

1-[3-Cyano-2-methoxy-6-(4-methoxyphenyl)-4-pyridyl]-3-methoxycarbonylazulene (**9c**).

This compound was obtained as violet needles (from methanol) in a yield of 93 mg (44%), mp 297-298 °C ; ir (potassium bromide): ν max 2214 (CN), 1685 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.88 (3H, s, 4"-OCH_3), 3.98 (3H, s, $COOCH_3$), 4.23 (3H, s, 2'-OCH_3), 7.01 (2H, d, *J* = 8.6 Hz, 3"-,5"-H), 7.49 (1H, s, 2-H), 7.58 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.70 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.94 (1H, t, *J* = 9.9 Hz, 6-H), 8.09 (2H, d, *J* = 8.6 Hz, 2"-,6"-H), 8.51 (1H, t, *J* = 9.6 Hz, 8-H), 8.62 (1H, s, 5'-H), 9.81 (1H, d, *J* = 9.6 Hz, 4-H).

Anal. Calcd. for $C_{26}H_{20}N_2O_4$: C, 73.57; H, 4.75; N, 6.60. Found: C, 73.35; H, 4.69; N, 6.51.

1-[6-(4-Chlorophenyl)-3-cyano-2-methoxy-4-pyridyl]-3-methoxycarbonylazulene (**9d**).

This compound was obtained as violet needles (from methanol) in a yield of 96 mg (45%), mp 287-288 °C; ir (potassium bromide): ν max 2221 (CN), 1698 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 4.00 (3H, s, $COOCH_3$), 4.23 (3H, s, OCH_3), 7.47 (2H, d, *J* = 8.9 Hz, 3"-,5"-H), 7.54 (1H, s, 2-H), 7.60 (1H, t, *J* = 9.9 Hz, 5-H), 7.72 (1H, t, *J* = 9.9 Hz, 7-H), 7.96 (2H, t, *J* = 9.9 Hz, 6-H), 8.06 (2H, d, *J* = 8.9 Hz, 2"-,6"-H), 8.50 (1H, d, *J* = 9.9 Hz, 8-H), 8.62 (1H, s, 5'-H), 9.83 (1H, d, *J* = 9.9 Hz, 4-H).

Anal. Calcd. for $C_{25}H_{17}ClN_2O_3$: C, 70.01; H, 4.00; N, 6.53. Found: C, 70.37; H, 4.04; N, 6.40.

Deesterification of 1-(6-Aryl-3-cyano-2-methoxy-4-pyridyl)-3-methoxycarbonylazulenes (**9a-d**).

General Procedure.

The ester compound **9a-d** (0.5 mmole) was heated in 100% phosphric acid (10 ml) for 30 minutes at 95-100 °C in an oil bath. The mixture was poured into water and extracted with benzene. The extract was washed with water and dried over sodium sulfate. The evaporation residue was purified by using a silica gel column (Merck, Kieselgel 60, 10 g) with benzene to give 1-(6-aryl-3-cyano-2-methoxy-4-pyridyl)azulenes **10a-d**.

1-(6-Phenyl-3-cyano-2-methoxy-4-pyridyl)azulene (**10a**).

This compound was obtained as green needles (from benzene) in a yield of 116 mg (69%), mp 122-123 °C; ir (potassium bromide): ν max 2213 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 4.21 (3H, s, OCH_3), 7.31 (2H, dd, *J* = 9.9, 9.6 Hz, 5'-,7'-H), 7.46 (3H, m, 3"-,4"-,5"-H), 7.47 (1H, d, *J* = 4.1 Hz, 3-H), 7.57 (1H, s, 5'-H), 7.70 (1H, t, *J* = 9.9 Hz, 6-H), 8.08 (2H, d, *J* = 8.1 Hz, 2'-,6"-H), 8.22 (1H, d, *J* = 4.1 Hz, 2-H), 8.42 (1H, d, *J* = 9.6 Hz, 4-H), 8.44 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.4 (OCH_3), 94.1 (=C<), 115.1 (=CH-), 116.3 (=C<), 118.2 (=CH-), 124.4 (=C<), 125.1 (=CH-), 127.3 (=CH-), 128.8 (=CH-), 130.2 (=CH-), 135.4 (=CH-), 136.6 (=C<), 137.6 (=C<), 137.9 (=CH-), 138.1 (=CH-), 138.9 (=CH-), 142.8 (=C<), 152.4 (=CH-), 157.2 (=C<), 165.3 (CN).

Anal. Calcd. for $C_{23}H_{16}N_2O$: C, 82.12; H, 4.80; N, 8.33. Found: C, 81.97; H, 4.86; N, 8.24.

1-[3-Cyano-2-methoxy-6-(4-methylphenyl)-4-pyridyl]-azulene (**10b**).

This compound was obtained as blue needles (from benzene) in a yield of 98 mg (56%), mp 145-146 °C; ir (potassium bromide): ν max 2217 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 2.42 (3H, s, CH_3), 4.21 (3H, s, OCH_3), 7.29 (2H, d, J = 8.4 Hz, 3"-,5"-H), 7.33 (2H, t, J = 9.9 Hz, 5-,7-H), 7.49 (1H, d, J = 3.9 Hz, 3-H), 7.56 (1H, s, 5'-H), 7.72 (1H, t, J = 9.9 Hz, 6-H), 7.99 (2H, d, J = 8.4 Hz, 2"-,6"-H), 8.23 (1H, d, J = 3.9 Hz, 2-H), 8.45 (2H, d, J = 9.9 Hz, 4'-,8'-H); ^{13}C nmr (deuteriochloroform): δ 54.4 (OCH_3), 93.7 (=C<), 114.8 (=CH-), 116.4 (=C<), 118.2 (=CH-), 124.5 (=C<), 125.1 (=CH-), 126.4 (=C<), 127.3 (=CH-), 129.6 (=CH-), 134.9 (=CH-), 135.4 (=C<), 136.6 (=C<), 137.9 (=CH-), 138.1 (=CH-), 138.9 (=CH-), 140.6 (=CH-), 142.8 (=C<), 152.3 (=CH-), 157.3 (=C<), 165.3 (CN).

Anal. Calcd. for $C_{24}H_{18}N_2O$: C, 82.26; H, 5.18; N, 8.00. Found: C, 82.08; H, 5.27; N, 7.81.

1-[3-Cyano-2-methoxy-6-(4-methoxyphenyl)-4-pyridyl]-azulene (**10c**).

This compound was obtained as blue needles (from benzene) in a yield of 110 mg (60%), mp 195-196 °C; ir (potassium bromide): ν max 2216 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 3.87 (3H, s, 4"-OCH_3), 4.21 (3H, s, 2'-OCH_3), 6.99 (2H, d, J = 7.4 Hz, 3"-,5"-H), 7.32 (2H, dd, J = 9.9, 9.6 Hz, 5-,7-H), 7.48 (1H, d, J = 3.9 Hz, 3-H), 7.51 (1H, s, 5'-H), 7.72 (1H, t, J = 9.9 Hz, 6-H), 8.07 (2H, d, J = 7.4 Hz, 2"-,6"-H), 8.22 (1H, d, J = 3.9 Hz, 2-H), 8.44 (1H, d, J = 9.6 Hz, 4-H), 8.45 (1H, d, J = 9.6 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.4 (OCH3), 55.4 (OCH_3), 93.2 (=C<), 114.2 (=CH-), 116.6 (=C<), 118.2 (=CH-), 124.6 (=C<), 125.0 (=CH-), 128.8 (=CH-), 130.2 (=C<), 135.5 (=CH-), 136.6 (=C<), 137.9 (=CH-), 138.1 (=CH-), 138.9 (=CH-), 142.8 (=C<), 152.2 (=C<), 156.9 (=C<), 161.5 (=C<), 165.3 (CN).

