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A NEW SYNTHETIC APPROACH TO AZULENO[1,2-*c*]THIOPHENES

Kimiaki Imafuku [a,*] and Dao-Lin Wang [b]

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

b *Graduate School of Science and Technology, Kumamoto University, Kurokami, Kumamoto 860-8555, Japan*

Dedicated to Professor A. I. Meyers on the occasion of his 70th birthday.

Abstract - A variety of methyl 3-acetyl-2-bromomethylazulene-1-carboxylates (**4aa**-**ae**) and 3-acetyl-2-bromomethylazulene-1-carbonitriles (**4ba**-**be**) were obtained by the bromination of the corresponding 1-methoxycarbonyl- and 1-cyano-substituted 3-acetyl-2-methylazulenes (**2aa**-**ae**, **2ba**-**be**), respectively, with *N*-bromosuccinimide. These azulenes (**4aa**-**ae**, **4ba**-**be**) reacted with thioacetamide to give azuleno[1,2-*c*]thiophenes (**7aa**-**ae**, **7ba**-**be**) in moderate yields. This reaction provides a new procedure for synthesis of thiophene-fused azulenes.

From the viewpoints of physical and chemical properties and biological activities, syntheses of a variety of azulene derivatives fused with heterocycles, such as furan,[1-3] thiophene,[4-9] pyrrole,[2,3,10] pyrazole,[11] imidazole,[12] thiazole,[13,14] pyridine,[15-18] pyridazine,[19,20] pyrimidine,[12,21] pyrazine,[12,22] etc., have been reported. Of them, thiophene-fused azulenes were prepared by using different types of starting materials as followings. Vetivazulene was heated with sulfur to convert to 3,5,9-trimethylazuleno[1,2-*b*]thiophene.[4] When 2-azulenylthioglycolic acid esters having an ester group at the 1-position were treated with alkaline solution, ethyl azuleno[2,1-*b*]thiophene-5-carboxylates were obtained.[5,6] 1-Thiocyano-8-phenacylazulenes were also heated in the presence of potassium hydroxide to yield 9-benzoyl-9*H*-azuleno[1,8-*bc*]thiophene.[7] On the other hand, methyl 2-oxo-2*H*-cyclohepta[*b*]furan-3-carboxylate reacted with a mixture of tautomeric morpholino enamines of 3-oxotetrahydrothiophene to afford two isomeric dihydroazuleno[1,2-*b*]thiophene and dihydroazuleno[1,2-*c*]thiophene which were dehydrogenated using 2,3-dichloro-5,6-dicyano-

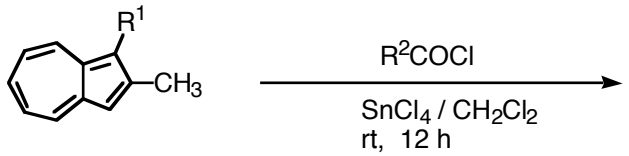
benzoquinone to give methyl azuleno[1,2-*b*]thiophene-9-carboxylate and methyl azuleno[1,2-*c*]thiophene-9-carboxylate, respectively.[8] Recently, 4-(3-oxo-2-butenyl)azuleno[1,2-*b*]thiophene was obtained by cyclization and ring-opening of 2-tropylio-3-(2-furyl)thiophene.[9]

In the present work, we found a new synthetic method of azuleno[1,2-*c*]thiophenes by the reactions of new building blocks, 1-acyl-2-bromomethylazulenes, with thioacetamides.

RESULTS AND DISCUSSION

Preparation of 1-Methoxycarbonyl- and 1-Cyano-substituted 3-Acyl-2-bromomethylazulenes.

It is well-known that the electrophilic substitution of azulene takes place at the 1- and 3-positions. In this work, methyl 2-methylazulene-1-carboxylate (**1a**)[23] and 2-methylazulene-1-carbonitrile (**1b**)[24] were used as starting materials, because the one position of the 1- and 3-positions was blocked by a substituent to prevent the reaction at two positions. In a previous paper, we obtained methyl 3-acetyl-2-methylazulene-1-carboxylate (**2aa**) and 3-acetyl-2-methylazulene-1-carbonitrile (**2ba**), respectively, by Friedel-Crafts acylation of the above 2-methylazulenes (**1a**,**b**).[25] Similarly, a solution of methyl 2-methylazulene-1-carboxylate (**1a**) and propionyl chloride, benzoyl chloride, or cinnamoyl chloride in dichloromethane was stirred for 12 h, except for cinnamoyl chloride (1 h), at room temperature in the presence of tin(IV) chloride to give methyl 2-methyl-3-propionylazulene-1-carboxylate (**2ab**), methyl 3-benzoyl-2-methylazulene-1-carboxylate (**2ac**), and methyl 3-cinnamoyl-2-methylazulene-1-carboxylate (**2ad**) in good yields, respectively. From the reactions of 2-methylazulene-1-carbonitrile (**1b**), 3-propionyl-, 3-benzoyl-, and 3-cinnamoyl-2-methylazulene-1-carbonitriles (**2bb**-**be**) were obtained in good yields. In the reactions with benzoyl chloride, the starting



1 a,**b** **2 aa-ae**, **ba-be**

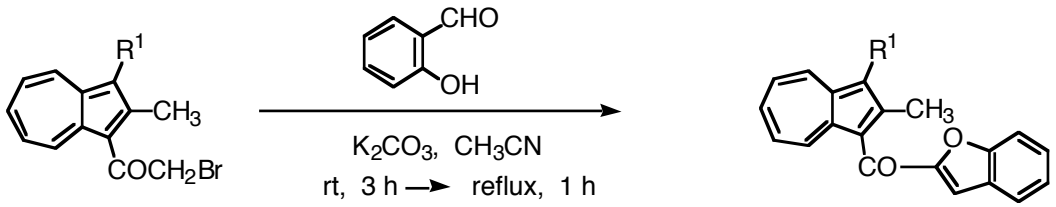
a $R^1 = COOCH_3$
b $R^1 = CN$

aa $R^1 = COOCH_3$, $R^2 = CH_3$
ab $R^1 = COOCH_3$, $R^2 = CH_2CH_3$
ac $R^1 = COOCH_3$, $R^2 = Ph$
ad $R^1 = COOCH_3$, $R^2 = CH{=}CH\text{-}Ph$
ba $R^1 = CN$, $R^2 = CH_3$
bb $R^1 = CN$, $R^2 = CH_2CH_3$
bc $R^1 = CN$, $R^2 = Ph$
bd $R^1 = CN$, $R^2 = CH{=}CH\text{-}Ph$

Scheme 1

materials (**1a**,**b**) were recovered in 27% and 34% yield, respectively.

Furthermore, methyl 3-bromoacetyl-2-methylazulene-1-carboxylate (**3a**) and 3-bromoacetyl-2-methylazulene-1-carbonitrile (**3b**) were prepared by bromination of the corresponding compounds (**2aa**,**ba**) with trimethylphenylammonium tribromide. The reactions of these compounds (**3a**,**b**) with salicylaldehyde in the presence of potassium carbonate gave respectively methyl 3-(2-benzo[*b*]furoyl)-2-methylazulene-1-carboxylate (**2ae**) (78%) and 3-(2-benzo[*b*]furoyl)-2-methylazulene-1-carbonitrile (**2be**) (57%) *via* substitution at the methylene carbon atom of the bromoacetyl group and cyclization by nucleophilic attack of the enolizable methylene carbon atom at the formyl group.



