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NEW SYNTHETIC APPROACH TO AZULENO[1,2-*c*]PYRROLES AND CONVERSION TO BENZ[*a*]AZULENES

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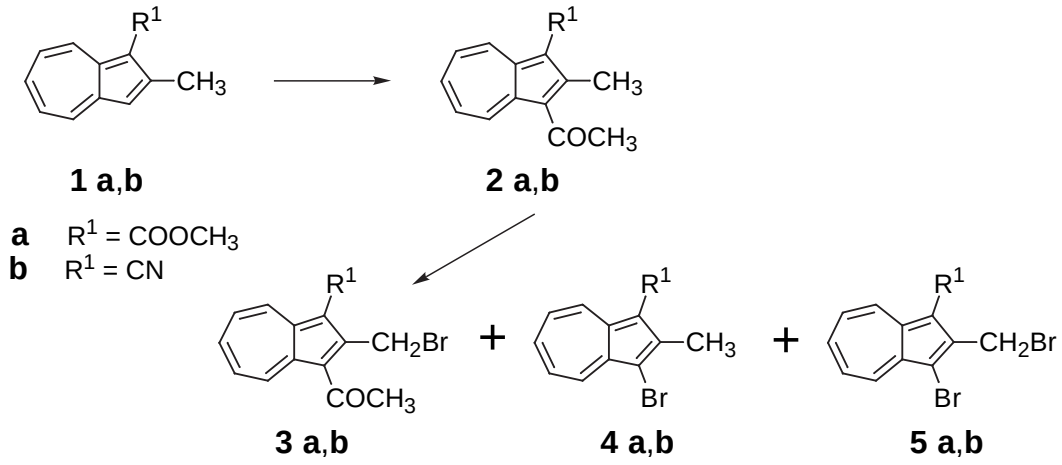
Dedicated to Professor Sho Ito on the occasion of his 77th birthday.

Abstract - 1-Acetyl-2-(bromomethyl)azulenes were obtained as new synthons directed to heterocycle-fused azulenes. 3-Methoxycarbonyl- and 3-cyano-substituted 1-acetyl-2-(bromomethyl)azulenes (**3a**,**b**) reacted with anilines (**6a-d**) in the presence of potassium carbonate to afford 9-substituted 2-aryl-3-methylazuleno-[1,2-*c*]pyrrole (**7aa-ad**,**ba-bd**) in moderate to good yields. These azuleno-[1,2-*c*]pyrroles (**7aa-ad**,**ba-bd**) were condensed with acetylenedicarboxylates to give 1-anilino-2,3-dialkoxycarbonyl-4-methylbenz[*a*]azulenes (**8aa-ad**,**ba**, **bb**,**bd**; **10aa-ad**,**ba-bd**) and 2-aryl-1-(1,2-dialkoxycarbonylethenyl)-4-methyl-azuleno[1,2-*c*]pyrroles (**9ab-ad**,**ba-bd**; **11aa-ad**,**ba-bd**) *via* cycloadducts.

On the viewpoints of physical and chemical properties and biological activities, syntheses of a variety of heterocycle-fused azulenes have been reported.[1-4] Of them, pyrrole-fused azulenes were prepared by using different types of starting materials as followings. 1-Acetyl-9-ethoxycarbonyl-2-phenylazuleno[2,1-*b*]-pyrrole was obtained by the reaction of 2-acetamido-1-iodo-3-ethoxycarbonylazulene with phenylacetyl-ide.[1] On the other hand, 3-methoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one reacted with a mixture of tautomeric morpholino enamines of 1-ethoxycarbonyl-3-oxopyrrolidine to give isomeric 3-ethoxycarbonyl-9-methoxycarbonyl-1,2-dihydroazuleno[1,2-*b*]pyrrole and 2-ethoxycarbonyl-9-methoxycarbonyl-1,3-di-hydroazuleno[1,2-*c*]pyrrole which were dehydrogenated to yield the corresponding azuleno[1,2-*b*]pyrrole and azuleno[1,2-*c*]pyrrole, respectively.[4] In this paper, we describe a new synthetic method of azuleno-[1,2-*c*]pyrroles by the reactions of new synthons with anilines.

RESULTS AND DISCUSSION

Synthesis of 1-Acetyl-2-(bromomethyl)azulenes. It is known that a methyl group at the 2-position of azulene ring is reactive. For example, 2-methylazulenes were condensed with benzaldehydes to afford 2-styrylazulenes.[5] Then, the conversion of the 2-methyl group of 2-methylazulene derivatives to a electrophilic functional group was attempted. 1-Acetyl-2-methylazulenes (**2a**,**b**), which were obtained by Friedel-Crafts acylation of 1-methoxycarbonyl-2-methylazulene (**1a**)[6] and 1-cyano-2-methylazulene (**1b**),[7] were treated with *N*-bromosuccinimide to give 1-acetyl-2-(bromomethyl)azulenes (**3a**,**b**) as major products and 1-bromo-2-methylazulenes (**4a**,**b**) and 1-bromo-2-(bromomethyl)azulemes (**5a**,**b**) as minor ones. Since compounds (**3a**,**b**) have two reactive functional groups, an acetyl and bromomethyl groups, at the neighboring positions, they seem to be useful building blocks for heterocycle-fused azulenes.



Scheme 1

Reactions of New Building Blocks (3a,b) with Anilines. A solution of 1-acetyl-3-methoxy-carbonyl-2-(bromomethyl)azulene (**3a**) and aniline (**6a**) (1.2 eq) in dichloromethane was stirred for 24 h at room temperature in the presence of potassium carbonate (4 eq) to give 2-anilino-9-methoxy-carbonyl-3-methyl-azuleno[1,2-*c*]pyrrole (**7aa**) in 40% yield. The reactions with *p*-methyl, *p*-methoxy, and *p*-bromo-substituted anilines (**6b-d**) were carried out under several conditions to give the corresponding azuleno[1,2-*c*]pyrroles (**7ab-ad**). In a similar manner, 9-cyano-substituted azuleno[1,2-c]pyrroles (**7ba-bd**) were obtained in the reactions of 1-acetyl-3-cyano-2-(bromomethyl)azulene (**3b**) with anilines (**6a-d**). These results are summarized in Table 1. From these results, it was found that good results were obtained in the reactions using 3 molar equivalents of aniline in the presence of 4 molar equivalents of potassium carbonate in chloroform as the solvent and at refluxing temperature. It was found that 1-acetyl-2-(bromo-methyl)azulenes (**3a**,**b**) were useful starting materials for syntheses of azuleno[1,2-*c*]pyrroles. Furthermore, compounds (**3a**,**b**) are expected as building blocks for other heterocycle-fused azulene derivatives and their reations are now in progress.

2 a,**b** **5 a**-**d** **6 aa**-**ad**, **ba**-**bd**

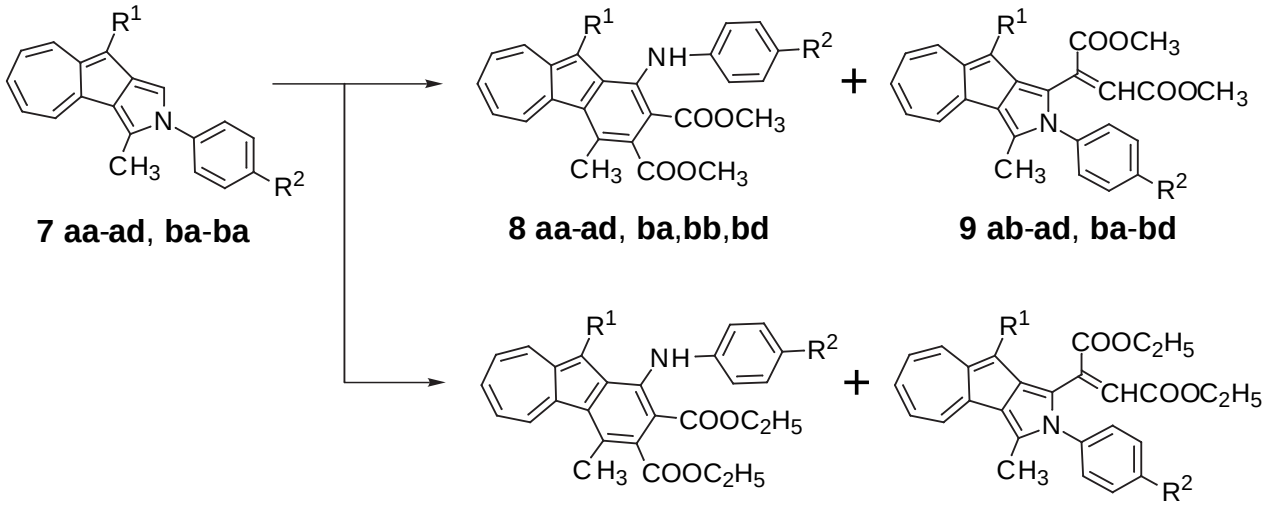
Scheme 2

Table 1. Reactions of 1-Acetyl-2-(bromomethyl)azulenes (**3a**,**b**) with Anilines (**6a**-**d**)

3	R^1	**6**	R^2	Molar ratio[a)]	Solvent	Temp.	Time h	Product **7**	Yield / %
a	$COOCH_3$	**a**	H	1 : 1.2 : 4	CH_2Cl_2	RT	24	**aa**	40
a	$COOCH_3$	**a**	H	1 : 2 : 4	$CHCl_3$	Reflux	24	**aa**	52
a	$COOCH_3$	**a**	H	1 : 3 : 4	$CHCl_3$	Reflux	8	**aa**	79
a	$COOCH_3$	**b**	CH_3	1 : 1.2 : 4	CH_2Cl_2	RT	24	**ab**	67
a	$COOCH_3$	**b**	CH_3	1 : 3 : 4	$CHCl_3$	Reflux	5	**ab**	86
a	$COOCH_3$	**c**	OCH_3	1 : 1.2 : 4	CH_2Cl_2	RT	24	**ac**	67
a	$COOCH_3$	**c**	OCH_3	1 : 3 : 4	$CHCl_3$	Reflux	2	**ac**	92
a	$COOCH_3$	**d**	Br	1 : 2 : 4	CH_2Cl_2	Reflux	24	**ad**	45
a	$COOCH_3$	**d**	Br	1 : 3 : 4	$CHCl_3$	Reflux	24	**ad**	61
b	CN	**a**	H	1 : 1.2 : 4	$CHCl_3$	Reflux	6	**ba**	31
b	CN	**a**	H	1 : 2 : 4	$CHCl_3$	Reflux	48	**ba**	42
b	CN	**a**	H	1 : 3 : 4	$CHCl_3$	Reflux	24	**ba**	57
b	CN	**b**	CH_3	1 : 3 : 4	$CHCl_3$	Reflux	12	**bb**	63
b	CN	**c**	OCH_3	1 : 3 : 4	$CHCl_3$	Reflux	12	**bc**	61
b	CN	**d**	Br	1 : 3 : 4	$CHCl_3$	Reflux	48	**bd**	50

a) **3** : **6** : K_2CO_3

Cycloaddition of Azuleno[1,2-*c*]pyrroles with Acetylenedicarboxylic Acid Esters. Azuleno[1,2-*c*]pyrrole skeleton has a diene moiety in the pyrrole ring and might undergo cycloaddition with dienophiles. Then, a mixed solution of 9-methoxycarbonyl-3-methyl-2-phenylazuleno[1,2-*c*]pyrrole (**7aa**) and dimethyl acetylenedicarboxylate in tetrahydrofuran was refluxed for 12 h to afford 1-anilino-2,3,10-trimethoxycarbonyl-4-methylbenz[*a*]azulene (**8aa**) in 62% yield. From the reactions of azuleno[1,2-*c*]-pyrrole (**7ab**) with the same reagent, 2,3,10-trimethoxycarbonyl-4-methyl-1-(4-methylanilino)benz[*a*]-



Scheme 3

Table 2. Reactions of 2-Aryl-3-methylazulenno[1,2-*c*]pyrroles (**6aa-ad**,**ba-bd**) with Acetylenedicarboxylic Acid Esters