Anal. Calcd. for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.82; H, 5.11; N, 7.76.

1-[6-(4-Chlorophenyl)-3-cyano-2-methoxy-4-pyridyl]azulene (**10d**).

This compound was obtained as green needles (from benzene) in a yield of 87 mg (47%), mp 225-226 °C; ir (potassium bromide): ν max 2221 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 4.21 (3H, s, OCH_3), 7.35 (2H, dd, J = 9.9, 9.6 Hz, 5-,7-H), 7.46 (2H, d, J = 7.7 Hz, 3"-,5"-H), 7.49 (1H, d, J = 3.9 Hz, 3-H), 7.56 (1H, s, 5'-H), 7.74 (1H, t, J = 9.9 Hz, 6-H), 8.04 (2H, d, J = 7.7 Hz, 2"-,6"-H), 8.22 (1H, d, J = 3.9 Hz, 2-H), 8.44 (1H, d, J = 9.6 Hz, 4-H), 8.46 (1H, d, J = 9.6 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.5 (OCH_3), 94.4 (=C<), 115.0 (=CH-), 116.2 (=C<), 118.3 (=CH-), 124.2 (=C<), 125.2 (=CH-), 125.3 (=CH-), 128.5 (=CH-), 129.0 (=CH-), 135.4 (=CH-), 136.1 (=C<), 136.4 (=C<), 136.6 (=C<), 137.9 (=CH-), 138.2 (=CH-), 139.0 (=CH-), 142.9 (=C<), 152.2 (=C<), 155.9 (=C<), 165.3 (CN).

Anal. Calcd. for $C_{23}H_{15}ClN_2O$: C, 74.49; H, 4.08; N, 7.56. Found: C, 74.23; H, 4.16; N, 7.54.

Preparation of 1-(4-Aryl-3-cyano-2-methoxy-6-pyridyl)-3-methoxycarbonylazulenes (**11a-l**).

General Procedure.

A solution of 1-cinnamoyl-3-methoxycarbonylazulene **6a-l** (0.5 mmole) and malononitrile (46 mg, 0.75 mmole) in methanol (10 ml) was stirred for 2-20 hours at 50 °C in the presence of sodium methoxide, prepared from sodium (46 mg, 2.0 mmoles) and aboslute methanol (5 ml). The reaction mixture was diluted with water and extracted with chloroform. The evaporation redidue was recrystallized from ethanol to give 1-(4-aryl-3-cyano-2-methoxy-6-pyridyl)-3-methoxycarbonylazulenes **11a-l**.

1-(3-Cyano-2-methoxy-4-phenyl-6-pyridyl)-3-methoxycarbonylazulene (**11a**).

This compound was obtained as brown needles (from ethanol) in a yield of 99 mg (50%), mp 234-235 °C; ir (potassium bromide): ν max 2220 (CN), 1712 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.97 (3H, s, $COOCH_3$), 4.23 (3H, s, OCH_3), 7.51 (1H, s, 2-H), 7.52-7.54 (3H, m), 7.61-7.70 (4H, m), 7.92 (1H, t, J = 9.6 Hz, 6-H), 8.77 (1H, s, 5'-H), 9.75 (1H, d, J = 9.6 Hz, 8-H), 10.04 (1H, d, J = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.4 ($COOCH_3$), 54.8 (OCH_3), 90.9 (=C<), 115.6 (=CH-), 115.9 (=CH<), 116.2 (=C<), 128.4 (=CH-), 129.0 (=CH-), 129.4 (=CH-), 129.8 (=CH-), 129.9 (=CH-), 136.4 (=C<), 138.9 (=CH-), 139.6 (=CH-), 140.8 (=CH-), 140.9 (=CH-), 141.5 (=C<), 143.9 (=C<), 155.9 (=C<), 156.6 (=C<), 164.9 (CN), 165.3 ($COOCH_3$).

Anal. Calcd. for $C_{25}H_{18}N_2O_3$: C, 76.13; H, 4.60; N, 7.10. Found: C, 76.19; H, 4.61; N, 7.14.

1-[3-Cyano-2-methoxy-4-(2-methylphenyl)-6-pyridyl]-3-methoxycarbonylazulene (**11b**).

This compound was obtained as brown needles (from ethanol) in a yield of 82 mg (40%), mp 260-261 °C; ir (potassium bromide): ν max 2224 (CN), 1684 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.32 (3H, s, CH_3), 3.95 (3H, s, $COOCH_3$), 4.26 (3H, s, OCH_3), 7.28-7.38 (4H, m), 7.42 (1H, s, 2-H), 7.66 (1H, t, J = 9.9 Hz, 7-H), 8.76 (1H, s, 5'-H), 9.76 (1H, d, J = 9.9 Hz, 8-H), 10.04 (1H, d, J = 10.2 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 19.9 (CH_3), 51.4 ($COOCH_3$), 54.7 (OCH_3), 92.9 (=C<), 115.4 (=C<), 116.3 (=CH-), 116.7 (=C<), 124.5 (=C<), 126.1(=CH-), 128.7 (=CH-), 129.3 (=CH-), 129.4 (=CH-), 129.9 (=CH-), 130.7 (=CH-), 135.2 (=C<), 136.4 (=C<), 139.0 (=CH-), 139.6 (=CH-), 140.9(=CH-), 141.5 (=C<), 143.9 (=C<), 156.4 (=C<), 156.9 (=C<), 164.3 (CN), 165.3 ($COOCH_3$).

Anal. Calcd. for $C_{26}H_{20}N_2O_3$: C, 76.45; H, 4.94; N, 6.86. Found: C, 76.45; H, 4.97; N, 6.97.

1-[3-Cyano-2-methoxy-4-(3-methylphenyl)-6-pyridyl]-3-methoxycarbonylazulene (**11c**).

This compound was obtained as brown needles (from ethanol) in a yield of 74 mg (36%), mp 235-236 °C; ir (potassium bromide): ν max 2226 (CN), 1678 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.47 (3H, s, CH_3), 3.98 (3H, s, $COOCH_3$), 4.25 (3H, s, OCH_3), 7.33 (1H, d, J = 7.5 Hz, 4"-H), 7.43 (1H, t, J = 7.5 Hz, 5"-H), 7.50 (1H, s, 2-H), 7.49 (1H, d, J = 7.5 Hz, 6"-H), 7.53 (1H, s, 2"-H), 7.66 (1H, t, J = 9.9 Hz, 5-H), or 7'-H), 7.69 (1H, t, J = 9.9 Hz, 7-H), 7.94 (1H, t, J = 9.9 Hz, 6-H), 8.80 (1H, s, 5'-H), 9.76 (1H, d, J = 9.9 Hz, 8-H), 10.06 (1H, d, J = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 21.4 (CH_3), 51.4 ($COOCH_3$), 54.8 (OCH_3), 115.7 (=CH-), 115.9 (=C<), 116.6 (=C<), 124.7 (=C<), 125.5 (=CH-), 128.8 (=CH-), 128.9 (=CH-), 129.4 (=CH-), 129.8 (=CH-), 130.7 (=CH-), 134.3 (=C<), 136.4 (=C<), 138.7 (=CH-), 139.0 (=CH-), 139.6 (=CH-), 140.9 (=CH-), 141.5 (=C<), 143.9 (=C<), 156.4 (=C<), 156.2 (=C<), 156.5 (=C<), 164.3 (CN), 165.4 ($COOCH_3$).

