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Functionalization of 1*H*-Pyrrolo[2,3-*b*]pyridine

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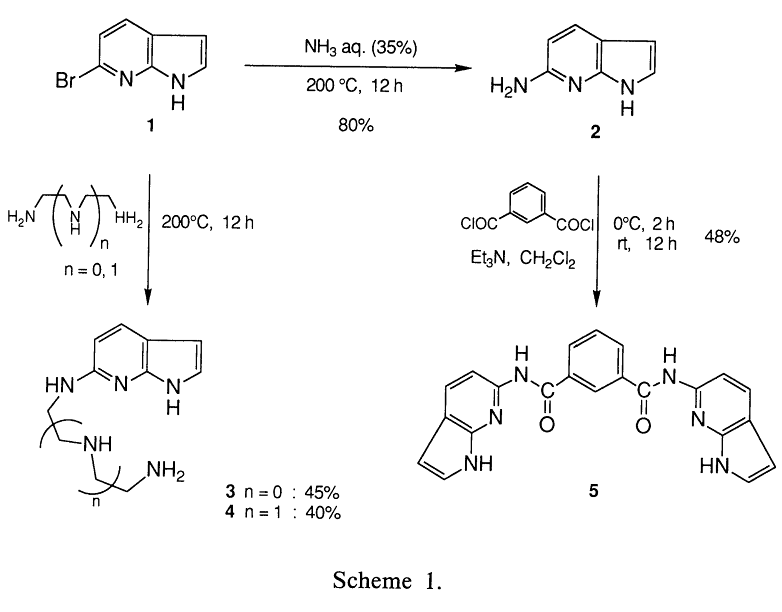
Functionalization of 1*H*-pyrrolo[2,3-*b*]pyridine (7-azaindole) was studied to provide new compounds directing toward agrochemicals and/or functional materials. Amino groups such as NH_2, $NH(CH_2)_2NH_2$, and $NH(CH_2)_2NH(CH_2)_2NH_2$ were introduced onto 6-position of 7-azaindole to form multidentate agents. 6-Amino and 6-iodo derivatives were easily converted to podant-type compounds, *N,N′*-bis(1*H*-pyrrolo[2,3-*b*]pyridin-6-yl)-1,3-benzenedicarboxamide and bis(1*H*-pyrrolo[2,3-*b*]pyridin-6-yl)acetylene, respectively. Polyacetylene having 1*H*-pyrrolo[2,3-*b*]pyridyl group as a pendant was obtained by polymerization of 6-ethynyl-7-azaindole synthesized by ethynylation of 6-bromo derivative. As functionalization at 3-position of 7-azaindole, syntheses of 3,3′-selenobis[1*H*-pyrrolo[2,3-*b*]pyridine] and the corresponding 3,3′-thio compound, as well as 3-carboxyethenyl- and 3-vinyl-7-azaindoles were performed. Some of these products exhibited high fungicidal activity.

1*H*-Pyrrolo[2,3-*b*]pyridine (7-azaindole) derivatives have been drawing much attention in physicochemical and biochemical studies[1] because of their characteristic condensed ring systems consisting of pyridine and pyrrole rings which have opposite π-electron densities. Thus studies on biological activities of 7-azaindole derivatives have been expanded significantly in recent years,[2] since they are aza analogues of indoles whose skeleton is often found in natural alkaloids and in synthetic pharmaceuticals.[3] As azaindoles contain a basic nitrogen atom of the pyridine ring and an acidic hydrogen atom of the pyrrole ring, they readily form complexes with metals[4] and may be applicable also to molecular recognition agents. Furthermore, it will be interesting to synthesize polymers containing 7-azaindole rings, which are hitherto unknown, directing toward materials science. Hence, it is of great importance to functionalize the azaindole ring for development of new or improved properties. Nevertheless, synthesis of functionalized azaindoles has been studied to very limited extent. From these points of view, we wish to report introduction of various functional groups to 7-azaindole ring.[5] Some of the products showed biological activities as agrochemicals and an acetylenic derivative was successfully polymerized to give the first example of azaindole-containing polymer.

