Condensed Heteroaromatic Ring Systems. XXI.[1] Synthesis of Pyrrolo[2,3-*d*]pyrimidines and Pyrrolo[3,2-*d*]pyrimidines

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Pyrrolo[2,3-*d*]pyrimidines and pyrrolo[3,2-*d*]pyrimidines were synthesized in high yields by the palladium-catalyzed reaction of 4-acetylamino-5-bromopyrimidines and 5-acetylamino-4-iodopyrimidines with (*Z*)-1-ethoxy-2-(tributylstannyl)ethene followed by cyclization under acidic conditions.

Keywords pyrrolo[2,3-*d*]pyrimidine; pyrrolo[3,2-*d*]pyrimidine; palladium-catalyzed reaction

Pyrrolopyrimidine rings may have interesting biological activities: for example, it was recently reported that pyrrolo[2,3-*d*]pyrimidine and pyrrolo[3,2-*d*]pyrimidine derivatives have antiviral activities.[2,3] Pyrrolo[2,3-*d*]pyrimidine and pyrrolo[3,2-*d*]pyrimidine derivatives are usually constructed from an appropriate pyrimidine or pyrrole derivatives, but there are relatively few reports on the synthesis of pyrrolopyrimidine derivatives having no substituent at the pyrrole ring moiety.[4,5] On the other hand, we have reported that (*Z*)-1-ethoxy-2-(tributylstannyl)-ethene (**1**) is a useful reagent to introduce a 2-ethoxyethenyl group, an acetaldehyde equivalent group, into aromatic rings by palladium-catalyzed reaction.[5] Furthermore, application of the palladium-catalyzed reaction to 2-substituted halobenzenes provides a method to construct some condensed heterocycles, *e.g.* indole, isocoumarin, and so on.[6]

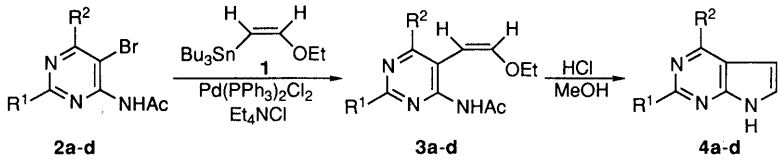
Here, we report the synthesis of both pyrrolo[2,3-*d*]-pyrimidines and pyrrolo[3,2-*d*]pyrimidines without substituents on the pyrrole ring moiety *via* the palladium-catalyzed reaction of acetylaminohalopyrimidines with (*Z*)-1-ethoxy-2-(tributylstannyl)ethene (**1**) as a key reaction.

Synthesis of Pyrrolo[2,3-*d*]pyrimidines The palladium-catalyzed reaction of 4-acetylamino-5-bromopyrimidines (**2a—d**) prepared by usual methods with **1** in the presence of dichlorobis(triphenylphosphine)palladium and tetraethylammonium chloride in several solvents was examined. The reaction in dimethylformamide (DMF) generally gave the corresponding (*Z*)-4-acetylamino-5-(2-ethoxyethenyl)-pyrimidines (**3a—d**) in 48—95% yields, and acetonitrile was also a useful solvent, as shown in Table I.

Since the proton magnetic resonance (^{1}H-NMR) spectra of the products (**3a—d**) show a pair of doublet signals with coupling constants of 7 hertz (Hz), it was decided that the 2-ethoxyethenyl group has *Z*-configuration, except in **3'a**, which was obtained as a minor product from the reaction of 4-acetylamino-5-bromopyrimidine (**2a**) with **1** in acetonitrile.

As shown in Table II, **3a—d** were easily cyclized by treatment with hydrochloric acid in methanol under reflux to give pyrrolo[2,3-*d*]pyrimidines (**4a—d**).

Synthesis of Pyrrolo[3,2-*d*]pyrimidines The palladium-catalyzed reaction of 4-chloro-6-methoxy-5-nitropyrimidine (**5a**), prepared by the known method with **1** in the presence of tetraethylammonium chloride in DMF at 140 °C, gave an unexpected product, (*E*)-4-(2-ethoxyethenyl)-1-methyl-5-nitro-6(1*H*)-pyrimidinone (**6a**). The infrared (IR) spectrum of **6a** shows a band at 1690 cm^{-1}, which is assigned to C=O stretching of an α-pyridinone type carbonyl group. The ^{1}H-NMR spectrum of **6a** shows a singlet signal at 3.53 ppm (N–Me) and a pair of doublet signals at



	R^1	R^2
a	H	H
b	Me	Me
c	OMe	H
d	OMe	OMe

Chart 1

TABLE I. The Palladium-Catalyzed Reaction of **2a—d** with **1**

Starting compd. No.	R^1	R^2	Solvent	Reaction temp. (°C)	Reaction time (h)	Product No.	Yield (%)
2a	H	H	DMF	120	5	**3a**	48
2b	Me	Me	DMF	140	1	**3b**	95
2c	OMe	H	DMF	110	1	**3c**	64
2d	OMe	OMe	DMF	140	1	**3d**	78
2a	H	H	MeCN	Reflux	2	**3a**+**3'a**	65+11 (*E*-isomer)
2c	OMe	H	MeCN	Reflux	3	**3c**	71
2d	OMe	OMe	MeCN	Reflux	24	**3d**	81
2a	H	H	THF	Reflux	24	**3a**	69
2d	OMe	OMe	THF	Reflux	14	**3d**	12