Anal. Calcd. for $C_{26}H_{20}N_2O_3$: C, 76.45; H, 4.94; N, 6.86. Found: C, 76.22; H, 4.98; N, 6.70.

1-[3-Cyano-2-methoxy-4-(4-methylphenyl)-6-pyridyl]-3-methoxycarbonylazulene (**11d**).

This compound was obtained as brown needles (from ethanol) in a yield of 86 mg (42%), mp 242-243 °C; ir (potassium bromide): ν max 2222 (CN), 1698 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 2.44 (3H, s, CH_3), 3.97 (3H, s, $COOCH_3$), 4.21 (3H, s,OCH_3), 7.33 (2H, d, J = 7.7 Hz, 3"-,5"-H), 7.47 (1H, s, 2-H), 7.57 (2H, d, J = 7.7 Hz, 2"-,6"-H), 7.61 (1H, t, J = 9.7 Hz, 5-H), 7.64 (1H, dd, J = 9.9, 9.7 Hz, 7-H), 7.90 (1H, t, J = 9.7 Hz, 6'-H), 8.74 (1H, s, 5'-H), 9.73 (1H, d, J = 9.9 Hz, 8-H), 10.01 (1H, d, J = 9.7 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 21.4 (CH_3), 51.3 ($COOCH_3$), 54.7 (OCH_3), 90.9 (=C<), 115.5 (=CH-), 115.7 (=C<), 116.0 (=C<), 116.6 (=C<), 124.7 (=C<), 128.3 (=CH-), 129.3 (=CH-), 129.6 (=CH-), 129.7 (=CH-), 133.5 (=C<), 138.9 (=CH-), 139.6 (=CH-), 140.2 (=CH-), 140.8 (=CH-), 141.5 (=C<), 143.8 (=C<), 155.9 (=C<), 156.4 (=C<), 165.0 (CN), 165.3 ($COOCH_3$).

Anal. Calcd. for $C_{26}H_{20}N_2O_3$: C, 76.45; H, 4.94; N, 6.86. Found: C, 76.42; H, 4.96; N, 6.77.

1-[3-Cyano-2-methoxy-4-(2-methoxyphenyl)-6-pyridyl]-3-methoxycarbonylazulene (**11e**).

This compound was obtained as brown needles (from acetic acid) in a yield of 100 mg (47%), mp 261-262 °C; ir (potassium bromide): ν max 2217 (CN), 1687 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.90 (3H, s, 2"-OCH_3), 3.97 (3H, s, $COOCH_3$), 4.24 (3H, s, 2'-OCH_3), 7.06 (1H, dd, J = 7.5, 7.2 Hz, 5"-H), 7.07 (1H, dd, J = 7.7, 7.2 Hz, 4"-H), 7.35 (1H, d, J = 7.7 Hz, 3"-H), 7.45 (1H, d, J = 7.5 Hz, 6"-H), 7.49 (1H, s, 2-H), 7.64 (1H, dd, J = 9.9, 9.6 Hz, 5-H), 7.67 (1H, t, J = 9.9 Hz, 7-H), 7.92 (1H, t, J = 9.9 Hz, 6-H), 8.77 (1H, s, 5'-H), 9.75 (1H, d, J = 9.9 Hz, 8-H), 10.03 (1H, d, J = 9.6 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.3 ($COOCH_3$), 54.6 (OCH_3), 91.3 (=C<), 115.5 (=CH-), 115.8 (=C<), 116.5 (=C<), 116.9 (=CH-), 120.9 (=CH-), 125.0 (=C<), 125.6 (=C<), 129.2 (=CH-), 129.6 (=CH-), 130.2 (=CH-), 131.2 (=CH-), 135.7 (=C<), 138.9 (=CH-), 139.6 (=CH-), 140.7 (=CH-), 140.9 (=CH-), 143.8 (=C<), 148.8 (=C<), 153.7 (=C<), 156.3 (=C<), 164.3 (CN), 165.4 ($COOCH_3$).

Anal. Calcd. for $C_{26}H_{20}N_2O_4$: C, 73.57; H, 4.75; N, 6.60. Found: C, 73.57; H, 4.66; N, 6.52.

1-[3-Cyano-2-methoxy-4-(3-methoxyphenyl)-6-pyridyl]-3-methoxycarbonylazulene (**11f**).

This compound was obtained as brown needles (from acetic acid) in a yield of 49 mg (23%), mp 226-227 °C; ir (potassium bromide): ν max 2217 (CN), 1706 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.90 (3H, s, 3"-OCH_3), 3.98 (3H, s, $COOCH_3$), 4.24 (3H, s, 2'-OCH_3), 7.05 (1H, d, J = 8.0 Hz, 4"-H), 7.20 (1H, dd, J = 8.0, 7.5 Hz, 5"-H), 7.45 (1H, t, J = 9.6 Hz, 5-H), 7.49 (1H, d, J = 7.5 Hz, 6"-H), 7.50 (1H, s, 2-H), 7.63 (1H, s, 2"-H), 7.66 (1H, dd, J = 9.9, 9.3 Hz, 7-H), 7.68 (1H, t, J = 9.6 Hz, 6-H), 8.79 (1H, s, 5'-H), 9.76 (1H, d , J = 9.3 Hz, 8-H), 10.06 (1H, d, J = 9.6 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.3 ($COOCH_3$), 54.8 (OCH_3), 55.5 (OCH_3), 91.0 (=C<), 113.9 (=CH-), 115.6 (=C<), 115.8 (=C<), 116.7 (=CH-), 120.7 (=CH-), 124.6 (=C<), 125.8 (=C<), 129.4 (=CH-), 129.8 (=CH-), 130.1 (=CH-), 137.7 (=C<), 139.0 (=CH-), 139.6 (=CH-), 140.9 (=CH-), 141.5 (=CH-), 143.9 (=CH-), 154.1 (=C<), 155.8 (=C<), 156.6 (=C<), 159.8 (=C<), 164.9 (CN), 165.3 ($COOCH_3$).

Anal. Calcd. for $C_{26}H_{20}N_2O_4$: C, 73.57; H, 4.75; N, 6.60. Found: C, 73.33; H, 4.88; N, 6.54.

1-[3-Cyano-2-methoxy-4-(4-methoxyphenyl)-6-pyridyl]-3-methoxycarbonylazulene (**11g**).

