Color Change (Yellow ⇌ Orange) of 4,6,7-Tri(alkoxy-substituted aryl)-1,2,5-thiadiazolo[3,4-*c*]pyridines in the Solid Phase

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Reversible color change of 4,6,7-tri(alkoxy-substituted phenyl)-1,2,5-thiadiazolo[3,4-*c*]pyridines **5** in the solid state was observed: on grinding, yellow crystals of **5** became an orange amorphous solid which, on heating or washing with an appropriate solvent, gave the original yellow crystals.

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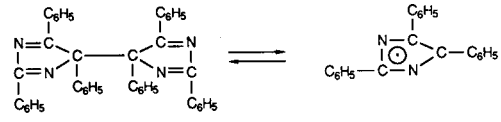
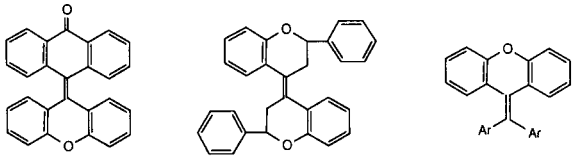
Piezochromism of organic compounds [1] having a



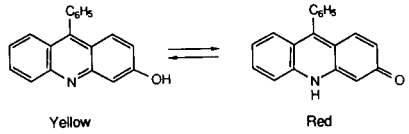
light yellow red purple

highly crowded C(sp^3)-C(sp^3) bond is considered due to a radical formation by fission of the C-C bond by pressure.



1 2 3

On the other hand, although so-called "thermochromic ethylenes" [2] such as **1-3**, show color change (lemon yellow ⇌ green) in the solid state by pressing or grinding, the color change was not caused by pressure but *via* a thermal process; when **1** was ground in an apparatus cooled in liquid nitrogen, such a color change was not observed [3].

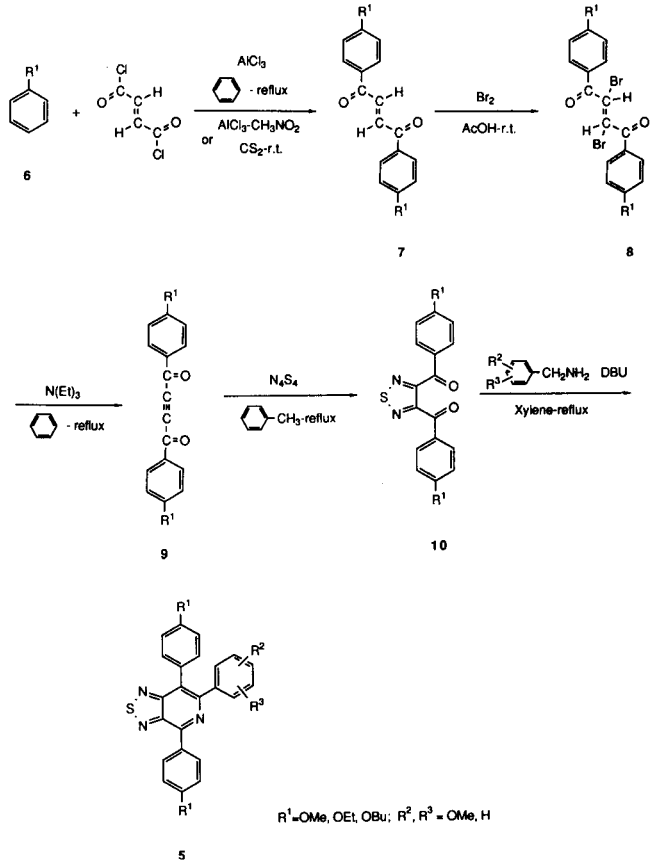


Yellow Red

4

A similar color change of 3-hydroxy-9-phenylacridine (**4**) (yellow ⇌ red) was explained [4] in terms of thermal lactim (**4-A**)-lactam (**4-B**) tautomerism; grinding of the yellow-colored lactim **4-A** causes local heating, leading to local melting and a partial tautomeric change of **4-A** into the red-colored lactam **4-B** and, as the melt contains a mixture of tautomers, it crystallizes very slowly, thus, converting into a glass which is rich in the metastable red-colored lactam **4-B**. The initial colors of compounds **1-4** can be regained by heating or washing with an appropriate solvent.

