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SYNTHESIS OF PYRIDO[1,2-*a*]BENZIMIDAZOLES FROM 2-ACYLMETHYL-1H-BENZIMIDAZOLES

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Methods are proposed for the synthesis of previously unknown pyrido[1,2-a]benzimidazoles via the cyclocondensation of 2-acylmethyl-1H-benzimidazoles with malononitrile, triethylorthoformate ester, or ethoxymethylenemalononitrile.

Keywords: benzimidazoles, ethoxymethylenemalononitrile, malononitrile, pyrido[1,2-*a*]-benzimidazoles, triethylorthoformate ester.

Pyrido[1,2-*a*]benzimidazoles possess a broad spectrum of biological activity [1-6] and fluorescent properties [7] and they appear in the composition of light sensitive materials [8, 9]. The synthesis of their novel compounds is of current interest, in particular with the attachment of a pyridine ring to benzimidazoles with an activated methylene group at position 2 [1,10, 11]. We have, for the first time, investigated 2-acylmethyl-1H-benzimidazoles **1a-g** as starting materials for such a synthesis.

We have found that the reaction of compounds **1a-g** with malononitrile does not stop at the stage of formation of the dicyanomethylene-substituted compounds **2a-g** but is accompanied by the intramolecular addition of the benzimidazole imino group to the nitrile giving the 1-amino-2-cyano-3-methyl(or aryl)pyrido[1,2-*a*]benzimidazoles **3a-g**. The reaction with 2-acetonylbenzimidazole **1a** takes place when refluxing in 2-propanol or for the less reactive carbonyl group containing 2-aroylbenzimidazoles **1b-g** using refluxing DMF and is complete after 30 min. The yields are close to quantitative.

Attachment of a pyridine ring to compounds **1a-g** also occurs *via* their reaction with triethylorthoformate ester. The reaction takes place with a molar ratio of reagents of 2:1, very likely by joining two molecules of the starting keto compound at the active methylene group in compounds **4a-g** to give compounds **4a-g** and then undergoing cyclocondensation of a benzimidazole imino group at the keto group to give the 4-acetyl(or aroyl)-2-(benzimidazol-2-yl)-1-methyl(or aryl)pyrido[1,2-*a*]benzimidazoles **5a-g**. The reaction with compounds **1a-d** occurs more smoothly even with the use of a one an a half or three fold excess of triethylorthoformate ester with heating to 140°C or refluxing in DMF and is complete within 15-30 min. Under the same conditions compounds **1e-g**, having an R substituent with marked electron-donor properties, react to give mixtures of products difficult to separate. In order to achieve a selective conversion using the desired scheme it was necessary to introduce the triethylorthoformate ester stepwise into the reaction mixture and also to increase the length of the reaction to 1 h.

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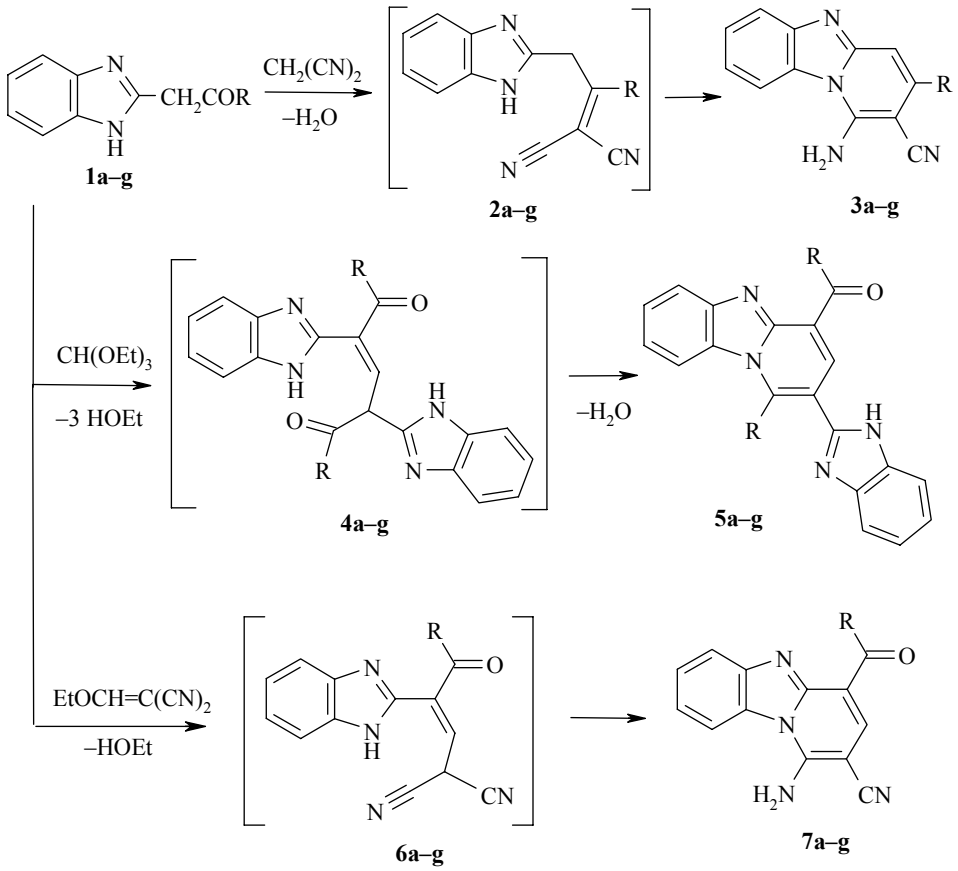

