Synthesis and Characterization of Fluorescent 4,6-Disubstituted-3-cyano-2-methylpyridines

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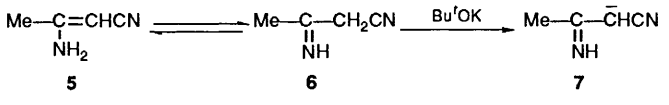
4,6-Disubstituted-3-cyano-2-methylpyridines, easily prepared by treating α,β-unsaturated carbonyl compounds with β-aminocrotononitrile in the presence of potassium *tert*-butoxide, have been found to show intense fluorescence in the region of 400–552 nm. 3-Cyano-4,6-bis(4-methoxyphenyl)- and 3-cyano-4,6-di(2-furyl)-2-methylpyridines show more intense fluorescence than 7-diethylamino-4-methylcoumarin. The 3-cyano group of pyridines increases the fluorescence intensities and improves photostabilities.

Many aromatic compounds containing two non-fused rings such as 2-stilbazoles,[1] and thienylpyridines [2] have been reported to show fluorescence. In the course of our study on the synthesis of pyridines,[3] some 4,6-disubstituted-3-cyano-2-methylpyridines were found to be intensely fluorescent compounds. This report describes the synthesis, fluorescence, and photostabilities of 4,6-disubstituted-3-cyano-2-methylpyridines.

Results and Discussion

α,β-Unsaturated carbonyl compounds **1**, prepared by an aldol condensation of methylketones with aldehydes, were reacted with β-aminocrotononitrile in the presence of potassium *tert*-butoxide at room temperature to give 3-cyano-2-methylpyridines **2**. The products gave satisfactory spectral data consistent with the structures.



5 **6** **7**

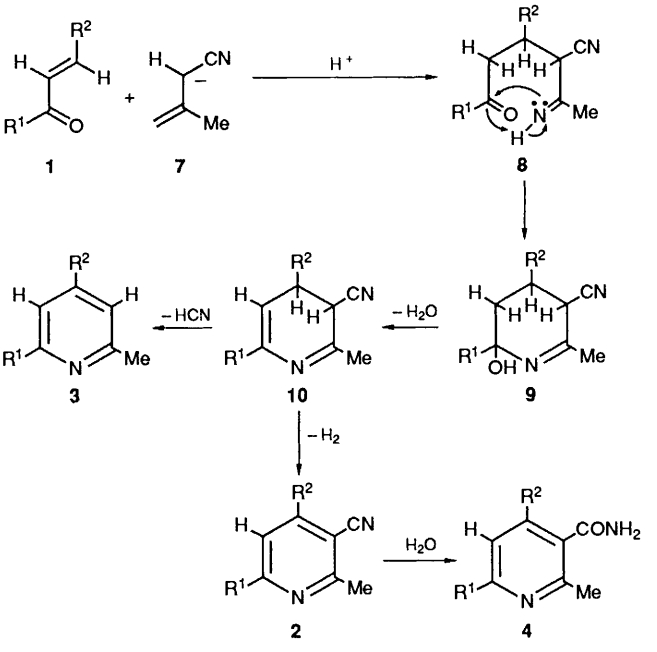
4,6-Bis(4-methoxyphenyl)- and 4,6-di(2-furyl)-2-methyl-pyridines **3k** and **3t** were obtained by treating **1** with β-aminocrotononitrile in the presence of sodium hydroxide at 120–130 °C under Ar atmosphere, together with the corresponding 4,6-disubstituted 2-methylpyridine-3-carboxamides **4**. Their structures were confirmed by NMR and mass spectral data.

Table 1 summarizes the yields of **1** and **2**. The products were obtained in moderate to good yields except in the cases of **1e** and **2e**. Thus, this method is useful and convenient for preparing 3-cyano-2-methylpyridines.

Scheme 1 shows a probable mechanism for the formation of **2** and **3**. β-Aminocrotononitrile can exist as amino (**5**) and imino isomers (**6**) in solution. A Michael addition of the carbanion of the imino isomer **7** to **1**, followed by intramolecular cyclization and dehydration, can give the key intermediate **10**. At room temperature, dehydrogenation of **10** can give **2**. Under severe conditions (120–130 °C), not only the dehydrogenation process of **10** followed by the hydrolysis of the cyano moiety but also the elimination of hydrogen cyanide from **10** can proceed to afford **4** and **3**, respectively.

Fig 1. shows the fluorescence spectrum of 3-cyano-4,6-bis(4-methoxyphenyl)-2-methylpyridine (**2k**). The fluorescence excitation maximum (λ_{ex}) and emission maximum (λ_{em}) were observed at 335 and 400 nm, respectively.

Table 2 summarizes the absorption and fluorescence spectra of **2** and **3**. 4- And/or 6-[4-(dimethylamino)phenyl]pyridines



Scheme 1

2a–m showed absorption maxima (λ_{max}) at 290–406 nm, and pyridines **2n–dd** at 258–334 nm. Thus the feature of λ_{max} of **2** could be classified into two groups. The λ_{max} of 3-unsubstituted pyridines **3k** and **3t** showed small hypochromic shifts (60 and 13 nm) compared with the 3-cyanopyridines **2k** and **2t**. The λ_{em} of **2a–m** were observed at longer wavelength (455–552 nm) than **2n–dd** (400–455 nm). The λ_{em} of **3k** and **3t** also showed hypochromic shifts (25 and 20 nm) compared with **2k** and **2t**.

ε Values of **2** were calculated to be *ca.* 30 000 except for bulky 6-(1-naphthyl)pyridines **2n–p** (ε = 12 000–23 600).

Fluorescence intensities of **2** and **3** were compared with 7-diethylamino-4-methylcoumarin, a standard fluorescence dye (λ_{max}: 370 nm, ε: 23 800; λ_{ex}: 378 nm, λ_{em}: 445 nm, in ethanol). Pyridines whose 4- and/or 6-positions were substituted with electron-releasing phenyl groups and/or π-sufficient heteroaromatics showed stronger fluorescence intensities. In particular, **2k** and **2t** had stronger fluorescence intensities than 7-diethylamino-4-methyl-coumarin. Besides, relative fluorescence intensities (RFI) of **2k** and **2t** were stronger than those of **3k** and **3t**, suggesting that the introduction of a cyano group at the 3-position of pyridines (**2**) was effective for the increase of fluorescence intensities.

Table 1 Syntheses of α,β-unsaturated carbonyl compounds (**1**) and 3-cyano-2-methylpyridines (**2**)

Compound	Substituent		Isolated yield (%)	
	R^1	R^2	**1**	**2**
a	4-$Me_2NC_6H_4$	C_6H_5	48	60
b	4-$Me_2NC_6H_4$	4-$CF_3C_6H_4$	44	71
c	4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4$	34	75
d	4-$Me_2NC_6H_4$	4-$MeOC_6H_4$	82	68
e	4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4CH$=CH	9	8
f	4-$Me_2NC_6H_4$	2-Furyl	75	70
g	4-$Me_2NC_6H_4$	2-Thienyl	81	72
h	4-$Me_2NC_6H_4$	2-Pyridyl	68	48
i	C_6H_5	4-$Me_2NC_6H_4$	20	81
j	4-$MeOC_6H_4$	4-$Me_2NC_6H_4$	39	91
k	4-$MeOC_6H_4$	4-$MeOC_6H_4$	67	82
l	4-$MeOC_6H_4$	2-Furyl	52	59
m	4-$Me_2NC_6H_4CH$=CH	4-$Me_2NC_6H_4$	26	32
n	1-Naphthyl	2-Furyl	60	47
o	1-Naphthyl	2-Thienyl	24	60
p	1-Naphthyl	1-Naphthyl	89	81
q	2-Furyl	4-$Me_2NC_6H_4$	33	40
r	2-Furyl	4-$MeOC_6H_4$	39	93
s	2-Furyl	1-Naphthyl	23	68
t	2-Furyl	2-Furyl	88	93
u	2-Furyl	2-Thienyl	73	74
v	2-Furyl	2-Pyrrolyl	82	63
w	2-Thienyl	4-$Me_2NC_6H_4$	63	97
x	2-Thienyl	1-Naphthyl	74	77
y	2-Thienyl	2-Furyl	72	70
z	2-Thienyl	2-Thienyl	65	86
aa	2-Thienyl	2-Pyrrolyl	68	74
bb	2-Pyridyl	4-$Me_2NC_6H_4$	60	70
cc	2-Pyridyl	4-$MeOC_6H_4$	25	37
dd	2-Pyridyl	2-Furyl	75	65