Scheme 1



6 7 8 9 10 5

R^1=OMe, OEt, OBu; R^2, R^3 = OMe, H

In our search [5] for a strongly fluorescent colored dye stuff, we found that 4,6,7-tri(alkoxy-substituted phenyl)-1,2,5-thiadiazolo[3,4-*c*]pyridines (**5**) of a different fun-

Table 1

Preparation of **5**

5	R^1	R^2	R^3	Yield (%)	Color [1]	max (log) [2]
aa	MeO	2-MeO	H	71	Yellow [3] 435	(4.04)
ab	MeO	3-MeO	H	66	Yellow [4] 436	(4.02)
ac	MeO	4-MeO	H	68	Orange [3] 444	(3.87)
ad	MeO	4-MeO	3-MeO	71	Yellow [4] 445	(3.99)
ae	MeO	H	H	68	Orange [3] 436	(4.04)
ba	EtO	2-MeO	H	67	Yellow [3] 435	(4.03)
bb	EtO	3-MeO	H	12	Yellow [4] 435	(4.03)
bc	EtO	4-MeO	H	81	Yellow [4] 446	(4.02)
bd	EtO	4-MeO	3-MeO	64	Yellow [4] 446	(4.01)
be	EtO	H	H	70	Yellow [4] 439	(4.06)
ca (1)	BuO	2-MeO	H	9	Yellow [4] 436	(4.06)
ca (2)	BuO	2-MeO	H	65	Orange [4] 436	(4.06)
cd	BuO	4-MeO	3-MeO	80	Yellow [4] 447	(3.99)

[1] Recrystallized from ethanol. [2] In chloroform. [3] Prisms. [4] Needles.

damental skeleton from the above two types, shows a similar type of reversible color change (yellow ⇌ orange). In the present article, we report the preparation, color change and thermal behavior (DSC analysis) of **5**.

Results and Discussion.

Preparation of **5**.

Compound **5** was prepared according to a modified method of that previously reported (Scheme 1) [6]. Friedel-Crafts acylation of alkoxybenzenes **6** gave the desired diaroylethylenes **7** in low yields. Acetylenes **9** were prepared from **7** as usual and reacted with tetrasulfur tetranitride (N_4S_4) to give 3,4-diaroyl-1,2,5-thiadiazoles **9**. Reaction of **9** with benzylamines **10** afforded **5**. Yield, physical properties, and spectral data of **5** were given in Table 1.

Color Change and Thermal Behavior of **6**.

Although the color of the solution of **5** in an usual organic solvent is orange, **5aa, 5ab, 5ad, 5ba, 5bb, 5bc, 5bd, 5be**, and **5cd** were obtained as yellow needles on recrystallization from ethanol, whilst **5ac** and **5ae** as orange needles from the same solvent. When being ground or rubbed, a part of the yellow crystals of **5** turned into an orange solid. Color change is clearer in 4-methoxy-substituted **5ad, 5bc, 5bd**, and **5cd** than in 2- or 3-methoxy-substituted **5aa, 5ab, 5ba**, and **5bb** and in un-substituted **5be**. The yellow color is easily retained by heating or washing the orange solid with an appropriate solvent.

$$\text{Yellow color} \underset{\text{Heat or Solvent}}{\overset{\text{Shear (Grinding)}}{\rightleftharpoons}} \text{Orange color}$$

Interestingly, both yellow and orange needles were formed when **5ca** was recrystallized from ethanol. When yellow needles **5ca-1** were ground or rubbed, they turned into orange solids. Microscopic and X-ray powder diffraction studies (Figure 1) revealed that the red part is an amorphous solid. When **5ca-1** was rubbed in an apparatus cooled by liquid nitrogen, no color change was observed as in the case of **1**. This suggests that the above mentioned color change is caused by heat but not pressure. Although a color change was not apparent, orange needles **5ca-2** gave an orange glass on grinding. The visible spectra of yellow needles **5ca-1** and orange glass of **5ca** were measured as a thin film (Figure 2). As expected, the max value of the orange glass of **5ca** is very near to those in solution.

