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PREPARATION OF 4,7-DIHETARYL-1,2,5-OXADIAZOLO[3,4-*c*]-PYRIDINES AS RED FLUORESCENT MATERIALS

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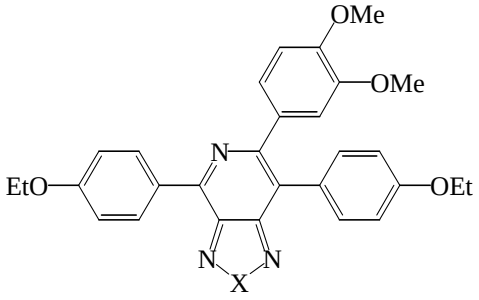
Abstract- A series of 1,2,5-oxadiazolo[3,4-*c*]pyridines (**6**, **7**, **8** and **10**) with thiophene, furan, and benzothiophene rings at the 4 and 7 positions were prepared, in quest of a red fluorescent material useful in OLED devices. Compound (**6**, **7**, **8** and **10**) emit fluorescence of orange to red color in solution and in the solid state. 6-Cyano derivatives (**6**) show a higher quantum yield than the corresponding esters (**7**), the phenyl derivative (**8**), and the unsubstituted compound (**10**). Red EL light at λ = 680 nm was obtained in an OLED device when 4,7-bis(5-phenylthien-2-yl) ester (**7h**) was used as a dopant emitter.

INTRODUCTION

Organic light-emitting diodes (OLEDs) are being developed for the realization of full color OLED displays.[1] Certain blue-[2] and green-color[3] OLEDs already have efficiencies sufficient for practical use. On the other hand, the choice of compounds, which emit red fluorescence for organic EL devices, is limited.[4]



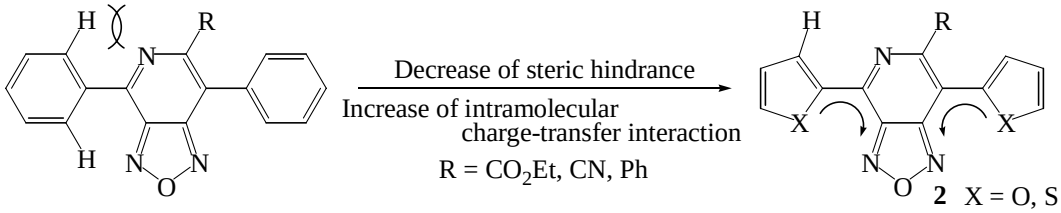
1a X = S, **1b** X = O

Scheme 1

Recently, the authors have prepared a number of heterocyclic-ring annelated pyridines, which are strongly fluorescent in solution and in the solid state.[5] Of these, 4,7-bis(4'-ethoxyphenyl)-6-(3",4"-dimethoxyphenyl)-1,2,5-thia(oxa)diazolo[3,4-*c*]pyridine (**1**) was found useful in orange color OLED[6] (Scheme 1). It was considered that replacement of the phenyl groups on the 4- and 7-positions of **1** with thiophene and furan units might decrease the steric repulsion between the thia(oxa)diazolopyridine ring and the aromatic rings, which would lead to greater conjugation of the π-system. Moreover, the replacement might cause an intramolecular charge-transfer interaction between the electron-rich thiophene or furan ring and the

electron-withdrawing thia(oxa)diazolopyridine ring in the molecule (Scheme 2).

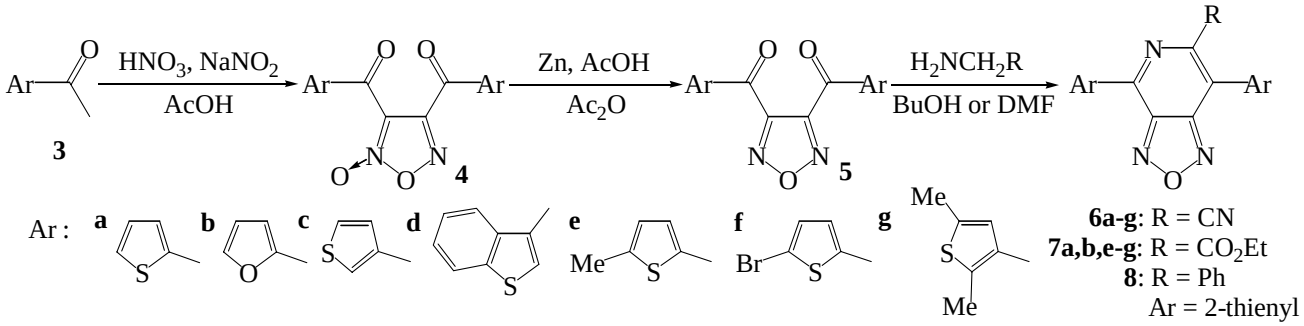
Aiming for red fluorescent compounds, 1,2,5-oxadiazolo[3,4-*c*]pyridines (**2**) with heteroaromatic thiophene- and furan-rings at the 4,7-positions were designed and prepared, and their spectral properties were studied.



Scheme 2

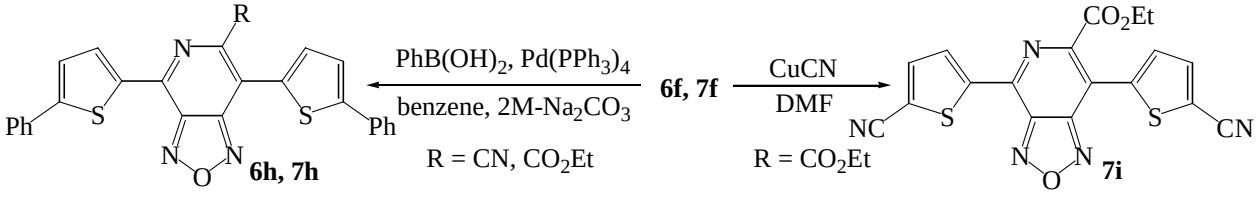
RESULTS AND DISCUSSION

Preparation. The preparation of 1,2,5-oxadiazolo[3,4-*c*]pyridines (**6**-**8** and **10**) with electron-rich thiophene, benzothiophene, and furan rings at the 4- and 7-positions is shown in Schemes 3-5. Derivatives (**6**, **7** and **8**) with a cyano, ethoxycarbonyl, or phenyl group at the 6-position were prepared from the corresponding heteroaromatic methyl ketones (**3**) *via* a sequence of oxidative dimerization with nitric acid to 3,4-dihetaroyl-1,2,5-oxadiazole-*N*-oxide (**4**), reduction of **4** with zinc powder to 1,2,5-oxadiazole (**5**), and then condensation of **5** with methylamine derivatives (Scheme 3).[7,8]

