# Transformations of 2-Ethyl-2-methyl-2,3-dihydro-1*H*-indole at the 3-Position

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Received July 3, 2019; revised November 10, 2019; accepted November 22, 2019

Abstract—The oxidation of *N*-acetyl-2-ethyl-2-methyl-2,3-dihydro-1*H*-indole with pyridinium chlorochromate,  $CrO_3 \cdot 2Py$ , or  $CrO_3$  gave *N*-acetyl-2-ethyl-2-methyl-2,3-dihydro-1*H*-indol-3-one which was hydrolyzed to 2-ethyl-2-methyl-2,3-dihydro-1*H*-indol-3-one. The latter was reduced with sodium tetrahydridoborate in ethanol to 3-hydroxy derivative and converted to the corresponding oxime by treatment with hydroxylamine hydrochloride in methanol. Baeyer–Villiger oxidation of 2-ethyl-2-methyl-2,3-dihydro-1*H*-indol-3-one and Beckmann rearrangement of its oxime were studied.

**Keywords:** 2-ethyl-2-methyl-2,3-dihydro-1*H*-indole, oxidation, oxime, Beckmann rearrangement, Baeyer–Villiger reaction.

DOI: 10.1134/S1070428020010133

Indole derivatives exhibit high biological activity, and their chemical modification could significantly affects the activity and give rise to new useful properties [1–4]. We previously showed that nitro, amino, and halogen derivatives of 2-ethyl-2-methyl-2,3-dihydro-1*H*-indole (1) possess antioxidant, antimicrobial, and growth-regulating properties [5]. In continuation of our studies aimed at searching for new biologically active compounds among dihydroindole derivatives like 1, the goal of the present work was to synthesize 3-oxo derivative of 1 and study its transformations. It should be noted that modifications of structure 1 at the 3-position attract interest since known synthetic and natural isatins (2,3-dioxoindoles) were found to exhibit important biological activities [6].

We tested several synthetic approaches to ketone **3**, in particular those based on oxidation with pyridinium chlorochromate (PCC),  $CrO_3 \cdot 2Py$ , and  $SeO_2$ . Attempt to oxidize initial 2-ethyl-2-methyl-2,3-dihydro-1*H*-indole (**1**) with PCC,  $CrO_3 \cdot 2Py$ , or  $CrO_3$  were unsuccessful, and only tars were obtained. Therefore, the NH

group of 1 was protected by acylation with acetic anhydride in 1,2-dichloroethane (DCE). Acetate 2 was isolated in 91% yield (Scheme 1) and was subjected to oxidation under different conditions (Table 1). The conversion of 2 on prolonged treatment with 4 equiv of PCC in methylene chloride at room temperature [7] was very low (the yield of **3** did not exceed 36%). We succeeded in improving the yield to 45% using  $CrO_3 \cdot 2Py$  as an oxidant, other conditions being equal. Further increase of the reaction time was not accompanied by increase of the yield. The best result was obtained by the oxidation of 2 with CrO<sub>3</sub> in acetic acid for 8 h; in this case, the yield of 3 increased to 85%. Further increase of the reaction time led to reduced yield, presumably because of decomposition of the product. The acetyl protection was readily removed by heating compound **3** in methanolic KOH under reflux; ketone 4 was thus formed in 75% yield.

The structure of the synthesized compounds was confirmed by <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR spectra, as well as 2D COSY, HSQC, HMBC, and NOESY experiments.





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Reagent	Amount, equiv	Solvent	Time, h	Yield of <b>3</b> , %
PCC	1.5	CH <sub>2</sub> Cl <sub>2</sub>	12	10
PCC	4	_	20	30
PCC	4	_	30	36
$CrO_3 \cdot 2Py$	1.5	$CH_2Cl_2$	12	21
$CrO_3 \cdot 2Py$	4	_	20	33
$CrO_3 \cdot 2Py$	4	_	30	45
CrO <sub>3</sub>	1	AcOH	8	85
CrO <sub>3</sub>	1	_	12	73

Table 1. Oxidation of N-acetyl-2-ethyl-2-methyl-2,3-dihydro-1H-indole and yields of compound 3

The carbonyl carbon of **3** resonated at  $\delta_C$  202.24 ppm in the <sup>13</sup>C NMR spectrum.