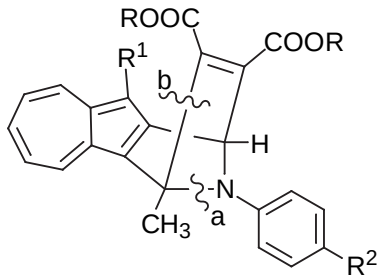
7				Reagent [a]	Time	Product			
R^1		R^2			h		Yield / %		
a	$COOCH_3$	**a**	H	A	12	**8aa**	62		---
a	$COOCH_3$	**b**	CH_3	A	12	**8ab**	61	**9ab**	9
a	$COOCH_3$	**c**	OCH_3	A	4	**8ac**	36	**9ac**	25
a	$COOCH_3$	**d**	Br	A	12	**8ad**	50	**9ad**	23
b	CN	**a**	H	A	12	**8ba**	56	**9ba**	35
b	CN	**b**	CH_3	A	6	**8bb**	81	**9bb**	3
b	CN	**c**	OCH_3	A	8		---	**9bc**	77
b	CN	**d**	Br	A	10	**8bd**	87	**9bd**	6
a	$COOCH_3$	**a**	H	B	12	**10aa**	45		---
a	$COOCH_3$	**b**	CH_3	B	12	**10ab**	67	**11ab**	19
a	$COOCH_3$	**c**	OCH_3	B	12	**10ac**	54	**11ac**	22
a	$COOCH_3$	**d**	Br	B	12	**10ad**	58	**11ad**	19
b	CN	**a**	H	B	12	**10ba**	69	**11ba**	11
b	CN	**b**	CH_3	B	6	**10bb**	88	**11bb**	7
b	CN	**c**	OCH_3	B	6	**10bc**	50	**11bc**	12
b	CN	**d**	Br	B	24	**10bd**	45	**11bd**	42

a) A : Dimethyl acetylenedicarboxylate, B : Diethyl acetylenedicarboxylate

azulene (**8ab**) and 1-(1,2-dimethoxycarbonylethenyl)-9-methoxycarbonyl-3-methyl-2-(4-methylphenyl)-azuleno[1,2-*c*]pyrrole (**9ab**) were obtained in 61 and 9% yields, respectively.

In a similar manner, the reactions of azuleno[1,2-*c*]pyrroles (**7aa-ad**,**ba-bd**) with dimethyl and diethyl acetylenedicarboxylates were carried out to give two types of products, 1-anilino-substituted benz[*a*]-azulenes (**8aa-ad**,**ba**,**bb**,**bd**; **10aa-ad**,**ba-bd**) and 1-[1,2-di(methoxycarbonyl)ethenyl]-substituted azuleno[1,2-*c*]pyrrole (**9ab-ad**,**ba-bd**; **11ab-ad**,**ba-bd**), by collapse and aromatization of cycloadducts. These results are summarized in Table 2.

It was elucidated that both of the products were formed from bond-cleavage of the cycloadducts [**A**] of azuleno[1,2-*c*]pyrroles (**7aa-ad**,**ba-bd**) with acetylenic dienophile. Namely, the benz[*a*]azulene (**8aa-ad**, **ba**,**bb**,**bd**; **10aa-ad**,**ba-bd**) and the azuleno[1,2-*c*]pyrroles (**9ab-ad**,**ba-bd**; **11ab-ad**,**ba-bd**) were respectively formed by bond fission at the *a* and *b* positions and by aromatization.



[**A**]

EXPERIMENTAL

All the melting points were determined with a Yanagimoto 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 ^{1}H and 75.5 MHz for ^{13}C). The MS spectra were obtained by a JEOL JMX-DX 303HF instrument. All the elemental analyses were performed at the Instrumental Analysis Center, Kumamoto University. Merck Kieselgel 60 was used for column chromatography.

Materials. 1-Methoxycarbonyl-2-methylazulene (**1a**)[6] and 1-cyano-2-methylazulene (**1b**)[7] were prepared according to the methods described in the literatures.

Preparation of 1-Acetyl-2-methylazulenes (2a,b). General Procedure. A solution of 2-methylazulene (**1a,b**) (0.5 mmol) and acetic anhydride (1 mL, 10 mmol) in dichloromethane (10 mL) was stirred for 2 h in the presence of tin(IV) chloride (156 mg, 0.6 mmol). The mixture was poured onto crashed ice and acidified with 12M hydrochloric acid. The organic layer was separated and the aqueous portion was extracted with dichloromethane. The combined organic layer was dried over sodium sulfate. The evaporation residue was chromatographed on silica gel column with benzene and red fraction was collected to give 1-acetyl-3-methoxycarbonyl-2-methylazulene (**2a**) and 1-acetyl-2-methylazulene-3-carbonitrile (**2b**).

Methyl 1-Acetyl-2-methylazulene-3-carboxylate (2a). Red crystals (from benzene); yield 220 mg (91%); mp 84-85 °C; IR (KBr) ν 1691 (C=O), 1640 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.67 (3H, s, CH_3), 2.92 (3H, s, $COCH_3$), 3.97 (3H, s, $COOCH_3$), 7.54 (1H, dd, *J* = 10.2, 9.6 Hz, 7-H), 7.55 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.74 (1H, t, *J* = 9.6 Hz, 6-H), 9.14 (1H, d, *J* = 10.2 Hz, 8-H), 9.39 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 17.3 (CH_3), 32.7 ($CO\underline{C}H_3$), 51.2 ($COO\underline{C}H_3$), 116.5 (=C<), 128.0 (=C<), 130.1 (=CH-), 130.5 (=CH-), 137.0 (=CH-), 137.2 (=CH-), 139.2 (=CH-), 141.7 (=C<), 142.7 (=C<), 153.5 (=C<), 166.3 ($\underline{C}OOCH_3$), 198.6 ($\underline{C}OCH_3$). *Anal*. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.56; H, 5.94.

1-Acetyl-2-methylazulene-3-carbonitrile (2b). Red crystals (from benzene); yield 176 mg (84%); mp 132-133 °C; IR (KBr) ν 2206 (C≡N), 1642 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.69 (3H, s, CH_3), 2.91 (3H, s, $COCH_3$), 7.68 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.68 (1H, dd, *J* = 10.2, 9.9 Hz, 5-H), 7.93 (1H, t, *J* = 9.9 Hz, 6-H), 8.50 (1H, d, *J* = 9.6 Hz, 8-H), 9.50 (1H, d, *J* = 10.2 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 17.5 (CH_3), 32.4 ($CO\underline{C}H_3$), 100.1 (=C<), 126.2 (=C<), 125.5 (=C<), 130.5 (=CH-), 132.2 (=CH-), 135.9 (=CH-), 139.4 (=CH-), 142.1 (=C<), 144.6 (=C<), 154.3 (C ≡ N), 196.2 ($\underline{C}OCH_3$). *Anal*. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.25; H, 5.30; N, 6.79.

Bromination of 1-Acetyl-2-methylazulenes (2a,b). General Procedure. To a solution of 1-acetyl-2-methylazulene (**2a**,**b**) (0.5 mmol) in carbon tetrachloride (20 mL) was added *N*-bromosuccinimide (178 mg, 1.0 mmol) and benzoyl peroxide (10 mg). The mixed solution was refluxed for 30 min for **2a** and 1 h for **2b**. The reaction mixture was diluted with water and extracted with dichloromethane. The evaporation residue from the extract was chromatographed on a silica gel column (Merck, Kieselgel 60) with benzene to give 1-acetyl-2-methylazulene (**3a**,**b**), 1-bromo-2-methylazulene (**4a**,**b**), and 1-bromo-2-(bromomethyl)azulene (**5a**,**b**).

Methyl 1-Acetyl-2-(bromomethyl)azulene-3-carboxylate (3a). Violet needles (from benzene); yield 115 mg (76%); mp 85-86 °C; IR (KBr) ν 1690 (C=O), 1651 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.80 (3H, s, $COCH_3$), 4.05 (3H, s, $COOCH_3$), 5.61 (2H, s, CH_2Br), 7.84 (1H, t, *J* = 9.6 Hz, 5-H), 7.91 (1H, dd, *J* = 10.4, 9.6 Hz, 7-H), 8.99 (1H, t, *J* = 9.6 Hz, 6-H), 9.46 (1H, d, *J* = 10.4 Hz, 8-H), 9.95 (1H, d, *J* =9.6 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 25.5 ($CO\underline{C}H_3$), 32.4 (CH_2Br), 51.6 ($COO\underline{C}H_3$), 115.1(=C<), 127.3 (=C<), 130.5 (=CH-), 138.9 (=CH-), 139.6 (=CH-), 141.0 (=CH-), 141.4 (=C<), 142.4 (=C<), 149.1 (=C<), 165.3 ($\underline{C}OOCH_3$), 198.1 ($\underline{C}OCH_3$). *Anal*. Calcd for $C_{15}H_{13}O_3Br$: C, 56.09; H, 4.08. Found: C, 56.34; H, 4.33.

Methyl 1-Bromo-2-methylazulene-3-carboxylate (4a). Blue crystals (from benzene); yield 10 mg (7%); mp 88-89 °C; IR (KBr) ν 1694 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.78 (3H, s, CH_3), 3.95 ($COOCH_3$), 7.37 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.44 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.64 (1H, t, *J* = 9.6 Hz, 6-H), 8.30 (1H, d, *J* = 9.9 Hz, 8-H), 9.35 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 17.1 (CH_3), 51.0 ($COO\underline{C}H_3$), 108.6 (=C<), 114.4 (=C<), 127.2 (=CH-), 128.1 (=CH-), 135.4 (=CH-), 136.3 (=CH-), 138.3 (=CH-), 138.6 (=C<), 140.6 (=C<), 151.1 (=C<), 165.7 (C=O). *Anal*. Calcd for $C_{13}H_{11}O_2Br$: C, 55.94; H, 3.97. Found: C, 56.19; H, 3.94.

Methyl 1-Bromo-2-(bromomethyl)azulene-3-carboxylate (5a). Dark violet crystals (from benzene); yield 11 mg (6%); mp 99-101 °C; IR (KBr) ν 1679 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 4.02 ($COOCH_3$), 5.17 (2H, s, CH_2Br), 7.46 (1H, dd, *J* = 10.2, 9.9 Hz, 5-H), 7.53 (1H, dd, *J* = 11.2, 9.9 Hz, 7-H), 7.77 (1H, t, *J* = 9.6 Hz, 6-H), 8.46 (1H, d, *J* = 11.2 Hz, 8-H), 9.52 (1H, d, *J* = 10.2 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 26.4 (CH_2Br), 51.5 ($COO\underline{C}H_3$), 108.1 (=C<), 113.3 (=C<), 127.9 (=CH-), 128.8 (=CH-), 137.8 (=CH-), 138.9 (=C<), 139.0 (=CH-), 140.5 (=CH-), 140.7 (=C<), 147.0 (=C<), 164.9 ($\underline{C}OOCH_3$). *Anal*. Calcd for $C_{13}H_{10}O_3Br_2$: C, 43.61; H, 2.81. Found: C, 43.52; H, 2.81.

1-Acetyl-2-(bromomethyl)azulene-3-carbonitrile (3b). Violet needles (from benzene); yield 99 mg (69%); mp 129 °C (decomp); IR (KBr) ν 2211 (C≡N), 1651 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.86 (3H, s, $COCH_3$), 5.07 (2H, s, CH_2Br), 7.77 (1H, dd, *J* = 10.2, 9.9 Hz, 5-H), 7.81 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 8.03 (1H, t, *J* = 9.9 Hz, 6-H), 8.69 (1H, d, *J* = 9.6 Hz, 8-H), 9.47 (1H, d, *J* = 10.2 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 23.8 ($COCH_3$), 31,9 (CH_2Br), 99.2 (=C<), 115.1 (=C<), 125.0 (=C<), 130.9 (=CH-), 132.2 (=CH-), 138.2 (=CH-), 141.4 (=CH-), 142.2 (=C<), 144.4 (=C<), 150.4 (C≡N), 195.7 ($\underline{C}OCH_3$). *Anal*. Calcd for $C_{14}H_{10}NOBr$: C, 58.15; H, 3.52; N, 4.98. Found: C, 58.03; H, 3.67; N, 5.01.