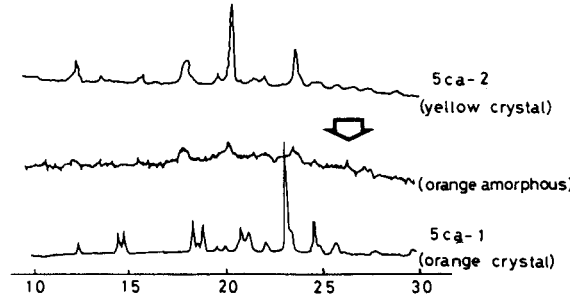


Fig 1. X-ray Diffraction patterns.

The DSC diagram of **5** was measured and, as summarized in Table 2 and Figure 3, classified into 3 types. When melted and then cooled, compound **5ca** forms an orange glass, whose Tg was observed at 33°. On heating, this glass gave an exothermic peak and, both orange and yellow crystals were formed. Then, two endothermic peaks were

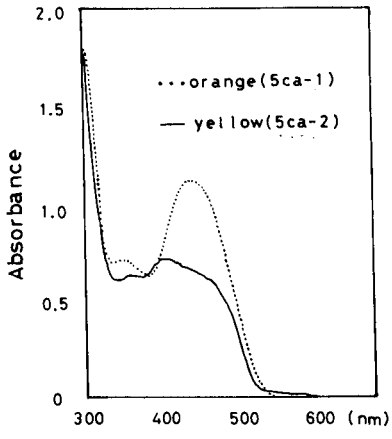


Fig 2. Absorption spectra in solid.

observed, which correspond to the melting points of the orange and the yellow crystals. The ratio of the two is dependent on the experimental conditions. Compounds **5ba** gave a similar DSC diagram with **5ca**.

When each orange melt of yellow crystals of compounds **5ab, 5ad, 5bc, 5bd, 5be**, and **5cd**, was heated, a very complex diagram of exothermic peaks was observed and orange crystals were formed. Further heating caused transformation of the orange crystals into yellow one, whose melting point are identical with the initial yellow crystals. The orange melt of the orange crystals of **5ae** behaved similarly, but, finally gave orange crystals. This means that, in compounds **5ab, 5ad, 5bc, 5bd, 5be**, and **5cd**, yellow crystals are the stable form, whilst the orange ones are the stable form in **5ae**. On the other hand, when each orange melt of compounds **5aa, 5ac**, and **5bb** was heated, both endothermic and exothermic peak was not observable. An apparent color change was not noticed during the re-heating period.

Table 2

Classification of DSC Diagram of **5**

Pattern	Compound
A	**5ba, 5ca**
A'	**5ab, 5ad, 5ae, 5bc, 5bd, 5be, 5cd**
B	**5aa, 5ac, 5bb**

EXPERIMENTAL

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. The ir spectra were recorded on a Nippon Bunko A-102 spectrophotometer as potassium bromide pellets. The ^{1}H-nmr (internal TMS) spectra were taken on a Nippon Denshi JEOL FT-100 NMR spectrometer in deuteriochloroform unless otherwise stated. Mass spectra were recorded on a Nippon Denshi JMS-01SG-2 mass spectrometer at 75 eV using a direct-inlet system. Electronic spectra were taken on a Hitachi 220 spectrophotometer.

Preparation of Diaroylethylene **7**. General Procedure.

