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Synthesis of 1,5,6,7-Tetrahydro-4*H*-benzimidazol-4-one Derivatives from 2,6-Bis(hydroxyimino)cyclohexan-1-one

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Abstract—The reaction of 2,6-bis(hydroxyimino)cyclohexan-1-one with aldehydes and ammonia afforded 2-substituted 4-hydroxyimino-4,5,6,7-tetrahydro-1*H*-benzimidazol-1-ols which were hydrolyzed to 1-hydroxy-2-R-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-ones. The *N*-hydroxy group in the latter can readily by removed by the action of chloroacetone in the presence of a base (potassium carbonate or triethylamine); as a result, 2-substituted 1,5,6,7-tetrahydro-4*H*-benzimidazol-4-ones were obtained.

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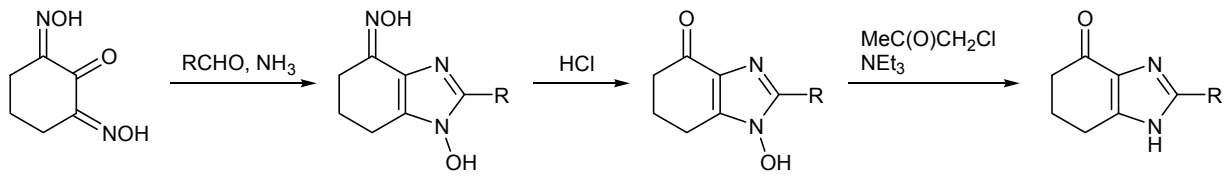
Imidazole and benzimidazole derivatives are components of natural substances, and they play an important role in biochemical processes occurring in living organisms [1–6]. A number of natural and synthetic derivatives of imidazole and benzimidazole are used in medical practice for the treatment of various diseases [7].

Transcription factor modulators [8–11] and urease inhibitors [12] have been found among substituted 1,5,6,7-tetrahydro-4*H*-benzimidazol-4-ones. These compounds were synthesized from 2-acylcyclohexane-1,3-dione *O*-alkyloximes [13], from nitroso enaminones via condensation with benzylamine [14], from halo ketones and amidines [15], from 2-aminodimedone hydrochloride and phenyl isothiocyanate [16], from 2-nitrodimedone [17], from isonitroso ketones, amines, and 4-oxo-4*H*-chromene-3-carbaldehyde [18], and from isonitroso ketones, aromatic amines, and formaldehyde [19, 20].

The most widely known general synthesis of imidazoles is based on the reaction of monooximes derived from 1,2-dicarbonyl compounds with aldehydes in the presence of amines. If ammonia is used as amine component, 1-hydroxyimidazoles are formed. Removal of the hydroxy group yields 1*H*-imidazoles [21]. Herein I report a simple procedure for the synthesis of functionalized 1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one derivatives from an accessible ketone, cyclohexanone, which is produced in Russia in an amount of ~500000 tons annually.

The nitrosation of cyclohexanone gave 2,6-bis(hydroxyimino)cyclohexan-1-one (**1**) in a high yield [22]. Bis-oxime **1** reacted with aldehydes in the presence of ammonia to produce 2-substituted 4-hydroxyimino-4,5,6,7-tetrahydro-1*H*-benzimidazol-1-ols **2a**–**2i**. Compounds **2a**–**2c**, **2e**, and **2f** were synthesized by reacting the corresponding aldehydes with ketone **1** in ethanol while passing gaseous ammonia through the reaction mixture. Compounds **2d** and **2h** were obtained by reaction of aldehydes with ketone **1** and ammonium acetate in ethanol. The hydroxyimino group in **2a**–**2f** was readily hydrolyzed on heating in concentrated

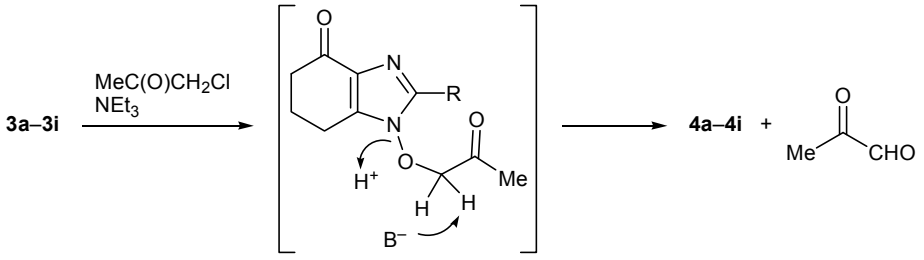
Scheme 1.



1 **2a–2i** **3a–3i** **4a–4i**

R = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 2-HOC_6H_4 (**c**), 3-$O_2NC_6H_4$ (**d**), 4-ethylpyridin-2-yl (**e**), furan-2-yl (**f**), Me (**g**), H (**h**), *i*-Pr (**i**).

Scheme 2.



A

aqueous HCl to afford ketones **3a**–**3f**. The hydroxyimino group was removed from **2g**–**2i** by treatment with sodium nitrite in acid medium [23].

N-Hydroxyimidazoles can be converted into 1*H*-imidazoles by the action of reducing agents [16, 18, 21, 24]. Treatment of **3a**–**3i** with chloroacetone in the presence of a base (triethylamine or potassium carbonate) readily afforded ketones **4a**–**4i** (Scheme 1). Removal of the *N*-hydroxy group from *N*-hydroxyindoles was accomplished in a similar way [25–27].