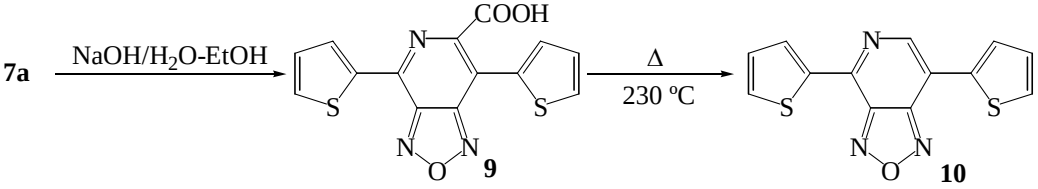


Scheme 3

Bis(5-phenylthien-2-yl) derivatives (**6h**) and (**7h**) with an extended π-system were prepared by Suzuki coupling[9] of the corresponding bromo derivatives (**6f**) and (**7f**) with phenylboronic acid in the presence of a palladium(0) catalyst (Scheme 4). 4,7-Bis(5-cyanothien-2-yl)-1,2,5-oxadiazolo-[3,4-*c*]pyridine (**7i**) was obtained in the reaction of 5-bromo derivative (**7f**) with copper(I) cyanide.



Scheme 4



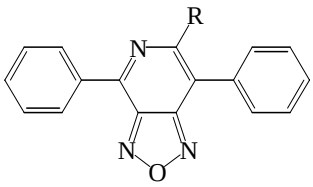
Scheme 5

6-Unsubstituted 4,7-bis(2-thienyl) derivative (**10**) was prepared by hydrolysis of ester (**7a**) and the thermal decarboxylation of the carboxylic acid (**9**) (Scheme 5).

Table 1. Absorption and emission spectra of **6**, **7**, **11** and **12**

Compound	Ar	Absorption[a] λ max (log ε) [nm]	Emission[b] Solution[a] [nm]	Φ[a,c]	Solid [nm]	Compound	Ar	Absorption[a] λ max (log ε) [nm]	Emission[b] Solution[a] [nm]	Φ[a,c]	Solid [nm]
6 (R = CN)						**7** (R = CO_2Et)					
6a	2-thienyl	474 (4.32)	563	0.46	623	**7a**	2-thienyl	457 (4.21)	567	0.28	594
6b	2-furyl	478 (4.31)	562	0.49	-	**7b**	2-furyl	470 (4.23)	567	0.33	594
6c	3-thienyl	433 (4.23)	537	0.59	572						
6d	benzo[*b*] thien-3-yl	471 (4.22)	562	0.51	604						
6e	5-methyl-thien-2-yl	504 (4.36)	594	0.41	661	**7e**	5-methyl-thien-2-yl	481 (4.26)	596	0.15	647
6f	5-bromo-thien-2-yl	494 (4.41)	579	0.49	667	**7f**	5-bromo-thien-2-yl	471 (4.34)	579	0.24	622
6g	2,5-dimethyl-thien-3-yl	457 (4.10)	556	0.17	589	**7g**	2,5-dimethyl-thien-3-yl	437 (4.01)	558	0.02	546
6h	5-phenyl-thien-2-yl	547 (4.58)	634	0.34	-	**7h**	5-phenyl-thien-2-yl	517 (4.49)	627	0.26	669
						7i	5-cyano-thien-2-yl	439 (4.34)	549	0.50	595
11	phenyl	400 (4.20)	508	0.45	504	**12**	phenyl	389 (4.11)	516	0.16	494

a) in $CHCl_3$. b) Emission spectra were obtained from excitation of the molecules at the λ max observed in the UV/VIS spectra. c) Fluorescence quantum yields (Φ) were determined using rhodamine-B in ethanol as a standard (Φ = 1.00[10]).



11: R = CN
12: R = CO_2Et

Scheme 6

Table 2. Absorption and emission spectra of **6a, 7a, 8** and **10**

Compound	Ar	R	Absorption[a] λ max (log ε) [nm]	Emission[b] Solution[a] [nm]	Φ[a,c]	Solid [nm]
6a	2-thienyl	CN	474 (4.32)	563	0.46	623
7a	2-thienyl	CO_2Et	457 (4.21)	567	0.28	594
8	2-thienyl	Ph	468 (4.34)	590	0.16	614
10	2-thienyl	H	464 (3.94)	570	0.35	621

a) in $CHCl_3$. b) Emission spectra were obtained from excitation of the molecules at the λ max observed in the UV/VIS spectra. c) Fluorescence quantum yields (Φ) were determined using rhodamine-B in ethanol as a standard (Φ = 1.00[10]).

UV/VIS and fluorescence spectra. The UV/VIS and fluorescence spectral data of 4,7-di(hetaryl)oxadiazolopyridines (**6**, **7**, **8** and **10**) are summarized in Tables 1-2. Those of the diphenyl derivatives (**11**) and (**12**) are shown for comparison (Tables 1-2).

UV/VIS spectra. As expected, both the 2-thienyl and 2-furyl rings at the 4- and 7-positions of the 1,2,5-oxadiazolo[3,4-*c*]pyridine cause a large bathochromic shift in the UV/VIS spectra and **6a-b** and **7a-b** show λ max at a wavelength 68-81 nm longer than that of the corresponding diphenyl derivatives[11] (**11**) and (**12**). Further bathochromic shift was observed in the spectra of **6e**, **6f**, **7e**, and **7f**, where a methyl group or a bromo funcitionality was introduced in the thiophene rings at the 4- and 7-positions. Introduction of a phenyl group causes a large bathochromic shift (73 nm for **6h** and 60 nm for **7h**, as compared to **6a** and **7a**, respectively). The electron-withdrawing cyano group causes a hypsochromic shift of λ max, due to an unfavorable electronic situation for an intramolecular charge transfer interaction.

Compound (**6c**) with two 3-thienyl groups shows a bathochromic shift, though the shift is smaller than that of **6a**. This may be because of a less favorable mesomeric effect in **6c**, in addition to the steric hindrance between the central oxadiazolopyridine ring and the 3-thienyl substituents. Benzo[*b*]thien-3-yl group causes a bathochromic shift, but λ max of **6d** does not exceed those of **6a-b**. The λ max of **6g** and **7g** show a shift to shorter wavelengths, due to a decreased conjugation between the bulky 2,5-dimethylthiophene rings and the central oxadiazolopyridine ring. Compound (**8**) which has a phenyl group at the 6-position exhibits a bathochromic shift as compared to unsubstituted compound (**10)**.