1-Bromo-2-methylazulene-3-carbonitrile (4b). Blue crystals (from benzene); yield 4 mg (3%); mp 154-156 °C; IR (KBr) ν 2203 cm^{-1} (C≡N); ^1H NMR ($CDCl_3$) δ 2.61 (3H, s, CH_3), 7.40 (1H, t, *J* = 9.9 Hz, 5-H), 7.44 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.72 (1H, t, *J* = 9.9 Hz, 6-H), 8.20 (1H, d, *J* = 9.9 Hz, 4-H), 8.26 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 15.3 (CH_3), 96.8 (=C<), 106.1 (=C<), 116.1 (=C<), 127.5 (=CH-), 127.9 (=CH-), 134.7 (=CH-), 136.0 (=CH-), 137.9 (=C<), 139.2 (=CH-), 142.2 (=C<), 150.8 (C≡N). *Anal*. Calcd for $C_{12}H_8NBr$: C, 58.56; H, 3.28; N, 5.69. Found: C, 58.52; H, 3.26; N, 5.76.

1-Bromo-2-(bromomethyl)azulene-3-carbonitrile (5b). Dark violet crystals (from benzene); yield 10 mg (6%); mp 125-127 °C; IR (KBr) ν 2205 cm^{-1} (C≡N); ^1H NMR ($CDCl_3$) δ 4.87 (CH_2Br), 7.58 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.63 (1H, dd, *J* = 9.9, 9.3 Hz, 7-H), 7.91 (1H, t, *J* = 9.9 Hz, 6-H), 8.51 (1H, d, *J* = 9.3 Hz, 8-H), 8.57 (1H, *J* = 9.6 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 23.1 (CH_2Br), 105.8 (=C<), 115.1 (=C<), 128.2 (=C<), 128.3 (=CH-), 128.6 (=CH-), 137.5 (=CH-), 138.5 (=C<), 138.8 (=CH-), 141.5 (=CH-), 142.7 (=C<), 147.2 (C≡N). *Anal*. Calcd for $C_{12}H_7NBr_2$: C, 44.35; H, 2.17; N, 4.31. Found: C, 44.6; H, 2.30; N, 4.31.

Reactions of 1-Acetyl-2-(bromomethyl)azulenes (3a,b) with Anilines (6a-d). A solution of azulene (**3a**,**b**) (0.5 mmol) and aniline (**6a-d**) (1.5 mmol) in dichloromethane (20 mL) for **3a** [or chloroform (20 mL) for **3b**] was refluxed in the presence of potassium carbonate (276 mg, 2.0 mmol). The reaction mixture was diluted with water. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was washed with water and dried over sodium sulfate. The evaporation residue was passed through a silica gel column with chloroform to yield 2-aryl-9-methoxycarbonyl-3-methylazuleno[1,2-*c*]pyrroles (**7aa-ad**) and 2-aryl-9-cyano-3-methylazuleno[1,2-*c*]-pyrroles (**7ba-bd**).

9-Methoxycarbonyl-3-methyl-2-phenylazuleno[1,2-*c*]pyrroles (7aa). Dark violet needles (from benznene); yield 125 mg (79%); mp 127-128 °C; IR (KBr) ν 1692 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.65 (3H, s, CH_3), 3.93 (3H, s, $COOCH_3$), 7.00-7.04 (3H, m, 3'-,4'-,5'-H), 7.14 (1H, s, 1-H), 7.34-7.43 (3H, m, 5-,6-,7-H), 7.48 (2H, d, *J* = 7.8 Hz, 2'-,6'-H), 7.79-7.81 (1H, m, 4-H), 8.99-9.03 (1H, m, 8-H); ^{13}C NMR ($CDCl_3$) δ 12.8 (CH_3), 51.0 ($COO\underline{C}H_3$), 107.8 (=C<), 108.6 (=CH-), 121.9 (=C<), 122.9 (=C<), 126.6 (=CH-), 127.1 (=CH-), 127.6 (=CH-), 128.8 (=CH-), 129.1 (=CH-), 129.4 (=CH-), 130.4 (=C<), 132.5 (=CH-), 133.7 (=CH-), 140.0 (=C<), 141.9 (=C<), 148.4 (=C<), 166.5 ($\underline{C}OOCH_3$); MS (EI) *m/z* 315 (M^+, 100), 284 (25), 256 (20). *Anal*. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44. Found: C, 79.97; H, 5.56; N, 4.13.

9-Methoxycarbonyl-3-methyl-2-(4-methylphenyl)azuleno[1,2-*c*]pyrrole (7ab). Dark violet needles (from benzene); yield 142 mg (86%); mp 106-107 °C; IR (KBr) ν 1683 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.44 (3H, s, 3-CH_3), 2.65 (3H, s, 4'-CH_3), 3.94 (3H, s, $COOCH_3$), 7.00-7.07 (2H, m, 3'-,5'-H), 7.12 (1H, s, 1-H), 7.34-7.43 (3H, m, 5-,6-,7-H), 7.28 (2H, m, 2'-,6'-H), 7.77-7.81 (1H, m, 4-H), 8.99-9.03 (1H, m, 8-H); MS (EI) *m/z* 329 (M^+, 100), 298 (13), 270 (11). *Anal*. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 79.98; H, 5.78; N, 4.19.

9-Methoxycarbonyl-2-(4-methoxyphenyl)-3-methylazuleno[1,2-*c*]pyrrole (7ac). Dark violet needles (from benzene); yield 159 mg (92%); mp 174-175 °C; IR (KBr) ν 1687 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.61 (3H, s, CH_3), 3.85 (3H, s, OCH_3), 3.93 (3H, s, $COOCH_3$), 6.98 (2H, d, *J* = 8.7 Hz, 3'-,5'-H), 7.01-7.04 (3H, m, 5-,6-,7-H), 7.09 (1H, s, 1-H), 7.29 (2H, d, *J* = 8.7 Hz, 2'-,6'-H), 7.77-7.81 (1H, m, 4-H), 8.99-9.03 (1H, m, 8-H); ^{13}C NMR ($CDCl_3$) δ 12.7 (CH_3), 51.0 ($COO\underline{C}H_3$), 55.6 (OCH_3), 107.7 (=C<), 108.8 (=CH-), 114.2 (=CH-), 121.5 (=C<), 123.2 (=C<), 127.0 (=CH-), 127.8 (=CH-), 128.7 (=C<), 129.3 (=CH-), 130.1 (=C<), 132.4 (=CH-), 132.9 (=CH-), 133.6 (=CH-), 141.9 (=C<), 148.3 (=C<), 158.9(=C<), 166.5 ($\underline{C}OOCH_3$). *Anal*. Calcd for $C_{21}H_{17}NO_2$: C, 76.50; H, 5.54; N, 4.06. Found: C, 76.73; H, 5.59; N, 4.14.

2-(4-Bromophenyl)-9-methoxycarbonyl-3-methylazuleno[1,2-*c*]pyrrole (7ad). Dark violet needles (from benzene); yield 120 mg (61%); mp 127-128 °C; IR (KBr) ν 1692 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.64 (3H, s, CH_3), 3.94 (3H, s, $COOCH_3$), 7.00-7.04 (3H, m, 5-,6-,7-H), 7.09 (1H, s, 1-H), 7.26 (2H, d, *J* = 8.6 Hz, 3'-,5'-H), 7.62 (2H, d, *J* = 8.6 Hz, 2'-,6'-H), 7.77-7.81 (1H, m, 4-H), 8.99-9.03 (1H, m, 8-H); ^{13}C NMR ($CDCl_3$) δ 12.8 (CH_3), 51.0 ($COO\underline{C}H_3$), 107.8 (=C<), 108.4 (=CH-), 121.5 (=C<), 122.2 (=C<), 126.6 (=CH-), 127.3 (=CH-), 128.0 (=CH-), 129.0 (=CH-), 129.4 (=CH-), 130.6 (=C<), 132.3 (=CH-), 132.7 (=CH-), 133.7 (=CH-), 139.9 (=C<), 141.8 (=C<), 148.6 (=C<), 166.4 ($\underline{C}OOCH_3$); MS (EI) *m/z* 395 ($[M+2]^+$, 100), 393 (M^+, 98), 254 (28). *Anal*. Calcd for $C_{21}H_{16}NO_2Br$: C, 63.97; H, 4.09; N, 3.55. Found: C, 64.01; H, 3.88; N, 3.51.

9-Cyano-3-methyl-2-phenylazuleno[1,2-*c*]pyrrole (7ba). Dark violet oil; yield 80 mg (57%); IR ($CHCl_3$) ν 2129 cm^{-1} (C≡N); ^1H NMR ($CDCl_3$) δ 2.63 (3H, s, CH_3), 6.90-6.99 (3H, m, 5-,6-,7-H), 7.01 (1H, s, 1-H), 7.35 (2H, d, *J* = 8.4 Hz, 2'-,6'-H), 7.44-7.54 (3H, m, 3'-,4'-,5'-H), 7.67 (1H, d, *J* = 9.6 Hz, 4-H), 7.84 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 12.7 (CH_3), 88.6 (=C<), 106.8

(=CH-), 118.2 (=C<), 122.0 (=C<), 123.7 (=C<), 126.5 (=CH-), 126.7 (=CH-), 128.0 (=CH-), 128.1 (=CH-), 128.3 (=C<), 129.3 (=CH-), 129.7 (=CH-), 132.1 (=CH-), 132.2 (=CH-), 139.5 (=C<), 139.9 (=C<), 151.3 (C≡N); MS (EI) *m/z* 282 (M+, 100), 240 (13), 178 (11). *Anal.* Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.11; H, 4.97; N, 9.87.

9-Cyano-3-methyl-2-(4-methylphenyl)azuleno[1,2-*c*]pyrrole (7bb). Dark violet needles (from benzene); yield 93 mg (63%); mp 157-158 °C; IR (KBr) ν 2195 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$) δ 2.44 (3H, s, 4'-CH_3), 2.62 (3H, s, 4-CH_3), 6.88-6.97 (3H, m, 5-,6-,7-H), 6.99 (1H, s, 1-H), 7.23 (2H, d, *J* = 8.7 Hz, 3'-,5'-H), 7.30 (2H, d, *J* = 8.7 Hz, 2'-,6'-H), 7.67 (1H, d, *J* = 9.3 Hz, 4-H), 7.83 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 12.7 (3-CH_3), 21.2 (4'-CH_3), 88.4 (=C<), 106.8 (=CH-), 118.3 (=C<), 121.8 (=C<), 123.7 (=C<), 126.3 (=CH-), 126.6 (=CH-), 127.9 (=CH-), 128.3 (=C<), 129.3 (=C<), 129.6 (=CH-), 129.8 (=CH-), 132.0 (=CH-), 132.1 (=CH-), 136.9 (=C<), 138.0 (=C<), 139.8 (=C<), 151.2 (C ≡ N); MS (EI) *m/z* 296 (M^+, 100), 240 (10), 178 (12). *Anal.* Calcd for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45. Found: C, 85.21; H, 5.36; N, 9.31.

9-Cyano-2-(4-methoxyphenyl)-3-methylazuleno[1,2-*c*]pyrrole (7bc). Dark violet oil; yield 95 mg (61%); IR (neat) ν 2191 cm^{-1} (C ≡ N); ^{1}H NMR ($CDCl_3$) δ 2.58 (3H, s, CH_3), 3.86 (3H, s, OCH_3), 6.85-6.98 (3H, m, 5-,6-,7-H), 6.96 (2H, d, *J* = 6.6 Hz, 3'-,5'-H), 7.00 (1H, s, 1-H), 7.24 (2H, d, *J* = 6.6 Hz, 2'-,6'-H), 7.65 (1H, d, *J* = 9.3 Hz, 4-H), 7.82 (1H, d, *J* = 10.2 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 12.5 (CH_3), 55.5 (OCH_3), 88.2 (4'-=C<), 106.9 (=CH-), 114.3 (=C<), 118.2 (=C<), 121.5 (=C<), 123.9 (=CH-), 126.5 (=CH-), 127.6 (=CH-), 127.9 (=CH-), 128.2 (=C<), 128.5 (=C<), 129.6 (=CH-), 131.9 (=CH-), 132.0 (=CH-), 132.3 (=C<), 139.7 (=C<), 151.1 (=C<), 159.2 (C≡N); MS (EI) *m/z* 312 (M^+, 100), 297 (38), 178 (11). *Anal.* Calcd for $C_{21}H_{16}N_2O$: C, 80.75; H, 5.16; N, 8.97. Found: C, 79.93; H, 5.22; N, 8.79.

