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# PREPARATION OF NOVEL HETEROISOINDOLES FROM NITROPYRIDINES AND NITROPYRIDONES

Takashi Murashima,[*a] Keiji Nishi,[a] Ken-ichi Nakamoto,[a] Atsushi Kato,[a] Ryuji Tamai,[a] Hidemitsu Uno,[b] and Noboru Ono[*a]

[a] Department of Chemistry, Faculty of Science, Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, Japan

[b] Advanced Instrumentation Center for Chemical Analysis, Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, Japan

*Dedicated to Professor A. I. Meyers on the occasion of his 70th birthday.*

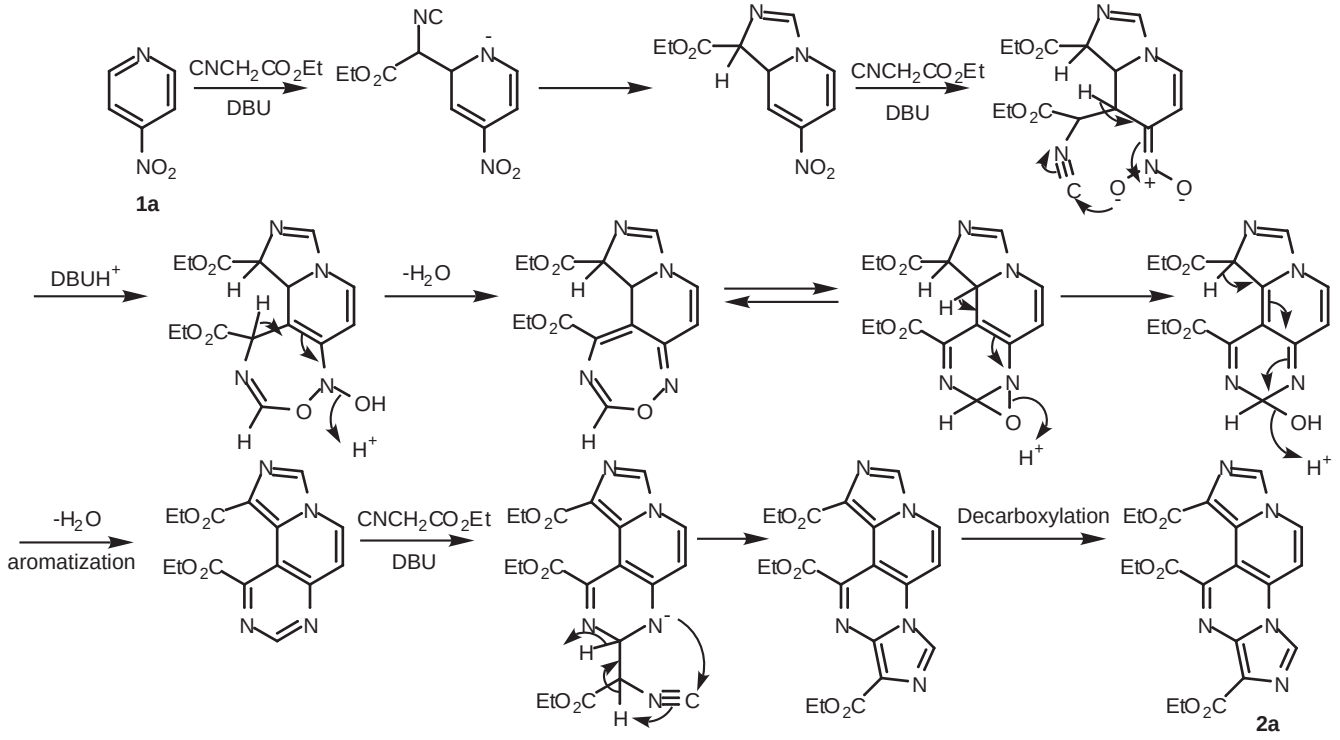
**Abstract**– The reaction of nitropyridine derivatives with ethyl isocyanoacetate in the presence of 1,8-diazabicyclo[5.4.0]undecene proceeded tandem cyclization to give polycyclic pyrrolopyridines or imidazopyridines. On the other hand, *N*-protected 3-nitro- and 5-nitropyridones and *N*,*N*-diprotected 5-nitrouracil gave corresponding bicyclic pyrroles in good yields under the similar conditions.