1 a,**b** **2 ae**, **be**

a $R^1 = COOCH_3$ **ae** $R^1 = COOCH_3$

b $R^1 = CN$ **be** $R^1 = CN$

Scheme 2

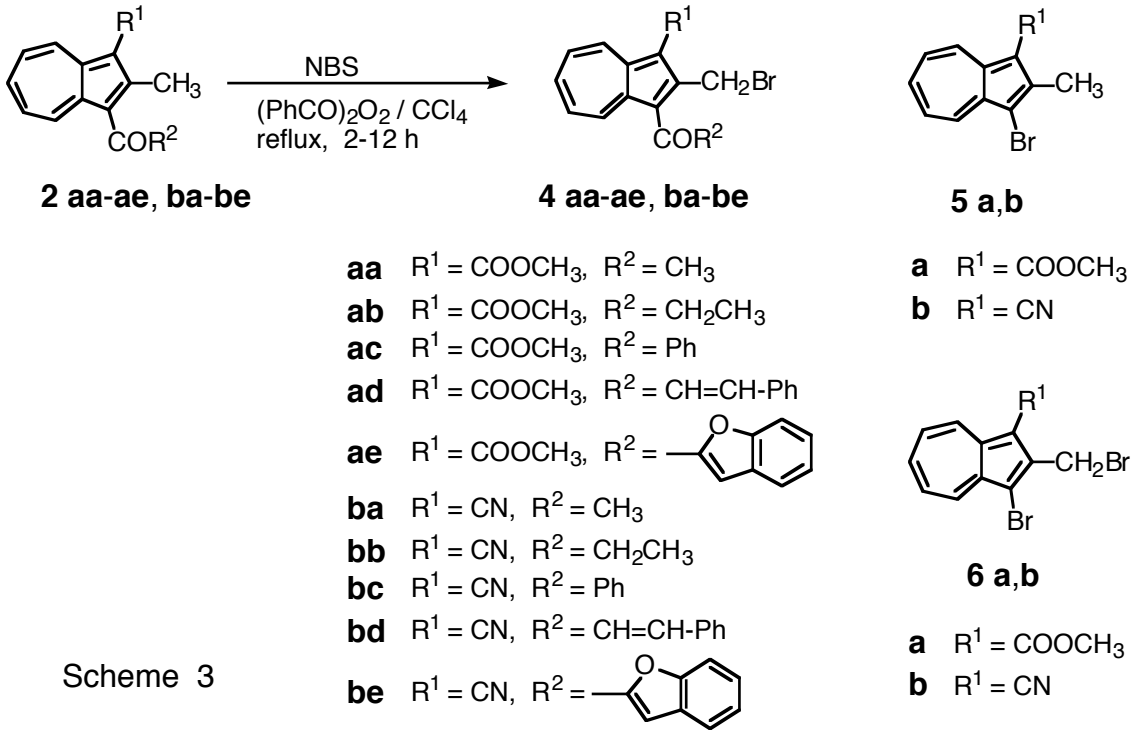
A methyl group of 2-methylazulenes bearing a methoxycarbonyl or cyano group at the 1- and/or 3-position is reactive, since 2-methylazulenes were condensed with benzaldehydes to give 2-styrylazulenes [26] and were brominated with *N*-bromosuccinimide (NBS) to afford 2-bromomethylazulenes.[27]

When a solution of methyl 3-acyl-2-methylazulene-1-carboxylates (**2aa**-**ae**) and 1.2 molar equivalents of NBS in carbon tetrachloride was refluxed for 2-12 h in the presence of benzoyl peroxide (0.2 molar equivalent) to give methyl 3-acyl-2-bromomethylazulene-1-carboxylate (**4aa**-**ae**). These redults are summarized in Table 1. In a similar manner, the brominations of 3-acyl-2-methylazulene-1-carbonitriles (**2ba**-**be**) gave the corresponding 3-acyl-2-bromomethylazulene-1-carbonitriles (**4ba**-**be**) (Table 1).

Since 1-acyl-2-bromomethylazulenes (**4aa**-**ae**, **4ba**-**be**) have two reactive functional groups, an acyl and bromomethyl groups, at the neighboring positions, they seem to be useful building blocks for heterocycle-fused azulenes.

Reactions of New Building Blocks with Thioacetamide.

A solution of methyl 3-acetyl-2-bromomethylazulene-1-carboxylate (**4aa**) and 1.5 molar equivalents of thioacetamide in ethanol was refluxed for 1 h to afford methyl 3-methylazuleno[1,2-*c*]thiophene-9-carboxylate (**7aa**) in 88% yiled. The reactions of methyl 3-acyl-2-bromomethyazulene-1-carboxylates



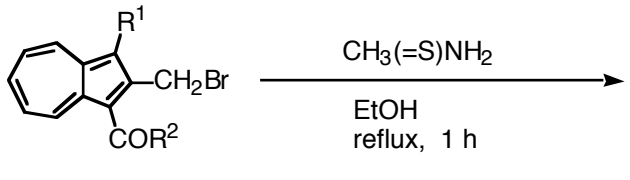
Scheme 3

Table 1. Bromination of Compounds (**2aa**-**ae**, **ba**-**be**)

Substrate	Time / h	Product	Yield / %				
2aa	10	**4aa**	72	**5a**	5	**6a**	4
2ab	2	**4ab**	61	**5a**	6	**6a**	22
2ac	4	**4ac**	88			**6a**	4
2ad	12	**4ad**	76				
2ae	3	**4ae**	89				
2ba	6	**4ba**	78	**5b**	2	**6b**	7
2bb	2	**4bb**	59	**5b**	10	**6b**	20
2bc	4	**4bc**	90				
2bd	12	**4bd**	64				
2be	8	**4be**	76				

(**4ab**-**ae**) having the diverse acyl group also gave the corresponding azuleno[1,2-*c*]thiophenes (**7ab**-**ae**) in good yields. 3-Acyl-2-bromomethylazulene-1-carbonitriles (**4ba**-**be**) reacted with thioacetamide to give the corresponging azuleno[1,2-*c*]thiophenes (**7ba**-**be**) in good yields. The results are summarized in Table 2. From these results, it was found that the reactions of 1-methoxycarbonyl- or 1-cyano-substituted 3-acyl-2-

bromomethylazulene (**4aa**-**ae**, **4ba**-**be**) with thioacetamide provided a new and useful synthetic procedure for azuleno[1,2-*c*]thiophenes.



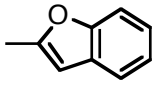
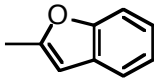
4 aa-ae, **ba-be** **7 aa-ae**, **ba-be**

aa $R^1 = COOCH_3$, $R^2 = CH_3$ **ba** $R^1 = CN$, $R^2 = CH_3$

ab $R^1 = COOCH_3$, $R^2 = CH_2CH_3$ **bb** $R^1 = CN$, $R^2 = CH_2CH_3$

ac $R^1 = COOCH_3$, $R^2 = Ph$ **bc** $R^1 = CN$, $R^2 = Ph$

ad $R^1 = COOCH_3$, $R^2 = CH{=}CH\text{-}Ph$ **bd** $R^1 = CN$, $R^2 = CH{=}CH\text{-}Ph$

ae $R^1 = COOCH_3$, $R^2 =$  **be** $R^1 = CN$, $R^2 =$ 

Scheme 4

Table 2. Reaction of Compounds (**4aa**-**ae**, **ba**-**be**) with Thioacetamide

Substrate	Product	Yield / %
4aa	**7aa**	88
4ab	**7ab**	79
4ac	**7ac**	89
4ad	**7ad**	62
4ae	**7ae**	88
4ba	**7ba**	92
4bb	**7bb**	95
4bc	**7bc**	76
4bd	**7bd**	73
4be	**7be**	84

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 A-102 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). All the elemental analyses were performed at the Instrumental Analysis Center, Kumamoto University. Merck Kieselgel 60 was used for column chromatography.

Acylation of Methyl 2-Methylazulene-1-carboxylate (1a). General Procedure: A solution of methyl 2-methylazulene-1-carboxylate (**1a**) (100 mg, 0.5 mmol) and acyl chloride (1.0 mmol) in dichloromethane (10 mL) was stirred for 12 h at rt in the presence of tin(IV) chloride (156 mg, 0.6 mmol). The reaction mixture was shaken with water (50 mL) and extracted with benzene. The evaporation residue from the extract was purified by silica gel column chromatography with benzene as eluent.