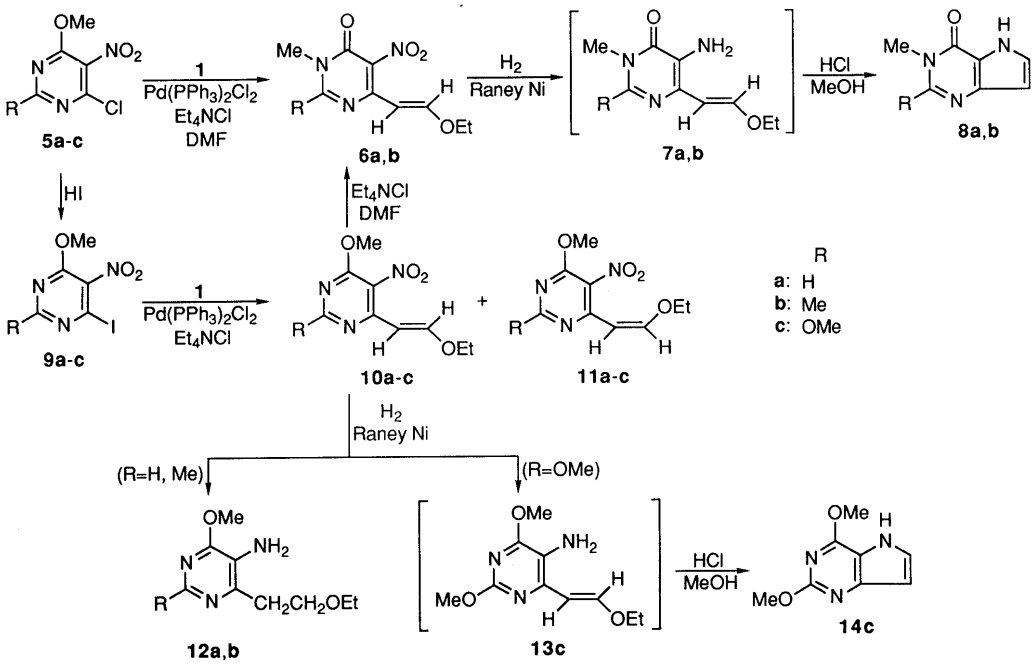


Chart 2

Table II. Cyclization of **3a—d** to **4a—d**

4	R^1	R^2	Reaction time (min)	Yield (%)
a	H	H	30	71
b	Me	Me	40	91
c	OMe	H	20	85
d	OMe	OMe	20	96

Table III. The Palladium-Catalyzed Reaction of **9a—c** with **1**

Starting compd. No.	R	Reaction time (h)	Yield		Yield	
			10	(%)	**11**	(%)
9a	H	5	**a**	72	**a**	8
9b	Me	4	**b**	44	**b**	50
9b	Me	24	**b**	73	**b**	21
9c	OMe	2	**c**	32	**c**	51
9c	OMe	15	**c**	73	**c**	11

5.80 and 8.00 ppm with a coupling constant of 12 Hz; these signals were assigned to the ethenyl group having *E*-configuration. The X-ray crystal analysis excluded the possibility of **6a** being (*E*)-4-(2-ethoxyethenyl)-3-methyl-5-nitro-6(3*H*)-pyrimidinone.

The palladium-catalyzed reaction of 4-chloro-2-methyl-6-methoxy-5-nitropyrimidine (**5b**) with **1** gave a similar product (**6b**), but the reaction of 4-chloro-2,6-dimethoxy-5-nitropyrimidine (**5c**) with **1** gave resinous products.

The pathway to **6a, b** by the reaction of **5a, b** with **1** is considered to be as follows. The normal palladium-catalyzed reaction product, (*Z*)- (**10a, b**) or (*E*)-4-(2-ethoxyethenyl)-6-methyl-5-nitropyrimidines (**11a, b**), whose preparation will be discussed below, reacts with tetraethylammonium chloride in DMF at 140 °C to produce the 4-(2-ethoxyethenyl)-5-nitro-6(1*H*)-pyrimidinones and methyl chloride. The resulting methyl chloride attacks **10a, b** or **11a, b** to yield **6a, b**.

This interpretation was supported by the results that **6a** was obtained in 82% yield from the reaction of **10a** with tetraethylammonium chloride in DMF at 140 °C for 15 min, and **6a** was not obtained under the cross-coupling reaction conditions excluding tetraethylammonium chloride.

Since the formation of **6a, b** by the reaction of **5a, b** with **1** is considered to be due to the relatively higher reaction temperature, we tried the palladium-catalyzed reaction under milder conditions. Namely, the chloronitropyrimidines (**5a—c**) were converted into the iodonitropyrimidines (**9a—c**) with hydroiodic acid at room temperature in 74—78% yields. The reaction of **9a—c** with **1** in tetrahydrofuran (THF) under refluxing conditions gave a mixture of the (*E*)- (**10a—c**) and the (*Z*)-4-(2-ethoxyethenyl)-5-nitropyrimidines (**11a—c**), as shown in Table III.

The palladium-catalyzed reaction of aryl halides with **1** affords primarily (*Z*)-1-aryl-2-ethoxyethenes. As reported in the previous paper, however, (*Z*)-1-aryl-2-ethoxyethenes isomerize to thermally stable (*E*)-1-aryl-2-ethoxyethenes during a prolonged reaction.[7] Furthermore, the reaction of aryl halides with electron-withdrawing groups tends to give a mixture of (*Z*)- and (*E*)-2-ethoxyethenylarenes as described above. This isomerization is presumably caused by the co-ordination of the palladium catalyst to the 2-ethoxyethenyl groups and/or by the π-electron delocalization of the 2-ethoxyethenyl groups due to electron deficiency of the aryl groups.

Catalytic hydrogenation of **10a, b** on Raney nickel did not give the expected products, 5-amino-4-(2-ethoxyethenyl)-6-methoxypyrimidines, but afforded 5-amino-4-(2-ethoxyethyl)-6-methoxypyrimidines (**12a, b**) in high yields.[8] On the other hand, the same reaction of **10c** gave **13c**, which cyclized to 2,4-dimethoxypyrrolo[3,2-*d*]pyrimidine (**14c**) on treatment with hydrochloric acid. The results suggest that the ethoxyethenyl groups of relatively electron-

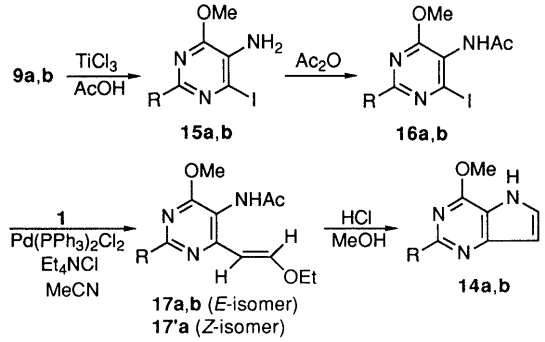


Chart 3

deficient pyrimidine derivatives (**10a, b**) are more easily reduced to 2-ethoxyethyl groups.

In order to synthesize **14a, b**, we examined another synthetic route, as shown in Chart 3. Namely, 5-acetylamino-4-iodo-6-methoxypyrimidines (**16a, b**) were synthesized by the reduction of 4-iodo-6-methoxy-5-nitropyrimidines (**9a, b**) with titanium trichloride,[9] followed by acetylation. The palladium-catalyzed reaction of **16a, b** with **1** gave the expected products (**17a, b**), which were transformed to the pyrrolo[3,2-*d*]pyrimidine (**14a, b**) in good yields.

This paper deals with the cyclization of the (*E*)- or (*Z*)-acetylamino(2-ethoxyethenyl)pyrimidines obtained as the main products of the palladium-catalyzed reaction of acetylaminohalopyrimidines with **1**. The cyclization of the acetylamino(2-ethoxyethenyl)pyrimidines to the pyrrolopyrimidines would be possible regardless of the configuration of the 2-ethoxyethenyl groups. Therefore, the method is expected to be useful to construct pyrrolo[2,3-*d*]- and pyrrolo[3,2-*d*]pyrimidines having no substituent on the pyrrole ring moiety.