It was presumed that initial alkylation of the *N*-hydroxy group with chloroacetone gives intermediate **A**. Proton abstraction from the CH_2 group by base B promotes electron density transfer to the oxygen atom with simultaneous proton addition to the imidazole nitrogen atom. As a result, ketone **4a**–**4i** and methylglyoxal are obtained (Scheme 2).

Oximes and ketones derived from tetrahydrobenzimidazole may be interesting as starting compounds for the synthesis of benzimidazole derivatives. Delyatitskaya and Strakov [28] reviewed numerous examples of modification of the carbocyclic moiety of ketones based on cyclohexene-fused heterocycles.

EXPERIMENTAL

The analytical and spectral studies were performed at the Joint Chemical Service Center, Siberian Branch, Russian Academy of Sciences. The IR spectra were recorded from samples pressed with KBr (concentration 0.25%) on a Bruker Vector spectrometer. The UV spectra were measured in ethanol on a Specord M-40 spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded at 25°C from 10% solutions in $CDCl_3$, DMSO-d_6, or H_2SO_4 (chemically pure grade, GOST 4204-77) on a Bruker AV 400 spectrometer (400.13 MHz for ^1H and 100.61 MHz for ^{13}C); the chemical shifts were measured relative to the residual proton and carbon signals of the deuterated solvent ($CHCl_3$, δ 7.24 ppm; $CDCl_3$, δ_C 76.90 ppm; DMSO-d_5, δ 2.50 ppm, DMSO-d_6, δ_C 39.50 ppm); when H_2SO_4 was used as solvent, CH_2Cl_2 was added as internal standard (δ 5.33, δ_C 54.0 ppm). Multiplicities of signals in the ^{13}C NMR spectra were determined using *J* modulation (JMOD) technique. The mass spectra (electron impact, 70 eV) were obtained on a Thermo Scientific DFS mass spectrometer with direct sample admission into the ion source (ion source temperature 180°C); given below are ion peaks with an intensity higher than 10%. The progress of reactions and the purity of the isolated compounds were monitored by TLC on Sorbfil UV-254 plates; spots were visualized under UV light or by treatment with iodine vapor. The melting points were determined on a Kofler micro hot stage. The elemental analyses were obtained at the Microanalysis Laboratory, Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences.

4-Hydroxyimino-2-phenyl-4,5,6,7-tetrahydro-1*H*-benzimidazol-1-ol (2a). Gaseous ammonia was passed at a moderate rate through a mixture of 78 g (0.5 mol) of 2,6-bis(hydroxyimino)cyclohexan-1-one (**1**) and 56 g (0.53 mol) of benzaldehyde in 500 mL of methanol under stirring and cooling with cold water. The mixture initially thickened, the precipitate dissolved, and a solid separated on further passing ammonia. The mixture was stirred for 3 h and left overnight at room temperature. The precipitate was filtered off, washed with methanol on a filter, and dried. Yield 112 g (91%), white powder, mp 276–278°C (from EtOH). UV spectrum, λ_{max}, nm (logε): 253 (3.53), 312 (3.64). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.80–1.94 m (2H, CH_2), 2.56–2.73 m (4H, CH_2), 7.32–7.52 m (3H, H_{arom}), 7.97–8.12 m (2H, H_{arom}), 10.48 br.s (1H, OH), 11.91 br.s (1H, OH). ^{13}C NMR spectrum (H_2SO_4), δ_C, ppm: 16.77, 17.46, 22.54 (CH_2); 126.95, 128.40, 134.00 (CH_{arom}); 110.77, 116.10, 145.13, 145.56, 155.76. Mass spectrum, *m*/*z* (I_{rel}, %): 243 (100) $[M]^+$, 227 (58), 209 (31), 208 (33), 196 (72), 182 (15), 105 (85). Found, %: C 64.20; H 5.40; N 17.27.

$[M]^+$ 243.1000. $C_{13}H_{13}N_3O_2$. Calculated, %: C 64.18; H 5.39; N 17.28. *M* 243.1002.

Compounds **2b**–**2g** and **2i** were synthesized in a similar way.

4-Hydroxyimino-2-(4-methoxyphenyl)-4,5,6,7-tetrahydro-1*H*-benzimidazol-1-ol (2b). Yield 87%, white powder, mp 267–269°C (from EtOH). IR spectrum: ν 1608 cm^{-1} (C=N). UV spectrum, λ_{max}, nm (log ε): 241 (3.54), 317 (3.68). ^{1}H NMR spectrum (H_2SO_4), δ, ppm: 2.41 m (2H, CH_2), 3.20 m (2H, CH_2), 3.34 m (2H, CH_2), 4.14 s (3H, OCH_3), 7.36 d (2H, H_{arom}, *J* = 8.9 Hz), 8.17 d (2H, H_{arom}, *J* = 8.9 Hz), 12.08 br.s (1H, OH), 12.34 br.s (1H, OH). ^{13}C NMR spectrum (H_2SO_4), δ_C, ppm: 17.55, 18.23, 23.29 (CH_2); 56.15 (OCH_3); 115.15, 130.37 (CH); 111.20, 111.28, 145.23, 146.44, 156.57, 161.44. Mass spectrum, *m*/*z* (I_{rel}, %): 273 (61) $[M]^+$, 257 (100), 241 (66), 226 (90), 211 (72), 196 (16), 185 (16), 159 (17), 135 (76). Found, %: C 61.48; H 5.35; N 15.43. $[M]^+$ 273.1108. $C_{14}H_{15}N_3O_3$. Calculated, %: C 61.53; H 5.33; N 15.38. *M* 273.1104.

