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SYNTHESIS AND FLUORESCENCE OF 4-METHYLSULFANYL-6-PYRIDYL-2*H*-PYRAN-2-ONES IN SOLID STATE

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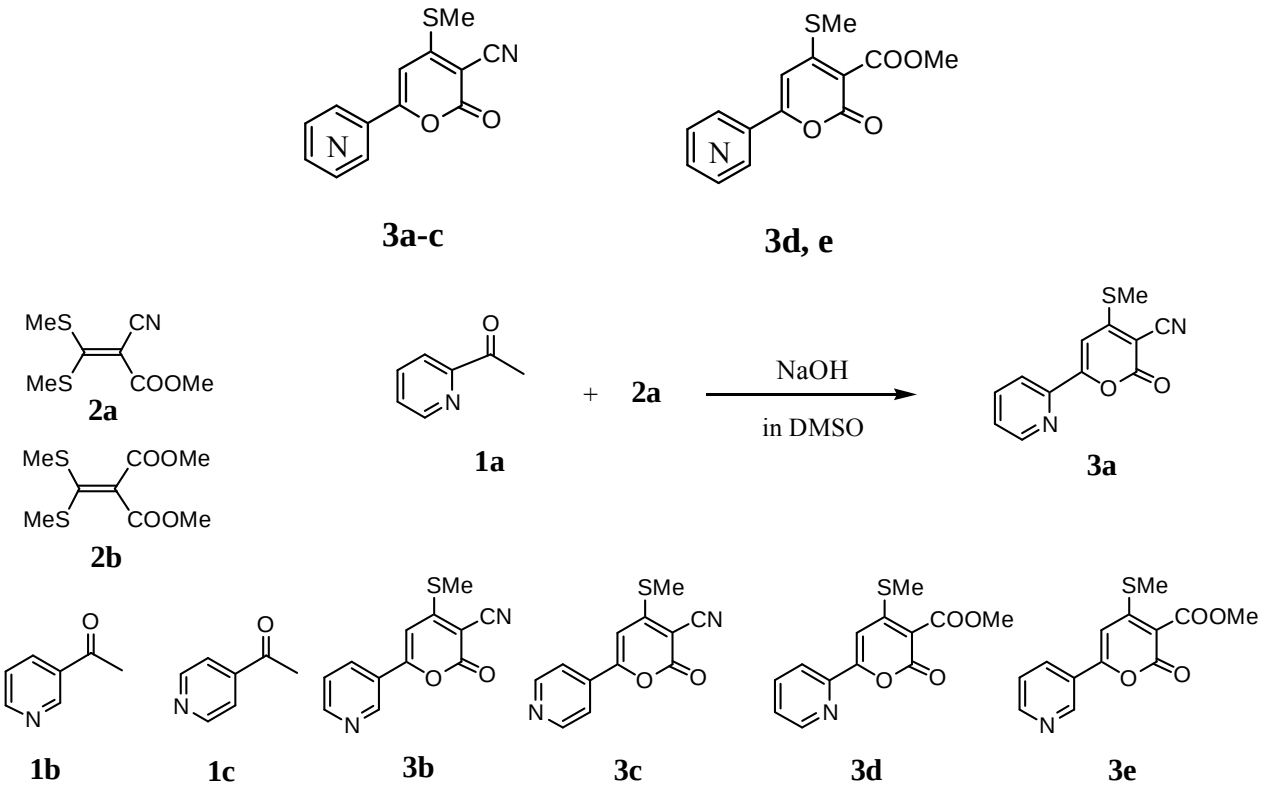
Abstract – Various 4-methylsulfanyl-6-pyridyl-2*H*-pyran-2-one derivatives were synthesized by the reaction of ketene dithioacetals with active methyl or methylene compounds in the presence of powdered sodium hydroxide in dimethyl sulfoxide (DMSO). Among these 2-pyrone derivatives, 3-aryl-4-methylsulfanyl-6-pyrid-2-yl-2*H*-pyran-2-ones show strong fluorescence in the solid state.

Heterocyclic compounds showing fluorescent properties have been the subject of much interest in the area of dye chemistry because of their potential in various applications, such as emitters for electroluminescence (EL) devices, copy-preventing inks, solar energy-collecting materials, and fluorescent colorants.[1] Recently, we reported the development of 2-pyrone derivatives as promising electroluminescent materials. These 2-pyrones have an aryl group, such as a phenyl group, at position 6, and it was found that compounds bearing electron-rich aryl groups show greater fluorescence. In particular, 6-(4-dimethylaminophenyl)-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitrile shows very strong red fluorescence, which is very important in the field of organic electroluminescence.[2] It was also found that 4-methylsulfanyl-2-oxo-6-pyrid-3-yl-2*H*-pyran-3-carbonitrile, bearing an electron-deficient pyridyl group at position 6, did not emit light. We also reported the synthesis and steady-state spectroscopic studies of new solid-state fluorescent compounds 5-aryl[2,2']bipyridyls.[3] It was anticipated that the introduction of both an aryl and an electron-poor pyridyl groups in the 2-pyrone moiety would

result in strong fluorescence. These fluorescent heterocyclic compounds were prepared by the reaction of ketene dithioacetals with the corresponding active methylene compounds (Scheme 1).