Results and Discussion

Functionalization on Pyridine Ring. Recently we reported[5] the facile direct introduction of halogen atoms onto 6-position of 7-azaindole via its *N*-oxide. Although chemical transformations of 6-haloazaindoles have been less studied, they must be useful intermediates for functionalization of 7-azaindole. Thus 6-bromo-7-azaindole (**1**)[5] was treated with 35% aqueous ammonia solution in a sealed tube at 200 °C for 12 h to give 6-amino-7-azaindole (**2**) in 80% yield. We found that this type of reaction can be applied to synthesis of ethylenediamine and diethylenetriamine derivatives, **3** and **4**, which would be interesting novel multidentate agents. However, 6-chloro-7-azaindole was not reactive with



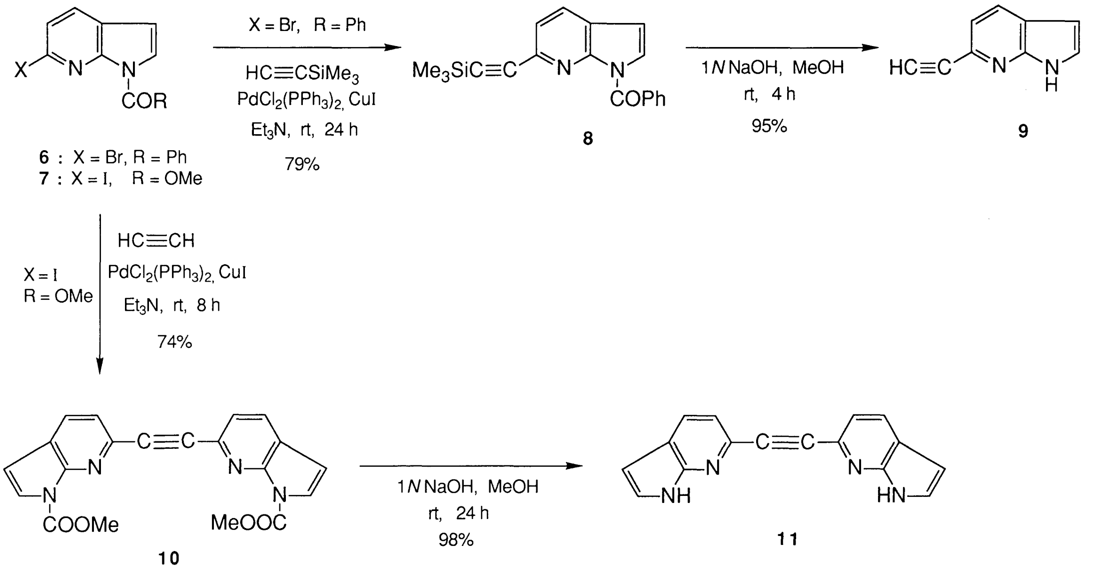
Scheme 1.

the amines under these conditions. Further treatment of 6-amino-7-azaindole (**2**) with isophthaloyl dichloride in the presence of triethylamine afforded a podant-type chelating agent, *N,N'*-bis(1*H*-pyrrolo[2,3-*b*]pyridin-6-yl)-1,3-benzenedicarboxamide (**5**), in 48% yield.

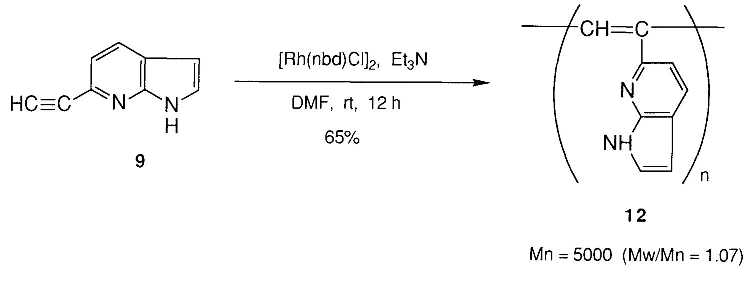
On the other hand, ethynylation of halogenated aromatic compounds is one of the useful methods in organic synthesis. Palladium-catalyzed cross-coupling reaction of haloarenes with acetylenes6) was applied to the halogenated azaindoles. 1-Benzoyl-6-bromo-7-azaindole reacted with trimethylsilylacetylene in the presence of copper(I) iodide and palladium/triphenylphosphine complex to give 1-benzoyl-6-trimethylsilylethynyl-7-azaindole (**8**). Compound **8** was readily desilylated and deacylated to 6-ethynyl-7-azaindole (**9**) by treatment with methanolic sodium hydroxide at room temperature. When gaseous acetylene was used instead of trimethylsilylacetylene, the anticipated diethynylated product was not obtained from the bromo derivative. But the more active 6-iodo-1-methoxycarbonyl-7-azaindole (**7**) reacted with acetylene in the presence of the same catalyst to give the disubstituted acetylene **10**. Compound **10** was easily deacylated to bis(1*H*-pyrrolo[2,3-*b*]pyridin-6-yl)acetylene (**11**) with methanolic sodium hydroxide. Compounds **5** and **11** are expected to possess molecular recognition ability since they have several sites for hydrogen bonding.

