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Reactions of pyridoxal with aromatic diamines

Roza Kh. Bagautdinova[1]*, Lyudmila K. Kibardina[1], Alexander R. Burilov[1], Anna G. Strelnik[1], Mikhail A. Pudovik[1]

[1] *Arbuzov Institute of Organic and Physical Chemistry, Federal Research Center "Kazan Scientific Center of the Russian Academy of Sciences", 8 Akademika Arbuzova St., Kazan 420088, Russia; e-mail: bagrosa@iopc.ru*

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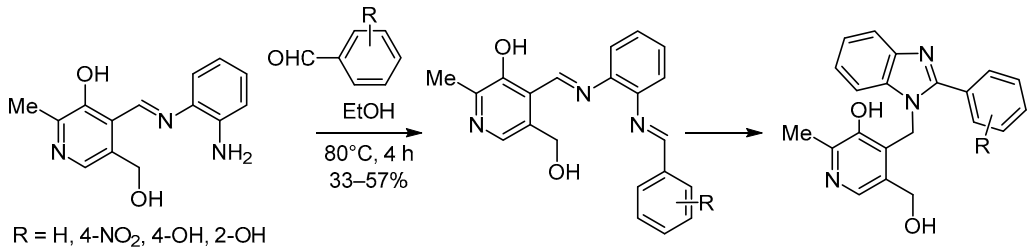


Pyridoxal monoimines were obtained by the reaction of pyridoxal with aromatic diamines. A change in the ratio of the reagents or introduction of another aromatic aldehyde into the reaction leads to the formation of symmetric and asymmetric diimines. In some cases, the initially formed diimines are transformed into the corresponding benzimidazoles. The products of the reaction of pyridoxal with 1,3-diaminobenzene have a furopyridine structure.

Keywords: aromatic aldehydes, aromatic diamines, benzimidazoles, diimines, imines, furopyridines, pyridoxal.

Interest in the synthesis of functionalized derivatives of pyridoxal (vitamin B_6) and the study of their biological activity has been ongoing from the moment of synthesis of the first representatives of this class of compounds up to the present. The central place among pyridoxal derivatives is occupied by imino derivatives (Schiff bases)[1–3] due to their wide use as ligands in coordination chemistry.[4,5] They are also successfully used as biologically active compounds,[6–8] analytical reagents,[9] catalysts.[10]

Pyridoxal readily reacts with primary aliphatic and aromatic amines to form the corresponding azomethines.[11–13] At the same time, various diamines were reacted with pyridoxal. The bisazomethines formed in this process are promising ligands for the production of metal complexes employed, for example, to determine nitrate and nitrite anions and as catalysts in various chemical transformations.[14–21] It is noted that when alkylene diamines are employed, regardless of the ratio and nature of the starting aldehydes, only the corresponding bisazomethines are formed.[11,22] Data on the reaction of aromatic diamines with pyridoxal are scarce and contradictory.

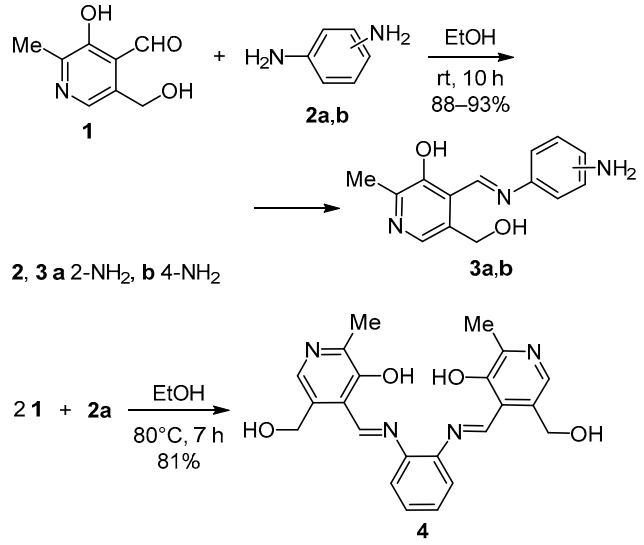
We used 1,2-, 1,3-, and 1,4-diaminobenzenes **2a**–**c** as the objects of study (Schemes 1, 2). There is information in the literature that the reaction of pyridoxal (**1**) hydrochloride and 1,2-diaminobenzene (**2a**) in MeOH solution in the presence of KOH leads to the formation of monoimine **3a**.[14] Moreover, this result was obtained using both equimolar amounts of reagents and a twofold excess of pyridoxal. The formation of diimine in this reaction was not recorded. In another work, a diimine was obtained as a result of the reaction of 1,2-diaminobenzene (**2a**) with pyridoxal (**1**) hydrochloride under similar conditions using Et_3N as the base.[23]