2-(4-Bromophenyl)-9-cyano-3-methylazuleno[1,2-*c*]pyrroles (7bd). Dark violet needles (from benzene); yield 90 mg (50%); mp 181-182 °C; IR (KBr) ν 2197 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$) δ 2.62 (3H, s, CH_3), 6.86-7.00 (3H, m, 5-,6-,7-H), 6.96 (1H, s, 1-H), 7.22 (2H, d, *J* = 6.6 Hz, 3'-,5'-H), 7.63 (2H, d, *J* = 6.6 Hz, 2'-,6'-H), 7.63-7.67 (1H, m, 4-H), 7.81 (1H, d, *J* = 10.5 Hz, 8-H); ^{13}C NMR $(CDCl)_3$ δ 12.7 (CH_3), 88.3 (=C<), 106.6 (=CH-), 118.0 (=C<), 121.9 (=C<), 122.2 (=C<), 123.4 (=CH-), 132.5 (=CH-), 138.4 (=C<), 139.6 (=C<), 151.4 (C≡N); MS (EI) *m/z* 362 ($[M+2]^+$, 1), 360 (M^+, 1), 312 (55), 282 (100), 240 (20), 178 (21). *Anal.* Calcd for $C_{20}H_{13}N_2Br$: C, 66.50; H, 3.63; N, 7.76. Found: C, 66.67; H, 3.41; N, 7.59.

Reactions of *N*-Aryl-substituted Azuleno[1,2-*c*]pyrroles (7aa-bd) with Dimethyl Acetylenedicarboxylate. A solution of *N*-aryl-substituted azuleno[1,2-*c*]pyrroles (**7aa-ad**,**ba-bc**) (0.5 mmol) and dimethyl acetylenedicarboxylate (106 mg, 0.75 mmol) in tetrahydrofuran (20 mL) was heated under reflux for 12 h. The evaporation residue was chromatographed on a silica gel column with benzene. The green fraction gave 1-anilino-2,3-dimethoxycarbonyl-4-methylbenz[*a*]azulenes (**8aa-bd**,**ba**, **bb**,**bd**), while brownish green fraction gave 2-aryl-8-methoxycarbonyl-1-(1,2-dimethoxycarbonylethenyl)-4-methylazuleno[1,2-*c*]pyrroles (**9ab-ad**,**ba-bc**).

1-Anilino-2,3,10-trimethoxycarbonyl-4-methylbenz[*a*]azulene (8aa). Green prisms (from benzene); yield 142 mg (62%); mp 218-220 °C; IR (KBr) ν 3308 (NH), 1730 (C=O), 1604 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.97 (3H, s, CH_3), 3.69 (3H, s, $COOCH_3$), 3.74 (3H, s, $COOCH_3$), 3.94 (3H, s, $COOCH_3$), 6.62 (2H, dd, *J* = 8.1, 7.5 Hz, 3'-,5'-H), 6.79 (1H, t, *J* = 7.5 Hz, 4'-H), 7.09 (2H, d, *J* = 8.1 Hz, 2'-,6'-H), 7.18 (1H, dd, *J* = 9.6, 9.0 Hz, 8-H), 7.30 (1H, dd, *J* = 11.1, 9.9 Hz, 6-H), 7.47 (1H, dd, *J* = 9.9, 9.9 Hz, 7-H), 7.97 (1H, s, NH), 8.52 (1H, d, *J* = 11.1 Hz, 5-H), 8.74 (1H, d, *J* = 9.0 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 19.7 (CH_3), 52.1 ($COOCH_3$), 52.4 ($COOCH_3$), 52.6 ($COOCH_3$), 115.9 (=CH-), 116.8 (=C<), 119.9 (=CH-), 123.9 (=C<), 127.7 (=C<), 128.1 (=CH-), 128.5 (=CH-), 128.9 (=CH-), 129.7 (=C<), 130.7 (=C<), 132.9 (=C<), 135.1 (=C<), 135.9 (=CH-), 136.6 (=CH-), 138.1 (=CH-), 141.5 (=C<), 141.6 (=C<), 144.9 (=C<), 167.2 ($COOCH_3$), 168.3 ($COOCH_3$), 169.7 ($COOCH_3$). *Anal*. Calcd for $C_{27}H_{23}NO_6$: C, 70.88; H, 5.07; N, 3.06. Found: C, 70.66; H, 5.03; N, 3.07.

2,3,10-Trimethoxycarbonyl-4-methyl-1-(4-methylanilino)benz[*a*]azulene (8ab). Green prisms (from benzene); yield 144 mg (61%); mp 203-204 °C; IR (KBr) ν 3331 (NH), 1725 (C=O), 1673 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.21 (3H, s, 4'-CH_3), 3.94 (3H, s, 4-CH_3), 3.67 (3H, s, $COOCH_3$), 3.75 (3H, s, $COOCH_3$), 3.97 (3H, s, $COOCH_3$), 6.54 (2H, d, *J* = 8.4 Hz, 2'-,6'-H), 6.90 (2H, dd, *J* = 8.4, 8.4 Hz, 3'-,5'-H), 7.16 (1H, dd, *J* = 9.9, 9.0 Hz, 8-H), 7.31 (1H, dd, *J* = 11.1, 9.9 Hz, 6-H), 7.44 (1H, t, *J* = 9.9 Hz, 7-H), 8.02 (1H, s, NH), 8.51 (1H, d, *J* = 11.1 Hz, 5-H), 8.82 (1H, d, *J* = 9.0 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 19.7 (CH_3), 20.5 (CH_3), 52.1 ($COOCH_3$), 52.4 ($COOCH_3$), 52.5 ($COOCH_3$), 116.2 (=CH-), 116.8 (=C<), 123.0 (=C<), 127.0 (=C<), 128.0 (=CH-), 128.4 (=CH-), 129.4 (=CH-), 129.7 (=CH-), 130.7 (=C<), 133.7 (=C<), 134.8 (=C<), 135.9 (=CH-), 136.6 (=CH-), 138.0 (=CH-), 141.4 (=C<), 141.5 (=C<), 142.4 (=C<), 167.1 ($COOCH_3$), 168.3 ($COOCH_3$), 169.8 ($COOCH_3$). *Anal*. Calcd for $C_{28}H_{25}NO_6$: C, 71.32; H, 5.34; N, 2.97. Found: C, 71.10; H, 5.07; N, 2.98.

1-(1,2-Dimethoxycarbonylethenyl)-9-methoxycarbonyl-3-methyl-2-(4-methylphenyl)-azuleno[1,2-*c*]pyrrole (9ab). Green prisms (from benzene); yield 21 mg (9%); mp 215-216 °C; IR (KBr) ν 1724 (C=O), 1699 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.30 (3H, s, 4'-CH_3), 2.71 (3H, s, 4-CH_3), 3.26 (3H, s, $COOCH_3$), 3.74 (3H, s, $COOCH_3\times 2$), 7.04-7.07 (4H, m, 2'-,3'-,5'-,6'-H), 7.43 (1H, dd, *J* = 11.2, 9.9 Hz, 7-H), 7.46 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.71 (1H, t, *J* = 9.9 Hz, 6-H), 7.92 (1H, s, 1-C=CH), 8.46 (1H, d, *J* = 9.6 Hz, 4-H), 9.10 (1H, d, *J* = 11.2 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 20.5 (CH_3), 23.8 (CH_3), 50.8 ($COOCH_3$), 51.7 ($COOCH_3$), 51.9 ($COOCH_3$), 55.6 (OCH_3), 109.5 (=C<), 113.4 (=CH-), 122.6 (=C<), 125.6 (=C<), 127.4 (=C<), 127.8 (=CH-), 129.2 (=C<), 129.6 (=CH-), 131.1 (=C<), 135.8 (=CH-), 135.9 (=CH-), 137.7 (=C<), 138.1 (=CH-), 142.6 (=CH<), 143.0 (=C<), 144.8 (=C<), 147.4 (=CH-), 156.4 (=C<), 164.7 ($COOCH_3$), 167.0 ($COOCH_3$), 167.8 ($COOCH_3$). *Anal*. Calcd for $C_{28}H_{25}NO_6$: C, 71.32; H, 5.34; N, 2.97. Found: C, 70.98; H, 5.07; N, 3.06.

1-(4-Methoxyanilino)-2,3,10-trimethoxycarbonyl-4-methylbenz[*a*]azulene (8ac). Green prisms (from benzene); yield 88 mg (36%); mp 197-198 °C; IR (KBr) ν 3323 (NH), 1731 (C=O), 1673

cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.93 (3H, s, CH_3), 3.66 (3H, s, $COOCH_3$), 3.69 (3H, s, $COOCH_3$), 3.76 (3H, s, $COOCH_3$), 3.93 (3H, s, OCH_3), 6.63 (2H, d, *J* = 9.0 Hz, 3'-,5'-H), 6.68 (2H, dd, *J* = 9.0, 9.0 Hz, 2'-,6'-H), 7.15 (1H, dd, *J* = 11.4, 9.6 Hz, 6-H), 7.27 (1H, dd, *J* = 9.9, 9.0 Hz, 8-H), 7.44 (1H,dd, *J* = 9.9, 9.6 Hz, 7-H), 8.01 (1H, s, NH), 8.51 (1H, d, *J* = 11.4 Hz, 5-H), 8.81 (1H, d, *J* = 9.0 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 19.6 (CH_3), 52.1 ($COO\underline{C}H_3$), 52.3 ($COO\underline{C}H_3$), 52.5 ($COO\underline{C}H_3$), 55.5 (OCH_3), 114.3 (=CH-), 116.7 (=C<), 117.9 (=CH-), 122.0 (=C<), 126.4 (=C<), 128.0 (=CH-), 128.2 (=CH-), 128.3 (=C<), 129.8 (=C<), 130.8 (=C<), 134.4 (=C<), 134.5 (=C<), 135.9 (=CH-), 136.6 (=CH-), 138.1 (=CH-), 138.5 (=C<), 141.4 (=C<), 141.5 (=C<), 153.9 (=C<), 167.1 ($\underline{C}OOCH_3$), 168.4 ($\underline{C}OOCH_3$), 169.9 ($\underline{C}OOCH_3$). *Anal*. Calcd for $C_{28}H_{25}NO_7$: C, 68.98; H, 5.17; N, 2.87. Found: C, 68.94; H, 5.18; N, 2.98.

1-(1,2-Dimethoxycarbonylethenyl)-9-methoxycarbonyl-2-(4-methoxyphenyl)-3-methylazuleno[1,2-*c*]pyrrole (9ac). Green prisms (from benzene); yield 61 mg (25%); mp 192-193 °C; IR (KBr) ν 1722 (C=O), 1715 (C=O), 1673 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.70 (3H, s, CH_3), 3.54 (3H, s, $COOCH_3$), 3.67 (3H, s, $COOCH_3$), 3.75 (3H, s, $COOCH_3$), 3.85 (3H, s, OCH_3), 6.84 (2H, d, *J* = 9.0 Hz, 3'-,5'-H), 7.12 (2H, d, *J* = 9.0 Hz, 2'-,6'-H), 7.41 (1H, dd, *J* = 9.9, 9.6 Hz, 8-H), 7.44 (1H, dd, *J* = 9.9, 9.4 Hz, 6-H), 7.66 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.92 (1H, s, 1-C=CH), 8.42 (1H, d, *J* = 9.4 Hz, 5-H), 9.04 (1H, d, *J* = 9.9 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 23.7 (CH_3), 50.9 ($COO\underline{C}H_3$), 51.7 ($COO\underline{C}H_3$), 51.9 ($COO\underline{C}H_3$), 55.7 (OCH_3), 109.3 (=C<), 114.5 (=CH-), 114.9 (=CH-), 122.2 (=C<), 125.5 (=C<), 127.5 (=C<), 127.6 (=CH-), 129.2 (=CH-), 134.5 (=C<), 135.5 (=CH-), 135.7 (=CH-), 137.7 (=C<), 137.9 (=CH-), 138.9 (=C<), 144.8 (=C<), 147.9 (=CH-), 154.9 (=C<), 156.9 (=C<), 164.7 ($\underline{C}OOCH_3$), 167.0 ($\underline{C}OOCH_3$), 167.8 ($\underline{C}OOCH_3$). *Anal*. Calcd for $C_{28}H_{25}NO_7$: C, 68.98; H, 5.17; N, 2.87. Found: C, 68.93; H, 5.20; N, 2.90.