This compound was obtained as brown needles (from acetic acid) in a yield of 55 mg (26%), mp 246-247 °C; ir (potassium bromide): ν max 2221 (CN), 1713 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.89 (3H, s, 4"-OCH_3), 3.98 (3H, s, $COOCH_3$), 4.23 (3H, s, 2'-OCH_3), 7.05 (2H, d, J = 6.9 Hz, 3"-,5"-H), 7.50 (1H, s, 2-H), 7.65 (1H, dd, J = 9.9, 9.6 Hz, 5-H), 7.66 (2H, d, J = 6.9 Hz, 2"-,6"-H), 7.67 (1H, dd, J = 9.9, 9.6 Hz, 7-H), 7.93 (1H, t, J = 9.9 Hz, 6-H), 8.78 (1H, s, 5'-H), 9.75 (1H, d, J = 9.6 Hz, 8-H), 10.04 (1H, d, J = 9.6 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.4 ($COOCH_3$), 54.7 (OCH_3), 55.4 (OCH_3), 114.3 (=CH-), 114.8 (=C<), 115.4 (=CH-), 116.3 (=C<), 124.8 (=C<), 128.6 (=C<), 129.3 (=CH-), 129.7 (=CH-), 129.9 (=CH-), 138.9 (=CH-), 139.6 (=CH-), 140.7 (=CH-), 140.8 (=CH-), 141.5 (=C<), 143.8 (=C<), 154.1 (=C<), 155.5 (=C<), 156.4 (=C<), 161.0 (=C<), 165.1 (CN), 165.4 ($COOCH_3$).

Anal. Calcd. for $C_{26}H_{20}N_2O_4$: C, 73.57; H, 4.75; N, 6.60. Found: C, 73.33; H, 4.75; N, 6.57.

1-[3-Cyano-4-(2,4-dimethoxyphenyl)-2-methoxy-6-pyridyl]-3-methoxycarbonylazulene (**11h**).

This compound was obtained as brown needles (from acetic acid) in a yield of 98 mg (43%), mp 286-287 °C; ir (potassium bromide): ν max 2223 (CN), 1684 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.88 (6H, s, 2 x OCH_3), 3.97 (3H, s, $COOCH_3$), 4.23 (3H, s, 2-OCH_3), 6.61 (1H, s, 3"-H), 6.63 (1H, d, J = 8.6 Hz, 5"-H), 7.31 (1H, d, J = 8.6 Hz, 6"-H), 7.49 (1H, s, 2-H), 7.64 (1H, dd, J = 10.2, 9.9 Hz, 5-H), 7.67 (1H, d, J = 9.9 Hz, 7-H), 7.93 (1H, t, J = 9.9 Hz, 6-H), 8.78 (1H, s, 5'-H), 9.75 (1H, d, J = 9.9 Hz, 8-H), 10.02 (1H, d, J = 10.2 Hz, 4-H).

Anal. Calcd. for $C_{27}H_{22}N_2O_5$: C, 71.35; H, 4.88; N, 6.17. Found: C, 71.41; H, 5.00; N, 6.14.

1-[3-Cyano-4-(2,5-dimethoxyphenyl)-2-methoxy-6-pyridyl]-3-methoxycarbonylazulene (**11i**).

This compound was obtained as brown needles (from acetic acid) in a yield of 141 mg (62%), mp 234-235 °C; ir (potassium bromide): ν max 2223 (CN), 1683 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.83 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), 3.97 (3H, s, $COOCH_3$), 4.24 (3H, s, 2'-OCH_3), 6.99 (2H, s, 3"-,4"-H), 7.26 (1H, s, 6"-H), 7.49 (1H, s, 2-H), 7.65 (1H, dd, J = 10.2, 9.6 Hz, 5-H), 7.67 (1H, t, J = 9.9 Hz, 7-H), 7.93 (1H, t, J = 9.6 Hz, 6-H), 8.78 (1H, s, 5'-H), 9.76 (1H, d, J = 9.9 Hz, 8-H), 10.03 (1H, d, J = 10.2 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.3 ($COOCH_3$), 54.7 (OCH_3), 55.9 (OCH_3), 56.1 (OCH_3), 93.3 (=C<), 112.6 (=CH-), 115.7 (=C<), 115.9 (=CH-), 116.6 (=C<), 116.8 (=CH-), 124.9 (=C<), 126.1 (=C<), 129.2 (=CH-), 129.6 (=CH-), 138.9 (=CH-), 139.6 (=CH-), 140.7 (=CH-), 140.9 (=CH-), 141.4 (=C<), 143.8 (=C<), 150.5 (=C<), 153.4 (=C<), 153.5 (=C<), 156.4 (=C<), 164.3 (CN), 165.4 ($COOCH_3$).

Anal. Calcd. for $C_{27}H_{22}N_2O_5$: C, 71.35; H, 4.88; N, 6.17. Found: C, 71.60; H, 4.98; N, 6.10.

1-[4-(2-Chlorophenyl)-3-cyano-2-methoxy-6-pyridyl]-3-methoxycarbonylazulene (**11j**).

This compound was obtained as brown needles (from acetic acid) in a yield of 109 mg (51%), mp 252-253 °C; ir (potassium

bromide): ν max 2221 (CN), 1690 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 4.00 (3H, s, $COOCH_3$), 4.26 (3H, s, OCH_3), 7.51 (1H, s, 2-H), 7.52-7.63 (4H, m), 7.64 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.70 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.95 (1H, t, *J* = 9.6 Hz, 6-H), 8.80 (1H, s, 5'-H), 9.78 (1H, d, *J* = 9.9 Hz, 8-H), 10.06 (1H, d, *J* = 9.9 Hz, 4-H).

Anal. Calcd. for $C_{25}H_{17}ClN_2O_3$: C, 70.01; H, 4.00; N, 6.53. Found: C, 70.07; H, 3.96; N, 6.36.

1-[4-(4-Chlorophenyl)-3-cyano-2-methoxy-6-pyridyl]-3-methoxycarbonylazulene (**11k**).

This compound was obtained as brown needles (from acetic acid) in a yield of 96 mg (45%), mp 233-234 °C; ir (potassium bromide): ν max 2224 (CN), 1694 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.98 (3H, s, $COOCH_3$), 4.26 (3H, s, OCH_3), 7.51 (1H, s, 2-H), 7.52 (2H, d, *J* = 6.6 Hz, 2"-,6"-H), 7.63 (2H, d, *J* = 6.6 Hz, 3"-,5"-H), 7.68 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.72 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.96 (1H, t, *J* = 9.9 Hz, 6-H), 8.80 (1H, s, 5'-H), 9.78 (1H, d, *J* = 9.3 Hz, 8-H), 10.07 (1H, d, *J* = 9.3 Hz, 4-H).

Anal. Calcd. for $C_{25}H_{17}ClN_2O_3$: C, 70.01; H, 4.00; N, 6.53. Found: C, 70.05; H, 4.10; N, 6.41.

1-[3-Cyano-4-(3,4-dihlorophenyl)-2-methoxy-6-pyridyl]-3-methoxycarbonylazulene (**11l**).

This compound was obtained as brown needles (from acetic acid) in a yield of 127 mg (55%), mp 288-289 °C; ir (potassium bromide): ν max 2222 (CN), 1708 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 4.00 (3H, s, $COOCH_3$), 4.26 (3H, s, OCH_3), 7.50 (1H, s, 2-H), 7.55 (1H, d, *J* = 8.1 Hz, 5"-H), 7.63 (2H, d, *J* = 8.1 Hz, 6"-H), 7.69 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.73 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.75 (1H, d, *J* = 1.8 Hz, 2"-H), 7.97 (1H, t, *J* = 9.9 Hz, 6-H), 8.82 (1H, s, 5'-H), 9.79 (1H, d, *J* = 9.6 Hz, 8-H), 10.08 (1H, d, *J* = 9.6 Hz, 4-H).

