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$Fe(CrO_2)_2$-catalyzed, photoactivated oxidative one-pot tandem synthesis of substituted quinolines from primary alcohols and arylamines

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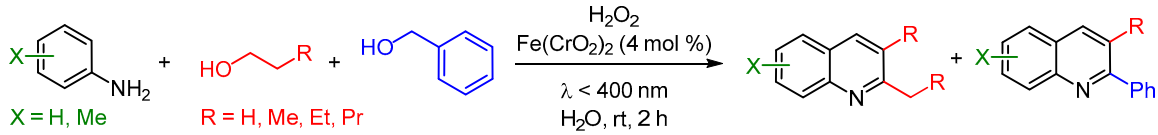


A one-pot tandem synthesis of substituted quinolines involving selective catalytic oxidation of primary alcohols to the corresponding aldehydes and their subsequent condensation with arylamines has been developed. $Fe(CrO_2)_2$ has been used as a catalyst, and oxidation has been performed with aqueous H_2O_2. To accelerate the catalytic oxidation of alcohols, photoactivation method has been applied.

Keywords: arylamines, primary alcohols, substituted quinolines, iron-containing catalyst, photoactivation.

Development of processes based on catalytic oxidation of alcohols to the corresponding aldehydes or ketones and their exploitation in subsequent synthesis of various classes of organic substances is of special scientific and practical interest. As a rule, these chemical transformations are related to tandem syntheses involving two or more bond-forming transformations and proceeding in a one-pot mode where the subsequent reaction is the consequence of the active intermediate formation in the previous chemical transformation. The considerable availability and stability of alcohols make them valuable reagents. The tandem approach has been successfully implemented in synthesis of esters,[1] amides,[2] alkenes,[3] heterocyclic compounds,[4] C–H activation products,[5] and acetals.[6] Catalytic systems in these syntheses possess two main functions. The first function is oxidation of the alcohol to the corresponding carbonyl compound (mainly *via* transfer of hydrogen atoms to the acceptor compounds). The second function is catalysis of the reaction of aldehydes or ketones with various organic substrates to afford the desired products. Catalytic systems based on ruthenium complexes $[Ru(PPh_3)_3(CO)(H)_2]$ and $[Ru(p\text{-cymene})Cl_2]_2$ have been described in detail.[7] Crotononitrile has been usually exploited as a hydrogen acceptor, and anhydrous and anaerobic environment is essential for tandem synthesis involving ruthenium catalysts.

Tandem syntheses have been successfully used to construct practically important nitrogen heterocyclic compounds. For example, 2,3-dialkylindoles were obtained in the reaction of aniline and vicinal diols in the presence of iridium and ruthenium complexes at 170°C within 24 h.[8] Synthesis of substituted quinolines from alcohols and arylamines in CCl_4 has been also described.[9] The reaction proceeded in a pulp digester at 140°C with a fractional charge of the reagents within 4 h. Iron-containing compounds were screened for effective catalytic activity in this chemical transformation.

A feature of iron compounds is their variable valency ($Fe^{3+} + e^- \leftrightarrow Fe^{2+}$) which allows them to act as mediators of redox processes.[10] As a rule, trivalent iron compounds are oxidants of organic substances.[11] The oxidative properties of Fe^{3+} ions are excellently activated not only thermally but also under ultraviolet (UV) irradiation. Thus, photooxidation of primary aliphatic alcohols using $FeCl_3$ has been described.[11,12] The reaction is completed with total reduction of Fe^{3+} ions, and the composition of the mixture of products depends on the conditions of the process (pH, the presence of H_2O in the system, etc.). Aerobic photocatalytic oxidation of H_2O–alcohol mixtures in the presence of $FeCl_3$ and $NaNO_2$ leads to selective formation of aldehydes.[12]

In this paper, we present the results of the study of a one-pot tandem synthesis of substituted quinolines based on selective catalytic oxidation of primary alcohols to aldehydes and their subsequent condensation reaction with arylamines promoted by iron chromite ($Fe(CrO_2)_2$) and an oxidizer – 5 wt % aq H_2O_2. The investigated tandem synthesis, in contrast to the known methods,[7,9] was carried out in a single batch at room temperature and atmospheric pressure in an environmentally safe aqueous medium. To accelerate the chemical transformations, the photoactiva-

tion method was tested. The heterogeneous catalyst – $Fe(CrO_2)_2$ was synthesized by a photochemical method.

Photochemical synthesis of the $Fe(CrO_2)_2$ catalyst. $Fe(CrO_2)_2$ was chosen as a heterogeneous catalyst for the tandem synthesis of substituted quinolines. The uniqueness of the selected catalyst lies in the fact that it exhibits catalytic activity both in the oxidation of primary alcohols to the corresponding aldehydes with aq H_2O_2 and the condensation reaction of aldehydes and arylamines. This feature of $Fe(CrO_2)_2$ made it possible to combine the oxidation and condensation reactions into a single tandem synthesis.