We repeated this reaction using pyridoxal (**1**) and 1,2-diaminobenzene (**2a**) or 1,4-diaminobenzene (**2b**) and obtained the corresponding monoimines **3a**,**b** (Scheme 1).

At the same time, the use of a double amount of pyridoxal in the reaction with 1,2-diaminobenzene (**2a**) when heating a solution in EtOH under reflux allowed us to obtain the corresponding symmetric diimine **4**. In the case of diamine **2b**, the reaction stopped at the stage of formation of monoimine **3b** even when using a double amount of pyridoxal (**1**) (Scheme 1).

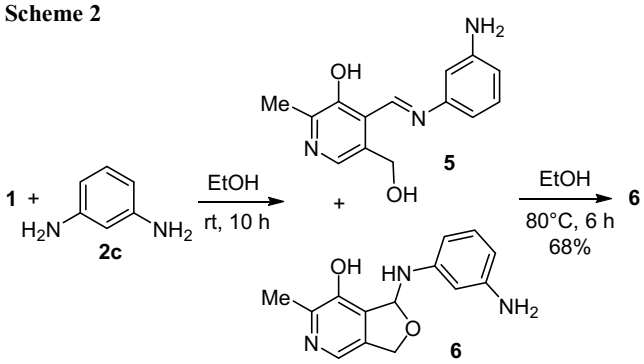
It should be noted that in the reaction of pyridoxal (**1**) with 1,3-diaminobenzene (**2c**) under similar conditions using aldehyde and diamine in a 1:1 ratio, a mixture of two tautomeric forms is formed, according to ^{1}H NMR

Scheme 1



spectroscopy: azomethine (compound **5**) and aminoacetal (compound **6**). Heating the reaction mixture in an EtOH solution under reflux for 6 h made it possible to isolate the thermodynamically more stable tautomer **6** (Scheme 2).

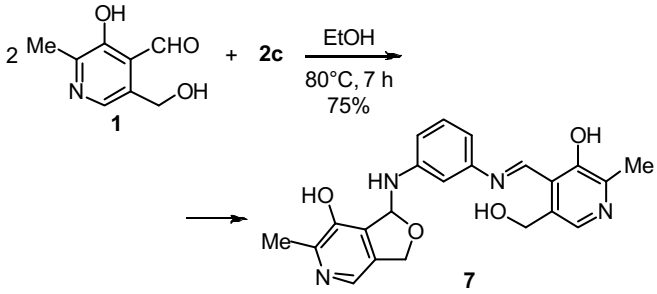
Scheme 2



There is no absorption band characteristic of the C=N bond in the IR spectrum of compound **6**, but there is an absorption band of stretching vibrations of the NH group at 3343 cm^{-1}. In the ^1H NMR spectrum of compound **6**, the protons of the methylene group appear as two doublets with chemical shifts of 5.08 and 5.23 ppm and an identical constant of 12 Hz. The singlet signal of the methine proton of the furan ring is observed at 6.13 ppm. It should be noted that there are few examples in the literature of stabilization of pyridoxal azomethines as an isomeric aminoacetal form, the formation of which is determined by the structural features of the aromatic amine reagent. For example, whereas the reaction of pyridoxal with phenylamine leads to the formation of azomethine, furopyridine is formed when 2-aminopyridine is used in this reaction.[24]

