Synthesis of 1,2-Diazepino[3,4-*b*]quinoxalines and Pyrido[3′,4′:9,8][1,5,6]oxadiazonino[3,4-*b*]quinoxalines *via* a 1,3-Dipolar Cycloaddition Reaction

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The reaction of 6-chloro-2-(1-methylhydrazino)quinoxaline 4-oxide **8** with furfural, 3-methyl-2-thiophenecarbaldehyde, 2-pyrrolecarbaldehyde, 4-pyridinecarbaldehyde and pyridoxal hydrochloride gave 6-chloro-2-[2-(2-furylmethylene)-1-methylhydrazino]quinoxaline 4-oxide **5a**, 6-chloro-2-[1-methyl-2-(3-methyl-2-thienylmethylene)hydrazino]quinoxaline 4-oxide **5b**, 6-chloro-2-[1-methyl-2-(2-pyrrolylmethylene)hydrazino]quinoxaline 4-oxide **5c**, 6-chloro-2-[1-methyl-2-(4-pyridylmethylene)hydrazino]quinoxaline 4-oxide **5d** and 6-chloro-2-[2-(3-hydroxy-5-hydroxymethyl-2-methyl-4-pyridylmethylene)-1-methylhydrazino]quinoxaline 4-oxide **5e**, respectively. The reaction of compound **5a** or **5b** with 2-chloroacrylonitrile afforded 8-chloro-3-(2-furyl)-4-hydroxy-1-methyl-2,3-dihydro-1*H*-1,2-diazepino[3,4-*b*]quinoxaline-5-carbonitrile **6a** or 8-chloro-4-hydroxy-1-methyl-3-(3-methyl-2-thienyl)-2,3-dihydro-1*H*-1,2-diazepino[3,4-*b*]quinoxaline-5-carbonitrile **6b**, respectively, while the reaction of compound **5e** with 2-chloroacrylonitrile furnished 11-chloro-7,13-dihydro-4-hydroxymethyl-5,14-methano-1,7-dimethyl-16-oxopyrido[3′,4′:9,8][1,5,6]oxadiazonino[3,4-*b*]quinoxaline **7**.

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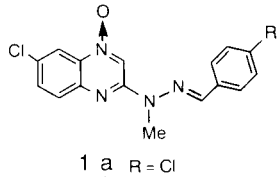
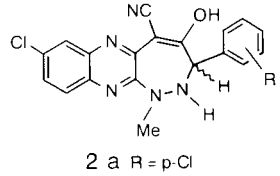
In previous papers [1,2], we reported that the 1,3-dipolar cycloaddition reaction of the quinoxaline 4-oxides **1** with 2-chloroacrylonitrile gave the 1,2-diazepino[3,4-*b*]quinoxalines **2**, whose alcoholysis afforded the 5-alkoxy-1,2-diazepino[3,4-*b*]quinoxalines **3** (Chart 1). Moreover, when the