A number of works have been devoted to the problems of catalytic oxidation of organic substances, including alcohols, by a solution of H_2O_2 in the presence of divalent iron compounds.[13] Such conditions are referred as the Fenton reaction. Usually, the oxidation process is directed to the complete destruction of organic substances. However, the Fenton reaction finds considerable application in synthetic practice.[14] Therefore, in order to avoid a complete oxidation of alcohols to carboxylic acids and CO_2, diluted aq H_2O_2 (5 wt %) and less active, insoluble divalent iron compound – $Fe(CrO_2)_2$ as a catalyst have been used in this work. Consequently, the stage of oxidation of alcohols in tandem synthesis can be considered as a special case of the Fenton reaction. The catalytic activity of iron compounds in the condensation reaction of aldehydes and aniline to afford different quinolines has been described previously.[15] A significant advantage of $Fe(CrO_2)_2$ lies in the possibility of carrying out heterogeneous catalysis because, after the completion of the tandem process, the catalyst may be easily separated from the reaction products by simple decantation or filtration. The catalytic activity of heterogeneous $Fe(CrO_2)_2$, as indicated by the conversion of the initial arylamines and the yield of the desired reaction products, is not inferior to the performance of the known homogeneous catalyst – $FeCl_3 \cdot 6H_2O$.[16]

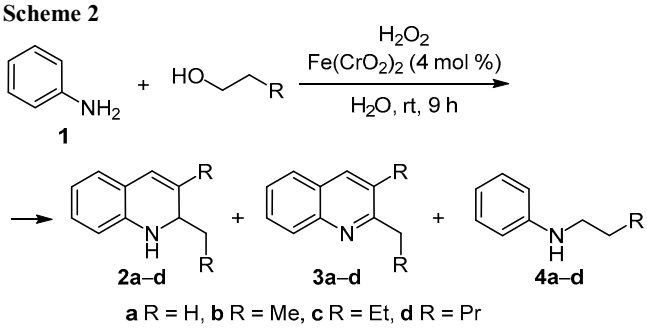
Catalyst $Fe(CrO_2)_2$ was synthesized in a photochemical reaction of $FeCl_3 \cdot 6H_2O$ and $K_2Cr_2O_7$ in H_2O–EtOH solution (Scheme 1). The reaction proceeded under the irradiation with Hg lamp at 20°C for 1 h. The developed photochemical method allowed to isolate $Fe(CrO_2)_2$ in quantitative yield. The resulting catalyst was a finely dispersed, black-brown powder.

Scheme 1

$$4FeCl_3 + 4K_2Cr_2O_7 + 7EtOH \xrightarrow[\text{rt, 1 h}]{\lambda < 400\ \text{nm}} 4Fe(CrO_2)_2 + 8KCl + 4HCl + 5H_2O + 7AcOH$$

Effect of the amount of H_2O_2 on the yield of tandem synthesis products. The $Fe(CrO_2)_2$-catalyzed reaction of aniline (**1**) and primary aliphatic alcohols in the presence of H_2O_2 is shown in Scheme 2. Products of the initially selected model reaction of EtOH and aniline (**1**) were 2-methyl-1,2-dihydroquinoline (**2a**), a stable precursor of the desired product 2-methylquinoline (**3a**), and a by-product *N*-ethylaniline (**4a**). The presented tandem process

Scheme 2



was developed on the basis of the previously studied two-stage catalytic synthesis of 2,3-dialkylquinolines by condensation of aniline (**1**) and photooxidation products of alcohols in the presence of $FeCl_3 \cdot 6H_2O$.[17]

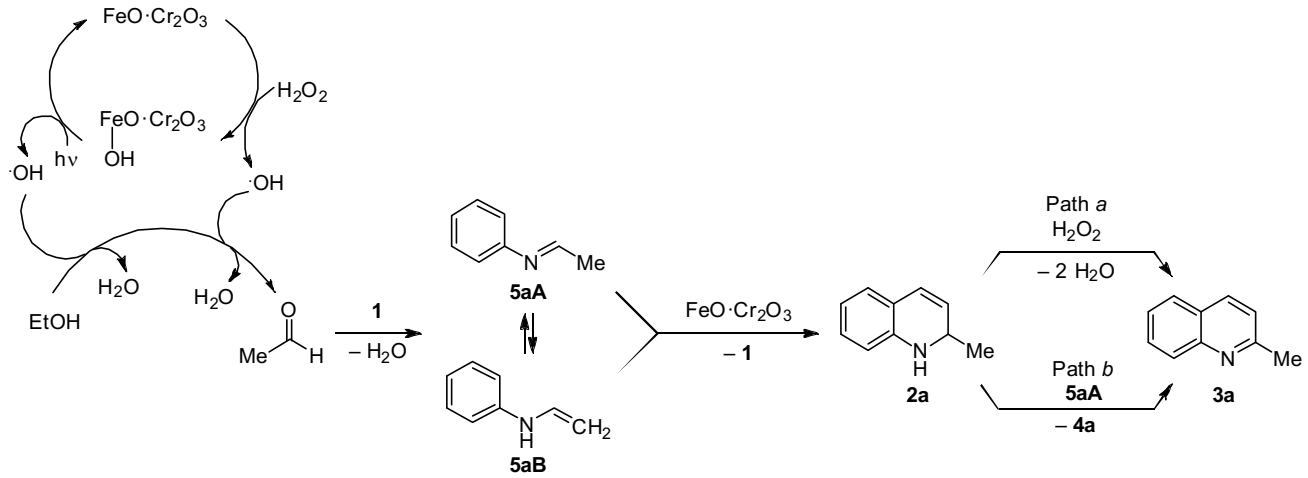
The efficiency of the tandem synthesis was estimated according to the conversion of the starting material **1**. The maximum conversion of compound **1** (62%) to afford product **3a** was achieved in the presence of 1.5 equiv (with respect to the alcohol) of H_2O_2 (Table 1, entry 1). In addition, decrease in the amount of H_2O_2 to equimolar reduced the conversion of aniline (**1**) to 44% and ensured