Methyl 2-Methyl-3-propionylazulene-1-carboxylate (2ab): This compound (**2ab**) was obtained by stirring for 12 h in yield 119 mg (93%) as red needles (from benzene); mp 73-74 °C; IR (KBr): ν = 1681 (C=O), 1645 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 1.28 (3H, t, J = 7.5 Hz, CH_2CH_3), 2.92 (2H, q, J = 7.5 Hz, CH_2CH_3), 2.95 (3H, s, CH_3), 4.00 (3H, s, $COOCH_3$), 7.60 (1H, dd, J = 9.9, 9.9 Hz, 5-H), 7.63 (1H, dd, J = 9.9, 9.9 Hz, 7-H), 7.82 (1H, dd, J = 9.9, 9.9 Hz, 6-H), 9.01 (1H, d, J = 9.9 Hz, 4-H), 9.49 (1H, d, J = 9.9 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 8.9 (CH_2CH_3), 17.2 (CH_3), 37.9 (CH_2CH_3), 51.2 ($COOCH_3$), 116.2 (=C<), 128.8 (=C<), 129.8 (=CH-), 130.0 (=CH-), 136.7 (=CH-), 137.2 (=CH-), 139.1 (=CH-), 141.5 (=C<), 142.5 (=C<), 152.3 (=C<), 166.4 (C=O), 203.3 (C=O). *Anal*. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.76; H, 6.43.

Methyl 3-Benzoyl-2-methylazulene-1-carboxylate (2ac): This compound (**2ac**) was obtained by stirring for 12 h in yield 107 mg (70%) as red needles (from benzene); mp 109-110 °C; IR (KBr): ν = 1691 (C=O), 1641 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 2.63 (3H, s, CH_3), 3.98 (3H, s, $COOCH_3$), 7.43 (2H, dd, J = 7.8, 7.8 Hz, 3'-,5'-H), 7.46 (1H, dd, J = 9.9, 9.9 Hz, 5-H), 7.56 (1H, dd, J = 7.5, 7.5 Hz, 4'-H), 7.63 (1H, dd, J = 9.9, 9.9 Hz, 6-H), 7.74-7.80 (3H, m, 2'-,6'-,7-H), 8.57 (1H, d, J = 9.9 Hz, 4-H), 9.61 (1H, d, J = 9.9 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 17.4 (CH_3), 51.1 ($COOCH_3$), 115.6 (=C<), 128.4 (=CH-), 129.3 (=CH-), 129.6 (=CH-), 129.7 (=CH-), 132.7 (=CH-), 136.2 (=CH-), 137.3 (=CH-), 138.9 (=CH-), 140.0 (=C<), 142.2 (=C<), 142.6 (=C<), 153.7 (=C<), 166.3 (C=O), 195.3 (C=O). *Anal*. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.65; H, 5.00.

Methyl 3-Cinnamoyl-2-methylazulene-1-carboxylate (2ad): This compound (**2ad**) was obtained by stirring for 1 h in yield 148 mg (89%) as red needles (from benzene); mp 98-99 °C; IR (KBr): ν = 1680 (C=O), 1656 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 2.92 (3H, s, CH_3), 3.97 (3H, s, $COOCH_3$), 7.21 (1H, d, J = 16.0 Hz, 3'-H), 7.31-7.33 (3H, m, 3"-,4"-,5"-H), 7.45-7.59 (4H, m, 2"-,5-,6"-,7-H), 7.50 (1H, d, J = 16.0 Hz, 2'-H), 7.73 (1H, dd, J = 9.9, 9.9 Hz, 6-H), 8.87 (1H, d, J = 9.9 Hz, 4-H), 9.51 (1H, d, J = 9.9

Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 17.3 (CH_3), 51.1 ($COOCH_3$), 115.8 (=C<), 128.2 (=C<), 128.3 (=CH-), 128.6 (=CH-), 128.9 (=CH-), 129.3 (=CH-), 129.7 (=CH-), 129.8 (=CH-), 130.4 (=CH-), 134.7 (=C<), 136.3 (=CH-), 137.3 (=CH-), 139.0 (=CH-), 141.9 (=C<), 142.7 (=C<), 143.9 (=C<), 153.2 (=C<), 166.3 (1-C=O), 192.3 (3-C=O). *Anal.* Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 80.26; H, 5.30.

Acylation of 2-Methylazulene-1-carbonitrile (**1b**). **General Procedure**: A solution of methyl 2-methylazulene-1-carbonitrile (**1b**) (84 mg, 0.5 mmol) and acyl chloride (1.0 mmol) in dichloromethane (10 mL) was stirred for 12 h at rt in the presence of tin(IV) chloride (156 mg, 0.6 mmol). The reaction mixture was worked up, as described above, and purified by silica gel column chromatography with benzene as eluent.

2-Methyl-3-propionylazulene-1-carbonitrile (**2bb**): This compound (**2bb**) was obtained by stirring for 12 h in yield 103 mg (92%) as red needles (from benzene); mp 109-110 °C; IR (KBr): ν = 2185 (CN), 1648 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 1.29 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 2.96 (3H, s, CH_3), 3.00 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 7.72 (1H, dd, *J* = 9.9, 9.9 Hz, 5-H), 7.75 (1H, dd, *J* = 9.9, 9.9 Hz, 7-H), 7.94 (1H, dd, *J* = 9.9, 9.9 Hz, 6-H), 8.63 (1H, d, *J* = 9.9 Hz, 4-H), 9.51 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 8.5 (CH_2CH_3), 17.4 (CH_3), 37.7 (CH_2CH_3), 100.1 (=C<), 116.4 (=C<), 126.0 (=C<), 130.2 (=CH-), 131.9 (=CH-), 136.1 (=C<), 139.2 (=CH-), 139.8 (=CH-), 140.3 (=C<), 142.2 (=C<), 144.6 (=C<), 153.5 (CN), 203.3 (C=O). *Anal.* Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.80; H, 6.00; N, 6.45.

3-Benzoyl-2-methylazulene-1-carbonitrile (**2bc**): This compound (**2bc**) was obtained by stirring for 12 h in yield 80 mg (59%) as red needles (from benzene); mp 121-122 °C; IR (KBr): ν 2205 (CN), 1627 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 2.54 (3H, s, CH_3), 7.48 (2H, dd, *J* = 7.8, 6.6 Hz, 3'-,5'-H), 7.61 (1H, dd, *J* = 6.9, 6.9 Hz, 4'-H), 7.62 (1H, dd, *J* = 9.9, 9.9 Hz, 5-H), 7.71 (1H, dd, *J* = 9.9, 9.9 Hz, 7-H), 7.75 (2H, d, *J* = 7.8 Hz, 2'-,6'-H), 7.91 (1H, dd, *J* = 9.9, 9.9 Hz, 6-H), 8.57 (1H, d, *J* = 9.9 Hz, 4-H), 9.61 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 16.0 (CH_3), 99.2 (=C<), 116.2 (=C<), 126.5 (=C<), 128.6 (=CH-), 129.5 (=CH-), 129.7 (=CH-), 130.5 (=CH-), 132.9 (=CH-), 135.9 (=CH-), 137.7 (=CH-), 139.8 (=C<), 140.0 (=CH-), 141.9 (=C<), 144.4 (=C<), 154.4 (CN), 193.7 (C=O). *Anal.* Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 83.78; H, 4.75; N, 5.38.