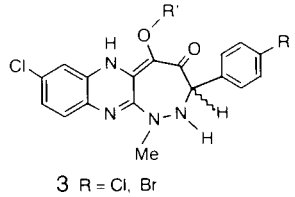
Chart 1



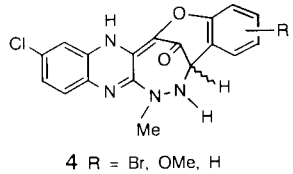
1 a R = Cl
b R = Br



2 a R = p-Cl
b R = p-Br



3 R = Cl, Br
R′ = Et, CH_2CH_2OH

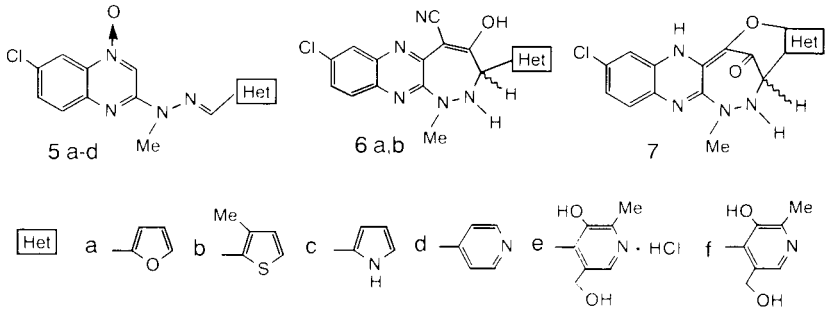


4 R = Br, OMe, H

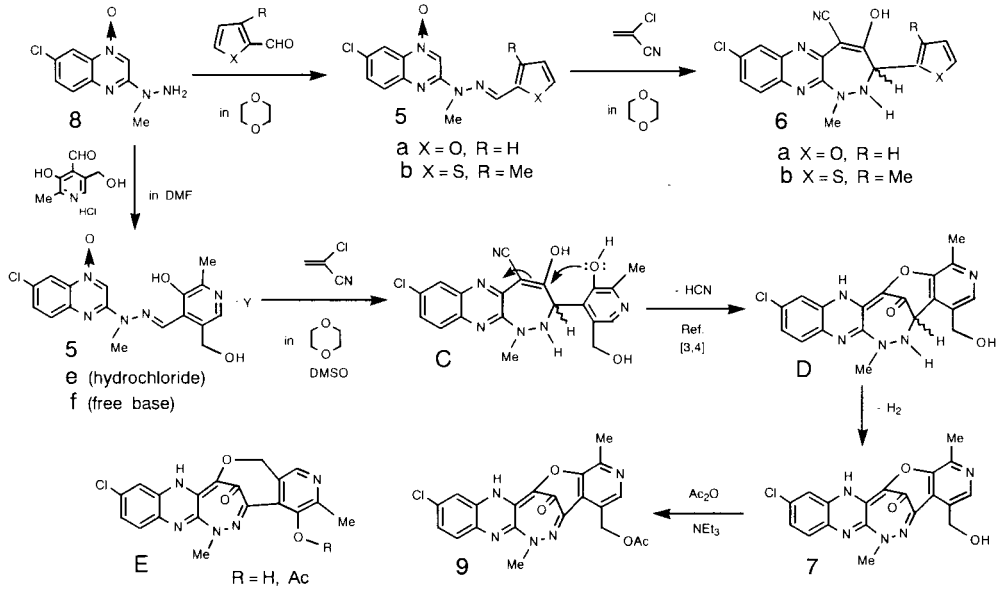
C_3-substituent was *o*-phenol residues in compounds **2**, an intramolecular alcoholysis took place to provide the 1,5,6-benzoxadiazonino[3,4-*b*]quinoxalines **4** [3,4]. From our recent screening data, the above compounds **1-4** were found to have only a weak antimicrobial activity [5], and some new candidates were synthesized in order to search for more active compounds. Accordingly, we undertook the synthesis of compounds **6** and **7** from compounds **5a-f** possessing heteroaryl moieties as shown in Chart 2. As the result, compounds **5a,b** and **5e,f** were clarified to be converted into the 1,2-diazepino[3,4-*b*]quinoxalines **6a,b** and pyrido[3′,4′:9,8][1,5,6]oxadiazonino[3,4-*b*]quinoxaline **7**, respectively. This paper describes the synthesis of novel compounds **5**, **6**, **7** and **9** (Scheme).

The reaction of 6-chloro-2-(1-methylhydrazino)quinoxaline 4-oxide **8** with furfural, 3-methyl-2-thiophenecarbaldehyde, 2-pyrrolecarbaldehyde, 4-pyridinecarbaldehyde and pyridoxal hydrochloride gave 6-chloro-2-[2-(2-furylmethylene)-1-methylhydrazino]quinoxaline 4-oxide **5a**, 6-chloro-2-[1-methyl-2-(3-methyl-2-thienylmethylene)hydrazino]-quinoxaline 4-oxide **5b**, 6-chloro-2-[1-methyl-2-(2-pyrrolylmethylene)hydrazino]quinoxaline 4-oxide **5c**, 6-chloro-2-[1-methyl-2-(2-pyridylmethylene)hydrazino]quinoxaline 4-oxide **5d** and 6-chloro-2-[2-(3-hydroxy-5-hydroxymethyl-2-methyl-4-pyridylmethylene)-1-methylhydrazino]quinoxaline 4-oxide hydrochloride **5e**, respectively. Treatment of the hydrochloride **5e** with sodium hydroxide afforded the

