POLYCYCLIC *N*-HETEROCYCLIC COMPOUNDS. 49

NEW SYNTHETIC METHOD OF FURO[3,2-f][1,7]NAPHTHYRIDINE SKELETON

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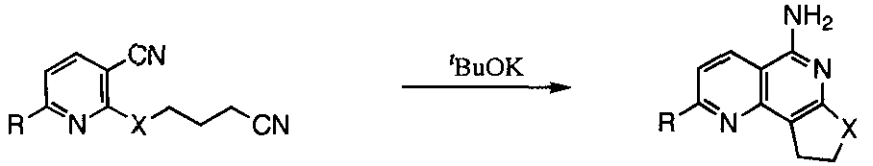
Abstract - An synthesis of 5-amino-1,2-dihydrofuro[3,2-*f*][1,7]naphthyridine (**6**) from 3-(3-cyanopropoxy)pyridine-2-carbonitrile (**5**) is described. Compound (**6**) was converted to mother skeleton (**12**). Treatment of **6** with conc. hydrochloric acid gave new spiroheterocycle (**7**).

In earlier paper, we have reported a new synthesis of 5-amino-1,2-dihydrothieno[2,3-*h*][1,6]-naphthyridines (**2a,b**) from 2-(3-cyanopropylthio)pyridine-3-carbonitriles (**1a,b**) using potassium *tert*-butoxide (^{t}BuOK)[1,2] as shown in Scheme 1. Similar reaction was achieved to 2-(3-cyanopropoxy)-6-methylpyridine-3-carbonitrile (**1c**) and expectedly gave 5-amino-8-methyl-1,2-dihydrofuro[2,3-*h*][1,6]-naphthyridine (**2c**).[3] We proposed the reaction mechanism for these products, which involved Smiles rearrangement followed by an intramolecular cyclization. These results prompted us to carry out the analogous reaction for 3-(3-cyanopropoxy)pyridine-2-carbonitrile (**5**).