1-7 a R = Me, **b** R = Ph, **c** R = 4-$O_2NC_6H_4$, **d** R = 3,4,5-$(MeO)_3C_6H_2$, **e** R = 4-$MeOC_6H_4$, **f** R = 2-furyl, **g** R = 2-thienyl

The reaction of compounds **1a-g** with the product of condensing triethylorthoformate ester with malononitrile (ethoxymethylenemalononitrile) also leads to the formation of a pyridobenzimidazole system. The process likely occurs *via* compounds **6a-g** which cyclize under the reaction conditions to give the 4-acyl-1-amino-2-cyanopyrido[1,2-*a*]benzimidazoles **7a-g**.

The composition and structure of the obtained compounds was proved by elemental analysis (Table 1) and from their IR and ^{1}H NMR spectra (Table 2).

It was notable that the ^{1}H NMR spectra of the methyl-substituted compound **5a** and its aryl-substituted structural analogs **5b-g** were markedly different. In the latter the proton signals for positions 9 and 8 are shifted to high field by 2.0 and 0.6 ppm respectively. This suggests that the aryl group in position 1 of the pyridobenzimidazole ring is twisted from planar due to steric hindrance and produces a strong shielding on the closest part of its *o*-phenylene fragment.

The assignment of signals in the spectrum of compound **7a** was made on the basis of a study of the nuclear Overhauser effect. Irradiation of the proton signal for the CH_3 group at 2.96 ppm caused an increase in the intensity of the H-3 signal at 8.15 ppm. The same procedure with the H-6 signal at 8.65 ppm had an effect on the H-7 signal at 7.41 ppm. This data confirms the location of the indicated protons in neighboring positions in the molecule. Hence it was possible to exclude an alternative 4-acetyl-3-amino-2-cyanopyrido[1,2-*a*]-benzimidazole structure which might have been expected from prior reasoning.

Hence 2-acylmethyl-1H-benzimidazoles are rather effective reagents for the synthesis of variously functionalized pyrido[1,2-*a*]benzimidazoles.