3-Cinnamoyl-2-methylazulene-1-carbonitrile (**2bd**): This compound (**2bd**) was obtained by stirring for 1 h in yield 141 mg (95%) as red needles (from benzene); mp 96-97 °C; IR (KBr): ν = 2209 (CN), 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 2.90 (3H, s, CH_3), 7.43 (1H, d, *J* = 16.0 Hz, 3'-H), 7.40-7.43 (3H, m, 3"-,4"-,5"-H), 7.58-7.61 (2H, m, 2"-,6"-H), 7.64 (1H, d, *J* = 16.0 Hz, 2'-H), 7.69 (2H, dd, *J* = 9.8, 9.8 Hz, 5-,7-H), 7.92 (1H, dd, *J* = 9.8, 9.8 Hz, 6-H), 8.61 (1H, d, *J* = 9.8 Hz, 4-H), 9.10 (1H, d, *J* = 9.8 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 16.4 (CH_3), 99.5 (=C<), 116.3 (=C<), 127.3 (=CH-), 127.5 (=CH-), 128.4 (=CH-), 129.0 (=CH-), 129.9 (=CH-), 130.6 (=CH-), 131.0 (=CH-), 134.6 (=C<), 136.0 (=CH-), 138.1 (=CH-), 140.1 (=CH-), 141.8 (=C<), 144.1 (=CH-), 144.5 (=C<), 153.7 (CN), 189.8

(C=O). *Anal.* Calcd for $C_{21}H_{15}NO$: C, 84.82; H, 5.09; N, 4.71. Found: C, 84.59; H, 5.01; N, 4.70.

Preparation of 3-Bromoacetyl-2-methylazulenes (3a,b): To a solution of methyl 3-acetyl-2-methylazulene-1-carboxylate (**2aa**) or 3-acetyl-2-methylazulene-1-carbonitrile (**2ba**) (0.5 mmol) in chloroform (20 mL) was added trimethylphenylammonium tribromide (206 mg, 0.55 mmol). After stirring for 2 h at 50 °C, the mixture was diluted with water (20 mL). The organic layer was separated and chromatographed on silica gel column with benzene to give the corresponding 3-bromoacetyl-2-methylazulenes (**3a**,**b**), respectively.

Methyl 3-Bromoacetyl-2-methylazulene-1-carboxylate (3a): This compound (**3a**) was obtained in yield 98 mg (61%) as red crystals (from benzene); mp 88-89 °C; IR (KBr): ν = 1681 (C=O), 1650 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 2.98 (3H, s, CH_3), 4.00 (3H, s, $COOCH_3$), 4.50 (2H, s, $COCH_2Br$), 7.67 (1H, dd, *J* = 9.8, 9.8 Hz, 5-H), 7.68 (1H, dd, *J* = 9.8, 9.8 Hz, 7-H), 7.87 (1H, dd, *J* = 9.8, 9.8 Hz, 6-H), 9.12 (1H, d, *J* = 9.8 Hz, 4-H), 9.48 (1H, d, *J* = 9.8 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 17.1 (CH_3), 36.1 (CH_2Br), 51.4 ($COO\mathit{C}H_3$), 116.9 (=C<), 124.8 (=C<), 130.8 (=CH-), 131.2 (=CH-), 139.7 (=CH-), 142.9 (=C<), 143.4 (=C<), 152.8 (=C<), 166.1 (C=O), 191.8 (C=O). *Anal.* Calcd for $C_{15}H_{13}O_4Br$: C, 56.27; H, 4.08. Found: C, 56.41; H, 4.28.

3-Bromoacetyl-2-methylazulene-1-carbonitrile (3b): This compound (**3b**) was obtained in yield 114 mg (79%) as red crystals (from benzene); mp 150-151 °C; IR (KBr): ν = 2213 (CN), 1632 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 3.99 (3H, s, CH_3), 4.48 (2H, s, $COCH_2Br$), 7.78 (1H, dd, *J* = 9.7, 9.7 Hz, 5-H), 7.82 (1H, dd, *J* = 9.7, 9.7 Hz, 7-H), 8.00 (1H, dd, *J* = 9.7, 9.7 Hz, 6-H), 8.59 (1H, d, *J* = 9.7 Hz, 4-H), 9.51 (1H, d, *J* = 9.7 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 17.1 (CH_3), 35.6 (CH_2Br), 100.8 (=C<), 115.9 (=C<), 122.3 (=C<), 131.3 (=CH-), 132.9 (=CH-), 136.4 (=CH-), 139.5 (=CH-), 140.9 (=CH-), 143.4 (=C<), 145.2 (=C<), 153.7 (CN), 189.3 (C=O). *Anal.* Calcd for $C_{14}H_{10}NOBr$: C, 58.35; H, 3.50; N, 4.86. Found: C, 58.4; H, 3.48; N, 4.86.

Reaction of 3-Bromoacetyl-2-methylazulenes (3a,b) with Salicylaldehyde: A solution of 3-bromoacetyl-2-methylazulene (**3a**,**b**) (0.3 mmol) and salicylaldehyde (56 mg, 0.45 mmol) in acetonitrile (10 mL) was stirred for 3 h at rt in the presence of potassium carbonate (83 mg, 0.6 mmol) and additionally refluxed for 1 h. The reaction mixture was diluted with water (40 mL) and extracted with benzene. The evaporation residue was purified by silica gel column chromatography with benzene as eluent.

Methyl 3-(2-Benzo[*b*]furoyl)-2-methylazulene-1-carboxylate (2ae): This compounds (**2ae**) was obtained in yield 75 mg (78%) as red needles (from benzene); mp 138-140 °C; IR (KBr): ν = 1690 (C=O), 1613 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 2.80 (3H, s, CH_3), 4.01 (3H, s, $COOCH_3$), 7.31 (1H, dd, *J* = 8.4, 7.8 Hz, 5'- or 6'-H), 7.33 (1H, d, *J* = 0.9 Hz, 3'-H), 7.48 (1H, dd, *J* = 8.4, 7.8 Hz, 5'- or 6'-H), 7.55 (1H, dd, *J* = 9.8, 9.8 Hz, 5-H), 7.60 (1H, d, *J* = 8.4 Hz, 4'-H), 7.67 (1H, d, *J* = 8.4 Hz, 7'-H), 7.69 (1H, dd, *J* = 9.8, 9.8 Hz, 7-H), 7.84 (1H, dd, *J* = 9.8, 9.8 Hz, 6-H), 8.70 (1H, d, *J* = 9.8 Hz, 4-H), 9.65

(1H, d, J = 9.8 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 17.3 (CH_3), 51.2 ($COOCH_3$), 112.5 (=CH-), 115.8 (=CH-), 115.9 (=C<), 123.2 (=CH-), 123.9 (=CH-), 126.9 (=C<), 127.2 (=CH-), 128.3 (=CH-), 129.7 (=CH-), 130.1 (=CH-), 136.2 (=CH-), 137.7 (=CH-), 139.2 (=CH-), 142.4 (=C<), 142.9 (=C<), 153.8 (=C<), 154.3 (=C<), 155.9 (=C<), 166.3 (C=O), 183.5 (C=O). *Anal.* Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.75; H, 4.68.

3-(2-Benzo[*b*]furoyl)-2-methylazulene-1-carbonitrile (**2be**): This compounds (**2be**) was obtained in yield 54 mg (58%) as red needles (from benzene); mp 231-232 °C. IR (KBr): ν = 2207 (CN), 1616 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 2.75 (3H, s, CH_3), 7.34 (1H, dd, J = 8.4, 7.8 Hz, 5'- or 6'-H), 7.43 (1H, d, J = 0.9 Hz, 3'-H), 7.50 (1H, dd, J = 8.4, 7.8 Hz, 5'- or 6'-H), 7.59 (1H, d, J = 8.4 Hz, 4'-H), 7.65 (1H, dd, J = 9.8, 9.8 Hz, 5- or 7-H), 7.71 (1H, d, J = 8.4 Hz, 7'-H), 7.73 (1H, dd, J = 9.8, 9.8 Hz, 5- or 7-H), 7.93 (1H, dd, J = 9.8, 9.8 Hz, 6-H), 8.68 (1H, d, J = 9.8 Hz, 4-H), 8.79 (1H, d, J = 9.8 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 15.7 (CH_3), 99.4 (=C<), 112.4 (=CH-), 115.6 (=CH-), 116.2 (=C<), 123.3 (=CH-), 124.1 (=CH-), 125.8 (=C<), 127.1 (=C<), 128.5 (=CH-), 129.9 (=CH-), 130.7 (=CH-), 136.2 (=CH-), 137.5 (=CH-), 140.2 (=CH-), 141.8 (=C<), 144.5 (=C<), 153.8 (=C<), 154.2 (=C<), 155.8 (CN), 181.7 (C=O). *Anal.* Calcd for $C_{21}H_{13}NO_2$: C, 81.01; H, 4.21; N, 4.50. Found: C, 80.90; H, 3.92; N, 4.63.