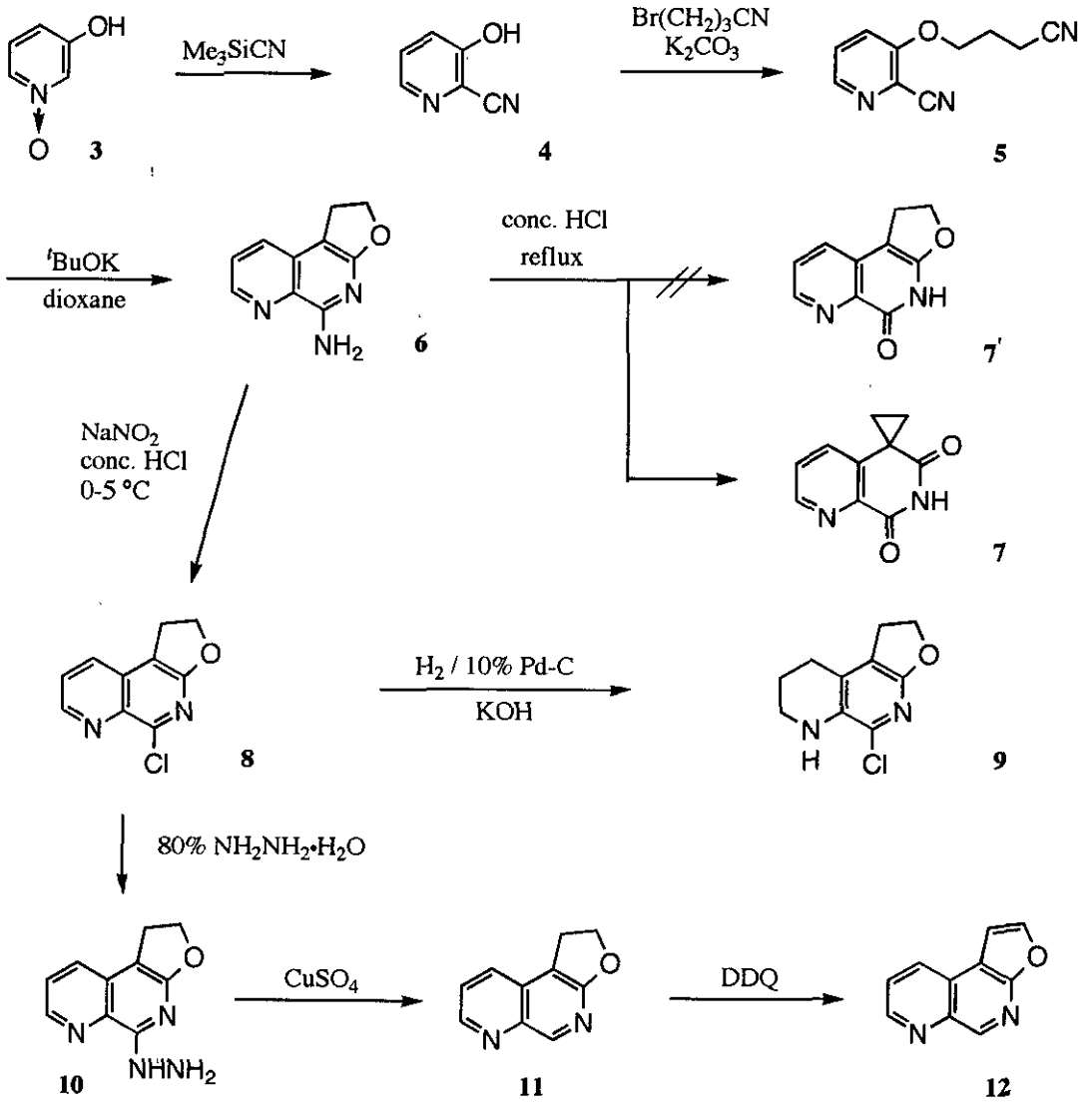


1a; R = H, X = S
1b; R = *Me*, X = *S*
1c; R = Me, X = O

2a; R = H, X = S
2b; R = *Me*, X = *S*
2c, R = Me, X = O

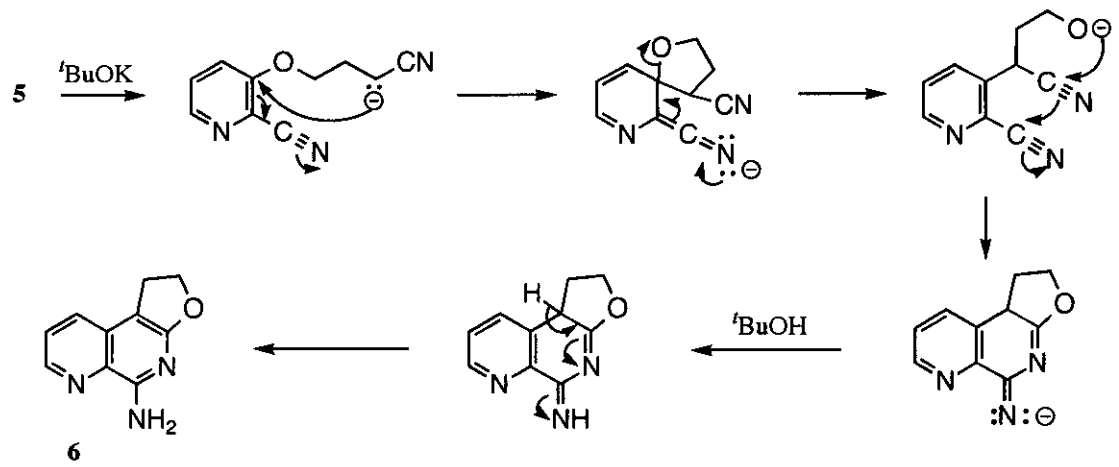
Scheme 1

As shown in Scheme 2, 3-hydroxypyridine-1-oxide (**3**) was converted to 3-hydroxypyridine-2-carbonitrile (**4**) with trimethylsilyl cyanide by using Vorbrüggen's method.[4] Reaction of **4** with 4-bromo-



