Reaction of 6-Aryl- or Styryl-4-methylsulfanyl-2-oxo-2*H*-pyrans with Active Methylene Compounds and Fluorescence Properties of the Products

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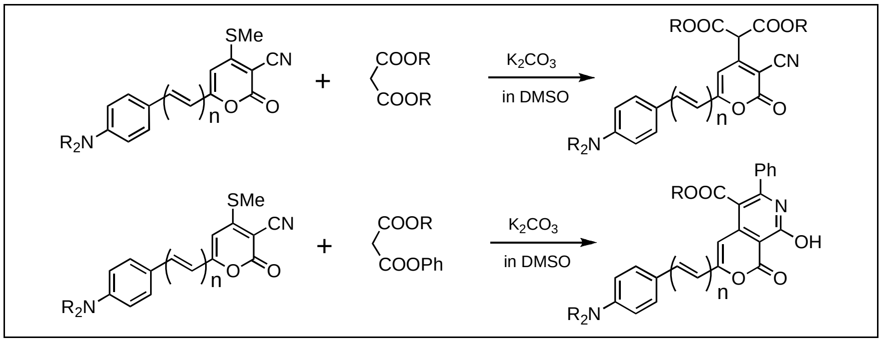

New 2-pyrone derivatives, dialkyl 3-cyano-6-phenyl-2-oxo-2*H*-pyran-4-ylmalonates and alkyl 3-cyano-6-phenyl-2-oxo-2*H*-pyran-4-ylacetates, which were easily prepared by the reaction of 6-aryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitriles with active methylene compounds in the presence of potassium carbonate, show fluorescence emission radiation. The light-emitting region of dimethyl 3-cyano-6-(4-*N*,*N*-dimethylamino)styryl-2-oxo-2*H*-pyran-4-ylmalonate (**7h**) was 620 nm in dichloromethane, making this compound a typical red fluorescent compound. Methyl 8-hydroxy-6-methyl-1-oxo-3-phenyl-1*H*-pyrano-[3,4-*c*]pyridine-5-carboxylate deriv-atives also showed fluorescence in the solid state. This is the first example of fluorescence in fused 2-pyrone derivatives.

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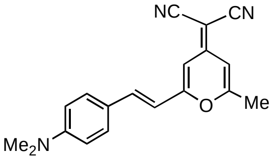
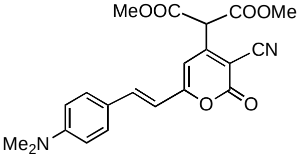
INTRODUCTION

Pyrones and fused pyrones are important in designing luminescent materials for organic light-emitting diodes (OLED), dye lasers, and luminescent labeling reagents for HPLC or capillary electrophoresis [1]. 2*H*-Pyrones containing aryl groups at position 6 continue to attract considerable attention in both synthetic and materials chemistry, and are highly interesting materials for applications in optoelectronic devices such as displays [2]. It has been reported that 6-aryl- or styryl-4-methylsulfanyl-2*H*-pyrones are easily prepared by the reaction of ketene dithioacetal with active methylene compounds in the presence of powdered sodium [3] and the resulting compounds are also useful synthetic intermediates for 6-aryl- and 6-styryl-4-alkoxy- or 4-amino-2-oxo-2*H*-pyran-3-carbonitriles [4,5]. In the field of organic electron luminescence, a red color is most desired. Compound 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran (DCM) and other 4*H*-pyran derivatives are important and well-known red materials in organic EL substances [6,7]. To prepare our final target compound **7h** possessing red fluorescence, we The previous procedure for preparing **3a-l** can be applied to 6-styryl-2*H*-pyrones. The reaction of 4-(*N*,*N*-disubstitutedaminophenyl)but-3-en-2-ones (**2m-o**) with synthesized 2*H*-pyrone derivatives bearing an active methylene group at the 4 position by the displacement of a 4-methylsulfanyl group with active methylene compounds.



DCM



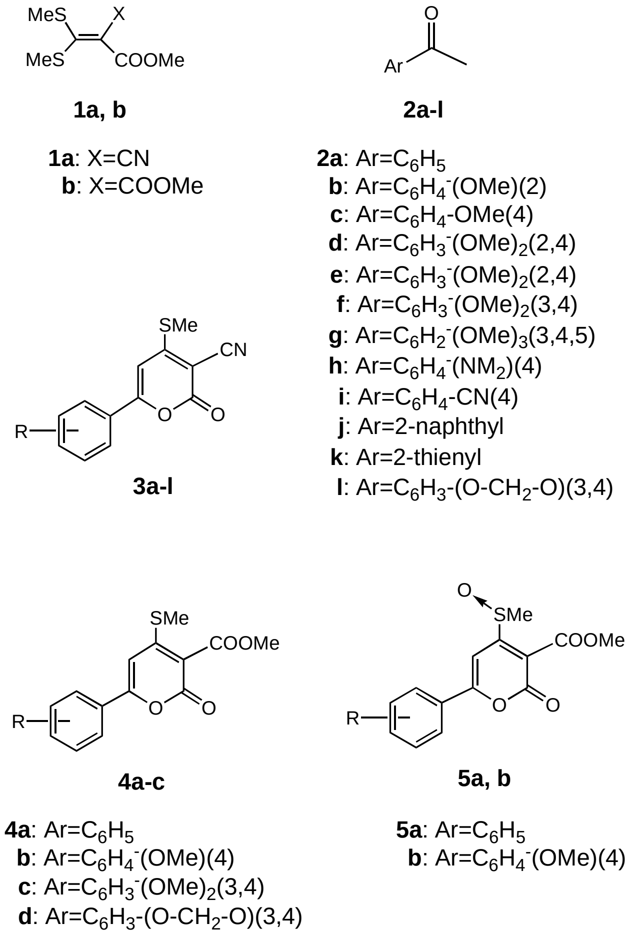
7h

Figure 1

RESULTS AND DISCUSSION

Synthesis of 2*H*-Pyrones and Fused 2*H*-Pyrone. The 2*H*-pyrone derivatives (**3a-l**) used in this study were easily prepared by the reaction of the corresponding aryl acetyl compounds (**2a-l**) with ketene dithioacetal (**1a**) [4b,d]. Methyl 6-aryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carboxylates (**4a-d**) were also prepared from **1b** and arylacetyl compounds (**2a**, **c, f, l**). Because compounds **4a-d** were not very active against nucleophiles, the

4-sulfinyl compounds **5a**-**c,** obtained by the oxidation of **5a-c** with *m*-chloroperbenzoic acid or hydrogen peroxide, were used in the reaction with active methylene compounds (See Figure 2).



1a, b

1a: X=CN
b: X=COOMe

2a-l

2a: Ar=C_6H_5
b: Ar=C_6H_4-(OMe)(2)
c: Ar=C_6H_4-OMe(4)
d: Ar=C_6H_3-$(OMe)_2$(2,4)
e: Ar=C_6H_3-$(OMe)_2$(2,4)
f: Ar=C_6H_3-$(OMe)_2$(3,4)
g: Ar=C_6H_2-$(OMe)_3$(3,4,5)
h: Ar=C_6H_4-(NM_2)(4)
i: Ar=C_6H_4-CN(4)
j: Ar=2-naphthyl
k: Ar=2-thienyl
l: Ar=C_6H_3-(O-CH_2-O)(3,4)

3a-l

4a-c

4a: Ar=C_6H_5
b: Ar=C_6H_4-(OMe)(4)
c: Ar=C_6H_3-$(OMe)_2$(3,4)
d: Ar=C_6H_3-(O-CH_2-O)(3,4)

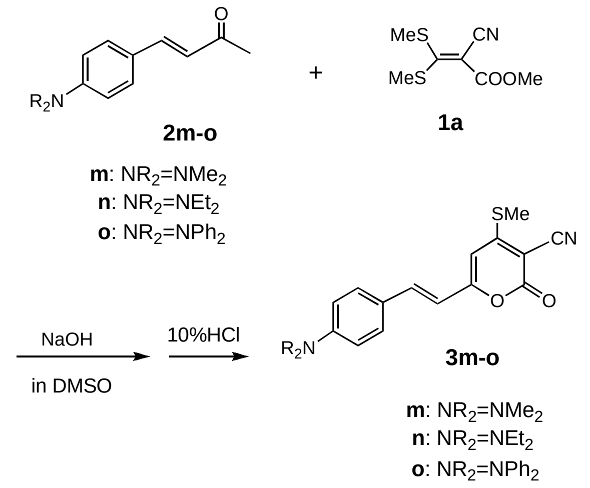
5a, b

5a: Ar=C_6H_5
b: Ar=C_6H_4-(OMe)(4)

Figure 2

The previous procedure for preparing **3a-l** can be applied to 6-styryl-2*H*-pyrones. The reaction of 4-(*N*,*N*-disubstituted aminophenyl)but-3-en-2-ones (**2m-o**) with methyl 3,3-bis(methylsulfanyl)-2-cyanoacrylate (**1a**) was carried out in the presence of sodium hydroxide as the base to give the desired products, 6-[2-(4-*N*,*N*'-disubstituted aminophenyl)vinyl]-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitriles (**3m-o**) in 32, 26, and 29% yields, respectively (Scheme 1).

Scheme 1



2m-o

m: NR_2=NMe_2
n: NR_2=NEt_2
o: NR_2=NPh_2

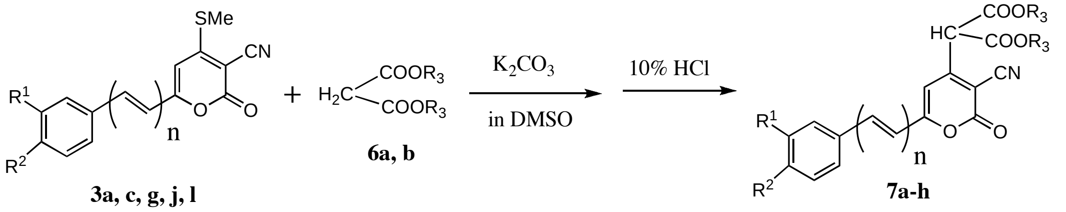
1a

3m-o

m: NR_2=NMe_2
n: NR_2=NEt_2
o: NR_2=NPh_2

It is well known that the reaction of ketene dithioacetals with active methylene compounds smoothly progresses in the presence of potassium carbonate as a base to give the corresponding mono-substituted products in good yield. The reaction of compound **3** with active methylene compounds was carried out under these experimental conditions. The reaction of **3a**, **c**, **g**, **j**, and **l** with methyl or ethyl malonates (**6a**, **b**) in the presence of potassium

Table 1. Synthesis of Dialkyl 3-Cyano-6-phenyl-2-oxo-2*H*-pyran-4-ylmalonates.



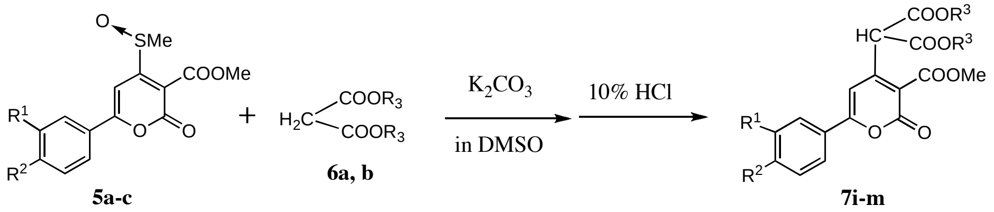
3a, c, g, j, l

6a, b

7a-h

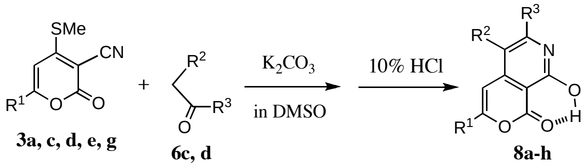
No.	R^1	R^2	R^3	n	Yield(%)	mp(°C)	Appearance
7a	H	H	Me	0	97	159-160	pale yellow needles
b	H	H	Et	0	82	158-159	pale yellow needles
c	H	OMe	Me	0	81	182-183	yellow needles
d	H	OMe	Et	0	72	194-198	pale yellow needles
e	H	NMe_2	Me	0	77	198-199	red needles
f	H	NMe_2	Et	0	74	194-198	red needles
g	thienyl		Me	0	83	174-175	yellow needles
h	H	NMe_2	Me	1	84	200-202	black red needles

Table 2. Synthesis of Dialkyl 3-Methoxycarbonyl-6-phenyl-2-oxo-2*H*-pyran-4-ylmalonates.