Appropriately functionalized ketene dithioacetals are versatile reagents which have been extensively utilized in organic synthesis.[3] One of these, α-oxoketene dithioacetal 3,3-bis(methylsulfanyl)-1-pyrid-2-yl-2-propenone (**4**), is also an extremely interesting synthon which is used for the synthesis of heterocycles bearing a 2-pyridyl group.[5] In an extension of our previous work on ketene dithioacetals, we here report the synthesis of new chromophores using ketene dithioacetals.[6]

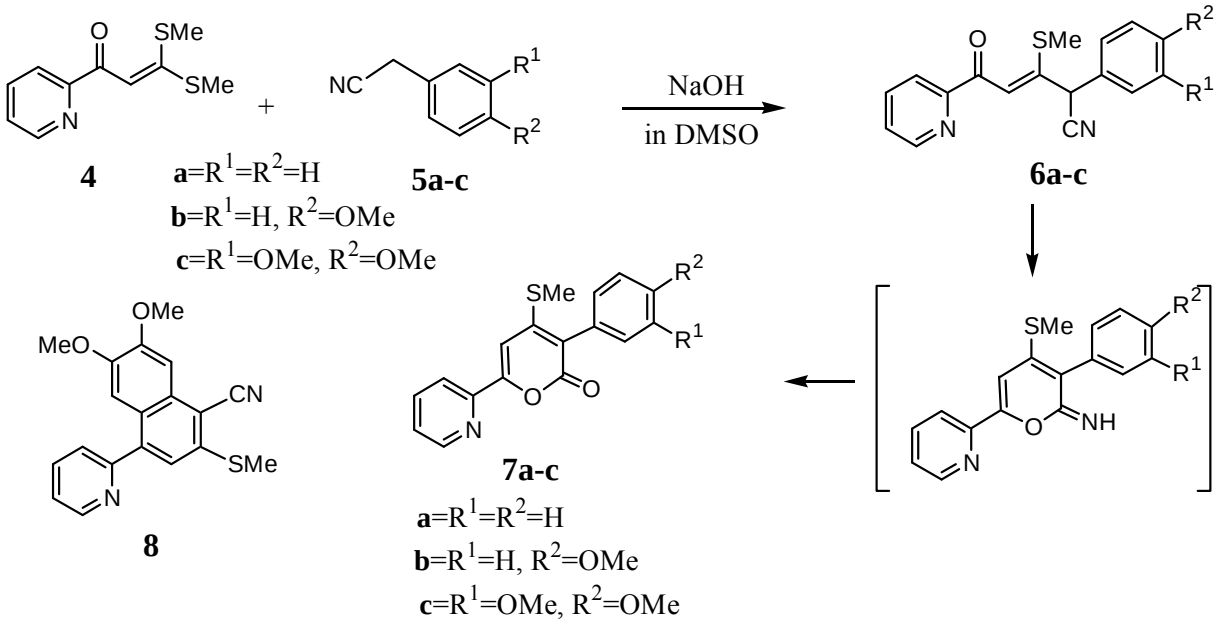


Scheme 1

In our recent synthesis of 2-pyrone derivatives showing strong fluorescence in the solid state,[2,7] we first attempted the synthesis of 4-methylsulfanyl-2-oxo-6-pyrid-2-yl-2*H*-pyran-3-carbonitrile (**3a**) by reaction of 2-acetylpyridine (**1**) with ketene dithioacetal (**2**) in the presence of sodium hydroxide in DMSO at room temperature. The reaction proceeded smoothly to give the desired product (**3a**) in 58% yield. However, this 2-pyrone derivative shows very weak fluorescence under many measurement conditions, such as in dichloromethane or ethanol solution, and even in the solid state. Position isomers 4-methylsulfanyl-2-oxo-6-pyrid-3-yl-2*H*-pyran-3-carbonitrile (**3b**)[8d] and 4-methylsulfanyl-2-oxo-6-pyrid-4-yl-2*H*-pyran-3-carbonitrile (**3c**), which were prepared from **1b** and **1c** with **2** in a manner similar to that described for the preparation of **3a**, also proved to be weakly fluorescent compounds. Similarly,

compounds methyl 4-methylsulfanyl-2-oxo-6-pyrid-2-yl-2*H*-pyran-3-carboxylate (**3d**) and methyl 4-methylsulfanyl-2-oxo-6-pyrid-3-yl-2*H*-pyran-3-carboxylate (**3e**), which were synthesized from **2b** and **1a** or **1b** in 48% and 34% yields, respectively,[8e] showed very weak fluorescence in dichloromethane.

The reaction of **4** with phenylacetonitrile (**5a**) in the presence of powdered sodium hydroxide in DMSO at room temperature gave the intermediate (**6a**), which was treated with hydrochloric acid to give the desired 3-phenyl-2-pyrone derivative (**7a**) in 58% yield. In a similar manner, compound (**7b**) was obtained from **5b** in 59% yield. In the reaction of **4** with **5c**, compound (**7c**) was obtained in 39% yield, together with 2-naphth-1-ylpyridine (**8**) in 35% yield (Scheme 2).