Since a large number of medicinally important natural products include azaarene skeletons in their structure,[1] these heteroarenes such as quinolines, indoles, isoindoles and azaisoindoles have generated interest as challenging targets for synthesis. There were various methods reported to prepare quinolines,[2] indoles[3] and isoindoles.[3] On the contrary, relatively little attention is given to heteroarene fused pyrroles such as pyrrolopyridinones,[4] pyrrolopyrimidines,[5] and pyrrolopyrroles[6] because of difficulties arose in the synthesis. Most of studies on the preparation of this class of molecules dealt with pyrrole fused with pyridine on its [1,2-x] and [2,3-x] position.[7] The synthesis of pyrrolo[3,4-x]pyridines described by

Armarego[8] is the only reported procedure, but the final products have protecting groups on the pyrrole ring nitrogen.

In a recent report, we have described various facets of the reaction of unsaturated nitro compounds with ethyl isocyanoacetate and discussed the formation of fused pyrroles,[9a,c] 1-hydroxypyrazoles[10] and fused pyrimidine *N*-oxides.[9b] Herein, we wish to report the reaction of simple nitroheteroarenes with ethyl isocyanoacetate.

According to our interest in the coordination ability of fused ring nitrogen, we have synthesized 1,10-phenanthrolinopyrrole, thiadiazolopyrrole, quinolinopyrroles and quinoxalinopyrroles[9] by the improved Barton-Zard methodology in moderate to good yields.[11] However, as Lash *et al.* reported, 3- and 4-nitropyridines were not suitable as a precursor for the pyridopyrrole.[12] The reaction of 4-nitropyridine with ethyl isocyanoacetate gave a complicated product, diethyl imidazo[3,4-*a*]imidazo[3',4':1,2]pyrido-[3,4-*e*]pyrimidine-1,10-dicarboxylate (**2a**) in quite low yield. This compound was diagnosed using NMR, MS and IR spectroscopies. The proton NMR spectrum for this product showed the presence of two non-equivalent ethyl esters and two doublets at 7.72 and 8.86 ppm. Proposed mechanism for the formation of the tetracyclic molecule is illustrated in Scheme 1.