4-Hydroxyimino-2-(2-hydroxyphenyl)-4,5,6,7-tetrahydro-1*H*-benzimidazol-1-ol (2c). Yield 84%, white powder, mp 259–261°C (from EtOH). UV spectrum: λ_{max} 322 nm (log ε 3.46). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.84–2.01 m (2H, CH_2), 2.62–2.78 m (4H, CH_2), 6.81–6.97 m (3H, H_{arom}), 7.28–7.41 m (1H, H_{arom}), 7.79 br.s (1H, OH), 11.07 br.s (1H, OH), 13.60 br.s (1H, OH). ^{13}C NMR spectrum (D_2O + NaOH), δ_C, ppm: 22.03, 24.26, 25.56 (CH_2); 115.63, 122.03, 132.85, 134.20 (CH); 122.43, 128.16, 132.35, 144.59, 155.70, 168.25. Mass spectrum, *m*/*z* (I_{rel}, %): 259 (100) $[M]^+$, 243 (36), 227 (63), 212 (80), 197 (29), 121 (77). Found, %: C 60.23; H 5.07; N 16.20. $[M]^+$ 259.0949. $C_{13}H_{13}N_3O_3$. Calculated, %: C 60.22; H 5.05; N 16.21. *M* 259.0951.

4-Hydroxyimino-2-(3-nitrophenyl)-4,5,6,7-tetrahydro-1*H*-benzimidazol-1-ol (2d). Yield 76%, yellow powder, mp 258°C (decomp., from EtOH). IR spectrum, ν, cm^{-1}: 1348, 1529 (NO_2). UV spectrum, λ_{max}, nm (log ε): 253 (3.52), 316 (3.68). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.81–1.93 m (2H, CH_2), 2.58–2.70 m (4H, CH_2), 7.73 m (1H, CH), 8.19 d.d (1H, CH, *J* = 8.2, 2.4 Hz), 8.45 d (1H, CH, *J* = 8.2 Hz), 8.86 m (1H, CH), 10.61 br.s (1H, OH), 12.48 br.s (1H, OH). ^{13}C NMR spectrum (H_2SO_4), δ_C, ppm: 17.69, 18.26, 23.52 (CH_2); 123.52, 129.00, 131.36, 135.08 (CH_{arom}); 112.59, 119.10, 142.92, 146.13, 146.70, 156.20. Mass spectrum, *m*/*z* (I_{rel}, %): 288 (100) $[M]^+$, 272 (70), 254 (34), 241 (62), 208 (34), 195 (26), 180 (18), 150 (96). Found, %: C 54.23; H 4.18; N 19.44. $[M]^+$ 288.0852. $C_{13}H_{12}N_4O_4$. Calculated, %: C 54.16; H 4.20; N 19.44. *M* 288.0853.

2-(4-Ethylpyridin-2-yl)-4-hydroxyimino-4,5,6,7-tetrahydro-1*H*-benzimidazol-1-ol (2e). Yield 86%, yellow powder, mp 149–152°C (from EtOH). UV spectrum, λ_{max}, nm (log ε): 248 (3.45), 331 (3.87). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.20 t (3H, CH_3, *J* = 6.12 Hz), 1.63–1.75 m (2H, CH_2), 2.30–2.40 m (2H, CH_2), 2.48–2.54 m (2H, CH_2), 2.56–2.68 m (2H, CH_2), 6.17 br.s (1H, OH), 7.58 d.d (1H, Py, *J* = 8.0, 1.8 Hz), 8.17 d (1H, Py, *J* = 8.0 Hz), 8.40 d (1H, Py, *J* = 1.8 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 15.18 (CH_3); 19.16, 21.51, 22.70, 25.17 (CH_2); 121.37, 135.36, 148.64 (CH_{arom}); 126.37, 132.33, 137.25, 139.58, 146.64, 149.32. Mass spectrum, *m*/*z* (I_{rel}, %): 272 (55) $[M]^+$, 255 (46), 225 (100), 210 (13), 149 (11), 133 (53). Found, %: C 61.80; H 5.90; N 20.62. $[M]^+$ 272.1274. $C_{14}H_{16}N_4O_2$. Calculated, %: C 61.75; H 5.92; N 20.58. *M* 272.1274.

2-(Furan-2-yl)-4-hydroxyimino-4,5,6,7-tetrahydro-1*H*-benzimidazol-1-ol (2f). Yield 72%, yellow powder, mp 265–267°C (from EtOH). UV spectrum, λ_{max}, nm (log ε): 248 (3.42), 322 (3.68). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.77–1.94 m (2H, CH_2), 2.58–2.74 m (4H, CH_2), 5.48 br.s (1H, OH), 6.67 d.d (1H, Fu, *J* = 3.4, 1.8 Hz), 7.09 d (1H, Fu, *J* = 3.4 Hz), 7.85 d (1H, Fu, *J* = 1.8 Hz), 10.85 br.s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 18.89, 21.02, 22.35 (CH_2); 111.12, 111.87, 144.05 (CH_{arom}); 122.47, 131.80, 133.58, 141.70, 147.68. Mass spectrum, *m*/*z* (I_{rel}, %): 233 (33) $[M]^+$, 217 (21), 199 (12), 186 (34), 162 (15), 149 (15), 121 (25), 95 (30), 91 (100). Found, %: C 56.70; H 4.77; N 17.93. $[M]^+$ 233.0797. $C_{11}H_{11}N_3O_3$. Calculated, %: C 56.65; H 4.75; N 18.02. *M* 233.0795.