Anal. Calcd. for $C_{25}H_{16}Cl_2N_2O_3$: C, 64.81; H, 3.48; N, 6.05. Found: C, 64.09; H, 3.68; N, 5.82.

Deesterification of 1-(4-Aryl-3-cyano-2-methoxy-6-pyridyl)-3-methoxycarbonylazulenes (**11a-l**).

General Procedure.

The ester compound **11a-l** (0.5 mmole) was heated in 100% phosphric acid (10 ml) for 30 minutes at 95-100 °C in an oil bath. The mixture was poured into water and extracted with benzene. The extract was washed with water and dried over sodium sulfate. The evaporation residue was purified by using a silica gel column (Merck, Kiesegel 60, 10 g) with benzene to give 1-(4-aryl-3-cyano-2-methoxy-6-pyridyl)azulenes **12a-l**.

1-(3-Cyano-2-methoxy-4-phenyl-6-pyridyl)azulene (**12a**).

This compound was obtained as green needles (from benzene) in a yield of 91 mg (54%), mp 145-146 °C; ir (potassium bromide): ν max 2219 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 4.21 (3H, s, OCH_3), 7.30-7.42 (5H, m), 7.46 (1H, s, 5'-H), 7.48-7.51 (2H, m), 7.64 (1H, d, *J* = 4.3 Hz, 3-H), 7.70 (1H, t, *J* = 9.9 Hz, 6-H), 8.28 (1H, d, *J* = 4.3 Hz, 2-H), 8.36 (1H, d, *J* = 9.9 Hz, 4-H), 9.89 (1H, d, *J* = 10.2 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.6 (OCH_3), 89.9 (=C<), 115.2 (=CH-), 116.2 (=C<), 118.8 (=CH-), 125.4 (=C<), 125.8 (=CH-), 126.3 (=CH-), 128.3 (=CH-), 128.8 (=CH-), 129.7 (=CH-), 136.6 (=C<), 137.4 (=CH-), 137.7 (=C<), 138.0 (=CH-), 138.3 (=CH-), 139.2 (=CH-), 144.7 (=C<), 155.5 (=C<), 157.2 (=C<), 164.9 (CN).

Anal. Calcd. for $C_{23}H_{16}N_2O$: C, 82.12; H, 4.79; N, 8.33. Found: C, 81.61; H, 4.85; N, 8.25.

1-[3-Cyano-2-methoxy-4-(2-methylphenyl)-6-pyridyl]azulene (**12b**).

This compound was obtained as bluish green needles (from benzene) in a yield of 152 mg (87%), mp 137-138 °C; ir (potassium bromide): ν max 2222 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 2.32 (3H, s, CH_3), 4.27 (3H, s, OCH_3), 7.27-7.47 (6H, m), 7.39 (1H, s, 5'-H), 7.40 (1H, d, *J* = 4.2 Hz, 3-H), 7.75 (1H, t, *J* = 9.9 Hz, 6-H), 8.28 (1H, d, *J* = 4.2 Hz, 2-H), 8.41 (1H, d, *J* = 9.9 Hz, 4-H), 9.95 (1H, d, *J* = 10.2 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 19.8 (CH_3), 54.6 (OCH_3), 115.6 (=C<), 115.9 (=CH-), 118.9 (=CH-), 125.4 (=C<), 125.8 (=CH-), 126.0 (=CH-), 126.4 (=CH-), 128.7 (=CH-), 129.2 (=CH-), 130.6 (=CH-), 135.3 (=C<), 135.5 (=C<), 136.7 (=C<), 137.5 (=CH-), 137.7 (=C<), 138.1 (=CH-), 138.4 (=CH-), 139.3 (=CH-), 144.8 (=C<), 156.5 (=C<), 157.1 (=C<), 164.4 (CN).

Anal. Calcd. for $C_{24}H_{18}N_2O$: C, 82.26; H, 5.18; N, 8.00. Found: C, 82.16; H, 5.43; N, 7.90.

1-[3-Cyano-2-methoxy-4-(3-methylphenyl)-6-pyridyl]azulene (**12c**).

This compound was obtained as bluish green needles (from benzene) in a yield of 93 mg (53%), mp 132-133 °C; ir (potassium bromide): ν max 2217 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 2.45 (3H, s, CH_3), 4.24 (3H, s, OCH_3), 7.29-7.46 (5H, m), 7.39 (1H, d, *J* = 4.5 Hz, 3-H), 7.41 (1H, s, 5'-H), 7.48 (1H, s, 2"-H), 7.73 (1H, t, *J* = 9.9 Hz, 6-H), 8.32 (1H, d, *J* = 4.2 Hz, 2-H), 8.39 (1H, d, *J* = 9.6 Hz, 4-H), 9.92 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 21.5 (CH_3), 54.7 (OCH_3), 115.3 (=CH-), 116.2 (=C<), 118.8 (=CH-), 125.4 (=C<), 125.5 (=CH-), 125.7 (=CH-), 126.3 (=CH-), 128.7 (=CH-), 129.9 (=CH-), 130.5 (=CH-), 136.6 (=C<), 137.4 (=CH-), 137.6 (=C<), 138.0 (=CH-), 138.3 (=CH-), 138.6 (=C<), 139.2 (=CH-), 144.7 (=C<), 155.7 (=C<), 157.2 (=C<), 164.9 (CN).

Anal. Calcd for $C_{24}H_{18}N_2O$: C, 82.26; H, 5.18; N, 8.00. Found: C, 81.96; H, 5.35; N, 7.79.

1-[3-Cyano-2-methoxy-4-(4-methylphenyl)-6-pyridyl]azulene (**12d**).

This compound was obtained as bluish green needles (from benzene) in a yield of 133 mg (76%), mp 162-163°C; ir (potassium bromide): ν max 2210 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 2.43 (3H, s, CH_3), 4.23 (3H, s, OCH_3), 7.32 (2H, d, *J* = 7.1 Hz, 3"-,5"-H), 7.34 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.40 (1H, d, *J* = 4.2 Hz, 3-H), 7.41 (1H, dd, *J* = 10.2, 9.9 Hz, 7-H), 7.48 (1H, s, 5'-H), 7.57 (2H, d, *J* = 7.1 Hz, 2"-,6" H), 7.72 (1H, t, *J* = 9.9 Hz, 6-H), 8.31 (1H, d, *J* = 4.2 Hz, 2-H), 8.39 (1H, d, *J* = 9.6 Hz, 4-H), 9.90 (1H, d, *J* = 10.2 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 21.4 (CH_3), 54.7 (OCH_3), 115.2 (=CH-), 116.4 (=C<), 118.8 (=CH-), 125.5 (=C<), 125.7 (=CH-), 126.2 (=CH-), 128.2 (=CH-), 129.6 (=CH-), 133.8 (=C<), 137.4 (=CH-), 137.6 (=C<), 138.0 (=CH-), 138.3 (=CH-), 139.2 (=CH-), 139.9 (=C<), 144.7 (=C<), 155.6 (=C<), 157.2 (=C<), 165.0 (CN).

Anal. Calcd. for $C_{24}H_{18}N_2O$: C, 82.26; H, 5.18; N, 8.00. Found: C, 81.96; H, 5.22; N, 7.98.