TABLE 1. Characteristics of the Compounds Synthesized

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	Yield, %
		C	H	N		
3a	$C_{13}H_{10}N_4$	70.14 / 70.26	4.37 / 4.54	25.18 / 25.21	300-302	91
3b	$C_{18}H_{12}N_4$	75.95 / 76.04	4.18 / 4.25	19.63 / 19.71	304.5-306	94
3c	$C_{18}H_{11}N_5O_2$	65.58 / 65.65	3.42 / 3.37	21.19 / 21.27	331-332.5	99
3d	$C_{21}H_{18}N_4O_3$	67.28 / 67.37	4.69 / 4.85	14.88 / 14.96	304-305.5	83
3e	$C_{19}H_{14}N_4O$	72.49 / 72.60	4.43 / 4.49	17.75 / 17.82	304-305.5	88
3f	$C_{16}H_{10}N_4O$	70.03 / 70.07	3.49 / 3.67	20.34 / 20.43	320-323	93
3g	$C_{16}H_{10}N_4S$	66.08 / 66.19	3.52 / 3.47	19.24 / 19.30	310-311.5	82
5a	$C_{21}H_{16}N_4O$	74.02 / 74.10	4.66 / 4.74	16.39 / 16.46	276.5-278	91
5b	$C_{31}H_{20}N_4O$	80.18 / 80.16	4.28 / 4.34	11.97 / 12.06	248-249.5	96
5c	$C_{31}H_{18}N_6O_5$	67.05 / 67.15	3.21 / 3.27	15.09 / 15.16	>300	94
5d	$C_{37}H_{32}N_4O_7$	68.78 / 68.93	5.12 / 5.00	8.53 / 8.69	240.5-242	61
5e	$C_{33}H_{24}N_4O_3$	75.44 / 75.56	4.52 / 4.61	10.53 / 10.68	253.5-255	74
5f	$C_{27}H_{16}N_4O_3$	72.83 / 72.97	3.49 / 3.63	12.47 / 12.61	288.5-290	61
5g	$C_{27}H_{16}N_4OS_2$	67.96 / 68.05	3.28 / 3.38	11.58 / 11.76	277-278.5	87
7a	$C_{14}H_{10}N_4O$	67.08 / 67.19	4.12 / 4.03	22.33 / 22.39	295-296.5	82
7b	$C_{19}H_{12}N_4O$	72.98 / 73.07	3.75 / 3.87	17.88 / 17.94	301-302.5	86
7c	$C_{19}H_{11}N_5O_3$	63.73 / 63.87	3.14 / 3.10	19.52 / 19.60	335-337.5	66
7d	$C_{22}H_{18}N_4O_4$	65.61 / 65.67	4.46 / 4.51	13.87 / 13.92	278.5-280	92
7e	$C_{20}H_{14}N_4O_2$	70.11 / 70.17	4.07 / 4.12	16.22 / 16.36	285-287	86
7f	$C_{17}H_{10}N_4O_2$	67.46 / 67.55	3.45 / 3.33	18.42 / 18.53	288-292	92
7g	$C_{17}H_{10}N_4OS$	64.07 / 64.14	3.23 / 3.17	17.48 / 17.60	305-312 (charring)	88

TABLE 2. Spectroscopic Characteristics of the Compounds Synthesized

Compound	IR spectrum, cm^{-1} (CO, CN, NH)	^{1}H NMR spectrum, δ, ppm (*J*, Hz)
1	2	3
3a	2220, 3300, 4350	2.41 (3H, s, CH_3); 6.84 (1H, s, H-4); 7.32 (1H, t, *J* = 7.2, H-7); 7.50 (1H, t, *J* = 7.2, H-8); 7.72-7.74 (3H, m, NH_2 + H-9); 8.46 (1H, d, *J* = 8.1, H-6)
3b	2220, 3125, 3490	6.95 (1H, s, H-4); 7.39 (1H, t, *J* = 7.8, H-7); 7.53-7.58 (4H, m, H-8 + + C_6H_5: H-3,4,5); 7.65-7.67 (2H, m, C_6H_5: H-2,6); 7.79 (1H, d, *J* = 7.8, H-9); 7.88 (2H, s, NH_2); 8.53 (1H, d, *J* = 7.8, H-6)
3c	2220, 3240, 3345	7.08 (1H, s, H-4); 7.42 (1H, t, *J* = 7.5, H-7); 7.57 (1H, t, *J* = 7.8, H-8); 7.82 (1H, d, *J* = 8.4, H-9); 7.94 and 8.38 (2 × 2H, two d, *J* = 8.7, $C_6H_4NO_2$); 8.01 (2H, s, NH_2); 8.56 (1H, d, *J* = 7.8, H-6)

TABLE 2 (continued)