Table 1. Effect of the structure of alcohol RCH_2CH_2OH, amount of H_2O_2, and photoactivation on the conversion of aniline (**1**) and composition of the mixture of tandem synthesis products **2a–d**, **3a–d**, and **4a–d***

Entry	R	Conversion of aniline (**1**)**, %	Composition of the mixture of reaction products**, %		
		15 mmol (1.5 equiv) H_2O_2			
1	H	62	**2a** (–)	**3a** (98)	**4a** (2)
2	Me	60	**2b** (–)	**3b** (96)	**4b** (4)
3	Et	57	**2c** (–)	**3c** (95)	**4c** (5)
4	Pr	52	**2d** (–)	**3d** (92)	**4d** (8)
		10 mmol (1.0 equiv) H_2O_2			
5	H	44	**2a** (50)	**3a** (38)	**4a** (12)
6	Me	41	**2b** (54)	**3b** (34)	**4b** (12)
7	Et	38	**2c** (56)	**3c** (31)	**4c** (13)
8	Pr	33	**2d** (61)	**3d** (24)	**4d** (15)
		5 mmol (0.5 equiv) H_2O_2			
9	H	29	**2a** (62)	**3a** (22)	**4a** (16)
10	Me	25	**2b** (63)	**3b** (20)	**4b** (17)
11	Et	22	**2c** (62)	**3c** (20)	**4c** (18)
12	Pr	20	**2d** (63)	**3d** (19)	**4d** (18)
		Photoactivation, 150 mmol (1.25 equiv) H_2O_2***			
13	H	98	**2a** (–)	**3a** (97)	**4a** (3)
14	Me	92	**2b** (–)	**3b** (95)	**4b** (5)
15	Et	89	**2c** (–)	**3c** (95)	**4c** (5)
16	Pr	87	**2d** (–)	**3d** (91)	**4d** (9)
17	H (Ph)*[4]	>99	**2a** (–)	**3a** (24) **3e** (66)	**4a** (8) **4e** (2)

* Reaction conditions: $Fe(CrO_2)_2$ (4 mol %), RCH_2CH_2OH (10 mmol), aq H_2O_2 (5 wt %), rt, 9 h, then aniline (**1**) (5 mmol), rt, 5 min.
** Determined by GC.
*** Reaction conditions: $Fe(CrO_2)_2$ (4 mol %), RCH_2CH_2OH (120 mmol), aq H_2O_2 (5 wt %, 150 mmol), λ <400 nm, rt, 2 h, then aniline (**1**) (50 mmol), rt, 5 min.
*[4] Equimolar mixture of EtOH and BnOH was exploited.

Scheme 3



the formation of products **2a**, **3a**, and **4a** with a molar ratio of 4:3:1 (entry 5). Intermediate **2a** could be easily oxidized to 2-methylquinoline (**3a**) by input of an additional amount of H_2O_2. With a further decrease in the amount of H_2O_2 to 0.5 equiv, the conversion of the starting material **1** was only 29%, and the formation of compound **4a** was slightly favored, as indicated by the molar ratio of the products (entry 9).

Oxidation of EtOH to acetaldehyde by H_2O_2 in the presence of the catalyst $Fe(CrO_2)_2$ (4 mol %) was the slowest reaction of the tandem synthesis and proceeded at 20°C for 9 h. An attempt to accelerate the oxidation step by increasing temperature favored the formation of a mixture of oxidation products and their derivatives – acetaldehyde, 1,1-diethoxyethane, AcOH, EtOAc, and CO_2. Consequently, the tendency of aldehyde formation decreases at elevated temperatures leading to poor selectivity in the condensation reaction stage of the tandem synthesis.

The photoactivation method for increasing the efficiency of tandem synthesis of 2-methylquinoline (3a). In order to accelerate the oxidation of EtOH and improve the selectivity toward acetaldehyde, the photoactivation method was applied. It is known that UV irradiation enhances the productivity of the photo-Fenton reaction due to the expedited hydroxyl radical generation stage: $Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \cdot OH$.[18] As established earlier, the photogenerated radicals ·OH can easily and selectively oxidize H_2O–alcohol mixtures to aldehydes in the presence of $FeCl_3 \cdot 6H_2O$.[12] The approach of the photogeneration of ·OH radicals allowed to improve the overall efficiency of the tandem synthesis of 2-methylquinoline (**3a**) by increasing the selectivity of the oxidation of EtOH and reducing the reaction time to 2 h.