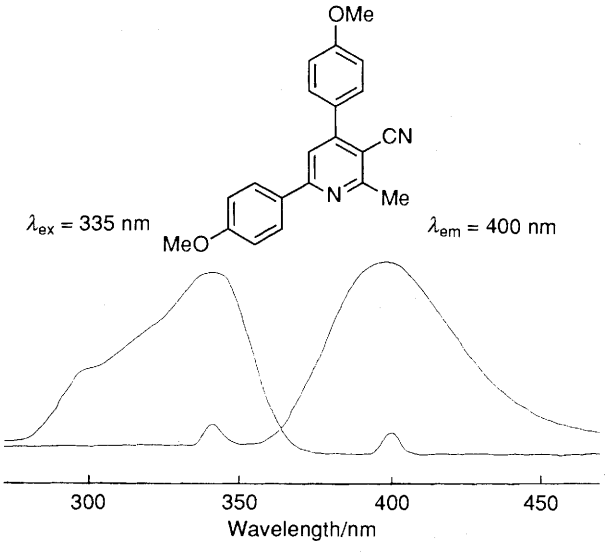


Fig. 1 Fluorescence spectrum of 3-cyano-4,6-bis(4-methoxyphenyl)-2-methylpyridine (**2k**)

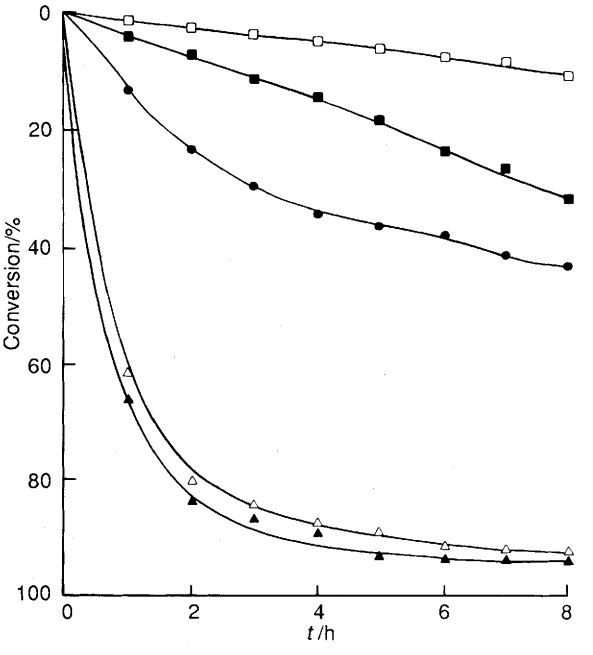


Fig. 2 Photostabilities of fluorescent pyridines. A methanol solution (50 cm^3) of the substrate (0.044 mmol dm^{-1}) in a borosilicate glass tube was irradiated with a 200 W high pressure mercury lamp under air atmosphere at room temperature. □: **2k**; ■: **3k**; ●: 7-Diethylamino-4-methylcoumarin; △: **2t**; ▲: **3t**.

Fig. 2 shows the photostabilities of **2k**, **3k**, **2t**, **3t** and 7-diethylamino-4-methylcoumarin. The stability was in the following order of compounds: **3t** < **2t** ≪ 7-diethylamino-4-methylcoumarin ≪ **3k** < **2k**. Furans are known to be easily oxidized to give hydroperoxides by UV irradiation under air atmosphere.[4] 7-Diethylamino-4-methylcoumarin has been reported to dimerize and oxidize under UV irradiation.[5,6] Therefore, 4-methoxyphenyl derivatives **2k** and **3k** could be most stable among them. Besides, the introduction of a 3-cyano group into pyridines **2** was effective in improving the photostabilities.

Experimental

NMR spectra ($CDCl_3$ solution) were taken on a JEOL JNM-270 GX spectrometer and mass spectra (70 eV) on a Shimadzu 9020-DF spectrometer. *J* Values are in Hz. IR spectra (KBr disk) were recorded on a Perkin-Elmer FT-IR 1640 spectrophotometer, UV spectra on a Hitachi 330, and fluorescence

Table 2 Absorption and fluorescent spectral data of **2** and **3**[a]

Compound	Substituent R[1]	Substituent R[2]	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}	λ_{ex}/nm	λ_{em}/nm	RFI[b]
2a	4-$Me_2NC_6H_4$	C_6H_5	380	32 800	385	520	0.192
2b	4-$Me_2NC_6H_4$	4-$CF_3C_6H_4$	384	30 400	397	545	0.010
2c	4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4$	378	38 200	396	495	0.352
2d	4-$Me_2NC_6H_4$	4-$MeOC_6H_4$	377	30 800	394	510	0.460
2e	4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4CH{=}CH$	387	20 100	420	545	0.022
2f	4-$Me_2NC_6H_4$	2-Furyl	392	30 300	397	545	0.126
2g	4-$Me_2NC_6H_4$	2-Thienyl	390	30 700	400	531	0.041
2h	4-$Me_2NC_6H_4$	2-Pyridyl	388	27 600	398	548	0.005
2i	C_6H_5	4-$Me_2NC_6H_4$	290	30 000	380	535	0.012
2j	4-$MeOC_6H_4$	4-$Me_2NC_6H_4$	304	27 600	330	525	0.032
2k	4-$MeOC_6H_4$	4-$MeOC_6H_4$	326	28 000	335	400	1.203
3k	4-$MeOC_6H_4$	4-$MeOC_6H_4$	266	30 000	292	375	0.355
2l	4-$MeOC_6H_4$	2-Furyl	283	25 600	248	415	0.752
2m	4-$Me_2NC_6H_4CH{=}CH$	4-$Me_2NC_6H_4$	406	28 800	423	552	0.135
2n	1-Naphthyl	2-Furyl	330	23 600	338	418	0.344
2o	1-Naphthyl	2-Thienyl	321	17 200	335	427	0.097
2p	1-Naphthyl	1-Naphthyl	280	12 000	330	417	0.097
2q	2-Furyl	4-$Me_2NC_6H_4$	317	29 600	335	535	0.005
2r	2-Furyl	4-$MeOC_6H_4$	334	26 800	341	402	0.848
2s	2-Furyl	1-Naphthyl	258	29 600	339	415	0.063
2t	2-Furyl	2-Furyl	289	42 000	295	405	1.240
3t	2-Furyl	2-Furyl	276	39 200	290	385	0.643
2u	2-Furyl	2-Thienyl	291	21 200	347	418	0.437
2v	2-Furyl	2-Pyrrolyl	296	31 200	305	450	0.182
2w	2-Thienyl	4-$Me_2NC_6H_4$	316	30 000	345	540	0.054
2x	2-Thienyl	1-Naphthyl	270	22 800	340	405	0.034
2y	2-Thienyl	2-Furyl	293	35 600	350	400	0.741
2z	2-Thienyl	2-Thienyl	293	28 000	350	405	0.485
2aa	2-Thienyl	2-Pyrrolyl	299	30 000	307	455	0.126
2bb	2-Pyridyl	4-$Me_2NC_6H_4$	295	31 200	308	455	0.004
2cc	2-Pyridyl	4-$MeOC_6H_4$	283	24 800	305	440	0.323
2dd	2-Pyridyl	2-Furyl	283	28 400	293	420	0.298

[a] Measured in EtOH at 25 °C. [b] Relative fluorescence intensity (1×10^{-6} mol dm^{-3}, 7-diethylamino-4-methylcoumarin = 1.000).

spectra on a Hitachi 650-10S spectrophotometer. M.p.s were measured with a Yanagimoto micro melting point apparatus and are uncorrected.