Bromination of Methyl 3-Acyl-2-methylazulene-1-carboxylates (**2aa**-**ae**). To a solution of methyl 3-acyl-2-methylazulene-1-carboxylate (**2aa**-**ae**) (0.5 mmol) in carbon tetrachloride (20 mL) were added NBS (107 mg, 0.6 mmol) and benzoyl peroxide (10 mg). The mixed solution was refluxed for 2-12 h. The mixture was quenched with water and extracted with dichloromethane. The evaporation residue was purified by silica gel column chromatography with benzene as eluent to give methyl 1-acyl-2-bromomethylazulene-3-carboxylates (**4ab**-**ae**). From the reactions of compound (**2aa**), methyl 3-bromo-2-methylazulene-1-carboxylate (**5a**) (8 mg, 6%) and methyl 3-bromo-2-bromomethylazulene-1-carboxylate (**6a**) (39 mg, 22%) were obtained as by products. The reaction of compound (**2ac**) gave also product (**6a**) (7 mg, 4%) as a minor product.

Methyl 2-Bromomethyl-3-propionylazulene-1-carboxylate (**4ab**): This compound (**4ab**) was obtained under refluxing for 2 h in yield 102 mg (61%) as violet needles (from benzene); mp 90-91 °C; IR (KBr): ν = 1692 (C=O), 1644 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 1.32 (3H, t, J = 7.2 Hz, CH_2CH_3), 3.13 (2H, q, J = 7.2 Hz, CH_2CH_3), 4.04 (3H, s, $COOCH_3$), 5.29 (2H, s, CH_2Br), 7.59 (1H, dd, J = 9.8, 9.8 Hz, 5-H), 7.64 (1H, dd, J = 9.8, 9.8 Hz, 7-H), 7.86 (1H, dd, J = 9.8, 9.8 Hz, 6-H), 8.90 (1H, d, J = 9.8 Hz, 4-H), 9.60 (1H, d, J = 9.8 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 8.9 (CH_2CH_3), 17.2 (CH_3), 25.4 (CH_2CH_3), 37.9 (CH_2Br), 51.5 ($COOCH_3$), 114.8 (=C<), 128.3 (=C<), 129.9 (=CH-), 130.1 (=CH-), 138.0 (=CH-), 139.6 (=CH-), 140.8 (=CH-), 140.9 (=C<), 142.2 (=C<), 148.4 (=C<), 165.4 (C=O), 202.7 (C=O). *Anal.* Calcd for $C_{16}H_{15}O_3Br$: C, 57.44; H, 4.26. Found: C, 57.34; H, 4.50.

Methyl 3-Benzoyl-2-bromomethylazulene-1-carboxylate (**4ac**): This compound (**4ac**) was

obtained under refluxing for 4 h in yield 169 mg (88%) as violet needles (from benzene); mp 125-128 °C; IR (KBr): ν = 1693 (C=O), 1640 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 4.05 (3H, s, $COOCH_3$), 5.15 (2H, s, CH_2Br), 7.43 (1H, dd, *J* = 9.7, 9.7 Hz, 5-H), 7.47 (2H, dd, *J* = 8,1, 7.5 Hz, 3'-,5'-H), 7.60 (1H, dd, *J* = 7.5 Hz, 4'-H), 7.68 (1H, dd, *J* = 9.9, 9.9 Hz, 6-H), 7.80 (1H, d, *J* = 8.1 Hz, 2'- or 6'-H), 7.84 (1H, dd, *J* = 9.7, 9.7 Hz, 7-H), 8.37 (1H, d, *J* = 9.7 Hz, 4-H), 9.68 (1H, d, *J* = 9.7 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 24.8 (CH_2Br), 51.6 ($COOCH_3$), 115.0 (=C<), 127.2 (=C<), 128.3 (=CH-), 128.6 (=CH-), 129.3 (=CH-), 129.9 (=CH-), 130.1 (=CH-), 133.2 (=CH-), 138.4 (=CH-), 139.7 (=CH-), 139.8 (=CH-), 140.7 (=CH-), 141.6 (=C<), 142.3 (=C<), 150.4 (=C<), 165.4 (C=O), 194.5 (C=O). *Anal.* Calcd for $C_{20}H_{15}O_3Br$: C, 62.88; H, 3.94. Found: C, 62.94; H, 4.00.

Methyl 2-Bromomethyl-3-cinnamoylazulene-1-carboxylate (**4ad**): This compound (**4ad**) was obtained under refluxing for 12 h in yield 155 mg (76%) as reddish violet needles (from benzene); mp 161-162 °C; IR (KBr): ν = 1692 (C=O), 1646 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 4.05 (3H, s, $COOCH_3$), 5.01 (2H, s, CH_2Br), 7.39-7.41 (3H, m, 3"-,4"-,5"-H), 7.54 (1H, d, *J* = 16.0 Hz, 3'-H), 7.63-7.70 (4H, m, 2"-,5-,6"-,7-H), 7.69 (1H, d, *J* = 16.0 Hz, 2'-H), 7.87 (1H, dd, *J* = 9.6 Hz, 6-H), 8.97 (1H, d, *J* = 9.6 Hz, 4-H), 9.66 (1H, d, *J* = 9.6 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 26.0 (CH_2Br), 51.5 ($COOCH_3$), 114.7 (=C<), 127.5 (=CH-), 128.1 (=C<), 128.7 (=CH-), 128.9 (=CH-), 130.1 (=CH-), 130.3 (=CH-), 130,6 (=CH-), 134.6 (=C<), 138.9 (=CH-), 139.7 (=CH-), 140.9 (=CH-), 141.6 (=C<), 142.6 (=C<), 144.9 (=CH-), 148.7 (=C<), 165.4 (COOCH3), 191.1 (C=O). *Anal.* Calcd for $C_{22}H_{17}O_3Br$: C, 64.56; H, 4.19. Found: C, 64.68; H, 4.34.

Methyl 3-(2-Benzo[*b*]furoyl)-2-bromomethylazulene-1-carboxylate (**4ae**): This compound (**4ae**) was obtained under refluxing for 3 h in yield 188 mg (89%) as violet needles (from benzene); mp 179 °C (dec); IR (KBr): ν = 1699 (C=O), 1632 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 4.06 (3H, s, $COOCH_3$), 5.24 (2H, s, CH_2Br), 7.31 (1H, dd, *J* = 7.5, 7.5 Hz, 5'- or 6'-H), 7.37 (1H, d, *J* = 0.9 Hz, 3'-H), 7.49 (1H, dd, *J* = 9.7, 9.7 Hz, 7-H), 7.50 (1H, d, *J* = 7.5 Hz, 7'-H), 7.60 (1H, d, *J* = 7.5 Hz, 4'-H), 7.67 (1H, dd, *J* = 9.7, 9.7 Hz, 5-H), 7.87 (1H, dd, *J* = 9.7, 9.7 Hz, 6-H), 8.59 (1H, d, *J* = 9.7 Hz, 4-H), 9.69 (1H, d, *J* = 9.7 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 24.7 (CH_2Br), 51.6 ($COOCH_3$), 112.6 (=CH-), 115.2 (=C<), 116.9 (=CH-), 123.4 (=CH-), 124.0 (=CH-), 126.1 (=C<), 127.0 (=C<), 128.6 (=CH-), 129.5 (=CH-), 130.3 (=CH-), 138.2 (=CH-), 139.9 (=CH-), 140.9 (=CH-), 141.7 (=C<), 142.3 (=C<), 149.9 (=C<), 153.8 (=C<), 156.0 (=C<), 165.3 (C=O), 182.3 (C=O). *Anal.* Calcd for $C_{22}H_{15}O_4Br$: C, 62.42; H, 3.57. Found: C, 62.22; H, 3.62.