The reaction of **1** with selenium(IV) oxide in boiling ethanol afforded 45% of selenide **5** (Scheme 2). It should be noted that indole **2** failed to react under similar conditions. Heating of **5** with Raney nickel in ethanol recovered initial indole **1** with elimination of selenium. The mass spectrum of **5** contained the molecular ion peak in support of the proposed structure.

In order to improve the solubility and bioavailability, ketone 4 was reduced to alcohol 7 with sodium tetrahydridoborate in ethanol. The reaction was complete in 5 h at 20°C, and the yield of 7 was 89% (Scheme 3). Compound 7 was formed as a racemate and was optically inactive. The formation of two epimeric alcohols was confirmed by the presence of two 3-H singlets at  $\delta$  4.61 and 4.73 ppm in the <sup>1</sup>H NMR spectrum and two C<sup>3</sup> signals at  $\delta_C$  79.31 and 78.84 ppm in the <sup>13</sup>C NMR spectrum.

We then proceeded with the synthesis of oxime **6** with a view to obtaining quinazoline derivatives via Beckmann rearrangement [8]. For this purpose, ketone **4** was treated with hydroxylamine hydrochloride [9], and crystalline oxime **6** was isolated in 70% yield as needles melting at 120–121°C (Scheme 3). *N*-Acetyl derivative failed to react under similar conditions. The C<sup>3</sup> signal of **6** was located at  $\delta_C$  162.02 ppm in the <sup>13</sup>C NMR spectrum.

Oxime **6** did not undergo rearrangement in polyphosphoric acid (PPA) (Scheme 4), and only the hydrolysis product, ketone **4**, was isolated in 23% yield. No quinazoline structure was obtained when oxime **6** 



RUSSIAN JOURNAL OF ORGANIC CHEMISTRY Vol. 56 No. 1 2020





was treated with thionyl chloride in methylene chloride according to [10]. However, in this case, we isolated from the reaction mixture 2-aminobenzonitrile (8, yield 60%). The formation of 8 may be rationalized by increased lability of the C<sup>2</sup>–N bond due to  $\pi$ -donor effect of the benzene fragment.

We also tried to oxidize ketone 4 under Baeyer-Villiger conditions to obtain benzoxazine derivative like 10. The oxidation of 4 with hydrogen peroxide as described in [11] gave no desired benzoxazine, whereas in the reaction with *m*-chloroperoxybenzoic acid (m-CPBA) as oxidant, we isolated from the reaction mixture regioisomeric dioxoindole N-oxides 11a and 11b in 36 and 13% yield, respectively (Scheme 5). The <sup>15</sup>N NMR spectra of **11a** and **11b** showed nitrogen signals at  $\delta_N$  319.13 and 335.34 ppm, respectively, against  $\delta_N$  88.41 ppm for initial ketone 4. The mass spectra of the products were in agreement with their molecular weight.

In summary, we have developed and optimized procedures for the synthesis of 2-ethyl-2-methyl-2,3dihydro-1H-indol-3-one and its oxime and studied their transformations under conditions of Baeyer-Villiger oxidation and Beckmann rearrangement. The structures of the isolated compounds have been confirmed by <sup>1</sup>H and <sup>13</sup>C NMR and mass spectra. Compounds 4, 6, and 7 are promising for further study of their biological and antioxidant activities.