1-[3-Cyano-2-methoxy-4-(2-methoxyphenyl)-6-pyridyl]-azulene (**12e**).

This compound was obtained as green needles (from benzene) in a yield of 130 mg (71%), mp 198-199 °C; ir (potassium bromide): ν max 2224 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 3.88 (3H, s, 2"-OCH_3), 4.23 (3H, s, 2'-OCH_3), 7.05 (1H, d, J = 8.1 Hz, 3"-H), 7.09 (1H, d, J = 7.5 Hz, 6"-H), 7.22-7.42 (5H, m), 7.46 (1H, s, 5'-H), 7.71 (1H, t, J = 9.9 Hz, 6-H), 8.28 (1H, d, J = 4.2 Hz, 2-H), 8.38 (1H, d, J = 9.6 Hz, 4-H), 9.88 (1H, d, J = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.5 (OCH_3), 55.5 (OCH_3), 92.3 (=C<), 111.5 (=CH-), 116.1 (=C<), 116.5 (=CH-), 118.7 (=CH-), 120.8 (=CH-), 125.5 (=CH-), 125.7 (=C<), 125.8 (=CH<), 126.1 (=CH-), 130.2 (=CH-), 131.1 (=CH-), 137.5 (=CH-), 137.9 (=C<), 138.2 (=CH-), 139.1 (=CH-), 144.6 (=C<), 153.2 (=C<), 156.4 (=C<), 157.0 (=C<), 164.3 (CN).

Anal. Calcd. for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.75; H, 5.02; N, 7.61.

1-[3-Cyano-2-methoxy-4-(3-methoxyphenyl)-6-pyridyl]-azulene (**12f**).

This compound was obtained as green needles (from benzene) in a yield of 92 mg (50%), mp 167-168 °C; ir (potassium bromide): ν max 2214 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 3.89 (3H, s, 3"-OCH_3), 4.24 (3H, s, 2'-OCH_3), 7.04 (1H, dd, J = 8.4, 2.4 Hz, 4"-H), 7.19-7.25 (2H, m), 7.33 (1H, dd, J = 9.9, 9.3 Hz, 5-H), 7.39-7.46 (2H, m), 7.41 (1H, s, 2"-H), 7.49 (1H, s, 5'-H), 7.73 (1H, t, J = 9.9 Hz, 6-H), 8.31 (1H, d, J = 4.2 Hz, 2-H), 8.40 (1H, d, J = 9.3 Hz, 4-H), 9.92 (1H, d, J = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.7 (OCH_3), 55.4 (OCH_3), 90.0 (=C<), 113.8 (=CH-), 115.3 (=CH-), 115.5 (=CH-), 116.2 (=C<), 118.5 (=CH-), 120.7 (=CH-), 120.8 (=CH-), 125.4 (=C<), 125.8 (=C<), 126.3 (=CH-), 129.7 (=CH-), 137.4 (=CH-), 137.6 (=C<), 138.1 (=CH-), 138.3 (=CH-), 139.3 (=CH-), 144.8 (=C<), 155.4 (=C<), 157.3 (=C<), 159.7 (=C<), 164.9 (CN).

Anal. Calcd. for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.41; H, 5.08; N, 7.50.

1-[3-Cyano-2-methoxy-4-(4-methoxyphenyl)-6-pyridyl]-azulene (**12g**).

This compound was obtained as green needles (from benzene) in a yield of 95 mg (52%), mp 177-178 °C; ir (potassium bromide): ν max 2220 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 3.88 (3H, s, 4"-OCH_3), 4.24 (3H, s, 2'-OCH_3), 7.04 (2H, d, J = 6.9 Hz, 3"-,5"-H), 7.33 (1H, d, J = 9.9, 9.6 Hz, 5-H), 7.41 (1H, d, J = 3.9 Hz, 3-H), 7.42 (1H, dd, J = 9.9, 9.3 Hz, 7-H), 7.48 (1H, s, 5' H), 7.65 (2H, d, J = 6.9 Hz, 2"-,6"-H), 7.73 (1H, t, J = 9.9 Hz, 6-H), 8.32 (1H, d, J = 3.9 Hz, 2-H), 8.40 (1H, d, J = 9.6 Hz, 4-H), 9.91 (1H, d, J = 9.3 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.7 (OCH_3), 55.4 (OCH_3), 89.7 (=C<), 114.3 (=CH-), 115.1 (=CH-), 116.6 (=C<), 118.8 (=CH-), 125.4 (=C<), 125.7 (=CH-), 126.2 (=CH-), 128.9 (=C<), 129.8 (=CH-), 137.4 (=CH-), 137.6 (=C<), 138.0 (=CH-), 138.3 (=CH-), 139.2 (=CH-), 144.7 (=C<), 155.3 (=C<), 157.1 (=C<), 160.9 (=C<), 165.1 (CN).

Anal. Calcd. for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.38; H, 4.98; N, 7.47.

1-[3-Cyano-4-(2,4-dimethoxyphenyl)-2-methoxy-6-pyridyl]azulene (**12h**).

This compound was obtained as green needles (from benzene) in a yield of 149 mg (75%), mp 234-236 °C; ir (potassium bromide): ν max 2210 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 3.87 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 4.24 (3H, s, 2'-OCH_3), 6.61 (1H, s, 3"-H), 6.62 (1H, d, J = 7.5 Hz, 6"-H), 7.32 (1H, dd, J = 9.9, 9.6 Hz, 5-H), 7.33 (1H, dd, J = 9.9, 9.3 Hz, 7-H), 7.39-7.45 (2H, m), 7.46 (1H, s, 5'-H), 7.72 (1H, t, J = 9.9 Hz, 6-H), 8.30 (1H, d, J = 4.2 Hz, 2-H), 8.39 (1H, d, J = 9.6 Hz, 4-H), 9.89 (1H, d, J = 9.3 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.5 (OCH_3), 55.5 (OCH_3), 55.6 (OCH_3), 92.4 (=C<), 99.1 (=CH-), 100.3 (=C<), 105.0 (=CH-), 110.4 (=C<), 116.4 (=C<), 116.8 (=CH-), 118.7 (=CH-), 125.5 (=CH-), 126.0 (=CH-), 131.0 (=CH-), 137.5 (=CH-), 137.9 (=CH-), 138.2 (=CH-), 139.1 (=CH-), 144.5 (=C<), 149.9 (=C<), 153.1 (=C<), 156.6 (=C<), 156.8 (=C<), 157.6 (=C<), 162.1 (CN).

Anal. Calcd. for $C_{25}H_{20}N_2O_3$: C, 75.74; H, 5.09; N, 7.07. Found: C, 75.78; H, 5.17; N, 7.03.

1-[3-Cyano-4-(2,5-dimethoxyphenyl)-2-methoxy-6-pyridyl]azulene (**12i**).