Scheme 2

butyronitrile in the presence of potassium carbonate afforded a key intermediate (**5**) which has not been mentioned in literatures. Treatment of **5** with ^{t}BuOK in dioxane around 95 °C gave 5-amino-1,2-dihydrofuro[3,2-*f*][1,7]naphthyridine (**6**) in 80% yield. Disappearance of nitrile absorption and appearance of amino bands at 3450 and 3280 cm^{-1} were observed in ir spectrum of **6.** Reaction mechanism of **5** to **6** was proposed in Scheme 3 with minor change to that of our earlier one.[1,2]



Scheme 3

Investigation of the reaction conditions for compound (**5**) to obtain **6** with ^{t}BuOK were performed. The results were summarized in Table 1. Run 5 exhibited the best yield.

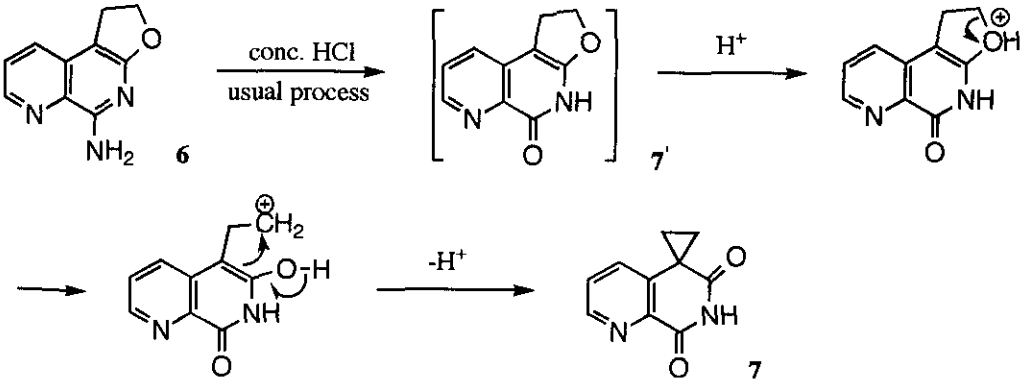
The skeleton of **6** has appeared in only one report as a Japanese patent,[5] which deals with only 6-alkyl-9-oxofuronaphthyridine derivatives. Our synthetic method of this skeleton is new and versatile one. Furthermore, compound (**6**) is a convenient material to synthesize the mother skeleton, furo[3,2-*f*][1,7]naphthyridine (**12**), which has not been reported by now. Hydrolysis of **6** with conc. hydrochloric acid under reflux to obtain 5-oxo derivative (**7'**) afforded unexpected product, spiro[cyclopropane-1,5'(6'*H*)-[1,7]naphthyridine]-6',8'(7'*H*)-dione (**7**). Formation mechanism of **7** was postulated in Scheme

Table 1. Reactions of Dinitrile (**5**) with ^{t}BuOK

Run	Solvent	Temperature (°C)	Reaction Time (h) [a]	Yield (%)[b]
1	DMF	room temperature	1	25
2	DMF	60 [c]	0.5	45
3	dioxane	room temperature	1	22
4	dioxane	60 [c]	0.5	67
5	dioxane	95 [d]	0.1	80

a) Color change of the reaction mixture to yellow and disappearance of **5** on tlc were confirmed. b) Isolated yield c) ^{t}BuOK was added at once to a warmed dinitrile solution around 60 °C and then the mixture was stirred at the same temperature. d) Similar manner as described in run 4 was performed around 95 °C and immediate color change to yellow was observed

4. It is not clear which preferentially occurred between hydrolysis of amino group and rearrangement of furan ring to spirocyclopropane. Compound (**7**) was a new type of spiroheterocyclic system produced by acid catalyzed rearrangement. Similar derivatives, spiro[cyclopropane-1,4'(1'*H*)-isoquinoline]-1',3'(2'*H*)-



Scheme 4

diones, were synthesized by Horning *et al.*[6] and Fujiwara *et al.*[7] with different method, however, our route is a new one. In order to confirm the structure (**7**), X-ray analysis was accomplished and its ORTEP drawing is shown in Figure 1. Diazotization of **6** with nitrous acid was performed to obtain **7'** as an alternative method but afforded 5-chloro derivative (**8**) in 67% yield. Compound (**8**) was submitted to a catalytic reduction with H_2 / 10% Pd-C containing potassium hydroxide to get a dechlorinated product (**11**),