Scheme 2

Alq_3 [tris(8-hydroxyquinolinato)aluminum][9] was used as a standard sample for absorption and fluorescence spectra. Measurements were carried out in dichloromethane and ethanol solution at room temperature. 3-Phenyl-2-pyrone derivatives show strong fluorescence; (Emission wavelength (Em) in solution and in the solid state are summarized in Table 1). The aryl group at position 6 of 2-pyrone derivatives also plays an important role in fluorescence expression. In 2-oxo-6-phenyl-2*H*-pyran-3-carbonitriles, it was shown that the fluorescence intensity of derivatives in which the phenyl group bore an electron-donating group was stronger than that of other compounds; in contrast, 6-(4-cyanophenyl)-2-oxo-2*H*-pyran-3-carbonitriles,[7] bearing an electron-withdrawing group on the aryl group at position 6, showed no fluorescence. Similarly, 4-methylsulfanyl-2-oxo-6-pyridyl-2*H*-pyran-3-carbonitriles (**3a-c**) and methyl 4-methylsulfanyl -2-oxo-6-pyridyl-2*H*-pyran-3-carboxylates (**3d**, **e**) also showed very weak fluorescence in solution and in the solid state. However, 3-phenyl-6-pyrid-2-yl-

2*H*-pyran-2-ones (**7a-c**), bearing an aryl group instead of a cyano group at position 3, showed fluorescence in the solid state. When measured in ethanol solution, the fluorescence of these 2-pyrone derivatives (**7a-c**) was less strong. When measured in dichloromethane, the fluorescence of them was nothing. At present, the reason for this fluorescence has not yet been elucidated, but it is likely that the simple reason between an electron-withdrawing and an electron-donating substituent on the 2-pyrone ring is not the only factor.

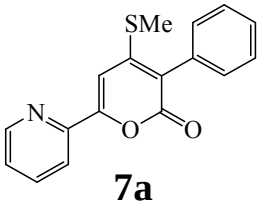
Table 1. UV and fluorescence spectra of 3-aryl-6-pyridin-2-yl-2*H*-pyran-2-ones in ethanol and in solid states.

		UV λmax[a]	Fluorescence(EtOH)				Fluorescence(solid)				
No.	mp(°)	(nm)(log ε)	Ex[b](nm)	Em[c](nm)	SS[d]	ϕ	Ex[b](nm)	Em[c](nm)	ΔF[e]	SS[d]	RI[f]
7a	181-183	254 (4.20)	282	439	157	0.01	349	474	35	125	7.02
7b	217-218	256 (4.20)	279	462	183	0.02	349	503	41	154	1.49
7c	164-166	297 (4.17)	284	435	151	0.15	340	529	94	189	0.25
Alq_3	-	-	-	-	-	-	341	510	-	169	1.00

[a]Measurement in EtOH. [b]Excitation Wavelength. [c]Emission Wavelength.
[d]Stoke's Shift, Em(nm)-Ex(nm) in EtOH. [d]Stoke's Shift, Em(nm)-Ex(nm) in solid state. [e]Em(solid)-Em(EtOH)
[f]Relative intensity of fluorescence in solid states, using Alq_3 as a standard compound.

The relative fluorescence intensity of the 3-phenyl-2-pyrone (**7a-c**) were 7.02, 1.49 and 0.25 respectively. These compounds generally show quite large Stoke's shifts: 125, 154, and 189 nm. No remarkable enhancement was observed by introduction of methoxy on the aryl group at position 3, however, the introduction of methoxy group as an electron-donating group results in a bathochromic shift in the absorption maximum (λ_{max}) together with an increase a just little absorption maxima (log ε) in UV spectrum. It has been reported that the twist angle between the two pyridyl groups in bipyridyl derivatives has a significant effect on fluorescence in the solid state.[3] The twist angle between pyridyl and pyranyl groups of the 3-phenyl-6-pyridyl-2*H*-pyrone (**7a**), which showed the strongest fluorescence, was 12.1°. This twist angle was smallest among other compounds (Table 2-3).[3, 7, 10] It is reported the fluorescence intensity is strongly affected by twist angle between the aryl at position 6 and pyranyl groups, which implies that molecular stacking is important factor in strong fluorescence. The twist angles of compounds (**9a-g**) were 13-26°, approximately. However, this angle was decreased to 12.1° on compound (**7a**). The smaller twist angle increased the delocalization of electrons between the pyridyl and the pyranyl groups. Introducing the phenyl group to position 3 and the pyridyl group to position 6, these groups played as an efficient donor and accepter, respectively. Therefore, compound (**7a**) showed strong fluorescence, it differed from compounds (**3a-e**).

Table 2. Crystallographic data of compound (**7a**).