Experimental

Melting points were determined in capillary tubes and are uncorrected. IR spectra were recorded on a JASCO IRA-1 spectrometer. ^{1}H-NMR spectra were recorded on a JEOL PMX-60 (60 MHz) using tetramethylsilane as an internal standard. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, dd=double doublet, m=multiplet, and br=broad. Mass spectra (MS) and high resolution mass spectra (HRMS) were recorded on a JEOL JMS-DX303 spectrometer. Elemental analyses were performed by the staff of the Central Analysis Room of the Pharmaceutical Institute, Tohoku University.

4-Amino-5-bromopyrimidine Bromine (5 ml) was added dropwise to a mixture of 4-aminopyrimidine[10] (4.75 g, 50 mmol), $CaCO_3$ (2.5 g, 25 mmol), and H_2O (60 ml) at 55—60 °C, and the mixture was stirred at the same temperature for 20 min, then made alkaline with 28% aqueous NH_3 and extracted with AcOEt. The AcOEt extract was dried over K_2CO_3. The residue obtained from the AcOEt extract was purified by Al_2O_3 column chromatography using AcOEt as an eluent to give colorless scales, which were recrystallized from MeOH. Yield 5.13 g (59%). mp 206—208 °C (dec.). Lit.[11] mp 208—210 °C (dec.). ^{1}H-NMR ($CDCl_3$): 6.7—7.4 (2H, br), 8.40 (1H, s), 8.47 (1H, s).

4-Acetylamino-5-bromopyrimidine (2a) A mixture of 4-amino-5-bromopyrimidine (3.0 g, 17 mmol), Ac_2O (5 ml), and AcOH (25 ml) was refluxed for 2 h. The mixture was made alkaline with aqueous K_2CO_3 and extracted with $CHCl_3$. The $CHCl_3$ extract was dried over K_2CO_3 and evaporated *in vacuo*. The residue were recrystallized from AcOEt–hexane to give colorless needles. Yield 3.49 g (95%). mp 108—110 °C. IR ($CHCl_3$) cm^{-1}: 3360, 1700. ^{1}H-NMR ($CDCl_3$): 2.60 (3H, s), 7.8—8.4 (1H, br), 8.70 (1H, s), 8.83 (1H, s). *Anal.* Calcd for $C_6H_6BrN_3O$: C, 33.36; H, 2.80; N, 19.45. Found: C, 33.25; H, 2.64; N, 19.31.

4-Acetylamino-5-bromo-2,6-dimethylpyrimidine (2b) A mixture of 4-amino-5-bromo-2,6-dimethylpyrimidine[12] (2.02 g, 10 mmol) and Ac_2O (20 ml) was heated at 70 °C for 2 h. After removal of the excess Ac_2O, the residue was treated as described in the preparation of **2a**. Recrystallization of the crude product from Et_2O–hexane gave colorless needles. Yield 1.98 g (81%). mp 90—91 °C. IR ($CHCl_3$) cm^{-1}: 3360, 1700. ^{1}H-NMR ($CDCl_3$): 2.5—2.6 (9H, br s), 7.8—8.3 (1H, br). *Anal.* Calcd for $C_8H_{10}BrN_3O$: C, 39.37; H, 4.13; N, 17.21. Found: C, 39.34; H, 4.09; N, 17.11.

4-Acetylamino-2-methoxypyrimidine A mixture of 4-amino-2-methoxypyrimidine[13] (0.62 g, 5 mmol) and Ac_2O (10 ml) was refluxed for 20 min. After removal of the excess Ac_2O, the residue was treated as described in the preparation of **2a**. Recrystallization of the crude product from AcOEt gave colorless prisms. Yield 0.73 g (88%). mp 166—168 °C. IR ($CHCl_3$) cm^{-1}: 3400, 1720. ^{1}H-NMR (DMSO-d_6): 2.23 (3H, s), 3.97 (3H, s), 7.78 (1H, d, J=6), 8.40 (1H, d, J=6), 10.3—10.8 (1H, br). *Anal.* Calcd for $C_7H_9N_3O_2$: C, 50.30; H, 5.43; N, 25.14. Found: C, 50.27; H, 5.46; N, 25.31.

4-Acetylamino-5-bromo-2-methoxypyrimidine (2c) A solution of Br_2 (2 ml, 40 mmol) in AcOH (20 ml) was added dropwise to a solution of 4-acetylamino-2-methoxypyrimidine (3.32 g, 20 mmol) in AcOH (20 ml) at room temperature. The mixture was stirred for 1 h, then the AcOH was removed *in vacuo*. The residue was made alkaline with 28% aqueous NH_3, and the resulting precipitates were recrystallized from AcOEt to give colorless needles. Yield 2.96 g (60%). mp 120—122 °C. IR ($CHCl_3$) cm^{-1}: 3360, 1700. ^{1}H-NMR ($CDCl_3$): 2.64 (3H, s), 4.00 (3H, s), 7.8—8.3 (1H, br), 8.44 (1H, s). *Anal.* Calcd for $C_7H_8BrN_3O_2$: C, 34.17; H, 3.28; N, 17.08. Found: C, 34.22; H, 3.44; N, 17.25.

4-Amino-5-bromo-2,6-dimethoxypyrimidine A solution of Br_2 (0.8 ml) in AcOH (10 ml) was added to a solution of 4-amino-2,6-dimethoxypyrimidine[14] (2.00 g, 13 mmol) in AcOH (10 ml) at room temperature. The mixture was stirred for 30 min, then the mixture was made alkaline with 28% aqueous NH_3. The resulting precipitates were recrystallized from Et_2O to give colorless prisms. Yield 2.39 g (78%). mp 169—171 °C. Lit.[14] mp 170—172 °C. ^{1}H-NMR ($CDCl_3$): 3.90 (3H, s), 4.00 (3H, s), 6.2—6.7 (2H, br).

4-Acetylamino-5-bromo-2,6-dimethoxypyrimidine (2d) A mixture of 4-amino-5-bromo-2,6-dimethoxypyrimidine (1.4 g, 6 mmol) and Ac_2O (10 ml) was refluxed for 18 h. After removal of the excess Ac_2O, the residue was diluted with H_2O and extracted with AcOEt. The AcOEt extract was dried over K_2CO_3. The crude product obtained from the AcOEt extract was recrystallized from AcOEt to give colorless needles. Yield 1.24 g (75%). mp 127—129 °C. IR ($CHCl_3$) cm^{-1}: 3370, 1700. ^{1}H-NMR ($CDCl_3$): 2.63 (3H, s), 3.98 (3H, s), 4.03 (3H, s), 7.8—8.3 (1H, br). *Anal.* Calcd for $C_8H_{10}BrN_3O_3$: C, 34.80; H, 3.65; N, 15.22. Found: C, 35.06; H, 3.44; N, 15.25.