Bromination of 3-Acyl-2-methylazulene-1-carbonitriles (**2bb-be**). To a solution of 3-acyl-2-methylazulene-1-carbonitrile (**2bb-be**) (0.5 mmol) in carbon tetrachloride (20 mL) were added NBS (107 mg, 0.6 mmol) and benzoyl peroxide (10 mg). The mixed solution was refluxed for 2-12 h. The mixture was quenched with water and extracted with dichloromethane. The evaporation residue was purified by silica gel column chromatography with benzene as eluent to give 3-acyl-2-bromomethylazulene-1-carbonitriles (**4bb-be**). From the reactions of compound (**2bb**), 3-bromo-2-methylazulene-1-carbonitrile (**5b**) (12 mg,

10%) and 3-bromo-2-bromomethylazulene-1-carbonitrile (**6b**) (33 mg, 20%) were obtained as by products.

2-Bromomethyl-3-propionylazulene-1-carbonitrile (**4bb**): This compound (**4bb**) was obtained under refluxing for 2 h in yield 89 mg (59%) as violet needles (from benzene); mp 162-164 °C; IR (KBr): ν = 2212 (CN), 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 1.33 (3H, t, J = 7.5 Hz, CH_2CH_3), 3.17 (2H, q, J = 7.5 Hz, CH_2CH_3), 5.06 (2H, s, CH_2Br), 7.76 (1H, dd, J = 9.8, 9.8 Hz, 5-H), 7.78 (1H, dd, J = 9.8, 9.8 Hz, 7-H), 8.02 (1H, dd, J = 9.8, 9.8 Hz, 6-H), 8.72 (1H, d, J = 9.8 Hz, 4-H), 9.37 (1H, d, J = 9.8 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 8.6 (CH_2CH_3), 23.8 (CH_2CH_3), 37.1 (CH_2Br), 99.1 (=C<), 115.1 (=C<), 125.6 (=CH-), 130.5 (=CH-), 131.7 (=CH-), 138.1 (=CH-), 140.8 (=CH-), 141.4 (=C<), 141.9 (=CH-), 144.2 (=C<), 149.8 (CN), 199.6 (C=O). *Anal.* Calcd for $C_{15}H_{12}NOBr$: C, 59.62; H, 4.00; N, 4.64. Found: C, 59.69; H, 4.13; N, 4.72.

3-Benzoyl-2-bromomethylazulene-1-carbonitrile (**4bc**): This compound (**4bc**) was obtained under refluxing for 4 h in yield 158 mg (90%) as violet needles (from benzene); mp 159-161 °C; IR (KBr): ν = 2212 (CN), 1631 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 4.81 (2H, s, CH_2Br), 7.45 (2H, d, J = 7.8, 7.5 Hz, 3'-,5'-H), 7.57 (1H, dd, J = 9.6, 9.6 Hz, 5-H), 7.64 (1H, dd, J = 7.5, 7.5 Hz, 4'-H), 7.74 (1H, dd, J = 9.6, 9.6 Hz, 7-H), 7.79 (2H, d, J = 7.8 Hz, 2'-,6'-H), 7.96 (1H, dd, J = 9.9, 9.9 Hz, 6-H), 8.55 (1H, d, J = 9.6 Hz, 4-H), 8.75 (1H, d, J = 9.6 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 22.7 (CH_2Br), 98.6 (=C<), 115.1 (=C<), 126.0 (=C<), 128.8 (=CH-), 129.7 (=CH-), 130.1 (=CH-), 130.5 (=CH-), 133.4 (=CH-), 138.2 (=CH-), 139.4 (=C<), 139.7 (=CH-), 141.3 (=C<), 144.4 (=C<), 151.2 (CN), 192.9 (C=O). *Anal.* Calcd for $C_{19}H_{12}NOBr$: C, 65.16; H, 3.45; N, 4.00. Found: C, 65.12; H, 3.28; N, 4.08.

2-Bromomethyl-3-cinnamoyl-1-carbonitrile (**4bd**): This compound (**4bd**) was obtained under refluxing for 12 h in yield 120 mg (64%) as violet needles (from benzene); mp 154-156 °C; IR (KBr): ν = 2211 (CN), 1649 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 5.03 (2H, s, CH_2Br), 7.40-7.45 (3H, m, 3"-,4"-, 5"-H), 7.54 (1H, d, J = 16.0 Hz, 3'-H), 7.66-7.69 (2H, m, 2"-,6"-H), 7.75 (1H, J = 16.0 Hz, 2'-H), 7.74-7.80 (2H, m, 5-,7-H), 8.02 (1H, dd, J = 9.8, 9.8 Hz, 6-H), 8.75 (1H, d, J = 9.8 Hz, 4-H), 9.18 (1H, d, J = 9.8 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 23.6 (CH_2Br), 98.6 (=C<), 115.1 (=C<), 126.6 (=CH-), 126.7 (=C<), 128.7 (=CH-), 129.0 (=CH-), 130.3 (=CH-), 130.8 (=CH-), 131.3 (=CH-), 134.4 (=C<), 137.9 (=CH-), 140.4 (=CH-), 141.2 (=C<), 141.9 (=CH-), 144.3 (=C<), 145.1 (=CH-), 149.5 (CN), 188.9 (C=O). *Anal.* Calcd for $C_{21}H_{14}NOBr$: C, 67.04; H, 3.75; N, 3.72. Found: C, 67.23; H, 3.98; N, 3.87.

3-(2-Benzo[*b*]furoyl)-2-bromomethylazulene-1-carbonitrile (**4be**): This compound (**4be**) was obtained under refluxing for 8 h in yield 148 mg (76%) as violet needles (from benzene); mp 215 °C (dec); IR (KBr): ν = 2212 (CN), 1627 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 4.94 (2H, s, CH_2Br), 7.35 (1H, dd, J = 8.4, 7.5 Hz, 5'- or 6'-H), 7.37 (1H, s, 3'-H), 7.52 (1H, dd, J = 8.4, 7.5 Hz, 5'- or 6'-H), 7.61 (1H, d, J = 8.4 Hz, 4'-H), 7.66 (1H, dd, J = 9.8, 9.8 Hz, 7-H), 7.73 (1H, d, J = 8.4 Hz, 7'-H), 7.78 (1H, dd, J = 9.8, 9.8 Hz, 5-H), 8.00 (1H, dd, J = 9.8, 9.8 Hz, 6-H), 8.76 (1H, d, J = 9.8 Hz, 4-H), 8.79 (1H, d, J = 9.8 Hz,

8-H); ^{13}C NMR ($CDCl_3$): δ = 22.7 (CH_2Br), 112.7 (=CH-), 115.0 (=C<), 116.5 (=CH-), 123.5 (=CH-), 124.3 (=CH-), 125.3 (=C<), 127.1 (=C<), 128.3 (=CH-), 128.8 (=CH-), 130.3 (=CH-), 130.8 (=CH-), 138.4 (=CH-), 139.4 (=CH-), 141.3 (=C<), 141.9 (=CH-), 144.2 (=C<), 150.8 (=C<), 153.5 (=C<), 156.1 (CN), 180.8 (C=O). *Anal.* Calcd for $C_{21}H_{12}NO_2Br$: C, 64.63; H, 3.10; N, 3.59. Found: C, 64.74; H, 3.02; N, 3.48.