7a

molecular formula	$C_{17}H_{13}NO_2S$	V (Å^3)	1451.7
formula weight	295.36	Z	4
color	yellow	R-factor	0.05
crystal shape	block	torsion angle(°)	12.1
crystal system	triclinic	6-aryl -pyrone (Å)	1.464
space group	Pī(#2)	C=O (Å)	1.209
a (Å)	5.9332	R.I.[a]	6.47
b (Å)	13.238	Stoke's Shift[b]	177
c (Å)	18.509		
β (°)	87.886		

[a] Relative Intensity of fluorescence in solid state, using Alq_3 as a standard.

[b] Value = Emission max(nm)-Excitation max(nm).

Additionally, the twist angle between the phenyl group at position 3 and the pyranyl ring was 64.5°. An efficient molecular stacking has been occurred because this angle also greatly contributed to the intermolecular interaction. The Em value indicates the difference in Em from solid state to solution which illustrates the effect of molecular stacking on the fluorescent spectra.

In conclusion, 3-aryl-6-pyrid-2-yl-2-oxo-2*H*-pyrans are valuable new fluorescent compounds which show previously unobserved fluorescence in the blue-green light region at 474 nm (**7a**), 503 nm (**7b**), and 529 nm (**7c**). 3-(4-Methoxyphenyl)-2-oxo-6-pyrid-2-yl-2*H*-pyrans (**7b**, **c**) showed a bathochromic shift in their λ_{max} and Em_{max} valves, and their ε_{max} values also increased in comparison with the parent compound (**7a**). However, the compound showing the strongest fluorescence among these 2-pyrone derivatives was 4-methylsulfanyl-3-phenyl-6-pyrid-2-yl-2*H*-pyran-2-one (**7a**), which bears an unsubstituted phenyl group at position 3 in the pyranyl ring. Among pyrone derivatives containing a pyridyl unit, compounds (**7a-c**) are the first to show strong light emission.

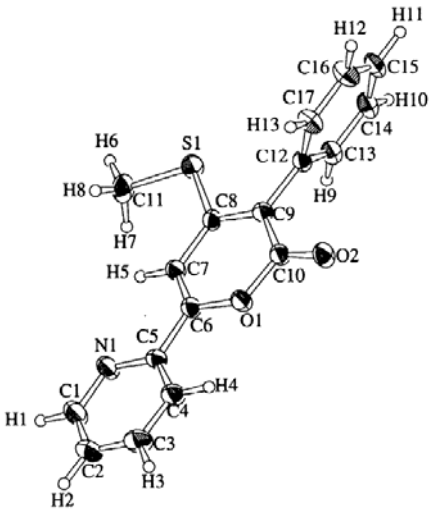


Figure 2. ORTEP of **7a**.

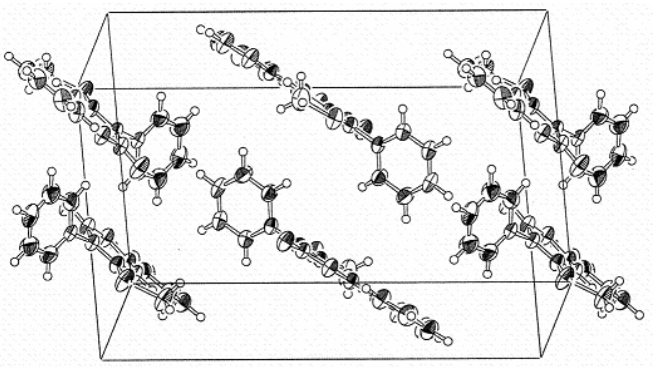
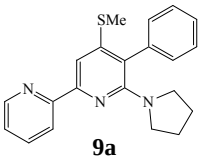
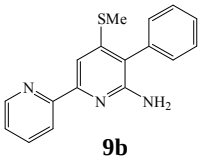


Figure 3. Molecular Packing Diagram of **7a**.

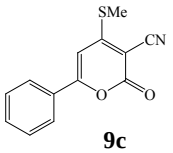
Table 3. Crystallographic data of compound (**9**).