General Procedure A. The Palladium-Catalyzed Reaction of Halopyrimidines with (*Z*)-1-Ethoxy-2-(tributylstannyl)ethene (1) A mixture of a halopyrimidine (**1**), Et_4NCl, and $Pd(PPh_3)_2Cl_2$ in a solvent (THF, MeCN, or DMF) was heated for an appropriate time with stirring. After removal of the solvent *in vacuo*, the residue was mixed with H_2O and $CHCl_3$ in the case of THF or MeCN as a solvent, or AcOEt in the case of DMF as a solvent. The mixture was filtered using a Celite® pad. The aqueous layer was extracted with $CHCl_3$ or AcOEt, and the organic layer was dried over $MgSO_4$. The residue obtained from the organic layer was purified by SiO_2 column chromatography.

(*Z*)- (3a) and (*E*)-4-Acetylamino-5-(2-ethoxyethenyl)pyrimidine (3'a) A mixture of **2a** (1.08 g, 5 mmol), **1** (2.16 g, 6 mmol), Et_4NCl (0.83 g, 5 mmol), and $Pd(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol) in MeCN (20 ml) was refluxed for 2 h. The residue was purified by SiO_2 column chromatography using AcOEt–hexane (1 : 4) as an eluent. The first eluate gave colorless needles (**3'a**), which were recrystallized from AcOEt–hexane. Yield 0.11 g (11%). mp 128—130 °C. IR ($CHCl_3$) cm^{-1}: 3350, 1690. ^{1}H-NMR ($CDCl_3$): 1.37 (3H, t, J=7), 2.53 (3H, s), 3.98 (2H, q, J=7), 5.67 (1H, d, J=13), 6.90 (1H, d, J=13), 8.1—8.8 (1H, br), 8.53 (1H, s), 8.82 (1H, s). *Anal.* Calcd for $C_{10}H_{13}N_3O_2$: C, 57.96; H, 6.32; N, 20.28. Found: C, 57.75; H, 6.40; N, 20.09.

The second eluate gave colorless needles (**3a**) which were recrystallized from Et_2O–hexane. Yield 0.67 g (65%). mp 87—89 °C. IR ($CHCl_3$) cm^{-1}: 3400, 1700. ^{1}H-NMR ($CDCl_3$): 1.37 (3H, t, J=7), 2.50 (3H, s), 4.08 (2H, q, J=7), 5.15 (1H, d, J=7), 6.42 (1H, d, J=7), 8.3—8.8 (1H, br), 8.77 (1H, s), 8.80 (1H, s). *Anal.* Calcd for $C_{10}H_{13}N_3O_2$: C, 57.96; H, 6.32; N, 20.28. Found: C, 57.80; H, 6.43; N, 20.26.

(*Z*)-4-Acetylamino-5-(2-ethoxyethenyl)-2,6-dimethylpyrimidine (3b) A mixture of **2b** (1.23 g, 5 mmol), **1** (2.16 g, 6 mmol), Et_4NCl (0.83 g, 5 mmol), and $Pd(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol) in DMF (20 ml) was heated at 140 °C for 1 h. Purification of the residue by SiO_2 column

chromatography using AcOEt–hexane (1 : 5) as an eluent gave a pale yellow viscous liquid. Yield 1.12 g (95%). IR ($CHCl_3$) cm^{-1}: 3380, 1690. ^1H-NMR ($CDCl_3$): 1.30 (3H, t, $J=7$), 2.43 (3H, s), 2.53 (3H, s), 2.60 (3H, s), 4.03 (2H, q, $J=7$), 5.13 (1H, d, $J=7$), 6.38 (1H, d, $J=7$), 7.8—8.5 (1H, br). MS *m/z*: 235 (M^+). HRMS Calcd for $C_{12}H_{17}N_3O_2$: 235.1321. Found: 235.1328.

(*Z*)-4-Acetylamino-5-(2-ethoxyethenyl)-2-methoxypyrimidine (3c) A mixture of **2c** (1.23 g, 5 mmol), **1** (2.16 g, 6 mmol), Et_4NCl (0.83 g, 5 mmol), and $Pd(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol) in MeCN (20 ml) was refluxed for 3 h. Purification of the residue by SiO_2 column chromatography using AcOEt–hexane (1 : 3) as an eluent gave colorless needles, which were recrystallized from AcOEt–hexane. Yield 0.84 g (71%). mp 88—90 °C. IR ($CHCl_3$) cm^{-1}: 3400, 1690. ^1H-NMR ($CDCl_3$): 1.37 (3H, t, $J=7$), 2.57 (3H, s), 4.00 (3H, s), 4.07 (2H, q, $J=7$), 5.12 (1H, d, $J=7$), 6.33 (1H, d, $J=7$), 8.4—8.8 (1H, br), 8.50 (1H, s). *Anal.* Calcd for $C_{11}H_{15}N_3O_3$: C, 55.69; H, 6.37; N, 17.71. Found: C, 55.78; H, 6.42; N, 17.90.

(*Z*)-4-Acetylamino-5-(2-ethoxyethenyl)-2,6-dimethoxypyrimidine (3d) A mixture of **2d** (1.38 g, 5 mmol), **1** (2.16 g, 6 mmol), Et_4NCl (0.83 g, 5 mmol), and $Pd(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol) in DMF (20 ml) was heated at 140 °C for 1 h. Purification of the residue by SiO_2 column chromatography using AcOEt–hexane (1 : 1) as an eluent gave a pale yellow viscous liquid. Yield 1.04 g (78%). IR ($CHCl_3$) cm^{-1}: 3400, 1700. ^1H-NMR ($CDCl_3$): 1.37 (3H, t, $J=7$), 2.53 (3H, s), 3.98 (6H, s), 4.03 (2H, q, $J=7$), 5.20 (1H, d, $J=7$), 6.23 (1H, d, $J=7$), 8.4—8.8 (1H, br). MS *m/z*: 267 (M^+). HRMS Calcd for $C_{12}H_{17}N_3O_4$: 267.1219. Found 267.1213.

General Procedure B. Cyclization of 3a—d to Pyrrolo[2,3-*d*]pyrimidines (4a—d) A mixture of a (*Z*)-4-acetylamino-5-(2-ethoxyethenyl)pyrimidine (**3**) (5 mmol) and concentrated HCl (3 ml) in MeOH (20 ml) was refluxed for the time shown in Table II. After removal of the solvent *in vacuo*, the residue was made alkaline with aqueous K_2CO_3 and extracted with $CHCl_3$ or AcOEt. The crude product obtained from the organic layer was purified by recrystallization.