Chart 2

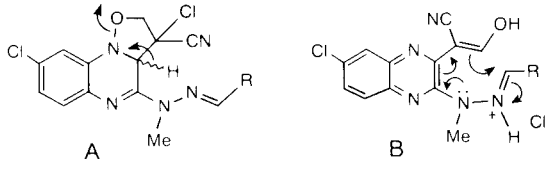


Scheme



free base **5f**. The reaction of compound **5a** or **5b** with 2-chloroacrylonitrile furnished 8-chloro-3-(2-furyl)-4-hydroxy-1-methyl-2,3-dihydro-1*H*-1,2-diazepino[3,4-*b*]quinoxaline-5-carbonitrile **6a** or 8-chloro-4-hydroxy-1-methyl-3-(3-methyl-2-thienyl)-2,3-dihydro-1*H*-1,2-diazepino[3,4-*b*]quinoxaline-5-carbonitrile **6b**, respectively, presumably *via* intermediates **A** and **B** (Chart 3) [1-4], while the reaction of

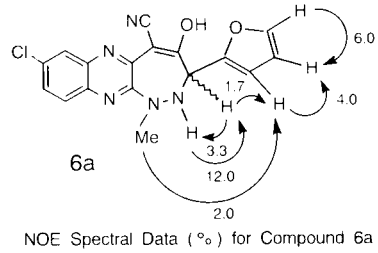
Chart 3



compound **5c** or **5d** (Chart 2) with 2-chloroacrylonitrile did not provide a 1,2-diazepino[3,4-*b*]quinoxaline derivative. On the other hand, the reaction of compound **5e** or **5f** with 2-chloroacrylonitrile gave 11-chloro-7,13-dihydro-4-hydroxymethyl-5,14-methano-1,7-dimethyl-16-oxopyrido[3′,4′:9,8][1,5,6]oxadiazonino[3,4-*b*]quinoxaline **7** presumably *via* intermediates **A**, **B**, **C** and **D** [1-4]. The 5,6-dihydro species **D** was easily dehydrogenated [4] to change into compound **7** and was not isolated in the present investigation. The reaction of compound **7** with acetic anhydride/triethylamine afforded 4-acetoxymethyl-11-chloro-7,13-dihydro-5,14-methano-1,7-dimethyl-16-oxopyrido[3′,4′:9,8][1,5,6]oxadiazonino[3,4-*b*]quinoxaline **9**.

The structural assignment of compounds **5**, **6**, **7** and **9** was based on the spectral and analytical data. Especially,

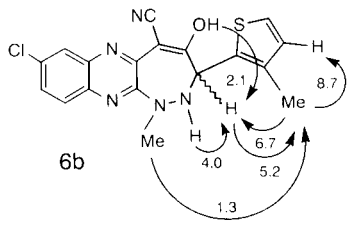
Chart 4



NOE Spectral Data (%) for Compound 6a

the structure of compounds **6a** and **6b** was ascertained by the NOE spectral data shown in Charts 4 and 5 [1-4]. The

Chart 5

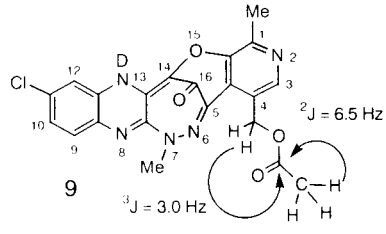


6b

NOE Spectral Data (%) for Compound 6b

^3J coupling (3.0 Hz) between the C_4-methylene proton (δ 5.37 ppm) and acetyl C=O carbon (δ 174.94 ppm) in compound **9** (Chart 6) excluded the structure **E** (Scheme). The