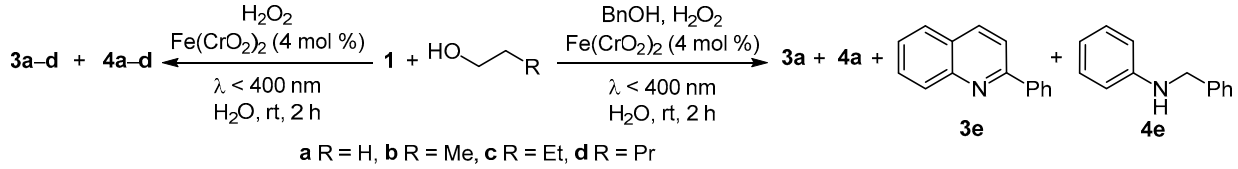
The presumptive mechanism of the photoactivated EtOH oxidation to acetaldehyde and its further condensation with aniline (**1**) in the presence of $Fe(CrO_2)_2$ and aq H_2O_2 (1.25 equiv relative to the alcohol) is shown in Scheme 3. As a result of interaction of H_2O_2 and FeO, the catalyst $Fe(CrO_2)_2$ (or $FeO \cdot Cr_2O_3$) is oxidized to Fe(OH)O, and hydroxyl radical ·OH is formed. Absorbing a quantum of the Hg lamp irradiation, the oxidized form of Fe(OH)O is degraded by releasing ·OH, and the catalyst is restored to the original form. Thus, there is a cyclic photoredox process that generates two hydroxyl radicals during one catalytic cycle.

In aqueous medium, EtOH is selectively oxidized to acetaldehyde by hydroxyl radicals.[12] The reaction of aniline (**1**) with acetaldehyde gives a Schiff base existing in two tautomeric forms: aldimine **5aA** and enamine **5aB**. Interaction of these compounds in the presence of catalyst $Fe(CrO_2)_2$ leads to 2-methyl-1,2-dihydroquinoline (**2a**).[19] The final product **3a** is formed in oxidation of compound **2a** by H_2O_2 according to path *a*. However, when H_2O_2 is deficient, azomethine **5aA** can also function as an oxidizing agent, and by-product **4a** is formed (path *b*). A more detailed study of the photoactivated catalytic tandem process mechanism is the subject of further work.

The influence of the structure of alcohol and arylamine on tandem synthesis. The influence of the structure of primary aliphatic alcohol on the conversion of the starting material **1** and the yield of the reaction products **2**, **3**, and **4 a–d** was studied (Scheme 2, Table 1). Increase in the length of the hydrocarbon radical of the alcohol caused a decrease in the conversion of aniline (**1**). In the presence of excess oxidant (1.5 equiv H_2O_2), selective conversion of starting material **1** to substituted quinolines **3a–d** occurred (Table 1, entries 1–4). However, as in the case of the model system, a decrease in the amount of oxidant affected the composition of the reaction product mixture. 1,2-Dihydroquinolines **2a–d** and *N*-alkylanilines **4a–d** were obtained along with products **3a–d** when an equimolar amount of H_2O_2 was used (entries 5–8). It is evident that the proportion of 1,2-dihydroquinolines increases with the length of the alkyl radical of the alcohol. Moreover, in the presence of 0.5 equiv of oxidizing agent, conversion of aniline (**1**) was significantly lower and the amount of *N*-alkylanilines **4a–d** in the reaction mixture increased with the length of the alkyl radical of the alcohol (entries 9–12).

Under the conditions of photoactivated tandem synthesis, conversion of the starting material **1** and the yield of the desired products **3a–d** were the highest and did not depend on the structure of the investigated alcohols

Scheme 4

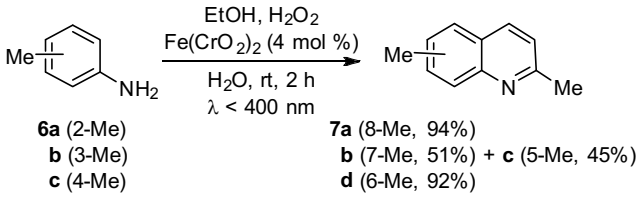


(Scheme 4, Table 1, entries 13–16). The products of tandem synthesis with aliphatic alcohols were 2,3-disubstituted quinolines **3a**–**d** and *N*-alkylanilines **4a**–**d**. 1,2-Dihydroquinolines **2a**–**d** were not found in the reaction mixture because they were completely oxidized by H_2O_2.

When equimolar mixture of EtOH and benzyl alcohol (BnOH) was exploited in the synthesis, formation of 2-phenylquinoline (**3e**), 2-methylquinoline (**3a**), and small amount of by-products **4a**,**e** was observed (Scheme 4). As indicated by the experimental data, the ratio of the products was shifted toward compound **3e** (Table 1, entry 17). Consequently, the more favorable direction of photoactivated tandem synthesis with a mixture of aliphatic and aromatic alcohols is the formation of 2-aryl-substituted quinolines.

The effect of the structure of arylamines was tested in the reaction of *o*-, *m*-, and *p*-toluidines **6a**–**c** and EtOH (Scheme 5). The presence and different location of the methyl group in the benzene ring did not affect the conversion of arylamines (in all cases 98%). The yield of the desired products – dimethylquinolines **7a**–**d** was up to 96%.