Pyrrolo[2,3-*d*]pyrimidine (**4a**): Colorless prisms from AcOEt. mp 128—130 °C. Lit.[15] mp 130—132 °C. IR ($CHCl_3$) cm^{-1}: 3450. ^1H-NMR ($CDCl_3$): 6.61 (1H, d, $J=4$), 7.48 (1H, d, $J=4$), 9.03 (1H, s), 9.13 (1H, s), 12.4—13.3 (1H, br).

2,4-Dimethylpyrrolo[2,3-*d*]pyrimidine (**4b**): Colorless prisms from AcOEt. mp 187—189 °C. IR ($CHCl_3$) cm^{-1}: 3450. ^1H-NMR ($CDCl_3$): 2.70 (3H, s), 2.80 (3H, s), 6.50 (1H, d, $J=3$), 7.23 (1H, d, $J=3$), 12.4—12.8 (1H, br). *Anal.* Calcd for $C_8H_9N_3$: C, 65.29; H, 6.16; N, 28.55. Found: C, 65.22; H, 6.19; N, 28.81.

2-Methoxypyrrolo[2,3-*d*]pyrimidine (**4c**): Colorless prisms from AcOEt–hexane. mp 180—182 °C. IR ($CHCl_3$) cm^{-1}: 3450. ^1H-NMR (DMSO-d_6): 4.00 (3H, s), 6.10 (1H, d, $J=3$), 7.13 (1H, d, $J=3$), 8.70 (1H, s), 10.9—11.7 (1H, br). *Anal.* Calcd for $C_7H_7N_3O$: C, 56.37; H, 4.73; N, 28.17. Found: C, 56.37; H, 4.56; N, 28.23.

2,4-Dimethoxypyrrolo[2,3-*d*]pyrimidine (**4d**): Colorless prisms from AcOEt–hexane. mp 217—219 °C. IR ($CHCl_3$) cm^{-1}: 3450. ^1H-NMR (DMSO-d_6): 3.97 (3H, s), 4.03 (3H, s), 6.33 (1H, dd, $J=2$, 3), 6.92 (1H, dd, $J=3$, 5), 11.2—11.8 (1H, br). *Anal.* Calcd for $C_8H_9N_3O_2$: C, 53.63; H, 5.06; N, 23.45. Found: C, 53.45; H, 4.90; N, 23.18.

(*E*)-4-(2-Ethoxyethenyl)-1-methyl-5-nitro-6(1*H*)-pyrimidinone (6a) According to the general procedure A, a mixture of 4-chloro-6-methoxy-5-nitropyrimidine[16] (**5a**) (7.58 g, 40 mmol), **1** (17.3 g, 48 mmol), Et_4NCl (6.63 g, 40 mmol), and $Pd(PPh_3)_2Cl_2$ (1.12 g, 1.6 mmol) in DMF (120 ml) was heated at 140 °C for 1 h. Purification of the residue by SiO_2 column chromatography using AcOEt–hexane (1 : 1) as an eluent gave yellow needles, which were recrystallized from AcOEt–hexane. Yield 2.97 g (33%). mp 123—125 °C. IR ($CHCl_3$) cm^{-1}: 1690. ^1H-NMR ($CDCl_3$): 1.36 (3H, t, $J=7$), 3.53 (3H, s), 4.08 (2H, q, $J=7$), 5.80 (1H, d, $J=12$), 8.00 (1H, d, $J=12$), 8.10 (1H, s). *Anal.* Calcd for $C_9H_{11}N_3O_4$: C, 48.00; H, 4.92; N, 18.66. Found: C, 48.21; H, 5.10; N, 18.85.

(*E*)-4-(2-Ethoxyethenyl)-1,2-dimethyl-5-nitro-6(1*H*)-pyrimidinone (6b) According to the general procedure A, a mixture of 4-chloro-6-methoxy-2-methyl-5-nitropyrimidine[17] (**5b**) (4.07 g, 20 mmol), **1** (8.65 g, 24 mmol), Et_4NCl (3.31 g, 20 mmol), and $Pd(PPh_3)_2Cl_2$ (0.56 g, 0.8 mmol) in DMF (80 ml) was heated at 140 °C for 30 min. Purification of the residue by SiO_2 column chromatography using AcOEt–hexane (1 : 1) as an eluent gave yellow needles, which were recrystallized from AcOEt–hexane. Yield 0.67 g (14%). mp 157—159 °C. IR ($CHCl_3$)cm^{-1}: 1680. ^1H-NMR ($CDCl_3$): 1.36 (3H, t, $J=7$), 2.53 (3H, s), 3.53 (3H, s), 4.07 (2H, q, $J=7$), 5.83 (1H, d, $J=12$), 8.03 (1H, d, $J=12$). *Anal.* Calcd for $C_{10}H_{13}N_3O_4$: C, 50.21; H, 5.48; N, 17.56. Found: C, 50.30; H, 5.61; N, 17.78.

3-Methylpyrrolo[3,2-*d*]pyrimidin-4(3*H*)-one (8a) A mixture of **6a** (0.90 g, 4 mmol) and W-2 Raney Ni (2 ml) in MeOH (70 ml) was hydrogenated under atmospheric pressure for 5 h. After removal of the catalyst by filtration, the filtrate was concentrated to *ca.* 20 ml. A mixture of the filtrate and concentrated HCl (2 ml) was refluxed for 70 min. The residue obtained from the reaction mixture was made alkaline with K_2CO_3 and extracted with AcOEt. The crude product obtained from the AcOEt extract was purified by SiO_2 column chromatography using AcOEt as an eluent to give colorless needles, which were recrystallized from acetone. Yield 0.35 g (59%). mp 225—226 °C. IR (KBr) cm^{-1}: 3200—3100, 1680. ^1H-NMR (DMSO-d_6): 3.59 (3H, s), 6.07 (1H, dd, $J=2$, 3), 7.28 (1H, dd, $J=3$, 5), 8.00 (1H, s), 11.1—12.6 (1H, br). *Anal.* Calcd for $C_7H_7N_3O$: C, 56.37; H, 4.73; N, 28.17. Found: C, 56.51; H, 4.78; N, 28.18.

2,3-Dimethylpyrrolo[3,2-*d*]pyrimidin-4(3*H*)-one (8b) A mixture of **6b** (0.48 g, 2 mmol) and W-2 Raney Ni (1 ml) in MeOH (50 ml) was hydrogenated for 7 h. Treatment as described for the preparation of **8a** gave colorless needles, which were recrystallized from acetone–hexane. Yield 0.25 g (77%). mp 235—236 °C. IR (KBr) cm^{-1}: 3200, 1670. ^1H-NMR (DMSO-d_6): 2.60 (3H, s), 3.63 (3H, s), 6.36 (1H, dd, $J=2$, 3), 7.30 (1H, dd, $J=3$, 5), 11.3—12.2 (1H, br). *Anal.* Calcd for $C_8H_9N_3O$: C, 58.89; H, 5.56; N, 25.75. Found: C, 58.83; H, 5.53; N, 25.69.