Calculation. Figures 1 and 2 show the relationship between the observed λ max of oxadiazolopyridines (**6**, **7a-b**, and **7e-h**) in the UV/VIS spectra and values calculated by winppp[12] and ZINDO on structures optimized by either MM2, PM3 or AM1. Calculations on a series of 6-cyano compounds (**6**) by using winppp alone could reproduce the observed λ max, but the method is less effective in case of **7** with a bulky ester and phenyl group at the 6-position. ZINDO methods (using MM2, PM3 or AM1) were unsatisfactory.

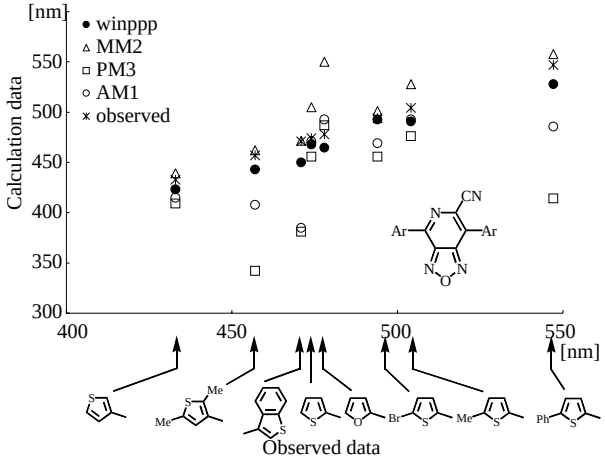


Figure 1 Observed and calculated values of absorption (λ max) of 6-cyano derivatives

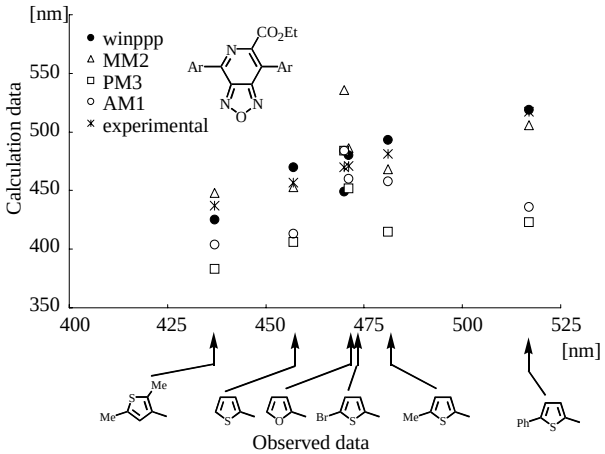


Figure 2 Observed and calculated values of absorption (λ max) 6-ethyl carboxylate derivatives

X-Ray structure determination of 7a. The ORTEP drawing of oxadiazolopyridine **7a** (Figure 3) shows that the two thiophene rings have the sulfur atoms positioned on the side of the pyridine ring of the 1,2,5-oxadiazolo[3,4-*c*]pyridine ring. The thiophene ring at the 4-position is almost planar with the central oxadiazolopyridine; the dihedral angle between the two rings is 1.1 degrees. On the other hand, the thiophene ring at the 7-position is not co-planar with the central ring, due to the bulky ester group at the 6-position. The two rings are twisted from co-planarity by 22 degrees.

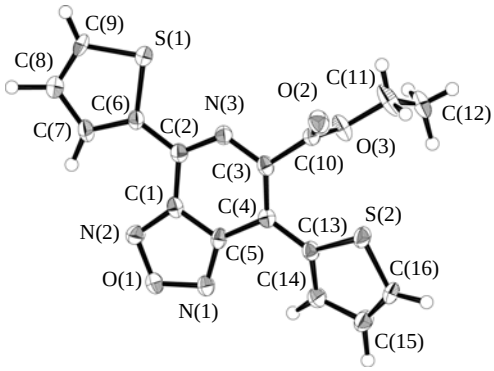


Figure 3 ORTEP view of **7a**

Fluorescence spectra. Oxadiazolopyridines (**6** - **8**, and **10**) prepared in this study, emit fluorescence of orange to red color (537-634 nm) in a chloroform solution. The Stokes shifts are large (84-122 nm), as previously found in 4,7-diphenyl-1,2,5-oxadiazolo[3,4-*c*]pyridine

derivatives.[11] Compounds (**6**, **7** and **8**) show fluorescence in the solid state, except for **6b** and **6h**. The emission peaks of **6**, **7**, **8** and **10** shift to longer wavelengths in the solid state. This fact is in contrast with the spectral data of **11** and **12**, which show a shift to shorter wavelengths, suggesting an intermolecular electronic interaction of the electron-poor 1,2,5-oxadiazolo[3,4-*c*]pyridine with the electron-rich thiophene and furan substituents.

The quantum yields of **6**, **7** and **8** were determined by employing rhodamine-B in ethanol as a standard.[10] Quantum yields of **6**, which have a cyano substituent at the 6-position, are higher than those of the corresponding **7** with a flexible ester function. It was found that a cyano group tends to increase the fluorescence of **6** and **7**, as noted in the comparison of 6-cyano derivative (**6a**) to unsubstituted compound (**10**), and **7i** with cyanothiophene rings to **7a** having unsubstituted thienyl substituents (Table 2). In the case of **8**, which has a phenyl group at the 6-position, the quantum yield decreased, if compared with **10**.

Finally, as a preliminary investigation, an organic light-emitting diode (OLED) using **7h** as a light-emitting dopant was fabricated by Kyushu Matsushita Electric Co. LTD. The device emitted red electroluminescence (680 nm), though the intensity was weak. The study on the application of **6** and **7** as light-emitting materials is now in progress.

EXPERIMENTAL

Melting points were determined on a Yanaco micromelting point apparatus (MP 500D) and are uncorrected. IR spectra were recorded on KBr pellets on JASCO IR-700 spectrophotometer. ^{1}H NMR spectra were obtained on a JEOL JNM-EX 270(270 MHz) in a $CDCl_3$ solution unless otherwise stated. MS spectra were obtained at 75 eV by using a JMS-01SA-2 mass spectrometer. Elemental analyses were performed at the Elemental Analytical Center, Kyushu University. UV-VIS spectra were obtained on JASCO V-570 spectrometer. Fluorescence spectra were performed on JASCO FP-777 spectrometer. Quantum yields were measured on a home-made fluorescence measurement system equipped with a CCD camera.[10] Column chromatography was carried out on silica gel (Wako gel C-300).