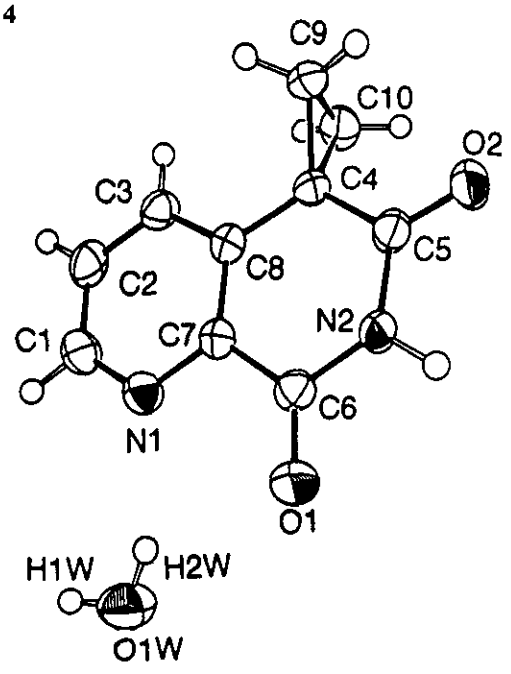


Figure 1. ORTEP drawing of compound (**7**)

however, 5-chloro-1,2,6,7,8,9-hexahydro derivative (**9**) was obtained. As an alternative method, reaction of **8** with 80% hydrazine hydrate was carried out to obtain hydrazino intermediate (**10**), which was treated with copper sulfate in acetic acid to get desired compound (**11**).[8] Dehydrogenation of **11** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in chlorobenzene gave the mother skeleton, furo[3,2-*f*][1,7]-naphthyridine (**12**).

In conclusion, we have successfully synthesized 5-amino-1,2-dihydrofuro[3,2-*f*][1,7]naphthyridine (**6**) on

a route involving Smiles rearrangement followed by cyclization. Furthermore, transformation of **6** afforded furo[3,2-*f*][1,7]naphthyridine (**12**) *via* several steps and also gave new spiroheterocycle, spiro[cyclopropane-1,5'(6'*H*)-[1,7]naphthyridine]-6',8'(7'*H*)-dione (**7**).

EXPERIMENTAL

All melting point were determined on a Yanagimoto micro-melting point apparatus, and are uncorrected. Elemental analyses were performed on a Yanagimoto MT-5 CHN Corder elemental analyzer. The EI-, FAB- and high resolution ms spectra were recorded on a VG 70-SE mass spectrometer, using glycerol or *m*-nitrobenzyl alcohol as a matrix agent. The ir spectra were recorded on a Japan Spectroscopic IRA-102 diffraction grating infrared spectrophotometer. They were measured as potassium bromide pellets and frequencies are expressed in cm^{-1}. The ^{1}H-nmr spectra were recorded on a Hitachi R-1500 FT-NMR spectrometer (60 MHz), Varian VXR-200 (200 MHz) or Varian VXR-500 (500MHz) instruments in the solvent indicated with tetramethylsilane as the internal standard. Chemical shifts are reported in ppm (δ) and *J* values in Hz, and the signals are designated as follows; s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; quin, quintet; br, broad.

3-Hydroxypyridine-2-carbonitrile (4)

Compound (**4**) was prepared from commercially available 3-hydroxypyridine-1-oxide (**3**) by using trimethylsilyl cyanide by Vorbrüggen's method[4] and was used for the next step without purification.