4-Hydroxyimino-2-methyl-4,5,6,7-tetrahydro-1*H*-benzimidazol-1-ol (2g). Yield 64%, mp 168–171°C (H_2O). UV spectrum: λ_{max} 268 nm (log ε 3.68). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.72–1.82 m (2H, CH_2), 2.14 s (3H, CH_3), 2.43–2.50 m (2H, CH_2), 2.50–2.58 m (2H, CH_2), 5.48 br.s (1H, OH), 10.64 br.s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 10.56 (CH_3); 19.17, 21.69, 22.70 (CH_2); 123.50, 130.48, 139.45, 148.08. Mass spectrum, *m*/*z* (I_{rel}, %): 181 (100) $[M]^+$, 165 (25), 146 (16), 134 (69), 122 (24). Found, %: C 53.00; H 6.08; N 23.22. $[M]^+$ 181.0847. $C_8H_{11}N_3O_2$. Calculated, %: C 53.03; H 6.12; N 23.19. *M* 181.0846.

4-Hydroxyimino-4,5,6,7-tetrahydro-1*H*-benzimidazol-1-ol (2h). A mixture of 15.6 g (0.1 mol) of compound **1**, 3.1 g (0.103 mol) of paraformaldehyde, and 8.0 g (0.104 mol) of ammonium acetate in 200 mL of methanol was heated to the boiling point with stirring. The heating bath was removed; when the exothermic reaction was over, the mixture was stirred for 1.5 h maintaining it slightly boiling and cooled, and the precipitate was filtered off, washed with methanol, and dried. Yield 11.3 g (68%), white powder, mp 225°C (decomp., from EtOH). UV spectrum: λ_{max} 261 nm (log ε 3.57). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.76–1.84 m (2H, CH_2), 2.52–2.60 m (4H, CH_2), 7.68 s (1H, CH), 10.47 br.s (1H, OH), 12.05 br.s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 18.76, 21.40, 22.40 (CH_2); 132.19 (CH); 126.77, 129.88, 148.58. Mass spectrum, *m*/*z* (I_{rel}, %): 167 (100) $[M]^+$, 151 (25), 132 (29), 119 (67), 106 (23). Found, %: C 50.32; H 5.45; N 25.15. $[M]^+$ 167.0691. $C_7H_9N_3O_2$. Calculated, %: C 50.29; H 5.43; N 25.14. *M* 167.0689.

4-Hydroxyimino-2-(propan-2-yl)-4,5,6,7-tetrahydro-1*H*-benzimidazol-1-ol (2i). Yield 74%, white powder, mp 240–242°C (from EtOH). UV spectrum: λ_{max} 267 nm (log ε 3.70). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.18 d (6H, CH_3, *J* = 7.6 Hz), 1.71–1.82 m (2H, CH_2), 2.41–2.58 m (4H, CH_2), 3.00–3.14 m (1H, CH), 3.42 br.s (1H, OH), 10.39 br.s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 20.36 (CH_3), 24.57 (CH); 18.84, 21.34, 22.36 (CH_2); 123.89, 130.03, 147.18, 148.20. Mass spectrum, *m*/*z* (I_{rel}, %): 209 (25) $[M]^+$, 193 (11), 178 (11), 162 (23), 149 (43), 105 (100). Found, %: C 57.35; H 7.23; N 20.12. $[M]^+$ 209.1237. $C_{10}H_{15}N_3O_2$. Calculated, %: C 57.40; H 7.23; N 20.08. *M* 209.1159.

1-Hydroxy-2-phenyl-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (3a). Compound **2a**, 122 g (0.5 mol), was added to 600 mL of concentrated aqueous HCl, and the mixture was heated to 80°C with stirring. Compound **2** dissolved, and then **3a** hydrochloride separated. The mixture was stirred for 30 min at 80°C, left to stand for 4 h at room temperature, and cooled to 5°C. The precipitate was filtered off, washed with ~50 mL of concentrated aqueous HCl, dried, and dissolved in 450 mL of 10% sodium hydroxide. The solution was carefully acidified to pH 6 with 10% aqueous HCl, and the precipitate was filtered off, washed with water, and dried. Yield 90 g (79%), white powder, mp 259–262°C (from EtOH). IR spectrum: ν 1670 cm^{-1} (C=O). UV spectrum, λ_{max}, nm (log ε): 269 (3.30), 293 (3.30), 316 (3.30). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.00–2.15 m (2H, CH_2), 2.38–2.48 m (2H, CH_2), 2.80–2.90 m (2H, CH_2), 7.40–7.55 m (3H, H_{arom}), 7.98–8.10 m (2H, H_{arom}), 12.3 br.s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.96, 23.08, 38.49 (CH_2); 127.51, 128.93, 129.52 (CH); 128.83, 129.95, 143.07, 143.59, 190.68 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 228 (14) $[M]^+$, 212 (55), 184 (19), 155 (9), 105 (34), 104 (100). Found, %: C 68.43; H 5.39; N 12.43. $[M]^+$ 228.0892. $C_{13}H_{12}N_3O_2$. Calculated, %: C 68.41; H 5.30; N 12.27. *M* 228.0893.