Chart 6

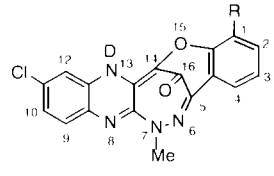


9

in deuteriotrifluoroacetic acid

nmr spectra of compounds **7** and **9** were measured in deuteriotrifluoroacetic acid because of their insolubility in most of other solvents, and hence the NOE between the C_{12}-H and N_{13}-H proton signals was not confirmed because of deuterization of the N_{13}-H proton. However, the C_9-H, C_{10}-H, C_{12}-H and N_7-Me proton signals of compounds **7** and **9** (Table) were observed in a similar magnetic field to those of compounds **10a,b** (Chart 7) [4], while

Chart 7



10 a R = H
b R = OMe

in deuteriotrifluoroacetic acid

the N_7-Me proton signals of compounds **7**,**9** and **10a,b** (δ 3.57-3.67 ppm) were observed in a lower magnetic field than those of compounds **4** (δ 3.30-3.31 ppm). Moreover, the nitrile carbon signals of compounds **2a,b** (Chart 2) [3] and compounds **6a,b** were observed at δ 113.30, 113.29, 114.09 and 114.07 ppm, respectively. The C_{16}=O carbon signals of compounds **7** and **9** were observed at δ 157.50 and 157.17 ppm, respectively.

Table

^{1}H-NMR Spectral Data for Compounds **7**,**9** and **10a,b**

Compound	Chemical Shift (δ ppm)			
	C_9-H	C_{10}-H	C_{12}-H	N_7-Me
7	6.73	6.82	6.89	3.59
9	6.69	6.79	6.86	3.57
10a	6.76	6.85	6.89	3.67
10b	6.74	6.83	6.88	3.64

EXPERIMENTAL

All melting points were determined on a Yazawa micro melting point BY-2 apparatus and are uncorrected. The ir spectra (potassium bromide) were recorded with a JASCO IRA-1 spectrophotometer. The nmr spectra were measured with VXR-300 spectrometer at 300 MHz. Chemical shifts are given on the δ scale. The mass spectra (ms) were determined with a JEOL JMS-01S spectrometer. Elemental analyses were performed on a Perkin-Elmer 240B instrument.

6-Chloro-2-[2-(2-furylmethylene)-1-methylhydrazino]quinoxaline 4-Oxide **5a**.

A solution of compound **8** (10 g, 44.5 mmoles) and furfural (6.41 g, 66.8 mmoles) in dioxane (200 ml) was refluxed in an oil bath for 1 hour. Cooling of the solution to room temperature precipitated yellow needles **5a**, which were collected by suction filtration and then washed with ethanol to give an analytically pure sample (12.46 g). Evaporation of the filtrate *in vacuo* afforded yellow needles **5a**, which were collected by suction filtration (0.70 g), total yield, 13.16 g (97%).

Compound **5a** had mp 237-238°; ir: ν 3130, 3080, 1605, 1565, 1525 cm^{-1}; ms: m/z 302 (M^+), 304 (M^+ +2); pmr (deuteriodimethyl sulfoxide): 8.83 (s, 1H, C_3-H), 8.27 (d, J = 2.0 Hz, 1H, furan C_5-H), 7.96 (s, 1H, hydrazone CH), 7.84 (dd, J = 2.0 Hz, J = 0.9 Hz, 1H, C_5-H), 7.83 (dd, J = 0.9 Hz, J = 9.0 Hz, 1H, C_8-H), 7.79 (dd, J = 9.0 Hz, J = 2.0 Hz, 1H, C_7-H), 6.95 (d, J = 3.0 Hz, 1H, furan C_3-H), 6.65 (dd, J = 2.0 Hz, J = 3.0 Hz, 1H, furan C_4-H), 3.67 (s, 3H, CH_3).