Synthesis of α,β-*Unsaturated Carbonyl Compounds* **1**.—In a general procedure, to an ethanol solution (20 cm^3) of methyl ketone (10 mmol) and aldehyde (10 mmol), was added 10% aqueous sodium hydroxide solution (5 cm^3). The mixture was stirred overnight at room temperature. After the reaction, the precipitate was filtered and recrystallized from ethanol. Physical and spectral data of α,β-unsaturated carbonyl compounds **1** are shown below.

1-[4-(Dimethylamino)phenyl)]-3-phenylprop-2-en-1-one **1a**: m.p. 173.0–174.0 °C (lit.,[7] 165–167 °C); δ_H 3.09 (6 H, s), 6.71 (2 H, d, *J* 8.9), 7.39–7.41 (3 H, m), 7.59 (1 H, d, *J* 15.9), 7.62–7.66 (2 H, m), 7.79 (1 H, d, *J* 15.9) and 8.01 (2 H, d, *J* 8.9); *m*/*z* 251 (M$^+$, 100%).

1-[4-(Dimethylamino)phenyl]-3-[4-(trifluoromethyl)phenyl]-prop-2-en-1-one **1b**: m.p. 158.5–160.0 °C (Found: C, 67.7; H, 4.9; N, 4.35. $C_{18}H_{16}F_3NO$ requires C, 67.70; H, 5.05; N, 4.39%); δ_H 3.10 (6 H, s), 6.65 (2 H, d, *J* 9.4), 7.70 (6 H, s) and 8.02 (2 H, d, *J* 9.4); *m*/*z* 319 (M$^+$, 100%).

1,3-Bis[4-(dimethylamino)phenyl]prop-2-en-1-one **1c**: m.p. 158.0–160.0 °C (lit.,[8] 157 °C); δ_H 3.03 (6 H, s), 3.07 (6 H, s), 6.70 (2 H, d, *J* 8.8), 6.71 (2 H, d, *J* 9.2), 7.41 (1 H, d, *J* 15.6), 7.55 (2 H, d, *J* 9.2), 7.77 (1 H, d, *J* 15.6) and 8.01 (2 H, d, *J* 8.8); *m*/*z* 294 (M$^+$, 100%).

1-[4-(Dimethylamino)phenyl]-3-(4-methoxyphenyl)prop-2-en-1-one **1d**: m.p. 123.0–125.0 °C (Found: C, 77.0; H, 6.6; N, 4.9. $C_{18}H_{19}NO_2$ requires C, 76.84; H, 6.81; N, 4.98%); δ_H 3.07 (6 H, s), 3.85 (3 H, s), 6.70 (2 H, d, *J* 9.2), 6.93 (2 H, d, *J* 8.5), 7.47 (1 H, d, *J* 15.9), 7.60 (2 H, d, *J* 8.5), 7.76 (1 H, d, *J* 15.9) and 8.00 (2 H, d, *J* 9.2); *m*/*z* 281 (M$^+$, 100%).

1,5-Bis[4-(dimethylamino)phenyl]penta-2,4-dien-1-one **1e**: m.p. 157.0–160.0 °C (lit.,[9] 158 °C); δ_H 3.01 (3 H, s), 3.07 (6 H, s), 6.68 (2 H, d, *J* 9.2), 6.69 (2 H, d, *J* 9.2), 6.87 (1 H, d, *J* 12.8), 7.05 (1 H, d, *J* 12.8), 7.39 (2 H, d, *J* 9.2), 7.58 (1 H, d, *J* 14.6), 7.62 (1 H, d, *J* 14.6) and 7.96 (2 H, d, *J* 9.2); *m*/*z* 320 (M$^+$, 100%).

1-[4-(Dimethylamino)phenyl]-3-(2-furyl)prop-2-en-1-one **1f**: m.p. 195.0–196.5 °C (Found: C, 74.5; H, 6.2; N, 5.8. $C_{15}H_{15}NO_2$ requires C, 74.67; H, 6.27; N, 5.81%); δ_H 3.08 (6 H, s), 6.49 (1 H, dd, *J* 3.4 and 1.8), 6.65 (1 H, d, *J* 3.4), 6.70 (2 H, d, *J* 9.2), 7.50 (1 H, d, *J* 15.3), 7.51 (1 H, d, *J* 1.8), 7.58 (1 H, d, *J* 15.3) and 8.01 (2 H, d, *J* 9.2); *m*/*z* 241 (M$^+$, 100%).

1-[4-(Dimethylamino)phenyl]-3-(2-thienyl)prop-2-en-1-one **1g**: m.p. 194.5–196.5 °C (Found: C, 69.75; H, 5.7; N, 5.45. $C_{15}H_{15}NOS$ requires C, 70.00; H, 5.88; N, 5.44%); δ_H 3.07 (6 H, s), 6.70 (2 H, d, *J* 9.2), 7.07 (1 H, dd, *J* 4.9 and 3.4), 7.31 (1 H, d, *J* 3.4), 7.37 (1 H, d, *J* 15.3), 7.39 (1 H, d, *J* 4.9), 7.91 (1 H, d, *J* 15.3) and 7.99 (2 H, d, *J* 9.2); *m*/*z* 257 (M$^+$, 100%).

1-[4-(Dimethylamino)phenyl]-3-(2-pyridyl)prop-2-en-1-one **1h**: m.p. 167.0–168.0 °C (Found: C, 76.05; H, 6.35; N, 11.05. $C_{16}H_{16}N_2O$ requires C, 76.17; H, 6.39; N, 11.10%); δ_H 3.09 (6 H, s), 6.70 (2 H, d, *J* 9.2), 7.27 (1 H, dd, *J* 6.7 and 4.8), 7.46 (1 H, d, *J* 7.5), 7.72 (1 H, dd, *J* 7.5 and 6.7), 7.75 (1 H, d, *J* 15.3), 8.08 (2 H, d, *J* 9.2), 8.16 (1 H, d, *J* 15.3) and 8.68 (1 H, d, *J* 4.8); *m*/*z* 252 (M$^+$, 63%) and 223 (100).

3-[4-(Dimethylamino)phenyl]-1-phenylprop-2-en-1-one **1i**: m.p. 113.0–114.0 °C (lit.,[10] 114–115 °C); δ_H 3.05 (6 H, s), 6.73 (2 H, d, *J* 8.6), 7.34 (1 H, d, *J* 15.6), 7.46–7.53 (3 H, m), 7.56 (2 H, d, *J* 8.6), 7.79 (1 H, d, *J* 15.9) and 7.98–8.01 (2 H, m); *m*/*z* 251 (M$^+$, 100%).

3-[4-(Dimethylamino)phenyl]-1-(4-methoxyphenyl)prop-2-en-1-one **1j**: m.p. 124.0–125.0 °C (Found: C, 77.0; H, 6.75; N, 4.85. $C_{18}H_{19}NO_2$ requires C, 76.84; H, 6.81; N, 4.98%); δ_H 3.04

(6 H, s), 3.89 (3 H, s), 6.70 (2 H, d, *J* 9.2), 6.97 (2 H, d, *J* 8.9), 7.35 (1 H, d, *J* 15.3), 7.55 (2 H, d, *J* 9.2), 7.79 (1 H, d, *J* 15.3) and 8.03 (2 H, d, *J* 8.9); *m/z* 281 (M^+, 100%).