Compounds **3b**–**3f** were synthesized in a similar way.

1-Hydroxy-2-(4-methoxyphenyl)-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (3b). Yield 74%, white powder, mp 246–249°C (from EtOH). IR spectrum: ν 1666 cm^{-1} (C=O). UV spectrum, λ_{max}, nm (log ε): 267 (3.40), 324 (3.60). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.03–2.14 m (2H, CH_2), 2.37–2.46 m (2H, CH_2), 2.78–2.86 m (2H, CH_2), 3.82 s (3H, OCH_3), 7.05 d (2H, H_{arom}, *J* = 8.9 Hz), 7.98 d (2H, H_{arom}, *J* = 8.9 Hz), 12.17 br.s (1H, OH). ^{13}C NMR spectrum (H_2SO_4), δ_C, ppm: 18.91, 20.28, 33.06 (CH_2); 56.83 (OCH_3); 115.95, 132.03 (CH); 110.98, 118.21, 149.27, 157.02, 163.33, 198.20 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 258 (8) $[M]^+$, 242 (76), 212 (16), 149 (14), 134 (100). Found, %: C 65.12; H 5.50; N 10.90. $[M]^+$ 258.1002. $C_{14}H_{14}N_2O_3$. Calculated, %: C 65.10; H 5.46; N 10.85. *M* 258.0999.

1-Hydroxy-2-(2-hydroxyphenyl)-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (3c). Yield 68%, white powder, mp 248–251°C (from EtOH). IR spectrum: ν 1685 cm^{-1} (C=O). UV spectrum, λ_{max}, nm (log ε): 321 (3.48), 263 (3.67). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.07–2.18 m (2H, CH_2), 2.45–2.53 m (2H, CH_2), 2.81–2.90 m (2H, CH_2), 6.91–6.98 m (2H, H_{arom}), 7.32–7.40 m (1H, H_{arom}), 7.49–8.09 m (1H, H_{arom}), 11.18 br.s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.38, 22.63, 37.83 (CH_2); 118.12, 119.06, 127.64, 132.13 (CH); 111.99, 126.34, 142.14, 142.67, 158.05, 189.44 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 244 (97) $[M]^+$, 228 (100), 199 (27), 172 (28), 121 (76). Found, %: C 63.89; H 5.05; N 11.55. $[M]^+$ 244.0849. $C_{13}H_{12}N_2O_3$. Calculated, %: C 63.92; H 4.95; N 11.47. *M* 244.0842.

1-Hydroxy-2-(3-nitrophenyl)-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (3d). Yield 56%, yellow powder, mp 265–267°C (from EtOH). IR spectrum, ν, cm^{-1}: 1670 (C=O), 1350, 1510 (NO_2). UV spectrum, λ_{max}, nm (log ε): 268 (3.63), 319 (3.60). ^{1}H NMR spec-

trum (DMSO-d_6), δ, ppm: 2.05–2.18 m (2H, CH_2), 2.40–2.53 m (2H, CH_2), 2.82–2.94 m (2H, CH_2), 7.81 d.d (1H, H_{arom}, J = 7.9, 7.9 Hz), 8.29 d (1H, H_{arom}, J = 8.6 Hz), 8.49 d (1H, H_{arom}, J = 7.9 Hz), 8.87 m (1H, H_{arom}), 12.61 br.s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.65, 22.68, 38.20 (CH_2); 121.19, 123.63, 130.48, 132.91 (CH_{arom}); 129.97, 130.20, 140.50, 143.72, 147.97, 190.50 (C=O). Mass spectrum, m/z (I_{rel}, %): 273 (54) $[M]^+$, 257 (100), 229 (22), 218 (23), 200 (29), 150 (67). Found, %: C 57.20; H 4.10; N 15.44. $[M]^+$ 273.0742. $C_{13}H_{11}N_3O_4$. Calculated, %: C 57.14; H 4.06; N 15.38. M 273.0744.

2-(4-Ethylpyridin-2-yl)-1-hydroxy-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (3e). Yield 52%, white powder, mp 144–146°C (from EtOH). IR spectrum: ν 1670 cm^{-1} (C=O). UV spectrum: λ_{max} 318 nm (logε 3.76). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.23 t (3H, CH_3, J = 8.3 Hz), 2.11–2.20 m (2H, CH_2), 2.50–2.56 m (2H, CH_2), 2.61–2.70 m (2H, CH_2), 2.84–2.90 m (2H, CH_2), 7.70 d.d (1H, Py, J = 8.4, 2.1 Hz), 8.17 d (1H, Py, J = 8.2 Hz), 8.25 d (1H, Py, J = 2.1 Hz), 14.16 br.s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.66 (CH_3); 19.50, 22.85, 25.83, 38.17 (CH_2); 120.51, 138.12, 144.89 (CH_{arom}); 130.30, 135.21, 138.84, 140.01, 146.66, 191.27 (C=O). Mass spectrum, m/z (I_{rel}, %): 257 (83) $[M]^+$, 241 (60), 213 (19), 201 (12), 185 (10), 149 (34), 133 (100). Found, %: C 65.30; H 5.90; N 16.38. $[M]^+$ 257.1156. $C_{14}H_{15}N_3O_2$. Calculated, %: C 65.35; H 5.88; N 16.33. M 257.1159.