A mixture of fumaryl chloride (46 g, 0.30 mole) and alkoxybenzene (0.90 mole) in carbon disulfide (200 ml) was added dropwise during 15 minutes at room temperature to a stirred mixture of an aluminium chloride-nitromethane complex in carbon disulfide [prepared from aluminum chloride (133 g, 1 mole), nitromethane (145 g, 2.3 moles), and carbon disulfide (700 ml)]. After the reaction mixture was stirred at room temperature for 3 hours, it was poured into a large amount of ice water, extracted with methylene chloride dried over magnesium sulfate, and evaporated *in vacuo*, giving **7**.

trans-1,2-Di(4-methoxybenzoyl)ethylene (**7a**).

This compound was obtained in 33% yield (29 g) as pale orange prisms (benzene), mp 167-169° (lit [7] mp 162-164°).

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 73.02; H, 5.51. Found: C, 72.96; H, 5.44.

trans-1,2-Di(4-ethoxybenzoyl)ethylene (**7b**).

This compound was obtained in 15% yield (15 g) as yellow prisms (benzene), mp 163-165°; ir: ν CO 1630 cm^{-1}; ^{1}H-nmr: δ 1.44 (6H, t, J = 7 Hz), 4.12 (4H, q, J = 7 Hz), 6.92 (4H, d, J = 9 Hz), 7.92 (2H, s), 8.04 (4H, d, J = 7 Hz); ms: m/e 324 (M$^+$).

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 74.19; H, 6.29.

trans-1,2-Di(4-butoxybenzoyl)ethylene (**7c**).

This compound was obtained in 13% yield (11 g) as yellow needles (ethanol), mp 118-120°; ir: ν CO 1640 cm^{-1}; ^{1}H-nmr: δ 1.00 (6H, t, J = 7 Hz), 1.20-2.00 (8H, m), 4.08 (4H, t, J = 7 Hz), 7.00 (4H, d, J = 9 Hz), 8.00 (2H, s), 8.08 (4H, d, J = 9 Hz); ms: m/e 280 (M$^+$).

Anal. Calcd. for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42. Found: C, 75.65; H, 7.43.

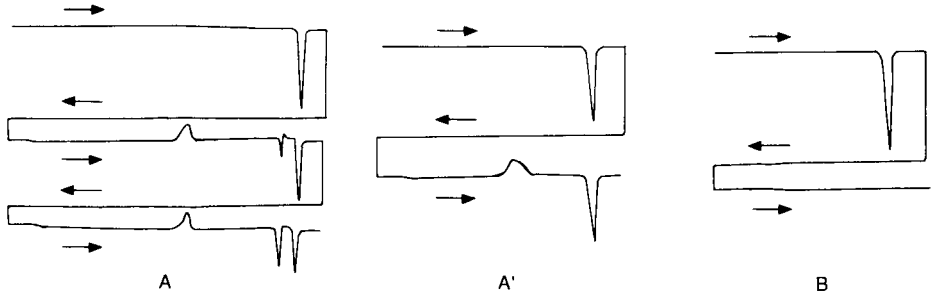


Figure 3. DSC diagram patterns of 5.

Preparation of 1,2-Diaroyl-1,2-dibromoethane (**8**). Typical Procedure.

Compound **7a** (29 g, 98 mmoles) in acetic acid (250 ml) was brominated with bromine (70 mmoles) in acetic acid (25 ml) at 0-5° and worked up as usual, giving **8a** (31 g, 70%). Compounds **8b** and **8c** were similarly prepared.

1,2-Dibromo-1,2-di(4-methoxybenzoyl)ethane (**8a**).

This compound was obtained as white needles (benzene), mp 180-182°; ir: ν CO 1660 cm^{-1}; ^{1}H-nmr: δ 3.78 (6H, s), 5.88 (2H, s), 7.00 (4H, d, J = 9 Hz), 8.03 (4H, d, J = 9 Hz); ms: m/e 454 (M$^+$), 456 (M$^+$), 458 (M$^+$).