Scheme 5



6a (2-Me)
b (3-Me)
c (4-Me)

7a (8-Me, 94%)
b (7-Me, 51%) + **c** (5-Me, 45%)
d (6-Me, 92%)

In conclusion, study of the tandem synthesis consisting of selective catalytic oxidation of primary alcohols to the corresponding aldehydes and their condensation with arylamines in the presence of a heterogeneous catalyst – $Fe(CrO_2)_2$ and an oxidizer H_2O_2 has been presented. The catalyst $Fe(CrO_2)_2$ was obtained by the photochemical synthesis. The developed reaction sequence afforded the desired products – alkyl- and aryl-substituted quinolines in high yield. The concentration of the oxidizer and exploitation of photoactivation has the greatest effect on the yield of the products. In the case of photoactivation, the tandem synthesis of substituted quinolines is accelerated and their yield is increased. A probable mechanism of photoactivated tandem synthesis of 2-methylquinoline is proposed.

Experimental

^1H and ^{13}C NMR spectra were acquired on a Bruker Avance III pulsed spectrometer (500 and 125 MHz, respectively) using $CDCl_3$ as a solvent and TMS as internal standard. A gas chromatograph–mass spectrometer Shimadzu QP2010 Ultra, equipped with a Restek Rtx-5MS column (length 30 m, internal diameter 0.25 mm, thickness of a liquid film 0.25 μm), was used to identify the products of the tandem synthesis; electron ionization (70 eV). The composition of the mixture of reaction products was established using a hardware-software complex based on Khromatek Kristall 5000.1 (with an electron capture detector – ECD) and 5000.2 (with a flame ionization detector – FID) chromatographs, equipped with Agilent Technologies 19091F-413 HP-FFAP (30 m × 0.32 mm, 0.25 μm) and SGE Analytical Science (30 m × 0.32 mm, 0.5 μm) columns, respectively. For calibration, standard solutions of reaction products **3a**–**e** and **4a**–**e** with a concentration of 0.01 M, 0.05 M, and 0.1 M in Et_2O were used. Standard compounds **3a**–**e** and **4a**–**e** were synthesized and isolated according to the method reported previously.[17] Commercially available substituted anilines **6a**–**c** (Acros), aliphatic alcohols (EKOS-1) were distilled prior to use as the starting materials. Chemically pure $FeCl_3 \cdot 6H_2O$ (Brom) and $K_2Cr_2O_7$ (Russkiy khrom) were exploited without additional purification.

Tandem synthesis of substituted quinolines 3a–d without photoactivation (General method). The synthesis was carried out in a 20-ml glass vial with constant stirring by means of a magnetic stirrer. To a finely dispersed $Fe(CrO_2)_2$ (90 mg, 4 mol %), the corresponding alcohol (10 mmol) was added. The mixture was then shaken and left for 24 h. Just before the reaction, the suspension of the catalyst in alcohol was subjected to ultrasonic treatment for 10 min. To the obtained suspension, aq H_2O_2 (5 wt %, 10 ml, 15 mmol) was added. The reaction mixture was stirred at room temperature and atmospheric pressure for 9 h. Then aniline (**1**) (466 mg, 5 mmol) was added and stirring was continued for 5 min. After completion of the reaction, the mixture was extracted with Et_2O (10 ml). The upper organic phase was separated, dried with anhydrous $MgSO_4$, and Et_2O was removed under reduced pressure. The residue was fractionally distilled under reduced pressure to afford products **3a**–**d**.

Photoactivated tandem synthesis of substituted quinolines 3a–e, 4a–e, and 7a–d (General method). Synthesis was carried out in a Lelesil Innovative Systems photocatalytic reactor with a 500-ml quartz reactor. $Fe(CrO_2)_2$ (1.07 g, 4 mol %) and the corresponding alcohol (120 mmol) were placed in the reactor flask, shaken, and left for 24 h. Just before the reaction, the suspension of the catalyst in alcohol was subjected to ultrasonic treatment for 10 min. To the obtained suspension, aq H_2O_2 (5 wt %, 102 ml, 150 mmol) was added. The reactor was connected to the installation in accordance with the manufacturer's instructions. The source of the radiation was a medium-pressure

Hg lamp with a power of 250 W. The spectral composition of the radiation was as follows (in terms of energy): UV (48%), visible (43%), and IR (9%). The range of wavelengths was 222–1368 nm. A light flux reached the reaction system passing through an aqueous layer thermostated at 20°C. Photoactivation was performed within 2 h. Then, aniline (**1**) (4.66 g, 50 mmol) or arylamine **6a**–**c** (50 mmol) was added. The reaction mixture was stirred for 5 min. After completion of the reaction, the mixture was extracted with Et_2O (100 ml). The upper organic phase was separated, dried with anhydrous $MgSO_4$, and Et_2O was removed under reduced pressure. The residue was fractionally distilled under reduced pressure to afford products **3a**–**e**, **4a**–**e**, and **7a**–**d**.

The physicochemical parameters and spectroscopic characteristics of the reaction products **3a**–**e**, **4a**–**e**, and **7a**–**d** correspond to the literature data.[9,20]

2-Methyl-1,2-dihydroquinoline (2a). Mass spectrum, *m*/*z* (I_{rel}, %): 145 $[M]^+$ (23), 144 (33), 143 (97), 130 (100).

2-Ethyl-3-methyl-1,2-dihydroquinoline (2b). Mass spectrum, *m*/*z* (I_{rel}, %): 173 $[M]^+$ (19), 172 (41), 171 (94), 144 (100).