2-(Furan-2-yl)-1-hydroxy-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (3f). Yield 68%, yellow powder, mp 271–272°C (decomp., from EtOH). IR spectrum: ν 1664 cm^{-1} (C=O). UV spectrum, λ_{max}, nm (logε): 230 (3.40), 275 (3.60), 303 (3.78), 314 (3.80). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.04–2.14 m (2H, CH_2), 2.37–2.47 m (2H, CH_2), 2.78–2.86 m (2H, CH_2), 6.67 d.d (1H, Fu, J = 3.5, 1.8 Hz), 7.07 d (1H, Fu, J = 3.4 Hz), 7.86 d (1H, Fu, J = 1.8 Hz), 12.30 br.s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.47, 22.68, 38.16 (CH_2); 110.85, 111.70, 144.10 (CH_{arom}); 129.92, 136.35, 142.63, 142.70, 190.30 (C=O). Mass spectrum, m/z (I_{rel}, %): 218 (12) $[M]^+$, 202 (49), 174 (10), 149 (51), 104 (18), 94 (78), 85 (100). Found, %: C 60.50; H 4.60; N 12.82. $[M]^+$ 218.0685. $C_{11}H_{10}N_2O_3$. Calculated, %: C 60.54; H 4.62; N 12.84. M 218.0686.

1-Hydroxy-2-methyl-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (3g). A solution of 28.0 g (0.406 mol) of sodium nitrite in 50 mL of water was added dropwise to a solution of 72.4 g (0.4 mol) of compound **2g** in a mixture of 800 mL of water and 35 mL (0.41 mol) of concentrated aqueous HCl, maintaining the temperature at 28–30°C by cooling with water over a period of 1 h. The mixture was stirred for 1 h at room temperature and evaporated to dryness under reduced pressure (20 mm). The residue was dissolved on heating in 200 mL of propan-2-ol, the solution was filtered, the filtrate was treated with charcoal, evaporated to a volume of ~50 mL, and cooled, and the precipitate was filtered off. Yield 31.2 g (47%), white powder, mp 222–225°C (decomp.). IR spectrum: ν 1672 cm^{-1} (C=O). UV spectrum: λ_{max} 285 nm (logε 3.87). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.98–2.07 m (2H, CH_2), 2.25 s (3H, CH_3), 2.31–2.37 m (2H, CH_2), 2.70–2.76 m (2H, CH_2), 11.97 br.s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.51, 22.92, 37.98 (CH_2); 11.23 (CH_3); 128.52, 141.43, 142.56; 189.81 (C=O). Mass spectrum, m/z (I_{rel}, %): 166 (28) $[M]^+$, 150 (100), 128 (32), 122 (46), 110 (13), 94 (30). Found, %: C 57.86; H 5.96; N 16.80. $[M]^+$ 166.0737. $C_8H_{10}N_2O_2$. Calculated, %: C 57.82; H 6.07; N 16.86. M 166.0740.

Compounds **3h** and **3i** were synthesized in a similar way.

1-Hydroxy-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (3h). Yield 58%, white powder, mp 185–186°C. IR spectrum, ν, cm^{-1}: 1656, 1679 (C=O). UV spectrum: λ_{max} 262 nm (logε 3.80). ^{1}H NMR spectrum (H_2SO_4), δ, ppm: 2.12–2.28 m (2H, CH_2), 2.72–2.89 m (2H, CH_2), 2.90–3.00 m (2H, CH_2), 8.69 s (1H, CH), 12.15 s (1H, OH). ^{13}C NMR spectrum (H_2SO_4), δ_C, ppm: 15.99, 18.83, 32.46 (CH_2); 134.73, 118.71, 147.40, 195.56 (C=O). Mass spectrum, m/z (I_{rel}, %): 152 (59) $[M]^+$, 136 (100), 124 (48), 108 (62), 96 (43), 80 (61). Found, %: C 55.34; H 5.36; N 18.49. $[M]^+$ 152.0582. $C_7H_8N_2O_2$. Calculated, %: C 55.25; H 5.30; N 18.41. M 152.0580.

1-Hydroxy-2-(propan-2-yl)-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (3i). Yield 66%, white powder, mp 241–244°C. IR spectrum: ν 1668 cm^{-1} (C=O). UV spectrum: λ_{max} 267 nm (logε 3.86). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.24 d (6H, CH_3, J = 7.6 Hz), 2.00–2.10 m (2H, CH_2), 2.33–2.39 m (2H, CH_2), 2.67–2.74 m (2H, CH_2), 3.23–3.33 m (1H, CH), 14.13 br.s (1H, OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.57, 22.93, 37.75 (CH_2); 19.78 (CH_3), 25.18 (CH), 125.83, 142.10, 151.50, 189.19 (C=O). Mass spectrum, m/z (I_{rel}, %): 194 (29) $[M]^+$, 177 (9), 163 (16), 149 (8), 121 (15), 71 (16). Found, %: C 61.79;

H 7.32; N 14.40. $[M]^+$ 194.1053. $C_{10}H_{14}N_2O_2$. Calculated, %: C 61.83; H 7.27; N 14.42. *M* 194.1050.