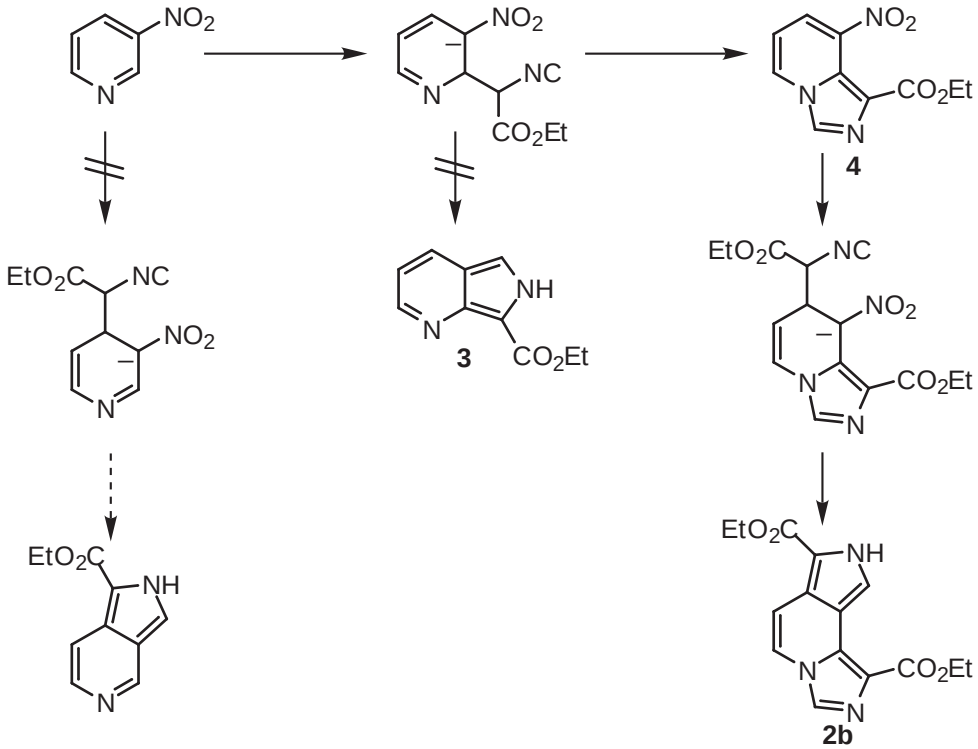



**Scheme 1**. Proposed Mechanism for the Formation of Tetracyclic Heteroarene (**2a**)

When 3-nitropyridine (**1b**) was reacted with two equivalents of carbanion derived from ethyl isocyanoacetate and DBU, tandem cyclization occurred to give the tricyclic compound, diethyl 8*H*-

imidazo[1,5-*a]*pyrrolo[3,4-*c*]pyridine-1,7-dicarboxylate (**2b**).[12] With the exception of recovered substrate, the compound (**2b**) was the only isolated product. The use of equimolar amounts of ethyl isocyanoacetate and **1b** also led to the production of **2b** and no mono cyclization product was obtained. Therefore, the second cyclization was faster than the first one.

Since the key step of this reaction is the nucleophilic attack of carbanions to substrates, the existence of nitro group is essential for the progress of each reaction. Thus, the initial product may be not pyrrolo[3,4-*b*]pyridine (**3**) but imidazo[1,5-*a*]pyridine (**4**). Once imidazo[1,5-*a*]pyridine (**4**) was formed, it was readily reacted with another carbanion and the nitro moiety was removed at the final stage of reaction to give the tricyclic compound (**2b**). (Scheme 2) The structures of compounds (**2b**) and other pyrrolic compounds (**2c,e,f**) were confirmed in comparison with the reported data.[12]



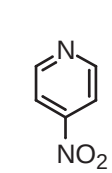
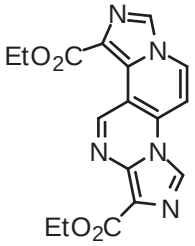
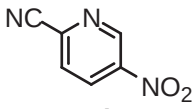
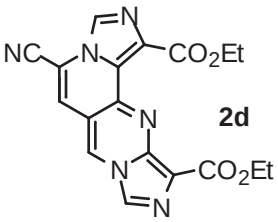
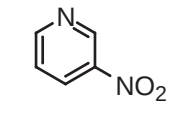
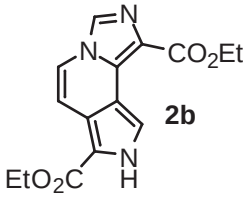
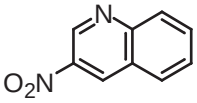
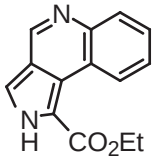
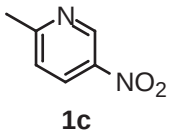
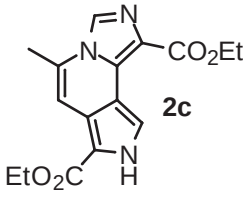
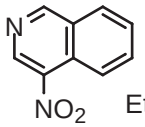
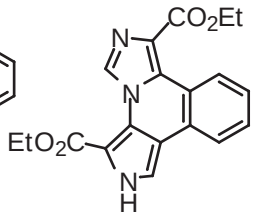