1-(4-Bromoanilino)-2,3,10-trimethoxycarbonyl-4-methylbenz[*a*]azulene (8ad). Green prisms (from benzene); yield 134 mg (50%); mp 221-222 °C; IR (KBr) ν 3338 (NH), 1727 (C=O), 1676 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.98 (3H, s, CH_3), 3.71 (3H, s, $COOCH_3$), 3.78 (3H, s, $COOCH_3$), 3.94 (3H, s, $COOCH_3$), 6.47 (2H, d, *J* = 8.7 Hz, 2'-,6'-H), 7.17 (2H, dd, *J* = 8.7, 8.7 Hz, 3'-,5'-H), 7.26 (1H, dd, *J* = 10.2, 9.0 Hz, 8-H), 7.38 (1H, dd, *J* = 11.4, 9.6 Hz, 6-H), 7.54 (1H, dd, *J* = 10.2, 9.6 Hz, 7-H), 7.79 (1H, s, NH), 8.57 (1H, d, *J* = 11.4 Hz, 5-H), 8.86 (1H, d, *J* = 9.0 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 19.7 (CH_3), 52.2 ($COO\underline{C}H_3$), 52.5 ($COO\underline{C}H_3$), 52.6 ($COO\underline{C}H_3$), 111.5 (=CH-), 116.3 (=C<), 117.1 (=CH-), 125.4 (=C<), 128.3 (=C<), 128.8 (=CH-), 129.5 (=C<), 130.7 (=C<), 131.6 (=CH-), 131.9 (=C<), 135.6 (=C<), 135.9 (=CH-), 136.8 (=CH-), 138.2 (=CH-), 141.5 (=C<), 141.7 (=C<), 142.0 (=C<), 144.4 (=C<), 167.3 ($\underline{C}OOCH_3$), 168.1 ($\underline{C}OOCH_3$), 169.5 ($\underline{C}OOCH_3$). *Anal*. Calcd for $C_{27}H_{22}NO_6Br$: C, 60.46; H, 4.14; N, 2.61. Found: C, 60.51; H, 4.12; N, 2.63.

1-(1,2-Dimethoxycarbonylethenyl)-9-methoxycarbonyl-3-methyl-2-(4-bromophenyl)-azuleno[1,2-*c*]pyrrole (9ad). Green prisms (from benzene); yield 62 mg (23%); mp 224-225 °C; IR (KBr) ν 1731 (C=O), 1704 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.75 (3H, s, CH_3), 3.34 (3H, s, $COOCH_3$), 3.74 (3H, s, $COOCH_3$), 3.75 (3H, s, $COOCH_3$), 7.01 (2H, d, *J* = 9.0 Hz, 2'-,6'-H), 7.37 (2H, d, *J* = 9.0 Hz, 3'-,5'-H), 7.45 (1H, dd, *J* = 11.1, 9.6 Hz, 7-H), 7.49 (1H, dd, *J* = 11.1, 9.3 Hz,

5-H), 7.76 (1H, t, *J* = 11.1 Hz, 6-H), 7.80 (1H, s, 1-C=CH), 8.52 (1H, d, *J* = 9.3 Hz, 4-H), 9.23 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 23.9 (CH_3), 50.9 ($COO\underline{C}H_3$), 51.8 ($COO\underline{C}H_3$), 52.1 ($COO\underline{C}H_3$), 109.0 (=C<), 113.6 (=C<), 114.7 (=CH-), 124.1 (=C<), 125.7 (=C<), 127.1 (=C<), 128.1 (=CH-), 129.5 (=CH-), 132.0 (=CH-), 136.5 (=CH-), 136.6 (=CH-), 137.8 (=C<), 138.8 (=CH-), 143.1 (=C<), 144.2 (=C<), 145.0 (=C<), 145.7 (=C<), 155.0 (=CH-), 164.4 ($\underline{C}OOCH_3$), 166.7 ($\underline{C}OOCH_3$), 167.6 ($\underline{C}OOCH_3$). *Anal*. Calcd for $C_{27}H_{22}NO_6Br$: C, 60.46; H, 4.14; N, 2.61. Found: C, 60.70; H, 4.21; N, 2.60.

1-Anilino-10-cyano-2,3-dimethoxycarbonyl-4-methylbenz[*a*]azulene (8ba). Green prisms (from benzene); yield 119 mg (56%); mp 237-238 °C; IR (KBr) ν 3378 (NH), 2204 (C ≡ N), 1726 (C=O), 1706 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.99 (3H, s, CH_3), 3.82 (3H, s, $COOCH_3$), 3.96 (3H, s, $COOCH_3$), 6.63 (2H, d, *J* = 7.5 Hz, 2'-,6'-H), 6.86 (1H, t, *J* = 7.5 Hz, 4'-H), 7.14 (2H, t, *J* = 7.5 Hz, 3'-,5'-H), 7.39 (1H, dd, *J* = 11.4, 9.9 Hz, 6-H), 7.53 (1H, dd, *J* = 9.9, 9.3 Hz, 8-H), 7.56 (1H, s, NH), 7.68 (1H, t, *J* = 9.9 Hz, 7-H), 8.38 (1H, d, *J* = 11.4 Hz, 5-H), 8.95 (1H, d, *J* = 9.3 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 19.5 (CH_3), 52.7 ($COO\underline{C}H_3$), 52.9 ($COO\underline{C}H_3$), 95.4 (=C<), 115.9 (=CH-), 116.7 (=C<), 120.6 (=CH-), 124.5 (=C<), 129.2 (=CH-), 129.4 (=C<), 129.6 (=CH-), 129.9 (=CH-), 130.0 (=C<), 130.2 (=C<), 132.9 (=C<), 136.2 (=CH-), 137.3 (=C<), 137.8 (=CH-), 139.3 (=CH-), 141.2 (=C<), 146.2 (=C<), 148.4 (C≡N), 167.6 ($\underline{C}OOCH_3$), 169.4 ($\underline{C}OOCH_3$). *Anal*. Calcd for $C_{26}H_{20}N_2O_4$: C, 73.57; H, 4.75; N, 6.60. Found: C, 73.76; H, 4.58; N, 6.69.

9-Cyano-1-[1,2-di(methoxycarbonyl)ethenyl]-3-methyl-2-phenylazuleno[1,2-*c*]pyrrole (9ba). Yellowish brown prisms (from benzene); yield 74 mg (35%); mp 190-191 °C; IR (KBr) ν 2204 (C ≡ N), 1723 (C=O), 1704 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.53 (3H, s, CH_3), 3.72 (3H, s, $COOCH_3$), 3.75 (3H, s, $COOCH_3$), 7.38-7.48 (5H, m, 3'-,4-,4'-,5'-,6-H), 7.49 (2H, d, *J* = 6.9 Hz, 2'-,6'-H), 7.58 (1H, t, *J* = 9.9 Hz, 6-H), 7.88 (1H, s, 1-C=CH), 8.15 (1H, d, *J* = 10.5 Hz, 9-H), 8.18 (1H, d, *J* = 9.0 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 23.5 (CH_3), 51.8 ($COO\underline{C}H_3$), 52.0 ($COO\underline{C}H_3$), 89.2 (=CH-), 113.7 (=C<), 118.7 (=C<), 122.2 (=CH-), 122.8 (=C<), 126.9 (=CH-), 128.1 (=C<), 128.3 (=C<), 129.2 (=CH-), 129.8 (=CH-), 129.9 (=CH-), 133.5 (=CH-), 135.5 (=CH-), 137.7 (=CH-), 138.4 (=C<), 143.1 (=C<), 143.3 (=CH-), 146.9 (=C<), 151.4 (C≡N), 166.7 ($\underline{C}OOCH_3$), 168.0 ($\underline{C}OOCH_3$). *Anal*. Calcd for $C_{26}H_{20}N_2O_4$: C, 73.57; H, 4.75; N, 6.60. Found: C, 73.76; H, 4.58; N, 6.69.

10-Cyano-2,3-dimethoxycarbonyl-4-methyl-1-(4-methylanilino)benz[*a*]azulene (8bb). Green prisms (from benzene); yield 178 mg (81%); mp 202-203 °C; IR (KBr) ν 3378 (NH), 2201 (C ≡ N), 1724 (C=O), 1708 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.23 (3H, s, 4'-CH_3), 3.00 (3H, s, 4-CH_3), 3.82 (3H, s, $COOCH_3$), 3.96 (3H, s, $COOCH_3$), 6.55 (2H, d, *J* = 8.4 Hz, 2'-,6'-H), 6.94 (1H, dd, *J* = 8.4 Hz, 3'-,5'-H), 7.40 (1H, dd, *J* = 9.9, 9.3 Hz, 8-H), 7.50 (1H, dd, *J* = 10.0, 9.9 Hz, 6-H), 7.59 (1H, s, NH), 7.68 (1H, t, *J* = 9.9 Hz, 7-H), 8.41 (1H, d, *J* = 10.5 Hz, 5-H), 8.95 (1H, d, *J* = 9.3 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 19.4 (4'-CH_3), 20.6 (4-CH_3), 52.7 ($COO\underline{C}H_3$), 52.8 ($COO\underline{C}H_3$), 94.3 (=C<), 116.1 (=CH-), 116.7 (=C<), 123.8 (=C<), 128.3 (=C<), 128.9 (=C<), 129.5 (=CH-), 129.7 (=CH-), 129.8 (=CH-), 129.9 (=C<), 130.1 (=C<), 133.4 (=C<), 135.9 (=CH-), 137.0 (=C<), 137.7 (=CH-), 139.2 (=CH-), 141.0 (=C<), 143.8 (=C<), 148.1 (C≡N), 167.5 ($\underline{C}OOCH_3$), 169.5 ($\underline{C}OOCH_3$).

Anal. Calcd for $C_{27}H_{22}N_2O_4$: C, 73.96; H, 5.06; N, 6.39. Found: C, 74.15; H, 5.27; N, 6.43.

9-Cyano-1-(1, 2-dimethoxycarbonylethenyl)-3-methyl-2-(4-methylphenyl)azuleno[1,2-*c*]-pyrrole (9bb). Yellowish brown prisms (from benzene); yield 7 mg (3%); mp 135-136 °C; IR (KBr) ν 2206 (C≡N), 1723 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.42 (3H, s, 4'-CH_3), 2.49 (3H, s, 4-CH_3), 3.71 (3H, s, $COOCH_3$), 3.75 (3H, s, $COOCH_3$), 7.18 (2H, d, *J* = 9.0 Hz, 3'-,5'-H), 7.28 (2H, d, *J* = 9.0 Hz, 2'-,6'-H), 7.40 (1H, dd, *J* = 10.5, 9.9 Hz, 7-H), 7.43 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.55 (1H, t, *J* = 9.9 Hz, 5-H), 7.82 (1H, s, 1-C=CH), 8.10 (1H, d, *J* = 9.6 Hz, 4-H), 8.12 (1H, d, *J* = 10.5 Hz, 8-H). *Anal*. Calcd for $C_{27}H_{22}N_2O_5$: C, 73.96; H, 5.06; N, 6.39. Found: C, 74.23; H, 4.93; N, 6.35.