## **EXPERIMENTAL**

The <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR spectra were recorded on a Bruker Avance III 500 spectrometer at 500, 125, and 51 MHz, respectively, using CDCl<sub>3</sub> as solvent and reference (for <sup>1</sup>H and <sup>13</sup>C); the <sup>15</sup>N chemical shifts are given relative to liquid ammonia. The mass spectra were obtained on a Thermo Finnigan MAT 95 XP instrument (electron impact, 70 eV, ion source temperature 200°C). Elemental analyses were carried out with a Euro 2000 CHNS(O) analyzer. The melting points were measured on a Boetius hot stage with a PHMK 05 microscope. Analytical thin-layer chroma-



tography was performed on Sorbfil PTSKh-AF-A plates manufactured by Sorbpolimer (Krasnodar, Russia). Silica gel 60 (grain size 0.063–0.2 mm; Macherey-Nagel) was used for column chromatography.

2-Ethyl-2-methyl-2,3-dihydro-1*H*-indole (1) was synthesized as described in [12].

1-(2-Ethyl-2-methyl-2,3-dihydro-1*H*-indol-1-yl)ethanone (2). Acetic anhydride, 9.5 g (93.2 mmol), was added to a solution of 5.0 g (31.1 mmol) of compound 1 in 20 mL of 1,2-dichloroethane, and the mixture was stirred for 24 h at room temperature (TLC). The mixture was treated with 10 mL of water and stirred for 30 min, the organic phase was separated and dried over MgSO<sub>4</sub>, the solvent was distilled off, and the residue was purified by silica gel column chromatography using petroleum ether-ethyl acetate (8:1) as eluent. Yield 5.7 g (91%), light yellow oil. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.83 t (3H, CH<sub>3</sub>CH<sub>2</sub>, J = 7.3 Hz), 1.56 s (3H, 2-CH<sub>3</sub>), 1.74–1.78 m and 2.22– 2.26 m (1H each, 2-CH<sub>2</sub>), 2.38 s (3H, CH<sub>3</sub>CO), 2.81 d and 3.11 d (1H each, 3-H, J = 16.1 Hz), 6.95 t (1H, 5-H, J = 7.6 Hz), 7.11–7.14 m (3H, 4-H, 6-H, 7-H). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 8.63 (CH<sub>3</sub>CH<sub>2</sub>), 25.73 (2-CH<sub>3</sub>), 26.31 (CH<sub>3</sub>CO), 31.16 (2-CH<sub>2</sub>), 41.81 (C<sup>3</sup>),  $69.62 (C^2)$ , 114.56 (C<sup>7</sup>), 122.94 (C<sup>5</sup>), 125.26 (C<sup>6</sup>), 127.20 (C<sup>4</sup>), 130.74 (C<sup>3a</sup>), 142.90 (C<sup>7a</sup>), 168.88 (C=O). Mass spectrum: *m*/*z* 203.13 [*M*]<sup>+</sup>. Found, %: C 76.74; H 8.29; N 6.94. C<sub>13</sub>H<sub>17</sub>NO. Calculated, %: C 76.81; H 8.43; N 6.89.