3-(3-Cyanopropoxy)pyridine-2-carbonitrile (5)

To a solution of **4** (29 g, 0.24 mol) in DMF (300 ml) was added 4-bromobutyronitrile (107 g, 0.73 mol) and K_2CO_3 (100 g, 0.73 mol) and the mixture was refluxed for 9 h with stirring. Ice-water (2000 g) was added to the mixture and the precipitated solid was collected by suction. The resulting solid mass was recrystallized from ethyl acetate to give compound (**5**) as colorless plates (17 g, overall yield from **3** 49%), mp 110-112 °C; ir: 2240 (CN); ^{1}H-nmr (200 MHz, $CDCl_3$): 2.26 (2H, br quin, $J_{2',1'}$ = 5.7 Hz, $J_{2',3'}$ = 6.8 Hz, H-2'), 2.72 (2H, t, $J_{3',2'}$ = 6.8 Hz, H-3'), 4.26 (2H, t, $J_{1',2'}$ = 5.7 Hz, H-1'), 7.37 (1H, dd, $J_{4,5}$ =

8.6 Hz, $J_{4,6}$ = 1.2 Hz, H-4), 7.51 (1H, dd, $J_{5,4}$ = 8.6 Hz, $J_{5,6}$ = 4.6 Hz, H-5), 8.34 (1H, dd, $J_{6,4}$ = 1.2 Hz, $J_{6,5}$ = 4.6 Hz, H-6); FAB-ms *m/z*: 188 (MH^+); *Anal.* Calcd for $C_{10}H_9N_3O$: C, 64.16; H, 4.84; N, 22.44. Found: C, 64.15; H, 4.95; N, 22.50.

5-Amino-1,2-dihydrofuro[3,2-*f*][1,7]naphthyridine (6)

Run 1: To a solution of **5** (200 mg, 1.1 mmol) in DMF (5 ml) was added ^{t}BuOK (240 mg, 2.2mmol), which was stirred at room temperature for 1 h. Ice-water (50 g) was added to the reaction mixture and the mixture was extracted with ethyl acetate (50 ml × 3). The organic layer was washed with saturated aqueous NaCl solution, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was recrystallized from ethyl acetate to give 50 mg (25%) of **6** as yellow needles, mp 232-234 °C; ir: 3450, 3280 (NH); ^{1}H-nmr (200 MHz, $CDCl_3$): 3.30 (2H, t, $J_{1,2}$ = 8.8 Hz, H-1), 4.73 (2H, t, $J_{2,1}$ = 8.8 Hz, H-2), 5.92 (2H, br, D_2O exchangeable, NH_2), 7.42 (1H, dd, $J_{8,7}$ = 4.2 Hz, $J_{8,9}$ = 8.4 Hz, H-8), 7.72 (1H, dd, $J_{9,7}$ = 1.6 Hz, $J_{9,8}$ = 8.4 Hz, H-9), 8.49 (1H, dd, $J_{7,8}$ = 4.2 Hz, $J_{7,9}$ = 1.6 Hz, H-7); EI-ms *m/z*: 187 (M^+); *Anal.* Calcd for $C_{10}H_9N_3O$: C, 64.16; H, 4.84; N, 22.44. Found: C, 64.12; H, 4.95; N, 22.42.

Run 2: To a solution of **5** (200 mg, 1.1 mmol) in DMF (5 ml) warmed around 60 °C was added ^{t}BuOK (240 mg, 2.2mmol) at once, and the mixture was stirred at the same temperature for 0.5 h. Ice-water (50 g) was added to the reaction mixture and the mixture was extracted with ethyl acetate (50 ml × 3). The organic layer was washed with saturated aqueous NaCl solution, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was recrystallized from ethyl acetate to give 90 mg (45%) of **6** as yellow needles.

Run 3: To a solution of **5** (200 mg, 1.1 mmol) in dioxane (15 ml) was added ^{t}BuOK (240 mg, 2.2 mmol) and the mixture was stirred at room temperature for 1 h. Ice-water (50 g) was added to the reaction mixture, which was extracted with ethyl acetate (50 ml × 3). The organic layer was washed with saturated aqueous NaCl solution, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was recrystallized from ethyl acetate to give 44 mg (22%) of **5** as yellow needles.