Anal. Calcd. for $C_{14}H_{11}ClN_4O_2$: C, 55.55; H, 3.66; Cl, 11.71; N, 18.51. Found: C, 55.70; H, 3.65; Cl, 11.60; N, 18.39.

6-Chloro-2-[1-methyl-2-(3-methyl-2-thienylmethylene)hydrazino]-quinoxaline 4-Oxide **5b**.

A solution of compound **8** (10 g, 44.5 mmoles) and 3-methyl-2-thiophenecarbaldehyde (9.36 g, 66.8 mmoles) in dioxane (200 ml) was refluxed in an oil bath for 1 hour. Cooling of the solution to room temperature precipitated yellow needles **5b**, which were collected by suction filtration and washed with ethanol to give an analytically pure sample (14.32 g, 97%), mp 228-229°; ir: ν 1570, 1520, 1480 cm^{-1}; ms: m/z 332 (M^+), 334 (M^+ +2); pmr (deuteriotrifluoroacetic acid): 8.87 (s, 1H, C_3-H), 8.38 (s, 1H, C_5-H), 8.21 (s, 1H, hydrazone CH), 7.65 (s, 2H, C_7-H and C_8-H), 7.29 (d, J = 5.0 Hz, 1H, thiophene C_5-H), 6.71 (d, J = 5.0 Hz, 1H, thiophene C_4-H), 3.60 (s, 3H, NCH_3), 2.18 (s, 3H, thiophene C_3-CH_3).

Anal. Calcd. for $C_{15}H_{13}ClN_4OS$: C, 54.14; H, 3.94; Cl, 10.65; N, 16.84; S, 9.63. Found: C, 53.99; H, 3.86; Cl, 10.70; N, 16.70; S, 9.48.

6-Chloro-2-[1-methyl-2-(2-pyrrolylmethylene)hydrazino]quinoxaline 4-Oxide **5c**.

A solution of compound **8** (10 g, 44.5 mmoles) and 2-pyrrolecarbaldehyde (6.35 g, 66.8 mmoles) in dioxane (200 ml) was refluxed in an oil bath for 1 hour. The solution was allowed to stand overnight to precipitate orange needles **5c**, which were collected by suction filtration and washed with ethanol to afford an analytically pure sample (9.70 g). Evaporation of the filtrate *in vacuo* provided orange needles **5c**, which were triturated with ethanol and collected by suction filtration (3.0 g), total yield, 12.70 g (95%).

Compound **5c** had mp 270-271°; ir: ν 3240, 3090, 1605, 1570, 1530 cm^{-1}; ms: m/z 301 (M^+), 303 ($M^+ + 2$); pmr (deuteriodimethyl sulfoxide): 11.73 (br s, 1H, pyrrole NH), 9.47 (s, 1H, C_3-H), 8.24 (s, 1H, C_5-H), 7.87 (s, 1H, hydrazone CH), 7.73 (s, 1H, C_8-H), 7.72 (s, 1H, C_7-H), 6.96 (dd, J = 4.0 Hz, J = 2.5 Hz, 1H, pyrrole C_5-H), 6.45 (dd, J = 4.0 Hz, J = 6.0 Hz, 1H, pyrrole C_4-H), 6.14 (dd, J = 2.5 Hz, J = 6.0 Hz, 1H, pyrrole C_3-H), 3.56 (s, 3H, CH_3).

Anal. Calcd. for $C_{14}H_{12}ClN_5O$: C, 55.73; H, 4.01; Cl, 11.75; N, 23.21. Found: C, 55.76; H, 3.95; Cl, 11.92; N, 23.17.

6-Chloro-2-[1-methyl-2-(4-pyridylmethylene)hydrazino]quinoxaline 4-Oxide **5d**.