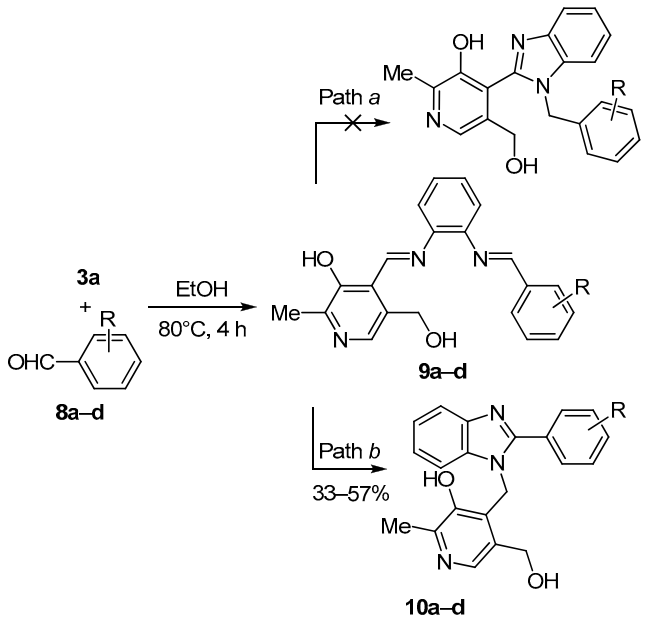
As a result of the reaction of 1,3-diaminobenzene (**2c**) with pyridoxal (**1**) in a 1:2 ratio, compound **7** was obtained containing both furopyridine and azomethine fragments. Apparently, the initially formed diimine undergoes an intramolecular transformation with the participation of one azomethine group and the formation of a furan fragment (Scheme 3).

Scheme 3



Since the reactions of pyridoxal (**1**) with aromatic diamines initially give rise to stable monoimines, the latter can be subjected to reactions with other aromatic aldehydes in order to obtain new asymmetric diimines. However, it turned out that the reactions of azomethine **3a** with a number of aromatic aldehydes (benzaldehyde (**8a**), 4-nitrobenzaldehyde (**8b**), 4-hydroxybenzaldehyde (**8c**), 2-hydroxybenzaldehyde (**8d**)) produce a different synthetic result (Scheme 4). The initially formed bisazomethines **9a**–**d** in this case undergo intramolecular cyclization, which is accompanied by a 1,3-proton shift from the carbon atom of the aryl fragment to the carbon atom in the pyridoxal, to the corresponding benzimidazoles **10a**–**d**.

Scheme 4



8–**10 a** R = H, **b** R = 4-NO_2
c R = 4-OH, **d** R = 2-OH

In the examined cases, ring closure in compounds **9a**–**d** can occur with the participation of one of two nonequivalent nitrogen atoms of azomethine fragments and lead to structurally different benzimidazoles (Scheme 4, paths *a*, *b*). Based on the fact that the protons of the methylene group in compounds **10a**–**d** have close chemical shifts, it can be assumed that path *b* is realized, and the methylene group becomes the bridging link between the pyridoxal and benzimidazole moieties.