Preparation of 4. Typical procedure. A solution of nitric acid (60 %, d=1.38, 63 mL, 0.825 mol) in acetic acid (100 mL) was added dropwise to a solution of 2-acetylthiophene (**3a**) (41.9 g, 0.33 mol) and sodium nitrite (0.68 g, 0.01 mol) in acetic acid (100 mL) at rt for 1 h. After the reaction mixture was stirred at rt for 72 h, it was poured into water (200 mL) and the precipitate was filtered. The filtrate was neutralized with sodium hydrogen carbonate and extracted with chloroform (100 mL x 3). The extract was dried over magnesium sulfate, and evaporated in *vacuo* to give a solid. The solid and the precipitate were combined, and recrystallized from ethanol, giving **4a** (19.2 g, 38%).

3,4-Bis(2-thienoyl)-1,2,5-oxadiazole-*N*-oxide (4a): yield 38%, colorless needles (ethanol), mp 117-118 ºC (lit.,[7] 112-113 ºC); IR ν 1625, 1512, 1408, 1358, 1049, 830, 677 cm^{-1}; ^{1}H-NMR δ: 7.19-7.31 (m, 2H), 7.61 (d, 1H, *J* = 4.0 Hz), 7.88-7.91 (m, 2H), 8.31 (d, 1H, *J* = 4.0 Hz); MS: *m/z* 290 (M^+ - 16). *Anal*. Calcd for $C_{12}H_6N_2O_4S_2$: C, 47.05; H, 1.97; N, 9.15. Found; C, 47.08; H, 1.98; N, 9.13.

3,4-Bis(2-furoyl)-1,2,5-oxadiazole-*N*-oxide (4b): yield 27%, colorless needles (ethanol), mp 114-115 ºC; IR ν 1663, 1601, 1562, 1463, 1388, 1330, 1283 cm^{-1}; ^{1}H-NMR δ: 6.65-6.87 (2H, m),

7.48 (1H, d, *J* = 4.0 Hz), 7.61 (1H, d, *J* = 1.0 Hz), 7.78-7.82 (2H, m); MS: *m/z* 258 (M^+ - 16). *Anal.* Calcd for $C_{12}H_6N_2O_6$: C, 52.57; H, 2.21; N, 10.22. Found; C, 2.20; H, 52.55; N, 10.19.

3,4-Bis(3-thienoyl)-1,2,5-oxadiazole-*N*-oxide (4c): yield 27%, yellow prisms (chloroform), mp 99-100 ºC; IR ν 1660, 1467, 1511, 1479, 1420, 1309, 1230 cm^{-1}; ^{1}H-NMR δ: 7.40-7.44 (m, 2H), 7.57 (d, 1H, *J* = 5.0 Hz), 7.76 (d, 1H, *J* = 5.0 Hz), 8.17 (s, 1H), 8.68 (s, 1H); MS: *m/z* 290 (M^+ - 16). *Anal.* Calcd for $C_{12}H_6N_2O_4S_2$: C, 1.97; H, 47.05; N, 9.15. Found; C, 1.99; H, 46.98; N, 9.07.

3,4-Bis(benzo[*b*]thien-3-oyl)-1,2,5-oxadiazole-*N*-oxide (4d): yield 29%, colorless prisms (ethanol), mp 196-198 ºC; IR ν 1642, 1615, 1492, 1421, 1204, 1036 cm^{-1}; ^{1}H-NMR δ: 7.43-7.59 (4H, m), 7.88-7.94 (2H, m), 8.36 (1H, s), 8.63-8.71 (2H, m), 9.07 (1H, s); MS: *m/z* 390 (M^+ - 16). *Anal.* Calcd for $C_{20}H_{10}N_2O_4S_2$: C, 2.48; H, 59.10; N, 6.84. Found; C, 59.08; H, 2.45; N, 6.95.

3,4-Bis(5-methylthien-2-oyl)-1,2,5-oxadiazole-*N*-oxide (4e): yield 62%, pale yellow prisms (chloroform), mp 152-154 ºC; IR ν 1657, 1614, 1469, 1446, 1343, 1260, 1234 cm^{-1}; ^{1}H-NMR δ: 2.59 (s, 3H), 2.61 (s,3H), 6.88 (d, 1H, *J* = 4.0 Hz), 7.37 (d, 1H, *J* = 4.0 Hz), 7.54 (d, 1H, *J* = 4.0 Hz), 8.11 (d, 1H, *J* = 4.0 Hz); MS: *m/z* 318 (M^+ - 16). *Anal.* Calcd for $C_{14}H_{10}N_2O_4S_2$: C, 50.29; H, 3.01; N, 8.38. Found; C, 50.21; H, 3.03; N, 8.59.

3,4-Bis(5-bromothien-2-oyl)-1,2,5-oxadiazole-*N*-oxide (4f): yield 47%, yellow prisms (chloroform), mp 148-150 ºC; IR ν 1660, 1621, 1473, 1403, 1337, 1056 cm^{-1}; ^{1}H-NMR δ: 7.19 (d, 1H, *J* = 4.3 Hz), 7.25 (d, 1H, *J* = 4.3 Hz), 7.47 (d, 1H, *J* = 4.0 Hz), 8.05 (d, 1H, *J* = 4.0 Hz); MS: *m/z* 462, 464, 466 (M^+). *Anal.* Calcd for $C_{12}H_4N_2O_4Br_2S_2$: C, 31.05; H, 0.87; N, 6.04. Found; C, 31.30; H, 0.94; N, 6.04.

3,4-Bis(2,5-dimethylthien-3-oyl)-1,2,5-oxadiazole-*N*-oxide (4g): yield 29%, colorless needles (chloroform), mp 126-129 ºC; IR ν 1656, 1614, 1553, 1481, 1448, 1380, 1231, 1128 cm^{-1}; ^{1}H-NMR δ: 2.38 (s, 3H), 2.45 (s, 3H), 2.68 (s, 3H), 2.69 (s, 3H), 6.76 (s, 1H), 7.37 (s, 1H); MS: *m/z* 362 (M^+), 346 (M^+ - 16). *Anal.* Calcd for $C_{16}H_{14}N_2O_4S_2$: C, 53.02; H, 3.89; N, 7.73. Found; C, 53.02; H, 3.88; N, 7.82.