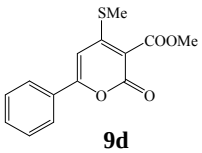
9a



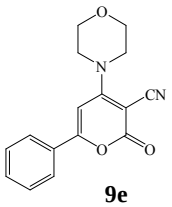
9b



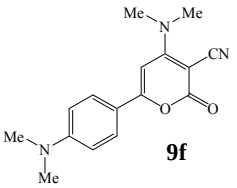
9c



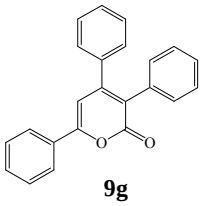
9d



9e



9f



9g

	9a[3]	**9b**[3]	**9c**[c, 7]	**9d**[7]	**9e**[7]	**9f**[7]	**9g**[10]
molecular formula	$C_{21}H_{21}N_3S$	$C_{17}H_{15}N_3S$	$C_{13}H_9NO_2S$	$C_{14}H_{12}O_4S$	$C_{16}H_{14}N_2O_3$	$C_{16}H_{17}N_3O_2$	$C_{23}H_{16}O_2$
formula weight	347.48	293.39	243.04	276.31	282.30	283.33	324.38
color	clear	clear	yellow	pale yellow	clear	pale greenish yellow	yellow
crystal shape	block	block		prism	prism	crystal	prism
crystal system	monoclinic	monoclinic		monoclinic	monoclinic	orthohombic	orthohombic
space group	$P2_1/n$(#14)	$P\bar{1}$(#2)		$P2_1/n$(#14)	$P2_12_12_1$(#19)	$P2_12_12_1$(#19)	P*bca*
a (Å)	5.6971	6.1102		14.137	7.3096	7.5938	18.267
b (Å)	19.222	10.474		7.0687	12.7257	14.0254	20.298
c (Å)	16.6632	12.966		13.9118	14.8169	27.4606	8.975
β (°)	91.4901	79.627		111.283	-	-	-
V (Å^3)	1824.2	751.1		1295.4	1378.26	2924.72	3327
Z	4	2		4	4	8	8
R-factor	0.074	0.062		0.054	0.021	0.050	0.059
torsion angle(°)	13.4	19.8	23.2	24.3	26.5	16.9	25.9
6-aryl -pyrone (Å)	1.485	1.489	1.463	1.464	1.466	1.460	
C=O or C-NR_2(Å)	1.379	1.375	1.228	1.205	1.211	1.221	
R.I.[a]	2.18	0.16	1.54	6.31	3.08	3.86	
Stoke's Shift[b]	130	91	122	176	99	223	

[a] Relative Intensity of fluorescence in solid state, using Alq_3 as a standard.

[b] Value = Emission max(nm)-Excitation max(nm).

[c] Computational caluculated result by MOPAC/AM1.

EXPERIMENTAL

Identification of compounds and property measurements were carried out by general procedures using the equipment described below. All melting points were determined in a capillary tube and are uncorrected. Infrared (IR) spectra were recorded in KBr pellets on a JASCO 810 or a Shimadzu IR-460 spectrometer, and ultraviolet (UV) absorption spectra were determined in 95% EtOH on a Hitachi 323 spectrometer. Fluorescence spectra were determined on a Shimadzu RF-1500 pc and Shimadzu RF-5300 pc. Nuclear magnetic resonance (NMR) spectra were obtained on Gemini 300NMR (300 MHz) and 500NMR (500 MHz) spectrometers with tetramethylsilane as an internal standard. Mass spectra (MS) were recorded on JEOL DX-303 mass spectrometers. Microanalysis was 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.

Fluorescence Measurements

a) Solid state

A powder sample of the subject compound was heaped on a tray. After covering the sample with a quartz plate, the tray was fixed in the fluorescence spectrometer (Shimadzu RF5300pc). After setting the fluorescent wavelength, the excitation spectrum was determined by scanning at the fluorescent wavelength. Similarly, the fluorescent spectrum was obtained by scanning at the excitation wavelength. The excitation wavelength was determined and the fluorescence spectrum was measured.
Relative fluorescence intensities were determined using Alq_3 as a standard sample. The fluorescence of the standard sample and all subject compounds were measured at 345 nm excitation.

b) In solution

The fluorescence quantum yields (ϕ) of the subject compound were compared with those of 9,10-diphenylanthracene or anthracene which was used as the standard. The concentrations of the measured samples in the excitation wavelength region were adjusted using a molar absorption coefficient of 0.05. The solution fluorescence spectra were obtained on Shimadzu RF1500pc in a manner similar to that described for measurement in the solid state. The quantum yields of 9,10-diphenylanthracene and anthracene used were $\phi = 0.81$ and $\phi = 0.25$ under measurement at 366 nm and 254 nm excitation, respectively.

4-Methylsulfanyl-2-oxo-6-pyrid-2-yl-2*H*-pyran-3-carbonitrile (**3a**).

A mixture of ketene dithioacetal (**2a**) (6.0 g, 30.0 mmol), 2-acetylpyridine (**1a**) (3.63 g, 30 mmol), NaOH (2.40 g, 60 mmol), and 60 mL of DMSO was stirred for 4 h at rt. During stirring, the color of the reaction mixture changed from yellow to reddish brown. After the reaction, the mixture was poured into 500 ml of water. This solution was stirred for another 4 h. The precipitates that appeared were collected by filtration and washed with water. After drying in air, the product was recrystallized from toluene to give 1.68 g (6.9 mmol) of pale yellow crystals in 23% yield. An analytical sample was recrystallized from MeOH to obtain yellow needles, mp 180-182ºC; IR (KBr): ν cm^{-1} 2213 (CN), 1720 (CO), 1609, 1563, 1488; UV (EtOH) λ_{max} nm (insufficient solubility): 248, 324, 370; Fl (CH_2Cl_2): Ex 264 nm, Em 559 nm; $\phi = 0.02$. Fl (solid): Ex 354 nm, Em 467 nm; RI < 0.01; ^{1}H-NMR ($CDCl_3$): δ 2.76 (3H, s, SMe), 7.57 (1H, s, 5-H), 7.46 (2H, dd, J = 4.8 Hz, 6.6 Hz, 5'-H), 7.89 (1H, ddd, J = 1.3, 6.6, 7.7 Hz, 4'-H), 8.00 (1H, d, J = 7.7 Hz, 3'-H), 8.70 (1H, dd, J = 1.3, 4.8 Hz, 6'-H); MS *m/z*: 245 (M^++1, 8), 244 (M^+, 52), 228 (32), 197 (100), 106 (25), 106 (27), 78 (52), 51 (73), 44 (33). *Anal*. Calcd for $C_{12}H_8N_2O_2S$: C, 59.00; H, 3.30; N, 11.47. Found: C, 59.12; H, 3.32; N, 11.45.