A solution of compound **8** (10 g, 44.5 mmoles) and 4-pyridinecarbaldehyde (5.71 g, 53.4 mmoles) in *N,N*-dimethylformamide (200 ml) was refluxed in an oil bath for 1 hour, and the solution was allowed to stand overnight to precipitate yellow needles **5d**, which were collected by suction filtration and washed with ethanol to afford an analytically pure sample (12.08 g). Evaporation of the filtrate *in vacuo* provided yellow needles **5d**, which were triturated with ethanol and then collected by suction filtration (1.31 g), total yield, 13.39 g (96%).

Compound **5d** had mp 248-250°; ir: ν 1590, 1575, 1535, 1525 cm^{-1}; ms: m/z 313 (M^+), 315 ($M^+ + 2$); pmr (deuteriodimethyl sulfoxide): 9.03 (s, 1H, C_3-H), 8.63 (d, J = 6.0 Hz, 2H, pyridine C_2-H and C_6-H), 8.28 (d, J = 2.0 Hz, 1H, C_5-H), 8.02 (s, 1H, hydrazone CH), 7.85 (d, J = 9.0 Hz, 1H, C_8-H), 7.80 (dd, J = 2.0 Hz, J = 9.0 Hz, 1H, C_7-H), 7.79 (d, J = 6.0 Hz, 2H, pyridine C_3-H and C_5-H), 3.72 (s, 3H, CH_3).

Anal. Calcd. for $C_{15}H_{13}ClN_5O$: C, 57.24; H, 4.16; Cl, 11.26; N, 22.25. Found: C, 57.27; H, 3.88; Cl, 11.03; N, 22.25.

6-Chloro-2-[2-(3-hydroxy-5-hydroxymethyl-2-methyl-4-pyridylmethylene)-1-methylhydrazino]quinoxaline 4-Oxide Hydrochloride **5e**.

A suspension of compound **8** (10 g, 44.5 mmoles) and pyridoxal hydrochloride (10.88 g, 53.5 mmoles) in *N,N*-dimethylformamide (400 ml) was heated at 160° in an oil bath for 30 minutes stirring with an overhead stirrer to precipitate yellow needles **5e**, which were collected by suction filtration and then washed with ethanol to afford an analytically pure sample (17.19 g, 91%), mp 288-290°; ir: ν 3200, 3080, 3040, 2620, 1990, 1610, 1560, 1530, 1510 cm^{-1}; ms: m/z 373 (M^+), 375 ($M^+ + 2$); pmr (deuteriotrifluoroacetic acid): 8.99 (s, 1H, C_3-H), 8.54 (s, 1H, pyridine C_6-H), 8.33 (d, J = 2.0 Hz, 1H, C_5-H), 8.18 (s, 1H, hydrazone CH), 7.87 (d, J = 9.0 Hz, 1H, C_8-H), 7.76 (dd, J = 2.0 Hz, J = 9.0 Hz, 1H, C_7-H), 4.99 (s, 2H, pyridine C_5-methylene), 3.79 (s, 3H, N-CH_3), 2.64 (s, 3H, pyridine C_2-CH_3).

Anal. Calcd. for $C_{17}H_{16}ClN_5O_3 \cdot HCl$: C, 49.77; H, 4.18; Cl, 17.28; N, 17.07. Found: C, 49.69; H, 4.22; Cl, 17.02; N, 16.92.

6-Chloro-2-[2-(3-hydroxy-5-hydroxymethyl-2-methyl-4-pyridylmethylene)-1-methylhydrazino]quinoxaline 4-Oxide **5f**.

A solution of sodium hydroxide (22.15 g, 53.7 mmoles) in water (50 ml) was added dropwise to a suspension of the hydrochloride **5e** (20 g, 48.8 mmoles) in *N,N*-dimethylformamide (450 ml) stirring with an overhead stirrer at room temperature to precipitate the free base **5f** as yellow needles, which were collected by suction filtration and washed with water and then ethanol to give an analytically pure sample (17.97 g, 99%), mp 238-240°; ir: ν 3270, 3080, 2960, 1570, 1520 cm^{-1}; ms: m/z 373 (M^+), 375 ($M^+ + 2$).