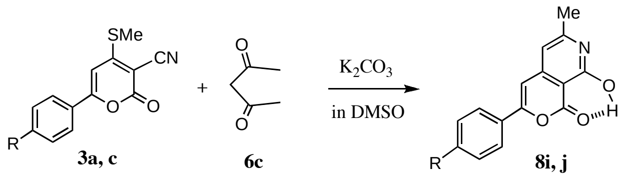


No.	R^1	R^2	R^3	Yield(%)	mp(°C)	Appearance
7i	H	H	Me	88	120-121	yellow needles
j	H	H	Et	80	80-90	yellow needles
k	H	OMe	Me	90	120-121	yellow needles
l	H	OMe	Et	79	89-92	yellow needles
m	-O-CH_2-O-		Me	53	143-146	yellow needles

Table 3. Synthesis of 1*H*-pyrano[3,4-*c*]pyridines



No.	R^1	R^2	R^3	Yield(%)	Mp(°C)
8a	C_6H_5	COOMe	Me	52	>300
b	C_6H_4-OMe(4)	COOMe	Me	30	296-297
c	C_6H_5	COOEt	Me	70	295-297
d	C_6H_4-OMe(4)	COOEt	Me	31	287-288
e	C_6H_3-OMe_2(2,4)	COOEt	Me	30	298-299
f	C_6H_3-OMe_2(3,4)	COOEt	Me	28	303-304
g	C_6H_4-NMe_2(4)	COOEt	Me	9	298-299
h	C_6H_4-OMe(4)	SO_2-C_6H_4-Me(4)	Me	22	260-270



3a: R=H
c: R=OMe

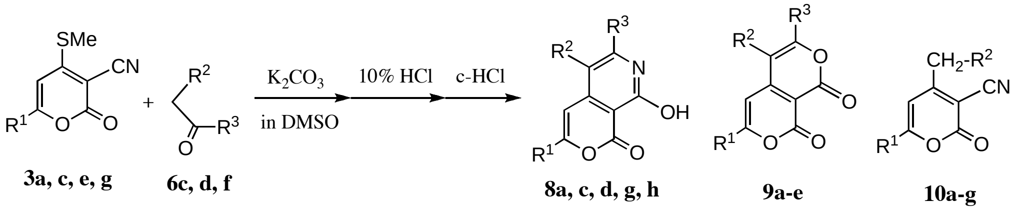
8i: R=H
j: R=OMe

carbonate in DMSO gave the corresponding dialkyl 3-cyano-6-phenyl- or 6-styryl-2-oxo-2*H*-pyran-4-yl-malonates (**7a-h**) in 72-97% yields, respectively (shown in Table 1).

Similarly, dialkyl 3-methoxycarbonyl-6-phenyl-2-oxo-2*H*-pyran-4-ylmalonates (**7i-m**) were readily obtained from 6-aryl-4-sulfinyl-2*H*-pyran-2-ones (**5a-c**) and active methylene compounds (**6a**, **b**) in good yields (shown in Table 2).

On the other hand, the reactions of **3a c, d, e, g** with methyl or ethyl acetoacetates (**6c, d**) under the same reaction conditions did not give the corresponding displacement products **7a-e**. The products of these reactions were determined to be 8-hydroxy-6-methyl-3-phenyl-1-oxo-1*H*-pyrano[3,4-*c*]pyridine-5-carboxylates (**8a-h**) (in Table 3) by spectroscopic (IR, UV, NMR, and MS) and elemental analyses. In the NMR spectra of **8a-h**, the hydroxy protons at position 8 appear at 12.0-12.5 ppm due to hydrogen bonding with a O=C group. In the case of **8i** and **f**, the hydroxy protons were not shown due to strong hydrogen bonds in the ^{1}H-NMR spectra. In the final step of this reaction, the reaction mixture was acidified with 10% HCl solution and then the intermediates, e.g., **3,** were treated with concentrated HCl to give separable mixtures of **8**, **9**, and **10**. These compounds were easily separated by their differential solubilities in solvents such as dichloromethane, DMF, and ethanol to give compounds **8**, **9** and **10**, respectively. The structures of these compounds were determined by spectroscopic (IR, NMR, UV, and MS) and elemental

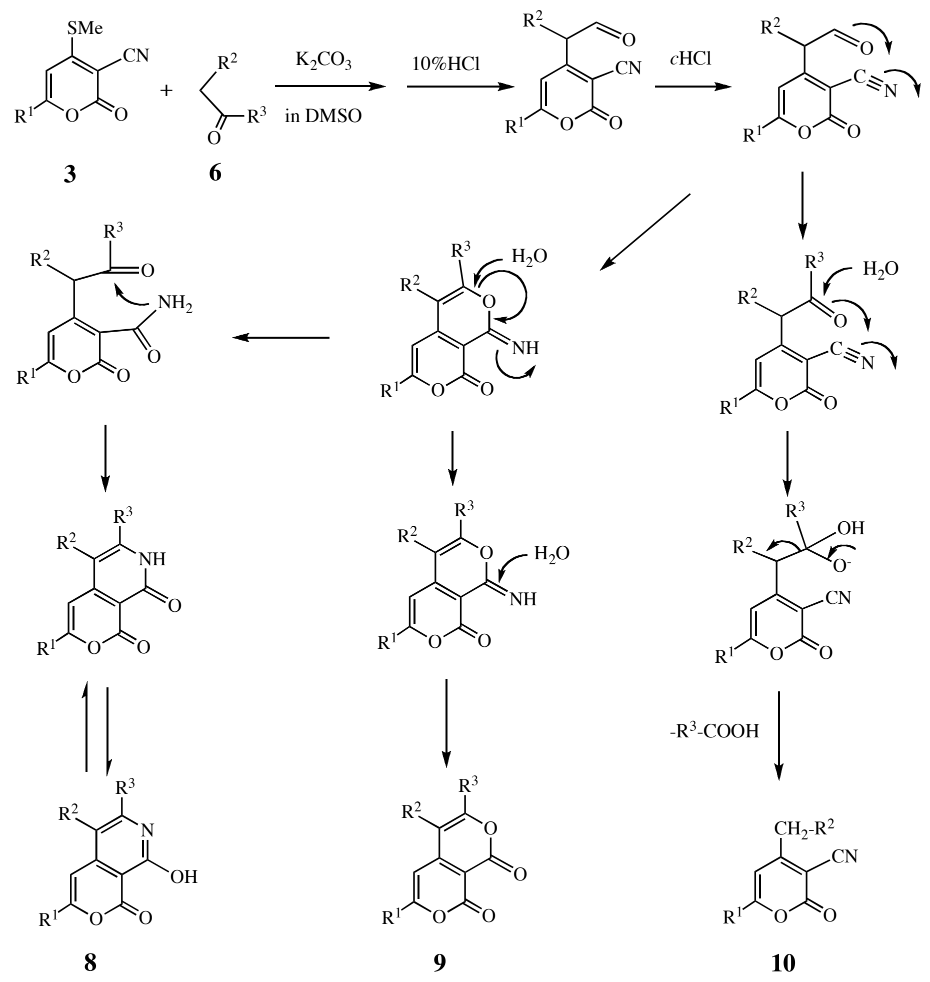
Table 4. Synthesis of 1*H*-pyrano[3,4-*c*]pyridines



3a, c, e, g **6c, d, f** **8a, c, d, g, h** **9a-e** **10a-g**

Entry	R^1	R^2	R^3	**8** Yield(%)	**9** Yield(%)	**10** Yield(%)
1	C_6H_5	COOMe	Me	**8a** 10	-- --	**10a** 60
2	C_6H_5	COOEt	Me	**8c** 12	**9a** 11	**10b** 36
3	C_6H_4-OMe(4)	COOEt	Me	**8d** 30	**9b** 21	**10c** 22
4	$C_6H_3(OMe)_2(3,4)$	COOEt	Me	-- --	**9c** 14	**10d** 45
5	C_6H_4-NMe_2(4)	COOEt	Me	**8g** 9	-- --	**10e** 2
6	C_6H_5	COOEt	Ph	-- --	**9d** 11	**10b** 69
7	C_6H_4-OMe(4)	COOEt	Ph	-- --	**9e** 14	**10c** 43
8	C_6H_5	SO_2-C_6H_4-Me(4)	Me	-- --	-- --	**10f** 66
9	C_6H_4-OMe(4)	SO_2-C_6H_4-Me(4)	Me	**8h** 22	-- --	**10g** 18

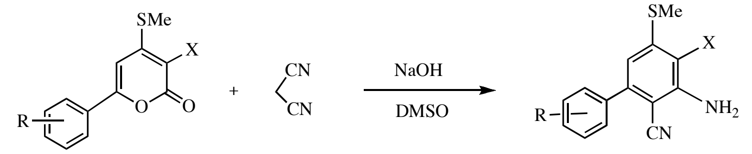
Scheme 2. Reaction Pathway



analyses. The reaction pathway of each product (**8**, **9**, **10**) is shown in Scheme 2.

The above reaction of 2-pyrones with active methylene compounds in the presence of potassium carbonate

Table 5. Synthesis of Biaryl Derivatives from 2-Pyrones



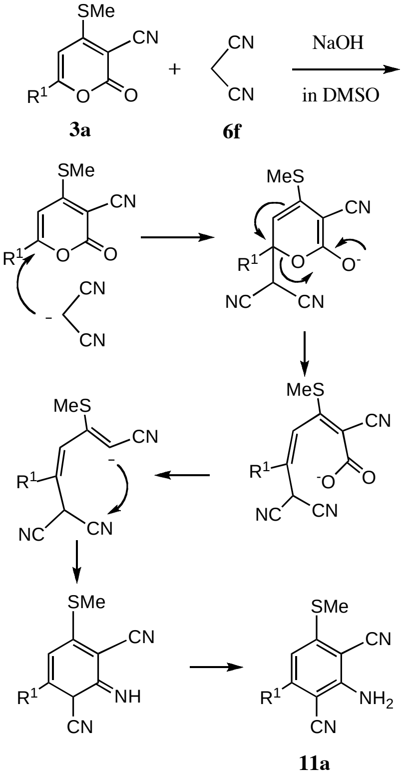
3a-d, f, 4a-c **6f** **11a-j**

No.	Aryl	X	Yield(%)	Appearance	mp (°C)
3a	C_6H_5	CN	85	colorless needles	240-242
b	C_6H_4-OMe(2)	CN	76	colorless needles	216-219
c	C_6H_4-OMe(4)	CN	99	colorless needles	212-213
d	C_6H_3-(OMe)$_2$(2,4)	CN	85	coloroless prisms	259-261
e	C_6H_2-(OMe)$_3$(3,4,5)	CN	90	colorless leaflets	263-265
f	C_6H_4-NMe$_2$(4)	CN	73	pale yellow needles	257-259
g	C_6H_4-(CN)(4)	CN	94	colorless needles	312-314
h	C_6H_5	COOMe	80	colorless needles	138-140
i	C_6H_4-OMe(4)	COOMe	68	colorless needles	124-126
j	C_6H_3O-CH$_2$-O-	COOMe	74	colorless needles	182-184

proceeds first with carbon nucleophilic attack at position 4, followed by displacement of the methylsulfanyl group to give the corresponding 4-substituted 2-pyrone derivatives.

Electron donating and accepting substituents are recognized as molecular subunits that display non-linear optical properties due to their high polarizability. These molecules not only exhibit optical properties but also display diverse pharmacological activities. Ram et al. have reported the synthesis of biaryl compounds by the reaction of 2*H*-pyrone derivatives (**3**) with malononitrile in the presence of potassium hydroxide [8]. This reaction proceeds initially by carbanion attack at position 6 with ring opening followed by ring transformation to yield biaryl compounds. While this reaction conveniently synthesizes polyfunctionalized biaryl compounds, the yield is low. We reexamined our reaction conditions to increase the yield of products. Compound **3a** was allowed to react with malononitrile (**6f**) in the presence of powdered sodium hydroxide in DMSO at room temperature for 5 hours. The reaction mixture was poured +into a large amount of water and stirred at room temperature for about 12 hours until nso more products precipitated. The product was recrystallized from methanol to give colorless needles, mp 240-242 °, in 85% yield. The structure of this compound was determined to be 4-amino-5-methylsulfanyl-biphenyl-2,4-di-carbonitrile (**11a**), which was identical spectroscopically with the compound prepared by Ram. Similarly, other new biphenyl compounds (**11b-j**) were synthesized from the corresponding 4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitriles (**3b-d, f, 4a-c**) and **6f** under similar reaction conditions. In reactions of **4a b**, and **c** with **6f**, 3-amino-biphenyl-4-carboxylates (**11a-j**) were also obtained in 73-99% yield (see Table 5).

Scheme 3. Reaction Pathway



Fluorescence properties. The UV-vis absorption and fluorescence emission radiation of the 4-substituted 2-oxo-2*H*-pyran-3-carbonitriles and 3-carboxylates and fused 2*H*-pyrones were analyzed. DCM and AlQ$_3$[tris(8-hydroxy-quinolinato)aluminum] were used as standards for absorption and fluorescence spectra. The measurements of both absorption and fluorescence spectra were performed in dichloromethane and ethanol solutions at room temperature. The spectroscopic properties, absorption maxima (λ_{max}), molar absorptivities (ε), fluorescence maxima (E_m max) and relative fluorescent intensities (RI) are described in part of Experimental. The aryl and styryl moieties bearing *N*,*N*-disubstituted amino groups at position 6 of the 2-pyrone derivatives fulfill the important condition for fluorescent expression. Compounds (**3l-m**) showed longer wavelength shifts in comparison with the most basic 2-pyrone, 4-methylsulfanyl-6-phenyl-2-oxo-2*H*-pyan-3-carbonitrile (**3a**). However, their relative fluorescence intensities have a tendency to decrease, while the ε values increase in the absorption spectra. In general, 4-amino-6-aryl-2-oxo-2*H*-pyran-3-carbonitriles show stronger intensity than the corresponding 4-methylsulfanyl compounds and their light-emission regions show a 40-50 nm blue shift. On the other hand, 4-substituted compounds (**7** and **9**) show a small batho-chromic shift and stronger fluorescence emission radiation than that of compound **3** in the solid state. In particular, the light-emitting region of compound **7h** was 620 nm in dichloromethane, making this compound a typical red fluorescent compound (See Figure 3). Compounds **7e**, **f** also showed red fluorescence in ethanol solution and can be used as a fluorescence reagent in an oxalate chemiluminescence system.