2-Phenyl-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (4a). *a*. Compound **3a**, 1.14 g (0.005 mol), was dissolved in 10 mL of acetone, 0.54 g (0.0065 mol) of chloroacetone and 1.30 g (0.0125 mol) of triethylamine were added, and the mixture was kept for 24 h at room temperature. The solvent was distilled off, the residue was dispersed in water, and the precipitate was filtered off, washed with water, and dried. Yield 0.90 g (89%).

b. Compound **3a**, 1.14 g (0.005 mol), was dissolved in 10 mL of dimethylformamide, 0.54 g (0.0065 mol) of chloroacetone and 2.80 g (0.02 mol) of potassium carbonate were added, and the mixture was stirred for 24 h at room temperature. The precipitate was filtered off, the solvent was distilled off under reduced pressure, the residue was dispersed in water, and the precipitate was filtered off, washed with water, and dried. Yield 0.85 g (88%), white powder, mp 220–223°C (from EtOH). IR spectrum: ν 1665 cm^{-1} (C=O). UV spectrum: λ_{max} 298 nm (log ε 3.87). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.01–2.14 m (2H, CH_2), 2.40–2.48 m (2H, CH_2), 2.73–2.90 m (2H, CH_2), 7.37–7.51 m (3H, H_{arom}), 7.93–8.17 m (2H, H_{arom}), 12.30 br.s (1H, NH). ^{13}C NMR spectrum (H_2SO_4), δ_C, ppm: 20.85, 21.50, 33.11 (CH_2); 128.18, 130.49, 136.87 (CH); 118.33, 123.15, 152.94, 160.25, 199.45 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 212 (88) $[M]^+$, 184 (26), 156 (8), 104 (100). Found, %: C 75.57; H 5.70; N 13.30. $[M]^+$ 212.0939. $C_{13}H_{12}N_2O$. Calculated, %: C 75.56; H 5.70; N 13.20. *M* 212.0944.

Compounds **4b**–**4i** were synthesized in a similar way.

2-(4-Methoxyphenyl)-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (4b). Yield 76%, white powder, mp 247–249°C (from EtOH). IR spectrum: ν 1633 cm^{-1} (C=O). UV spectrum, λ_{max}, nm (log ε): 312 (3.87), 246 (3.40). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.00–2.12 m (2H, CH_2), 2.37–2.47 m (2H, CH_2), 2.71–2.84 m (2H, CH_2), 3.80 s (3H, OCH_3), 7.02 d (2H, H_{arom}, *J* = 9.35 Hz), 8.06 br.s (2H, H_{arom}), 12.83 br.s and 13.10 br.s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 23.54, 24.10, 37.54 (CH_2); 55.23 (OCH_3), 114.20, 127.93 (CH); 121.99, 126.85, 149.97, 156.07, 160.40, 187.45 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 242 (98) $[M]^+$, 227 (10), 214 (10), 186 (9), 134 (100). Found, %: C 69.34; H 5.65; N 11.43. $[M]^+$ 242.1048. $C_{14}H_{14}N_2O_2$. Calculated, %: C 69.40; H 5.83; N 11.56. *M* 242.1050.

2-(2-Hydroxyphenyl)-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (4c). Yield 78%, white powder, mp 264–266°C (from EtOH). IR spectrum: ν 1652 cm^{-1} (C=O). UV spectrum, λ_{max}, nm (log ε): 323 (3.76), 294 (3.40). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.07–2.18 m (2H, CH_2), 2.45–2.53 m (2H, CH_2), 2.81–2.90 m (2H, CH_2), 6.91–6.98 m (2H, H_{arom}), 7.32–7.40 m (1H, H_{arom}), 7.49–8.09 m (1H, H_{arom}), 10.35 br.s and 12.35 br.s (1H each, OH, NH). ^{13}C NMR spectrum (DMSO-d_6),[1] δ_C, ppm: 22.93, 23.64, 37.67 (CH_2); 116.83, 118.56, 125.78, 130.36 (CH); 113.83, 129.90, 150.24, 150.71, 157.64, 188.71 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 228 (100) $[M]^+$, 172 (18), 120 (53). Found, %: C 68.35; H 5.35; N 12.32. $[M]^+$ 228.0892. $C_{13}H_{12}N_2O_2$. Calculated, %: C 68.41; H 5.30; N 12.27. *M* 228.0893.

2-(3-Nitrophenyl)-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (4d). Yield 66%, white powder, mp 295°C (decomp., from EtOH). IR spectrum, ν, cm^{-1}: 1637 (C=O); 1350, 1516 (NO_2). UV spectrum: λ_{max} 296 nm (log ε 3.74). ^{1}H NMR spectrum (H_2SO_4), δ, ppm: 1.67–1.86 m (2H, CH_2), 2.42–2.55 m (2H, CH_2), 2.55–2.67 m (2H, CH_2), 7.30 t (1H, H_{arom}, *J* = 7.6 Hz), 7.67 d (1H, H_{arom}, *J* = 7.6 Hz), 7.98 d (1H, H_{arom}, *J* = 8.1 Hz), 8.25 s (1H, H_{arom}), 12.06 s and 12.27 s (1H, NH). ^{13}C NMR spectrum (H_2SO_4), δ_C, ppm: 20.00, 20.89, 33.19 (CH_2); 122.91, 129.52, 131.78, 134.18 (CH_{arom}); 120.20, 123.46, 147.07, 148.50, 156.96, 199.10 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 257 (100) $[M]^+$, 229 (13.5), 211 (8), 149 (32). Found, %: C 60.67; H 4.28; N 16.32. $[M]^+$ 257.0791. $C_{13}H_{11}N_3O_3$. Calculated, %: C 60.69; H 4.31; N 16.34. *M* 257.0795.