1	2	3
3d	2220, 3320, 3480	3.75 (3H, s, OCH_3); 3.88 (6H, s, $2OCH_3$); 6.98 (2H, s, C_6H_2); 7.06 (1H, s, H-4); 7.38 (1H, t, *J* = 7.8, H-7); 7.55 (1H, t, *J* = 7.5, H-8); 7.79 (1H, d, *J* = 8.1, H-9); 7.85 (2H, s, NH_2); 8.52 (1H, d, *J* = 8.1, H-6)
3e	2220, 3200, 3320, 3445	3.84 (3H, s, OCH_3); 6.90 (1H, s, H-4); 7.10 and 7.61 (2 × 2H, two d, *J* = 8.7, $C_6H_4OCH_3$); 7.37 (1H, t, *J* = 7.2, H-7); 7.54 (1H, t, *J* = 7.5, H-8); 7.78 (1H, d, *J* = 8.1, H-9); 7.83 (2H, s, NH_2); 8.51 (1H, d, *J* = 7.8, H-6)
3f	2220, 3300, 3400	6.74 (1H, m, 2-furyl: H-4); 7.21 (1H, s, H-4); 7.34 (1H, d, *J* = 3.6, 2-furyl: H-3); 7.35 (1H, t, *J* = 7.8, H-7); 7.53 (1H, t, *J* = 7.8, H-8); 7.76 (1H, d, *J* = 8.1, H-9); 7.82 (2H, s, NH_2); 7.94 (1H, d, *J* = 1.3, 2-furyl: H-5); 8.48 (1H, d, *J* = 8.1, H-6)
3g	2215, 3300, 3440	7.04 (1H, s, H-4); 7.25 (1H, m, 2-thienyl: H-4); 7.38 (1H, t, *J* = 7.8, H-7); 7.55 (1H, t, *J* = 7.5, H-8); 7.68 (1H, d, *J* = 2.7, 2-thienyl: H-3); 7.76 (1H, d, *J* = 4.2, 2-thienyl: H-5); 7.78 (1H, d, *J* = 7.8, H-9); 7.80 (2H, s, NH_2); 8.49 (1H, d, *J* = 8. 4, H-6)
5a	1670	3.06 (3H, s, CH_3CO); 3.50 (3H, s, CH_3); 7.25-7.27 (2H, m, H-5',6'), 7.44 (1H, t, *J* =7.5, H-7); 7.59-7.64 (2H, m, H-8 + H-7'); 7.74 (1H, m, H-4'); 7.97 (1H, d, *J* = 7.8, H-9); 8.42 (1H, s, H-3); 8.47 (1H, d, *J* = 8.7, H-6); 13.05 (1H, s, H-1')
5b	1675	5.97 (1H, d, *J* = 9.0, H-9); 6.99 (1H, t, *J* = 8.4, H-8); 7.09-7.17 (2H, m, H-5',6'); 7.39-7.44 (2H, m, H-7 + H-7'); 7.50 (1H, d, *J* = 6.6, H-4'); 7.55-7.79 (9H, m, H-6 + C_6H_5 + COC_6H_5: H-3,4,6); 7.99 (2H, d, *J* = 7.2, COC_6H_5: H-2,6); 8.08 (1H, s, H-3); 12.28 (1H, s, H-1')
5c	1685	6.11 (1H, d, *J* = 8.4, H-9); 7.06 (1H, t, *J* = 7.8, H-8); 7.13 (2H, m, H-5',6'); 7.43 (3H, m, H-7 + H-4',7'); 7.78 (1H, d, *J* = 8.4, H-6); 8.03 and 8.37 (2H + 2H, two d, *J* = 8.7, $C_6H_4NO_2$); 8.24 and 8.51 (2 × 2H, two d, *J* = 8.4, $COC_6H_4NO_2$); 8.35 (1H, s, H-3); 12.64 (1H, s, H-1')
5d	1660	3.68 (6H, s, $2OCH_3$); 3.79 (6H, s, $2OCH_3$); 3.80 (6H, s, $2OCH_3$); 6.20 (1H, d, *J* = 8.7, H-9); 7.06 (2H, s, C_6H_2); 7.10-7.20 (3H, m, H-8 + H-5',6'); 7.32 (2H, s, COC_6H_2); 7.43-7.48 (2H, m, H-7 + H-7'); 7.53 (1H, d, *J* = 7.5, H-4'); 7.83 (1H, d, *J* = 8.1, H-6); 8.13 (1H, s, H-3); 11.98 (1H, s, H-1')
5e	1670	3.87 (3H, s, OCH_3); 3.88 (3H, s, OCH_3); 6.14 (1H, d, *J* = 8.7, H-9); 7.03-7.19 (7H, m, H-8 + H-5',6' + COC_6H_4 : H-3,5 + C_6H_4 : H-3,5); 7.42 (1H, t, *J* = 8.1, H-7); 7.48 (2H, m, H-4',7'); 7.62 (2H, d, *J* = 8.7, C_6H_4 : H-2,6); 7.79 (1H, d, *J* = 8.1, H-6); 7.97 (2H, d, *J* = 8.4, COC_6H_4: H-2,6); 8.05 (1H, s, H-3); 12.20 (1H, s, H-1')
5f	1670	6.14 (1H, d, *J* = 8.1, H-9); 6.81 (2H, m, furyl: H-4 + CO-furyl: H-4); 6.95 (1H, d, *J* = 3.0, furyl: H-3); 7.20-7.23 (2H, m, H-5',6'); 7.26 (1H, t, *J* = 7.2, H-8); 7.51-7.57 (4H, m, CO-furyl: H-3 + H-4',7' + H-7); 7.89 (1H, d, *J* = 8.1, H-6); 8.16 (2H, m, furyl: H-5 + CO-furyl: H-5); 8.21 (1H, s, H-3); 12.58 (1H, s, H-1')
5g	1660	6.17 (1H, d, *J* = 8.7, H-9); 7.11-7.17 (3H, m, H-8 + H-5',6'); 7.28 (1H, m, thienyl: H-4); 7.38 (1H, m, CO-thienyl: H-4); 7.46-7.57 (3H, m, H-7 + + H-4',7'); 7.65 (1H, m, thienyl: H-3); 7.85-7.89 (2H, m, H-6 + CO-thienyl: H-3); 7.98 (1H, d, *J* = 7.8, thienyl: H-5); 8.17 (1H, s, H-3); 8.21 (1H, d, *J* = 7.8, CO-thienyl: H-5); 12.28 (1H, s, H-1')
7a	1665, 2225, 3265	2.75 (3H, s, CH_3); 7.42 (1H, t, *J* = 7.8, H-7); 7.57 (1H, t, *J* = 7.5, H-8); 7.85 (1H, d, *J* = 8.1, H-9); 8.18 (1H, s, H-3); 8.40 (2H, br. s, NH_2); 8.67 (1H, m, H-6)
7b	1650, 2230, 3300	7.43 (1H, t, *J* = 7.5, H-7); 7.50-7.57 (3H, m, H-8 + C_6H_5 : H-3,5), 7.63 (1H, m, C_6H_5: H-4); 7.75-7.78 (2H, m, C_6H_5: H-2,6); 7.82 (1H, s, H-3); 8.37 (2H, br. s, NH_2); 8.68 (1H, m, H-6)
7c	1740, 2225, 3290	7.44 (1H, t, *J* = 7.2, H-7); 7.55 (1H, t, *J* = 7.5, H-8); 7.77 (1H, m, H-9); 7.94 (1H, s, H-3); 7.95 and 8.33 (2 × 2H, two d, *J* = 8.4, $C_6H_4NO_2$); 8.54 (2H, br. s, NH_2); 8.72 (1H, m, H-6)
7d	1660, 2225, 3265	3.77 (9H, s, $3OCH_3$); 7.08 (2H, s, C_6H_2); 7.43 (1H, t, *J* = 8.1, H-7); 7.56 (1H, t, *J* = 8.1, H-8); 7.79 (1H, d, *J* = 8.4, H-9); 7.83 (1H, s, H-3); 8.25 (2H, br. s, NH_2); 8.68 (1H, m, H-6)