Although polyacetylenes are of great interest as electroconducting materials, synthesis of polyacetylenes having heteroaromatic substituents has rarely been reported.7) 6-Ethynyl-7-azaindole (**9**) was not polymerized by irradiation with γ-ray in DMF solution. So we attempted to polymerize the ethynylazaindole **9** by employing Tabata's method8) for aromatic acetylenes. To a solution of 0.1 equiv of [Rh(2,5-norbornadiene)Cl]$_2$ and 10 equiv of triethylamime in DMF was added dropwise a solution of 6-ethynyl-7-azindole in DMF at room temperature over 4 h. After stirring for 8 h at the same temperature, the polyacetylene **12** was obtained in 65% yield. Molecular weight of the isolated polymer was $\overline{M}_n$=5,000 ($\overline{M}_w/\overline{M}_n$=1.07). This is not only the first example of 7-azaindole-containing polyacetylene but also that of azaindole-containing polymer.

Functionalization on Pyrrole Ring. It is known that electrophilic substitution occurs at 3-position of 7-azaindole.9) Thus we studied the introduction of chalcogen atoms on the pyrrole ring of 7-azaindole since chalcogen atoms often give rise to characteristic properties in functional materials. The reaction of 7-azindole (**13**) with selenium dioxide in refluxing ethanol for 24 h gave 3,3'-selenobis[1*H*-pyrrolo[2,3-*b*]pyridine] (**14**) in 44% yield. This reaction is considered to proceed



Scheme 2.



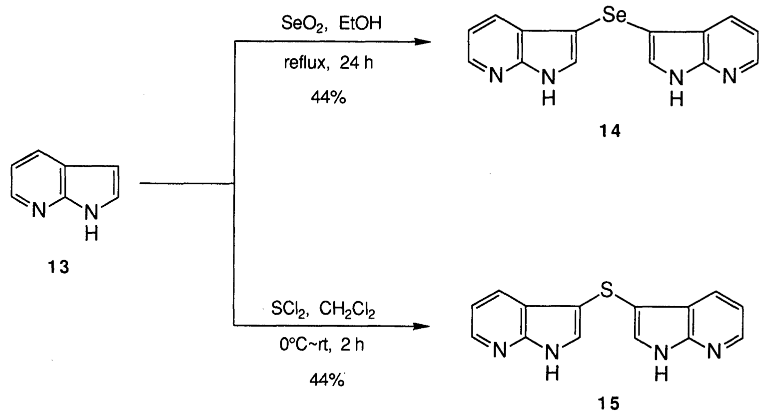
Scheme 3.

by the nucleophilic attack of C-3 of 7-azaindole to the selenium atom of diethyl selenite generated from 1 equiv of selenium dioxide and 2 equiv of ethanol. As a sulfur analog of **14**, the sulfide derivative **15** was prepared by the reaction of 7-azaindole with sulfur dichloride in 44% yield. These two chalcogen derivatives showed marked difference in biological activity (vide infra).

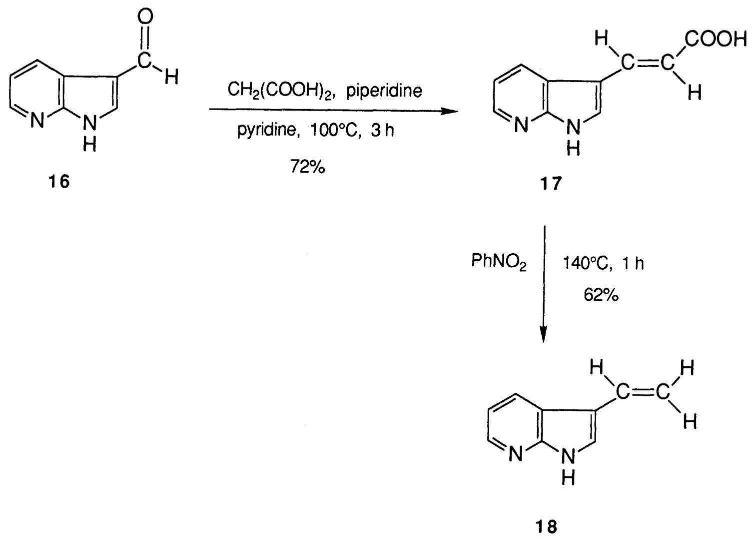
Polyethylenes containing heterocyclic compounds are well-known as electronic materials[10] and biologically active substances,[11] but azaindole-containing polyethylene has not been reported. So the introduction of vinyl group onto 3-position of 7-azaindole was investigated. As a precursor of 3-vinylazaindole, 3-formyl-7-azaindole (**16**) was prepared from 7-azaindole by the known procedure.[12] Although Wittig reaction was considered to be a facile method to transform formyl group of 7-azaindole into vinyl group, this reaction was not appropriate to this compound under conventional reaction conditions using methylenetriphenylphosphorane probably because of acidic hydrogen on pyrrole nitrogen. When 3-formylazaindole **16** was reacted with malonic acid in the presence of a catalytic amount of piperidine at 100 °C for 3 h, the acrylic acid derivative **17** in *trans*-form was poroduced in 72% yield. Decarboxylation of the compound **17** easily proceeded by thermal treatment in nitrobenzene to give 3-vinyl-7-azaindole (**18**) in 62% yield.