Preparation of 5. Typical procedure. To a mixture of *N*-oxide (**4a**) (10.0 g, 33 mmol), acetic acid (4.0 g, 66.6 mmol), and acetic anhydride (20 mL) in ethanol (300 mL) was added zinc powder (5.0 g, 76.5 mmol) in small portions (1.0 g for every 10 min). After the addition was complete, the mixture was stirred at rt for 2 h and insoluble materials were filtered off. The filtrate was evaporated in *vacuo* to give the residue, which was dissolved in chloroform (100 mL). After insoluble materials were filtered off, the filtrate was treated with saturated aq. sodium hydrogen carbonate to remove remaining acetic acid, washed with saturated aq. sodium chloride, dried over magnesium sulfate, and evaporated in *vacuo* to give a residue, which, on trituration with ethanol, gave **5a**. Recrystallization from ethanol gave **5a** in 28% yield as colorless needles. The mother liquor was evaporated in *vacuo* and the residue was subjected to column chromatography (chloroform/hexane=1/2) to afford another crop of **5a** (2.11 g, 22%).

In place of ethanol, acetonitrile was employed as a solvent in the preparation of **5c**, **5e**, **5f**, and a 1:1-mixture (v/v) of acetonitrile and dichloromethane in the preparation of **5d**.

3,4-Bis(2-thienoyl)-1,2,5-oxadiazole (5a): yield 50%, colorless needles (ethanol), mp 111-112 ºC; IR ν 1646, 1508, 1413, 1360, 1315, 1142, 1056 cm^{-1}; ^{1}H-NMR δ: 7.25 (dd, 4H, *J* = 4.0, 4.2 Hz), 7.90 (d, 2H, *J* = 4.2 Hz), 8.06 (d, 2H, *J* = 4.0 Hz). MS: m/z 290 (M^+). *Anal.* Calcd for $C_{12}H_6N_2O_3S_2$: C, 49.65; H, 2.08; N, 9.65. Found: C, 49.77; H, 2.16; N, 9.51.

3,4-Bis(2-furoyl)-1,2,5-oxadiazole (5b): yield 23%, colorless needles (chloroform/hexane =1/1), mp 123-124 ºC; IR ν 1654, 1558, 1460, 1394, 1326, 1030 cm^{-1}; ^{1}H-NMR δ: 6.69 (dd, 2H, *J* = 1.7, 3.6 Hz), 7.64 (d, 2H, *J* = 3.6 Hz), 7.79 (d, 2H, *J* = 1.7 Hz); MS: *m/z* 258 (M^+). *Anal.* Calcd for $C_{12}H_6N_2O_5$: C, 55.82; H, 2.34; N, 10.85. Found; C, 55.88; H, 2.33; N, 10.84.

3,4-Bis(3-thienoyl)-1,2,5-oxadiazole (5c): yield 44%, colorless prisms (ethanol), mp 99-100 ºC; IR ν 1657, 1512,1421, 1292, 1135, 973, 880 cm^{-1}; ^{1}H-NMR δ: 7.44 (d, 2H, *J* = 5.3 Hz), 7.75 (d, 2H, *J* = 5.3 Hz), 8.46 (s 2H); MS: *m/z* 290 (M^+). *Anal.* Calcd for $C_{12}H_6N_2O_3S_2$: C, 49.64; H, 2.08; N, 9.65. Found; C, 49.45; H, 2.03; N, 9.70.

3,4-Bis(benzo[*b*]thien-3-oyl)-1,2,5-oxadiazole (5d): yield 32%, colorless prisms (chloroform), mp 203-205 ºC; IR ν 1657, 1638, 1490, 1461, 1420, 1376, 1246 cm^{-1}; ^{1}H-NMR δ: 7.47 (4H, m), 7.93 (2H, d, J=8.9 Hz), 8.06 (4H, m); MS: *m/z* 390 (M^+). *Anal.* Calcd for $C_{20}H_{10}N_2O_3S_2$: C, 61.52; H, 2.58; N, 7.17. Found; C, 61.20; H, 2.54; N, 7.10.

3,4-Bis(5-methylthien-2-oyl)-1,2,5-oxadiazole (5e): yield 34%, colorless prisms (ethanol), mp 130-131 ºC; IR ν 1653, 1538, 1446, 1340, 1322, 1232, 1166, 1059 cm^{-1}; ^{1}H-NMR δ: 2.61 (6H, s), 6.91 (2H, d, *J* = 4.0 Hz), 7.84 (2H, d, *J* = 4.0 Hz); MS: *m/z* 318 (M^+). *Anal.* Calcd for $C_{14}H_{10}N_2O_3S_2$: C, 52.82; H, 3.17; N, 8.80. EA Found; C, 52.90; H, 3.24; N, 8.85.

3,4-Bis(5-bromothien-2-oyl)-1,2,5-oxadiazole (5f): yield 31%, colorless prisms (chloroform), mp 139-140 ºC; IR ν 3100, 1661, 1633, 1516, 1403, 1327, 1137, 1059 cm^{-1}; ^{1}H-NMR δ: 7.22 (2H, d, *J* = 4.3 Hz), 7.79 (2H, d, *J* = 4.3 Hz); MS: *m/z* 446, 448, 450 (M^+). *Anal.* Calcd for $C_{12}H_4N_2O_3Br_2S_2$: C, 32.16; H, 0.90; N, 6.25. Found; C, 32.34; H, 0.92; N, 6.27.

3,4-Bis(2,5-dimethylthien-3-oyl)-1,2,5-oxadiazole (5g): yield 28%, colorless needles (ethanol), mp 110-112 ºC; IR ν 1660, 1647, 1511, 1479, 1309, 1230 cm^{-1}; ^{1}H-NMR δ: 2.41(6H, s), 2.72(6H, s), 7.13 (2H, s); MS: *m/z* 346 (M^+). *Anal.* Calcd for $C_{16}H_{14}N_2O_3S_2$: C, 55.47; H, 4.07; N, 8.09. Found; C, 55.56; H, 4.16; N, 8.15.

Preparation of 6a-g. Typical procedure. A solution of **5a** (500 mg, 1.7 mmol) and aminoacetonitrile hydrogen sulfate (1.59 g, 10.3 mmol) in butanol (50 mL) was heated under reflux for 18 h and the solvent was evaporated in *vacuo*. The residue obtained was dissolved in chloroform (50 mL) and the chloroform layer was washed with 10% hydrochloric acid (50 mL x 3), dried over magnesium sulfate, and evaporated in *vacuo* to give a residue, which, on column chromatography (chloroform/hexane=2/1), afforded **6a** (316 mg) in 59% yield.