3-Ethyl-2-propyl-1,2-dihydroquinoline (2c). Mass spectrum, *m*/*z* (I_{rel}, %): 201 $[M]^+$ (22), 200 (37), 199 (96), 156 (100).

2-Butyl-3-propyl-1,2-dihydroquinoline (2d). Mass spectrum, *m*/*z* (I_{rel}, %): 229 $[M]^+$ (28), 228 (35), 227 (91), 172 (100).

2-Methylquinoline (3a). Yield 6.7 g (97%), yellow oily liquid, bp 80–81°C (2 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.78 (3H, s, CH_3); 7.22 (1H, d, *J* = 8.0, H-3); 7.46 (1H, t, *J* = 7.5, H-6); 7.68 (1H, t, *J* = 7.5, H-7); 7.73 (1H, d, *J* = 9.2, H-5); 7.97 (1H, d, *J* = 8.0, H-8); 8.03 (1H, d, *J* = 7.5, H-4). ^{13}C NMR spectrum, δ, ppm: 25.1; 121.7; 125.4; 126.3; 127.4; 128.8; 129.2; 135.8; 147.8; 158.7. Mass spectrum, *m*/*z* (I_{rel}, %): 143 $[M]^+$ (100), 128 (20), 115 (22).

2-Ethyl-3-methylquinoline (3b). Yield 7.5 g (95%), yellow oily liquid, bp 97–99°C (2 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.38 (3H, t, *J* = 7.2, $CH_2C\underline{H}_3$); 2.38 (3H, s, CH_3); 2.96 (2H, q, *J* = 7.6, CH_2); 7.40 (1H, t, *J* = 8.0, H-7); 7.58 (1H, t, *J* = 8.0, H-6); 7.62 (1H, d, *J* = 8.0, H-5); 7.70 (1H, s, H-4); 8.06 (1H, d, *J* = 8.0, H-8). ^{13}C NMR spectrum, δ, ppm: 12.8; 18.6; 29.4; 125.6; 126.7; 127.3; 128.2; 128.5; 129.3; 135.6; 146.7; 163.2. Mass spectrum, *m*/*z* (I_{rel}, %): 172 (12), 171 $[M]^+$ (100), 170 (73), 168 (21), 143 (26), 128 (16), 77 (13).

3-Ethyl-2-propylquinoline (3c). Yield 8.3 g (95%), yellow oily liquid, bp 118°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.97 (3H, t, *J* = 7.2, $CH_2CH_2C\underline{H}_3$); 1.11 (3H, t, *J* = 7.2, $CH_2C\underline{H}_3$); 1.80–1.90 (2H, m, $CH_2C\underline{H}_2CH_3$); 2.82 (2H, q, *J* = 7.2, $C\underline{H}_2CH_3$); 2.99 (2H, t, *J* = 8.0, $C\underline{H}_2CH_2CH_3$); 7.44 (1H, t, *J* = 8.0, H-7); 7.62 (1H, t, *J* = 7.2, H-6); 7.72 (1H, d, *J* = 7.6, H-5); 7.84 (1H, s, H-4); 8.08 (1H, d, *J* = 8.0, H-8). ^{13}C NMR spectrum, δ, ppm: 14.4; 14.5; 22.9; 25.2; 37.8; 125.6; 126.9; 127.5; 128.4; 129.2; 133.9; 146.4; 162.1. Mass spectrum, *m*/*z* (I_{rel}, %): 199 $[M]^+$ (27), 170 (14), 158 (17), 157 (100).

2-Butyl-3-propylquinoline (3d). Yield 9.0 g (91%), yellow oily liquid, bp 143°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.13 (3H, t, *J* = 7.2, $(CH_2)_2CH_2C\underline{H}_3$); 1.25 (3H, t, *J* = 7.2, $CH_2CH_2C\underline{H}_3$); 1.38 (2H, m, $(CH_2)_2C\underline{H}_2CH_3$); 1.71 (2H, m, $CH_2C\underline{H}_2CH_3$); 1.75 (2H, m, $CH_2C\underline{H}_2CH_2CH_3$); 2.72 (2H, t, *J* = 7.5, $C\underline{H}_2(CH_2)_2CH_3$); 2.81 (2H, t, *J* = 7.2, $C\underline{H}_2CH_2CH_3$); 7.53 (1H, t, *J* = 7.8, H-6); 7.62 (1H, t, *J* = 7.8, H-7); 7.65 (1H, s, H-4); 7.78 (1H, d, *J* = 7.8, H-5); 8.01 (1H, d, *J* = 7.9, H-8). ^{13}C NMR spectrum, δ, ppm: 13.4; 13.9; 22.8; 23.2; 31.9; 34.4; 35.7; 125.5; 126.9; 127.2; 128.3; 128.5; 130.2; 134.2; 146.8; 161.1. Mass spectrum, *m*/*z* (I_{rel}, %): 227 $[M]^+$ (25), 184 (11), 157 (100), 115 (12).

2-Phenylquinoline (3e). Yield 6.7 g (66%), pale-yellow powder, mp 82°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.46–7.74 (5H, m, H Ar); 7.79 (1H, d, *J* = 8.4, H-4); 7.89 (1H, d, *J* = 8.8, H-3); 8.11–8.16 (3H, m, H-5,6,7); 8.19–8.22 (1H, m, H-8). ^{13}C NMR spectrum, δ, ppm: 119.5; 127.1; 127.2; 127.7; 127.8; 128.2; 129.1; 130.4; 131.8; 137.2; 139.0; 145.9; 157.9. Mass spectrum, *m*/*z* (I_{rel}, %): 206 (21), 205 $[M]^+$ (100), 204 (53), 102 (20).