Biological Activities. Although biological properties of some azaindoles in animals have been studied, their activities in plants have rarely been investigated.[13] Therefore, we have synthesized some azaindole derivatives in addition to the aforementioned products and tested their biological activities as agricultural fungicides. The results of the screening are summarized in Table 1 as relative activities.

We found that a series of the synthesized 7-azaindoles exhibited considerable fungicidal activity toward *Pyricularia oryzae*, which is a fungus of rice blast, in vivo. 6-Amino-7-azaindole (**2**) showed fungicidal activity only against rice blast. 6-Ethynyl-7-azaindole (**9**) and 3-vinyl-7-azaindole (**18**), which have carbon–carbon unsaturated functional groups, exhibited the similar extent of activity, but the fungi controlled by these compounds were different. Since many chalcogen



Scheme 4.

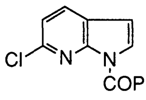


Scheme 5.

Table 1. Relative Fungicidal Activity of 7-Azaindole Derivatives[a)]

Compound	In vivo	In vitro			
	Rice	Rice		Cucumber	Apple
	Blast	Helminthosporium leat spot	Bacterial leaf blight	Anthracnose	Scab
2	△	×	×	×	×
9	△	×	△	×	—
14	×	×	×	×	×
15	○	△	×	×	—
17	×	△	×	×	○
18	△	△	×	△	—
19	×	×	○	○	○
20	○	×	×	×	—
21	×	×	×	×	—
22	○	×	×	×	—

a) Activity: ○=high, △=medium, ×=low or none, —=not tested.



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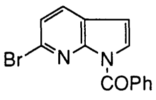

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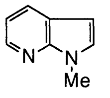

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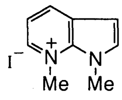

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derivatives are known as agrochemicals, the selenide **14** and the sulfide **15** were also tested. Although the sulfide **15** showed fungicidal activity against rice blast and helminthosporium leaf spot, the selenide **14** did not show any activity toward these fungi in spite of our expectation. Among other 3-substituted derivatives of 7-azaindole, the acrylic acid derivative **17** and 3-vinyl-7-azaindole (**18**) had some extent of biological activities. While the chloro derivative **19**[5)] showed strong inhibitory activity toward some fungi, the bromo derivative **20**[5)] was not so effective and was a good inhibitor only for rice blast. 1-Methyl-7-azaindole (**21**)[14)] did not exhibit any activity, but its pyridinium salt **22**[14)] revealed high activity for rice blast.

With these results in hand, we will continue synthesis of some other derivatives of 7-azaindoles to attain better activity.

Experimental

Measurement. Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were taken on a Hitachi 270-30 infrared spectrometer. ^{1}H and ^{13}C NMR were recorded on a JEOL JNM-FX-90Q or a JEOL JNM-EX270 spectrometer with tetramethylsilane as an internal standard. Mass spectra were obtained by electron impact (EI) on a Shimadzu GCMS-QP2000 or a JEOL JMS-DX303 mass spectrometer. The molecular weight distribution of the polymer **12** was determined by gel permeation chromatography (GPC) using Toyo Soda HLC CP8000 with TSKGEL G2500HXL, and a UV detector operating at 254 nm with DMF as an eluent. Fungicidal activity of azaindoles was evaluated by Dainippon Ink and Chemicals, Inc.