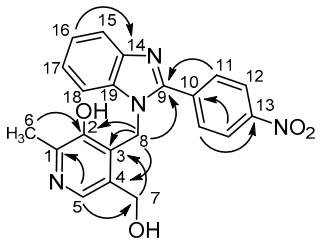
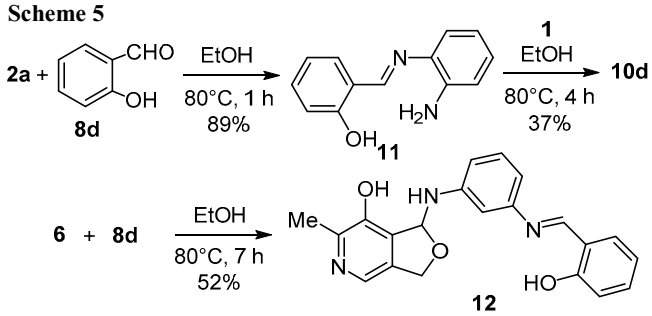


Figure 1. Key correlations in $^{1}H–^{13}C$ HMBC spectrum of compound **10b**.

Scheme 5



To confirm this assumption, a set of NMR correlation experiments (DEPT, COSY, $^{1}H–^{13}C$ HSQC, $^{1}H–^{13}C$ HMBC) was performed for compounds **10a**–**d**. For compound **10b**, for example, the chain of successive correlations between the atoms H-5/C-1, H-5/C-7, H-6/C-2, and H-7/C-3 (Fig. 1) allows one to differentiate in the spectrum the signal corresponding to the CH_2OH group (7-CH_2) from a signal of another methylene group (8-CH_2). Moreover, correlations between the H-8/C-3, H-8/C-4, and H-8/C-2 atoms unambiguously indicate the location of the methylene group within the structure. The correlation between the H-11/C-9 atoms is an additional argument in favor of the fact that, in compound **10b**, the nitrophenyl moiety is bonded to the imidazole directly rather than *via* the methylene group. The structures of compounds **10a**,**c**,**d** were similarly established.

Examples of the formation of benzimidazoles in the reactions of 1,2-diaminobenzene (**2a**) with aromatic aldehydes are known, and for this process to occur, the presence of mineral or organic acids (H_2SO_4, AcOH), a high-boiling solvent, ultrasonic irradiation is required.[25–27] In the case of imines based on pyridoxal (**1**), only brief heating under reflux in an EtOH solution is sufficient for this reaction to take place. Compound **10d** was also obtained by counter synthesis: the reaction of 1,2-diaminobenzene (**2a**) with salicylic aldehyde **8d** gave monoimine **11**,[28] treatment of which with pyridoxal (**1**) leads to the formation of compound **10d** (Scheme 5). The reaction of furopyridine **6** with salicylic aldehyde **8d** yields compound **12** containing both azomethine and furopyridine moieties.

To conclude, it was found as a result of the study that the reactions of pyridoxal with aromatic diamines proceed in two steps, and the initially formed monoimines can be used in successive synthesis of symmetric and asymmetric diimines. For some of them, an unusual transformation was observed, leading to the construction of a compound containing both azomethine and furopyridine fragments. Benzimidazoles with a pyridoxal moiety were obtained for the first time.

Experimental

IR spectra were registered on a Bruker Tensor-27 spectrometer over 400–3600 cm^{-1} range in KBr pellets. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance-400 spectrometer (400 and 101 MHz, respectively) in DMSO-d_6, using residual solvent signals as internal standard (2.50 ppm for ^{1}H nuclei and 39.5 ppm for ^{13}C nuclei). MALDI-TOF mass spectra were recorded on an Ultraflex III TOF/TOF Bruker spectrometer (*p*-nitroaniline matrix). Elemental analysis was performed on an Euro Vector EA-3000 CHNS-analyzer.