***N*-Ethylaniline (4a)**. Yield 178 mg (3%), pale-yellow oily liquid, bp 72–73°C (10 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.30 (3H, t, *J* = 7.2, CH_3); 3.21 (2H, q, *J* = 7.2, CH_2); 3.65 (1H, br. s, NH); 6.66 (2H, d, *J* = 7.6, H-2,6); 6.74 (1H, t, *J* = 7.6, H-4); 7.21 (2H, t, *J* = 7.6, H-3,5). ^{13}C NMR spectrum, δ, ppm: 14.9; 38.5; 112.9; 117.2; 129.3; 148.5. Mass spectrum, *m*/*z* (I_{rel}, %): 121 $[M]^+$ (50), 106 (100), 93 (10), 79 (15), 77 (20), 44 (15).

***N*-Propylaniline (4b)**. Yield 310 mg (5%), yellow oily liquid, bp 96°C (10 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.13 (3H, t, *J* = 7.2, CH_3); 1.77 (2H, m, $CH_2C\underline{H}_2CH_3$); 3.20 (2H, t, *J* = 7.0, $C\underline{H}_2CH_2CH_3$); 3.72 (1H, br. s, NH); 6.75 (2H, d, *J* = 8.2, H-2,6); 6.84 (1H, t, *J* = 8.1, H-4); 7.24 (2H, t, *J* = 8.0, H-3,5). ^{13}C NMR spectrum, δ, ppm: 11.8; 22.9; 45.9; 112.8; 117.2; 129.5; 148.7. Mass spectrum, *m*/*z* (I_{rel}, %): 135 $[M]^+$ (17), 106 (100), 77 (21).

***N*-Butylaniline (4c)**. Yield 332 mg (5%), yellow oily liquid, bp 112–113°C (10 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.35 (3H, t, *J* = 7.6, CH_3); 1.38–1.52 (2H, m, $(CH_2)_2C\underline{H}_2CH_3$); 1.52–1.70 (2H, m, $CH_2C\underline{H}_2CH_2CH_3$); 3.10 (2H, t, *J* = 6.8, $C\underline{H}_2(CH_2)_2CH_3$); 3.81 (1H, br. s, NH); 6.61 (2H, d, *J* = 7.6, H-2,6); 6.71 (1H, t, *J* = 6.8, H-4); 7.19 (2H, t, *J* = 7.2, H-3,5). ^{13}C NMR spectrum, δ, ppm: 13.8; 22.9; 30.2; 43.3; 112.7; 117.1; 129.2; 148.6. Mass spectrum, *m*/*z* (I_{rel}, %): 149 $[M]^+$ (20), 106 (100), 77 (14).

***N*-Pentylaniline (4d)**. Yield 639 mg (9%), yellow oily liquid, bp 124–125°C (10 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.39 (3H, t, *J* = 7.0, CH_3); 1.42–1.53 (2H, m, $(CH_2)_3C\underline{H}_2CH_3$); 1.55–1.70 (2H, m, $(CH_2)_2C\underline{H}_2CH_2CH_3$); 1.74–1.98 (2H, m, $CH_2C\underline{H}_2(CH_2)_2CH_3$); 3.06 (2H, t, *J* = 7.4, $C\underline{H}_2(CH_2)_3CH_3$); 3.92 (1H, br. s, NH); 6.76 (2H, d, *J* = 8.0, H-2,6); 7.03 (1H, t, *J* = 8.0, H-4); 7.24 (2H, t, *J* = 8.0, H-3,5). ^{13}C NMR spectrum, δ, ppm: 13.9; 22.6; 29.5; 32.3; 43.2; 112.9; 124.7; 129.2; 147.7. Mass spectrum, *m*/*z* (I_{rel}, %): 163 $[M]^+$ (11), 107 (11), 106 (100), 77 (20), 51 (12), 41 (10).

***N*-Benzylaniline (4e)**. Yield 183 mg (2%), pale-yellow crystalline powder, mp 35–38°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.05 (1H, br. s, NH); 4.38 (2H, s, CH_2);

6.78 (2H, d, *J* = 8.2, H-2,6); 6.87 (1H, t, *J* = 8.1, H-4); 7.24 (2H, t, *J* = 8.2, H-3,5); 7.26–7.33 (5H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 48.6; 112.9; 124.8; 127.2; 127.7; 129.2; 140.2; 147.9. Mass spectrum, *m*/*z* (I_{rel}, %): 183 $[M]^+$ (50), 182 (19), 106 (17), 91 (100), 77 (14), 65 (13).

2,8-Dimethylquinoline (7a). Yield 7.2 g (94%), yellow oily liquid, bp 65–66°C (0.3 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.65 (3H, s, CH_3); 2.87 (3H, s, CH_3); 6.98 (1H, d, *J* = 8.0, H-5); 7.24 (1H, d, *J* = 7.6, H-3); 7.38 (1H, t, *J* = 8.0, H-6); 7.65 (1H, d, *J* = 8.0, H-7); 7.89 (1H, d, *J* = 7.6, H-4). ^{13}C NMR spectrum, δ, ppm: 21.6; 25.7; 121.6; 125.3; 126.9; 127.3; 128.3; 136.5; 137.5; 144.7; 157.9. Mass spectrum, *m*/*z* (I_{rel}, %): 157 $[M]^+$ (100), 156 (31), 143 (10).