1,3-Bis(4-methoxyphenyl)prop-2-en-1-one **1k**: m.p. 102.0–104.0 °C (lit.,[11] 100 °C); δ_H 3.85 (3 H, s), 3.89 (3 H, s), 6.93 (2 H, d, *J* 9.2), 6.98 (2 H, d, *J* 8.6), 7.43 (1 H, d, *J* 15.6), 7.60 (2 H, d, *J* 8.6), 7.78 (1 H, d, *J* 15.6) and 8.05 (2 H, d, *J* 9.2); *m/z* 268 (M^+, 100%).

3-(2-Furyl)-1-(4-methoxyphenyl)prop-2-en-1-one **1l**: m.p. 78.0–80.0 °C (Found: C, 73.7; H, 5.35. $C_{14}H_{12}O_3$ requires C, 73.67; H, 5.30%); δ_H 3.87 (3 H, s), 6.50 (1 H, dd, *J* 3.4 and 1.8), 6.69 (1 H, d, *J* 3.4), 6.87 (2 H, d, *J* 9.2), 7.46 (1 H, d, *J* 15.3), 7.52 (1 H, d, *J* 1.8), 7.59 (1 H, d, *J* 15.3) and 8.04 (2 H, d, *J* 9.2); *m/z* 228 (M^+, 100%).

1,5-Bis[4-(dimethylamino)phenyl]penta-1,4-diene-3-one **1m**: m.p. 199.0–200.0 °C (Found: C, 78.55; H, 7.3; N, 8.5. $C_{21}H_{24}N_2O$ requires C, 78.72; H, 7.55; N, 8.74%); δ_H 3.04 (12 H, s), 6.70 (4 H, d, *J* 9.0), 6.89 (2 H, d, *J* 15.8), 7.40 (4 H, d, *J* 9.0), 7.69 (2 H, d, *J* 15.8); *m/z* 320 (M^+, 100%).

3-(2-Furyl)-1-(1-naphthyl)prop-2-en-1-one **1n**: m.p. oil (lit.,[12] oil); δ_H 6.45 (1 H, dd, *J* 3.4 and 1.8), 6.63 (1 H, d, *J* 3.4), 7.20 (1 H, d, *J* 15.6), 7.38 (1 H, d, *J* 15.6), 7.46–7.96 (7 H, m) and 8.37 (1 H, d, *J* 1.8); *m/z* 248 (M^+, 100%).

1-(1-Naphthyl)-3-(2-thienyl)prop-2-en-1-one **1o**: m.p. 64.0–65.0 °C (lit.,[13] 68 °C); δ_H 7.08 (1 H, dd, *J* 4.9 and 3.7), 7.11 (1 H, d, *J* 15.9), 7.29 (1 H, d, *J* 3.7), 7.43 (1 H, d, *J* 4.9), 7.51–8.33 (7 H, m) and 7.73 (1 H, d, *J* 15.9); *m/z* 264 (M^+, 92%) and 127 (100).

1,3-Di(1-naphthyl)prop-2-en-1-one **1p**: m.p. 70.0–72.0 °C; (Found: C, 89.3; H, 5.5. $C_{23}H_{16}O$ requires C, 89.58; H, 5.23%); δ_H 7.41 (1 H, d, *J* 15.8), 7.48–7.62 (6 H, m), 7.85–7.95 (4 H, m), 8.01–8.11 (2 H, m), 8.42–8.45 (2 H, m) and 8.50 (1 H, d, *J* 15.8); *m/z* 308 (M^+, 100%).

3-[4-(Dimethylamino)phenyl]-1-(2-furyl)prop-2-en-1-one **1q**: m.p. 93.5–95.0 °C (Found: C, 74.35; H, 6.25; N, 5.85. $C_{15}H_{15}O_2N$ requires C, 74.67; H, 6.27; N, 5.81%); δ_H 3.04 (6 H, s), 6.57 (1 H, dd, *J* 3.4 and 1.8), 6.69 (2 H, d, *J* 8.9), 7.26 (1 H, d, *J* 15.3), 7.28 (1 H, d, *J* 3.4), 7.55 (2 H, d, *J* 8.9), 7.62 (1 H, d, *J* 1.8) and 7.86 (1 H, d, *J* 15.3); *m/z* 241 (M^+, 100%).

1-(2-Furyl)-3-(4-methoxyphenyl)prop-2-en-1-one **1r**: m.p. 79.0–80.0 °C (lit.,[14] 81–82 °C); δ_H 3.86 (3 H, s), 6.59 (1 H, dd, *J* 3.7 and 1.8), 6.94 (2 H, d, *J* 8.8), 7.31 (1 H, d, *J* 3.7), 7.34 (1 H, d, *J* 15.6), 7.62 (2 H, d, *J* 8.8), 7.65 (1 H, d, *J* 1.8) and 7.86 (1 H, d, *J* 15.6); *m/z* 228 (M^+, 100%).

1-(2-Furyl)-3-(1-naphthyl)prop-2-en-1-one **1s**: m.p. 96.0–98.0 °C (Found: C, 82.15; H, 4.75. $C_{17}H_{12}O_2$ requires C, 82.24; H, 4.87%); δ_H 6.62 (1 H, dd, *J* 3.4 and 1.7), 7.37 (1 H, d, *J* 3.4), 7.55 (1 H, d, *J* 15.6), 7.91 (1 H, d, *J* 1.7), 8.74 (1 H, d, *J* 15.6) and 7.38–8.31 (7 H, m); *m/z* 248 (M^+, 100%).

1,3-Di(2-furyl)prop-2-en-1-one **1t**: m.p. 88.0–89.0 °C (lit.,[15] 88–89 °C); δ_H 6.51 (1 H, dd, *J* 3.3 and 1.8), 6.58 (1 H, dd, *J* 3.3 and 1.8), 6.71 (1 H, d, *J* 3.3), 7.31 (1 H, d, *J* 3.3), 7.32 (1 H, d, *J* 15.6), 7.52 (1 H, d, *J* 1.8), 7.63 (1 H, d, *J* 15.6) and 7.64 (1 H, d, *J* 1.8); *m/z* 188 (M^+, 76%) and 95 (100).

1-(2-Furyl)-3-(2-thienyl)prop-2-en-1-one **1u**: m.p. 78.0–79.0 °C (lit.,[15] 81–82 °C); δ_H 6.59 (1 H, dd, *J* 3.7 and 1.5), 7.09 (1 H, dd, *J* 5.2 and 3.7), 7.23 (1 H, d, *J* 15.3), 7.32 (1 H, d, *J* 3.7), 7.37 (1 H, d, *J* 3.7), 7.43 (1 H, d, *J* 5.2), 7.65 (1 H, d, *J* 1.5) and 7.99 (1 H, d, *J* 15.3); *m/z* 204 (M^+, 96%) and 147 (100).

1-(2-Furyl)-3-(2-pyrrolyl)prop-2-en-1-one **1v**: m.p. 182.0–183.0 °C (Found: C, 70.55; H, 4.6; N, 7.2. $C_{11}H_9NO_2$ requires C, 70.58; H, 4.85; N, 7.48%); δ_H 6.33 (1 H, dd, *J* 2.5 and 2.1), 6.57 (1 H, dd, *J* 1.7 and 1.7), 6.72 (1 H, d, *J* 2.5), 7.00 (1 H, d, *J* 2.1), 7.06 (1 H, d, *J* 15.7), 7.27 (1 H, d, *J* 1.7), 7.61 (1 H, d, *J* 1.7), 7.80 (1 H, d, *J* 15.7) and 8.99 (1 H, br s); *m/z* 187 (M^+, 100%).