4-{[(2-Aminophenyl)imino]methyl}-5-(hydroxymethyl)-2-methylpyridin-3-ol (3a). 1,2-Diaminobenzene (**2a**) (0.65 g, 6 mmol) was added with stirring to a suspension of 3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carbaldehyde (**1**) (1.00 g, 6 mmol) in EtOH (20 ml). After 10 h, the precipitate was filtered off, washed with EtOH (50 ml), and dried. Yield 1.28 g (88%), yellow powder, mp 197–200°C (mp 182–184°C[14]). IR spectrum, ν, cm^{-1}: 1620 (C=N), 3332 (NH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.45 (3H, s, CH_3); 4.77 (2H, s, CH_2O); 5.16 (1H, s, OH); 5.42 (2H, s, NH_2); 6.67–7.21 (4H, m, H Ar); 7.99 (1H, s, H pyridine); 9.09 (1H, s, CH); 13.77 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 19.2; 59.0; 116.3; 117.4; 119.4; 121.0; 129.3; 133.8; 134.0; 138.7; 143.5; 148.5; 153.3; 159.0. Mass spectrum, *m*/*z*: 258 $[M+H]^+$. Found, %: C 65.00; H 6.21; N 16.31. $C_{14}H_{15}N_3O_2$. Calculated, %: C 65.34; H 5.89; N 16.33.

4-{[(4-Aminophenyl)imino]methyl}-5-(hydroxymethyl)-2-methylpyridin-3-ol (3b) was obtained by the same procedure as compound **3a** from 3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carbaldehyde (**1**) (1.32 g, 8 mmol) and 1,4-diaminobenzene (**2b**) (0.86 g, 8 mmol). Yield 1.89 g (93%), yellow powder, mp 226–228°C. IR spectrum, ν, cm^{-1}: 1635 (C=N), 3351 (NH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.41 (3H, s, CH_3); 4.74 (2H, s, CH_2O); 5.36 (1H, s, OH); 5.57 (2H, s, NH_2); 6.66 (2H, d, *J* = 7.4, H Ar); 7.30 (2H, d, *J* = 7.4, H Ar); 7.93 (1H, s, H pyridine); 9.07 (1H, s, CH); 14.49 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 19.2; 59.0; 114.6; 121.0; 123.5; 133.3; 135.5; 136.5; 148.1; 150.2; 153.5; 154.0. Mass spectrum, *m*/*z*: 258 $[M+H]^+$. Found, %: C 65.10; H 6.08; N 16.72. $C_{14}H_{15}N_3O_2$. Calculated, %: C 65.34; H 5.89; N 16.33.

4,4'-{[1,4-Phenylenebis(azanylylidene)]bis(methanylidene)}bis[5-(hydroxymethyl)-2-methylpyridin-3-ol] (4). A mixture of 3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carbaldehyde (**1**) (0.25 g, 1.5 mmol), 1,2-diaminobenzene (**2a**) (0.08 g, 0.75 mmol), and EtOH (10 ml) was heated under reflux for 7 h. The formed precipitate was separated, washed with EtOH (40 ml), and dried. Yield 0.26 g (81%), orange powder, mp 193–195°C (mp 199°C[23]). IR spectrum, ν, cm^{-1}: 1611 (C=N), 3332 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.38 (3H, s, CH_3); 2.40 (3H, s, CH_3); 4.77 (2H, s, OH); 5.17 (2H, s, CH_2O); 5.40 (2H, s, CH_2O); 6.66 (1H, t, *J* = 7.5, H Ar); 6.83 (1H, d, *J* = 7.9, H Ar); 7.07 (1H, t, *J* = 7.5, H Ar); 7.20 (1H, d, *J* = 7.6, H Ar); 7.99

(1H, s, H pyridine); 8.02 (1H, s, H pyridine); 9.09 (1H, s, CH); 9.18 (1H, s, CH)); 13.59 (2H, s, OH). ^{13}C NMR spectrum, δ, ppm: 19.2; 58.9; 59.0; 116.3; 117.3; 119.4; 120.4; 120.9; 129.8; 133.8; 134.0; 138.6; 138.7; 142.3; 143.5; 148.5; 148.8; 153.3; 153.6; 159.0; 163.5. Mass spectrum, *m*/*z*: 407 $[M+H]^+$. Found, %: C 64.70; H 5.34; N 13.42. $C_{22}H_{22}N_4O_4$. Calculated, %: C 65.00; H 5.47; N 13.79.