4,7-Bis(2-thienyl)-6-cyano-1,2,5-oxadiazolo[3,4-*c*]pyridine (6a): yield 59%, red needles (chloroform), mp 244-246 ºC; IR ν 1537, 1471, 1435, 1198, 1061 cm^{-1}; ^{1}H-NMR δ: 7.29-7.34 (2H, m), 7.75-7.78 (2H, m), 8.41 (1H, d, *J* = 4.8 Hz), 8.58 (1H, d, *J* = 2.6 Hz); MS: *m/z* 310 (M^+). *Anal.* Calcd for $C_{14}H_6N_4OS_2$: C, 54.18; H, 1.95; N, 18.05. Found; C, 54.23; H, 1.93; N, 18.16.

4,7-Bis(2-furyl)-6-cyano-1,2,5-oxadiazolo[3,4-*c*]pyridine (6b): yield 11%, dark red needles (chloroform/hexane =1/1), mp 229-230 ºC; IR ν 3118, 2228, 1589, 1562, 1488, 1384, 1197, 1026, 966, 886 cm^{-1}; ^{1}H-NMR δ: 6.76-6.78 (2H, m), 7.84-7.90 (4H, m); MS: *m/z* 278 (M^+). *Anal.* Calcd for $C_{14}H_6N_4O_3$: C, 60.44; H, 2.17; N, 20.14. Found; C, 60.41; H, 2.24; N, 19.97.

4,7-Bis(3-thienyl)-6-cyano-1,2,5-oxadiazolo[3,4-*c*]pyridine (6c): yield 39%, red needles (ethanol), mp 151-152 ºC; IR ν 2230, 1574, 1526, 1481, 1443, 1341, 1229, 1147 cm^{-1}; ^{1}H-NMR δ: 7.52 (d, 1H, *J* = 5.0 Hz), 7.60 (d, 1H, *J* = 5.3 Hz), 8.06 (d, 1H, *J* = 5.0 Hz), 8.17(d, 1H, *J* = 5.0 Hz), 8.49 (s, 1H); MS: *m/z* 310 (M^+). *Anal.* Calcd for $C_{14}H_6N_4OS_2$: C, 54.18; H, 1.95; N, 18.05. Found;

C, 54.26; H, 1.93; N, 18.13.

4,7-Bis(benzo[*b*]thien-3-yl)-6-cyano-1,2,5-oxadiazolo[3,4-*c*]pyridine (6d): yield 32%, orange prisms (chloroform/hexane =1/1), mp 313-314 ºC; IR ν 3102, 2236, 1514, 1178, 1026, 899, 823, 761 cm^{-1}; ^{1}H-NMR δ: 7.48-7.71 (5H, m), 7.98-8.04 (2H, m), 8.12 (1H, s), 9.29 (1H, d, *J* =8.6 Hz), 9.45 (1H, s); MS: *m/z* 410 (M^+). *Anal.* Calcd for $C_{22}H_{10}N_4OS_2$: C, 64.37; H, 2.46; N, 13.65. Found; C, 64.25; H, 2.43; N, 13.62.

4,7-Bis(5-methylthien-2-yl)-6-cyano-1,2,5-oxadiazolo[3,4-*c*]pyridine (6e): yield 60%, dark red needles (chloroform), mp 231-232 ºC; IR ν 2230, 1544, 1468, 1375, 1198, 1166 cm^{-1}; ^{1}H-NMR δ: 2.62 (s, 3H), 2.63 (s, 3H), 6.87-6.98 (m, 2H), 8.22 (d, 1H *J* = 4.0 Hz), 8.36 (d, 1H, *J* = 3.6 Hz); MS: *m/z* 338 (M^+). *Anal.* Calcd for $C_{16}H_{10}N_4OS_2$: C, 56.79; H, 2.98; N, 16.56. Found; C, 56.42; H, 2.99; N, 16.26.

4,7-Bis(5-bromothien-2-yl)-6-cyano-1,2,5-oxadiazolo[3,4-*c*]pyridine (6f): yield 17%, dark red prisms (chloroform), mp 236-237 ºC; IR ν 2226, 1540, 1470, 1434, 1400, 1379, 1308, 1194 cm^{-1}; ^{1}H-NMR δ: 7.26-7.30 (2H, m), 8.20 (1H, d, *J* = 4.3 Hz), 8.31 (1H, d, *J* = 4.0 Hz); MS: *m/z* 466, 468, 470 (M^+). *Anal.* Calcd for $C_{14}H_4N_4OBr_2S_2$: C, 35.92; H, 0.86; N, 11.97. Found; C, 36.17; H, 0.95; N, 11.89.

4,7-Bis(2,5-dimethylthien-3-yl)-6-cyano-1,2,5-oxadiazolo[3,4-*c*]pyridine (6g): yield 76%, orange needles (chloroform), mp 186-187 ºC; IR ν 2226, 1552, 1502, 1475, 1442, 1197, 1140 cm^{-1}; ^{1}H-NMR δ: 2.49 (3H, s), 2.51 (3H, s), 2.53 (3H, s), 2.89 (1H, s), 6.92 (1H, s), 7.88 (1H, s); MS: *m/z* 366 (M^+). *Anal.* Calcd for $C_{18}H_{14}N_4OS_2$: C, 58.99; H, 3.85; N, 15.29. Found; C, 59.11; H, 3.82; N, 15.28.

4,7-Bis(5-phenylthien-2-yl)-6-cyano-1,2,5-oxadiazolo[3,4-*c*]pyridine (6i). To a mixture of **6f** (200 mg, 0.46 mmol), tetrakis(triphenylphosphine)palladium (16 mg, 13 μmol), benzene (6 mL) and aq. 2M-sodium carbonate (3 mL) was added a solution of phenylboronic acid (134 mg, 1.1 mmol) in degassed ethanol (1.5 mL) under argon. The reaction mixture was refluxed for 6 h, poured into water (100 mL) and was extracted with dichloromethane (50 mL x 3). The dichloromethane layer was washed with water (50 mL x 3), dried over magnesium sulfate, and evaporated in *vacuo* to give a residue, which on column chromatography (chloroform) afforded **6i** in 50% yield (99 mg) as dark red needles (benzene), mp 281-283 ºC; IR ν 2224, 1542, 1458, 1440, 1212, 1199 cm^{-1}; ^{1}H-NMR δ: 7.36 (m, 8H), 7.73-7.78 (m, 4H), 8.45 (d, 1H, *J* = 4.3 Hz), 8.54 (d, 1H, *J* = 4.3 Hz); FAB-MS (3-nitrobenzyl alcohol): *m/z* 463 (MH^+). *Anal.* Calcd for $C_{26}H_{14}N_4OS_2$: C, 67.51; H, 3.05; N, 12.11. Found; C, 67.67; H, 3.05; N, 11.79.