1-Acetyl-2-ethyl-2-methyl-2,3-dihydro-1H-indol-3-one (3). A solution of 1.0 g (4.88 mmol) of compound 2 in 6 mL of acetic acid was cooled to 0°C, 0.9 g (9.7 mmol) of CrO<sub>3</sub> was added, and the mixture was allowed to warm up to room temperature and stirred until the reaction was complete (TLC). The mixture was treated with a saturated solution of sodium hydrogen carbonate and extracted with chloroform  $(3 \times$ 20 mL), the combined extracts were dried over MgSO<sub>4</sub> and evaporated, and the residue was purified by silica gel chromatography using petroleum ether-ethyl acetate (6:1) as eluent. Yield 0.9 g (85%), light brown crystals, mp 71–72°C. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.60 t (3H, CH<sub>3</sub>CH<sub>2</sub>, J = 7.3 Hz), 1.58 s (3H, 2-CH<sub>3</sub>), 2.11–2.15 m (2H, CH<sub>2</sub>CH<sub>3</sub>), 2.22 s (3H, CH<sub>3</sub>CO), 7.22 t (1H, 6-H, J = 7.6 Hz), 7.36 d.d (1H, 7-H, J = 7.6, 1.4 Hz), 7.67 d.d (1H, 5-H, J = 7.6, 1.4 Hz), 7.79 d (1H, 4-H, J = 7.6 Hz). <sup>13</sup>C NMR spectrum,  $\delta_{\rm C}$ , ppm: 7.98 (CH<sub>3</sub>CH<sub>2</sub>), 21.05 (CH<sub>3</sub>CO), 23.06 (2-CH<sub>3</sub>), 30.10 (CH<sub>2</sub>CH<sub>3</sub>), 72.36 (C<sup>2</sup>), 123.88 (C<sup>6</sup>), 124.21 (C<sup>4</sup>), 126.41 (C<sup>3a</sup>), 137.14 (C<sup>7</sup>), 137.22 (C<sup>5</sup>), 153.45 (C<sup>7a</sup>), 168.23 (CH<sub>3</sub>C=O), 202.24 (C<sup>3</sup>). Mass spectrum: *m/z* 217.11 [*M*]<sup>+</sup>. Found, %: C 71.79; H 6.88; N 6.51. C<sub>13</sub>H<sub>15</sub>NO<sub>2</sub>. Calculated, %: C 71.87; H 6.96; N 6.45.

2-Ethyl-2-methyl-2,3-dihydro-1H-indol-3-one (4). Compound 3, 0.6 g (2.8 mmol), was dissolved in 10 mL of THF, a solution of 0.8 g (13.8 mmol) of potassium hydroxide in 10 mL of methanol was added, and the mixture was refluxed until the initial compound disappeared (TLC). The mixture was then treated with a saturated solution of ammonium chloride and extracted with ethyl acetate  $(3 \times 20 \text{ mL})$ , the combined extracts were dried over MgSO4 and evaporated, and the residue was purified by silica gel column chromatography using petroleum ether-ethyl acetate (8:1) as eluent. Yield 0.4 g (75%), light green oil. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.82 t (3H, CH<sub>3</sub>CH<sub>2</sub>, J = 7.4 Hz), 1.30 s (3H, 2-CH<sub>3</sub>), 1.63–1.70 m and 1.76–1.82 m (1H each,  $CH_2CH_3$ ), 6.81 t (1H, 5-H, J = 7.5 Hz), 8.88 d (1H, 7-H, J = 8.0 Hz), 7.44 d.d (1H, 6-H, J = 8.0,7.5 Hz), 7.59 d (1H, 4-H, J = 7.5 Hz). <sup>13</sup>C NMR spectrum, δ<sub>C</sub>, ppm: 8.07 (CH<sub>3</sub>CH<sub>2</sub>), 22.91 (2-CH<sub>3</sub>), 30.88  $(CH_2CH_3)$ , 67.44  $(C^2)$ , 112.56  $(C^7)$ , 118.86  $(C^5)$ , 120.75 (C<sup>3a</sup>), 124.74 (C<sup>4</sup>), 137.14 (C<sup>6</sup>), 159.92 (C<sup>7a</sup>), 205.15 (C<sup>3</sup>). Mass spectrum: m/z 175.23 [M]<sup>+</sup>. Found, %: C 75.32; H 7.38; N 8.05. C<sub>11</sub>H<sub>13</sub>NO. Calculated, %: C 75.40; H 7.48; N 7.99.