6-Amino-1*H*-pyrrolo[2,3-*b*]pyridine (2). 6-Bromo-7-azaindole[5)] (**1**: 197 mg, 1.0 mmol) in 35% aqueous ammonia (10 ml) was sealed in a stainless steel tube and heated at 200 °C for 12 h. Solid patassium carbonate was added to the reaction mixture and extracted with chloroform (20 ml×3). The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The reaction products were separated by thin-layer chromatography with ethyl acetate as an eluent to give **2** (107 mg, 80%) as pale yellow plates: Mp 118—119 °C; IR (KBr) 3436 cm^{-1} (NH_2); ^{1}H NMR ($CDCl_3$) δ=5.0—5.5 (2H, brs, NH_2), 6.34 (1H, dd, J=1.7, 3.7 Hz, H-3), 6.35 (1H, d, J=8.3 Hz, H-5), 7.0 (1H, dd, J=2.0, 3.7 Hz, H-2), 7.69 (1H, d, J=8.3 Hz, H-4), 8.5—9.0 (1H, brs, H-1); MS (EI) m/z (rel intensity) 133 (M$^+$, 100), 106 (M$^+$—HCN, 37). Found: C, 63.08; H, 5.31; N, 31.47%. Calcd for $C_7H_7N_3$: C, 63.14; H, 5.30; N, 31.56%.

***N*-(1*H*-Pyrrolo[2,3-*b*]pyridin-6-yl)ethylenediamine (3).** 6-Bromo-7-azaindole (**1**: 197 mg, 1.0 mmol) in ethylenediamine (10 ml) was heated in a sealed tube at 200 °C for 12 h. Excess ethylenediamine was removed and the residue was purified by thin-layer chromatography with ethyl acetate as an eluent to give **3** (80.1 mg, 45%) as pale yellow plates: Mp 133—134 °C; IR (KBr) 3420 cm^{-1} (NH_2); ^{1}H NMR ($CDCl_3$) δ=1.8—2.0 (3H, brs, amino H), 2.99 (2H, t, J=6.3 Hz, -NHC$\underline{H}_2$-), 3.42 (2H, t, J=6.3 Hz, -C$\underline{H}_2$NH$_2$), 6.25 (1H, d, J=4.0 Hz, H-3), 6.28 (1H, d, J=8.6 Hz, H-5), 6.93 (1H, d, J=4.0 Hz, H-2), 7.65 (1H, d, J=8.6 Hz, H-4); MS (EI) m/z (rel intensity) 176 (M$^+$, 20), 146 (M$^+$—CH_2NH_2, 100), 117 (M$^+$—$NHCH_2CH_2NH_2$, 52). Found: C, 61.58; H, 6.83; N, 31.62%. Calcd for $C_9H_{12}N_4$: C, 61.34; H, 6.86; N, 31.79%.

***N*-(1*H*-Pyrrolo[2,3-*b*]pyridin-6-yl)diethylenetriamine (4).** Following the procedure for preparation of **3**, **1** (197 mg, 1.0 mmol) was treated with diethylenetriamine (10 ml) to afford **4** (88.0 mg, 40%) as yellow oil: IR (KBr) 3296 cm^{-1} (NH_2); ^{1}H NMR (CD_3OD) δ=2.5—3.6 (8H, m, -CH_2-×4), 6.23 (1H, d, J=3.4 Hz, H-3), 6.31 (1H, d, J=8.6 Hz, H-5), 6.92 (1H, d, J=3.4 Hz, H-2), 7.69 (1H, d, J=8.6 Hz, H-4): MS (EI) m/z (rel intensity) 219 (M$^+$, 25), 117 (100). Found: m/z 219.1478. Calcd for $C_{11}H_{17}N_4$: M, 219.1484.

***N,N′*-Bis(1*H*-pyrrolo[2,3-*b*]pyridin-6-yl)-1,3-benzenedicarboxamide (5).** To a solution of 6-amino-7-azaindole (**2**: 133 mg, 1 mmol) and triethylamine (400 mg, 4 mmol) in dichloromethane (10 ml) was added dropwise isophthaloyl dichloride (100 mg, 0.5 mmol) in dichloromethane (30 ml) under nitrogen atmosphere at 0 °C over 2 h. After stirring for 12 h at room temperature, the precipitated solid was filtered and extracted with chloroform (20 ml×3) and saturated $NaHCO_3$ aq (10 ml×3). The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by chromatography on a silica-gel column eluted with hexane–ethyl acetate (1:9) to give **5** (95 mg, 48%) as colorless plates: Mp>300 °C; IR (KBr) 1658 cm^{-1} (-NHCO-); ^{1}H NMR (DMSO-d_6) δ=5.80 (2H, brs, -NHCO-×2), 6.48 (2H, dd, J=1.7, 2.9 Hz, H-3′×2), 7.40 (2H, dd, J=2.9, 2.9 Hz, H-2′×2), 7.66 (1H, t, J=8.0 Hz, H-5), 7.9—8.4 (6H, m, H-4, H-6, H-4′×2, H-5′×2), 8.68 (1H, s, H-2); MS (EI) m/z (rel intensity) 396 (M$^+$, 67), 264 (100). Found: C, 66.90; H, 4.03; N, 20.83%. Calcd for $C_{22}H_{16}N_6O_2$: C, 66.65; H, 4.07; N, 21.20%.