Anal. Calcd. for $C_{18}H_{16}Br_2O_4$: C, 47.40; H, 3.53. Found: C, 47.50; H, 3.68.

1,2-Dibromo-1,2-di(4-ethoxybenzoyl)ethylene (**8b**).

This compound was obtained in 66% yield (15 g from 15 g of **7b**) as white needles (benzene), mp 203-205°; ir: ν CO 1660 cm^{-1}; ^{1}H-nmr: δ 1.56 (6H, t, J = 7 Hz), 4.14 (4H, q, J = 7 Hz), 5.92 (2H, s), 6.98 (4H, d, J = 9 Hz), 8.06 (4H, d, J = 9 Hz); ms: m/e 482 (M$^+$), 484 (M$^+$), 486 (M$^+$).

Anal. Calcd. for $C_{20}H_{20}Br_2O_4$: C, 49.61; H, 4.16. Found: C, 49.56; H, 4.17.

1,2-Dibromo-1,2-di(4-butoxybenzoyl)ethylene (**8c**).

This compound was obtained in 46% yield (8 g from 11 g of **7c**) as white needles (benzene), mp 145-147°; ir: ν CO 1670 cm^{-1}; ^{1}H-nmr: δ 0.96 (6H, t, J = 7 Hz), 1.28-2.96 (8H, m), 4.04 (4H, t, J = 7 Hz), 5.88 (2H, s), 6.94 (4H, d, J = 9 Hz), 8.04 (4H, d, J = 9 Hz); ms: m/e 538 (M$^+$), 540 (M$^+$), 542 (M$^+$).

Anal. Calcd. for $C_{24}H_{28}Br_2O_4$: C, 53.34; H, 5.22. Found: C, 53.16; H, 5.24.

Preparation of Diaroylacetylenes **9**. Typical Procedure.

A mixture of **8a** (31 g, 66 mmoles) and triethylamine (67 g, 660 mmoles) in benzene (300 ml) was heated at reflux for 5 hours. Triethylammonium hydrochloride was filtered and the filtrate was evaporated *in vacuo* to leave a residue which, on recrystallization from ethanol, gave **9a** (16 g, 80%).

Compounds **9b** and **9c** were similarly prepared.

Di(4-methoxybenzoyl)acetylene (**9a**).

This compound was obtained as white needles, mp 136-138°; ir: ν CO 1630 cm^{-1}; ^{1}H-nmr: δ 3.88 (6H, s), 6.92 (4H, d, J = 9 Hz), 8.04 (4H, d, J = 9 Hz); ms: m/e 294 (M$^+$).

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found: C, 73.33; H, 4.91.

Di(4-ethoxybenzoyl)acetylene (**9b**).

This compound was obtained in 58% yield (5.8 g from 15 g of **8b**) as white needles, mp 120-122°; ir: ν CO 1630 cm^{-1}; ^{1}H-nmr: δ 1.28 (6H, t, J = 7 Hz), 4.12 (4H, q, J = 7 Hz), 6.96 (4H, d, J = 9 Hz), 8.12 (4H, d, J = 9 Hz); ms: m/e 322 (M$^+$).

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.35; H, 5.67.

Di(4-butoxybenzoylacetylene (**9c**).

This compound was obtained in 65% yield (3.6 g from 8.0 g of **8c**) as white needles, mp 74-76°; ir: ν CO 1640 cm^{-1}; ^{1}H-nmr: δ 0.96 (6H, t, J = 7 Hz), 1.08-1.96 (8H, m), 4.04 (4H, t, J = 7 Hz), 6.92 (4H, d, J = 9 Hz), 8.10 (4H, d, J = 9 Hz); ms: m/e 378 (M$^+$), 377.

Anal. Calcd. for $C_{24}H_{26}O_4$: C, 76.16; H, 6.93. Found: C, 76.30; H, 6.92.

3,4-Diaroyl-1,2,5-thiadiazole **10**.

Compound **10** was prepared according to the reported procedure [5].