4-Methylsulfanyl-2-oxo-6-pyrid-3-yl-2*H*-pyran-3-carbonitrile (**3b**).[8d]

This compound (4.39 g, 18.0 mmol) was synthesized in 60% yield from 3-acetylpyridine (**1b**) (3.63 g, 30 mmol) and **2a** (6.0 g, 30 mmol) in manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from DMF to give pale yellow needles, mp 190-192°C; UV (EtOH) λ_{max} nm (log ε): 247 (4.16) 327 (4.24), 365 (4.10); Fl (CH_2Cl_2): Ex 263 nm, Em 525 nm, ϕ = 0.04. Fl (solid): Ex 297 nm, Em 468 nm; RI = 0.06; ^{1}H-NMR ($CDCl_3$): δ 2.76 (3H, s, SMe), 7.57 (1H, s, 5-H), 6.78 (1H, s, 5-H), 7.50 (1H, m, 5'-H), 8.19 (1H, m, 4'-H), 8.79 (1H, dd, J = 1.6, 4.8 H, 6'-H), 9.09 (1H, d, J = 1.6 Hz, 2'-H).

4-Methylsulfanyl-2-oxo-6-pyrid-4-yl-2*H*-pyran-3-carbonitrile (**3c**).

This compound (3.68 g, 15.1 mmol) was synthesized in 50% yield from 4-acetypyridine (**1c**) and **2a** (6.0 g, 30 mmol) in manner similar to that described for the preparation of **3a**. An analytical sample was recrystallized from MeOH to give pale yellow needles, mp 207-209°C; IR (KBr): ν cm^{-1} 2210 (CN), 1720 (CO), 1610, 1590, 1550, 1490, 810; UV (EtOH) λ_{max} nm (log ε): 365 (4.08), 324 (4.28), 254 (4.16), 241 (4.10), 231 (4.07). Fl (CH_2Cl_2): Ex 264 nm, Em 527 nm, ϕ = 0.04. Fl (solid): no fluorescence; ^{1}H-NMR ($CDCl_3$): δ 2.27 (3H, s, SMe), 6.84 (1H, s, 5-H), 7.71 (2H, dd, J = 1.6 Hz, 4.6 Hz, 3,5-H), 8.83 (2H, d, J = 4.6 Hz, 2, 6-H); MS *m/z*: 245 (M^++1, 20), 244 (M^+, 100), 229 (10), 216 (41), 166 (10), 106 (27), 78 (24), 51 (13), 44 (15). *Anal*. Calcd for $C_{12}H_8N_2O_2S$: C, 59.01; H, 3.30; N, 11.47. Found: C, 59.22; H, 3.46; N, 11.38.

Methyl 4-Methylsulfanyl-2-oxo-6-pyrid-2-yl-2*H*-pyran-3-carboxylate (**3d**).[8e]

This compound was prepared from ketene dithioacetal (**2b**) and 2-acetylpyridine (**1a**) by the previous method to give pale yellow needles, mp 192-194°C.[8e] UV (CH_2Cl_2) λ_{max} nm (log ε): 246 (4.60), 323 (4.47); Fl (CH_2Cl_2): Ex 281 nm; Em 560 nm; ϕ = 0.15. Fl (solid): Ex 357 nm, Em 469 nm, RI = 0.06.

Methyl 4-Methylsulfanyl-2-oxo-6-pyrid-3-yl-2*H*-pyran-3-carboxylate (**3e**).[8e]

This compound was prepared from ketene dithioacetal (**2b**) and 3-acetylpyridine (**1b**) by the previous method to give pale yellow needles, mp 191-193°.[8e] UV (CH_2Cl_2) λ_{max} nm (log ε): 227 (4.68), 244 (4.59), 319 (4.48), 352 (4.38); Fl (CH_2Cl_2): Ex 264 nm; Em 527 nm; ϕ = 0.01; Fl (solid): Ex 354, Em 470 nm, RI = 0.11.

4-Methylsulfanyl-3-phenyl-6-pyrid-2-yl-2*H*-pyran-2-one (**7a**).