**Scheme 2**. Reaction Course of the Formation of Pyrrolopyridine (**2b**)

To improve the yields of pyrrolic compounds such as **2b**, some 3-nitropyridine derivatives were used as starting materials. Nitropyridines were prepared by the nitration of substituted pyridines with modified *kyodai* nitration[13] which was the improved Bakke method.[14]

The reaction of 2-methyl-5-nitropyridine (**1c**) with ethyl isocyanoacetate in the presence of DBU resulted in the production of similar tricyclic heteroarene, diethyl 5-methyl-8*H*-imidazo[1,5-*a*]pyrrolo[3,4-*c*]pyridine-1,7-dicarboxylate (**2c**) in 9% yield. Since these cyclization reactions were accelerated in the presence of an electron withdrawing group, it would be expected to facilitate the

production of pyrrolic compound by the use of 2-cyano-5-nitropyridine (**1d**) as the starting material. This, however, was not the case, the product formed being the imidazole type compound, diethyl 5-cyanoimidazo[3,4-*a*]imidazo[1',5':1,2]pyrido[3,4-*d*]pyrimidine-1,11-dicarboxylate (**2d**) derived from **1d** in 6% yield. The proton NMR spectral feature was analogous to that of **2a** except that one of the two doublets (7.72 ppm) was disappeared and another doublet (8.86 ppm) was changed into singlet. The existence of cyano group was confirmed by IR spectrum.

Table 1. Products and Yields of the Reaction of Nitropyridines

| Substrate | Product | Yield/% | Substrate | Product | Yield/% |
|---|---|---|---|---|---|
|  **1a** |  **2a** | 4[a] (12[c]) |  **1d** |  **2d** | 6[a] (18[c]) |
|  **1b** |  **2b** | 15[b] |  **1e** |  **2e** | 54[a] |
|  **1c** |  **2c** | 9[b] |  **1f** |  **2f** | 12[a] (24[c]) |

[a] Reagents: $CNCH_2CO_2Et$/DBU 1.0 eq. [b] Reagents: $CNCH_2CO_2Et$/DBU 2.0 eq.
[c] Yields based on isocyanoacetate.

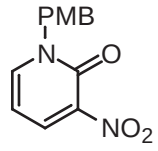
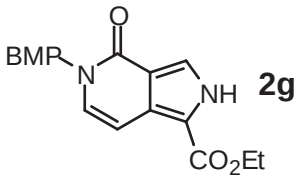
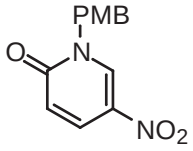
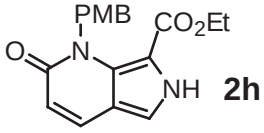
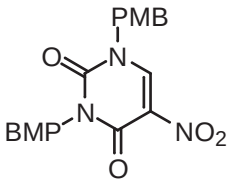
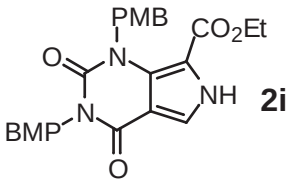
In spite of the use of only one equivalent of ethyl isocyanoacetate and DBU, 4-nitroisoquinoline (**1f**) was also subject to tandem cyclization to give tetracyclic compound, diethyl 2*H*-imidazo[4,3-*a*]pyrrolo[3,4-*c*]isoquinoline-3,7-dicarboxylate (**2f**) in 12% yield.

On the contrary, 3-nitroquinoline (**1e**) was reacted with equimolar amount of reagent giving single cyclization product, ethyl 2*H*-pyrrolo[3,4-*c*]quinoline-1-carboxylate (**2e**) in the yield of 54%. When an excess amount of reagent was used for this reaction, we have observed no tandem cyclization product such as **2b**, **2c** and **2f**. These results suggest that the initial nucleophilic attack occurred on the 4-position of 3-nitroquinoline (**1e**) and a pyrrole ring was constructed instead of an imidazole ring or a pyrimidine

ring as observed in the cases of **1a-d** and **1f**. The product (**2e**) was no longer subject to nucleophilic attack, thus the subsequent cyclization could not proceed.