Anal. Calcd. for $C_{17}H_{16}ClN_5O_3$: C, 54.62; H, 4.32; Cl, 9.48; N, 18.74. Found: C, 54.70; H, 4.37; Cl, 9.68; N, 18.88.

8-Chloro-3-(2-furyl)-4-hydroxy-1-methyl-2,3-dihydro-1*H*-1,2-diazepino[3,4-*b*]quinoxaline-5-carbonitrile **6a**.

A solution of compound **5a** (10 g, 33.1 mmoles) and 2-chloroacrylonitrile (11.59 g, 132.4 mmoles) in dioxane (500 ml) was refluxed in an oil bath for 1 hour, and the solvent was immediately evaporated *in vacuo* to give an oily product. Crystallization of the oily product from dioxane/*n*-hexane afforded brownish yellow needles **6a**, which were collected by suction filtration (11.50 g, 98%), mp 191-192°; ir: ν 2220, 1590, 1550, 1510 cm^{-1}; ms: m/z 353 (M^+), 355 ($M^+ + 2$); pmr (deuteriodimethyl sulfoxide): 13.85 (br s, 1H, OH), 8.03 (d, J = 2.0 Hz, 1H, C_7-H), 7.66 (dd, J = 2.0 Hz, J = 0.8 Hz, 1H, furan C_5-H), 7.47 (d, J = 9.0 Hz, 1H, C_{10}-H), 7.40 (dd, J = 2.0 Hz, J = 9.0 Hz, 1H, C_9-H), 6.39 (dd, J = 2.0 Hz, J = 3.1 Hz, 1H, furan C_4-H), 6.29 (dd, J = 0.8 Hz, J = 3.1 Hz, 1H, furan C_3-H), 6.15 (s, 1H, N_2-H), 5.30 (s, 1H, C_3-H), 3.13 (s, 3H, CH_3).

Anal. Calcd. for $C_{17}H_{12}ClN_5O_2$: C, 57.72; H, 3.42; Cl, 10.02; N, 19.80. Found: C, 57.81; H, 3.39; Cl, 9.95; N, 19.63.

8-Chloro-4-hydroxy-1-methyl-3-(3-methyl-2-thienyl)-2,3-dihydro-1*H*-1,2-diazepino[3,4-*b*]quinoxaline-5-carbonitrile **6b**.

A solution of compound **5b** (5 g, 15.0 mmoles) and 2-chloroacrylonitrile (5.26 g, 60.1 mmoles) in dioxane (200 ml) was refluxed in an oil bath for 2 hours, and the solvent was immediately evaporated *in vacuo* to give an oily product. Crystallization of the oily product from dioxane/*n*-hexane afforded brick red prismic needles **6b**, which were collected by suction filtration (3.36 g, 58%), mp 205-206°; ir: ν 1590, 1555, 1510 cm^{-1}; ms: m/z 383 (M^+), 385 ($M^+ + 2$); pmr (deuteriodimethyl sulfoxide): 13.80 (br s, 1H, OH), 8.08 (d, J = 2.0 Hz, 1H, C_7-H), 7.52 (d, J = 9.0 Hz, 1H, C_{10}-H), 7.43 (dd, J = 2.0 Hz, J = 9.0 Hz, 1H, C_9-H), 7.28 (d, J = 5.0 Hz, 1H, thiophene C_5-H), 6.93 (d, J = 5.0 Hz, 1H, thiophene C_4-H), 6.12 (br s, 1H, N_2-H), 5.55 (s, 1H, C_3-H), 3.08 (s, 3H, N_1-CH_3), 2.35 (s, 3H, thiophene C_3-CH_3).

Anal. Calcd. for $C_{18}H_{14}ClN_5OS$: C, 56.32; H, 3.68; Cl, 9.24; N, 18.24; S, 8.35. Found: C, 56.03; H, 3.73; Cl, 9.41; N, 17.98; S, 8.26.

11-Chloro-7,13-dihydro-4-hydroxymethyl-5,14-methano-1,7-dimethyl-16-oxopyrido[3′,4′:9,8][1,5,6]oxadiazonino[3,4-*b*]quinoxaline **7**.