Powdered sodium hydroxide (0.80 g, 10.0 mmol) was added to a solution of 1.13 g (5.0 mmol) of **4** and 0.70 g (6.0 mmol) of phenylacetonitrile (**5a**) in 50 mL of DMSO and the mixture was stirred for 2 h at rt. The reaction mixture was poured into 300 mL of ice water and neutralized with 10% hydrochloric acid

solution. The mixture was extracted with 100 mL of CH_2Cl_2 three times. The organic layer was washed with water and dried over anhydrous sodium sulfate. Removal of the solvent by evaporation gave a brown residue. A mixture of the residue and 20 mL of 2*N* HCl was refluxed for 30 min. After the reaction, the reaction mixture was poured into 300 mL of the water and neutralized with 10% aqueous $NaHCO_3$. The precipitate that appeared from the mixture was collected by filtration to give a brown solid, which was purified by silica gel column chromatography by using toluene as an eluent to give 0.56 g (1.9 mmol, 38%) of **7a** as yellow needles. An analytical sample was recrystallized from MeOH to give pale yellow needles, mp 181-183˚C. IR (KBr) ν cm^{-1}: 1700 (C=O), 1620, 1570, 1470, 1430, 1360, 1315, 1185, 1070; UV (EtOH) λ_{max} nm (log ε): 360 (4.08), 318 (4.11), 309 (4.13), 254 (4.20); UV (CH_2Cl_2) λ_{max} nm (log ε): 359 (4.43), 305 (4.49), 255 (4.64); Fl (EtOH): Ex 282 nm; Em 439 nm; ϕ = 0.01; Fl (CH_2Cl_2): no fluorescence; Fl (solid): Ex 349, Em 474 nm, RI = 7.02; ^{1}H-NMR ($CDCl_3$) δ: 2.51 (3H, s, SMe), 7.37 (1H, dd, J = 7.8, 7.8 Hz, 5’’-H), 7.35-7.50 (5H, m, phenyl-H), 7.56 (1H, s, 5-H), 7.85 (2H, ddd, J = 1.8, 7.8, 8.0 Hz, 4’’-H), 8.08 (1H, ddd, J = 0.9, 1.2, 8.0 Hz, 3’’-H), 8.66 (1H, ddd, J = 0.9, 1.8, 4.8, 6’’-H); ^{13}C-NMR ($CDCl_3$) δ: 15.2 (SMe), 159.7 (2), 148.8 (3), 120.78 (4), 100.4 (5), 156.7 (6), 133.5 (1’), 129.9 (2’, 6’), 128.6 (3’, 5’), 128.7 (4’), 156.0 (2”), 120.81 (3”), 137.2 (4”), 125.0 (5”), 149.7 (6”); MS *m/z* : 296 (M^++1, 23), 295 (M^+, 100), 252 (25), 248 (43), 191 (20), 161 (27), 115 (23), 106 (22), 95 (21), 85 (37), 83 (57), 81 (41), 78 (71), 71 (20), 69 (94), 68 (20), 57 (42), 55 (40), 51 (44), 47 (24), 44 (66), 43 (47), 42 (13), 41 (56). ***Anal.*** Calcd for $C_{17}H_{13}NO_2S$: C, 69,13; H, 4.56; N, 4.74. Found: C, 69.06; H, 4.56; N, 4.99.

Crystal data of **7a**: lemon yellow block crystal ($C_{17}H_{13}NO_2S$ = 295.36, 0.10 x 0.10 x 0.45 mm^3), triclinic, space group = P1 (#2), Z = 4, a = 5.9332 (6) Å, b = 13.238 (3) Å, c = 18.509 (3) Å, V = 1451.7 (4) $Å^3$, α = 87.778 (4)°, β = 87.886 (1)°, γ = 89.723 (2)°, $D_{(calcd)}$ = 1.35 g/cm^3, μ (MoKα) = 2.26 cm^{-1}, F (000) = 616.00, Reflection = 12645, Residuals = 0.054 (R1), 0.092 (R), 0.170 (Rw).

4-Methylsulfanyl-3-(4-methoxyphenyl)-6-pyrid-2-yl-2*H*-pyran-2-one (**7b**)

This compound (0.39 g, 1.2 mmol) was prepared in 46% yield from 1.13 g (5.0 mmol) of **4** and 0.88 g (6.0 mmol) of *p*-methoxyphenylacetonitrile (**5b**) in a manner similar to that described for the synthesis of **7a**. An analytical sample was recrystallized from MeOH to give yellow leaflets, mp 217-218˚C. IR (KBr) ν cm^{-1}: 1700 (C=O), 1620, 1580, 1560, 1490, 1465, 1430, 1365, 1335, 1290, 1245, 1175, 1070; UV (EtOH) λ_{max} nm (log ε): 371 (4.12), 308 (4.11), 256 (4.20); UV (CH_2Cl_2) λ_{max} nm (log ε): 255 (4.71), 360 (4.48) ; Fl (EtOH): Ex 279 nm; Em 462 nm; ϕ = 0.02; Fl (CH_2Cl_2): no fluorescence; Fl (solid): Ex 349, Em 503 nm, RI = 1.49; ^{1}H-NMR ($CDCl_3$) δ: 2.53 (3H, s, SMe), 3.85 (3H, s, OMe), 7.00 (2H, d, J = 8.8 Hz, 3’, 5’-H), 7.32-7.49 (3H, m, 2’, 6’, 5’’-H), 7.54 (1H, s, 5-H), 7.84 (1H, ddd, J = 1.8, 7.8, 8.0 Hz,