1-Benzoyl-6-trimethylsilylethynyl-1*H*-pyrrolo[2,3-*b*]pyridine (8). To a solution of 1-benzoyl-6-bromo-7-azaindole (**6**: 301 mg, 1.0 mmol), bis(triphenylphosphine)palladium(II) chloride (36 mg, 0.05 mmol) and Copper(I) iodide (16 mg, 0.085 mmol) in triethylamine (25 ml) was added dropwise trimethylsilylacetylene (196 mg, 2.0 mmol) under nitrogen atmosphere at room temperature. After stirring for 24 h at the same temperature, the solvent was removed and the residue was extracted with ether (30 ml×3), dried ($MgSO_4$), and concentrated in vacuo. The crude product was separated by chromatography on a silica-gel column eluted with hexane–ethyl acetate (9:1) to give **8** (259 mg, 79%) as colorless needles: MP 112—113 °C; IR (KBr) 2160 (C≡C), 1688 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=0.26 (9H, s, SiMe$_3$), 6.62 (1H, d, J=4.0 Hz, H-3), 7.37 (1H, d, J=8.0 Hz, H-5), 7.4—8.0 (7H, m, H-2, H-4, Ph); MS (EI) m/z (rel intensity) 319 (M$^+$+1, 3), 318 (M$^+$, 9), 290 (M$^+$−CO, 26), 105 (PhCO$^+$, 100). Found: C, 71.58; H, 5.73; N, 8.69%. Calcd for $C_{19}H_{18}N_2OSi$: C, 71.66; H, 5.70; N, 8.80%.

6-Ethynyl-1*H*-pyrrolo[2,3-*b*]pyridine (9). 1-Benzoyl-6-trimethylsilylethynyl-7-azaindole (**8**: 318 mg, 1.0 mmol) was dissolved in MeOH (10 ml) and 1 mol dm^{-3} NaOH (20 ml). After stirring for 4 h at room temperature, MeOH was removed and the residue was extracted with ether (20 ml×3), dried ($MgSO_4$) and concentrated in vacuo to give **9**. The crude product was subjected to recrystallization from chloroform/ether to give pure **9** (135 mg, 95%) as colorless needles: Mp 176—177 °C; IR (KBr) 3296 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ=3.18 (1H, s, -C≡CH), 6.53 (1H, d, J=3.4 Hz, H-3), 7.31 (1H, d, J=8.1 Hz, H-5), 7.50 (1H, d, J=3.4 Hz, H-2), 7.93 (1H, d, J=8.1 Hz, H-4), 11.5—12.3 (1H, brs, NH); MS (EI) m/z (rel intensity) 142 (M$^+$, 100), 116 (7), 115 (22). Found: C, 76.20; H, 4.32; N, 19.56%. Calcd for $C_9H_6N_2$: C, 76.04; H, 4.25; N, 19.71%.

Dimethyl 6,6′-Ethynylenebis[1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate] (10). Copper(I) iodide (40 mg, 0.21 mmol) was added to a mixture of bis(triphenylphosphine)palladium(II) chloride (70 mg, 0.1 mmol) and 6-iodo-1-methoxycarbonyl-7-azaindole (**7**: 302 mg, 1.0 mmol) in triethylamine (20 ml) under nitrogen atmosphere in a flask equipped with a gas inlet tube. A slow current of acetylene was passed through the reaction mixture for 8 h at room temperature. After removal of triethylamine under reduced pressure, 10 ml of water was added to the residue. The reaction mixture was extracted with chloroform (25 ml×4), dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by chromatography on a silica-gel column eluted with hexane–ethyl acetate (1:9) to give **10** (139 mg, 74%) as colorless plates: Mp>300 °C; IR (KBr) 1718 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=4.14 (6H, s, -CO-OMe×2), 6.60 (2H, d, J=4.2 Hz, H-3×2), 7.60 (2H, d, J=8.1 Hz, H-5×2), 7.82 (2H, d, J=4.2 Hz, H-2×2), 7.90 (2H, d, J=8.1 Hz, H-4×2); ^{13}C NMR ($CDCl_3$) δ=54.5 (OMe), 89.0 (C≡C), 105.5 (C-3), 123.3 (C-5), 127.5 (C-2), 128.1 (C-4), 129.3 or 130.2 (C-3a or C-7a), 135.2 (C-6), 151.4 (C=O); MS (EI) m/z (rel intensity) 374 (M$^+$, 28), 330 (M$^+$−CO$_2$, 44), 286 (M$^+$−2CO$_2$, 100). Found: C, 64.03; H, 3.42; N, 14.86%. Calcd for $C_{20}H_{14}N_4O_4$: C, 64.17; H, 3.77; N, 14.97%.