**5,5'-(Selanediyl)bis(2-ethyl-2-methyl-2,3-dihydro-1***H***-indole) (5). Compound 1, 0.1 g (0.6 mmol), was dissolved in 5 mL of ethanol, 0.07 g (0.6 mmol) of SeO<sub>2</sub> in 5 mL of ethanol was added, and the mixture was refluxed until the initial compound disappeared (TLC). The mixture was diluted with 10 mL of water, the organic phase was separated and dried over MgSO<sub>4</sub>, the solvent was distilled off, and the residue was subjected to silica gel column chromatography (petroleum ether–EtOAc, 8:1). Yield 0.1 g (45%), light brown oil. <sup>1</sup>H NMR spectrum, \delta, ppm: 0.92 t (3H, CH<sub>3</sub>CH<sub>2</sub>,** *J* **= 7.3 Hz), 1.23 s (3H, 2-CH<sub>3</sub>), 1.58–1.62 m (2H, CH<sub>2</sub>CH<sub>3</sub>), 2.72 d and 2.85 d (1H each, 3-H,** *J* **= 15.7 Hz), 6.46 d (1H, 7-H,** *J* **= 7.9 Hz), 7.16 d.d (1H,**  6-H, J = 7.9, 1.4 Hz), 7.19 d (1H, 4-H, J = 1.4 Hz). <sup>13</sup>C NMR spectrum,  $\delta_{\rm C}$ , ppm: 9.02 (CH<sub>3</sub>CH<sub>2</sub>), 26.50 (2-CH<sub>3</sub>), 34.64 (CH<sub>2</sub>CH<sub>3</sub>), 41.70 (C<sup>3</sup>), 64.37 (C<sup>2</sup>), 109.49 (C<sup>7</sup>), 119.18 (C<sup>5</sup>), 129.65 (C<sup>3a</sup>), 130.27 (C<sup>4</sup>), 132.73 (C<sup>6</sup>), 149.83 (C<sup>7a</sup>). Mass spectrum: m/z 400.17  $[M]^+$ . Found, %: C 66.09; H 7.02; N 7.13. C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>Se. Calculated, %: C 66.15; H 7.07; N 7.01.

2-Ethyl-N-hydroxy-2-methyl-2,3-dihydro-1H-indol-3-imine (6). Hydroxylamine hydrochloride, 0.2 g (2.8 mmol), was added to a solution of 0.1 g (0.6 mmol) of ketone 4 in 10 mL of methanol, and the mixture was refluxed for 15 h (TLC). The solvent was distilled off, 10 mL of water was added to the residue, and the mixture was extracted with ethyl acetate  $(3 \times$ 10 mL). The combined extracts were dried over MgSO<sub>4</sub> and evaporated, and the residue was purified by silica gel chromatography (petroleum ether-EtOAc, 4:1). Yield 0.08 g (70%), yellow crystals, mp 120–121°C. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.89 t (3H, CH<sub>3</sub>CH<sub>2</sub>, J = 7.4 Hz), 1.41 s (3H, 2-CH<sub>3</sub>), 1.68–1.72 m and 1.77– 1.81 m (1H each, CH<sub>2</sub>CH<sub>3</sub>), 6.71 d (1H, 7-H, J =8.1 Hz), 6.76 t (1H, 5-H, J = 7.6 Hz), 7.26 d.d (1H, 6-H, J = 8.1, 7.6 Hz), 8.20 d (1H, 4-H, J = 7.6 Hz). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 8.16 (CH<sub>3</sub>CH<sub>2</sub>), 27.04 (2-CH<sub>3</sub>), 34.37 (CH<sub>2</sub>CH<sub>3</sub>), 64.48 (C<sup>2</sup>), 110.36 (C<sup>7</sup>), 118.42 (C<sup>5</sup>), 118.59 (C<sup>3a</sup>), 130.00 (C<sup>4</sup>), 133.02 (C<sup>6</sup>), 153.59 (C<sup>7a</sup>), 162.02 (C<sup>3</sup>). Mass spectrum: m/z 190.11 [*M*]<sup>+</sup>. Found, %: C 69.37; H 7.38; N 14.84. C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O. Calculated, %: C 69.45; H 7.42; N 14.73.