4”-H), 8.09 (1H, ddd, J = 0.9, 1.2, 8.0 Hz, 3”-H), 8.66 (1H, ddd, J = 0.9 1.8, 4.8 Hz, 6”-H); ^{13}C-NMR ($CDCl_3$) δ: 15.2 (SMe), 55.2 (OMe), 159.6 (2), 137.2 (3), 120.5 (4), 100.4 (5), 155.7 (6), 156.4 (1’), 149.7 (3’), 124.9 (4’), 148.7 (5’), 120.7 (6’), 125.6 (1”), 131.2 (2”, 6”), 114.0 (3”, 5”), 159.9 (4”); Ms *m/z* : 326 (M^++1, 16), 325 (M^+, 72), 297 (36), 282 (14), 278 (18), 191 (14), 78 (29), 57 (12), 55 (12), 45 (12), 44 (100), 43 (32). *Anal.* Calcd for $C_{18}H_{15}NSO_3$: C, 66.44; H, 4.65; N, 4.30. Found: C, 66.42; H, 4.64; N, 4.21.

3-(3,4-Dimethoxyphenyl)-4-methylsulfanyl-6-pyrid-2-yl-2*H*-pyran-2-one (**7c**)

This compound (0.69 g, 2.0 mmol) was prepared in 39% yield from 1.13 g (5.0 mmol) of **4** and 0.88 g (6.0 mmol) of 3,4-dimethoxyphenylacetonitrile (**5c**) in a manner similar to that described for the synthesis of **7a**. In this case, the reaction product was a separable mixture of **7c** and 2-(1-cyano-6,7-dimethoxy-2-methylsulfanyl-4-naphthyl)pyridine (**8**), which separated to give the products 7c and 8 through recrystallization using MeOH. **8** was more soluble than **7c** in MeOH. An analytical sample was recrystallized from MeOH to give yellow needles, mp 164-166°C. IR (KBr) ν cm^{-1}: 1730 (C = O), 1640, 1620, 1590, 1540, 1515, 1480, 1450, 1420, 1380, 1355, 1330, 1280, 1230, 1180, 1160, 1110, 1085, 1045; UV (EtOH) λ_{max} nm (log ε): 369 (4.13), 334 (4.00), 315 (4.17), 305 (4.19), 297 (4.17), 255 (4.31), 244 (4.32); UV (CH_2Cl_2) λ_{max} nm (log ε): 249 (4.62) 369 (4.37) ; Fl (EtOH): Ex 284 nm; Em 435 nm; ϕ = 0.15; Fl (CH_2Cl_2): no fluorescence; Fl (solid): Ex 340, Em 529 nm, RI = 0.25; ^{1}H-NMR ($CDCl_3$) δ: 2.53 (3H, s, SMe), 3.90 (3H, s, OMe), 3.92 (3H, s, OMe) 6.96 (1H, dd, J = 1.9, 8.2 Hz, 6’-H), 6.98 (1H, d, J = 8.2 Hz, 5’-H), 6.99 (1H, dd, J = 1.9 Hz, 2’-H), 7.37 (1H, dd, J = 1.1, 4.8, 7.8 Hz, 5”-H), 7.55 (1H, s, 5-H), 7.85 (1H, ddd, J = 1.8, 7.8, 8.0 Hz, 4”-H), 8.09 (1H, ddd, J = 0.9, 1.1, 8.0 Hz, 3”-H), 8.67 (1H, ddd, J = 0.9, 1.8, 4.8 Hz, 6”-H); MS *m/z*: 356 (M^++1, 8), 355 (M^+, 30), 327 (10), 83 (10), 78 (18), 71 (10), 69 (12), 57 (18), 55 (16), 45 (12), 44 (100), 43 (24). *Anal.* Calcd for $C_{19}H_{17}NO_4S$: C, 64.21; H, 4.82; N, 3.94. Found: C, 64.47; H, 4.91; N, 4.17.

2-(1-Cyano-6,7-dimethoxy-2-methylsulfanyl-4-naphthyl)pyridine (**8**).

A analytical sample was recrystallized from MeOH to give colorless needles, mp 163-164°C; IR (KBr) ν cm^{-1}: 2210 (CN), 1590, 1500, 1260; UV (EtOH) λ_{max} nm (log ε): 242 (4.65), 267 (4.34), 336 (3.93), 371 (4.01); ^{1}H-NMR ($CDCl_3$) δ: 2,66 (3H, s, SMe), 3.85 (3H, s, OMe), 4.08 (3H, s, OMe), 7.38 (1H, s, 5’-H), 7.41 (1H, s, 6’-H), 7.43 (1H, m, 5-H), 7.48 (1H, s, 2’-H), 7.60 (1H, near d, J = 7.7 Hz, 3-H), 7.90 (1H, ddd, J = 1.8, 6.7, 7.7 Hz, Hz, 4-H), 8.83 (1H, near d, J = 5.9 Hz, 6-H); MS *m/z* : 337 (M^++1, 20), 356 (M^+, 100), 321 (39), 256 (16), 95 (23). *Anal.* Calcd for $C_{19}H_{16}N_2O_2S$: C, 67.84; H, 4.79; N, 8.33. Found: C, 67.57; H, 4.88; N, 8.12.

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