This compound was obtained as green needles (from benzene) in a yield of 168 mg (85%), mp 195-196 °C; ir (potassium bromide): ν max 2218 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 3.81 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 4.24 (3H, s, 2-OCH_3), 6.92 (1H, d, J = 1.8 Hz, 6"-H), 6.98 (2H, s, 3"-,4"-H), 7.32 (1H, dd, J = 9.9, 9.3 Hz, 5-H), 7.39 (1H, d, J = 4.2 Hz, 3-H), 7.40 (1H, dd, J = 10,2, 9.9 Hz, 7-H), 7.46 (1H, s, 5'-H), 7.72 (1H, t, J = 9.9 Hz, 6-H), 8.29 (1H, d, J = 4.2 Hz, 2-H), 8.39 (1H, d, J = 9.3 Hz, 4-H), 9.89 (1H, d, J = 10.2 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.6 (OCH_3), 55.9 (OCH_3), 56.1 (OCH_3), 92.2 (=C<), 112.6 (=CH-), 115.8 (=CH-), 115.9 (=CH-), 116.1 (=C<), 116.5 (=CH-), 118.7 (=CH-), 125.6 (=CH-), 125.7 (=C<), 126.1 (=CH-), 126.4 (=C<), 137.5 (=C<), 137.9 (=CH-), 138.2 (=CH-), 139.1 (=CH-), 144.6 (=C<), 150.5 (=C<), 152.9 (=C<), 153.5 (=C<), 157.1 (=C<), 164.3 (CN).

Anal. Calcd. for $C_{25}H_{20}N_2O_3$: C, 75.74; H, 5.09; N, 7.07. Found: C, 75.61; H, 5.18; N, 7.15.

1-[4-(2-Chlorophenyl)-3-cyano-2-methoxy-6-pyridyl]azulene (**12j**).

This compound was obtained as green needles (from benzene) in a yield of 169 mg (91%), mp 235-236 °C; ir (potassium bromide): ν max 2222 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 4.25 (3H, s, OCH_3), 7.32 (1H, dd, J = 9.9, 9.6 Hz, 5-H), 7.38-7.41 (5H, m), 7.44 (1H, s, 5'-H), 7.53-7.56 (1H, m), 7.72 (1H, t, J = 9.9 Hz, 6-H), 8.28 (1H, d, J = 4.2 Hz, 2-H), 8.38 (1H, d, J = 9.6 Hz, 4-H), 9.92 (1H, d, J = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.6 (OCH_3), 91.6 (=C<), 99.1 (=CH-), 115.4 (=C<), 116.2 (=CH-), 118.9 (=CH-), 125.3 (=C<), 125.9 (=CH-), 126.4 (=CH-), 127.1 (=CH-), 130.2 (=CH-), 130.4 (=CH-), 130.6 (=CH-), 132.3 (=C<), 135.6 (=C<), 137.5 (=CH-), 137.7 (=C<), 138.1 (=CH-), 139.3 (=CH-), 144.8 (=C<), 153.4 (=C<), 157.1 (=C<), 164.3 (CN).

Anal. Calcd. for $C_{23}H_{15}ClN_2O$: C, 74.49; H, 4.08; N, 7.56. Found: C, 74.46; H, 4.03; N, 7.41.

1-[4-(4-Chlorophenyl)-3-cyano-2-methoxy-6-pyridyl]azulene (**12k**).

This compound was obtained as green needles (from benzene) in a yield of 113 mg (61%), mp 155-156 °C; ir (potassium bromide): ν max 2219 cm^{-1} (CN); ^1H nmr (deuteriochloroform): δ 4.26 (3H, s, OCH_3), 7.36 (1H, dd, J = 9.9, 9.3 Hz, 5-H), 7.42 (1H, d, J = 4.2 Hz, 3-H), 7.44 (1H, dd, J = 10.2, 9.9 Hz, 7-H),

7.46 (1H, s, 5'-H), 7.50 (2H, d, J = 6.6 Hz, 3"-,5"-H), 7.62 (2H, d, J = 6.6 Hz, 2"-,6"-H), 7.76 (1H, t, J = 9.9 Hz, 6-H), 8.32 (1H, d, J = 4.2 Hz, 2-H), 8.42 (1H, d, J = 9.3 Hz, 4-H), 9.93 (1H, d, J = 10.2 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.8 (OCH_3), 89.9 (=C<), 115.0 (=CH-), 116.0 (=C<), 118.9 (=CH-), 125.3 (=C<), 125.9 (=CH-), 126.5 (=CH-), 129.2 (=CH-), 129.7 (=CH-), 135.1 (=C<), 136.1 (=C<), 137.4 (=CH-), 137.8 (=C<), 138.2 (=CH-), 138.4 (=CH-), 139.4 (=CH-), 144.9 (=C<), 154.3 (=C<), 157.5 (=C<), 165.0 (CN).

Anal. Calcd. for $C_{23}H_{15}ClN_2O$: C, 74.49; H, 4.08; N, 7.56. Found: C, 74.69; H, 4.05; N, 7.65.

1-[3-Cyano-4-(3,4-dihlorophenyl)-2-methoxy-6-pyridyl]-azulene (**12l**).

This compound was obtained as green needles (from benzene) in a yield of 152 mg (75%), mp 244-245 °C; ir (potassium bromide): ν max 2217 cm^{-1} (CN); ^{1}H nmr (deuteriochloroform): δ 4.26 (3H, s, OCH_3), 7.42 (1H, d, J = 4.2 Hz, 3-H), 7.45 (1H, dd, J = 9.9, 9.0 Hz, 5-H), 7.44 (1H, s, 5'-H), 7.45 (1H, t, J = 9.9 Hz, 7-H), 7.53 (1H, dd, J = 8.1, 2.1 Hz, 6"-H), 7.61 (1H, d, J = 8.1 Hz, 5"-H), 7.73 (1H, d, J = 2.1 Hz, 2"-H), 7.77 (1H, t, J = 9.9 Hz, 6-H), 8.32 (1H, d, J = 4.2 Hz, 2-H), 8.43 (1H, d, J = 9.0 Hz, 4-H), 9.94 (1H, d, J = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.8 (OCH_3), 114.8 (=CH-), 115.7 (=C<), 119.0 (=CH-), 125.0 (=C<), 126.1 (=CH-), 126.6 (=CH-), 127.7 (=CH-), 130.2 (=CH-), 130.9 (=CH-), 133.9 (=C<), 134.2 (=C<), 136.5 (=C<), 137.5 (=CH-), 137.9 (=C<), 138.3 (=CH-), 138.4 (=CH-), 139.4 (=CH-), 145.0 (=C<), 150.1 (=C<), 152.8 (=C<), 157.8 (=C<), 165.0 (CN).

Anal. Calcd. for $C_{23}H_{14}Cl_2N_2O$: C, 68.16; H, 3.48; N, 6.91. Found: C, 68.40; H, 3.51; N, 6.97.

Preparation of 1-(4-Heterocycle-substituted 3-Cyano-2-methoxy-6-pyridyl)-3-methoxycarbonylazulenes (**13a,b**).

General Procedure.

A solution of 1-(3-heterocycle-substituted 2-propenoyl)-3-methoxycarbonylazulene **8a,b** (0.5 mmole) and malononitrile (46 mg, 0.75 mmole) in methanol (10 ml) was refluxed for 3-5 hours in the presence of sodium methoxide, prepared from sodium (46 mg, 2.0 mmoles) and aboslute methanol (5 ml). The reaction mixture was worked up, as described above, to give 1-(4-heterocycle-substituted 3-cyano-2-methoxy-6-pyridyl-pyridines **13a,b**.

1-[3-Cyano-4-(2-furyl)-2-methoxy-6-pyridyl]-3-methoxy-carbonylazulene(**13a**).