Run 4: To a solution of **5** (300 mg, 1.6 mmol) in dioxane (10 ml) warmed around 60 °C was added ^{t}BuOK (360 mg, 3.2 mmol) and the mixture was stirred at the same temperature for 0.5 h. Ice-water (50 g) was added to the reaction mixture, which was allowed to stand about 1 h. The deposited solid mass was collected by suction and the filtrate was extracted with ethyl acetate (50 ml × 3). The organic layer

was washed with saturated aqueous NaCl solution, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue and the above solid mass were combined, which was recrystallized from ethyl acetate to give 201 mg (67%) of **6**.

Run 5: To a solution of **5** (300 mg, 1.6 mmol) in dioxane (10 ml) heated around 95 °C was added ^{t}BuOK (360 mg, 3.2 mmol) at once. The color of the solution changed to yellow immediately (about 0.1 h). The mixture was cooled to room temperature as soon as possible. Ice-water (50 g) was added to the mixture and then allowed to stand for 1 h. The deposited solid mass was collected by suction and the resulting mass was recrystallized from ethyl acetate to give 240 mg (80%) of **6**.

Spiro[cyclopropane-1,5'(6'*H*)-[1,7]naphthyridine]-6',8'(7'*H*)-dione (7)

A solution of **6** (1.0 g, 5.4 mmol) in conc. hydrochloric acid (10 ml) was refluxed for 6 h. The reaction mixture was cooled to the room temperature and neutralized with saturated aqueous $NaHCO_3$ solution. The precipitated solid mass was collected by suction. The filtrate was extracted with ethyl acetate (30 ml × 3). The organic layer was washed with saturated aqueous NaCl solution, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue and the above solid mass were combined and recrystallized from acetone to give 470 mg (47%) of **7** as colorless plates, mp >300 °C; ir: 3200, 3090 (NH), 1710, 1685 (CO); ^{1}H-nmr (500 MHz, DMSO-d_6): 1.73, 1.91(each 2H, each dd, J_a = 8 Hz, J_b = 4 Hz, spiro-CH_2), 7.56 (1H, dd, $J_{4,3}$ = 8.2 Hz, $J_{4,2}$ = 1.5 Hz, H-4), 7.63 (1H, dd, $J_{3,4}$ = 8.2 Hz, $J_{3,2}$ = 4.4 Hz, H-3), 8.67 (1H, dd, $J_{2,3}$ = 4.4 Hz, $J_{2,4}$ = 1.5 Hz, H-2), 11.68 (1H, br s, D_2O exchangeable, NH); FAB-ms *m/z*: 189 (MH^+); *Anal.* Calcd for $C_{10}H_8N_2O_2$: C, 63.82; H, 4.28; N, 14.88. Found: C, 63.70; H, 4.43; N, 14.79.

X-Ray structure analysis of **7** showed containing 1 mol of H_2O as crystal water. This analytical sample was dried around 100 °C under vaccum to remove crystal water.

Crystal structure analysis of a monohydrate of **7**. Crystal data: $C_{10}H_8N_2O_2 \cdot H_2O$; Mr = 206.20; monoclinic, space group $P2_1/c$, a = 7.781(2), b = 23.381(4), c = 5.336(3) Å, β = 106.25(3)°, V = 932(1) Å^3; Z = 4; D_C = 1.469 g cm^{-3}. The crystals were grown from an acetone solution by slow evaporation. A crystal of size 0.13 x 0.33 x 0.33 mm was examined by using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Cell dimensions were obtained from 24 reflections ($26 < 2\theta < 29°$). In total 2066 reflections were measured by the ω-2θ scan method, and 1866 of these were unique (R_{int} = 0.016).

Refinements were carried out including all the hydrogen atoms by using 1091 reflections with $I > 3\sigma(I)$ within $2\theta_{max}$ of 52°. $R = 0.035$, $R_W = 0.027$, $S = 1.38$.

In the crystal an N-H•••O hydrogen bond is formed between the molecules of **7** related by a center of symmetry [N(2)•••O(2) 2.906(3) Å]. N(1) accepts a hydrogen bond from a water molecule [N(1)•••O(W) 2.961(3) Å]. There is an additional hydrogen bond of 2.900(2) Å between the water molecules related by a *c* glide plane.