(3RS)-2-Ethyl-2-methyl-2,3-dihydro-1H-indol-3ol (7). Sodium tetrahydridoborate, 0.04 g (1.1 mmol), was added in portions with vigorous stirring to a solution of 0.1 g (0.6 mmol) of ketone 4 in 10 mL of ethanol, and the mixture was stirred until the initial ketone disappeared (TLC). The mixture was evaporated, the residue was treated with 5 mL of water and extracted with ethyl acetate  $(3 \times 10 \text{ mL})$ , the combined extracts were dried over  $MgSO_4$  and evaporated, and the residue was purified by silica gel chromatography (petroleum ether-EtOAc, 5:1). Yield 0.09 g (89%), white crystals, mp 86–87°C. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.03 [0.94] t (3H, CH<sub>3</sub>CH<sub>2</sub>, J = 7.4 Hz), 1.15 [1.24] s (3H, 2-CH<sub>3</sub>), 1.65–1.80 [1.54–1.59] m (2H, CH<sub>2</sub>CH<sub>3</sub>), 4.61 [4.73] s (1H, 3-H), 6.64 [6.60] d (1H, 7-H, *J* = 7.8 Hz), 6.77 [6.75] t (1H, 5-H, *J* = 7.3 Hz), 7.14 [7.12] d.d (1H, 6-H, J = 7.8, 7.3 Hz), 7.32 [7.28] d (1H, 4-H, J = 7.3 Hz). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 8.36 [8.58] (CH<sub>3</sub>CH<sub>2</sub>), 23.76 [18.93] (2-CH<sub>3</sub>), 27.39 [33.01] (CH<sub>2</sub>CH<sub>3</sub>), 66.43 [67.16] (C<sup>2</sup>), 79.31 [78.84]  $(C^3)$ , 110.56 [110.05]  $(C^7)$ , 119.03 [118.73]  $(C^5)$ ,

126.13 [125.66] (C<sup>4</sup>), 129.86 [129.66] (C<sup>6</sup>), 130.15 [129.97] (C<sup>3a</sup>), 149.59 [149.43] (C<sup>7a</sup>). Mass spectrum: m/z 177.12  $[M]^+$ . Found, %: C 74.49; H 8.47; N 7.98. C<sub>11</sub>H<sub>15</sub>NO. Calculated, %: C 74.54; H 8.53; N 7.90.

2-Aminobenzonitrile (8). A solution of 0.1 mL of thionyl chloride in 5 mL of methylene chloride was added dropwise to a solution of 0.1 g (0.5 mmol) of oxime 6 in 5 mL of methylene chloride, and the mixture was stirred until the initial oxime disappeared (TLC). The mixture was treated with 20 mL of a saturated aqueous solution of sodium chloride, the organic phase was separated, and the aqueous phase was extracted with methylene chloride ( $3 \times 10$  mL). The combined extracts were dried over MgSO4 and evaporated, and the residue was subjected to silica gel chromatography (petroleum ether-EtOAc, 8:1) to isolate 0.04 g (60%) of 8 as a light yellow oily material. <sup>1</sup>H NMR spectrum, δ, ppm: 6.74 d.d.d (1H, 5-H, J = 8.2, 7.3, 1.6 Hz), 6.76 d.d (1H, 6-H, J = 7.3, 1.6 Hz), 7.33 t.d (1H, 4-H, J = 8.2, 1.6 Hz), 8.39 d.d (1H, 3-H, J = 8.2, 1.6 Hz). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 96.04 (CN), 115.15 (C<sup>6</sup>), 117.63 (C<sup>1</sup>), 118.03 (C<sup>5</sup>), 132.38 (C<sup>3</sup>), 134.03 (C<sup>4</sup>), 149.56 (C<sup>2</sup>). Mass spectrum: m/z 118.05  $[M]^+$ . Found, %: C 71.11; H 5.08; N 23.81. C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>. Calculated, %: C 71.17; H 5.12; N 23.71.