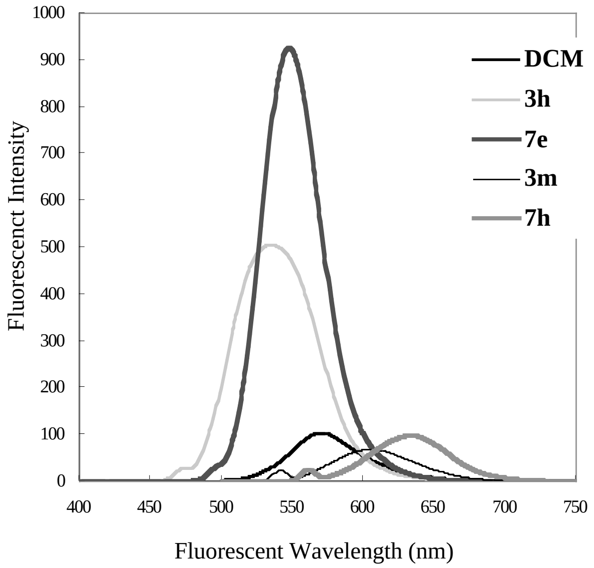


Figure 3. Comparison og fluorescent intensity of 2*H*-pyrone with that of DCM in CH_2Cl_2 solution.

The fluorescence emission radiation of fused pyrones such as compounds **8** and **9** were analyzed. The 1*H*-pyrano[3,4-*c*]pyridin-1-one derivatives (**8**) exhibit moderately strong fluorescent radiation, while the 1*H*,8*H*-pyrano[3,4-*c*]pyran-1,8-dione derivatives (**9**) did not show appreciable fluorescence emission radiation in the solid state. In a similar case with compound **3**, 3-phenyl pyrano[3,4-*c*]pyridin-1-one bearing electron-donating groups such as a methoxy group on the phenyl group showed strong fluorescence. For example, ethyl 8-hydroxy-3-(2,4-dimethoxyphenyl)-6-methyl-1-oxo-1*H*-pyrano[3,4-*c*]pyridine-5-carboxylate (**8e**) showed fluorescence emission radiation at 490 nm with a relative intensity of 4.88 in the solid state. The reason why the fluorescence of these chemical compounds increases seems to be the strong packing by the flat molecules due to hydrogen bonding of a –C=O----H-O- system. This fact suggests the possibility of developing fluorescence in other fused 2*H*-pyrone derivatives. Biaryl derivatives (**11a-j**) showed weak fluorescence emission radiation in the solid state.

In conclusion, new 2-pyrone derivatives, dialkyl 3-cyano-2-oxo-6-phenyl-2*H*-pyran-4-ylmalonates and alkyl 3-cyano-2-oxo-6-phenyl-2*H*-pyran-4-ylacetates, which were easily prepared by the reaction of 6-aryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitriles with active methylene compounds in the presence of potassium carbonate, show fluorescence emission radiation. Methyl 8-hydroxy-6-methyl-1-oxo-3-phenyl-1*H*-pyrano[3,4-*c*]-pyridine-5-carboxylate derivatives also showed fluorescence in the solid state. This is the first example of fluorescence in fused 2-pyrone derivatives.

EXPERIMENTAL

Identifications of compounds and measurements of properties were carried out by general procedures using the following equipment. All melting points were determined in a capillary tube and are uncorrected. The infrared (IR) spectra were recorded in potassium bromide pellets on JASCO 810 or Shimazu IR-460 spectrometer, and the ultraviolet (UV) absorption spectra were determined in 95% ethanol on a Hitachi 323 spectrometer. The fluorescence spectra were determined on Shimazu RF-1500. The nuclear magnetic resonance (NMR) spectra were obtained on Gemini 300NMR (300 MHz) and 500NMR (500 MHz) spectrometers with tetramethylsilane as an internal standard. The mass spectra (MS) were recorded on JEOL DX-303 mass spectrometers. Microanalyses were performed by Y. Ohwatari on a Perkin Elmer 2002 at Nagasaki University. All chemicals were reagent grade and used without further purification unless otherwise specified.

Method of Measurement of Fluorescence.

In solid states. A powder sample of subject compound is heaped in the tray. After covering the sample with quartz plate, this part was fixed in fluorescence spectrometer. After fixing the fluorescent wavelength, the excitation spectrum was determined by the scanning with the fluorescent wavelength. Similarly, Fluorescent spectrum was obtained after scanning with the excitation wavelength. After obtaining these results, the excitation wavelength was decided and the fluorescence spectrum was measured.

The fluorescent relative intensity was determined by using AlQ$_3$ as standard sample. Fluorescence of standard sample and all subject compounds were measured on 272 nm excitation.

In solution. The concentration of measuring samples in the excitation wavelength region was adjusted under 0.05 on the molar absorption. The fluorescence spectra in solution were obtained in a manner similar to that described for the measurement in the solid states. Relative intensity of fluorescence in solution was determined by using DCM as a standard compound. Fluorescence of standard sample and all subject compounds were measured on 366 nm excitation.

6-(4-*N,N*-Dimethylamino)styryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitrile (3m). A mixture of 1.89 g (10 mmoles) of **2l**, 2.03 g (10 mmoles) of **1a**, 0.8 g (20 mmoles) powdered sodium hydroxide, and 40 ml of DMSO was stirred at room temperature for 1 hour. The reaction mixture was poured into 500 ml of ice-water and stirred at room temperature for 2 hours. The brown precipitates that appeared were collected by filtration, washed with water, and recrystallized from a mixture of dichloromethane and methanol to give 0.998 g (3.20 mmoles, 32% yield) of black violet leaflets, mp 280-284°; ir(potassium bromide) υ cm^{-1}: 2202(CN), 1705(C=O), 1595, 1560, 1465, 1360, 1162); uv(EtOH) λ nm(log ε): 253 (4.19), 309 (4.29), 374 (3.67), 397 (3.64), 513 (4.67); fluorescence (EtOH):Ex: 366 nm; Em: 624 nm. (CH$_2$Cl$_2$): Ex: 541nm, Em:612 nm: RI=1.25. ^{1}H nmr(CDCl$_3$) δ: 2.65(s, 3, SMe), 3.10(s, 6, 2xNMe$_2$), 6.12(s, 1, 6-H), 6.44(d, 1, =CH, J=15.7 Hz), 6.72(d, 2, 3', 5'-H, J=9.1 Hz), 7.48(d, 2, 2', 6'-H, J=9.1 Hz), 7.68 (d, 2, =CH, J=15.7 Hz); ms: m/z 312 (M$^+$, 100), 284(6), 241(5), 209(15), 174(16), 44(35). *Anal.* Calcd for $C_{17}H_{16}N_2O_2S$: C, 65.36; H, 5.16; N, 8.97. Found. C, 65.19; H, 5.14; N, 8.88.

6-(4-*N,N*-Diethylamino)styryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitrile (3n). A mixture of 2.17 g (10 mmoles) of **2m**, 2.03 g (10 mmoles) of **1a**, 0.8 g (20 mmoles) powdered sodium hydroxide, and 40 ml of DMSO was stirred at room temperature for 1 hour. The reaction mixture was poured into 500 ml of ice-water and stirred at room temperature for 10 hours. The brown oil that appeared were collected and crystallized by the treatment with methanol to give 0.892 g (2.62 mmoles, 26% yield) of black solids. An analytical sample was recrystallized from a mixture of dichloromethane and methanol to give black violet leaflets, mp 242-246°; ir(potassium bromide) ν cm^{-1}: 2202 (CN), 1700 (CO), 1590, 1560, 1460, 1180; uv (EtOH) λ nm(log ε):252 (4.09), 315 (4.25), 374 (3.52), 397 (3.42), 529 (4.69); fluorescence (CH$_2$Cl$_2$): Em: 550 nm; Ex: 613 nm. RI=0.65; ^{1}H nmr (CDCl$_3$) δ: 1.21 (t, 6, N-CH$_2$-*CH$_3$*, J=7.1 Hz), 2.61 (s, 3, SMe), 3.43 (q, 4, N-CH$_2$-, J=7.1 Hz), 6.07 (s, 1, 5-H), 6.37 (d, 1, =CH, J=15.7 Hz), 6.65 (d, 2, 3', 5'-H, J=9.1 Hz), 7.42 (d, 2, 2', 6'-H, J=9.1 Hz), 7.63 (d, 1, =CH, J=15.7 Hz); ms: m/z 340 (M$^+$, 76), 325 (100), 297 (3), 158 (6). *Anal.* Calcd for $C_{19}H_{20}N_2O_2S$: C, 67.03; H, 5.92; N, 8.23. Found. C, 66.89; H, 5.96; N, 8.20.

6-(4-*N,N*-Diphenylamino)styryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitrile(3o). A mixture of 3.13 g(10 mmoles) of **2n**, 2.03 g (10 mmoles) of **1a**, 0.8 g (20 mmoles) powdered sodium hydroxide, and 40 ml of DMSO was stirred at room temperature for 1 hour. The reaction mixture was poured into 500 ml of ice-water and stirred at room temperature for 2 hours. The brown precipitates that appeared were collected by filtration, washed with water, and recrystallized from a mixture of dichloromethane and methanol to give 1.25 g (2.87 mmoles, 29% yield) of red brown leaflets, mp 210-216°; ir(potassium bromide) υ cm^{-1}: 2205 (CN), 1720 (CO), 1590, 1565, 1494, 1460, 1330, 1280; uv (EtOH) λ nm(log ε): 305 (4.48), 502 (4.19); fluorescence (EtOH): Em, 285 nm; Ex, 620 nm(weak); ^{1}H nmr (CDCl$_3$) δ: 2.62 (s, 3, SMe), 6.18 (s, 1, 5-H), 6.48 (d, 1, =CH, J=15.1 Hz), 6.75-7.40 (m, 14, phenyl-H), 7.61 (d, 1, =CH, J=15.1 Hz); ms: m/z 437 (M$^+$+1, 12), 436 (M$^+$, 38), 313 (8), 298 (7), 53 (33), 42 (100). *Anal.* Calcd for $C_{27}H_{20}N_2O_2S$: C, 74.29; H, 4.62; N, 6.42. Found. C, 74.22; H, 4,71; N, 6,43.

Dimethyl 3-Cyano-2-oxo-6-phenyl-2*H*-pyran-4-yl-malonate (7a). This compound (0.635 g, 1.94 mmoles) was prepared in 97% yield from **3a** (0.487 g, 2.0 mmoles) and dimethyl malonate (**6a**)(0.528 g, 4.0 mmoles) by the previous method [4d]. This product was recrystallized from methanol to give pale yellow needles, mp 159-160°; ir(potassium bromide) ν_{max} cm^{-1}: 3450 (OH, br), 2210 (CN), 1750 (CO), 1620, 1530; uv(EtOH) λ_{max} nm (log ε): 256 (3.93), 372 (4.35); fluorescence (solid): Ex, 337 nm; Em, 479 nm; RI=7.51; ^{1}H nmr(CDCl$_3$) δ: 3.90 (s, 6, OMeX2), 5.09 (s, 1, CH), 6.76 (s, 1, 5-H), 7.58 (m, 3, 3', 4', 5'-H), 7.92 (m, 2, 2', 6'-H); ms m/z: 328 (M$^+$+1, 19), 327 (M$^+$, 100), 295 (75), 267 (47), 105 (82), 77 (56). *Anal.* Calcd. for $C_{17}H_{13}NO_6$: C, 62.39 ; H, 4.00 ; N, 4.28. Found: C, 62.33; H, 3.84; N, 4.30.

Diethyl 3-Cyano-2-oxo-6-phenyl-2*H*-pyran-4-ylmalonate (7b). A mixture of 0.486 g(2.0 mmoles) of **3a**, 0.64 g (4.0 mmoles) of diethyl malonate (**6b**), and 0.936 g (3 mmoles) of potassium carbonate in 20 ml of DMSO was stirred for 2 hours at room temperature. The reaction mixture was poured into 200 ml of ice-water and acidified with 10% hydrochloric acid. The precipitate that appeared was collected by filtration, washed with water, and recrystallized from ethanol to give 0.582 g(1.64 mmoles, 82% yield) of colorless needles, mp 158-159°; ir(potassium bromide) ν cm^{-1}: 2230 (CN), 1740 (CO), 1530; uv(EtOH) λ nm(log ε): 290 (4.50), 324 (4.40), 390 (4.25); fluoresence (solide): Ex, 263 nm; Em, 470 nm; RI=4.30; ^{1}H nmr(CDCl$_3$) δ: 1.34(t, 6-CH$_2$-*CH$_3$*, J=7.2 Hz,), 4.29 (m, 4, O-CH$_2$-), 5.02 (s, 1, CH), 7.17 (s, 1, 5-H), 7.48-7.58 (m, 3, phenyl-H), 7.88-7.92 (m, 2, phenyl-H); ms :m/z 356 (M$^+$+1, 23), 355 (M$^+$, 100), 309 (11), 281 (51), 255 (16), 238 (18), 211 (16), 105 (81), 77 (46). *Anal.* Calcd for $C_{19}H_{17}NO_6$: C, 64.22; H, 4.82; N, 3.94. Found. C, 64.32; H, 4.82; N, 3.86.

Dimethyl 3-Cyano-6-(4-methoxyphenyl)-2-oxo-2*H*-pyran-4-ylmalonate (7c). A mixture of 0.546 g(2.0 mmoles) of **3d**, 0.53 g (4.0 mmoles) of **6a**, and 0.936 g (3.0 mmoles) of potassium carbonate in 20 ml of DMSO was stirred for 2 hours at room temperature. The reaction mixture was poured into 200 ml of ice-water and acidified with 10% hydrochloric acid. The precipitate that appeared was collected by filtration, washed with water, and recrystallized from methanol to give 0.577 g(1.62 mmoles, 81% yield) of colorless needles, mp 180-183°; ir(potassium bromide) υ cm^{-1}: 2220 (CN), 1750 (CO), 1515; uv(EtOH) λ nm(log ε): 255 (3.93), 372 (4.35); fluoresence (solid): Ex, 270 nm; Em, 512 nm; RI=1.15; ^{1}H nmr(CDCl$_3$) δ: 3.86 (s, 6, OMe), 3.90 (s, 3, OMe), 5.03 (s, 1, CH), 7.00 (d, 2, 3', 5'-H, J=8.5 Hz), 7.03 (s, 1, 5-H), 7.87 (d, 2, 2', 6'-H, J=8.5 Hz); ms: m/z 358 (M$^+$+1, 21), 357 (M$^+$, 100), 329 (11), 297 (13), 13 (32). *Anal.* Calcd for $C_{18}H_{15}NO_7$: C, 60.51; H, 4.23; N, 3.92. Found. C, 60.49; H, 4.23; N, 4.11.