4-Iodo-6-methoxy-5-nitropyrimidines (9a—c) A mixture of a 4-choloro-6-methoxy-5-nitropyrimidine[16-18] (**5**) (10 mmol) and 57% HI (6 ml) was stirred at room temperature for 24 h. The mixture was diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with aqueous Na_2SO_3 and dried over K_2CO_3. The crude product obtained from the $CHCl_3$ extract was purified by recrystallization.

4-Iodo-6-methoxy-5-nitropyrimidine (**9a**): Yellow needles from acetone–hexane. Yield 74%. mp 170 °C. ^1H-NMR (DMSO-d_6): 4.17 (3H, s), 8.62 (1H, s). *Anal.* Calcd for $C_5H_4IN_3O_3$: C, 21.37; H, 1.43; N, 14.95. Found: C, 21.33; H, 1.28; N, 14.84.

4-Iodo-6-methoxy-2-methyl-5-nitropyrimidine (**9b**): Yellow needles from Et_2O–hexane. Yield 77%. mp 103—105 °C. ^1H-NMR ($CDCl_3$): 2.66 (3H, s), 4.07 (3H, s). *Anal.* Calcd for $C_6H_6IN_3O_3$: C, 24.43; H, 2.05; N, 14.24. Found: C, 24.48; H, 2.13; N, 14.30.

4-Iodo-2,6-dimethoxy-5-nitropyrimidine (**9c**): Yellow prisms from AcOEt–hexane. Yield 78%. mp 143—145 °C. ^1H-NMR ($CDCl_3$): 4.06 (3H, s), 4.09 (3H, s). *Anal.* Calcd for $C_6H_6IN_3O_4$: C, 23.17; H, 1.94; N, 13.51. Found: C, 23.09; H, 1.96; N, 13.75.

(*E*)- (10a—c) and (*Z*)-4-(2-Ethoxyethenyl)-6-methoxy-5-nitropyrimidines (11a—c) According to the general procedure A, a mixture of **9** (10 mmol), **1** (4.32 g, 12 mmol), Et_4NCl (1.66 g, 10 mmol), and $Pd(PPh_3)_2Cl_2$ (280 mg, 0.4 mmol) in THF (60 ml) was refluxed for the time shown in Table III. The crude product was purified by SiO_2 column chromatography using AcOEt–hexane (1 : 9) as an eluent. The first eluate gave the *E*-isomer (**10**) and the second eluate gave the *Z*-isomer (**11**).

(*E*)-4-(2-Ethoxyethenyl)-6-methoxy-5-nitropyrimidine (**10a**): Yellow needles from AcOEt–hexane. mp 114—116 °C. ^1H-NMR ($CDCl_3$): 1.30 (3H, t, $J=7$), 3.96 (2H, q, $J=7$), 4.00 (3H, s), 5.70 (1H, d, $J=12$), 8.00 (1H, d, $J=12$), 8.43 (1H, s). *Anal.* Calcd for $C_9H_{11}N_3O_4$: C, 48.00; H, 4.92; N, 18.66. Found: C, 47.77; H, 4.70; N, 18.57.

(*Z*)-4-(2-Ethoxyethenyl)-6-methoxy-5-nitropyrimidine (**11a**): Yellow needles from AcOEt–hexane. mp 114—115 °C. ^1H-NMR ($CDCl_3$): 1.37 (3H, t, $J=7$), 4.10 (3H, s), 4.13 (2H, q, $J=7$), 5.33 (1H, d, $J=7$), 6.63 (1H, d, $J=7$), 8.73 (1H, s). *Anal.* Calcd for $C_9H_{11}N_3O_4$: C, 48.00; H, 4.92; N, 18.66. Found: C, 47.84; H, 4.88; N, 18.61.

(*E*)-4-(2-Ethoxyethenyl)-6-methoxy-2-methyl-5-nitropyrimidine (**10b**): Yellow needles from Et_2O–hexane. mp 90—92 °C. ^1H-NMR ($CDCl_3$): 1.37 (3H, t, $J=7$), 2.57 (3H, s), 4.03 (2H, q, $J=7$), 4.05 (3H, s), 5.80 (1H, d, $J=12$), 8.15 (1H, d, $J=12$). *Anal.* Calcd for $C_{10}H_{13}N_3O_4$: C, 50.21; H, 5.48; N, 17.56. Found: C, 50.08; H, 5.31; N, 17.49.

(*Z*)-4-(2-Ethoxyethenyl)-6-methoxy-2-methyl-5-nitropyrimidine (**11b**): Yellow needles from Et_2O–hexane. mp 89—90 °C. ^1H-NMR ($CDCl_3$): 1.33 (3H, t, $J=7$), 2.60 (3H, s), 4.03 (3H, s), 4.05 (2H, q, $J=7$), 5.33 (1H, d, $J=7$), 6.55 (1H, d, $J=7$). *Anal.* Calcd for $C_{10}H_{13}N_3O_4$: C, 50.21; H, 5.48; N, 17.56. Found: C, 50.14; H, 5.36; N, 17.29.

(*E*)-4-(2-Ethoxyethenyl)-2,6-dimethoxy-5-nitropyrimidine (**10c**): Yellow needles from Et_2O–hexane. mp 125—127 °C. ^1H-NMR ($CDCl_3$): 1.40 (3H, t, $J=7$), 4.03 (3H, s), 4.05 (2H, q, $J=7$), 4.07 (3H, s), 5.92 (1H, d, $J=12$), 8.10 (1H, d, $J=12$). *Anal.* Calcd for $C_{10}H_{13}N_3O_5$: C, 47.06; H, 5.13; N, 16.46. Found: C, 47.11; H, 5.09; N, 16.43.

(*Z*)-4-(2-Ethoxyethenyl)-2,6-dimethoxy-5-nitropyrimidine (**11c**): Yellow needles from Et_2O–hexane. mp 108 °C. ^1H-NMR ($CDCl_3$): 1.33 (3H, t, $J=7$), 4.05 (3H, s), 4.07 (3H, s), 4.13 (2H, q, $J=7$), 5.37 (1H, d, $J=7$),

6.60 (1H, d, $J=7$). *Anal.* Calcd for $C_{10}H_{13}N_3O_5$: C, 47.06; H, 5.13; N, 16.46. Found: C, 47.26; H, 5.20; N, 16.49.