2-Ethyl-2-methyl-2*H*-indole-3,5-dione 1-oxide (11a) and 2-ethyl-2-methyl-2*H*-indole-3,7-dione 1-oxide (11b). A solution of 0.17 g (1.0 mmol) of ketone 4 in 5 mL of methylene chloride was added dropwise to a suspension of 0.84 g (4.8 mmol) of *m*-chloroperoxybenzoic acid in 10 mL of anhydrous methylene chloride, and the mixture was stirred at room temperature until the initial ketone disappeared (TLC). The mixture was treated with a saturated aqueous solution of sodium hydrogen carbonate and extracted with methylene chloride ( $3 \times 15$  mL), the combined extracts were washed with brine, dried over magnesium sulfate, and evaporated, and the products were isolated by silica gel chromatography (petroleum ether–EtOAc, 9:1).

Compound **11a**. Yield 0.07 g (36%), dark red oily material. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.72 t (3H, C**H**<sub>3</sub>CH<sub>2</sub>, J = 7.4 Hz), 1.50 s (3H, 2-CH<sub>3</sub>), 1.95–2.04 m (2H, C**H**<sub>2</sub>CH<sub>3</sub>), 6.68 s (1H, 4-H), 6.76 d (1H, 6-H, J = 9.7 Hz), 7.72 d (1H, 7-H, J = 9.7 Hz). <sup>13</sup>C NMR spectrum,  $\delta_{\rm C}$ , ppm: 7.79 (CH<sub>3</sub>CH<sub>2</sub>), 20.33 (2-CH<sub>3</sub>), 28.61 (CH<sub>2</sub>CH<sub>3</sub>), 82.54 (C<sup>2</sup>), 119.84 (C<sup>4</sup>), 122.07 (C<sup>7</sup>), 135.21 (C<sup>3a</sup>), 135.22 (C<sup>6</sup>), 142.69 (C<sup>7a</sup>), 186.33 (C<sup>5</sup>), 196.04 (C<sup>3</sup>). Mass spectrum: m/z 205.08 [M]<sup>+</sup>.

Found, %: C 62.75; H 6.37; N 11.36.  $C_{11}H_{11}NO_3$ . Calculated, %: C 62.89; H 6.50; N 11.28.

Compound **11b**. Yield 0.03 g (13%), light red oily material. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.75 t (3H, C**H**<sub>3</sub>CH<sub>2</sub>, *J* = 7.4 Hz), 1.53 s (3H, 2-CH<sub>3</sub>), 1.99–2.10 m (2H, C**H**<sub>2</sub>CH<sub>3</sub>), 6.91 d (1H, 4-H, *J* = 9.6 Hz), 7.05 d (1H, 6-H, *J* = 6.3 Hz), 7.41 d.d (1H, 5-H, *J* = 9.6, 6.3 Hz). <sup>13</sup>C NMR spectrum,  $\delta_{\rm C}$ , ppm: 7.75 (CH<sub>3</sub>CH<sub>2</sub>), 20.53 (2-CH<sub>3</sub>), 28.82 (CH<sub>2</sub>CH<sub>3</sub>), 84.15 (C<sup>2</sup>), 118.44 (C<sup>6</sup>), 131.22 (C<sup>3a</sup>), 136.72 (C<sup>6</sup>), 137.00 (C<sup>5</sup>), 142.40 (C<sup>7a</sup>), 173.73 (C<sup>7</sup>), 194.88 (C<sup>3</sup>). Mass spectrum: *m*/*z* 205.08 [*M*]<sup>+</sup>. Found, %: C 62.71; H 6.39; N 11.39. C<sub>11</sub>H<sub>11</sub>NO<sub>3</sub>. Calculated, %: C 62.89; H 6.50; N 11.28.

### ACKNOWLEDGMENTS

The analytical data were obtained using the equipment of the Chemistry joint center (Ufa Institute of Chemistry, Russian Academy of Sciences).

#### FUNDING

This study was performed in the framework of state assignment (project nos. AAAA-A19-119020890014-7, AAAA-A17-117011910027-0.

## CONFLICT OF INTEREST

The authors declare the absence of conflict of interest.

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