Reactions of 3-Acyl-2-bromomethylazulenes (**4aa-ae**, **4ba-be**). A solutioin of 3-acyl-2-bromomethylazulene (**4aa**-**ae**, **4ba**-**be**) (0.3 mmol) and thioacetamide (34 mg, 0.45 mmol) in dry ethanol (10 mL) was heated under refluxing for 1 h. The mixture was quenched with water (10 mL) and extracted with chloroform (2 x 10 mL). The evaporation residue was purified by silica gel column chromatography with benzene as eluent to give the correponding methyl azuleno[1,2-*c*]thiophene-9-carboxylates (**7aa**-**ae**) and azuleno[1,2-*c*]thiophene-9-carbonitriles (**7ba**-**be**).

Methyl 3-Methylazuleno[1,2-*c*]thiophene-9-carboxylate (**7aa**): This compound (**7aa**) was obtained in yield 68 mg (88%) as yellowish green needles (from benzene); mp 142-144 °C; IR (KBr): ν = 1682 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 2.82 (3H, s, CH_3), 3.94 (3H, s, $COOCH_3$), 6.87-6.99 (3H, m, 5-,6-,7-H), 7.14 (1H, s, 1-H), 7.56-7.64 (1H, m, 4-H), 8.81-8.88 (1H, m, 8-H); ^{13}C NMR ($CDCl_3$): δ = 14.8 (CH_3), 51.0 ($COO\mathit{C}H_3$), 105.7 (=CH-), 110.0 (=C<), 129.1 (=CH-), 130.4 (=CH-), 130.5 (=CH-), 133.4 (=C<), 134.0 (=CH-), 134.5 (=C<), 134.8 (=CH-), 140.0 (=C<), 145.2 (=C<), 151.7 (=C<), 166.0 (C=O). *Anal.* Calcd for $C_{15}H_{12}O_2S$: C, 70.28; H, 4.72. Found: C, 70.38; H, 4.77.

Methyl 3-Ethylazuleno[1,2-*c*]thiophene-9-carboxylate (**7ab**): This compound (**7ab**) was obtained in yield 64 mg (79%) as yellowish green needles (from benzene); mp 104-105 °C; IR (KBr): ν = 1688 (C=O), 1640 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 1.47 (3H, t, J = 7.5 Hz, $CH_2C\mathit{H}_3$), 3.23 (2H, q, J = 7.5 Hz, $C\mathit{H}_2CH_3$), 3.95 (3H, s, $COOCH_3$), 6.91-6.97 (3H, m, 5-,6-,7-H), 7.20 (1H, s, 1-H), 7.60-7.65 (1H, m, 4-H), 8.84-8.91 (1H, m, 8-H); ^{13}C NMR ($CDCl_3$): δ = 14.4 ($CH_2\mathit{C}H_3$), 23.0 ($\mathit{C}H_2CH_3$), 51.0 ($COO\mathit{C}H_3$), 105.7 (=CH-), 110.3 (=C<), 129.1 (=CH-), 130.3 (=CH-), 130.4 (=CH-), 133.6 (=C<), 134.0 (=CH-), 134.8 (=C<), 139.9 (=CH-), 141.7 (=C<), 145.4 (=C<), 151.7 (=C<), 166.0 (C=O). *Anal.* Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22. Found: C, 71.02; H, 5.21.

Methyl 3-Phenylazuleno[1,2-*c*]thiophene-9-carboxylate (**7ac**): This compound (**7ac**) was obtained in yield 85 mg (89%) as dark green needles (from benzene); mp 118-119 °C; IR (KBr): ν = 1672 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ = 3.96 (3H, s, $COOCH_3$), 6.71-6.97 (3H, m, 5-,6-,7-H), 7.41-7.49 (3H, m, 3'-,4'-,5'-H), 7.46 (1H, s, 1-H), 7.65 (1H, d, J = 8.1 Hz, 2'- or 6'-H), 7.66 (1H, d, J = 8.1 Hz, 2'- or 6'-H), 7.97 (1H, d, J = 9.0 Hz, 4-H), 8.91-8.95 (1H, m, 8-H); ^{13}C NMR ($CDCl_3$): δ = 51.1 ($COO\mathit{C}H_3$), 109.3 (=CH-), 109,9 (=CH-), 128.1 (=CH-), 128.5 (=CH-), 128.9 (=CH-), 129.4 (=CH-), 130.2 (=CH-), 130.6 (=CH-), 133.8 (=C<), 133.9 (=C<), 135.2 (=CH-), 137.4 (=C<), 139.1 (=C<), 145.8 (=C<), 151.8 (=C<), 165.9 (C=O). *Anal.* Calcd for $C_{20}H_{14}O_2S$: C, 75.44; H, 4.33. Found: C, 75.63; H, 4.21.

Methyl 3-Styrylazuleno[1,2-*c*]thiophene-9-carboxylate (**7ad**): This compound (**7ad**) was obtained in yield 58 mg (62%) as yellowish green needles (from benzene); mp 152-153 °C; IR (KBr): □ = 1689 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): □ = 3.94 (3H, s, $COOCH_3$), 6.59-6.70 (3H, m, 5-,6-,7-H), 7.17 (1H, d, *J* = 15.5 Hz, 3'-H), 7.30 (1H, s, 1-H), 7.32-7.42 (3H, m, 3"-,4"-,5"-H), 7.54 (2H, d, *J* = 7.2 Hz, 2"-, 6"-H), 7.71 (1H, d, *J* = 15.5 Hz, 2'-H), 7.86 (1H, d, *J* = 9.8 Hz, 4-H), 8.88 (1H, d, *J* = 9.8 Hz, 8-H); ^{13}C NMR ($CDCl_3$): □ = 51.1 ($COOCH_3$), 108.2 (=CH-), 109,9 (=CH-), 120.1 (=CH-), 126.7 (=CH-), 128.2 (=CH-), 128.8 (=CH-), 130.4 (=CH-), 130.7 (=CH-), 131.6 (=CH-), 134.7 (=C<), 134.9 (=CH-), 135.2 (=CH-), 136.3 (=C<), 136.7 (=C<), 139.9 (=C<), 145.7 (=C<), 151.9 (=C<), 165.8 (C=O). *Anal*. Calcd for $C_{22}H_{16}O_2S$: C, 76.72; H, 4.68. Found: C, 76.68; H, 4.72.

Methyl 3-(2-Benzo[*b*]furyl)azuleno[1,2-*c*]thiophene-9-carboxylate (**7ae**): This compound (**7ae**) was obtained in yield 95 mg (88%) as yellowish green needles (from benzene); mp 101-102 °C; IR (KBr): □ = 1676 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): □ = 3.90 (3H, s, $COOCH_3$), 6.84-6.93 (3H, m, 5-,6-, 7-H), 6.96 (1H, s, 1-H), 7.24 (1H, dd, *J* = 7.8, 7.2 Hz, 5'- or 6'-H), 7.30 (1H, dd, *J* = 7.8, 7.2 Hz, 5'- or 6'-H), 7.40 (1H, s, 2'-H), 7.49 (1H, d, *J* = 7.2 Hz, 7'-H), 7.53 (1H, d, *J* = 7.2 Hz, 4'-H), 8.56 (1H, d, *J* = 9.8 Hz, 4-H), 8.85 (1H, d, *J* = 9.8 Hz, 8-H); ^{13}C NMR ($CDCl_3$): □ = 51.0 ($COOCH_3$), 104.9 (=CH-), 109.5 (=CH-), 110.3 (=CH-), 111.1 (=CH-), 120.9 (=CH-), 123.3 (=CH-), 124.6 (=CH-), 124.7 (=C<), 128.7 (=C<), 130.3 (=CH-), 130.6 (=CH-), 131.5 (=CH-), 134.8 (=C<), 135.3 (=CH-), 135.7 (=CH-), 138.4 (=C<), 146.4 (=C<), 150.2 (=C<), 151.7 (=C<), 154.5 (=C<), 165.6 (C=O). *Anal.* Calcd for $C_{22}H_{14}O_3S$: C, 73.72; H, 3.91. Found: C, 73.83; H, 3.69.