Isomerization of 10a to 6a A mixture of **10a** (0.45 g, 2 mmol) and Et_4NCl (0.33 g, 2 mmol) in DMF (5 ml) was heated at 140 °C for 5 min. After evaporation of the solvent, the residue was purified by SiO_2 column chromatography using AcOEt–hexane (1 : 1) to give yellow prisms, which were identical with the specimen prepared from **5a** and **1**. Yield 0.37 g (82%).

5-Amino-4-(2-ethoxyethyl)-6-methoxypyrimidine (12a) A mixture of **10a** (0.45 g, 2 mmol) and W-2 Raney Ni (1 ml) in MeOH (40 ml) was hydrogenated for 3 h. The crude product was purified by SiO_2 column chromatography using AcOEt as an eluent to give a pale yellow viscous liquid. Yield 0.36 g (93%). IR ($CHCl_3$) cm^{-1}: 3400, 3350. ^{1}H-NMR ($CDCl_3$): 1.17 (3H, t, $J=7$), 2.97 (2H, t, $J=6$), 3.47 (2H, q, $J=7$), 3.80 (2H, t, $J=6$), 4.00 (3H, s), 3.7—4.3 (2H, br), 8.23 (1H, s). MS *m/z*: 197 (M^+). HRMS calcd for $C_9H_{15}N_3O_2$: 197.1163. Found: 197.1160.

5-Amino-4-(2-ethoxyethyl)-6-methoxy-2-methylpyrimidine (12b) A mixture of **10b** (0.48 g, 2 mmol) and W-2 Raney Ni (1 ml) in MeOH (40 ml) was hydrogenated for 2.5 h. The crude product was purified by SiO_2 column chromatography using AcOEt as an eluent to give a colorless viscous liquid. Yield 0.40 g (95%). IR ($CHCl_3$) cm^{-1}: 3420, 3340. ^{1}H-NMR ($CDCl_3$): 1.13 (3H, t, $J=7$), 2.1—2.7 (2H, br), 2.47 (3H, s), 2.87 (2H, t, $J=5$), 3.46 (2H, q, $J=7$), 3.37 (2H, t, $J=5$), 3.98 (3H, s). MS *m/z*: 211 (M^+). HRMS Calcd for $C_{10}H_{17}N_3O_2$: 211.1321. Found: 211.1330.

The same product (**12b**) was obtained from the hydrogenation of **11b** (0.48 g, 2 mmol) under the same reaction conditions. Yield 0.41 g (97%).

The Palladium–Charcoal Catalyzed Hydrogenation of 10b A mixture of **10b** (0.48 g, 2 mmol) and 5% Pd–C (80 mg) in MeOH (40 ml) was hydrogenated under atmospheric pressure for 45 min. Removal of the catalyst by filtration and evaporation of the filtrate gave a residue, which was purified by SiO_2 column chromatography using AcOEt–hexane (1 : 9) as an eluent. The first eluate gave colorless needles, (*E*)-5-amino-4-(2-ethoxyethenyl)-6-methoxy-2-methylpyrimidine (**13b**), which were recrystallized from AcOEt–hexane. Yield 0.14 g (33%). mp 125—127 °C. IR ($CHCl_3$) cm^{-1}: 3450, 3300. ^{1}H-NMR ($CDCl_3$): 1.36 (3H, t, $J=7$), 2.50 (3H, s), 2.8—3.7 (2H, br), 3.98 (3H, s), 4.00 (2H, q, $J=7$), 5.82 (1H, d, $J=12$), 7.65 (1H, d, $J=12$). *Anal.* Calcd for $C_{10}H_{15}N_3O_2$: C, 57.40; H, 7.23; N, 20.08. Found: C, 57.28; H, 7.05; N, 19.87.

The second eluate gave a viscous colorless liquid (**12b**), which was identical to the specimen described above. Yield 0.27 g (64%).

2,4-Dimethoxypyrrolo[3,2-*d*]pyrimidine (14c) A mixture of **10c** (0.51 g, 2 mmol) and W-2 Raney Ni (1 ml) in MeOH (40 ml) was hydrogenated for 2 h. After filtration to remove the catalyst, the filtrate was concentrated to *ca.* 10 ml. A mixture of the MeOH solution and concentrated HCl (1 ml) was refluxed for 70 min. The residue obtained from the mixture was diluted with H_2O, made alkaline with K_2CO_3, and extracted with AcOEt. The AcOEt extract was dried over K_2CO_3 and evaporated to give the crude product, which was purified by SiO_2 column chromatography using AcOEt–hexane (1 : 1) as an eluent. The product obtained from the eluate was recrystallized from acetone–hexane to give colorless needles. Yield 0.19 g (53%). mp 181—183 °C. Lit.[19] mp 183—184 °C. IR ($CHCl_3$) cm^{-1}: 3460. ^{1}H-NMR (DMSO-d_6): 3.98 (3H, s), 4.10 (3H, s), 6.38 (1H, dd, $J=2$, 3), 7.33 (1H, dd, $J=3$, 5), 10.9—11.3 (1H, br).

5-Amino-4-iodo-6-methoxypyrimidine (15a) A mixture of **9a** (2.81 g, 10 mmol), 20% $TiCl_3$ (46.5 g, 60 mmol), AcOH (30 ml), and H_2O (30 ml) was stirred at room temperature for 18 h. The mixture was made alkaline with 3 N NaOH and filtered through a Celite® pad. The pad was washed well with $CHCl_3$, and the filtrate was extracted with $CHCl_3$. The combined $CHCl_3$ layer was dried over $MgSO_4$ and evaporated *in vacuo*. The residue was recrystallized from Et_2O–hexane to give colorless needles. Yield 2.25 g (85%). mp 79—81 °C. IR ($CHCl_3$) cm^{-1}: 3500, 3400. ^{1}H-NMR ($CDCl_3$): 3.8—4.4 (2H, br), 4.00 (3H, s), 7.93 (1H, s). *Anal.* Calcd for $C_5H_6IN_3O$: C, 23.92; H, 2.41; N, 16.74. Found: C, 23.81; H, 2.35; N, 16.81.

5-Amino-4-iodo-6-methoxypyrimidine (15b) According to the procedure described above, colorless needles was obtained from the reaction of **9b** (1.97 g, 7 mmol), 20% $TiCl_3$ (32.7 g, 42 mmol), AcOH (20 ml), and H_2O (20 ml) and recrystallized from Et_2O–Hexane. Yield 1.43 g (78%). mp 88—90 °C. IR ($CHCl_3$) cm^{-1}: 3480, 3380. ^{1}H-NMR ($CDCl_3$): 2.47 (3H, s), 3.7—4.2 (2H, br), 3.97 (3H, s). *Anal.* Calcd for $C_6H_8IN_3O$: C, 27.19; H, 3.04; N, 15.85. Found: C, 26.97; H, 2.95; N, 15.66.