The reactions of nitropyridine derivatives, except 3-nitroquinoline, did not give expected pyrrolic compounds in good yields. Thus, to improve the yields of heteroarene annulated pyrroles, we have tried the similar reactions with nitropyridones and nitrouracil. The commercially available nitro-2-pyridones and nitrouracil were reacted with *p*-methoxybenzyl chloride to give *N*-protected starting materials. The reactions of 3-nitro-*N*-*p*-methoxybenzyl-2-pyridone (**1g**), 5-nitro-*N*-*p*-methoxybenzyl-2-pyridone (**1h**) and 5-nitro-*N*,*N*-di-*p*-methoxybenzyluracil (**1i**) with ethyl isocyanoacetate in the presence of DBU resulted in the production of expected bicyclic pyrroles (**2g-i**) in the yields of 65, 50 and 88%, respectively.

Table 2. Products and Yields of the Reaction of Nitropyridones and Nitrouracil

| Substrate | Product | Yield/% |
|---|---|---|
|  **1g** |  **2g** | 65 |
|  **1h** |  **2h** | 50 |
|  **1i** |  **2i** | 88 |

Reagents: $CNCH_2CO_2Et$/DBU 1.0 eq.

The nitroalkene moiety of nitropyridone derivatives was less aromatic than that of nitropyridines, thus compounds (**1g-i**) were more reactive toward nucleophilic attack. Another advantage is that once nucleophilic attack occurred, the resulting compounds (**2g-i**) have no reaction points because their reactive *N*-positions were protected with *p*-methoxybenzyl groups. Therefore, *N*-protected nitropyridones and nitrouracil were good precursors for the preparation of heteroarene annulated pyrroles.

In summary, we have described the preparation of heteroarene annulated pyrroles starting from nitropyridine derivatives and nitropyridone derivatives. Some nitropyridines gave expected

azaisoindoles, but others yielded imidazopyridines. These types of polycyclic heteroarenes are known to have extremely high fluorescence quantum efficiencies in the visible spectra, therefore these organic materials are ideal for electro luminescence materials. Investigations are in progress to apply these azaheterocycles to EL materials. On the other hand, *N*-protected nitropyridones and nitrouracil were better precursors for azaisoindoles. When the *N*-protected groups of these compounds are removed, the resulting NH protons could form hydrogen bonds to adjacent carbonyl groups of neighboring molecules to give dimers.

## EXPERIMENTAL

Melting points were measured by a Yanaco hot stage apparatus and are uncorrected. NMR spectra were recorded on a JEOL-JNM-GSX 270 or JNM-EX 400 spectrometer at ambient temperature by using $CDCl_3$ or DMSO-$d_6$ as a solvent and tetramethylsilane as an internal standard for $^1H$ and $^{13}C$ and *J* values are given in Hz. IR and UV-VIS spectra were obtained with a Hitachi 270-30 and Shimadzu UV-2200 spectrophotometer, respectively. MS spectra were measured with a Hitachi M80B-LCAPI spectrometer under the following ionizing conditions: electron impact, 20 eV, high boiling PFK as a standard. THF was freshly distilled from sodium benzophenone ketyl. Acetonitrile was distilled from $P_2O_5$. Ethyl isocyanoacetate was prepared from ethyl *N*-formylglycinate using $POCl_3$ and triethylamine.[15] Unless otherwise specified, all nitro aromatics which were not commercially available were prepared by *kyodai*-nitration methods of heteroaromatics using $NO_2/O_3$ and sodium hydrogen sulfite.

### Nitropyridine derivatives (1b-f)

Into a solution of liquid nitrogen dioxide (1 mL) in dry $CH_2Cl_2$ (50 mL) ozonized oxygen was slowly introduced for 1.5 h at –78 °C. Pyridines (10 mmol) were added in one portion to the solution and the resulting suspension was stirred for 1 h at rt, then the mixture was poured into 5% sodium hydrogen sulfite. The reaction mixture was worked up as usual, and the residue was purified by recrystallization from methanol.