From the Hydrochloride **5e**.

A solution of the hydrochloride **5e** (8 g, 19.5 mmoles) and 2-chloroacrylonitrile (3.37 g, 38.5 mmoles) in dimethyl sulfoxide (200 ml)/dioxane (200 ml) was refluxed in an oil bath for 2 hours. The solution was allowed to stand overnight to precipitate red needles, which were collected by suction filtration and then

washed with ethanol. Further refluxing of the above insoluble red needles in ethanol for 2 hours gave analytically pure red needles **7** (3.62 g, 47%).

From the Free Base **5f**.

A solution of the free base **5f** (5 g, 13.4 mmoles) and 2-chloroacrylonitrile (1.76 g, 20.1 mmoles) in dimethyl sulfoxide (150 ml)/dioxane (100 ml) was refluxed in an oil bath for 1 hour. The solution was allowed to stand overnight to precipitate red needles, which were collected by suction filtration and then washed with ethanol. Subsequent refluxing of the above insoluble red needles in ethanol (100 ml) for 2 hours afforded analytically pure red needles **7** (2.33 g, 44%).

Compound **7** had mp 343-345°; ir: ν 1680, 1600, 1580, 1540, 1510 cm^{-1}; ms: m/z 395 (M^+), 397 ($M^+ + 2$); pmr (deuteriotrifluoroacetic acid): 8.57 (s, 1H, C_3-H), 6.89 (d, J = 2.0 Hz, 1H, C_{12}-H), 6.82 (dd, J = 2.0 Hz, J = 8.5 Hz, 1H, C_{10}-H), 6.73 (d, J = 8.5 Hz, 1H, C_9-H), 5.05 (s, 2H, C_4-methylene), 3.59 (s, 3H, N_7-CH_3), 2.58 (s, 3H, C_1-CH_3).

Anal. Calcd. for $C_{19}H_{14}ClN_5O_3$: C, 57.66; H, 3.56; Cl, 8.96; N, 17.70. Found: C, 57.46; H, 3.70; Cl, 9.06; N, 17.44.

4-Acetoxymethyl-11-chloro-7,13-dihydro-5,14-methano-1,7-dimethyl-16-oxopyrido[3',4':9,8][1,5,6]oxadiazonino[3,4-*b*]quinoxaline **9**.

A solution of compound **7** (1 g, 2.53 mmoles) and triethylamine (1 ml) in acetic anhydride (200 ml) was refluxed in an oil bath for 4 hours. After the solution was filtered, the filtrate was allowed to stand overnight to precipitate red needles **9**, which were collected by suction filtration and washed with ethanol and then *n*-hexane to give an analytically pure sample (800 mg, 72%), mp 320-321°; ir: ν 3200, 3040, 2920, 1740, 1680, 1600, 1580, 1545, 1510 cm^{-1}; ms: m/z 437 (M^+), 439 ($M^+ + 2$); pmr (deuteriotrifluoroacetic acid): 8.35 (s, 1H, C_3-H), 6.86 (d, J = 2.0 Hz, 1H, C_{12}-H), 6.79 (dd, J = 2.0 Hz, J = 8.5 Hz, 1H, C_{10}-H), 6.69 (d, J = 8.5 Hz, 1H, C_9-H), 5.37 (s, 2H, C_4-methylene), 3.57 (s, 3H, N_7-CH_3), 2.57 (s, 3H, C_1-CH_3), 1.97 (s, 3H, acetyl CH_3).

Anal. Calcd. for $C_{21}H_{16}ClN_5O_4$: C, 57.61; H, 3.68; Cl, 8.10; N, 16.00. Found: C, 57.87; H, 3.68; Cl, 8.39; N, 15.81.

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[5] Unpublished data: Compounds **1-4** showed a weak *in vitro* antifungal activity (20-80% growth inhibition) against *Pythium debaryanum*, *Rhizoctonia solani* and *Pyricularia oryzae* at a concentration of 100 ppm.