5-Acetylamino-4-iodo-6-methoxypyrimidine (16a) A mixture of **15a** (1.50 g, 6 mmol) and Ac_2O (10 ml) was heated at 100 °C for 2 h. The mixture was made alkaline with aqueous K_2CO_3 and extracted with $CHCl_3$. The $CHCl_3$ extract was dried over K_2CO_3 and evaporated. The residue was recrystallized from AcOEt–hexane to give colorless needles. Yield 1.32 g (75%). mp 146—147 °C. IR ($CHCl_3$) cm^{-1}: 3400, 1700. ^{1}H-NMR ($CDCl_3$): 2.17 (3H, s), 3.98 (3H, s), 7.1—7.5 (1H, br), 8.33 (1H, s). *Anal.* Calcd for $C_7H_8IN_3O_2$: C, 28.69; H, 2.75; N, 14.34. Found: C, 28.91; H, 2.93; N, 14.28.

5-Acetylamino-4-iodo-6-methoxy-2-methylpyrimidine (16b) According to the procedure described above, colorless needles were obtained from the reaction of **15b** (0.53 g, 2 mmol) and Ac_2O (5 ml) and recrystallized from AcOEt–hexane. Yield 0.39 g (64%). mp 189—190 °C. IR ($CHCl_3$) cm^{-1}: 3420, 1700. ^{1}H-NMR ($CDCl_3$): 2.17 (3H, s), 2.63 (3H, s), 3.97 (3H, s), 6.7—7.1 (1H, br). *Anal.* Calcd for $C_8H_{10}IN_3O_2$: C, 31.29; H, 3.28; N, 13.68. Found: C, 31.12; H, 3.07; N, 13.56.

(*E*)- (17a) and (*Z*)-5-Acetylamino-4-(2-ethoxyethenyl)-6-methoxypyrimidine (17′a) According to the general procedure A, a mixture of **16a** (1.17 g, 4 mmol), **1** (1.73 g, 4.8 mmol), Et_4NCl (0.66 g, 4 mmol), and $Pd(PPh_3)_2Cl_2$ (110 mg, 0.15 mmol) in MeCN (20 ml) was refluxed for 33 h. The crude product was purified by SiO_2 column chromatography using AcOEt–hexane (3 : 1) as an eluent. The first eluate gave colorless needles (**17a**), which were recrystallized from AcOEt–hexane. Yield 0.35 g (37%). mp 143—145 °C. IR ($CHCl_3$) cm^{-1}: 3420, 1700. ^{1}H-NMR ($CDCl_3$): 1.33 (3H, t, $J=7$), 2.18 (3H, s), 3.94 (3H, s), 4.00 (2H, q, $J=7$), 5.80 (1H, d, $J=12$), 6.7—7.1 (1H, br), 7.85 (1H, d, $J=12$), 8.41 (1H, s). *Anal.* Calcd for $C_{11}H_{15}N_3O_3$: C, 55.69; H, 6.37; N, 17.71. Found: C, 55.49; H, 6.31; N, 17.64.

The second eluate gave colorless needles (**17′a**), which were recrystallized from acetone–hexane. Yield 0.28 g (30%). mp 117—118 °C. IR ($CHCl_3$) cm^{-1}: 3420, 1700. ^{1}H-NMR ($CDCl_3$): 1.37 (3H, t, $J=7$), 2.10 (3H, s), 4.00 (3H, s), 4.13 (2H, q, $J=7$), 5.45 (1H, d, $J=7$), 6.45 (1H, d, $J=7$), 7.3—8.2 (1H, br), 8.62 (1H, s). *Anal.* Calcd for $C_{11}H_{15}N_3O_3$: C, 55.69; H, 6.37; N, 17.71. Found: C, 55.52; H, 6.30; N, 17.59.

(*E*)-5-Acetylamino-4-(2-ethoxyethenyl)-6-methoxy-2-methylpyrimidine (17b) According to the general procedure A, a mixture of **16b** (0.50 g, 1.6 mmol), **1** (0.70 g, 2 mmol), Et_4NCl (0.27 g, 1.6 mmol), and $Pd(PPh_3)_2Cl_2$ (42 mg, 0.06 mmol) in MeCN (10 ml) was refluxed for 31 h. The crude product was purified by SiO_2 column chromatography using AcOEt–hexane (2 : 3) as an eluent to give colorless needles, which were recrystallized from AcOEt–hexane. Yield 0.30 g (75%). mp 153—154 °C. IR ($CHCl_3$) cm^{-1}: 3350, 1690. ^{1}H-NMR ($CDCl_3$): 1.33 (3H, t, $J=7$), 2.07 (3H, s), 2.53 (3H, s), 2.96 (3H, s), 4.00 (2H, q, $J=7$), 5.37 (1H, d, $J=7$), 6.33 (1H, d, $J=7$), 7.4—7.9 (1H, br). *Anal.* Calcd for $C_{12}H_{17}N_3O_3$: C, 57.36; H, 6.82; N, 16.72. Found: C, 57.12; H, 6.86; N, 16.49.

4-Methoxypyrrolo[3,2-*d*]pyrimidine (14a) According to the general procedure B, a mixture of **17a** (119 mg, 0.5 mmol) and concentrated HCl (0.3 ml) in MeOH (5 ml) was refluxed for 5 h. The crude product was recrystallized from acetone to give colorless needles. Yield 70 mg (94%). mp 164—165 °C. IR ($CHCl_3$) cm^{-1}: 3470. ^{1}H-NMR (CD_3OD): 4.14 (3H, s), 6.75 (1H, d, $J=3$), 7.50 (1H, d, $J=3$), 8.42 (1H, s). *Anal.* Calcd for $C_7H_7N_3O$: C, 56.37; H, 4.73; N, 28.18. Found: C, 56.43; H, 4.74; N, 27.88.

4-Methoxy-2-methylpyrrolo[3,2-*d*]pyrimidine (14b) According to the general procedure B, a mixture of **17b** (176 mg, 0.7 mmol) and concentrated HCl (0.3 ml) in MeOH (7 ml) was refluxed for 2.5 h. The crude product was recrystallized from AcOEt–hexane to give colorless needles. Yield 90 mg (79%). mp 181—182 °C. IR ($CHCl_3$) cm^{-1}: 3470. ^{1}H-NMR ($CDCl_3$): 2.70 (3H, s), 4.08 (3H, s), 6.57 (1H, dd, $J=2$, 5), 7.33 (1H, dd, $J=3$, 5), 9.6—10.3 (1H, br). *Anal.* Calcd for $C_8H_9N_3O$: C, 58.89; H, 5.56; N, 25.75. Found: C, 58.86; H, 5.49; N, 25.69.

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