This compound was obtained as brown needles (from acetic acid) in a yield of 83 mg (43%), mp 274-275 °C; ir (potassium bromide): ν max 2217 (CN), 1699 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 4.01 (3H, s, $COOCH_3$), 4.23 (3H, s, OCH_3), 6.64 (1H, dd, J = 3.6, 1.5 Hz, 4"-H), 7.63 (1H, d, J = 3.6 Hz, 3"-H), 7.66 (1H, d, J = 1.5 Hz, 5"-H), 7.69 (2H, dd, J = 9.6, 9.3 Hz, 5'-,7'-H), 7.91 (1H, s, 2-H), 7.94 (1H, t, J = 9.6 Hz, 6-H), 8.87 (1H, s, 5'-H), 9.77 (1H, d, J = 9.3 Hz, 8-H) 10.04 (1H, d, J = 9.3 Hz, 4-H).

Anal. Calcd. for $C_{23}H_{16}N_2O_4$: C, 71.86; H, 4.19; N, 7.29. Found: C, 72.10; H, 4.19; N, 7.35.

1-[3-Cyano-2-methoxy-4-(2-thienyl)-6-pyridyl]-3-methoxy-carbonylazulene (**13b**).

This compound was obtained as brown needles (from acetic acid) in a yield of 92 mg (46%), mp 231-232 °C; ir (potassium bromide): ν max 2217 (CN), 1703 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.99 (3H, s, $COOCH_3$), 4.19 (3H, s, OCH_3), 7.20 (1H, dd, J = 4.8, 3.6 Hz, 4"-H), 7.53 (1H, s, 2-H), 7.54 (1H, d, J = 5.4 Hz, 5"-H), 7.62 (1H, t, J = 9.9 Hz, 5-H), 7.64 (1H, d, J = 9.9 Hz, 7-H), 7.91 (1H, t, J = 9.9 Hz, 6-H), 7.93 (1H, dd, J = 3.6, 1.2 Hz, 2"-H), 8.71 (1H, s, 5'-H), 9.72 (1H, d, J = 9.9 Hz, 8-H) 9.97 (1H, d, J = 9.9 Hz, 4-H); ^{13}C nmr (deuteriochloroform): δ 51.3 ($COOCH_3$), 54.8 (OCH_3), 88.6 (=C<), 114.1 (=CH), 116.3 (=C<), 116.6 (=C<), 124.3 (=C<), 128.6 (=CH-), 128.8 (=CH-), 129.3 (=CH-), 129.4 (=CH-), 129.8 (=CH-), 137.7 (=C<), 138.9 (=CH-), 139.6 (=CH-), 140.6 (=C<), 140.8 (=CH-), 141.5 (=CH-), 143.8 (=C<), 147.1 (=C<), 156.5 (=C<), 165.2 (CN), 165.3 ($COOCH_3$).

Anal. Calcd. for $C_{23}H_{16}N_2O_3S$: C, 68.98; H, 4.03; N, 7.00. Found: C, 69.19; H, 3.97; N, 7.09.

Deesterification of 1-(4-Heterocycle-substituted 3-Cyano-2-methoxy-6-pyridyl)-3-methoxycarbonylazulenes (**13a,b**).

General Procedure.

The ester compound **13a,b** (0.5 mmole) was heated in 100% phosphric acid (10 ml) for 30 minutes at 95-100 °C in an oil bath. The mixture was poured into water and extracted with benzene. The extract was washed with water and dried over sodium sulfate. The evaporation residue was purified by using a silica gel column (Merck, Kieselgel 60, 10 g) with benzene to give 1-(4-heterocycle-substituted 3-cyano-2-methoxy-6-pyridyl)-azulenes **14a,b**.

1-[3-Cyano-4-(2-furyl)-2-methoxy-6-pyridyl]azulene (**14a**).

This compound was obtained as green prisms (from benzene) in a yield of 93 mg (57%), mp 150-151 °C; ir (potassium bromide): ν max 2213 cm^{-1} (CN); ^{1}H nmr (deuteriochloroform): δ 4.15 (3H, s, OCH_3), 6.59 (1H, dd, J = 3.6, 1.8 Hz, 4"-H), 7.30 (1H, dd, J = 9.9, 9.3 Hz, 5-H), 7.33 (1H, dd, J = 10.2, 9.9 Hz, 7-H), 7.37 (1H, d, J = 4.3 Hz, 3-H), 7.55 (1H, d, J = 3.6 Hz, 3"-H), 7.60 (1H, d, J = 1.8 Hz, 5"-H), 7.69 (1H, t, J = 9.9 Hz, 6-H), 7.77 (1H, s, 5'-H), 8.31 (1H, d, J = 4.3 Hz, 2-H), 8.35 (1H, d, J = 9.3 Hz, 4-H), 9.85 (1H, d, J = 10.2 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.6 (OCH_3), 84.6 (=C<), 110.2 (=CH-), 112.6 (=CH-), 113.5 (=CH-), 116.8 (=C<), 118.8 (=CH-), 125.4 (=C<), 125.7 (=CH-), 126.2 (=CH-), 137.4 (=CH-), 137.6 (=C<), 137.9 (=CH-), 138.3 (=CH-), 139.1 (=CH-), 141.8 (=C<), 144.2 (=CH-), 144.8 (=C<), 148.6 (=C<), 157.3 (=C<), 165.0 (CN).

Anal. Calcd. for $C_{21}H_{14}N_2O_2$: C, 77.28; H, 4.32; N, 8.59. Found: C, 77.46; H, 4.49; N, 8.54.

1-[3-Cyano-2-methoxy-4-(2-thienyl)-6-pyridyl]azulene (**14b**).

This compound was obtained as green prisms (from benzene) in a yield of 106 mg (62%), mp 118-119 °C; ir (potassium bromide): ν max 2208 cm^{-1} (CN); ^{1}H nmr (deuteriochloroform): δ 4.20 (3H, s, OCH_3), 7.19 (1H, dd, J = 5.1, 3.9 Hz, 4"-H), 7.32 (1H, dd, J = 9.9, 9.3 Hz, 5-H), 7.35-7.43 (1H, m), 7.41 (1H, t, J = 9.9 Hz, 7-H), 7.52 (1H, dd, J = 3.9, 1.2 Hz, 3"-H), 7.56 (1H, s, 5'-H), 7.72 (1H, t, J = 9.9 Hz, 6-H), 7.92 (1H, d, J = 4.2 Hz, 3-H), 8.31 (1H, d, J = 4.2 Hz, 2-H), 8.38 (1H, d, J = 9.3 Hz, 4-H), 9.87

(1H, d, J = 9.9 Hz, 8-H); ^{13}C nmr (deuteriochloroform): δ 54.7 (OCH_3), 114.0 (=CH-), 116.7 (=C<), 118.9 (=CH-), 125.2 (=C<), 125.8 (=CH-), 126.4 (=CH-), 128.3 (=C<), 128.5 (=CH-), 128.6 (=CH), 129.1 (=CH-), 137.4 (=CH-), 137.7 (=C<), 138.0 (=C<), 138.1 (=CH-), 138.3 (=CH-), 139.2 (=CH-), 144.8 (=C<), 146.8 (=C<), 157.3 (=C<), 165.4 (CN).

Anal. Calcd. for $C_{21}H_{14}N_2OS$: C, 73.66; H, 4.12; N, 8.18. Found: C, 73.88; H, 4.27; N, 8.20.

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