9-Cyano-1-[1,2-di(methoxycarbonyl)ethenyl]-2-(4-methoxyphenyl)-3-methylazuleno[1,2-*c*] pyrrole (9bc). Yellowish brown prisms (from benzene); yield 175 mg (77%); mp 218-219 °C; IR (KBr) ν 2204 (C ≡ N), 1709 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.35 (3H, s, CH_3), 3.62 (3H, s, $COOCH_3$), 3.67 (3H, s, $COOCH_3$), 3.77 (3H, s, OCH_3), 6.91 (2H, d, *J* = 9.0 Hz, 3'-,5'-H), 7.22 (2H, dd, *J* = 9.9, 9.6 Hz, 5-,7-H), 7.34 (2H, d, *J* = 9.0 Hz, 2'-,6'-H), 7.40 (1H, t, *J* = 9.9 Hz, 6-H), 7.63 (1H, s, 1-C=CH), 7.93 (2H, d, *J* = 9.6 Hz, 4-,8-H); ^{13}C NMR ($CDCl_3$) δ 23.5 (CH_3), 51.7 ($COO\underline{C}H_3$), 51.9 ($COO\underline{C}H_3$), 55.5 (OCH_3), 88.3 (=C<), 113.4 (=C<), 115.0 (=CH-), 116.9 (=C<), 121.7 (=C<), 125.9 (=CH-), 128.2 (=CH-), 129.2 (=CH-), 130.0 (=CH-), 132.6 (=CH-), 134.8 (=CH-), 136.5 (=C<), 136.9 (=C<), 137.0 (=CH-), 138.6 (=C<), 142.8 (=C<), 147.1 (=C<), 153.6 (=CH-), 159.1 (=C<), 162.7 (C≡N), 166.7 ($\underline{C}OOCH_3$), 168.2 ($\underline{C}OOCH_3$). *Anal*. Calcd for $C_{27}H_{22}N_2O_5$: C, 71.35; H, 4.88; N, 6.16. Found: C, 71.62; H, 4.69; N, 6.05.

1-(4-Bromoanilino)-10-cyano-2,3-dimethoxycarbonyl-4-methylbenz[*a*]azulene (8bd). Green prisms (from benzene); yield 219 mg (87%); mp 264-265 °C; IR (KBr) ν 3325 (NH), 2203 (C ≡ N), 1723 (C=O), 1706 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 3.00 (3H, s, CH_3), 3.83 (3H, s, $COOCH_3$), 3.97 (3H, s, $COOCH_3$), 6.48 (2H, d, *J* = 8.7 Hz, 2'-,6'-H), 7.22 (1H, d, *J* = 8.7 Hz, 3'-,5'-H), 7.39 (1H, s,NH), 7.44 (1H, dd, *J* = 9.9, 9.0 Hz, 8-H), 7.56 (1H, dd, *J* = 10.5, 9.9 Hz, 6-H), 7.71 (1H, t, *J* = 9.9 Hz, 7-H), 8.41 (1H, d, *J* = 10.5 Hz, 5-H), 8.98 (1H, d, *J* = 9.0 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 19.5 (CH_3), 52.8 ($COO\underline{C}H_3$), 53.0 ($COO\underline{C}H_3$), 94.2 (=C<), 112.5 (=C<), 116.7(=C<), 117.2 (=CH-), 125.5 (=C<), 128.3 (=CH-), 129.7 (=CH-), 130.0 (=C<), 130.1 (=C<), 130.2 (=CH-), 130.3 (=C<), 132.0 (=CH-), 136.3 (=CH-), 137.7 (=C<), 138.0 ((=CH-), 139.4 (=C<), 141.2 (=C<), 145.6 (C≡N), 167.4 ($\underline{C}OOCH_3$), 169.2 ($\underline{C}OOCH_3$). *Anal*. Calcd for $C_{26}H_{19}N_2O_4Br$: C, 62.04; H, 3.80; N, 5.57. Found: C, 62.25; H, 3.98; N, 5.53.

2-(4-Bromophenyl)-9-cyano-1-(1, 2-dimethoxycarbonylethenyl)-3-methylazuleno[1,2-*c*]-pyrrole (9bd). Yellowish brown prisms (from benzene); yield 15 mg (6%); mp 235-236 °C; IR (KBr) ν 2205 (C≡N), 1722 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.58 (3H, s, CH_3), 3.73 (3H, s, $COOCH_3$), 3.75 (3H, s, $COOCH_3$), 7.32 (2H, d, *J* = 6.6 Hz, 2'-,6'-H), 7.45 (1H, dd, *J* = 10.2, 9.9 Hz, 7-H), 7.47 (1H, dd, *J* = 9.9, 9.3 Hz, 5-H), 7.56 (2H, dd, *J* = 6.6 Hz, 3'-,5'-H), 7.67 (1H, t, *J* = 9.9 Hz, 6-H), 7.82 (1H, s, 1-C=CH), 8.25 (1H, d, *J* = 9.3 Hz, 4-H), 8.27 (1H, d, *J* = 9.9 Hz, 8-H). *Anal*. Calcd for $C_{26}H_{19}N_2O_4Br$: C, 62.04; H, 3.80; N, 5.57. Found: C, 62.24; H, 3.72; N, 5.56.

Reactions of *N*-Aryl-substituted Azuleno[1,2-*c*]pyrroles (7aa-bd) with Diethyl Acetylenedicarboxylate. A solution of *N*-aryl-substituted azuleno[1,3-*c*]pyrroles (**7aa-bd**) (0.5 mmol) and diethyl acetylenedicarboxylate (128 mg, 0.75 mmol) in tetrahydrofuran (20 mL) was heated under reflux for 12 h. The reaction mixture was worked up, as described above, to give 1-anilino-2,3-diethoxycarbonyl-4-methylbenz[*a*]azulenes (**10aa-bd**,**ba-bd**) and 2-aryl-3-methyl-1-(1,2-diethoxycarbonyl)azuleno[1,2-*c*]-pyrroles (**11ab-ad**,**ba-bd**).

1-Anilino-10-methoxycarbonyl-2,3-diethoxycarbonyl-4-methylbenz[*a*]azulene (10aa). Greenish prisms (from benzene); yield 109 mg (45%); mp 162-163 °C; IR (KBr) ν 3313 (NH), 1727 (C=O), 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.21 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.41 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 2.99 (3H, s, CH_3), 3.72 (3H, s, $COOCH_3$), 4.15 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.40 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 6.60 (2H, d, *J* = 7.8 Hz, 2'-,6'-H), 6.77 (1H, t, *J* = 7.5 Hz, 4'-H), 7.08 (2H, dd, *J* = 7.8, 7.5 Hz, 3'-,5'-H), 7.19 (1H, dd, *J* = 9.9, 9.0 Hz, 8-H), 7.31 (1H, dd, *J* = 11.1, 9.9 Hz, 6-H), 7.46 (1H, t, *J* = 9.9 Hz, 7-H), 7.84 (1H, s, NH), 8.51 (1H, d, *J* = 11.1 Hz, 5-H), 8.85 (1H, d, *J* = 9.0 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 13.8 ($CH_2\underline{C}H_3$), 14.1 ($CH_2\underline{C}H_3$), 19.7 (CH_3), 52.1 ($COO\underline{C}H_3$), 61.6 ($\underline{C}H_2CH_3$ × 2), 115.7 (=CH-), 116.9 (=C<), 119.7 (=CH-), 127.9 (=C<), 128.0 (=CH-), 128.4 (=CH-), 128.8 (=C<), 129.8 (=C<), 130.7 (=C<), 132.5 (=C<), 135.4 (=CH-), 135.8 (=CH-), 136.4 (=CH-), 138.0 (=CH-), 141.5 (=C<), 141.6 (=C<), 145.1 (=C<), 167.2 (=C<), 167.4 ($\underline{C}OOCH_3$), 167.9 ($\underline{C}OOC_2H_5$) 169.2 ($\underline{C}OOC_2H_5$). *Anal*. Calcd for $C_{29}H_{27}NO_6$: C, 71.74; H, 5.61; N, 2.89. Found: C, 71.90; H, 5.66; N, 2.72.

2,3-Diethoxycarbonyl-10-methoxycarbonyl-4-methyl-1-(4-methylanilino)benz[*a*]azulene (10ab). Greenish prisms (from benzene); yield 167 mg (67%); mp 167-168 °C; IR (KBr) ν 3342 (NH), 1739 (C=O), 1723 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.23 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.40 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 2.21 (3H, s, 4'-CH_3), 2.98 (3H, s, 4-CH_3), 3.74 (3H, s, $COOCH_3$), 4.14 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.40 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 6.52 (2H, d, *J* = 8.4 Hz, 2'-,6'-H), 6.89 (1H, d, *J* = 8.4 Hz, 3'-,5'-H), 7.18 (1H, dd, *J* = 9.9, 9.0 Hz, 8-H), 7.30 (1H, dd, *J* = 11.1, 9.9 Hz, 6-H), 7.46 (1H, t, *J* = 9.9 Hz, 7-H), 7.91 (1H, s, NH), 8.52 (1H, d, *J* = 11.1 Hz, 5-H), 8.84 (1H, d, *J* = 9.0 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 13.8 ($CH_2\underline{C}H_3$), 14.1 ($CH_2\underline{C}H_3$), 19.6 (CH_3), 20.5 (CH_3), 52.1 ($COO\underline{C}H_3$), 61.5 ($\underline{C}H_2CH_3$), 61.6 ($\underline{C}H_2CH_3$), 116.1 (=CH-), 117.0 (=C<), 124.0 (=C<), 127.2 (=CH-), 128.0(=CH-), 128.3 (=CH-), 129.2 (=C<), 129.3 (=C<), 129.9 (=C<), 130.7 (=C<), 133.3 (=C<), 135.0 (=C<), 135.9 (=CH-), 136.4 (=CH-), 137.9 (=CH-), 141.4 (=C<), 141.5 (=C<), 142.6 (=C<), 167.2 ($\underline{C}OOCH_3$), 168.0 ($\underline{C}OOC_2H_5$), 169.3 ($\underline{C}OOC_2H_5$). *Anal*. Calcd for $C_{30}H_{29}NO_6$: C, 72.13; H, 5.85; N, 2.80. Found: C, 72.27; H, 6.07; N, 2.70.

1-(1,2-Diethoxycarbonyl)-9-methoxycarbonyl-4-methyl-2-(4-methylphenyl)azuleno-[1,2-*c*]pyrrole (11ab). Greenish prisms (from benzene); yield 47 mg (19%); mp 209-210 °C; IR (KBr) ν 1725 (C=O), 1711 (C=O), 1701 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.27 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.28 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 2.30 (3H, s, CH_3), 2.71 (3H, s, CH_3), 3.26 (3H, s, $COOCH_3$), 4.16 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.21 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 7.07-7.09 (4H, m, 2'-,3'-,5'-,6'-H), 7.42 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.46 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.69 (1H, t,

J = 9.9 Hz, 6-H), 7.90 (1H, s, 1-C=CH), 8.46 (1H, d, *J* = 9.6 Hz, 4-H), 9.90 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 14.1 ($CH_2\underline{C}H_3$), 14.2 ($CH_2\underline{C}H_3$), 20.6 (CH_3), 23.8 (CH_3), 50.8 ($COO\underline{C}H_3$), 60.6 ($\underline{C}H_2CH_3$), 60.9 ($\underline{C}H_2CH_3$), 109.4 (=CH-), 113.4 (=CH-), 123.0 (=C<), 125.8 (=C<), 127.7 (=CH-), 128.3 (=C<), 129.1 (=CH-), 129.6 (=CH-), 131.1 (=C<), 135.7 (=C<), 135.9 (=CH-), 137.7 (=C<), 138.0 (=CH-), 142.7 (=C<), 143.0 (=C<), 144.3 (=C<), 147.0 (=CH-), 156.5 (=C<), 164.8 ($\underline{C}OOCH_3$), 166.7 ($\underline{C}OOC_2H_5$), 167.4 ($\underline{C}OOC_2H_5$). *Anal*. Calcd for $C_{30}H_{29}NO_6$: C, 72.13; H, 5.85; N, 2.80. Found: C, 71.99; H, 5.98; N, 2.60.