3,4-Di(4-methoxybenzoyl)-1,2,5-thiadiazole (**10a**).

This compound was obtained in 23% yield (4.4 g from 16 g of **9a**) as pale brown needles (ethanol), mp 166-167°; ir: ν CO 1660 cm^{-1}; ^{1}H-nmr: δ 3.85 (6H, s), 6.95 (4H, d, J = 9 Hz), 8.05 (4H, d, J = 9 Hz); ms: m/e 354 (M$^+$).

Anal. Calcd. for $C_{16}H_{14}N_2O_4S$: C, 72.90; H, 4.33; N, 10.63. Found: C, 72.97; H, 4.52; N, 10.29.

3,4-Di(4-ethoxybenzoyl)-1,2,5-thiadiazole (**10b**).

This compound was obtained in 40% yield (2.8 g from 5.8 g of **9b**) as white needles (ethanol), mp 145-147°; ir: ν CO 1650 cm^{-1}; ^{1}H-nmr: δ 1.40 (6H, t, J = 7 Hz), 4.12 (4H, q, J = 7 Hz), 6.94 (4H, d, J = 9 Hz), 8.20 (4H, d, J = 9 Hz); ms: m/e 382 (M$^+$).

Anal. Calcd. for $C_{20}H_{18}N_2O_4S$: C, 62.81; H, 4.74; N, 7.33. Found: C, 62.69; H, 4.70; N, 7.24.

3,4-Di(4-butoxybenzoyl)-1,2,5-thiadiazole (**10c**).

This compound was obtained in 11% yield (0.40 g from 3.1 g of *9c*) as white needles (hexane), mp 50-52°; ir: ν CO 1660 cm^{-1}; ^{1}H-nmr: δ 0.96 (6H, t, J = 7 Hz), 1.20-1.96 (8H, m), 4.04 (4H, t, J = 7 Hz), 6.92 (4H, d, J = 9 Hz), 8.00 (4H, d, J = 9 Hz); ms: m/e 438 (M$^+$), 437.

Anal. Calcd. for $C_{24}H_{26}N_2O_4S$: C, 65.72; H, 5.98; N, 6.39. Found: C, 65.59; H, 5.97; N, 6.44.

Preparation of **5**.

A 1:3:3-equimolar mixture of **10**, arylmethylamine, and DBU in xylene was refluxed for 24 hours. The solvent was evaporated *in vacuo* and a residue was column chromatographed on silica gel (Wako gel, C-300) using dichloromethane as an eluent, giving **5** in the yields in Table 1.

4,7-Di(4-methoxyphenyl)-6-(2-methoxyphenyl)-1,2,5-thiadiazolo[3,4-*c*]-pyridine (**5aa**).

This compound had mp 230-232°; ms: m/e 455 (M$^+$); ^{1}H-nmr: δ 3.40 (3H, s), 3.80 (3H, s), 3.92 (3H, s), 6.68-7.60 (10H, m), 8.86 (2H, d, J = 9 Hz).

Anal. Calcd. for $C_{26}H_{21}N_3O_3S$: C, 68.55; H, 4.65; N, 9.23. Found: C, 68.71; H, 4.49; N, 8.93.

4,7-Di(4-methoxyphenyl)-6-(3-methoxyphenyl)-1,2,5-thiadiazolo[3,4-*c*]-pyridine (**5ab**).

This compound had mp 170-172°; ms: m/e 455 (M$^+$); ^{1}H-nmr: δ 3.68 (3H, s), 3.84 (3H, s), 3.92 (3H, s), 6.72-7.42 (10H, m), 8.72 (2H, d, J = 9 Hz).

Anal. Calcd. for $C_{26}H_{21}N_3O_3S$: C, 68.55; H, 4.65; N, 9.23. Found: C, 68.66; H, 4.57; N, 8.96.

4,6,7-Tri(4-methoxyphenyl)-1,2,5-thiadiazolo[3,4-*c*]pyridine (**5ac**).