Diethyl 3-Cyano-6-(4-methoxyphenyl)-2-oxo-2*H*-pyran-4-ylmalonate (7d). A mixture of 0.546 g (2.0 mmoles) of **3d**, 0.64 g (4.0 mmoles) of **6b**, and 0.936 g (3.0 mmoles) of potassium carbonate in 20 ml of DMSO was stirred for 2 hours at room temperature. The reaction mixture was poured into 200 ml of ice-water and the whole was acidified with 10% hydrochloric acid. The precipitate that appeared was collected by filtration, washed with water, and recrystallized from methanol to give 0.553 g(1.44 mmoles, 72% yield) of pale yellow needles, mp 194-198°; ir(potassium bromide) υ cm^{-1}: 2210 (CN), 1735 (CO), 1605, 1505; uv(EtOH) λ nm(log ε): 249 (4.25), 291 (4.33), 339 (4.44); fluoresence (solide): Ex, 272 nm; Em, 506 nm; RI=0.47; ^{1}H nmr(CDCl$_3$) δ: 1.33 (t, 6, O-CH$_2$-*CH*$_3$, J=7.1 Hz), 3.90 (s, 6, OMe), 4.31 (m, 4, O-CH$_2$-), 5.00 (s, 1, CH), 7.00 (d, 2, 3', 5'-H, J=9.3 Hz), 7.04 (s, 1, 5-H), 7.86 (d, 2, 2', 6'-H, J=9.3 Hz); ms: m/z 386 (M$^+$+1, 23), 385 (M$^+$, 100), 357 (6), 297 (13), 340 (5), 311 (12), 135 (33). *Anal.* Calcd for $C_{20}H_{19}NO_7$: C, 62.33; H, 4.97; N, 3.63. Found. C, 62.43; H, 4.98; N, 3.50.

Dimethyl 3-Cyano-6-(4-*N,N*-dimethylaminophenyl)-2-oxo-2*H*-pyran-4-ylmalonate (7e). A mixture of 0.508 g(2.0 mmoles) of **3i**, 0.53 g (4.0 mmoles) of **6a**, and 0.936 g (3.0 mmoles) of potassium carbonate in 20 ml of DMSO was stirred for 2 hours at room temperature. The reaction mixture was poured into 200 ml of ice-water and the whole was acidified with 10% hydrochloric acid. The precipitate that appeared was collected by filtration, washed with water, and recrystallized from methanol to give 0.512 g(1.38 mmoles, 69% yield) of red needles, mp 198-199°; ir(potassium bromide) υ cm^{-1}: 2220 (CN), 1745 (CO), 1502, 1210; uv(EtOH) λ nm (log ε): 292 (3.98), 488 (4.78); fluoresence (solid): Ex, 272 nm; Em, 610 nm; RI=0.70; ^{1}H nmr(CDCl$_3$) δ: 3.12 (s, 6, NMe$_2$), 3.85 (s, 6, OMe), 4.99 (s, 1, -CH-), 6.69 (d, 2, 3', 5'-H, J=9.3 Hz), 6.89 (s, 1, 5-H), 7.79 (d, 2, 2', 6'-H, J=9.3 Hz); ms: m/z 371 (M$^+$+1, 21), 370 (M$^+$, 93), 342 (11), 148 (28), 43 (100). *Anal.* Calcd for $C_{19}H_{18}N_2O_6$: C, 61.62; H, 4.90; N, 7.56. Found. C, 61.47; H, 5.09; N, 7.61.

Diethyl 3-Cyano-6-(4-*N,N*-dimethylaminophenyl)-2-oxo-2*H*-pyran-4-ylmalonate (7f). A mixture of 0.508 g(2.0 mmoles) of **3i**, 0.64 g (4.0 mmoles) of **6b**, and 0.936 g (3.0 mmoles) of potassium carbonate in 20 ml of DMSO was stirred for 2 hours at room temperature. The reaction mixture was poured into 200 ml of ice-water and the whole was acidified with 10% hydrochloric acid. The precipitate that appeared was collected by filtration, washed with water, and re-crystallized from methanol to give 0.589 g(1.48 mmoles, 74% yield) of orange red needles, mp 194-198°; ir(potassium bromide) υ cm^{-1}: 2220 (CN), 1735 (CO), 1515; uv(EtOH) λ nm(log ε): 264 (4.24), 379 (4.56); fluoresence (solid): Ex, 272 nm; Em, 590 nm; RI=0.12; ^{1}H nmr(CDCl$_3$) δ: 1.33 (t, 6, O-CH$_2$-*CH*$_3$, J=7.2 Hz), 3.11 (s, 6, NMe$_2$), 4.30 (m, 4, O-CH$_2$-), 4.96 (s, 1, CH), 6.69 (d, 2, 3', 5'-H, J=9.3 Hz), 6.91 (s, 1, 5-H), 7.79 (d, 2, 2', 6'-H, J=9.3 Hz); ms: m/z 399 (M$^+$+1, 25), 398 (M$^+$, 100), 148 (17), 43 (91). *Anal.* Calcd for $C_{21}H_{22}N_2O_6$: C, 63.31; H, 5.57; N, 7.03. Found. C, 63.36; H, 5.57; N, 6.78.

Dimethyl 3-Cyano-6-thien-2-yl-2-oxo-2*H*-pyran-4-ylmalonate (7g). A mixture of 0.498 g(2.0 mmoles) of **3j**, 0.53 g (4.0 mmoles) of **6a**, and 0.936 g (3.0 mmoles) of potassium carbonate in 20 ml of DMSO was stirred for 2 hours at room temperature. The reaction mixture was poured into 200 ml of ice-water and the whole was acidified with 10% hydrochloric acid. The precipitate that appeared was collected by filtration, washed with water, and re-crystallized from methanol to give 0.552 g(1.66 mmoles, 83% yield) of yellow needles, mp 174-175°. ir(potassium bromide) υ cm^{-1}: 2230 (CN), 1750, 1735 (CO), 1525; uv(EtOH) λ nm(log ε): 249 (4.23), 255 (4.25), 261 (4.21), 296 (4.35), 348 (4.40); fluoresence (solid): Ex, 267 nm; Em, 527 nm; RI=2.47; ^{1}H nmr(CDCl$_3$) δ: 3.86 (s, 6, OMe), 5.02 (s, 1, -CH-), 6.94 (s, 1, 5-H), 7.20 (dd, 1, 4'-H, J=3.9, 5.0 Hz), 7.69 (dd, 1, 5'-H, J=1.3, 5.0 Hz), 7.78 (dd, 1, 3'-H, J=1. 3, 3.9 Hz); ms: m/z 334 (M$^+$+1, 19), 333 (M$^+$, 100), 301 (15), 273 (28), 111 (72), 59 (22). *Anal.* Calcd for $C_{15}H_{11}NO_6S$: C, 54.05; H, 3.333; N, 4.20. Found. C, 53.93; H, 3.33; N, 4.23.

Dimethyl 3-Cyano-6-(4-*N,N*-dimethylamino)styryl-2-oxo-2*H*-pyran-4-ylmalonate (7h). A mixture of 0.624 g (2.0 mmoles) of **3k**, 0.66 g (5.0 mmoles) of **6a**, 5.5 g (4.0 mmoles) of potassium carbonate, and 20 ml of DMSO was stirred for 2 hours at room temperature. The reaction mixture was poured into 200 ml of ice-water, and the whole was neutralized with 10% hydrochloric acid. The precipitates that appeared were collected by filtration to give black solid. After air drying, the product was recrystallized from methanol to give 0.667 g (1.68 mmoles, 84%) of black crystals, mp 200-202°; ir(potassium bromide) υ cm^{-1}: 2215 (CN), 1755, 1740, 1720 (CO), 1600, 1500; uv(EtOH) λ nm(log ε): 278 (3.94), 320 (4.08), 539 (4.70); fluoresence(CH$_2$Cl$_2$): Ex, 553 nm; Em, 620 nm. RI=0.44; ^{1}H nmr(CDCl$_3$) δ: 3.07 (s, 6, NMe$_2$), 3.04 (s, 3, OMe), 4.95 (s, 1, -CH-), 6.08 (s, 1, 5-H), 6.45 (d, 1, -CH, J=15.4 Hz), 6.67 (d, 2, 3', 5'-H, J=9.0 Hz), 7.44 (dd, 2, 2', 6'-H, J=2.2, 9.0 Hz), 7.63 (d, 1, =CH, J=15.4 Hz); ms: m/z 397 (M$^+$+1, 16), 396 (M$^+$, 65), 312 (27), 174 (6), 83 (6), 44 (100). *Anal* . Calcd for $C_{21}H_{20}N_2O_6$: C, 63.63; H, 5.09; N, 7.07. Found: C, 63.73, H, 4.98; N, 6.98.

Dimethyl 3-Methoxycarbonyl-2-oxo-6-phenyl-2*H*-pyran-4-ylmalonate (7i). This compound (0.639 g, 1.76 mmoles) was prepared in 88% yield from **5a** (0.585 g, 2.0 mmoles) and **6a** (0.528 g, 4.0 mmoles) by the previous method [4d]. This compound was recrystallized from methanol to give pale yellow needle, mp 120-121°; ir(potassium bromide) υ$_{max}$ cm^{-1}: 3450 (OH, br), 1750 (CO), 1730 (CO), 1710 (CO), 1625, 1540; uv(EtOH) λ$_{max}$ nm(log ε): 253 (4.26), 352 (4.27); fluorescence (solid): Ex, 336 nm; Em, 470 nm; RI=4.16; ^{1}H nmr(CDCl$_3$) δ: 3.82 (s,6,2xOMe), 3.94 (s, 3, OMe), 5.17 (s, 5, -CH-), 6.91 (s, 1, 5-H), 7.40-7.52 (m, 3, phenyl-H), 7.81-7.92 (m, 2, phenyl-H); ms m/z : 361 (M$^+$+1, 2), 360 (M$^+$, 12), 246 (85), 214 (38), 146 (35), 105 (100), 77 (47). *Anal.* Calcd. for $C_{18}H_{16}O_8$: C, 60.00; H, 4.48. Found: C, 60.01; H, 4.46.

Diethyl 3-Methoxycarbonyl-2-oxo-6-phenyl-2*H*-pyran-4-ylmalonate (7j). This compound (0.621 g, 1.6 mmoles) was synthesized in 80% yield from **5a** (0.585 g, 2.0 mmoles) and **6b** (0.641g, 4.0 mmoles) in manner similar to that described for the preparation of **7i**. An analytical sample was recrystallized from ethanol to give colorless needles, mp 80-90°; ir(potassium bromide) υ$_{max}$ cm^{-1}: 3450 (OH, br), 1760 (CO), 1730 (CO), 1720 (CO), 1620, 1540; uv(EtOH) λ$_{max}$ nm(log ε): 249 (4.30), 347 (4.36); fluorescence (solid): Ex, 341 nm; Em, 472 nm; RI=3.24; ^{1}H nmr(CDCl$_3$) δ: 1.31 (t, 6, O-CH$_2$-*CH*$_3$, J=7.2 Hz), 3.95 (s, 3, OMe), 4.26 (q, 2, O-CH$_2$-, J=7.2Hz), 4.28 (q, 2, O-CH$_2$-, J=7.2Hz), 5.11 (s, 1, CH), 6.95 (s, 1, 5-H), 7.42-7.50 (m, 3, phenyl-H), 7.86 (m, 2, phenyl-H); ms m/z: 388 (M$^+$, 100), 360 (30), 314 (15), 283 (15), 242 (32). *Anal.* Calcd. for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19. Found: C, 62.06; H, 5.08.

Dimethyl 3-Methoxycarbonyl-6-(4-methoxyphenyl)-2-oxo-2*H*-pyran-4-ylmalonate (7k). A mixture of 0.58 g (2.0 mmoles) of **5b**, 0.53 g (4.0 mmoles) of **6a**, and 0.936 g (3.0 mmoles) of potassium carbonate in 20 ml of DMSO was stirred for 2 hours at room temperature. The reaction mixture was poured into 200 ml of ice-water and the whole was acidified with 10% hydrochloric acid. The precipitate that appeared was collected by filtration, washed with water, and re-crystallized from methanol to give 0.392 g (0.972 mmole, 49% yield) of yellow needles, mp 143-146°; ir(potassium bromide) υ cm^{-1}: 1750

(CO), 1512, 1542, 1516; uv(EtOH) λ nm(log ε): 264 (4.06), 380 (4.37); fluoresence (solid): Ex, 337 nm; Em, 477 nm; RI=6.74; ^{1}H nmr(CDCl$_3$) δ: 3.83 (s, 3, OMe), 3.88 (s, 3, OMe), 3.93 (s, 3, OMe), 5.22 (s, 1, -CH-), 6.79 (s, 1, CH), 6.97 (d, 2, 3', 5'-H, J=9.3 Hz), 7.83 (d, 2, 2', 6'-H, J=9.3 Hz); ms: m/z 391 (M$^+$+1, 21), 390 (M$^+$, 100), 362 (62), 330 (78), 135 (77), 77 (13). *Anal.* Calcd for $C_{19}H_{18}O_9$: C, 58.46; H, 4.65. Found. C, 58.37; H, 4.56.