1-[(3-Aminophenyl)amino]-6-methyl-1,3-dihydrofuro-[3,4-*c*]pyridin-7-ol (6). A mixture of 3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carbaldehyde (**1**) (0.25 g, 1.5 mmol), 1,3-diaminobenzene (**2c**) (0.16 g, 1.5 mmol), and EtOH (20 ml) was heated under reflux for 6 h. After cooling, the formed precipitate was separated, washed with EtOH (50 ml), and dried. Yield 0.26 g (68%), orange powder, mp 137–140°C. IR spectrum, ν, cm^{-1}: 3343 (NH). 1H NMR spectrum, δ, ppm (*J*, Hz): 2.29 (3H, s, CH_3); 5.08 (1H, d, *J* = 12.0, CH_2O); 5.23 (1H, d, *J* = 12.0, CH_2O); 5.31 (2H, s, NH_2); 5.78–6.74 (4H, m, H Ar); 6.13 (1H, s, CH); 7.85 (1H, s, H pyridine); 13.99 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 19.4; 71.3; 80.1; 103.6; 104.2; 107.3; 126.9; 132.3; 134.5; 135.5; 142.9; 145.2; 146.4; 149.4. Mass spectrum, *m*/*z*: 258 $[M+H]^+$. Found, %: C 65.12; H 6.06; N 16.31. $C_{14}H_{15}N_3O_2$. Calculated, %: C 65.34; H 5.89; N 16.33.

1-[(3-{[2-Hydroxy-6-(hydroxymethyl)-3-methylbenzylidene]amino}phenyl)amino]-6-methyl-1,3-dihydrofuro-[3,4-*c*]pyridin-7-ol (7) was obtained by the same procedure as compound **4** from 3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carbaldehyde (**1**) (0.73 g, 4.37 mmol) and 1,3-diaminobenzene (**2c**) (0.24 g, 2.22 mmol). Yield 0.67 g (75%), brown powder, mp 222–224°C. IR spectrum, cm^{-1}: 1611 (C=N), 3332 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.34 (3H, s, CH_3); 2.37 (3H, s, CH_3); 4.74 (2H, s, CH_2O); 5.13 (1H, d, *J* = 12.1, CH_2O); 5.25 (1H, d, *J* = 12.1, CH_2O); 5.43 (1H, s, CH); 6.50 (1H, d, *J* = 2.1, H Ar); 6.81 (1H, d, *J* = 8.0, H Ar); 6.94 (1H, d, *J* = 2.1, H Ar); 7.03 (1H, d, *J* = 8.0, H Ar); 7.94 (1H, s, H pyridine); 7.98 (1H, s, H pyridine); 9.12 (1H, s, CH). ^{13}C NMR spectrum, δ, ppm: 19.2; 19.4; 58.9; 71.3; 79.8; 110.5; 112.5; 120.3; 126.9; 128.0; 132.8; 134.0; 135.0; 138.6; 145.3; 145.6; 146.3; 147.9; 148.7; 153.7; 161.2. Mass spectrum, *m*/*z*: 407 $[M+H]^+$. Found, %: C 64.70; H 5.34; N 13.42. $C_{22}H_{22}N_4O_4$. Calculated, %: C 65.00; H 5.47; N 13.79.