### Diethyl Imidazo[3,4-*a*]imidazo[3',4':1,2]pyrido[3,4-*e*]pyrimidine-1,10-dicarboxylate (2a)

DBU (1.52 g, 10 mmol) was added dropwise to a solution of 4-nitropyridine (**1a**) (1.24 g, 10 mmol) and ethyl isocyanoacetate (1.13 g, 10 mmol) in acetonitrile (50 mL) at 0 °C. The resulting mixture was stirred at ambient temperature for 96 h. After 10% hydrochloric acid (50 mL) was added, the crude mixture was extracted with ethyl acetate (3 x 20 mL). The organic phase was washed with 3% sodium hydrogen carbonate, water and brine, dried over $Na_2SO_4$. The solvent was removed and the residue was washed with ethanol to give pale yellow precipitate. This solid product was purified by recrystallization with chloroform and ethanol, giving the title compound (**2a**) (0.141 g, 3%), mp 268 °C (decomp); $^1$H-NMR ($CDCl_3$) δ 1.50 (t, 3H, *J* 7.32), 1.52 (t, 3H, *J* 7.32), 4.54 (q, 2H, *J* 7.32), 4.56 (q, 2H, *J* 7.32), 7.72 (d, 1H, *J* 5.37), 8.40 (s, 1H), 8.86 (d, 1H, *J* 5.37), 10.00 (s, 1H) and 10.86 (s, 1H); $^{13}$C-NMR ($CDCl_3$) δ 14.3, 30.9, 61.9, 62.0, 108.1, 111.0, 119.0, 124.5, 127.1, 127.2, 129.6, 132.9, 136.3, 150.7, 151.7, 162.1 and 163.1; *m/z* 353 ($M^+$, 65%), 308 ($M^+$-EtO) and 281 (100); HRMS Calcd for $C_{17}H_{15}N_5O_4$ 353.1124; Found: 353.1122.

**Diethyl 8*H*-Imidazo[1,5-*a*]pyrrolo[3,4-*c*]pyridine-1,7-dicarboxylate (2b)**

To a solution of 3-nitropyridine (**1b**) (1.24 g, 10 mmol) in THF (50 mL) was added dropwise ethyl isocyanoacetate (2.25 g, 20 mmol) then DBU (3.03 g, 20 mmol) at 0 °C. The resulting mixture was stirred at ambient temperature for 24 h, diluted with chloroform, and washed with 50 mL of water. The water phase was extracted with chloroform (50 mL). The combined organic phase was washed with 5% sodium hydrogen carbonate, water and brine, dried over sodium sulfate. The solvent was removed and the residue was purified by recrystallization with methanol to give the title compound (**2b**) (0.452 g, 15%), mp 242-243 °C; $^1$H-NMR ($CDCl_3$) δ 1.47 (t, 3H, *J* 7.32), 1.48 (t, 3H, *J* 7.32), 4.47 (q, 2H, *J* 7.32), 4.50 (q, 2H, *J* 7.32), 7.26 (d, 1H, *J* 9.27), 7.33 (d, 1H, *J* 3.42), 7.86 (d, 1H, *J* 9.77), 9.50 (s, 1H) and 9.68 (br s, 1H); $^{13}$C-NMR ($CDCl_3$) δ 14.4, 60.3, 113.7, 120.2, 120.6, 121.9, 124.5, 125.9, 126.9, 127.6, 129.3, 144.3, 148.0 and 160.3; *m/z* 301 ($M^+$, 100%), 255 ($M^+$-EtOH, 70), 229 (27), 210 (27) and 183 (46); HRMS Calcd for $C_{15}H_{15}N_3O_4$ 301.1063; Found: 301.1055.

The polyheterocyclic arenes (**2c-f**) were prepared by similar procedures to that described for the preparation of **2b**, under the conditions described in Table 1.