Preparation of 7a, 7b, 7e, 7f and 7g. Typical procedure. A solution of **5a** (1.00 g, 3.44 mmol) and ethyl glycinate hydrogen chloride (3.37 g, 24.1 mmol) in butanol (50 mL) was heated under reflux for 48 h and the solvent was evaporated in *vacuo*. The residue obtained was dissolved in chloroform (50 mL) and the chloroform layer was washed with 10% hydrochloric acid (50 mL x 3), dried over magnesium sulfate, and evaporated in *vacuo* to give a residue, which on column chromatography (chloroform/hexane =1/1) afforded **7a** in 49% yield (564 mg).

In place of butanol, dimethylformamide was employed as a solvent in the preparation of **7e** and **7g**.

Ethyl 4,7-bis(2-thienyl)-1,2,5-oxadiazolo[3,4-*c*]pyridine-6-carboxylate (7a): yield 49%, red needles (chloroform); mp 124-125 ºC; IR ν 1730, 1538, 1440, 1281, 1236, 1167, 1059 cm^{-1}; ^{1}H-NMR δ: 1.32 (t, 3H, *J* = 7.3 Hz), 4.44 (q, 2H, *J* = 7.3 Hz), 7.19-7.32 (m, 3H), 7.56 (1H, d, *J* =

5.3 Hz), 7.70-7.72 (m, 2H), 8.57 (d, 1H, *J* = 3.0 Hz); MS: *m/z* 357 (M^+). *Anal.* Calcd for $C_{16}H_{11}N_3O_3S_2$: C, 53.77; H, 3.10; N, 11.76. Found; C, 53.73; H, 3.01; N, 11.91.

Ethyl 4,7-bis(2-furyl)-1,2,5-oxadiazolo[3,4-*c*]pyridine-6-carboxylate (7b): yield 42%, red needles (ethanol); mp 141-143 ºC; IR ν 1774, 1596, 1499, 1386, 1270, 1022, 964 cm^{-1}; ^{1}H-NMR δ: 1.43 (t, 3H, *J* = 7.3 Hz), 4.55 (q, 2H, *J* = 7.3 Hz), 6.67 (dd, 1H, *J* = 1.7, 3.6 Hz), 6.73 (dd, 1H, *J* = 1.7, 3.6 Hz), 7.56 (d, 1H, *J* = 3.6 Hz), 7.62 (d, 1H, *J* = 1.7 Hz), 7.83 (d, 1H, *J* = 1.7 Hz), 7.88 (d, 1H, *J* = 3.6 Hz); MS: *m/z* 325 (M^+). *Anal.* Calcd for $C_{16}H_{11}N_3O_5$: C, 59.08; H, 3.41; N, 12.92. Found; C, 58.99; H, 3.51; N, 12.66.

Ethyl 4,7-bis(5-methylthien-2-yl)-1,2,5-oxadiazolo[3,4-*c*]pyridine-6-carboxylate (7e): yield 22%, red needles (chloroform), mp 170-171 ºC; IR ν 1741, 1544, 1474, 1280, 1230, 1177 cm^{-1}; ^{1}H-NMR δ: 1.35 (t, 3H, *J* = 6.9 Hz), 2.57 (s, 3H), 2.60 (s, 3H), 4.44 (q, 2H, *J* = 6.9 Hz), 6.85 (d, 1H, *J* = 3.3 Hz), 6.94 (d, 1H, *J* = 3.3 Hz), 7.53 (d, 1H, *J* = 3.3 Hz), 8.35 (d, 1H, *J* = 3.3 Hz); MS: *m/z* 318 (M^+). *Anal.* Calcd for $C_{18}H_{15}N_3O_3S_2$: C, 56.09; H, 3.92; N, 10.90. Found; C, 56.03; H, 3.91; N, 10.99.

Ethyl 4,7-bis(5-bromothien-2-yl)-1,2,5-oxadiazolo[3,4-*c*]pyridine-6-carboxylate (7f): yield 49%, red needles (chloroform), mp 159-160 ºC; IR ν 1733, 1540, 1481, 1440, 1384, 1276, 1151, 1068 cm^{-1}; ^{1}H-NMRδ: 1.37 (3H, t, *J* = 7.3 Hz), 4.46 (2H, q, *J* = 7.3 Hz), 7.17 (1H, d, *J* = 4.0 Hz), 7.25 (1H, d, *J* = 4.3 Hz), 7.49 (1H, d, *J* = 4.0 Hz), 8.30 (1H, d, *J* = 4.3 Hz); MS: *m/z* 513, 515, 517 (M^+). *Anal.* Calcd for $C_{16}H_9N_3O_3Br_2S_2$: C, 37.30; H, 1.76; N, 8.16. Found; C, 37.66; H, 1.79; N, 8.23.

Ethyl 4,7-bis(2,5-dimethylthien-3-yl)-1,2,5-oxadiazolo[3,4-*c*]pyridine-6-carboxylate (7g): yield 13%, yellow needles (ethanol), mp 132-134 ºC; IR ν 1734, 1507, 1267, 1181, 1137, 1016 cm^{-1}; ^{1}H-NMR δ: 1.22 (t, 3H, *J* = 7.3 Hz), 2.28 (s, 3H), 2.47 (s, 3H), 2.53 (s, 3H), 2.90 (s, 3H), 4.30 (q, 2H, *J* = 7.3 Hz), 6.72 (s, 3H), 7.85 (s, 3H); MS: *m/z* 413(M^+). *Anal.* Calcd for $C_{20}H_{19}N_3O_3S_2$: C, 58.09; H, 4.63; N, 10.16. Found; C, 58.01; H, 4.57; N, 10.18.

Preparation of ethyl 4,7-bis(5-phenylthien-2-yl)-1,2,5-oxadiazolo[3,4-*c*]pyridine-6-carboxylate (7i). To a mixture of **7f** (100 mg, 0.19 mmol), tetrakis(triphenylphosphine)palladium (6.7 mg, 5.8 μmol), benzene (2 mL) and aq. 2M-sodium carbonate (1.5 mL) was added a solution of phenylboronic acid (52 mg, 0.43 mmol) in degassed ethanol (0.5 mL) under argon. The reaction mixture was refluxed for 6 h, poured into water (20 mL) and was extracted with dichloromethane (10 mL x 3). The dichloromethane layer was washed with water (20 mL x 3), dried over magnesium salfate, and evaporated in *vacuo* to give a residue, which on column chromatography (chloroform) afforded **7i** in 67% yield (66 mg): dark red needles (chloroform), mp 188-189 ºC; IR ν 1737, 1538, 1459, 1385, 1275, 1250, 1176, 1136 cm^{-1}; ^{1}H-NMR δ: 1.38 (t, 3H, *J* = 7.3 Hz), 4.50 (q, 2H, *J* = 7.3 Hz), 7.31-7.52 (m, 8H), 7.68 (d, 2H, *J* = 8.2 Hz), 7.74-7.77(m, 3H), 8.54 (d, 1H, *J* = 4.0 Hz); FAB-MS (3-nitrobenzylalcohol): *m/z* 510 (MH^+). *Anal.* Calcd for $C_{28}H_{19}N_3O_3S_2$: C, 65.99; H, 3.76; N, 8.25. Found; C, 65.91; H, 3.73; N, 8.27.