5-(Hydroxymethyl)-2-methyl-4-[(2-phenyl-1*H*-benzimidazol-1-yl)methyl]pyridin-3-ol (10a). A mixture of imine **3a** (0.4 g, 1.6 mmol) and benzaldehyde (**8a**) (0.16 g, 1.6 mmol) in EtOH (10 ml) was heated under reflux with stirring for 4 h. After cooling, the formed precipitate was filtered off, washed with EtOH (40 ml), Et_2O (20 ml), and dried. Yield 0.18 g (33%), white powder, mp 224–226°C. IR spectrum, ν, cm^{-1}: 1619 (C=N), 3183 (OH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.30 (3H, s, CH_3); 4.26 (2H, d, *J* = 4.1, CH_2); 5.18 (1H, s, OH); 5.58 (2H, s, CH_2O); 7.08 (1H, t, *J* = 7.2, Ph); 7.17 (2H, dd, *J* = 14.0, *J* = 7.8, H Ph); 7.55 (3H, dd, *J* = 5.1, *J* = 1.8, H Ph); 7.65 (1H, d, *J* = 7.9, H Ph); 7.82 (2H, dd, *J* = 6.5, *J* = 3.0, H Ph); 7.92 (1H, s, H pyridine); 8.91 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 20.3; 41.6; 59.2; 111.6; 119.6; 122.1; 122.5; 128.5; 128.9; 129.9; 130.1; 131.4; 134.5; 135.8; 139.9; 143.1; 146.3; 149.9; 154.7. Mass spectrum, *m*/*z*: 346 $[M+H]^+$. Found, %: C 73.45; H 5.66; N 11.81. $C_{21}H_{19}N_3O_2$. Calculated, %: C 73.01; H 5.56; N 12.17.

5-(Hydroxymethyl)-2-methyl-4-{[2-(4-nitrophenyl)-1*H*-benzimidazol-1-yl]methyl}pyridin-3-ol (10b) was obtained by the same procedure as compound **10a** from imine **3a** (0.28 g, 1.1 mmol) and 4-nitrobenzaldehyde (**8b**) (0.16 g, 1.1 mmol). Yield 0.23 g (54%), white powder, mp 243–244°C. IR spectrum, ν, cm^{-1}: 1347, 1523 (NO_2), 1610 (C=N), 3098 (OH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.25 (3H, s, CH_3); 4.26 (2H, s, CH_2); 5.16 (1H, s, OH); 5.64 (2H, s, CH_2O); 7.16 (1H, d, *J* = 7.5, H Ar); 7.21 (1H, d, *J* = 7.5, H Ar); 7.32 (1H, d, *J* = 8.1, H Ar); 7.71 (1H, d, *J* = 7.6, H Ar); 7.90 (1H, s, H pyridine); 8.09 (2H, d, *J* = 8.2, H Ar); 8.37 (2H, d, *J* = 8.4, H Ar); 8.88 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 20.2; 41.6; 59.2; 111.9; 120.0; 122.6; 123.3; 123.9; 128.5; 131.4; 134.3; 136.1; 137.7; 140.1; 143.1; 146.4; 148.3; 149.8; 152.6. Mass spectrum, *m*/*z*: 391 $[M+H]^+$. Found, %: C 65.00; H 4.92; N 13.96. $C_{21}H_{18}N_4O_4$. Calculated, %: C 64.60; H 4.66; N 14.35.

5-(Hydroxymethyl)-4-{[2-(4-hydroxyphenyl)-1*H*-benzimidazol-1-yl]methyl}-2-methylpyridin-3-ol (10c) was obtained by the same procedure as compound **10a** from imine **3a** (0.31 g, 1.2 mmol) and 4-hydroxybenzaldehyde (**8c**) (0.15 g, 1.2 mmol). Yield 0.25 g (57%), white powder, mp 198–201°C. IR spectrum, ν, cm^{-1}: 1611 (C=N), 3064 (OH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.31 (3H, s, CH_3); 4.19 (2H, s, CH_2); 5.06 (1H, s, OH); 5.54 (2H, s, CH_2O); 6.92 (2H, d, *J* = 8.2, H Ar); 7.03 (1H, d, *J* = 7.3, H Ar); 7.11 (2H, d, *J* = 8.2, H Ar); 7.59 (1H, d, *J* = 7.6, H Ar); 7.64 (2H, d, *J* = 8.4, H Ar); 7.92 (1H, s, H pyridine); 9.80 (1H, s, OH); 14.96 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 20.3; 41.6; 59.1; 111.4; 115.7; 119.2; 121.7; 121.9; 122.1; 122.2; 128.6 (2C); 131.6; 134.6; 135.6; 139.6; 143.0; 146.2; 149.9; 155.0; 159.1. Mass spectrum, *m*/*z*: 362 $[M+H]^+$. Found, %: C 69.71; H 5.71; N 11.43. $C_{21}H_{19}N_3O_3$. Calculated, %: C 69.78; H 5.59; N 11.63.