3-[4-(Dimethylamino)phenyl]-1-(2-thienyl)prop-2-en-1-one **1w**: m.p. 116.0–117.0 °C (Found: C, 69.85; H, 5.9; N, 5.4. $C_{15}H_{15}NOS$ requires C, 70.00; H, 5.88; N, 5.44%); δ_H 3.04 (6 H, s), 6.69 (2 H, d, *J* 8.9), 7.16 (1 H, dd, *J* 4.9 and 3.7), 7.23 (1 H, d, *J* 15.3), 7.55 (2 H, d, *J* 8.9), 7.62 (1 H, dd, *J* 4.9 and 1.2), 7.82 (1 H, dd, *J* 3.7 and 1.2) and 7.83 (1 H, d, *J* 15.3); *m/z* 257 (M^+, 100%).

3-(1-Naphthyl)-1-(2-thienyl)prop-2-en-1-one **1x**: m.p. 85.0–86.0 °C (Found: C, 77.1; H, 4.55. $C_{17}H_{12}OS$ requires C, 77.24; H, 4.58%); δ_H 7.18 (1 H, dd, *J* 5.1 and 3.7), 7.46–7.61 (2 H, m), 7.49 (1 H, d, *J* 15.4), 7.51 (1 H, d, *J* 3.7), 7.68 (1 H, d, *J* 5.1), 7.86–7.92 (4 H, m), 8.23–8.26 (1 H, m) and 8.68 (1 H, d, *J* 15.4); *m/z* 264 (M^+, 69%) and 112 (100).

3-(2-Furyl)-1-(2-thienyl)prop-2-en-1-one **1y**: m.p. 71.0–72.0 °C (lit.,[16] 70.8–71.6 °C); δ_H 6.51 (1 H, dd, *J* 3.1 and 1.8), 6.72 (1 H, d, *J* 3.1), 7.17 (1 H, dd, *J* 4.9 and 3.7), 7.33 (1 H, d, *J* 15.3), 7.53 (1 H, d, *J* 1.8), 7.60 (1 H, d, *J* 15.3), 7.67 (1 H, dd, *J* 4.9 and 1.2) and 7.85 (1 H, dd, *J* 3.7 and 1.2); *m/z* 204 (M^+, 85%) and 111 (100).

1,3-Di(2-thienyl)prop-2-en-1-one **1z**: m.p. 99.0–100.0 °C (lit.,[16] 99.2–99.8 °C); δ_H 7.09 (1 H, dd, *J* 5.5 and 3.7), 7.18 (1 H, dd, *J* 4.9 and 3.7), 7.21 (1 H, d, *J* 15.3), 7.36 (1 H, d, *J* 3.7), 7.42 (1 H, d, *J* 5.5), 7.67 (1 H, d, *J* 4.9), 7.84 (1 H, d, *J* 3.7) and 7.96 (1 H, d, *J* 15.3); *m/z* 220 (M^+, 100%).

3-(2-Pyrrolyl)-1-(2-thienyl)prop-2-en-1-one **1aa**: m.p. 159.0–160.0 °C (lit.,[17] 158–160 °C); δ_H 6.34 (1 H, dd, *J* 3.4 and 2.4), 6.73 (1 H, d, *J* 3.7), 7.00 (1 H, d, *J* 2.4), 7.03 (1 H, d, *J* 15.3), 7.16 (1 H, dd, *J* 4.9 and 3.4), 7.64 (1 H, dd, *J* 4.9 and 1.2), 7.77 (1 H, d, *J* 15.3), 7.81 (1 H, dd, *J* 3.4 and 1.2) and 8.86 (1 H, br s); *m/z* 203 (M^+, 100%).

3-[4-(Dimethylamino)phenyl]-1-(2-pyridyl)prop-2-en-1-one **1bb**: m.p. 138.0–139.0 °C (Found: C, 76.05; H, 6.35, N, 11.0. $C_{16}H_{16}N_2O$ requires C, 76.17; H, 6.39; N, 11.10%); δ_H 3.03 (6 H, s), 6.68 (2 H, d, *J* 9.0), 7.64 (2 H, d, *J* 9.0) and 7.43–8.80 (6 H, m); *m/z* 252 (M^+, 100%).

3-(4-Methoxyphenyl)-1-(2-pyridyl)prop-2-en-1-one **1cc**: m.p. 203.0–205.0 °C (lit.,[18] 185–186 °C); δ_H 3.61 (3 H, s), 6.24 (1 H, d, *J* 12.8), 6.65 (2 H, d, *J* 8.6), 6.87 (1 H, dd, *J* 6.1 and 5.5), 7.22 (1 H, d, *J* 12.8), 7.45 (1 H, dd, *J* 7.9 and 6.1), 7.64 (1 H, d, *J* 7.9), 7.89 (2 H, d, *J* 8.6) and 8.48 (1 H, d, *J* 5.5); *m/z* 239 (M^+, 100%).

3-(2-Furyl)-1-(2-pyridyl)prop-2-en-1-one **1dd**: m.p. 49.0–51.0 °C (lit.[18] 53–54 °C); δ_H 6.52 (1 H, dd, *J* 3.7 and 1.8), 6.78 (1 H, d, *J* 3.7), 7.48 (1 H, dd, *J* 5.8 and 4.9), 7.55 (1 H, d, *J* 1.8), 7.70 (1 H, d, *J* 15.9), 7.87 (1 H, dd, *J* 7.3 and 5.8), 8.14 (1 H, d, *J* 15.9), 8.17 (1 H, d, *J* 7.3) and 8.74 (1 H, d, *J* 4.9); *m/z* 199 (M^+, 100%).

Synthesis of 4,6-*Disubstituted*-3-*cyano*-2-*methylpyridines* **2**.—In a general procedure, an acetonitrile suspension (50 cm^3) containing an α,β-unsaturated compound (1.0 mmol), β-aminocrotononitrile (1.2 mmol), and potassium *tert*-butoxide (5.0 mmol) was stirred overnight at room temperature. After filtration, the filtrate was extracted with diethyl ether (3 × 25 cm^3) and dried over sodium sulfate. After the evaporation of the solvent, the residue was recrystallized from ethanol. Physical and spectral data of 3-cyano-2-methylpyridines **2** are shown below.

3-Cyano-6-[4-(dimethylamino)phenyl]-2-methyl-4-phenylpyridine **2a**: m.p. 150.0–152.0 °C (Found: C, 80.3; H, 6.0; N, 13.25. $C_{21}H_{19}N_3$ requires C, 80.48; H, 6.11; N, 13.41%); δ_H 2.87 (3 H, s), 3.05 (6 H, s), 6.77 (2 H, d, *J* 9.2), 7.50–7.64 (6 H, m) and 8.02 (2 H, d, *J* 9.2); *m/z* 313 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2211 (C≡N).

3-Cyano-6-[4-(dimethylamino)phenyl]-2-methyl-4-[4-(trifluoromethyl)phenyl]pyridine **2b**: m.p. 190.0–192.5 °C (Found: C, 69.0; H, 4.7; N, 11.35%. $C_{22}H_{18}F_3N_3$ requires C, 69.28; H, 4.76; N, 11.02%); δ_H 2.89 (3 H, s), 3.07 (6 H, s), 6.84 (2 H, d, *J* 9.2), 7.55 (1 H, s), 7.73 (2 H, d, *J* 8.6), 7.80 (2 H, d, *J* 8.6) and 8.04 (2 H, d, *J* 9.2); *m/z* 381 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2214 (C≡N).