Diethyl 3-Methoxycarbonyl-6-(4-methoxyphenyl)-2-oxo-2*H*-pyran-4-ylmalonate (7l). A mixture of 0.584 g (2.0 mmoles) of **5b**, 0.64 g (4.0 mmoles) of **6b**, and 0.936 g (3.0 mmoles) of potassium carbonate in 20 ml of DMSO was stirred for 2 hours at room temperature. The reaction mixture was poured into 200 ml of ice-water and the whole was acidified with 10% hydrochloric acid. The precipitate that appeared was collected by filtration, washed with water, and recrystallized from ethanol to give 0.598 g (1.58 mmoles, 79% yield) of yellow needles, mp 89-92°; ir(potassium bromide) υ cm^{-1}: 1750, 1730 (CO), 1538, 1515; uv(EtOH) λ nm(log ε): 261 (3.75), 381 (4.25); fluoresence (solid): Ex, 332 nm; Em, 479 nm; RI=4.20; ^{1}H nmr(CDCl$_3$) δ: 1.31 (t, 6, O-CH$_2$-*CH$_3$*, J=7.1 Hz), 3.88 (s, 6, OMe), 3.93 (s, 3, OMe), 4.28 (m, 4, O-CH$_2$-), 5.15 (s, 1, CH), 6.82 (s, 1, 5-H), 6.97 (d, 2, 3', 5'-H, J=9.3 Hz), 7.82 (d, 2, 2', 6'-H, J=9.3 Hz); ms: m/z 418 (M$^+$, 100), 390 (32), 272 (11), 135 (71), 45 (100). *Anal.* Calcd for $C_{21}H_{22}O_9$: C, 60.26; H, 5.30. Found. C, 60.31; H, 5.28.

Dimethyl 6-Benzo[1,3]dioxol-5-yl-3-methoxy-carbonyl-2-oxo-2*H*-pyran-4-ylmalonate (7m). This compound (0.429 g, 1.06 mmoles) was synthesized in 53% yield from **5c** (0.673 g, 2.0 mmoles) and **6a** (0.528g, 4 mmoles) in manner similar to that described for the preparation of **7i**. An analytical sample was recrystallized from methanol to give yellow needles, mp 143-146°; ir(potassium bromide) υ $_{max}$ cm^{-1}: 1780 (CO), 1735 (CO), 1680 (CO), 1620, 1600; uv(EtOH) λ $_{max}$ nm(log ε): 244 (4.27), 249 (4.28), 254 (4.29), 383 (4.36); fluorescence (solid): Ex, 331 nm; Em, 504 nm; RI=0.87; ^{1}H nmr(CDCl$_3$) δ: 3.82 (s, 6, 2xOMe), 3.96 (s, 3, OMe), 5.20 (s, 1, -CH-), 6.06 (s, 2, O-CH$_2$-O), 6.76 (s, 1, 5-H), 6.89 (d, 1, J=8.3 Hz, 5'-H), 7.30 (d, 1, 2'-H, J=1.8 Hz), 7.45 (dd, 1, 6'-H, J=1.8, 8.3 Hz); ms m/z: 404 (M$^+$, 100), 376 (41), 373 (22), 344 (43), 341 (21), 290 (43)0, 258 (46), 190 (44), 149 (93). *Anal.* Calcd. for $C_{19}H_{16}O_{10}$: C, 56.44; H, 3.99. Found: C, 56.68; H, 3.79.

Methyl 8-Hydroxy-6-methyl-1-oxo-3-phenyl-1*H*-pyrano-[3,4-*c*]pyridine-5-carboxylate (8a). Potassium carbonate (0.691 g, 5.0 mmoles) was added to the soulution of **3a** (0.487 g, 2.0 mmoles) and methyl acetoacetate (**6c**)(0.464 g, 4.0 mmoles) in 20 ml of DMSO. After stirring at room temperature for 2 hours, the reaction mixture was poured into 200 ml of ice water and then acidified with 10% hydrochloric acid. The caramel oil product that appeared was collected by decantation and washed several tomes with water. This crude product was dissolved in 100 ml of methanol and this methanol solution was refluxed for 2 hours. After removal of the solvent by rotary evaporation, the residue was crystallized by treating with 10~20 ml of methanol. The resulting precipitate was collected by filtration and recrystallized from methanol to give 0.324 g (1.04 mmoles) of **8a** as pale yellow crystals, mp >300°, in 52% yield. ir(potassium bromide) υ $_{max}$ cm^{-1}: 3450 (OH, br), 1755 (CO), 1710 (CO), 1648, 1620, 1585, 1530; uv(EtOH) λ$_{max}$ nm(log ε): 268 (5.23), 346 (5.23); fluorescence (solid): Ex, 345 nm; Em, 462 nm; RI=1.23; ^{1}H nmr(CDCl$_3$+CF$_3$COOH) δ: 2.62 (s, 3, 6-Me), 4.03 (s, 3, OMe), 7.41 (s, 1, 4-H), 7.44-7.59 (m, 3, phenyl-H), 7.85-7.92 (m, 2, phenyl-H); ms m/z: 312 (M$^+$+1, 40), 311 (M$^+$, 100), 284 (15), 281 (11), 280 (38), 253 (13), 252 (58), 105 (64), 77 (27). *Anal.* Calcd. for $C_{17}H_{13}NO_5$: C, 65.59; H, 4.21; N, 4.50. Found: C, 65.34; H, 4.29; N, 4.44.

Methyl 8-Hydroxy-3-(4-methoxyphenyl)-6-methyl-1-oxo-1*H*-pyrano[3,4-*c*]pyridine-5-carboxylate (8b). This compound (0.203 g, 0.59 mmole) was synthesized in 30% yield from **3c** (0.547 g, 2.0 mmoles), **6c** (0.464 g, 4.0 mmoles), and K$_2$CO$_3$ (0.691 g, 5.0 mmoles) to that described for **8a**. This compound was recrystallized from methanol to give pale yellow needles, mp 296-297°; ir(potassium bromide) υ $_{max}$ cm^{-1}: 3450 (OH, br), 1755 (CO), 1706 (CO), 1648, 1635, 1580; uv(EtOH) λ $_{max}$ nm(log ε): 276 (4.48), 366 (4.60); fluorescence (solid): Ex, 335 nm; Em, 468 nm; RI=3.93; ^{1}H nmr(CDCl$_3$) δ: 2.39 (s, 3, 6-Me), 3.85 (s, 3, OMe), 3.90 (s, 3, OMe), 7.09 (m, 3, CH), 7.84 (m, 2, 3', 5'-H), 12.3 (s, 1, OH); ms m/z: 342 (M$^+$+1, 21), 341 (M$^+$, 100), 313 (36), 135 (33), 78 (27). *Anal.* Calcd. for $C_{18}H_{15}NO_6$: C, 63.34; H, 4.43; N, 4.10. Found: C, 63.14; H, 4.29; N, 4.04.

Ethyl 8-Hydroxy-6-methyl-1-oxo-3-phenyl-1*H*-pyrano[3,4-*c*]pyridine-5-carboxylate (8c). This compound (0.452 g, 1.4 mmoles) was synthesized in 70% yield from **3a** (0.487 g, 2.0 mmoles), ethyl acetoacetate (**6d**)(0.691 g, 5.0 mmoles), and potassium carbonate (0.691 g, 5.0 mmoles) to that described for **8a**. This compound was recrystallized from ethanol to give colorless needles, mp 295-296°; ir(potassium bromide) υ $_{max}$ cm^{-1}: 3450 (OH, br), 1775 (CO), 1720 (CO), 1650, 1625, 1580; uv(EtOH) λ $_{max}$ nm(log ε): 349 (4.25); fluorescence (solid): Ex, 340 nm; Em, 460 nm; RI=3.99; ^{1}H nmr(CDCl$_3$) δ: 1.34 (t, 3, O-CH$_2$-*CH$_3$*, J=7.0 Hz), 2.42 (s, 3, Me), 4.38 (q, 2, O-CH$_2$-, J=7.0 Hz), 7.26 (s, 1, CH), 7.58 (m, 3, 3', 4', 5'-H), 7.87 (m, 2, 2', 6'-H), 12.20 (s, 1, OH); ms m/z: 326 (M$^+$+1, 20), 325 (M$^+$, 100), 280 (39), 252 (31), 105 (50). *Anal.* Calcd. for $C_{18}H_{15}NO_5$: C, 66.46; H, 4.65; N, 4.31. Found: C, 66.39; H, 4.56; N, 4.31.

Ethyl 8-Hydroxy-3-(4-methoxyphenyl)-6-methyl-1-oxo-1*H*-pyrano[3,4-*c*]pyridine-5-carboxylate (8d). This compound (0.221 g, 0.622 mmole) was synthesized in 31% yield from **3c** (0.547 g, 2.0 mmoles), **6d** (0.521 g, 4.0 mmoles), and potassium carbonate (0.691 g, 5.0 mmoles) to that described for **7a**. This compound was recrystallized from methanol to give pale yellow needles, mp 287-288°; ir(potassium bromide) υ $_{max}$ cm^{-1}: 3450 (OH, br), 2220 (CN), 1750 (CO), 1515; uv(EtOH) λ $_{max}$ nm(log ε): 247 (4.05), 190 (4.30), 345 (4.34), 372 (4.36); fluorescence (solid): Ex, 339 nm; Em, 496 nm; RI=2.45; ^{1}H nmr(CDCl$_3$) δ: 1.34 (t, 3, O-CH$_2$-*CH$_3$*, J=7.3 Hz), 2.40 (s, 3, Me), 3.85 (s, 3, OMe), 4.38 (q, 2, O-*CH$_2$*-CH$_3$, J=7.3 Hz), 7.11 (d, 2, 3', 5'-H, J=8.8Hz), 7.13 (s, 1, CH), 7.83 (d, 2, 2', 6'-H, J=8.8 Hz), 12.25 (s, 1, OH); ms m/z: 356 (M$^+$+1, 10), 355 (M$^+$, 45), 355 (16), 313 (15), 135 (35). *Anal.* Calcd. for $C_{19}H_{17}NO_6$: C, 64.22; H, 4.82; N, 3.94. Found: C, 64.20; H, 4.71; N, 3.80.

Ethyl 8-Hydroxy-3-(2,4-dimethoxyphenyl)-6-methyl-1-oxo-1*H*-pyrano[3,4-*c*]pyridine-5-carboxylate (8e). This compound (0.234 g, 0.61 mmole) was synthesized in 31% yield from **3e** (0.607 g, 2.0 mmoles), **6d** (0.521 g, 4.0 mmoles), and potassium carbonate (0.691 g, 5.0 mmoles) to that described for **8a**. This compound was recrystallized from ethanol to give pale yellow needles, mp 298-299°; ir(Potassium bromide) υ $_{max}$ cm^{-1}: 3450 (OH, br), 1755 (CO), 1718 (CO), 1640, 1610, 1579, 1560, 1530, 1505; uv(EtOH) λ $_{max}$ nm(log ε): 274 (4.42), 377 (4.51); fluorescence (solid): Ex, 336 nm; Em, 490 nm; RI=4.88; ^{1}H nmr(CDCl$_3$) δ: 1.34 (t, 3, O-CH$_2$-*CH$_3$*, J=7.4 Hz), 2.37 (s, 3, Me), 3.86 (s, 3, OMe), 3.92 (s, 3, OMe), 4.36 (q, 2, 1/2O-*CH$_2$*-CH$_3$, J=7.4 Hz), 6.73 (d, 1, 3'-H, J=1.0 Hz), 7.76 (d, 1, 6'-H, J=9.4 Hz), 12.20 (brs, 1, OH); ms m/z: 386 (M$^+$+1, 23), 385 (M$^+$, 100), 340 (13), 285 (10), 165(33). *Anal.* Calcd. for $C_{20}H_{19}NO_7$: C, 62.33; H, 4.97; N, 3.63. Found: C, 62.45; H, 4.94; N, 3.82.

Ethyl 8-Hydroxy-3-(3,4-dimethoxyphenyl)-6-methyl-1-oxo-1*H*-pyrano[3,4-*c*]pyridine-5-carboxylate (8f). This compound (0.217 g, 0.56 mmole) was synthesized in 28% yield from **3e** (0.607 g, 2.0 mmoles), **6d** (0.521 g, 4.0 mmoles), and potassium carbonate (0.691 g, 5.0 mmoles) to that described for **8a**. This compound was recrystallized from ethanol to give yellow needles, mp 303-304°; ir(potassium bromide) υ_{max} cm^{-1}: 3450 (OH, br), 1775 (CO), 1718 (CO), 1640, 1620, 1570; uv(EtOH) λ_{max} nm(log ε): 269 (4.38), 273 (4.43); fluorescence (solid): Ex, 343 nm; Em, 495 nm; RI=2.08; ^{1}H nmr(CDCl$_3$) δ: 1.35 (t, 3/2H, 1/2O-CH$_2$-$\mathit{CH_3}$, J=7.1 Hz), 1.36(t, 3/2H, 1/2O-CH$_2$-$\mathit{CH_3}$, J=7.1 Hz), 2.46 (s, 3/2H, 1/2Me), 2.50 (s, 3/2H, 1/2Me), 3.85 (s, 3, OMe), 3.86 (s, 3, OMe), 4.40 (q, 2/2H, 1/2O-$\mathit{CH_2}$-CH$_3$, J=7.1 Hz), 4.42 (q, 2/2H, 1/2O-$\mathit{CH_2}$-CH$_3$, J=7.1 Hz), 7.10-7.17 (m, 2, 5, 5'-H), 7.33 (d, 1/2H, 2'-H, J=2.0 Hz), 7.38 (d, 1/2H, 2'-H, J=2.0 Hz), 7.47 (dd, 1/2H, 6'-H, J=2.0, 9.0 Hz), 7.58 (dd, 1/2H, 6'-H, J=2.0, 9.0 Hz), 12.25 (s, 1/2H, OH); ms m/z: 386 (M$^+$+1, 58), 385 (M$^+$, 100), 357 (11), 165 (36), 44 (20). *Anal.* Calcd. for $C_{20}H_{19}NO_7$: C, 62.33; H, 4.97; N, 3.63. Found: C, 62.02; H, 4.93; N, 3.30.