2,3-Diethoxycarbonyl-1-(4-methoxyanilino)-10-methoxycarbonyl-4-methylbenz[*a*]azulene (10ac). Greenish prisms (from benzene); yield 139 mg (54%); mp 142-143 °C; IR (KBr) ν 3331 (NH), 1727 (C=O), 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.23 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.40 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 2.99 (3H, s, CH_3), 3.70 (3H, s, OCH_3), 3.75 (3H, s, $COOCH_3$), 4.14 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.40 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 6.58 (2H, d, *J* = 9.0 Hz, 3'-,5'-H), 6.67 (1H, d, *J* = 9.0 Hz, 2'-,6'-H), 7.20 (1H, dd, *J* = 9.9, 9.3 Hz, 8-H), 7.33 (1H, dd, *J* = 11.4, 9.3 Hz, 6-H), 7.49 (1H, dd, *J* = 9.9, 9.3 Hz, 7-H), 7.99 (1H, s, NH), 8.53 (1H, d, *J* = 11.4 Hz, 5-H), 8.87 (1H, d, *J* = 9.3 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 13.9 ($CH_2\underline{C}H_3$), 14.1 ($CH_2\underline{C}H_3$), 19.7 (CH_3), 52.1 ($COO\underline{C}H_3$), 55.5 (OCH_3), 61.5 ($\underline{C}H_2CH_3$), 61.6 ($\underline{C}H_2CH_3$), 114.2 (=CH-), 117.0 (=C<), 117.7 (=CH-), 123.1 (=C<), 126.7 (=C<), 127.9 (=CH-), 128.2 (=CH-), 128.3 (=CH-), 130.1 (=C<), 130.9 (=C<), 134.1 (=C<), 134.7 (=C<), 135.9 (=CH-), 136.4 (=CH-), 137.9 (=CH-), 138.8 (=C<), 141.4 (=C<), 141.6 (=C<), 153.8 (=C<), 167.1 ($\underline{C}OOCH_3$), 168.1 ($\underline{C}OOC_2H_5$), 169.4 ($\underline{C}OOC_2H_5$). *Anal*. Calcd for $C_{30}H_{29}NO_7$: C, 69.89; H, 5.67; N, 2.72. Found: C, 70.01; H, 5.83; N, 2.74.

1-(1,2-Diethoxycarbonyl)-9-methoxycarbonyl-2-(4-methoxyphenyl)-4-methylazuleno-[1,2-*c*]pyrrole (11ac). Greenish prisms (from benzene); yield 57 mg (22%); mp 139-140 °C; IR (KBr) ν 1726 (C=O), 1671 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.27 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.29 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 2.70 (3H, s, CH_3), 3.30 (3H, s, $COOCH_3$), 3.78 (3H, s, OCH_3), 4.18 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.21 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 6.85 (2H,d, *J* = 9.0 Hz, 2'-,6'-H), 7.13 (2H, d, *J* = 9.0 Hz, 3'-,5'-H), 7.41 (1H, dd, *J* = 9.9, 9.6 Hz, 7-H), 7.44 (1H, dd, *J* = 9.9, 9.3 Hz, 5-H), 7.66 (1H, t, *J* = 9.9 Hz, 6-H), 7.90 (1H, s, 1-C=CH), 8.42 (1H, d, *J* = 9.3 Hz, 4-H), 9.03 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 14.1 ($CH_2\underline{C}H_3$), 14.2 ($CH_2\underline{C}H_3$), 23.8 (CH_3), 50.9 ($COO\underline{C}H_3$), 55.6 (OCH_3), 60.6 ($\underline{C}H_2CH_3$), 60.8 ($\underline{C}H_2CH_3$), 109.2 (=CH-), 114.5 (=CH-), 114.9 (=CH-), 122.6 (=C<), 125.7 (=C<), 127.7 (=CH-), 129.1 (=CH-), 135.4 (=CH-), 135.7 (=CH-), 137.6 (=C<), 137.8 (=CH-), 139.0 (=C<), 143.1 (=C<), 144.3 (=C<), 147.5 (=CH-), 154.9 (=C<), 157.1 (=C<), 164.8 ($\underline{C}OOCH_3$), 166.7 ($\underline{C}OOC_2H_5$), 167.4 ($\underline{C}OOC_2H_5$). *Anal*. Calcd for $C_{30}H_{29}NO_7$: C, 69.98; H, 5.67; N, 2.72. Found: C, 69.96; H, 5.73; N, 2.77.

1-(4-Bromoanilino)-2,3-diethoxycarbonyl-10-methoxycarbonyl-4-methylbenz[*a*]azulene (10ad). Greenish prisms (from benzene); yield 164 mg (58%); mp 196-197 °C; IR (KBr) ν 3336 (NH), 1739 (C=O), 1721 (C=O), 1674 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.21 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.41 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 3.00 (3H, s, CH_3), 3.77 (3H, s, $COOCH_3$), 4.16 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.41 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 6.47 (2H, d, *J* = 8.7 Hz, 2'-,6'-H), 7.16

(1H, d, *J* = 8.7 Hz, 3'-,5'-H), 7.22 (1H, dd, *J* = 9.6, 9.0 Hz, 8-H), 7.33 (1H, dd, *J* = 11.1, 9.9 Hz, 6-H), 7.49 (1H, t, *J* = 9.9 Hz, 7-H), 7.66 (1H, s, NH), 8.52 (1H, d, *J* = 11.1 Hz, 5-H), 8.86 (1H, d, *J* = 9.0 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 13.8 ($CH_2\underline{C}H_3$), 14.1 ($CH_2\underline{C}H_3$), 19.7 (CH_3), 52.2 ($COO\underline{C}H_3$), 61.6 ($\underline{C}H_2CH_3$), 61.7 ($\underline{C}H_2CH_3$), 111.2 (=C<), 116.4 (=C<), 117.0 (=CH-), 126.6 (=C<), 128.2 (=CH-), 128.7 (=CH-), 129.0 (=C<), 129.6 (=C<), 130.6 (=C<), 131.4 (=C<), 131.6 (=CH-), 135.8 (=CH-), 135.9 (=C<), 136.6 (=CH-), 138.1 (=CH-), 141.5 (=C<), 141.9 (=C<), 144.8 (=C<), 167.4 ($\underline{C}OOCH_3$), 167.7 ($\underline{C}OOC_2H_5$), 169.0 ($\underline{C}OOC_2H_5$). *Anal*. Calcd for $C_{29}H_{26}NO_6Br$: C, 61.71; H, 4.64; N, 2.48. Found: C, 61.55; H, 4.69; N, 2.47.

2-(4-Bromophenyl)-1-(1, 2-diethoxycarbonyl)-9-methoxycarbonyl-4-methylazuleno[1,2-*c*]pyrrole (11ad). Greenish prisms (from benzene); yield 54 mg (19%); mp 196-197 °C; IR (KBr) ν 1725 (C=O), 1702 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.28 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.29 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 2.74 (3H, s, CH_3), 3.35 (3H, s, $COOCH_3$), 4.18 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.22 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 7.02 (2H, d, *J* = 9.0 Hz, 2'-,6'-H), 7.37 (2H, d, *J* = 9.0 Hz, 3'-,5'-H), 7.48 (1H, dd, *J* = 10.5, 9.9 Hz, 7-H), 7.52 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.75 (1H, t, *J* = 9.9 Hz, 6-H), 7.78 (1H, s, 1-C=CH), 8.53 (1H, d, *J* = 9.6 Hz, 4-H), 9.22 (1H, d, *J* = 10.5 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 14.1 ($CH_2\underline{C}H_3$), 14.2 ($CH_2\underline{C}H_3$), 23.8 (CH_3), 50.9 ($COO\underline{C}H_3$), 60.7 ($\underline{C}H_2CH_3$), 61.1 ($\underline{C}H_2CH_3$), 108.9 (=C<), 113.5 (=C<), 114.7 (=CH-), 116.6 (=CH-), 124.5 (=C<), 125.9 (=C<), 127.5 (=C<), 128.0 (=CH-), 129.4 (=CH-), 131.8 (=C<), 131.9 (=CH-), 136.4 (=CH-), 137.8 (=C<), 138.7 (=CH-), 143.1 (=C<), 144.2 (=CH-), 144.5 (=C<), 145.4 (=CH-), 155.1 (=C<), 164.4 ($\underline{C}OOCH_3$), 166.4 ($\underline{C}OOC_2H_5$), 167.2 ($\underline{C}OOC_2H_5$). *Anal*. Calcd for $C_{29}H_{26}NO_6Br$: C, 61.71; H, 4.64; N, 2.48. Found: C, 61.76; H, 4.73; N, 2.56.

10-Cyano-2,3-diethoxycarbonyl-4-methyl-1-phenylbenz[*a*]azulene (10ba). Greenish prisms (from benzene); yield 156 mg (69%); mp 184-185 °C; IR (KBr) ν 3328 (NH), 2219 (C≡N), 1724 (C=O), 1710 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.27 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.42 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 3.02 (3H, s, CH_3), 4.27 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.43 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 6.63 (2H, d, *J* = 7.5 Hz, 2'-,6'-H), 6.88 (1H, d, *J* = 7.5 Hz, 4'-H), 7.17 (2H, t, *J* = 7.5 Hz, 3'-,5'-H), 7.43 (1H, dd, *J* = 9.9, 9.0 Hz, 8-H), 7.47 (1H, s, NH), 7.54 (1H, dd, *J* = 10.8, 9.9 Hz, 6-H), 7.69 (1H, t, *J* = 9.9 Hz, 7-H), 8.45 (1H, d, *J* = 10.8 Hz, 5-H), 8.97 (1H, d, *J* = 9.0 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 13.8 ($CH_2\underline{C}H_3$), 14.1 ($CH_2\underline{C}H_3$), 19.5 (CH_3), 61.8 ($\underline{C}H_2CH_3$), 62.1 ($\underline{C}H_2CH_3$), 94.6 (=C<), 115.7 (=CH-), 116.7 (=C<), 120.4 (=CH-), 125.5 (=C<), 129.2 (=CH-), 129.5 (=CH-), 129.6 (=C<), 129.9 (=CH-), 130.0 (=C<), 130.5 (=C<), 132.6 (=C<), 134.4 (=C<), 136.3 (=CH-), 137.7 (=CH-), 139.2 (=CH-), 141.4 (=C<), 146.4 (=C<), 148.4 (C≡N), 167.2 ($\underline{C}OOC_2H_5$), 168.0 ($\underline{C}OOC_2H_5$). *Anal*. Calcd for $C_{28}H_{24}N_2O_4$: C, 74.32; H, 5.35; N, 6.19. Found: C, 74.52; H, 5.52; N, 6.01.

9-Cyano-1-(1,2-diethoxycarbonyl)-4-methyl-2-phenylazuleno[1,2-*c*]pyrrole (11ba). Greenish prisms (from benzene); yield 25 mg (11%); mp 191-192 °C; IR (KBr) ν 2200 (C≡N), 1718 (C=O), 1695 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.27 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.29 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 2.53 (3H, s, CH_3), 4.18 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.22 (2H, q, *J* = 7.2 Hz,

$C\underline{H}_2CH_3$), 7.38 (1H, dd, *J* = 10.5, 9.6 Hz, 7-H), 7.39 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.49 (5H, m, Ph), 7.58 (1H, t, *J* = 9.6 Hz, 6-H), 7.87 (1H, s, 1-C=CH), 8.15 (1H, d, *J* = 9.9 Hz, 4-H), 8.19 (1H, d, *J* = 10.5 Hz, 8-H). *Anal*. Calcd for $C_{28}H_{24}N_2O_4$: C, 74.32; H, 5.35; N, 6.19. Found: C, 73.94; H, 5.48; N, 6.07.