3-Cyano-4,6-bis[4-(dimethylamino)phenyl]-2-methylpyridine **2c**: m.p. 208.0–209.0 °C (Found: C, 77.7; H, 6.85; N, 16.0. $C_{23}H_{24}N_4$ requires C, 77.50; H, 6.79; N, 15.72%); δ_H 2.84 (3 H, s), 3.04 (12 H, s), 6.77 (2 H, d, *J* 8.2), 6.80 (2 H, d, *J* 7.9), 7.53 (1 H, s), 7.58 (2 H, d, *J* 7.9) and 8.00 (2 H, d, *J* 8.2); *m/z* 356 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2211 (C≡N).

3-Cyano-6-[4-(dimethylamino)phenyl]-4-(4-methoxyphenyl)-2-methylpyridine **2d**: m.p. 201.5–204.0 °C (Found: C, 76.7; H, 5.85; N, 11.95. $C_{22}H_{21}N_3O$ requires C, 76.94; H, 6.16; N, 12.24%); δ_H 2.85 (3 H, s), 3.05 (6 H, s), 3.88 (3 H, s), 6.77 (2 H, d, *J* 8.6), 7.04 (2 H, d, *J* 8.9), 7.53 (1 H, s), 7.59 (2 H, d, *J* 8.9) and 8.01 (2 H, d, *J* 8.6); *m/z* 343 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2214 (C≡N).

3-Cyano-6-[4-(dimethylamino)phenyl]-4-[4-(dimethylamino)styryl]-2-methylpyridine **2e**: m.p. 200.0–201.5 °C (Found: C, 78.3; H, 6.65; N, 14.5. $C_{25}H_{26}N_4$ requires C, 78.50; H, 6.85; N, 14.65%); δ_H 2.81 (3 H, s), 3.04 (6 H, s), 3.05 (6 H, s), 6.72 (2 H, d, *J* 8.6), 6.80 (2 H, d, *J* 9.2), 7.16 (1 H, d, *J* 15.9), 7.46 (1 H, d, *J* 15.9), 7.52 (1 H, d, *J* 8.6), 7.74 (1 H, s) and 8.02 (2 H, d, *J* 9.2); *m/z* 382 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2211 (C≡N).

3-Cyano-6-[4-(dimethylamino)phenyl]-4-(2-furyl)-2-methylpyridine **2f**: m.p. 149.5–152.0 °C (Found: C, 75.05; H, 5.5; N, 13.85. $C_{19}H_{17}N_3O$ requires C, 75.23; H, 5.65; N, 13.85%); δ_H 2.83 (3 H, s), 3.05 (6 H, s), 6.61 (1 H, dd, *J* 3.7 and 1.5), 6.78 (2 H, d, *J* 9.2), 7.57 (1 H, d, *J* 3.7), 7.62 (1 H, d, *J* 1.5), 7.94 (1 H, s) and 8.04 (2 H, d, *J* 9.2); *m/z* 303 (M^+, 10%); ν_{max}(KBr)/cm^{-1} 2222 (C≡N).

3-Cyano-6-[4-(dimethylamino)phenyl]-2-methyl-4-(2-thienyl)-pyridine **2g**: m.p. 143.0–144.5 °C (Found: C, 71.1; H, 5.2; N, 13.05. $C_{19}H_{17}N_3S$ requires C, 71.44; H, 5.36; N, 13.15%); δ_H 2.85 (3 H, s), 3.05 (6 H, s), 6.79 (2 H, d, *J* 8.9), 7.21 (1 H, dd, *J* 5.5 and 4.0), 7.52 (1 H, d, *J* 5.5), 7.64 (1 H, s), 7.86 (1 H, d, *J* 4.0) and 8.01 (2 H, d, *J* 8.9); *m/z* 319 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2211 (C≡N).

3-Cyano-6-[4-(dimethylamino)phenyl]-2-methyl-2′,4-bipyridine **2h**: m.p. 139.0–140.0 °C (Found: C, 76.6; H, 5.7; N, 17.9. $C_{20}H_{18}N_4$ requires C, 76.41; H, 5.77; N, 17.82%); δ_H 2.89 (3 H, s), 3.05 (6 H, s), 6.77 (2 H, d, *J* 9.2 Hz), 7.42 (1 H, dd, *J* 7.6 and 6.4), 7.86 (1 H, s), 7.88 (1 H, d, *J* 7.6), 7.89 (1 H, dd, *J* 6.4 and 4.3), 8.07 (2 H, d, *J* 9.2) and 8.82 (1 H, d, *J* 4.3); *m/z* 314 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2210 (C≡N).

3-Cyano-4-[4-(dimethylamino)phenyl]-2-methyl-6-phenylpyridine **2i**: m.p. 213.0–215.0 °C (Found: C, 80.2, H, 6.1; N, 13.4. $C_{21}H_{19}N_3$ requires C, 80.48; H, 6.11; N, 13.41%); δ_H 2.89 (3 H, s), 3.05 (6 H, s), 6.82 (2 H, d, *J* 8.5), 7.46–7.56 (3 H, m), 7.61 (2 H, d, *J* 8.5), 7.65 (1 H, s) and 8.03–8.07 (2 H, m); *m/z* 313 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2211 (C≡N).

3-Cyano-4-[4-(dimethylamino)phenyl]-6-(4-methoxyphenyl)-2-methylpyridine **2j**: m.p. 194.0–196.0 °C (Found: C, 77.15; H, 6.1; N, 12.45. $C_{22}H_{21}N_3O$ requires C, 76.94; H, 6.16; N, 12.24%); δ_H 2.88 (3 H, s), 3.06 (6 H, s), 3.88 (3 H, s), 6.85 (2 H, d, *J* 9.0), 7.01 (2 H, d, *J* 8.8), 7.58 (1 H, s), 7.61 (2 H, d, *J* 8.8) and 8.04 (2 H, d, *J* 9.0); *m/z* 343 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2211 (C≡N).

3-Cyano-4,6-bis(4-methoxyphenyl)-2-methylpyridine **2k**: m.p. 172.0–173.0 °C (Found: C, 76.35; H, 5.55; N, 8.50. $C_{21}H_{18}N_2O_2$ requires C, 76.35; H, 5.49; N, 8.48%); δ_H 2.88 (3 H, s), 3.88 (3 H, s), 3.89 (3 H, s), 7.01 (2 H, d, *J* 8.8), 7.06 (2 H, d, *J* 8.8), 7.58 (1 H, s), 7.60 (2 H, d, *J* 8.8) and 8.05 (2 H, d, *J* 8.8); *m/z* 330 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2210 (C≡N).

3-Cyano-4-(2-furyl)-6-(4-methoxyphenyl)-2-methylpyridine **2l**: m.p. 124.0–125.0 °C (Found: C, 74.6; H, 4.7; N, 9.45. $C_{18}H_{14}N_2O_2$ requires C, 74.47; H, 4.86; N, 9.65%); δ_H 2.86 (3 H, s), 3.89 (3 H, s), 6.63 (1 H, dd, *J* 3.5 and 1.4), 7.02 (2 H, d, *J* 8.5), 7.61 (1 H, d, *J* 3.5), 7.64 (1 H, d, *J* 1.4), 7.99 (1 H, s) and 8.08 (2 H, d, *J* 8.5); *m/z* 290 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2222 (C≡N).

3-Cyano-4-[4-(dimethylamino)phenyl]-6-[4-(dimethylamino)styryl]-2-methylpyridine **2m**: m.p. 166.5–167.5 °C (Found: C, 78.25; H, 6.8; N, 14.65. $C_{25}H_{26}N_4$ requires C, 78.50; H, 6.85; N, 14.65%); δ_H 2.82 (3 H, s), 3.02 (6 H, s), 3.05 (6 H, s), 6.71 (2 H, d, *J* 8.8), 6.80 (2 H, d, *J* 8.8), 6.96 (1 H, d, *J* 15.8), 7.24 (2 H, d, *J* 8.8), 7.28 (1 H, s), 7.58 (2 H, d, *J* 8.8) and 7.70 (1 H, d, *J* 15.8); *m/z* 382 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2211 (C≡N).