Ethyl 8-Hydroxy-3-(4-*N,N*-dimethylaminophenyl)-6-methyl-1-oxo-1*H*-pyrano[3,4-*c*]pyridine-5-carboxylate (8g). This compound (0.066 g, 0.18 mmole) was synthesized in 9% yield from **3g** (0.573 g, 2.0 mmoles), **6d** (0.521 g, 4.0 mmoles), and potassium carbonate (0.691 g, 5.0 mmoles) to that described for **8a**. This compound was recrystallized from ethanol to give yellow needles, mp 298-299°; ir(potassium bromide) υ_{max} cm^{-1}: 3450 (OH, br), 1755 (CO), 1700 (CO), 1640, 1600, 1570, 1520; uv(EtOH) λ_{max} nm(log ε): 270 (4.32), 305 (4.16), 434 (4.61); fluorescence (solid): Ex, 331 nm; Em, 540 nm; RI=0.36; fluorescence (CH$_2$Cl$_2$): Ex, 441 nm; Em, 515 nm; ^{1}H nmr(CDCl$_3$) δ: 1.34 (t, 3, O-CH$_2$-$\mathit{CH_3}$, J=7.0 Hz), 2.37 (s, 3, Me), 3.03 (s, 6, NMe$_2$), 4.37 (q, 2, O-$\mathit{CH_2}$-CH$_3$, J=7.0 Hz), 6.82 (d, 2, 3', 5'-H, J=9.1Hz), 6.99 (s, 1, 5-H), 7.70 (d, 2, 2', 6'-H, J=9.1 Hz), 12.10 (brs, 1/2H, 1/2OH); ms m/z: 369 (M$^+$+1, 25), 368 (M$^+$, 100), 340 (17), 148 (28), 44 (56). *Anal.* Calcd. for $C_{20}H_{20}N_2O_5$: C, 65.21; H, 5.47; N, 7.60. Found: C, 65.24; H, 5.41; N, 7.48.

8-Hydroxy-3-(4-methoxyphenyl)-6-methyl-1-oxo-5-tolylmethyl-1*H*-pyrano[3,4-*c*]pyridine (8h). This compound (0.192 g, 0.44 mmole) was synthesized in 22% yield from **3b** (0.547 g, 2.0 mmoles), 4-toluenesulfonylacetoacetate(**6e**) (0.691 g, 5.0 mmoles), and potassium carbonate (0.691 g, 5.0 mmoles) to that described for **8a**. This compound was recrystallized from ethanol to give pale yellow needles, mp 260-270°; ir(potassium bromide) ν_{max} cm^{-1}: 3450 (OH, br), 1760 (CO), 1640, 1600, 1555, 1505; uv(EtOH) λ_{max} nm(log ε): 295 (4.40), 301 (4.40), 351 (4.06), 372 (4.15); fluorescence (solid): Ex, 345 nm; Em, 493 nm; RI=3.40; ^{1}H nmr(CDCl$_3$) δ: 2.43 (s, 3, 6-Me), 2.91 (s, 3, p-Me), 3.93 (s, 3, OMe), 7.03 (d, 2, 3', 5'-H, J=9.1 Hz), 7.38 (d, 1, 2'', 6''-H, J=8.3 Hz), 7.80 (d, 1, 2', 6'-H, J=9.1 Hz), 7.83 (d, 1, 3'', 5''-H, J=8.3 Hz), 8.05 (s, 1, 5-H); ms m/z: 438 (M$^+$+1, 18), 437 (M$^+$, 51), 372 (13), 345 (31), 344 (13), 273 (25), 239 (16), 238 (55), 237 (29), 140 (51), 135 (100), 134 (25), 91 (13), 77 (12), 57 (12). *Anal.* Calcd. for $C_{23}H_{19}NO_6S$: C, 63.15; H, 4.38; N, 3.20. Found: C, 63.02; H, 4.19; N, 3.02.

8-Hydroxy-6-methyl-3-phenyl-1*H*-pyrano[3,4-*c*]-pyridin-1-one (8i). Potassium carbonate (0.691 g, 5.0 mmoles) was added to the soulution of **3a** (0.487 g, 2.0 mmoles) and acetylacetone (**6f**) (0.400 g, 4.0 mmoles) in 20 ml of DMSO. This mixture was stirring at room temperature for 2 hours. The reaction mixture was poured into 200 ml of ice water and then acidified with 10% hydrochloric acid. This product was recrystallized with methanol to give 0.274 g(1.1 mmoles, 55% yield) of pale yellow crystals, mp >260°; ir(potassium bromide) υ_{max} cm^{-1}: 3500 (OH, br), 1750 (CO), 1735 (CO), 1640, 1600; uv(EtOH) λ_{max} nm(log ε): 260 (4.19), 347 (4.39); fluorescence (solid): Ex, 319 nm; Em, 468 nm; RI=0.22; ^{1}H nmr(CDCl$_3$) δ: 2.59 (s, 3, Me), 6.67 (s, 1, 5-H), 6.97 (s, 1, 4-H), 7.57 (m, 3, 3',4', 5'-H), 7.90 (m, 2, 2', 6'-H); ms m/z: 254 (M$^+$+1, 19), 253 (M$^+$, 100), 225 (24), 176 (25), 105 (13), 77 (18). *Anal.* Calcd. for $C_{15}H_{11}NO_3(C_{30}H_{22}N_2O_6 \cdot H_2O)$: C, 68.70; H, 4.61; N, 5.34. Found: C, 68.77; H, 4.56; N, 5.24.

8-Hydroxy-6-methyl-3-(4-methoxyphenyl)-1*H*-pyrano[3,4-*c*]pyridine-1-one (8j). This compound (0.470 g, 1.66 mmoles was prepared in 83% yeld from **3b** (0.547 g, 2.0 mmoles) and **6f** (0.400g, 4.0 mmoles) in a manner similar to that described from the preparation of **8a.** An analytical sample was recrystallized from methanol to give pale yellow needles mp >323°; ir(potassium bromide) $\upsilon\upsilon_{max}$ cm^{-1}: 3450 (OH, br), 1760 (CO), 1590, 1510; uv(EtOH) λ_{max} nm(log ε): 271 (4.34), 363 (4.57); fluorescence (solid): Ex, 337 nm; Em, 495 nm; RI=0.40; ^{1}H nmr(CDCl$_3$) δ: 2.25 (s, 3, Me), 3.84 (s, 3, OMe), 6.12 (s, 1, 5-H), 7.03 (s, 1, 4-H), 7.10 (d, 2, J=8.8Hz, 3', 5'-H), 7.86 (d, 2, J=8.8 Hz, 2', 6'-H); ms m/z: 284 (M$^+$+1, 18), 283 (M$^+$, 100), 255 (70), 212 (18), 135 (16), 127 (14), 77 (12). *Anal.* Calcd. for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.94. Found: C, 67.55; H, 4.65; N, 4.89.

The reaction of 6-Aryl-3-cyano-2*H*-pyran-2-ones (3a-c, e) with active methylene compounds (6c,d,f). Potassium carbonate (0.691 g, 5.0 mmoles) was added to the soulution of **3a** (0.487 g, 2.0 mmoles) and **6c** (0.464 g, 4.0 mmoles) in 20 ml of DMSO. This mixture was stirring at room temperature for 2 hours, poured into 200 mL of ice water and then acidified with 10% hydrochloric acid. The product that appeared was collected by decantation and washed several times with water. The crude product was dissolved in a solution of 150 ml of ethanol and 10 ml of concentrated-HCl solution. The solution was refluxed for 30 min. After removal of the solvent by rotary evaporation, the residue was crystallized by treatment with 10~20 ml of ethanol. The resulting precipitate was collected by filtration and washed with 50 mL of dichloromethane. This compound (**8a**) was recrystallized from DMF to give coloreless needles, mp >300°. Dichloromethane in the above filtrate was removed by rotary evaporation to give **10a** which was easily purified by recrystallization with ethanol. In the reaction of **3a** with **6d** under similar reaction conditions, a separable mixture of **8c**, **9a**, and **10b** was obtained, which was easily separated by recrystallization with ethanol. Though compound **9a** was not so soluble in ethanol, compound **10b** was easily solved in ethanol. Compound **9a** was recrystallized from DMF to give pure compound, mp 152-155°, for elemental analysis. Compound **10b** was easily recrystallized from ethanol to give pale yellow needles, mp 145-147°. The yields of each products were shown in **Table 4**.

Ethyl 1,8-Dioxo-3-methyl-6-phenyl-1*H*,8*H*-pyrano-[3,4-*c*]-pyran-4-carboxylate (9a). This compound (0.072g, 0.22 mmole) was obtained 11 % yield by the above method from **3a** (0.487 g, 2.0 mmoles) and **6d** (0.521 g, 4.0 mmoles) to give pale yellow leaflets mp 152-155°; ir(potassium bromide) υ_{max} cm^{-1}: 1780 (CO), 1705 (CO), 1623, 1585, 1575; uv(EtOH) λ_{max} nm(log ε): 261 (4.45), 334 (4.39), 359 (4.30); fluorescence (solid): Ex, 337 nm; Em, 457 nm; RI=0.82; ^{1}H nmr(CDCl$_3$) δ:

1.46(t, 3, O-CH_2-CH_3, J=7.1 Hz), 2.56 (s, 3, Me), 4.48 (q, 2, O-CH_2-CH_3, J=7.1 Hz), 4.80 (s, 2, CH_2), 7.53 (m, 3, 3',4', 5'-H), 7.92 (m, 2, 2', 6'-H); ms m/z: 327 (M^++1, 16), 326 (M^+, 84), 298 (22), 283 (22), 105 (100), 77 (57). *Anal.* Calcd. for $C_{18}H_{14}NO_6$: C, 66.26; H, 4.32. Found: C, 66.15; H, 4.17.

Ethyl 1,8-Dioxo-6-(4-methoxyphenyl)-3-methyl-1*H*,8*H*-pyrano[3,4-*c*]pyran-4-carboxylate (9b). This compound (0.152 g, 0.42 mmole) was prepared in 21% yield from **3c** (0.547 g, 2.0 mmoles) and **6d** (0.521 g, 4.0 mmoles) in manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized with DMF to give pale yellow needles, mp 215-219°; ir(potassium bromide) υ_{max} cm^{-1}: 1800 (CO), 1785 (CO), 1710 (CO), 1580, 1560; uv(EtOH) λ_{max} nm(log ε): 277 (4.26), 343 (4.31), 395 (4.43); fluorescence (solid): Ex, 343 nm; Em, 472 nm; RI=1.38; ^{1}H nmr($CDCl_3$) δ: 1.45 (t, 3, O-CH_2-CH_3, J=7.1 Hz), 2.54 (s, 3, Me), 3.90 (s, 3, OMe), 4.87 (q, 2, O-CH_2-CH_3, J=7.1 Hz), 7.00 (d, 2, 3', 5'-H, J=9.1Hz), 7.26 (s, 1, 5-H), 7.90 (d, 2, 2', 6'-H, J=9.1 Hz); ms m/z: 356 (M^+, 87), 328 (22), 311 (11), 135 (100), 77 (13), 43 (24). *Anal.* Calcd. for $C_{19}H_{16}O_7$: C, 64.04; H, 4.53. Found: C, 64.02; H, 4.40.

Ethyl 6-(3,4-Dimethoxyphenyl)-1,8-dioxo-3-methyl-1*H*,8*H*-pyrano[3,4-*c*]pyran-4-carboxylate (9c). This compound (0.108 g, 0.28 mmole) was prepared in 14% yield from **3e** (0.607 g, 2.0 mmoles) and ethyl acetoacetate(**6d**) (0.521 g, 4.0 mmoles) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from DMF to give yellow crystals, mp 213-217°; ir(potassium bromide) υ_{max} cm^{-1}: 1783 (CO), 1720 (CO), 1579; uv(EtOH) λ_{max} nm(log ε): 279 (4.44), 347 (4.36), 404 (4.48); fluorescence (solid): Ex, 341 nm; Em, 542 nm; RI=0.14; ^{1}H nmr($CDCl_3$) δ: 1.48 (t, 3, O-CH_2-CH_3, J=7.1 Hz), 2.55 (s, 3, Me), 3.97 (s, 3, OMe), 3.98 (s, 3, OMe), 4.47 (q, 2, O-CH_2-CH_3, J=7.1 Hz), 6.96 (d, 1, 5'-H, J=8.5 Hz), 7.17 (s, 1, 5-H), 7.41 (d, 1, 2'-H, J=2.2 Hz), 7.53 (dd, 1, 6'-H, J=2.2, 8.5Hz); ms m/z: 387 (M^++1, 22), 386 (M^+, 100), 165 (60), 135 (11), 97 (17), 85 (14). *Anal.* Calcd. for $C_{20}H_{18}O_8$: C, 62.17; H, 4.70. Found: C, 61.91; H, 4.61.