10-Cyano-2,3-diethoxycarbonyl-4-methyl-1-(4-methylphenyl)benz[*a*]azulene (10bb). Greenish prisms (from benzene); yield 205 mg (88%); mp 194-195 °C; IR (KBr) ν 3352 (NH), 2197 (C≡N), 1737 (C=O), 1715 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.27 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.42 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 2.22 (3H, s, 4'-CH_3), 3.00 (3H, s, 4-CH_3), 4.25 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.42 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 6.53 (2H, d, *J* = 8.4 Hz, 2'-,6'-H), 6.93 (1H, d, *J* = 8.4 Hz, 3'-,5'-H), 7.37 (1H, dd, *J* = 9.6, 9.3 Hz, 8-H), 7.45 (1H, s, NH), 7.49 (1H, dd, *J* = 10.5, 9.6 Hz, 6-H), 7.64 (1H, t, *J* = 9.6 Hz, 7-H), 8.31 (1H, d, *J* = 10.5 Hz, 5-H), 8.89 (1H, d, *J* = 9.3 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 14.8 ($CH_2\underline{C}H_3$), 15.0 ($CH_2\underline{C}H_3$), 19.3 (CH_3), 20.6 (CH_3), 61.7 ($\underline{C}H_2CH_3$), 61.9 ($\underline{C}H_2CH_3$), 94.3 (=C<), 115.9 (=CH-), 116.8 (=CH-), 124.7 (=C<), 128.2 (=C<), 129.0 (=C<), 129.4 (=CH-), 129.6 (=CH-), 129.7 (=C<), 129.8 (=CH-), 130.4 (=CH-), 133.1 (=C<), 135.9 (=CH-), 136.8 (=C<), 137.2 (=C<), 137.6 (=CH-), 140.0 (=C<), 141.1 (=C<), 143.9 (=C<), 148.2 (C≡N), 167.2 ($\underline{C}OOC_2H_5$), 168.9 ($\underline{C}OOC_2H_5$). *Anal*. Calcd for $C_{29}H_{26}N_2O_4$: C, 74.66; H, 5.62; N, 6.01. Found: C, 74.71; H, 5.53; N, 6.08.

9-Cyano-1-(1,2-diethoxycarbonyl)-4-methyl-2-(4-methylphenyl)azuleno[1,2-*c*]pyrrole (11bb). Greenish prisms (from benzene); yield 16 mg (7%); mp 179-180 °C; IR (KBr) ν 2202 (C≡N), 1716 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.26 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.29 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 2.42 (3H, s, 4'-CH_3), 2.49 (3H, s, CH_3), 4.17 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.22 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 7.28 (1H, d, *J* = 8.4 Hz, 2'-,6'-H), 7.34-7.36 (2H, m, 5-,7-H), 7.39 (2H, d, *J* = 8.4 Hz, 3'-,5'-H), 7.54 (1H, t, *J* = 9.6 Hz, 6-H), 7.81 (1H, s, 1-C=CH), 8.09 (1H, d, *J* = 9.6 Hz, 4-H), 8.13 (1H, d, *J* = 10.5 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 14.1 ($CH_2\underline{C}H_3$), 14.2 ($CH_2\underline{C}H_3$), 21.1 (CH_3), 23.5 (CH_3), 60.7 ($\underline{C}H_2CH_3$), 60.9 ($\underline{C}H_2CH_3$), 88.9 (=C<), 113.7 (=C<), 118.3 (=C<), 122.9 (=CH-), 128.3 (=C<), 128.7 (=C<), 129.1 (=CH-), 129.8 (=CH-), 130.4 (=CH-), 133.0 (=CH-), 135.2 (=CH-), 137.1 (=C<), 137.2 (=CH-), 138.5 (=C<), 140.9 (=C<), 142.6 (=C<), 147.1 (=C<), 152.0 (=CH-), 162.1 (C≡N), 166.5 ($\underline{C}OOC_2H_5$), 167.7 ($\underline{C}OOC_2H_5$). *Anal*. Calcd for $C_{29}H_{26}N_2O_4$: C, 74.66; H, 5.62; N, 6.01. Found: C, 74.86; H, 5.53; N, 6.00.

10-Cyano-2,3-diethoxycarbonyl-4-methyl-1-(4-methoxyphenyl)benz[*a*]azulene (10bc). Greenish prisms (from benzene); yield 121 mg (50%); mp 196-197 °C; IR (KBr) ν 3360 (NH), 2196 (C≡N), 1737 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.21 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.35 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 2.89 (3H, s, CH_3), 3.62 (3H, s, OCH_3), 4.18 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.35 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 6.51 (2H, d, *J* = 7.8 Hz, 3'-,5'-H), 6.62 (2H, d, *J* = 7.8 Hz, 2'-,6'-H), 7.26 (1H, dd, *J* = 9.9, 9.0 Hz, 8-H), 7.30 (1H, s, NH), 7.41 (1H, dd, *J* = 10.5, 9.9 Hz, 6-H), 7.56 (1H, t, *J* = 9.9 Hz, 7-H), 8.23 (1H, d, *J* = 10.5 Hz, 5-H), 8.82 (1H, d, *J* = 9.0 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 13.8 ($CH_2\underline{C}H_3$), 14.1 ($CH_2\underline{C}H_3$), 19.3 (CH_3), 55.4 (OCH_3), 61.7 ($\underline{C}H_2CH_3$), 62.0 ($\underline{C}H_2CH_3$), 94.2 (=C<), 114.5 (=CH-), 116.8 (=C<), 117.6 (=CH-), 124.0 (=C<), 128.6 (=C<), 129.4 (=CH-), 129.7

(=CH-), 129.9 (=C<), 130.4 (=C<), 133.9 (=C<), 135.9 (=CH-), 136.8 (=C<), 137.6 (=CH-), 139.2 (=CH-), 140.0 (=C<), 141.1 (=CH-), 148.1 (=C<), 154.1 (C ≡ N), 167.2 ($\underline{C}OOC_2H_5$), 169.0 ($\underline{C}OOC_2H_5$). *Anal*. Calcd for $C_{29}H_{26}N_2O_5$: C, 72.18; H, 5.43; N, 5.81. Found: C, 72.08; H, 5.66; N, 5.76.

9-Cyano-1-(1,2-di(ethoxycarbonyl)-4-methyl-2-(4-methoxyphenyl)azuleno[1,2-*c*]pyrrole (11bc). Greenish prisms (from benzene); yield 29 mg (12%); mp 201-202 °C; IR (KBr) 2202 (C≡N), 1698 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.25 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.29 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 2.45 (3H, s, CH_3), 3.86 (OCH_3), 4.15 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.22 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 7.00 (2H, d, *J* = 6.6 Hz, 3'-,5'-H), 7.31 (1H, dd, *J* = 9.9, 9.3 Hz, 7-H), 7.33 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.43 (2H, d, *J* = 6.6 Hz, 2'-,6'-H), 7.49 (1H, t, *J* = 9.9 Hz, 6-H), 7.71 (1H, s, 1-C=CH), 8.02 (1H, d, *J* = 9.6 Hz, 4-H), 8.06 (1H, d, *J* = 9.3 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 14.1 ($CH_2\underline{C}H_3$), 14.2 ($CH_2\underline{C}H_3$), 23.6 (CH_3), 55.8 (OCH_3), 60.7 ($\underline{C}H_2CH_3$), 60.9 ($\underline{C}H_2CH_3$), 88.3 (=C<), 113.6 (=C<), 115.1 (=CH-), 117.5 (=C<), 122.1 (=C<), 125.9 (=CH-), 128.8 (=C<), 129.1 (=CH-), 129.9 (=CH-), 132.6 (=CH-), 134.9 (=CH-), 136.7 (=C<), 136.9 (=CH-), 138.7 (=C<), 142.5 (=C<), 147.2 (=C<), 153.2 (=CH-), 159.2 (=C<), 163.0 (C≡N), 166.5 ($\underline{C}OOC_2H_5$), 167.9 ($\underline{C}OOC_2H_5$). *Anal*. Calcd for $C_{29}H_{26}N_2O_5$: C, 72.18; H, 5.43; N, 5.81. Found: C, 72.06; H, 5.30; N, 5.76.

1-(4-Bromophenyl)-10-cyano-2,3-diethoxycarbonyl-4-methylbenz[*a*]azulene (10bd). Greenish prisms (from benzene); yield 120 mg (45%); mp 234-235 °C; IR (KBr) ν 3316 (NH), 2204 (C≡N), 1718 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.27 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.43 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 3.03 (3H, s, CH_3), 4.28 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.44 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 6.48 (2H, d, *J* = 9.0 Hz, 2'-,6'-H), 7.21 (2H, d, *J* = 9.0 Hz, 3'-,5'-H), 7.29 (1H, s, NH), 7.46 (1H, dd, *J* = 9.9, 9.0 Hz, 8-H), 7.56 (1H, dd, *J* = 11.1, 9.9 Hz, 6-H), 7.72 (1H, t, *J* = 9.9 Hz, 7-H), 8.45 (1H, d, *J* = 11.1 Hz, 5-H), 8.89 (1H, d, *J* = 9.0 Hz, 9-H); ^{13}C NMR ($CDCl_3$) δ 13.9 ($CH_2\underline{C}H_3$), 14.1 ($CH_2\underline{C}H_3$), 19.5 (CH_3), 61.9 ($\underline{C}H_2CH_3$), 62.2 ($\underline{C}H_2CH_3$), 94.2 (=C<), 112.3 (=CH-), 116.7 (=C<), 117.1 (=CH-), 129.7 (=CH-), 129.9 (=C<), 130.1 (=CH-), 130.4 (=C<), 130.5 (=C<), 131.7 (=C<), 132.0 (=CH-), 136.3 (=CH-), 137.8 (=CH-), 137.9 (=C<), 139.3 (=CH-), 141.4 (=C<), 145.7 (=C<), 148.6 (=C<), 153.2 (C≡N), 167.0 ($\underline{C}OOC_2H_5$), 168.7 ($\underline{C}OOC_2H_5$). *Anal*. Calcd for $C_{28}H_{23}N_2O_4Br$: C, 63.28; H, 4.36; N, 5.27. Found: C, 63.57; H, 4.53; N, 5.27.

2-(4-Bromophenyl)-9-cyano-1-(1, 2-diethoxycarbonyl)-4-methylazuleno[1,2-*c*]pyrrole (11bd). Greenish prisms (from benzene); yield 112 mg (42%); mp 192-193 °C; IR (KBr) ν 2203 (C≡N), 1702 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.27 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 1.30 (3H, t, *J* = 7.2 Hz, $CH_2C\underline{H}_3$), 2.58 (3H, s, CH_3), 4.18 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.22 (2H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 7.33 (1H, dd, *J* = 9.0 Hz, 2'-,6'-H), 7.43 (1H, dd, *J* = 10.5, 9.9 Hz, 7-H), 7.46 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 7.55 (2H, d, *J* = 9.0 Hz, 3'-,5'-H), 7.66 (1H, t, *J* = 9.9 Hz, 6-H), 7.81 (1H, s, 1-C=CH), 8.24 (1H, d, *J* = 9.6 Hz, 4-H), 8.27 (1H, d, *J* = 10.5 Hz, 8-H); ^{13}C NMR ($CDCl_3$) δ 14.1 ($CH_2\underline{C}H_3$), 14.2 ($CH_2\underline{C}H_3$), 23.5 (CH_3), 60.8 ($\underline{C}H_2CH_3$), 61.1 ($\underline{C}H_2CH_3$), 89.5 (=C<), 114.0 (=C<), 118.7 (=C<), 120.7 (=C<), 121.9 (=CH-), 123.6 (=C<), 128.3 (=CH-), 129.2 (=CH-), 129.8 (=CH-), 132.7 (=CH-), 134.2 (=CH-), 136.0 (=CH-), 138.2 (=C<), 138.3 (=C<), 141.9 (=C<), 143.2 (=C<),

146.6 (=C<), 149.0 (=CH-), 159.8 (C≡N), 166.2 ($\underline{C}OOC_2H_5$), 167.2 ($\underline{C}OOC_2H_5$). *Anal.* Calcd for $C_{28}H_{23}N_2O_4Br$: C, 63.28; H, 4.36; N, 5.27. Found: C, 63.42; H, 4.38; N, 5.29.

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