3-Cyano-4-(2-furyl)-2-methyl-6-(1-naphthyl)pyridine **2n**: m.p. 145.0–146.0 °C (Found: C, 81.2; H, 4.45; N, 9.0. $C_{21}H_{14}N_2O$ requires C, 81.27; H, 4.55; N, 9.03%); δ_H 2.94 (3 H, s), 6.64 (1 H, dd, *J* 3.7 and 1.5), 7.48–7.67 (4 H, m), 7.52 (1 H, d, *J* 3.7), 7.62 (1 H, d, *J* 1.5), 7.92 (1 H, s) and 7.95–8.09 (3 H, m); *m/z* 310 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2220 (C≡N).

3-Cyano-2-methyl-6-(1-naphthyl)-4-(2-thienyl)pyridine **2o**: m.p. 142.0–143.0 °C (Found: C, 77.0; H, 4.3; N, 8.5. $C_{21}H_{14}N_2S$ requires C, 77.27; H, 4.32; N, 8.58%); δ_H 2.96 (3 H, s), 7.23 (1 H, dd, *J* 5.1 and 3.7), 7.51–7.64 (4 H, m), 7.61 (1 H, d, *J* 5.1), 7.66 (1 H, s), 7.92–8.09 (3 H, m) and 7.95 (1 H, d, *J* 3.7); *m/z* 326 (M^+, 70%) and 325 (100); ν_{max}(KBr)/cm^{-1} 2219 (C≡N).

3-Cyano-2-methyl-4,6-di(1-naphthyl)pyridine **2p**: m.p. 98.0–100.0 °C (Found: C, 87.4; H, 4.8; N, 7.5. $C_{27}H_{18}N_2$ requires C, 87.54; H, 4.90; N, 7.56%); δ_H 3.09 (3 H, s), 7.93 (1 H, s), 7.41–8.28 (14 H, m); *m/z* 370 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2212 (C≡N).

3-Cyano-4-[4-(dimethylamino)phenyl]-6-(2-furyl)-2-methylpyridine **2q**: m.p. 252.0–253.0 °C (Found: C, 75.5; H, 5.5; N, 13.85. $C_{19}H_{17}N_3O$ requires C, 75.23; H, 5.65; N, 13.85%); δ_H 2.83 (3 H, s), 3.05 (6 H, s), 6.57 (1 H, dd, *J* 3.7 and 1.8), 6.81 (2 H, d, *J* 9.2), 7.20 (1 H, d, *J* 3.7), 7.28 (1 H, d, *J* 1.8), 7.60 (1 H, s) and 7.61 (2 H, d, *J* 9.2); *m/z* 303 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2211 (C≡N).

3-Cyano-6-(2-furyl)-4-(4-methoxyphenyl)-2-methylpyridine **2r**: m.p. 188.0–191.0 °C (Found: C, 74.3; H, 4.85; N, 9.55. $C_{18}H_{14}N_2O_2$ requires C, 74.47; H, 4.86; N, 9.65%); δ_H 2.85 (3 H, s), 3.89 (3 H, s), 6.58 (1 H, dd, *J* 3.4 and 1.8), 7.05 (2 H, d, *J* 9.2), 7.23 (1 H, d, *J* 3.4), 7.60 (1 H, d, *J* 1.8), 7.61 (1 H, s) and 7.62 (2 H, d, *J* 9.2); *m/z* 290 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2210 (C≡N).

3-Cyano-6-(2-furyl)-2-methyl-4-(1-naphthyl)pyridine **2s**: m.p. 240.0–241.5 °C (Found: C, 81.5; H, 4.4; N, 8.95. $C_{21}H_{14}N_2O$ requires C, 81.27; H, 4.55; N, 9.03%); δ_H 2.80 (3 H, s), 6.51 (1 H, dd, *J* 3.4 and 1.7), 6.81 (1 H, d, *J* 3.4), 7.44–8.32 (7 H, m), 7.58 (1 H, d, *J* 1.7) and 7.59 (1 H, s); *m/z* 310 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2179 (C≡N).

3-Cyano-4,6-di(2-furyl)-2-methylpyridine **2t**: m.p. 144.5–145.5 °C (Found: C, 72.05; H, 4.1; N, 11.15. $C_{15}H_{10}N_2O_2$ requires C, 71.99; H, 4.03; N, 11.19%); δ_H 2.79 (3 H, s), 6.57 (1 H, dd, *J* 3.6 and 1.8), 6.61 (1 H, dd, *J* 3.6 and 1.8), 7.20 (1 H, d, *J* 3.6), 7.57 (1 H, d, *J* 3.6), 7.59 (1 H, d, *J* 1.8), 7.62 (1 H, d, *J* 1.8) and 7.91 (1 H, s); *m/z* 250 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2211 (C≡N).

3-Cyano-6-(2-furyl)-2-methyl-4-(2-thienyl)pyridine **2u**: m.p. 152.0–154.0 °C (Found: C, 67.5; H, 3.5; N, 10.6. $C_{15}H_{10}N_2OS$ requires C, 67.65; H, 3.78; N, 10.52%); δ_H 2.85 (3 H, s), 6.59 (1 H, dd, *J* 3.5 and 1.5), 7.22 (1 H, dd, *J* 5.1 and 3.9), 7.24 (1 H, d, *J* 3.5), 7.58 (1 H, dd, *J* 5.1 and 1.3), 7.61 (1 H, d, *J* 1.5), 7.72 (1 H, s) and 7.91 (1 H, dd, *J* 3.9 and 1.3); *m/z* 266 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2211 (C≡N).

3-Cyano-6-(2-furyl)-2-methyl-4-(2-pyrrolyl)pyridine **2v**: m.p. 207.0–208.0 °C (Found: C, 72.0; H, 4.2; N, 16.75. $C_{15}H_{11}N_3O$ requires C, 72.28; H, 4.45; N, 16.86%); δ_H 2.78 (3 H, s), 6.40 (1 H, dd, *J* 2.5 and 2.5), 6.57 (1 H, dd, *J* 1.7 and 1.7), 7.07 (1 H, d, *J* 2.5), 7.13 (1 H, d, *J* 2.5), 7.21 (1 H, d, *J* 1.7), 7.58 (1 H, d, *J* 1.7), 7.70 (1 H, s) and 9.56 (1 H, br s); *m/z* 249 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2211 (C≡N).

3 -Cyano-4-[4-(dimethylamino)phenyl]-2-methyl-6-(2-thienyl)pyridine **2w**: m.p. 220.0–221.0 °C (Found: C, 71.35; H, 5.3; N, 13.05. $C_{19}H_{17}N_3S$ requires C, 71.44; H, 5.36; N, 13.15%); δ_H 2.83 (3 H, s), 3.05 (6 H, s), 6.81 (2 H, d, *J* 9.2), 7.14 (1 H, dd, *J* 4.9 and 3.7), 7.48 (1 H, dd, *J* 4.9 and 1.2), 7.53 (1 H, s), 7.59 (2 H, d, *J* 9.2), 7.69 (1 H, dd, *J* 3.7 and 1.2); *m/z* 319 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2211 (C≡N).

3-Cyano-2-methyl-4-(1-naphthyl)-6-(2-thienyl)pyridine **2x**: m.p. 213.0–214.0 °C (Found: C, 77.05; H, 4.6; N, 8.35. $C_{21}H_{14}N_2S$ requires C, 77.27; H, 4.32; N, 8.58%); δ_H 2.90 (3 H, s), 7.14 (1 H, dd, *J* 5.1 and 3.9), 7.52 (1 H, dd, *J* 5.1 and 0.9), 7.62 (1 H, s), 7.66 (1 H, dd, *J* 3.9 and 0.9) and 7.49–8.10 (7 H, m); *m/z* 326 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2188 (C≡N).