2-(4-Ethylpyridin-2-yl)-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (4e). Yield 72%, mp 170–172°C (from EtOH). IR spectrum: ν 1664 cm^{-1} (C=O). UV spectrum: λ_{max} 303 nm (log ε 3.86). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.21 t (3H, CH_3, *J* = 7.3 Hz), 2.12–2.20 m (2H, CH_2), 2.50–2.56 m (2H, CH_2), 2.58–2.67 m (2H, CH_2), 2.84–2.89 m (2H, CH_2), 7.58 d (1H, Py, *J* = 7.8 Hz), 8.11 d (1H, Py, *J* = 7.8 Hz), 8.32 s (1H, Py), 11.23 br.s (1H, NH). ^{13}C NMR spectrum (H_2SO_4), δ_C, ppm: 11.52 (CH_3); 19.46, 20.51, 24.87, 35.55 (CH_2); 127.54, 143.13, 147.63 (CH_{arom}); 125.75, 127.92, 136.89, 149.90, 150.88, 195.45 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 241 (51) $[M]^+$, 213 (10), 185 (4), 133 (100). Found, %: C 69.73; H 6.30; N 17.54.

[1] With addition of ~5% of triethylamine; otherwise signals at δ_C 150.24 and 129.90 ppm were not observed because of strong broadening.

$[M]^+$ 241.1208. $C_{14}H_{15}N_3O$. Calculated, %: C 69.69; H 6.27; N 17.42. *M* 241.1211.

2-(Furan-2-yl)-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (4f). Yield 76%, white powder, mp 279–281°C (from EtOH). IR spectrum: ν 1664 cm^{-1} (C=O). UV spectrum, λ_{max}, nm (log ε): 275 (3.60), 303 (3.85), 314 (3.86). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.89–2.16 m (2H, CH_2), 2.34–2.57 m (2H, CH_2), 2.64–2.95 m (2H, CH_2), 6.64 s (1H, Fu), 7.09 s (1H, Fu), 7.81 s (1H, Fu), 13.30 br.s (1H, NH). ^{13}C NMR spectrum (H_2SO_4), δ_C, ppm: 20.72, 21.10, 32.32 (CH_2); 115.20, 124.59, 152.59 (CH_{arom}); 121.96, 134.40, 142.42, 161.56, 198.24 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 202 (100) $[M]^+$, 174 (20), 146 (24), 94 (72). Found, %: C 65.28; H 5.05; N 13.95. $[M]^+$ 202.0736. $C_{11}H_{10}N_2O_2$. Calculated, %: C 65.33; H 4.98; N 13.86. *M* 202.0737.

2-Methyl-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (4g). Yield 59%, white powder, mp 225–228°C (from EtOH). IR spectrum: ν 1658 cm^{-1} (C=O). UV spectrum: λ_{max} 268 nm (log ε 3.80). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.90–2.00 m (2H, CH_2), 2.22 s (3H, CH_3), 2.27–2.34 m (2H, CH_2), 2.59–2.66 m (2H, CH_2). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.23 (CH_3); 23.63, 23.99, 37.80 (CH_2); 128.25, 149.16, 153.24, 188.25 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 150 (100) $[M]^+$, 122 (46), 94 (35). Found, %: C 64.08; H 6.76; N 18.70. $[M]^+$ 150.0791. $C_8H_{10}N_2O$. Calculated, %: C 63.98; H 6.71; N 18.65. *M* 150.0788.

1,5,6,7-Tetrahydro-4*H*-benzimidazol-4-one (4h). Yield 68%, white powder, mp 190–192°C (from EtOH). IR spectrum, ν, cm^{-1}: 1656, 1678 (C=O). UV spectrum: λ_{max} 263 nm (log ε 3.78). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.99–2.06 m (2H, CH_2), 2.35–2.43 m (2H, CH_2), 2.73–2.80 m (2H, CH_2), 7.80 s (1H, 2-H), 10.56 br.s and 12.91 br.s (1H, NH). ^{13}C NMR spectrum (H_2SO_4), δ_C, ppm: 18.42, 21.28, 34.98 (CH_2); 136.92 (C^2), 121.24, 143.32, 197.61 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 136 (6) $[M]^+$, 69 (10), 58 (34), 43 (100). Found, %: C 61.90; H 5.85; N 20.50. $[M]^+$ 136.0630. $C_7H_8N_2O$. Calculated, %: C 61.75; H 5.92; N 20.58. *M* 136.0631.

2-(Propan-2-yl)-1,5,6,7-tetrahydro-4*H*-benzimidazol-4-one (4i). Yield 69%, white powder, mp 222–223°C (from EtOH). IR spectrum: ν 1661 cm^{-1} (C=O). UV spectrum: λ_{max} 269 nm (log ε 3.80). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 d (6H, CH_3, J = 7.4 Hz), 1.98–2.17 m (2H, CH_2), 2.40–2.50 m (2H, CH_2), 2.72–2.82 m (2H, CH_2), 3.04–3.18 m (1H, CH), 11.95 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.27, 24.02, 37.15 (CH_2); 20.86 (CH_3), 28.26 (CH), 126.05, 156.91, 159.97, 189.26 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 178 (34) $[M]^+$, 163 (100), 135 (7). Found, %: C 67.42; H 8.05; N 15.68. $[M]^+$ 178.1096. $C_{10}H_{14}N_2O$. Calculated, %: C 67.38; H 7.92; N 15.72. *M* 178.1101.

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