Bis(1*H*-pyrrolo[2,3-*b*]pyridin-6-yl)acetylene (11). Dimethyl ester (**10**: 187 mg, 0.5 mmol) was dissolved in MeOH (10 ml) and 1 mol dm^{-3} NaOH (15 ml). After stirring for 24 h at room temperature, the reaction mixture was filtered. The solid was washed with water and dried under reduced pressure at 60 °C for 6 h to give **11** (254 mg, 98%) as pale brown plates: Mp>300 °C; IR (KBr) 3460 cm^{-1} (NH); ^{1}H NMR (DMSO-d_6) δ=6.51 (2H, d, J=3.0 Hz, H-3×2), 7.35 (2H, d, J=8.0 Hz, H-5×2), 7.59 (2H, d, J=3.0 Hz, H-2×2), 8.00 (2H, d, J=8.0 Hz, H-4×2); MS (EI) m/z (rel intensity) 258 (M$^+$, 100). Found: C, 74.53; H, 3.99; N, 21.66%. Calcd for $C_{16}H_{10}N_4$: C, 74.40; H, 3.90; N, 21.70%.

Poly[1*H*-pyrrolo[2,3-*b*]pyridin-6-yl)acetylene] (12). To a solution of [Rh(norbornadiene)Cl]$_2$ (56 mg, 0.127 mmol) and triethylamine (1.3 g, 127 mmol) in DMF (3 ml) was added dropwise 6-ethynyl-7-azaindole (**9**: 180 mg, 1.27 mmol) in DMF (2 ml) under nitrogen atmosphere over 4 h. After stirring for 8 h at the same temperature, the solvent was removed in vacuo and the residue was subjected to reprecipitation from DMF–$CHCl_3$ to give **12** (117.3 mg, 65%) as dark purple powder: Mp>300 °C; IR (KBr) 1602, 894, 820, and 726 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=6—7 (2H, m, -C=CH-, H-3), 7—8 (3H, br, H-2, H-4, H-5), 11—12 (1H, br, NH). Found: C, 72.31; H, 4.20; N, 17.73%. Calcd for $C_9H_6N_2$: C, 76.04; H, 4.25; N, 19.71%.

3,3′-Selenobis[1*H*-pyrrolo[2,3-*b*]pyridine] (14). 7-Azaindole (**13**: 118 mg, 1.0 mmol) and selenium dioxide (222 mg, 2.0 mmol) were heated in EtOH (10 ml) at refluxing temperature for 24 h. The precipitates were filtered off, washed with EtOH, and dried under reduced pressure to give **14** (68.4 mg, 44%) as pale red powder: Mp 245—247 °C; IR (KBr) 3156 (NH), 1420, and 1292 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=7.09 (2H, dd, J=4.8, 8.1 Hz, H-5×2), 7.78 (2H, d, J=2.1 Hz, H-2×2), 8.01 (2H, dd, J=1.7, 8.1 Hz, H-4×2), 8.19 (2H, dd, J=1.7, 4.8 Hz, H-6×2), 11.7—12.0 (2H, brs, H-1×2); ^{13}C NMR (DMSO-d_6) δ=97.3 (C-3), 116.1 (C-5), 121.6 (C-3a), 127.3 (C-2), 131.1 (C-4), 143.9 (C-6), 148.5 (C-7a); MS (EI) m/z (rel intensity) 314 (M$^+$, 100), 234 (M$^+$−Se, 6). Found: C, 53.41; H, 3.01; N, 18.03%. Calcd for $C_{14}H_{10}N_4Se$: C, 53.69; H, 3.22; N, 17.89%.