3-Cyano-4-(2-furyl)-2-methyl-6-(2-thienyl)pyridine **2y**: m.p. 137.0–138.0 °C (Found: C, 67.1; H, 3.55; N, 10.75. $C_{15}H_{10}N_2OS$

requires C, 67.65; H, 3.78; N, 10.52%); δ_H 2.78 (3 H, s), 6.61 (1 H, dd, *J* 3.7 and 1.8), 7.13 (1 H, dd, *J* 5.1 and 3.8), 7.49 (1 H, d, *J* 5.1), 7.58 (1 H, d, *J* 3.7), 7.62 (1 H, d, *J* 1.8), 7.72 (1 H, d, *J* 3.8) and 7.87 (1 H, s); *m/z* 266 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2222 (C≡N).

3-Cyano-2-methyl-4,6-di(2-thienyl)pyridine **2z**: m.p. 158.0–158.5 °C (Found: C, 63.5; H, 3.4; N, 9.8. $C_{15}H_{10}N_2S_2$ requires C, 63.80; H, 3.57; N, 9.92%); δ_H 2.82 (3 H, s), 7.13 (1 H, dd, *J* 4.5 and 3.7), 7.19 (1 H, dd, *J* 4.5 and 3.7), 7.49 (1 H, d, *J* 4.5), 7.53 (1 H, d, *J* 4.5), 7.60 (1 H, s), 7.69 (1 H, d, *J* 3.7) and 7.86 (1 H, d, *J* 3.7); *m/z* 282 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2211 (C≡N).

3-Cyano-2-methyl-4-(2-pyrrolyl)-6-(2-thienyl)pyridine **2aa**: m.p. 212.0–214.0 °C (Found: C, 67.95; H, 4.0; N, 15.95. $C_{15}H_{11}N_3S$ requires C, 67.90; H, 4.18; N, 15.84%); δ_H 2.78 (3 H, s), 6.40 (1 H, dd, *J* 3.0 and 2.5), 7.07 (1 H, d, *J* 3.0), 7.14 (1 H, d, *J* 2.5), 7.15 (1 H, dd, *J* 3.8 and 3.4), 7.50 (1 H, d, *J* 3.8), 7.63 (1 H, s), 7.71 (1 H, d, *J* 3.4) and 9.56 (1 H, br s); *m/z* 265 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2212 (C≡N).

5-Cyano-4-[4-(dimethylamino)phenyl]-6-methyl-2,2′-bipyridine **2bb**: m.p. 263.5–264.5 °C (Found: C, 76.7; H, 5.7; N, 17.8. $C_{20}H_{18}N_4$ requires C, 76.41; H, 5.77; N, 17.82%); δ_H 2.90 (3 H, s), 3.05 (6 H, s), 6.82 (2 H, d, *J* 8.5), 7.35 (1 H, ddd, *J* 6.7, 4.2 and 1.8), 7.68 (2 H, d, *J* 8.5), 7.85 (1 H, ddd, *J* 8.0, 6.7 and 1.8), 8.40 (1 H, s), 8.50 (1 H, d, *J* 8.0) and 8.71 (1 H, dd, *J* 4.2 and 1.2); *m/z* 314 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2221 (C≡N).

5-Cyano-4-(4-methoxyphenyl)-6-methyl-2,2′-bipyridine **2cc**: m.p. 197.0–199.0 °C (Found: C, 75.65; H, 4.85; N, 13.95. $C_{19}H_{15}N_3O$ requires C, 75.73; H, 5.02; N, 13.94%); δ_H 2.92 (3 H, s), 3.89 (3 H, s), 7.06 (2 H, d, *J* 9.2), 7.41 (1 H, dd, *J* 7.9 and 4.3), 7.70 (2 H, d, *J* 9.2), 7.91 (1 H, dd, *J* 8.7 and 7.9), 8.47 (1 H, s), 8.55 (1 H, d, *J* 8.7), 8.73 (1 H, d, *J* 4.3); *m/z* 301 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2233 (C≡N).

5-Cyano-4-(2-furyl)-6-methyl-2,2′-bipyridine **2dd**: m.p. 167.0–168.0 °C (Found: C, 73.55; H, 4.1; N, 16.0. $C_{16}H_{11}N_3O$ requires C, 73.55; H, 4.24; N, 16.08%); δ_H 2.89 (3 H, s), 6.63 (1 H, dd, *J* 3.5 and 1.4), 7.38 (1 H, dd, *J* 6.4 and 4.9), 7.61 (1 H, d, *J* 3.5), 7.67 (1 H, d, *J* 1.4), 7.86 (1 H, dd, *J* 7.9 and 6.4), 8.50 (1 H, d, *J* 7.9), 8.75 (1 H, s) and 8.75 (1 H, d, *J* 4.9); *m/z* 261 (M^+, 100%); ν_{max}(KBr)/cm^{-1} 2229 (C≡N).

Synthesis of 4,6-*Disubstituted* 2-*Methylpyridines* **3k** *and* **3t**.—In a general procedure, to a 2-methoxyethanol solution (20 cm^3) of β-aminocrotononitrile (4 mmol) and sodium hydroxide (50 mmol) was slowly added a 2-methoxyethanol solution (20 cm^3) of α,β-unsaturated carbonyl compound (2 mmol) at 120–130 °C under an Ar atmosphere. The mixture was refluxed for 4 h. After the reaction, the products were extracted with dichloromethane, washed with 10% aqueous sodium hydrogensulfite and brine. Desired products were isolated using a column chromatograph (SiO_2, CH_2Cl_2). Physical and spectral data of 4,6-disubstituted 2-methylpyridines are shown below.

4,6-Bis(4-methoxyphenyl)-2-methylpyridine **3k**: yield 65%; m.p. 115.0–116.0 °C (Found: C, 78.45; H, 6.05; N, 4.7. $C_{20}H_{19}NO_2$ requires C, 78.66; H, 6.27; N, 4.59%); δ_H 2.66 (3 H, s), 3.87 (6 H, s), 7.00 (2 H, d, *J* 9.0), 7.02 (2 H, d, *J* 9.0), 7.23 (1 H, d, *J* 1.3), 7.63 (1 H, d, *J* 1.3), 7.63 (2 H, d, *J* 9.0) and 7.98 (2 H, d, *J* 9.0); *m/z* 305 (M^+, 100%).

4,6-Di(2-furyl)-2-methylpyridine **3t**: yield 49%; m.p. 98.0–99.0 °C (Found: C, 74.4; H, 5.1; N, 6.15. $C_{14}H_{11}NO_2$ requires C, 74.65; H, 4.92; N, 6.22%); δ_H 2.59 (3 H, s), 6.48 (1 H, dd, *J* 3.4 and 1.7), 6.51 (1 H, dd, *J* 3.4 and 1.7), 6.85 (1 H, d, *J* 3.4), 7.06 (1 H, d, *J* 3.4), 7.23 (1 H, d, *J* 1.3), 7.51 (1 H, d, *J* 1.7), 7.53 (1 H, d, *J* 1.7) and 7.71 (1 H, d, *J* 1.3); *m/z* 225 (M^+, 100%).

Photostability of Fluorescent Pyridines.—A methanol solution (50 cm^3) of substrate (0.044 mmol dm^{-1}) in a borosilicate glass tube was irradiated with a 200 W high pressure mercury lamp using a merry-go-round under air atmosphere at room temperature. The conversion was calculated based on the absorbance at λ_{max}.

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