This compound had mp 161-162°; ms: m/e 455 (M$^+$); ^{1}H-nmr: δ 3.84 (3H, s), 3.92 (3H, s), 3.94 (3H, s), 6.80-7.56 (10H, m), 8.76 (2H, d, J = 9 Hz).

Anal. Calcd. for $C_{26}H_{21}N_3O_3S$: C, 68.55; H, 4.65; N, 9.23. Found: C, 68.49; H, 4.63; N, 9.16.

4,7-Di(4-methoxyphenyl)-6-(3,4-dimethoxyphenyl)-1,2,5-thiadiazolo[3,4-*c*]-pyridine (**5ad**).

This compound had mp 144-145°; ms: m/e 455 (M$^+$); ^{1}H-nmr: δ 3.64 (3H, s), 3.86 (3H, s), 3.92 (3H, s), 3.94 (3H, s), 6.65-7.44 (6H, m), 8.72 (2H, d, J = 9 Hz).

Anal. Calcd. for $C_{27}H_{23}N_3O_4S$: C, 66.78; H, 4.74; N, 8.65. Found: C, 66.77; H, 4.64; N, 8.43.

4,7-Di(4-methoxyphenyl)-6-phenyl)-1,2,5-thiadiazolo[3,4-*c*]pyridine (**5ae**).

This compound had mp 198-199°; ms: m/e 425 (M$^+$); ^{1}H-nmr: δ 3.84 (3H, s), 3.90 (3H, s), 6.84-7.64 (11H, m), 8.72 (2H, d, J = 9 Hz).

Anal. Calcd. for $C_{25}H_{19}N_3O_2S$: C, 70.58; H, 4.50; N, 9.88. Found: C, 70.66; H, 4.63; N, 9.48.

4,7-Di(4-ethoxyphenyl)-6-(2-methoxyphenyl)-1,2,5-thiadiazolo[3,4-*c*]-pyridine (**5ba**).

This compound had mp 218-219°; ms: m/e 483 (M$^+$); ^{1}H-nmr: δ 1.40 (3H, t, J = 7 Hz), 1.44 (3H, t, J = 7 Hz), 3.40 (3H, s), 4.04 (2H, q, J = 7 Hz), 4.16 (2H, q, J = 7 Hz), 6.68-7.60 (10H, m), 8.68 (2H, d, J = 9 Hz).

Anal. Calcd. for $C_{26}H_{25}N_3O_3S$: C, 69.54; H, 5.21; N, 8.69. Found: C, 69.35; H, 5.16; N, 8.47.

4,7-Di(4-ethoxyphenyl)-6-(3-methoxyphenyl)-1,2,5-thiadiazolo[3,4-*c*]-pyridine (**5bb**).

This compound had mp 154-156°; ms: m/e 483 (M^+); ^{1}H-nmr: δ 1.44 (3H, t, J = 7 Hz), 1.48 (3H, t, J = 7 Hz), 3.68 (3H, s), 4.08 (2H, q, J = 7 Hz), 4.16 (2H, q, J = 7 Hz), 6.76-7.40 (10H, m), 8.72 (2H, d, J = 9 Hz).

Anal. Calcd. for $C_{28}H_{25}N_3O_3S$: C, 69.54; H, 5.21; N, 8.69. Found: C, 69.44; H, 5.22; N, 8.54.

4,7-Di(4-ethoxyphenyl)-6-(4-methoxyphenyl)-1,2,5-thiadiazolo[3,4-*c*]-pyridine (**5bc**).

This compound had mp 174-176°; ms: m/e 483 (M^+); ^{1}H-nmr: δ 1.44 (3H, t, J = 7 Hz), 1.48 (3H, t, J = 7 Hz), 3.80 (3H, s), 4.06 (2H, q, J = 7 Hz), 4.14 (2H, q, J = 7 Hz), 6.80-7.56 (10H, m), 8.72 (2H, d, J = 9 Hz).