**Diethyl 5-Methyl-8*H*-imidazo[1,5-*a*]pyrrolo[3,4-*c*]pyridine-1,7-dicarboxylate (2c)**

Yield 9%; mp >250 °C; $^{1}$H-NMR ($CDCl_3$) δ 1.47 (t, 3H, *J* 7.33), 1.49 (t, 3H, *J* 7.32), 2.66 (s, 3H), 4.46 (q, 2H, *J* 7.33), 4.50 (q, 2H, *J* 7.32), 7.27 (d, 1H, *J* 2.75), 8.02 (s, 1H), 8.57 (d, 1H, *J* 2.74) and 10.08 (br s, 1H); $^{13}$C-NMR ($CDCl_3$) δ 14.4, 14.5, 56.0, 59.6, 60.0, 106.5, 110.8, 113.3, 121.3, 121.8, 122.0, 130.0, 130.1, 130.3, 160.4 and 163.4; *m/z* 315 ($M^+$, 81%), 269 ($M^+$-EtOH, 100), 243 (11), 224 (37) and 197 (76); HRMS Calcd for $C_{16}H_{17}N_3O_4$ 315.1219; Found: 315.1222.

**Diethyl 5-Cyanoimidazo[3,4-*a*]imidazo[1',5':1,2]pyrido[3,4-*d*]pyrimidine-1,11-dicarboxylate (2d)**

Yield 6%; mp >250 °C; $^{1}$H-NMR ($CDCl_3$) δ 1.51 (t, 3H, *J* 7.02), 1.54 (t, 3H, *J* 7.02), 4.55 (q, 2H, *J* 7.02), 4.58 (q, 2H, *J* 7.02), 8.53 (s, 1H), 9.34 (s, 1H) and 10.11 (s, 2H); *m/z* 378 ($M^+$, 38%), 269 ($M^+$-EtO, 12) and 306 (100); IR (nujol mull) 1295 (C-O), 1297 (C-O), 1714 (C=O), 1716 (C=O) and 2227 (CN); HRMS Calcd for $C_{18}H_{14}N_6O_4$ 378.1077; Found: 378.1069.

**Ethyl 2*H*-Pyrrolo[3,4-*c*]quinoline-1-carboxylate (2e)**

Yield 54%; mp 233-234 °C; $^{1}$H-NMR ($CDCl_3$) δ 1.48 (t, 3H, *J* 7.02), 4.52 (q, 2H, *J* 7.02), 7.59-7.71 (m, 3H), 8.11 (dd, 1H, *J* 1.83, 7.62), 9.15 (s, 1H), 9.55 (d, 1H, *J* 1.83) and 9.58 (br s, 1H); $^{13}$C-NMR ($CDCl_3$) δ 14.4, 60.3, 113.7, 120.2, 120.6, 121.9, 124.5, 125.9, 126.9, 127.6, 129.3, 144.3, 148.0 and 160.3; *m/z* 240 ($M^+$, 79%) and 194 ($M^+$-EtOH, 100); Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.69; H, 5.05; N, 11.60.

**Diethyl 2*H*-Imidazo[4,3-*a*]pyrrolo[3,4-*c*]isoquinoline-3,7-dicarboxylate (2f)**

Yield 12%; mp 184-186 °C; $^{1}$H-NMR ($CDCl_3$) δ 1.47 (m, 6H), 4.47 (q, 2H, *J* 7.02), 4.55 (q, 2H, *J* 7.02), 7.50-7.54 (m, 2H), 7.58 (d, 1H, *J* 3.66), 7.86 (dd, 1H, *J* 3.66, 7.02), 9.69 (br s, 1H) and 9.71 (s, 2H); $^{13}$C-NMR ($CDCl_3$) δ 14.2, 14.5, 60.7, 61.9, 109.6, 114.1, 115.4, 116.5, 121.7, 124.5, 126.8, 127.7, 127.9, 128.2, 129.0, 131.7, 153.2, 160.0 and 172.0; *m/z* 351 ($M^+$, 100%), 305 ($M^+$-EtOH, 39), 279 (41), 260 (29) and 233 (55); HRMS Calcd for $C_{19}H_{17}N_3O_4$ 351.1219; Found: 351.1214