3-Methylazuleno[1,2-*c*]thiophene-9-carbonitrile (**7ba**): This compound (**7ba**) was obtained in yield 62 mg (92%) as yellowish needles (from benzene); mp 163-164 °C; IR (KBr): □ = 2296 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$): □ = 2.82 (3H, s, CH_3), 6.82-6.92 (2H, m, 5-,7-H), 6.93-6.97 (1H, m, 6-H), 6.96 (1H, s, 1-H), 7.52-7.55 (1H, m, 4-H), 7.65 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C NMR ($CDCl_3$): □ = 14.7 (CH_3), 91.3 (=C<), 103.8 (=CH-), 128.9 (=CH-), 130.1 (=CH-), 130.8 (=CH-), 133.4 (=CH-), 133.8 (=C<), 134.2 (=C<), 135.0 (=C<), 138.2 (=C<), 143.6 (=C<), 154.5 (CN). *Anal*. Calcd for $C_{14}H_9NS$: C, 75.30; H, 4.06; N, 6.27. Found: C, 75.08; H, 4.02; N, 6.33.

3-Ethylazuleno[1,2-*c*]thiophene-9-carbonitrile (**7bb**): This compound (**7bb**) was obtained in yield 68 mg (95%) as dark green needles (from benzene); mp 124-125 °C; IR (KBr): □ = 2196 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$): □ = 1.46 (3H, t, *J* = 7.5 Hz, CH_2CH_3), 3.18 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 6.65-6.89 (2H, m, 5-,7-H), 6.90-6.94 (1H, m, 6-H), 6.96 (1H, s, 1-H), 7.46-7.51 (1H, m, 4-H), 7.61 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C NMR ($CDCl_3$): □ = 14.3 (CH_2CH_3), 22.8 (CH_2CH_3), 91.4 (=C<), 103.7 (=CH-), 116.9 (=C<), 128.9 (=CH-), 129.9 (=CH-), 130.7 (=CH-), 133.1 (=CH-), 133.2 (=C<), 133.7 (=CH-), 137.9 (=C<), 143.2 (=C<), 143.6 (=C<), 154.3 (CN). *Anal*. Calcd for $C_{15}H_{11}NS$: C, 75.91; H, 4.67; N, 5.90. Found: C, 76.20; H, 4.41; N, 6.14.

3-Phenylazuleno[1,2-*c*]thiophene-9-carbonitrile (**7bc**): This compound (**7bc**) was obtained in

yield 65 mg (76%) as dark green needles (from benzene); mp 178-179 °C; IR (KBr): ν = 2198 cm^{-1} (CN); ^1H NMR ($CDCl_3$): δ = 6.79 (1H, dd, *J* = 9.8, 9.8 Hz, 6-H), 6.91 (1H, dd, *J* = 9.9, 9.8 Hz, 5-H), 6.97 (1H, dd, *J* = 9.8, 9.8 Hz, 7-H), 7.27 (1H, s, 1-H), 7.45-7.53 (3H, m, 3'-,4'-,5'-H), 7.66 (2H, d, *J* = 8.4 Hz, 2'- or 6'-H), 7.77 (1H, d, *J* = 9.9 Hz, 8-H), 7.89 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C NMR ($CDCl_3$): δ = 91.3 (=C<), 107.2 (=CH-), 116.8 (=C<), 128.1 (=CH-), 128.9 (=CH-), 129.1 (=CH-), 129.3 (=CH-), 130.2 (=CH-), 130.6 (=CH-), 133.1 (=C<), 133.4 (=C<), 133.8 (=CH-), 134.9 (=CH-), 137.4 (=C<), 138.9 (=C<), 144.2 (=C<), 154.6 (CN). *Anal.* Calcd for $C_{19}H_{11}NS$: C, 79.97; H, 3.86; N, 4.91. Found: C, 79.83; H, 3.85; N, 5.06.

3-Styrylazuleno[1,2-*c*]thiophene-9-carbonitrile (**7bd**): This compound (**7bd**) was obtained in yield 68 mg (73%) as yellowish green needles (from benzene); mp 186-187 °C (decomp); IR (KBr): ν = 2198 cm^{-1} (CN); ^1H NMR ($CDCl_3$): δ = 6.81-6.88 (1H, m, 6-H), 6.93-6.96 (2H, m, 5-,7-H), 7.03 (1H, s, 1-H), 7.14 (1H, d, *J* = 15.5 Hz, 3'-H), 7.32 (1H, dd, *J* = 7.2, 7.2 Hz, 4'-H), 7.39 (2H, dd, *J* = 7.5, 7.2 Hz, 3"-,5"-H), 7.51 (2H, d, *J* = 7.5 Hz, 2"-,6"-H), 7.57 (1H, d, *J* = 15.5 Hz, 2'-H), 7.63 (1H, d, *J* = 10.0 Hz, 4-H), 7.65-7.69 (1H, m, 8-H); ^{13}C NMR ($CDCl_3$): δ = 91.3 (=C<), 105.6 (=CH-), 116.6 (=C<), 119.2 (=CH-), 126.8 (=CH-), 128.5 (=CH-), 128.9 (=CH-), 130.0 (=CH-), 130.3 (=CH-), 130.7 (=CH-), 132.6 (=CH-), 133.6 (=CH-), 134.0 (=C<), 134.6 (=CH-), 136.3 (=C<), 137.7 (=C<), 138.1 (=C<), 144.1 (=C<), 154.6 (CN). *Anal.* Calcd for $C_{21}H_{13}NS$: C, 80.99; H, 4.21; N, 4.50. Found: C, 80,72; H, 4.18; N, 4.44.

3-(2-Benzo[*b*]furyl)azuleno[1,2-*c*]thiophene-9-carbonitrile (**7be**): This compound (**7be**) was obtained in yield 82 mg (84%) as yellowish green needles (from benzene); mp 174-175 °C (decomp); IR (KBr): ν = 2196 cm^{-1} (CN); ^1H NMR ($CDCl_3$): δ = 6.87-6.94 (1H, m, 6-H), 6.97-7.01 (2H, m, 5-,7-H), 7.06 (1H, s, 1-H), 7.23 (1H, s, 3'-H), 7.29 (1H, dd, *J* = 8.1, 7.5 Hz, 5'- or 6'-H), 7.36 (1H, dd, *J* = 8.1, 7.5 Hz, 5'- or 6'-H), 7.55 (1H, d, *J* = 8.1 Hz, 7'-H), 7.59 (1H, d, *J* = 8.1 Hz, 4'-H), 7,73 (1H, d, *J* = 9.9 Hz, 4-H), 8.58 (1H, d, *J* = 9.9 Hz, 8-H); ^{13}C NMR ($CDCl_3$): δ = 91.6 (=C<), 105.6 (=CH-), 105.6 (=CH-), 107.8 (=CH-), 111.2 (=CH-), 116.5 (=C<), 121.2 (=CH-), 123.6 (=CH-), 125.3 (=CH-), 126.4 (=C<), 128.6 (=C<), 130.4 (=CH-), 130.9 (=CH-), 131.7 (=CH-), 133.9 (=CH-), 134.2 (=CH-), 135.6 (=CH-), 136.9 (=C<), 144.9 (=C<), 149.5 (=C<), 154.6 (=C<), 154.7 (CN). *Anal.* Calcd for $C_{21}H_{11}NOS$: C, 77.51; H, 3.41; N, 4.31. Found: C, 77.52; H, 3.44; N, 4.57.

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