Anal. Calcd. for $C_{28}H_{25}N_3O_3S$: C, 69.54; H, 5.21; N, 8.69. Found: C, 69.55; H, 5.23; N, 8.47.

4,7-Di(4-ethoxyphenyl)-6-(3,4-dimethoxyphenyl)-1,2,5-thiadiazolo[3,4-*c*]-pyridine (**5bd**).

This compound had mp 168-171°; ms: m/e 513 (M^+); ^{1}H-nmr; δ 1.42 (3H, t, J = 7 Hz), 1.46 (3H, t, J = 7 Hz), 3.64 (3H, s), 3.88 (3H, s), 4.06 (2H, q, J = 7 Hz), 4.14 (2H, q, J = 7 Hz), 6.80-7.36 (10H, m), 8.72 (2H, d, J = 9 Hz).

Anal. Calcd. for $C_{29}H_{27}N_3O_4S$: C, 67.81; H, 5.30; N, 8.18. Found: C, 67.66; H, 5.34; N, 8.05.

4,7-Di(4-ethoxyphenyl)-6-phenyl-1,2,5-thiadiazolo[3,4-*c*]pyridine (**5be**).

This compound had mp 205-207°; ms: m/e 453 (M^+); ^{1}H-nmr; δ 1.44 (3H, t, J = 7 Hz), 1.48 (3H, t, J = 7 Hz), 4.04 (2H, q, J = 7 Hz), 4.12 (2H, q, J = 7 Hz), 6.80-7.60 (11H, m), 8.72 (2H, d, J = 9 Hz).

Anal. Calcd. for $C_{27}H_{22}N_3O_2S$: C, 71.50; H, 5.11; N, 9.26. Found: C, 71.38; H, 5.16; N, 9.06.

4,7-Di(4-butoxyphenyl)-6-(2-methoxyphenyl)-1,2,5-thiadiazolo[3,4-*c*]-pyridine (**5ca**)-(**1**).

This compound had mp 153-155°; ms: m/e 538 (M^+); ^{1}H-nmr: δ 0.96 (3H, t, J = 7 Hz), 0.98 (3H, t, J = 7 Hz), 1.32-2.00 (8H, m), 3.36 (3H, s), 3.92 (3H, t, J = 6 Hz), 4.04 (3H, t, J = 6 Hz), 6.68-7.60 (10H, m), 8.64 (2H, d, J = 9 Hz).

Anal. Calcd. for $C_{32}H_{33}N_3O_3S$: C, 71.08; H, 6.15; N, 7.77. Found: C, 71.23; H, 6.14; N, 7.65.

4,7-Di(4-butoxyphenyl)-6-(2-methoxyphenyl)-1,2,5-thiadiazolo[3,4-*c*]-pyridine (**5ca**)-(**2**).

This compound had mp 148-150°.

Anal. Calcd. for $C_{32}H_{33}N_3O_3S$: C, 71.08; H, 6.15; N, 7.77. Found: C, 70.99; H, 6.21; N, 7.95.

4,7-Di(4-butoxyphenyl)-6-(3,4-dimethoxyphenyl)-1,2,5-thiadiazolo[3,4-*c*]-pyridine (**5cd**).

This compound had mp 162-164°; ms: m/e 569; ^{1}H-nmr: δ 1.00 (3H, t, J = 7 Hz), 1.02 (3H, t, J = 7 Hz), 1.40-2.00 (8H, m), 3.62 (3H, s), 3.88 (3H, s), 4.00 (2H, t, J = 6 Hz), 4.04 (2H, t, J = 6 Hz), 6.80-7.16 (7H, m), 7.36 (2H, d, J = 9 Hz), 8.72 (2H, d, J = 9 Hz).

Anal. Calcd. for $C_{33}H_{35}N_3O_4S$: C, 69.57; H, 6.19; N, 7.38. Found: C, 69.66; H, 6.21; N, 7.21.

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