TABLE 2 (continued)

1	2	3
7e	1650, 2230, 3310	3.85 (3H, s, OCH_3); 7.03 and 7.78 (2 × 2H, two d, J = 8.7, $C_6H_4OCH_3$); 7.41 (1H, t, J = 8.1, H-7); 7.54 (1H, t, J = 7.2, H-8); 7.74-7.80 (2H, m, H-3,9); 8.34 (2H, br. s, NH_2); 8.64 (1H, m, H-6)
7f	1645, 2230, 3290	6.75 (1H, m, furyl: H-4); 7.40 (1H, t, J = 3.3, furyl: H-3); 7.46 (1H, t, J = 7.8, H-7); 7.57 (1H, t, J = 7.5, H-8); 7.82 (1H, d, J = 7.8, H-9); 8.07 (1H, s, H-3); 8.19 (1H, m, furyl: H-5); 8.41 (2H, br. s, NH_2); 8.70 (1H, m, H-6)
7g	1640, 2235, 3330, 3420	7.24 (1H, m, thienyl: H-4); 7.43 (1H, t, J = 7.2, H-7); 7.56 (1H, t, J = 7.5, H-8); 7.79-7.81 (2H, m, H-9 + thienyl: H-3); 8.00 (1H, s, H-3); 8.06 (1H, d, J = 4.5, thienyl: H-5); 8.41 (2H, br. s, NH_2); 8.65 (1H, d, J = 6.9, H-6)

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument for KBr tablets. ^{1}H NMR spectra were taken on a Varian VXR-300 (300 MHz) using DMSO-d_6 and TMS standard. The ^{1}H NMR spectrum of compound **7a** (with the Overhauser effect study) was carried out on a Varian Mercury-400 (400 MHz) spectrometer. Monitoring of the reaction course and the purity of the synthesized compounds were carried out on Silufol UV-254 plates using the solvent system benzene–ethanol (9:1) and revealed using UV light.