5-Chloro-1,2-dihydrofuro[3,2-*f*][1,7]naphthyridine (8)

To a solution of **6** (1.0 g, 5.4 mmol) in conc. hydrochloric acid (15 ml) under cooling at 0-5 °C was added $NaNO_2$ (0.74 g, 10.7 mmol) in water (2.7 ml) checking with potassium iodide-starch paper. The reaction mixture was basified with saturated aqueous $NaHCO_3$ solution and the precipitated solid was collected by suction. The filtrate was extracted with benzene. The organic layer was washed with saturated aqueous NaCl solution, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue and the above solid were combined, and then recrystallized from dioxane to give 0.74 g (67%) of **8** as colorless granules, mp 196-198 °C; ^{1}H-nmr (200 MHz, DMSO-d_6): 3.51 (2H, t, $J_{1,2}$ = 9.0 Hz, H-1), 4.82 (2H, t, $J_{2,1}$ = 9.0 Hz, H-2), 7.75 (1H, dd, $J_{8,7}$ = 4.0 Hz, $J_{8,9}$ = 8.5 Hz, H-8), 8.23 (1H, dd, $J_{9,7}$ = 1.5 Hz, $J_{9,8}$ = 8.5 Hz, H-9), 8.89 (1H, dd, $J_{7,8}$ = 4.0 Hz, $J_{7,9}$ = 1.5 Hz, H-7); FAB-ms *m/z*: 209 (MH^++2, 23%), 207 (MH^+, 70%); *Anal.* Calcd for $C_{10}H_7N_2OCl$: C, 58.12; H, 3.41; N, 13.55. Found:C, 58.00; H, 3.62; N, 13.41.

5-Chloro-1,2,6,7,8,9-hexahydrofuro[3,2-*f*][1,7]naphthyridine (9)

A mixture of **8** (0.5 g, 2.4 mmol), 10% Pd-C (385 mg, 3.6 mmol), and KOH (136 mg, 2.4 mmol) in dioxane (300 ml) was submmited to catalytic hydrogenation for 6 days. The reaction mixture was filtrated to remove Pd-C and the filtrate was evaporated. The residue was subjected to column chromatography on silica gel (Merck; Kieselgel 60, 70-230 mesh). The eluate of cyclohexane-ethyl acetate (4 : 1, v/v) was recrystallized from ethyl acetate to give 249 mg (49%) of **9** as colorless plates, mp 174-177 °C; ir: 3400 (NH); ^{1}H-nmr (200 MHz, $CDCl_3$): 1.96 (2H, br quin, J = about 6 Hz, H-8), 2.65 (2H, t, $J_{9,8}$ = 6.5 Hz, H-9), 3.05 (2H, t, $J_{1,2}$ = 8.5 Hz, H-1), 3.34 (2H, t, $J_{7,8}$ = 5.5 Hz, H-7), 4.00 (1H,

br, D_2O exchangeable, NH), 4.57 (2H, t, $J_{2,1}$ = 8.5 Hz, H-2); FAB-ms *m/z*: 210 (M^+, 100%), 211 (MH^+, 90%), 212 (M^++2, 45%), 213 (MH^++2, 30%); *Anal.* Calcd for $C_{10}H_{11}N_2OCl$: C, 57.01; H, 5.26; N, 13.29. Found: C, 57.15; H, 5.22; N, 13.26.

5-Hydrazino-1,2-dihydrofuro[3,2-*f*][1,7]naphthyridine (10)