Ethyl 1,8-Dioxo-3,6-diphenyl-1*H*,8*H*-pyrano[3,4-*c*]-pyran-4-carboxylate (9d). This compound (0.085 g, 0.22 mmole) was prepared in 11% yield from **3a** (0.487 g, 2.0 mmoles) and **6g** (0.769 g, 4.0 mmoles) in a manner simila to tha described for the preparation **9a**. An analytical sample was recrystallized from DMF to give pale yellow needles, mp 195-196°; ir(potassium bromide) υ_{max} cm^{-1}: 1793 (CO), 1778 (CO), 1728 (CO), 1625, 1585, 1563; uv(EtOH) λ_{max} nm(log ε): 276 (4.25), 354 (4.40); fluorescence (solid): Ex, 337 nm; Em, 476 nm; RI=0.62; ^{1}H nmr($CDCl_3$) δ: 0.99 (t, 3, O-CH_2-CH_3, J=7.1 Hz), 4.17 (q, 2, O-CH_2-CH_3, J=7.1 Hz), 7.17 (s, 1, 5-H), 7.43-7.60 (m, 6, phenyl-H), 7.65 (m, 2, 2', 6'-H), 7.95 (m, 2, 2'', 6''-H); ms m/z: 389 (M^++1, 14), 388 (M^+, 55), 360 (23), 255 (11), 105 (100), 77 (55). *Anal.* Calcd. for $C_{23}H_{16}O_6$: C, 71.13; H, 4.15. Found: C, 71.06; H, 4.06.

Ethyl 1,8-Dioxo-6-(4-methoxyphenyl)-3-phenyl-1*H*,8*H*-pyrano[3,4-*c*]pyran-4-carboxylate (9e). This compound (0.117 g, 0.28 mmole) was prepared in 14% yield from **9b** (0.547 g, 2.0 mmoles) and ethyl benzoylacetate (**6g**) (0.769 g, 4.0 mmoles) in a manner similar to that described for the preparation of **9a**. An analytical sample was recrystallized from DMF to give yellow needles, mp 212-213°; ir(potassium bromide) υ_{max} cm^{-1}: 1790 (CO), 1718 (CO), 1605 (CO), 1585, 1565, 1505; uv(EtOH) λ_{max} nm(log ε): 283 (4.59), 359 (4.61), 400 (4.54); fluorescence (solid): Ex, 337 nm; Em, 531 nm; RI=0.51; ^{1}H nmr($CDCl_3$) δ: 1.01 (t, 3, O-CH_2-CH_3, J=7.1 Hz), 3.90 (s, 3, OMe), 4.16 (q, 2, O-CH_2-CH_3, J=7.1 Hz), 7.00 (d, 2, 3', 5'-H, J=9.1 Hz), 7.04 (s, 1, 5-H), 7.48-7.60 (m, 3, 3'', 4'', 5''-H), 7.92 (d, 2, 2', 6'-H, J=9.1 Hz); ms m/z: 419 (M^++1, 5), 418 (M^+, 20), 314 (20), 313 (100), 285 (17), 135 (69), 105 (14), 77 (25), 44 (15). *Anal.* Calcd. for $C_{24}H_{18}O_7$: C, 68.90; H, 4.34. Found: C, 68.73; H, 4.17.

Methyl 3-Cyano-2-oxo-6-phenyl-2*H*-pyran-4-ylacetate (10a). This compound (0.323 g 0.120 mmole) was separated by th recrystallization with ethanol from a mixture of **8a** and **10a** which were obtained by the reaction of **3a** (0.487 g, 2.0 mmoles) and **6c** (0.464 g, 4.0 mmoles). An analytical sample was recrystallized from ethanol to give pale yellow leaflets, mp 196-201°; ir(potassium bromide) υ_{max} cm^{-1}: 2220 (CN), 1740 (CO), 1720 (CO), 1620, 1540; uv(EtOH) λ_{max} nm(log ε): 290 (4.11), 370 (4.22); Fluorescence (solid): Ex, 348 nm; Em, 474 nm; RI=1.00; ^{1}H nmr($CDCl_3$) δ: 3.81 (s, 3, OMe), 3.84 (s, 2, -CH_2-), 6.87 (s, 1, 5-H), 7.54 (m, 3, 3', 4', 5'-H), 7.87 (m, 2, 2', 6'-H); ms m/z: 270 (M^++1, 14), 269 (M^+, 84), 241 (25), 154 (20), 127 (20), 105 (100), 77 (62). *Anal.* Calcd. for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20. Found: C, 66.78; H, 3.85; N, 5.17.

Ethyl 3-Cyano-2-oxo-6-phenyl-2*H*-pyran-4-ylacetate (10b). This compound (0.391 g, 1.38 mmoles) was separated from a mixture of **8c**, **9a** and **10b**which was prepared from **3a** (0.487 g, 2.0 mmoles) and **6d** (0.769 g, 4.0 mmoles). An analytical sample was recrystallized from ethanol to give pale yellow leaflets, mp 145-147°; ir(potassium bromide) υ_{max} cm^{-1}: 2220 (CN), 1740 (CO), 1720 (CO), 1620, 1530; uv(EtOH) λ_{max} nm(log ε): 291 (4.71), 359 (4.32); fluorescence (solid): Ex, 322 nm; Em, 482 nm; RI=8.72; ^{1}H nmr($CDCl_3$) δ: 1.33 (t, 3, O-CH_2-CH_3, J=7.3 Hz), 3.82 (s, 2, -CH_2-), 4.26 (q, 2, O-CH_2-CH_3, J=7.3 Hz), 6.88 (s, 1, 5-H), 7.54 (m, 3, 3', 4', 5'-H), 7.87 (m, 2, 2', 6'-H); ms m/z: 284 (M^++1, 18), 283 (M^+, 100), 211 (29), 183 (28), 105 (87), 77 (65). *Anal.* Calcd. for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.94. Found: C, 67.84; H, 4.57; N, 5.15.

Ethyl 3-Cyano-6-(4-methoxyphenyl)-2-oxo-2*H*-pyran-4-ylacetate (10c). This compound (0.269 g 0.86 mmole) was separated from a mixture of **8d**, **9b** and **10c** which was prepared from **3b** (0.547 g, 2.0 mmoles) and **6d**(0.769 g, 4 mmoles). An analytical sample was recrystallized from ethanol to give yellow leaflets, mp 172-173°; ir(potassium bromide) υ_{max} cm^{-1}: 2220 (CN), 1740 (CO), 1720 (CO), 1620, 1610, 1540, 1515; uv(EtOH) λ_{max} nm(log ε): 291 (4.80), 329 (4.70), 359 (4.54); fluorescence (solid): Ex, 342 nm; Em, 513 nm; RI=2.32; ^{1}H nmr($CDCl_3$) δ: 1.32 (t, 3, O-CH_2-CH_3, J=7.3 Hz), 3.79 (s, 2, -CH_2-), 3.90 (s, 3, OMe), 4.25 (q, 2, O-CH_2-CH, J=7.3 Hz_3), 6.76 (s, 1, 5-H), 7.99 (d, 2, 3', 5'-H, J=9.1 Hz), 7.93 (d, 2, 2', 6'-H, J=9.1 Hz); ms m/z: 314 (M^++1, 19), 313 (M^+, 100), 285 (14), 135 (22). *Anal.* Calcd. for $C_{17}H_{15}NO_5$: C, 65.17; H, 4.83; N, 4.47. Found: C, 65.39; H, 4.66; N, 4.44.

Ethyl 3-Cyano-6-(3,4-dimethoxyphenyl)-2-oxo-2*H*-pyran-4-ylacetate (10d). This compound (0.309 g, 0.90 mmole) was separated in 45% yield from a mixture of **9c** and **10d** which was prepared from **3e** (0.607 g, 2.0 mmoles) and **6d** (0.521 g, 4.0 mmoles). An analytical sample was recrystallized from ethanol to give orange needles, mp 165-166°; ir(potassium bromide) υ_{max} cm^{-1}: 2220 (CN), 1740 (CO), 1718 (CO), 1610, 1600, 1505; uv(EtOH) λ_{max} nm(log ε): 292 (5.10), 231 (5.05), 386 (4.91); fluorescence (solid): Ex, 347 nm; Em, 567 nm; RI=0.15; ^{1}H nmr($CDCl_3$) δ: 1.33 (t, 3, O-CH_2-CH_3, J=7.0 Hz), 3.80 (s, 2, -CH_2-), 4.26 (q, 2, O-CH_2-CH_3, J=7.0 Hz), 6.78 (s, 1, 5-H), 6.95 (d, 1, 5'-H, J=8.8 Hz), 7.35 (d, 1, 2'-H, J=2.4 Hz), 7.51 (dd, 1, 6'-H, J=2.4 Hz); ms m/z: 344 (M^++1, 20), 343 (M^+, 100), 256 (20), 165 (19), 129 (11), 73 (13), 69 (16), 57 (14). *Anal.* Calcd. for

$C_{18}H_{17}NO_6$: C, 62.97; H, 4.99; N, 4.08. Found: C, 62.73; H, 5.02; N, 3.89.

Ethyl 3-Cyano-6-(4-*N,N*-dimethylaminophenyl)-2-oxo-2*H*-pyran-4-ylacetate (10e). This compound (0.013 g, 0.04 mmole) was separated in 2% yield from a mixture of **8g** and **10e** which was prepared from **3g** (0.573 g, 2.0 mmoles) and ethyl acetoacetate(**6d**) (0.521 g, 4.0 mmoles). An analytical sample was recycclazed from ethanol to give red needles, mp 174-178°; ir(potassium bromide) υ_{max} cm^{-1}: 2220 (CN), 1725 (CO), 1700 (CO), 1600, 1550; uv(EtOH) λ_{max} nm(log ε): 285 (4.20), 325 (3.89), 471 (4.80); fluorescence (solid): Ex, 343 nm; Em, 612 nm; RI=0.04; fluorescence (CH_2Cl_2): Ex, 476 nm; Em, 531 nm; ^{1}H nmr($CDCl_3$) δ: 1.32 (t, 3, O-CH_2-*CH_3*, J=7.1 Hz), 3.11 (s, 6, NMe_2), 3.74 (s, 2, -CH_2-), 4.24 (q, 2, O-*CH_2*-CH_3, J=7.1 Hz), 6.64 (s, 1, 5-H), 6.69 (d, 2, 2', 6'-H, J=9.0 Hz), 7.77 (d, 2, 3', 4'-H, J=9.0 Hz); ms m/z: 327 (M$^+$+1, 22), 326 (M$^+$, 100), 298 (15), 225 (12), 148 (40), 44 (30). *Anal.* Calcd. for $C_{18}H_{18}N_2O_4$: C, 66.25; H, 5.56; N, 8.58. Found: C, 65.96; H, 5.55; N, 8.45.

3-Cyano-6-phenyl-4-toluenesulfonylmethyl-2*H*-pyran-2-one (10f). This compound (0.482 g, 1.32 mmoles) was prepared in 66% yield from **3a** (0.487 g, 2.0 mmoles) and **6e** (0.849 g, 4.0 mmoles) in a manner similar to that described for the preparation of **10a**. An analytical sample was re-crystallized from methanol to give pale yellow needles, mp 267-268°; ir(potassium bromide) υ_{max} cm^{-1}: 1765, 1740, 1705 (CO), 1615, 1515; uv(EtOH) λ_{max} nm(log ε): 359 (4.13); fluorescence (solid): Ex, 342 nm; Em, 464 nm; RI=5.20; ^{1}H nmr($CDCl_3$) δ: 2.47 (s, 3 Me), 4.46 (s, 2, -CH_2-), 7.08 (s, 1, 5-H), 7.40 (d, 2, 3", 5"-H, J=8.2 Hz), 7.54 (m, 3, 3', 4', 5'-H), 7.77 (d, 2, 2", 6"-H, J=8.2 Hz), 7.91 (d, 2, 2', 6'-H, J=6.9 Hz); ms m/z: 366 (M$^+$+1, 15), 365 (M$^+$, 65), 155 (100), 105 (12), 91 (93), 77 (18). *Anal.* Calcd. for $C_{20}H_{15}NO_4S$: C, 65.74; H, 4.14; N, 3.83. Found: C, 65.87; H, 3.97; N, 3.78.

3-Cyano-6-(4-methoxyphenyl)-4-toluenesulfonyl-methyl-2*H*-pyran-2-one (10g). This compound (0.142 g 0.3 mmoles) was separated in 18% yield from a mixture of **8a** and **10g** which was prepared from **3c** (0.547 g, 2.0 mmoles) and 4-toluenesulphonylacetoacetone (**6e**) (0.849 g, 4.0 mmoles). An analytical sample was recyclized with ethanol to give yellow needles, mp 278-280°; ir(potassium bromide) υ_{max} cm^{-1}: 1720 (CO), 1615, 1600, 1530, 1505; uv(EtOH) λ_{max} nm(log ε): 312 (4.36), 319 (4.35), 388 (4.37); fluorescence (solid): Ex, 340 nm; Em, 497 nm; RI=0.08; ^{1}H nmr($CDCl_3$) δ: 2.48 (s, 3, Me), 3.92 (s, 3, OMe), 4.43 (s, 2, -CH_2-), 6.97 (s, 1, 5-H), 7.02 (d, 2, 3', 5'-H, J=9.1 Hz), 7.40 (d, 2, 3", 5"-H, J=8.5Hz), 7.75 (d, 2, 2", 6"-H, J=8.5 Hz), 7.88 (d, 2, 2', 6'-H, J=9.1 Hz); ms m/z: 396 (M$^+$+1, 24), 395 (M$^+$, 94), 155 (71), 149 (54), 135 (54), 91 (100). *Anal.* Calcd. for $C_{21}H_{17}NO_5S$: C, 63.79; H, 4.33; N, 3.54. Found: C, 63.52; H, 4.30; N, 3.50.