1-Amino-3-methylpyrido[1,2-*a*]benzimidazole-2-carbonitrile (3a). A mixture of compound **1a** (0.348 g, 2 mmol), malononitrile (0.264 g, 4 mmol), and 2-propanol (2 ml) was refluxed with stirring for 30 min. After cooling, the precipitate was filtered and washed with 2-propanol. The product is formed in an analytically pure state.

1-Amino-3-phenylpyrido[1,2-*a*]benzimidazole-2-carbonitrile (3b). A mixture of compound **1b** (0.472 g, 2 mmol), malononitrile (0.264 g, 4 mmol), DMF (2.0 ml), and glacial acetic acid (1 drop) was refluxed with stirring for 30 min. After cooling, the precipitate was filtered, washed with 2-propanol, and dried for 5 h using a water vacuum pump at 115°C. The product is formed in an analytically pure state.

Compounds 3c-g were formed similarly from compounds **1c-g**. Synthesis of compound **3c** was carried out in DMF (4 ml).

4-Acetyl-2-(1H-benzimidazol-2-yl)-1-methylpyrido[1,2-*a*]benzimidazole (5a). A mixture of compound **1a** (0.348 g, 2 mmol) and triethylorthoformate ester (0.444 g, 3 mmol) was held at 140°C for 10 min. It was cooled to 100°C, ethanol (2 ml) added, and stirred. After cooling, the precipitate was filtered off, washed with an ethanol-water mixture (1: 1), and recrystallized from a mixture of pyridine–water (2: 1).

Compounds 5b,d were prepared similarly from compounds **1b,d** by heating for 30 min. In the synthesis of compound **5d** triethylorthoformate ester (0.222 g, 1.5 mmol) was taken and the product was separated after dilution of the reaction mixture with toluene (2.0 ml).

2-(1H-Benzimidazol-2-yl)-4-(4-nitrobenzoyl)-1-(4-nitrophenyl)pyrido[1,2-*a*]benzimidazole (5c). A mixture of compound **1c** (0.281 g, 1 mmol), triethylorthoformate ester (0.222 g 1.5 mmol), and DMF (1.0 ml) was refluxed for 15 min. It was cooled to 100°C, water (2-3 drops added), and stirred. After cooling, the precipitate was filtered off, washed with 2-propanol, and dried for 5 h using a water vacuum pump at 115°C. The product is formed in an analytically pure state.

2-(1H-Benzimidazol-2-yl)-4-(4-methoxybenzoyl)-1-(4-methoxyphenyl)pyrido[1,2-*a*]benzimidazole (5e). A mixture of compound **1e** (0.266 g, 1 mmol) and triethylorthoformate ester (0.111 g, 0.75 mmol) was refluxed in DMF (1.0 ml). After 30 min 0.037 g (0.25 mmol) and then after 15 minutes more a further 0.037 g (0.25 mmol) of triethylorthoformate ester were added and refluxing was continued for 15 min. After cooling to 100°C water (1 ml) was added, and refluxed with stirring to complete product crystallization. After cooling, the precipitate was filtered off, washed with 2-propanol, and crystallized from a mixture of pyridine–water (2:1).

Compounds 5f,g were prepared similarly from compounds **1f,g**.

4-Acetyl-1-aminopyrido[1,2-*a*]benzimidazole-2-carbonitrile (7a). A mixture of compound **1a** (0.174 g, 1 mmol) and ethoxymethylenemalononitrile (0.146 g, 1.2 mmol) in DMF (1 ml) was heated with stirring to the formation of a homogenous solution and held at 110-115°C for 30 min. Ethanol (1 ml) was added with stirring. After cooling, the precipitate was filtered off and washed with 2-propanol.

Compounds 7b-g were prepared similarly from compounds **1b-g.**

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