To a stirred suspension of **8** (600 mg, 2.9 mmol) in ethanol (30 ml) was added 80% hydrazine hydrate (2.32 g, 58.1 mmol) and the mixture was refluxed for 2 h. The reaction mixture was evaporated, and water (50 ml) was added to the residue. The insoluble solid mass was collected by suction. The filtrate was extracted with benzene (50 ml × 3). The organic layer was washed with saturated aqueous NaCl solution, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue and the above solid mass were combined and recrystallized from benzene to give 455 mg (78%) of **10** as yellow plates, mp 165-168 °C; ir: 3250 ($NHNH_2$); ^{1}H-nmr (200 MHz, $CDCl_3$): 3.31 (2H, t, $J_{1,2}$ = 8.8 Hz, H-1), 4.04 (2H, br, D_2O exchangeable, NH_2), 4.76 (2H, t, $J_{2,1}$ = 8.8 Hz, H-2), 7.43 (1H, dd, $J_{8,9}$ = 8.5 Hz, $J_{8,7}$ = 4.1 Hz, H-8), 7.71 (1H, dd, $J_{9,7}$ = 1.6 Hz, $J_{9,8}$ = 8.5 Hz, H-9), 7.88 (1H, br s, D_2O exchangeable, NH), 8.46 (1H, dd, $J_{7,8}$ = 4.1 Hz, $J_{7,9}$ = 1.6 Hz, H-7); FAB-ms *m/z*: 202 (M^+, 100%) 203 (MH^+, 85%); *Anal.* Calcd for $C_{10}H_{10}N_4O$: C, 59.39; H, 4.98; N, 27.70. Found:C, 59.30; H, 4.92; N, 27.53.

1,2-Dihydrofuro[3,2-*f*][1,7]naphthyridine (11)

To a solution of **10** (697 mg, 3.5 mmol) in 50% aqueous acetic acid (v/v) under heating around 100 °C was dropwise added 10% $CuSO_4$ solution (10 ml) and the resulting mixture was refluxed for 2 h under stirring. The reaction mixture was cooled to the room temperature, made alkaline with 10% aqueous NaOH, and then extracted with ether (100 ml × 3). The organic layer was washed with saturated aqueous NaCl solution, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was recrystallized from cyclohexane-ethyl acetate (4 : 1, v/v) to give 549 mg (93%) of **11** as colorless fine crystalline solid, mp 142-144 °C; ^{1}H-nmr (200 MHz, $CDCl_3$): 3.53 (2H, t, $J_{1,2}$ = 8.9 Hz, H-1), 4.86 (2H, t, $J_{2,1}$ = 8.9 Hz, H-2), 7.50 (1H, dd, $J_{8,7}$ = 4.1 Hz, $J_{8,9}$ = 8.6 Hz, H-8), 7.94 (1H, dd, $J_{9,7}$ = 1.7 Hz, $J_{9,8}$ = 8.6 Hz, H-9), 8.82 (1H, dd, $J_{7,8}$ = 4.1 Hz, $J_{7,9}$ = 1.7 Hz, H-7), 9.09 (1H, s, H-5); FAB-ms *m/z*: 173 (MH^+); High resolution FAB-ms m/z: Calcd for $C_{10}H_9N_2O$: 173.0714. Found: 173.0693 (MH^+).

Furo[3,2-*f*][1,7]naphthyridine (12)

To a solution of **11** (230 mg, 1.3 mmol) in dry chlorobenzene (50 ml) was added DDQ (910 mg, 4.0 mmol), and then the mixture was refluxed for 2 h under stirring. The reaction mixture was evaporated *in vacuo* and the residue was subjected to column chromatography on silica gel (Merck; Kieselgel 60, 70-230 mesh). The eluate of cyclohexane-acetone (4 : 1, v/v) was recrystallized from cyclohexane to give 135 mg (59%) of **12** as colorless feathers, mp 154-156 °C; ^{1}H-nmr (200 MHz, $CDCl_3$): 7.26 (1H, d, $J_{1,2}$ = 2.4 Hz, H-1), 7.70 (1H, dd, $J_{8,7}$ = 4.2 Hz, $J_{8,9}$ = 8.4 Hz, H-8), 7.91 (1H, d, $J_{2,1}$ = 2.4 Hz, H-2), 8.49 (1H, dd, $J_{9,7}$ = 1.6 Hz, $J_{9,8}$ = 8.4 Hz, H-9), 9.05 (1H, dd, $J_{7,8}$ = 4.2 Hz, $J_{7,9}$ = 1.6 Hz, H-7), 9.26 (1H, s, H-5); FAB-ms *m/z*: 171 (MH^+); High resolution FAB-ms m/z: Calcd for $C_{10}H_7N_2O$: 171.0558. Found: 171.0586 (MH^+).

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