**Ethyl *5H*-5-*p*-Methoxybenzyl-4-oxopyrrolo[5,6-*c*]pyridine-1-carboxylate (2g)**

Yield 65%; mp 161-162 °C; $^{1}$H-NMR ($CDCl_3$) δ 1.35 (t, 3H, *J* 7.3), 3.75 (s, 3H), 4.34 (q, 2H, *J* 7.3), 5.08 (s, 2H), 6.76-6.92 (m, 4H), 7.25 (d, 2H, *J* 6.8), 7.80 (d, 1H, *J* 3.4) and 11.30 (br s, 1H); $^{13}$C-NMR ($CDCl_3$) δ 14.4, 50.0, 55.2, 60.4, 101.1, 114.2, 117.5, 122.6, 128.7, 129.2, 129.5, 131.8, 159.2, 160.2,

161.3; *m/z* 326($M^+$, 20%) and 121(100); Anal. Calcd for $C_{18}H_{18}N_2O_4$+$H_2O$: 62.78; H, 5.85; N, 8.13. Found: C, 62.64; H, 5.88; N, 8.04.

**Ethyl *7H*-7-*p*-Methoxybenzyl-6-oxopyrrolo[6,5-*c*]pyridine-1-carboxylate (2h)**

Yield 50%; mp 152-153 °C; $^1$H-NMR ($CDCl_3$) δ 1.24 (t, 3H, *J* 6.84), 3.71 (s, 3H) 4.24 (q, 2H, *J* 6.84), 6.00 ((s, 2H), 6.41 (d, 1H, *J* 9.28), 6.75 (d, 2H, *J* 8.79), 7.01 (d, 1H, *J* 3.42), 7.13 (d, 2H, *J* 8.79), 7.54 (d, 1H, *J* 9.28) and 10.27 (br s, 1H); $^{13}$C-NMR ($CDCl_3$) δ 14.3, 48.0, 55.1, 60.7, 105.8, 113.1, 113.5, 117.7, 128.2, 130.5, 132.8, 133.0, 158.2, 159.2 and 164.0; *m/z* 326 ($M^+$, 34%) and 21 (100); Anal. Calcd for $C_{18}H_{18}N_2O_4$+1/4MeOH: C, 65.69; H, 5.69; N, 8.42. Found: C, 65.69; H, 5.64; N, 8.42.

**Ethyl *5H,7H*-5,7-Di-*p*-methoxybenzyl-4,6-dioxopyrrolo[6,5-*c*]pyrimidine-1-carboxylate (2i)**

Yield 88%; mp 169-170 °C; $^1$H-NMR ($CDCl_3$) δ 1.21 (t, 3H, *J* 7.33), 3.72 (s, 3H), 3.74 (s, 3H), 4.22 (q, 2H, *J* 7.33), 5.14 (s, 2H), 5.75 (s, 2H), 6.77 (d, 2H, *J* 8.79), 6.79 (d, 2H, *J* 8.79), 7.13 (d, 2H, *J* 8.79), 7.40 (d, 2H, *J* 8.79), 7.45 (d, 1H, *J* 3.91) and 10.13 (br s, 1H); $^{13}$C-NMR ($CDCl_3$) δ 14.1, 43.8, 49.5, 55.1, 55.1, 61.1, 106.6, 108.2, 113.6, 113.6, 122.3, 128.2, 129.4, 129.7, 130.1, 132.1, 152.2, 158.5, 158.8 and 159.3; *m/z* 463 ($M^+$, 90%), 342 ($M^+$-$CH_2C_6H_4OMe$, 46) and 121(100); Anal. Calcd for $C_{25}H_{25}N_3O_6$+1/2MeOH: C, 63.87; H, 5.68; N, 8.76. Found: C, 63.76; H, 5.46; N, 8.95.

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