3-Amino-5-methylsulfanyl-biphenyl-2,4-dicarbonitrile (11a). A mixure of **3a** (0.481 g, 2.0 mmoles), malononitrile (**6h**)(0.40 g, 6.1 mmoles), powdered sodium hydroxide (0.20 g, 5.0 mmoles), and 20 ml of DMSO was stirred for 5 hours at room temperature. The color of the reaction mixture was changed from yellow to red brown. The reaction mixture was poured into 300 ml of water and this solution was stirred for 4-20 hours at room temperature The precipitate that appeared was collected by filtration. After drying in air, the product was recrystallized from methanol or ethanol to give pure products (0.446g, 1.68 mmoles) as colorless needles, in 84% yield, mp 240-242°[4f: mp 243-244°]; ir(potassium bromide) υ_{max} cm^{-1}: 3395 (NH), 3345 (NH), 3248, 2222 (CN), 2217 (CN), 1656, 1560, 1543, 1286; uv(EtOH) λ_{max} nm(log ε):252 (4.08), 306 (4.04), 252 (4.56) ; fluorescence (solid): Ex, 347 nm; Em, 430 nm; RI=0.25; ^{1}H nmr($CDCl_3$) δ: 2.57 (s, 3, SMe), 5.26 (brs, 2, NH_2), 6.56 (s, 1, 6-H), 7.48 (m, 5, phenyl-H); ms m/z: 266 (M$^+$+1, 24), 265 (M$^+$, 100), 232 (20), 206 (12).

3-Amino-2'-methoxy-5-methylsulfanyl-biphenyl-2,4-dicarbonitrile (11b). This compound (1.084 g, 3.81 mmoles) was prepared in 76% yield from **3b** (1.37 g, 5.0 mmoles) and **6h** (0.506 g, 10.0 mmoles) in a manner similar to that described for the preparation of **11a**. An analytical sample was re-crystallized from DMF to give colorless needles, mp 216-219°; ir(potassium bromide) υ_{max} cm^{-1}: 3465 (NH), 3352 (NH), 3231, 2221 (CN), 2206 (CN), 1635, 1566, 1543, 1289, 752; ^{1}H nmr($CDCl_3$) δ: 2.53(s, 3, SMe), 5.18 (brs, 2, NH_2), 6.52 (s, 1, 6-H), 7.06 (m, 2, phenyl-H), 7. 21 (m, 2, phenyl-H), 7.42 (m, 1, phenyl-H); ms m/z: 296 (M$^+$+1, 41), 295 (M$^+$, 100), 280 (32), 248 (28), 233 (38). *Anal.* Calcd. for $C_{16}H_{13}N_3OS$: C, 65.06; H, 4.44; N, 14.23. Found: C, 64.98; H, 4.51 N, 14.31.

3-Amino-4'-methoxy-5-methylsulfanyl-biphenyl-2,4-dicarbonitrile (11c). This compound (1.46 g, 4.9 mmoles) was prepared in 98% yield from **3c** (1.37 g, 5.0 mmoles) and **6h** (0.51 g, 7.7 mmoles) in a manner similar to that described for the preparation of **11a**. An analytical sample was re-crystallized from DMF to give colorless needles, mp 200-202[4f: mp 212-213°]; ir(potassium bromide) υ_{max} cm^{-1}: 3454 (NH), 3335 (NH), 2223 (CN), 2206 (CN), 1644, 1567, 1515, 1255; uv(EtOH) λ_{max} nm(log ε):255 (4.48), 293 (4.18), 316 (4.17), 362 (4.13); fluorescence (solid): Ex, 365 nm; Em, 422 nm; RI=0.13; ^{1}H nmr($CDCl_3$) δ:2.57 (s, 3, SMe), 3.87 (s, 3, OMe), 5.12 (brs, 2, NH_2), 6.54 (s, 1, 6-H), 7.02 (d, 2, 2', 6'-H, J=9.0 Hz), 7.49 (d, 2, 3', 5'-H, J=9.0 Hz); ms m/z: 296 (M$^+$+1, 20), 295 (M$^+$, 100), 262 (9), 236 (11).

3-Amino-2',4'-dimethoxy-5-methylsulfanyl-biphenyl-2,4-dicarbonitrile (11d). This compound (0.555 g, 1.69 mmoles) was prepared in 85% yield from **3d** (0.60 g, 2.0 mmoles) and **6h** (0.198 g, 3.0 mmoles) in a manner similar to that described for the preparation of **11a**. An analytical sample was recrystallized from DMF to give colorless needles, mp 259-261°; ir(potassium bromide) υ_{max} cm^{-1}: 3406 (NH), 3344 (NH), 3247, 2221 (CN), 2206 (CN), 1655, 1614, 1562, 1541, 1211, 831; uv(EtOH) λ_{max} nm(log ε): 298 (3.87), 325 (3.86), 359 (3.92) ; fluorescence (solid): Ex, 334 nm; Em, 428 nm; RI=0.13; ^{1}H nmr($CDCl_3$) δ: 2.56 (s, 3, SMe), 3.84 (s, 3, OMe), 3.92 (s, 3, OMe), 6,53 (s, 1, 6-H), 6.62 (s, 1, 3'-H), 6.64 (d, 1, 5'-H, J=8.7 Hz), 7.18 (d, 1, 6'-H, J=8.7 Hz); ms m/z: 326 (M$^+$+1, 59), 325 (M$^+$, 100, 310 (10), 278 (18), 263 (16), 248 (10). *Anal.* Calcd for $C_{17}H_{15}N_3O_2S$: C, 62.75; H, 4.65; N, 12.91. Found: C, 62.58; H, 4.75; N, 12.86.

3-Amino-3',4',5'-trimethoxy-5-methylsulfanyl-biphenyl-2,4-dicarbonitrile (11e). This compound (0.642 g, 1.81 mmoles) was prepared in 90% yield from **3f** (0.666 g, 2.0 mmoles) and **6h** (0.20 g, 3.0 mmoles) in a manner similar to that described for the preparation of **11a**. An analytical sample was re-crystallized from DMF to give colorless needles, mp 263-265°; ir(potassium bromide) υ_{max} cm^{-1}: 3404 (NH), 3338 (CN), 3246, 2219 (CN), 1648, 1585, 1542, 1282, 1240, 1124, 995; uv(EtOH) λ_{max} nm(log ε):254 (4.68), 308 (4.32), 365 (4.31) ; fluorescence (solid): Ex, 368 nm; Em, 434 nm; RI=0.13; ^{1}H nmr($CDCl_3$) δ:2.60 (s, 3, SMe), 3.93 (s, 6, 2xOMe), 3.98 (s, 3, 0Me), 6.57 (s, 1, 6-H), 6.73 (s, 2, 2', 6'-H); ms m/z: 356 (M$^+$+1, 30), 355 (M$^+$, 100), 340 (29), 312 (17), 282 (10). *Anal.* Calcd. for $C_{18}H_{17}N_3O_3S$: C, 60.83; H, 4.82; N, 11.82. Found: C, 60.53; H, 4.87; N, 11.64.

3-Amino-4'-*N,N*-dimethylamino-5-methylsulfanyl-biphenyl-2,4-dicarbonitrile (11f). This compound (0.675 g, 2.19 mmoles) was prepared in 73% yield from **3g** (0.858 g, 3.0 mmoles) and **6h** (0.504 g, 7.6 mmoles) in a manner similar to that described for the preparation of **11a**. An analytical sample was re-crystallized from DMF to give colorless needles; mp 257-259°; ir(potassium bromide) υ_{max} cm^{-1}: 3454 (NH), 3335 (NH), 3235, 2221 (CN), 2206 (CN), 1644, 1610, 1566, 1527, 1365, 1201, 805; uv(EtOH) λ_{max} nm(log ε):264 (4.58), 379 (4.51) ; fluorescence (solid): Ex, 375 nm; Em, 523 nm; RI=0.12; ^{1}H nmr(DMSO-d$_6$) δ: 2.60 (s, 3, SMe), 3.33 (s, 6, NMe$_2$), 6.60 (brs, 2, NH$_2$), 6.52 (s, 1, 6-H), 6.81 (d, 2, 3', 5'-H, J=9.0 Hz), 7.48 (d, 2, 2', 6'-H, J=9.0 Hz); ms m/z: 309 (M$^+$+1, 222), 308 (M$^+$, 100), 307 (39), 249 (10). *Anal.* Calcd for $C_{17}H_{16}N_4S$: C, 66.21, H, 5.23; N, 16.17. Found: C, 66.12; H, 5.22; N, 16.32.

3-Amino-4'-cyano-5-methylsulfanyl-biphenyl-2,4-dicarbonitrile (11g). This compound (0.545 g, 1.88 mmoles) was prepared in 94% yield from **3h** (0.534 g, 2.0 mmoles) and **6h** (0.198 g, 3.0 mmoles) in a manner similar to that described for the preparation of **11a**. An analytical sample was re-crystallized from DMF to give colorless needles; mp 312-314°; ir(potassium bromide) υ_{max} cm^{-1}: 3454 (NH), 3366 (NH), 2231 (CN), 2214 (CN), 2207 (CN), 1650, 1618, 1567, 1541, 1291, 830; ^{1}H nmr(CDCl$_3$ +CF$_3$COOH) δ: 2.61 (s, 3, SMe), 6.54 (s, 1, 6-H), 7.67 (d, 2, 3', 5'-H, J=8.7 Hz), 7.88 (d, 2, 2', 6'-H, J=8.7 Hz); ms m/z: 291 (M$^+$+1, 20), 290 (M$^+$, 100), 289 (6), 257 (12), 231 (8). *Anal.* Calcd for $C_{16}H_{10}N_4S$: C, 66.19; H, 3.47; N, 19.30. Found: C, 65.97; H, 3.67; N, 19.01.

Methyl 3-Amino-2-cyano-5-methylsulfanyl-biphenyl-4-carboxylate (11h). This compound (0.74 g, 1.59 mmoles) was prepared in 80% yield from **4a** (0.55 g, 2.0 mmoles) and **6h** (0.30 g, 4.0 mmoles) in a manner similar to that de-scribed for the preparation of **11a**. An analytical sample was re-crystallized from DMF to give colorless needles, mp 138-140°[4f: mp 169-170°]; ir(potassium bromide) υ_{max} cm^{-1}: 3445 (NH), 3343 (NH), 2210 (CN), 1671 (CO), 1597, 1427, 1335, 1266, 704; uv(EtOH) λ_{max} nm(log ε):252 (4.52), 308 (4.01), 368 (4.03); ^{1}H nmr(CDCl$_3$) δ: 2.44 (s, 3, SMe), 3.98 (s, 3, OMe), 6.41 (brs, 2, NH$_2$), 6.55 (s, 1, 6-H), 7.43-7.59 (m, 5, phenyl-H); ms m/z: 299 (M$^+$+1, 19), 298 (M$^+$, 100), 267 (26), 266 (65), 69 (11), 59 (17).

Methyl 3-Amino-2-cyano-4'-methoxy-5-methyl-sulfanyl-biphenyl-4-carboxylate (11i). This compound (1.12 g, 3.412 mmoles) was prepared in 68% yield from **4b** (1.53 g, 5.0 mmoles) and **6h** (0.462 g, 7.0 mmoles) in a manner similar to that described for the preparation of **11a**. An analytical sample was recrystallized from DMF to give colorless needles; mp 124-126°; ir(potassium bromide) υ_{max} cm^{-1}: 3457 (NH), 3341 (NH), 2210 (CN), 1690 (CO), 1603, 1512 1260; uv(EtOH) λ_{max} nm(log ε):254 (4.46), 312 (4.13), 369 (4.07); fluorescence (solid): Ex, 372 nm; Em, 435 nm; RI=0.15; ^{1}H nmr(CDCl$_3$) δ: 2.44 (s, 3, SMe), 3.87 (s, 3, OMe), 3.95 (s, 3, OMe), 6.41 (brs, 2, NH$_2$), 6.52 (s, 1, 6-H), 7.01 (d, 2, 3', 5'-H, J=8.9 Hz), 7.52 (d, 2, 2', 6'-H, J=8.9 Hz); ms m/z: 329 (M$^+$+1, 21), 328 (M$^+$, 100), 297 (25), 210 (10), 179 (14), 45 (12). *Anal.* Calcd for $C_{17}H_{16}N_2O_3S$: C, 62.18; H, 4.91; N, 8.53. Found. C, 61.96; H, 4.88; N, 8.55.

Methyl 6-Amino-4-benzo[1.3]dioxol-5-yl-5-cyano-2-(sulfanyl)-benzoate (11j). This compound (0.507 g, 1,47 mmoles) was prepared in 74% yield from **4c** (0.64 g, 2.0 mmoles) and **6h** (0.3 g, 4.0 mmoles) in a manner similar to that described for the preparation of **11a**. An analytical sample was re-crystallized from DMF to give colorless needles; mp 196-198°; ir(potassium bromide) υ_{max} cm^{-1}: 3464 (NH), 3352 (NH), 2208 (CN), 1676 (CO), 1564, 1503, 1274, 1243.; uv(EtOH) λ_{max} nm(log ε):254 (4.51), 316 (4.18), 368 (4.12); ^{1}H nmr(CDCl$_3$) δ: 2.44 (s, 3, SMe), 3.97 (s, 3, OMe), 6.04 (s, 2, O-CH$_2$-O), 6.41 (brs, 2, NH$_2$), 6.49 (s, 1, 6-H), 6.91 (d, 1, 5'-H, J=8.2 Hz), 7.00 (d, 1, 2'-H, J=1.6 Hz), 7.04 (dd, 1, 6'-H, J=1.6, 8.2 Hz); ms m/z: 343 (M$^+$+1, 9), 342 (M$^+$, 43), 311 (10), 310 (24), 262 (96), 234 (100). *Anal.* Calcd for $C_{17}H_{14}N_2O_4S$: C, 59.64; H, 4.12; N, 8.18. Found. C, 59.66; H, 4.11 N, 8.09.

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