5-(Hydroxymethyl)-4-{[2-(2-hydroxyphenyl)-1*H*-benzimidazol-1-yl]methyl}-2-methylpyridin-3-ol (10d) was obtained by the same procedure as compound **10a** from imine **3a** (0.12 g, 0.5 mmol) and 2-hydroxybenzaldehyde (**8d**) (0.06 g, 0.5 mmol). Yield 0.06 g (35%), white powder, mp 247–248°C. IR spectrum, ν, cm^{-1}: 1613 (C=N), 3052 (OH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.30 (3H, s, CH_3); 4.21 (2H, s, CH_2); 5.11 (1H, s, OH); 5.42 (2H, s, CH_2O); 6.94 (1H, t, *J* = 7.5, H Ar); 6.98–7.09 (2H, m, H Ar); 7.14 (1H, t, *J* = 7.7, H Ar); 7.29–7.40 (2H, m, H Ar); 7.50 (1H, dd, *J* = 7.6, *J* = 1.6, H Ar); 7.62 (1H, d, *J* = 7.9, H Ar); 7.88 (1H, s, H pyridine); 9.05 (1H, s, OH); 10.40 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 20.3; 41.4; 59.1; 111.4; 116.5; 117.9; 119.3; 119.5; 121.9; 122.4; 128.6; 131.7; 131.9; 134.7; 135.3; 139.8; 142.9; 146.3; 150.0; 153.2; 156.5. Mass spectrum, *m*/*z*: 362 $[M+H]^+$. Found, %: C 69.42; H 6.01; N 11.54. $C_{21}H_{19}N_3O_3$. Calculated, %: C 69.78; H 5.59; N 11.63.

1-[(3-{[(2-Hydroxyphenyl)methylidene]amino}phenyl)-amino]-6-methyl-1,3-dihydrofuro[3,4-*c*]pyridin-7-ol (12)

was obtained by the same procedure as compound **4** from furopyridine **6** (0.3 g, 1.165 mmol) and 2-hydroxybenzaldehyde (**8d**) (0.14 g, 1.165 mmol). Yield 0.22 g (52%), orange powder, mp 285–286°C. IR spectrum, ν, cm^{-1}: 1613 (C=N), 3042 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.37 (3H, s, CH_3); 5.13 (1H, d, *J* = 12.1, CH_2O); 5.25 (1H, d, *J* = 12.1, CH_2O); 6.62 (1H, s, CH=N); 7.00–7.05 (3H, m, H Ar); 7.27 (1H, s, H Ar); 7.43 (2H, s, H Ar); 7.67 (1H, s, H Ar); 7.75 (1H, s, H Ar); 8.00 (1H, s, H pyridine); 8.99 (1H, s, OCHN); 12.50 (1H, s, OH); 12.95 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 19.5; 71.1; 79.7; 112.4; 117.2; 119.8; 120.2; 128.7; 132.3; 133.1; 134.0; 134.2; 135.1; 135.7; 145.7; 146.3; 148.9; 149.6; 160.6; 164.4. Mass spectrum, *m*/*z*: 362 $[M+H]^+$. Found, %: C 69.71; H 5.71; N 11.43. $C_{21}H_{19}N_3O_3$. Calculated, %: C 69.78; H 5.59; N 11.63.

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