Preparation of ethyl 4,7-bis(5-cyanothien-2-yl)-1,2,5-oxadiazolo[3,4-*c*]pyridine-6-carboxylate (7j). After a solution of **7f** (100 mg, 0.19 mmol) and cuprous cyanide (40 mg, 0.44 mmol) in dimethylformamide (5 mL) was heated under reflux for 12 h, it was poured into a mixture of water (60 mL), concentrated hydrochloric acid (10 mL) and anhydrous iron(III) chloride (40 g). The mixture was stirred at 60ºC for 30 min, then extracted with chloroform (50 mL). The chloroform

layer was separated, washed with 10% hydrochloric acid (50 mL x 3), dried over magnesium sulfate, and evaporated *in vacuo* to give a residue, which, on column chromatography (ethyl acetate/hexane=1/3), afforded **7j** in 34% yield (20 mg): orange needles (hexane/chloroform =1/1), mp 195-196 ºC; IR ν 2222, 1736, 1527, 1460, 1413, 1286, 1178 cm^{-1}; ^{1}H-NMR δ: 1.38 (t, 3H, *J* = 7.3 Hz), 4.48 (q, 2H, *J* = 7.3 Hz), 7.71-7.74 (m, 2H), 7.78 (d, 1H, *J* = 4.0 Hz), 8.56 (d, 1H, *J* = 4.3 Hz); FAB-MS (3-nitrobenzyl alcohol) *m/z* 408(MH^+). *Anal.* Calcd for $C_{18}H_9N_5O_3S_2$: C, 53.06; H, 2.23; N, 17.19. Found; C, 52.92; H, 2.21; N, 17.15.

Preparation of 4,7-bis(2-thienyl)-1,2,5-oxadiazolo[3,4-*c*]pyridine-6-carboxylic acid (9). A mixture of **7a** (2.50 g, 6.99 mmol), potassium hydroxide (1.80 g, 32 mmol) in ethanol (50 mL) and water (50 mL) was heated under reflux for 2.5 h. After the reaction mixture was cooled to rt, it was poured into water (300 mL), and acidified with concentrated hydrochloric acid to pH 1. The mixture was stirred at rt for 2 h and the precipitate formed was filtered. The filtrate was extracted with chloroform (50 ml x 3), dried over magnesium sulfate, and evaporated *in vacuo* to give a solid. The solid and the precipitate were combined and recrystallized from 50% aqueous ethanol (v/v), giving **9** in 95% yield (2.20 g) as red plates; mp 220 ºC (decomp); IR ν 3262, 1733, 1538, 1481, 1435, 1299 cm^{-1}; ^{1}H-NMR (DMSO-d_6) δ: 7.30 (dd, 1H, *J* = 3.8, 5.0 Hz), 7.41 (dd, 1H, *J* = 3.8, 5.0 Hz), 7.74 (d, 1H, *J* = 3.8 Hz), 7.92 (d, 1H, *J* = 5.0 Hz), 8.08 (d, 1H, *J* = 5.0 Hz) 8.47 (d, 1H, *J* = 3.8 Hz); MS: *m/z* 329 (M^+). *Anal.* Calcd for $C_{14}H_7N_3O_3S_2$: C, 51.05; H, 2.14; N, 12.76. Found: C, 50.98; H, 2.37; N, 12.79.

Preparation of 4,7-bis(2-thienyl)-1,2,5-oxadiazolo[3,4-*c*]pyridine (10). Carboxylic acid (**9**) (0.30 g, 0.91 mmol) was heated at 220-240 ºC for 3 min in a silicon bath and cooled to rt. The pyrolysate was dissolved in chloroform (20 mL) and filtered to remove insoluble materials. The filtrate was evaporated in *vacuo* to give an orange residue, which on recrystallization from ethanol gave **10** in 33% yield (87 mg): orange needles; mp 215-216 ºC; IR ν 1530, 1489, 1437, 1244, 849 cm^{-1}; ^{1}H-NMR δ: 7.20-7.31 (m, 2H), 7.50 (d, 1H, *J* = 4.0 Hz), 7.67 (d, 1H, *J* = 4.3 Hz), 8.09 (d, 1H, *J* = 2.6 Hz) 8.56 (d, 1H, *J* = 2.6 Hz), 8.60 (s, 1H). MS: m/z 285 (M^+). Anal. Calcd for $C_{13}H_7N_3OS_2$: C, 54.72; H, 2.47; N, 14.73. Found: C, 54.78; H, 2.46; N, 14.73.

X-RAY CRYSTAL STRUCTURE DETERMINATION

Crystal data of 6a. Chemical Formula: $C_{16}H_{11}N_3O_3S_2$ *M*= 357.40. Crystal system monoclinic, unit cell dimensions *a* = 7.2111(4) Å, *b* = 16.495(1) Å, *c* = 13.1902(6) Å, *β* = 103.658(4)° *V* = 1524.6(1) $Å^3$, *Z*= 4, D_C = 1.557 g/cm^3, *μ*(Mo-Kα) = 0.7107 mm^{-1}. Space group $P2_1/n$ (No. 14). Crystal size 0.35 x 0.05 x 0.05 mm. *F*(000) 736. Temperature of Data Collection 153.2 K•.Index ranges $0 \leq h \leq 9$, $0 \leq k \leq 21$, $-17 \leq l \leq 16$. Reflections measured 3574. Independent Reflections 3444 [*R*(int) = 0.000, *R*(sigma) = 0.148]. The structure was solved by direct methods, SIR-92[13], and refinement method full-matrix least-squares refinement on F^2. Data/restraints/parameters 1648 / 0 / 218. Final *R* and R_W values 0.0611, 0.1460. All calculations were performed on a Gateway GP7-7000 using SIR92[13], Texsan[14]and SHELXL-97-2.[15]

The supplementary materials have been deposited at the Cambridge Crystallographic Data Center.

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