3,3′-Thiobis[1*H*-pyrrolo[2,3-*b*]pyridine] (15). To a solution of 7-azaindole (**13**: 118 mg, 1.0 mmol) in dichloromethane (2 ml) was added dropwise sulfur dichloride (206 mg, 2.0 mmol) in dichloromethane (3 ml) under nitrogen atmosphere at 0 °C over 1 h. After stirring for 1 h at room temperature, the reaction mixture was washed with 1 mol dm^{-3} NaOH (10 ml×3). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was washed with EtOH, dried in vacuo to give **15** (58.5 mg, 44%) as yellow plates: Mp 252—254 °C (decomp); IR (KBr) 3144 (NH), 1590, 1410, and 1284 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=7.08 (2H, dd, J=4.8, 7.6 Hz, H-5×2), 7.83 (2H, d, J=2.3 Hz, H-2×2), 8.08 (2H, dd, J=1.9, 7.6 Hz, H-4×2), 8.19 (2H, dd, J=1.9, 4.8 Hz, H-6×2), 11.5—12.0 (2H, brs, H-1×2); MS (EI) m/z (rel intensity) 268 (M$^+$+2, 10), 267 (M$^+$+1, 29), 266 (M$^+$, 100), 234 (M$^+$−S, 32). Found: C, 63.05; H, 3.81; N, 20.76; S, 12.01%. Calcd for $C_{14}H_{10}N_4S$: C, 63.14; H, 3.78; N, 21.04; S, 12.04%.

3-(2-Carboxyethenyl)-1*H*-pyrrolo[2,3-*b*]pyridine (17). To a solution of 3-formyl 7-azaindole (**16**: 584 mg, 4 mmol) and malonic acid (832 mg, 8 mmol) in pyridine (25 ml) was added piperidine (68 mg, 0.8 mmol) under nitrogen atmosphere. After heating the solution at 100 °C for 3 h, pyridine was removed under reduced pressure. The residue was washed with chloroform and filtered to give crude **17**. The product was purified by recrystallization from THF–hexane to give pure **17** (540 mg, 72%) as pale yellow plates: Mp 189—192 °C; IR (KBr) 1670 cm^{-1} (COOH); ^{1}H NMR (DMSO-d_6) δ=6.36 (1H, d, J=16.2 Hz, CH=C$\underline{\text{H}}$COOH), 7.20 (1H, dd, J=4.8, 7.7 Hz, H-5), 7.79 (1H, d, J=16.2 Hz, C$\underline{\text{H}}$=CHCOOH), 8.04 (1H, s, H-2), 8.14 (1H, dd, J=1.5, 7.7 Hz, H-4), 8.42 (1H, dd, J=1.5, 4.8 Hz, H-6), 12.0—12.4 (1H, brs, H-1); MS (EI) *m*/*z* (rel intensity) 188 (M$^+$, 100), 171 (M$^+$−OH, 42), 144 (M$^+$−CO$_2$, 11). Found: C, 63.95; H, 4.68; N, 14.88%. Calcd for $C_{10}H_8N_2O_2$: C, 63.82; H, 4.29; N, 14.87%.

3-Vinyl-1*H*-pyrrolo[2,3-*b*]pyridine (18). 3-(2-Carboxyethenyl)-7-azaindole (**17**: 188 mg, 1.0 mmol) was heated in nitrobenzene at 140 °C for 1 h. After removal of the solvent under reduced pressure, the residue was purified by chromatography on a silica-gel column eluted with hexane–ethyl acetate (8 : 2) to give **18** (89 mg, 62%) as colorless needles: Mp 112—115 °C (decomp); IR (KBr) 1632 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ=5.20 (1H, dd, J=1.2, 11.0 Hz, =C$\underline{\text{H}}$H), 5.68 (1H, dd, J=1.2, 17.6 Hz, =CH$\underline{\text{H}}$), 6.86 (1H, dd, J=11.0, 17.6 Hz, C$\underline{\text{H}}$=CH$_2$), 7.14 (1H, dd, J=4.8, 8.1 Hz, H-5), 7.39 (1H, s, H-2), 8.21 (1H, dd, J=1.5, 8.1 Hz, H-6), 8.34 (1H, dd, J=1.5, 4.8 Hz, H-6), 10.4—11.0 (1H, brs, H-1); MS (EI) *m*/*z* (rel intensity) 145 (M$^+$+1, 28), 144 (M$^+$, 90), 143 (M$^+$−1, 100). Found: C, 74.91; H, 5.56; N, 19.36%. Calcd for $C_9H_8N_2$: C, 74.97; H, 5.59; N, 19.43%.

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