2,6-Dimethylquinoline (7d). Yield 7.1 g (92%), pale-yellow crystalline powder, mp 56–60°C.[9a] ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.54 (3H, s, CH_3); 2.72 (3H, s, CH_3); 7.21 (1H, d, *J* = 7.6, H-3); 7.59 (1H, d, *J* = 8.4, H-7); 7.73 (1H, s, H-5); 7.95 (1H, d, *J* = 7.6, H-4); 7.93 (1H, d, *J* = 8.4, H-8). ^{13}C NMR spectrum, δ, ppm: 21.4; 25.1; 121.8; 126.4; 128.3; 131.5; 135.2; 135.4; 146.8; 157.8. Mass spectrum, *m*/*z* (I_{rel}, %): 157 $[M]^+$ (100), 156 (32).

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References

1. Yamamoto, N.; Obora, Y.; Ishii, Y. *J. Org. Chem.* **2011**, *76*, 2937.
2. Schley, N. D.; Dobereiner, G. E.; Crabtree, R. H. *Organometallics* **2011**, *30*, 4174.
3. Lee, E. Y.; Kim, Y.; Lee, J. S.; Park, J. *Eur. J. Org. Chem.* **2009**, 2943.
4. Obora, Y.; Ishii, Y. *Synlett* **2011**, 30.
5. Simon, M.-O.; Ung, G.; Darses, S. *Adv. Synth. Catal.* **2011**, *353*, 1045.
6. Gunanathan, C.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2009**, *131*, 3146.
7. (a) Watson, A. J. A.; Maxwell, A. C.; Williams, J. M. J. *Org. Biomol. Chem.* **2012**, *10*, 240. (b) Watson, A. J. A.; Maxwell, A. C.; Williams, J. M. J. *Org. Lett.* **2009**, *11*, 2667.
8. Tursky, M.; Lorentz-Petersen, L. L. R.; Olsen, L. B.; Madsen, R. *Org. Biomol. Chem.* **2010**, *8*, 5576.
9. (a) Khusnutdinov, R. I.; Bayguzina, A. R.; Aminov, R. I. *Russ. Chem. Bull., Int. Ed.* **2013**, *62*, 133. [*Izv. Akad. Nauk, Ser. Khim.* **2013**, 134.] (b) Khusnutdinov, R. I.; Bayguzina, A. R.; Aminov, R. I. *Russ. J. Gen. Chem.* **2015**, *85*, 2725. [*Zh. Obshch. Khim.* **2015**, 1993.] (c) Khusnutdinov, R. I.; Bayguzina, A. R.; Aminov, R. I. *Russ. J. Gen. Chem.* **2016**, *86*, 1613. [*Zh. Obshch. Khim.* **2016**, 1135.]
10. Eggins, B. R. *Chemical Sensors and Biosensors*; Wiley: Chichester, 2002, p. 142.
11. Makhmutov, A. R.; Usmanov, S. M. *Bashkir. Khim. Zh.* **2017**, *24*(1), 18.
12. Makhmutov, A. R.; Usmanov, S. M. *Bashkir. Khim. Zh.* **2017**, *24*(4), 33.
13. (a) Walling, C. *Acc. Chem. Res*. **1975**, *8*, 125. (b) Tyre, B. W.; Watts, R. J.; Miller, G. C. *J. Environ. Qual.* **1991**, *20*, 832.
14. Barbusiński, K. *Ecol. Chem. Eng*. S **2009**, *16*, 347.
15. Bulgakov, R. G.; Kuleshov, S. P.; Vafin, R. R.; Dzhemilev, U. M. *Russ. J. Org. Chem.* **2009**, *45*, 944. [*Zh. Org. Khim*. **2009**, 956.]
16. Makhmutov, A. R.; Usmanov, S. M. *Bashkir. Khim. Zh.* **2017**, *24*(3), 45.
17. Makhmutov, A. R. *J. Sib. Fed. Univ*., *Chem.* **2017**, *10*, 154.
18. (a) Pozdnyakov, I. P.; Vorobyev, D. Yu.; Glebov, E. M.; Plyusnin, V. F.; Grivin, V. P.; Ivanov, Y. V.; Bazhin, N. M. *Mendeleev Commun*. **2000**, *10*, 185. (b) Pozdnyakov, I. P.; Plyusnin, V. F.; Glebov, E. M.; Grivin, V. P.; Vorobyev, D. Yu.; Bazhin, N. M.; Sosedova, Yu. A. *Int. J. Photoenergy* **2004**, *6*, 89.
19. (a) Bulgakov, R. G.; Kuleshov, S. P.; Makhmutov, A. R.; Dzhemilev, U. M. *Kinet. Catal.* **2010**, *51*, 534. (b) Bulgakov, R. G.; Kuleshov, S. P.; Makhmutov, A. R. *Russ. Chem. Bull., Int. Ed.* **2007**, *56*, 443. [*Izv. Akad. Nauk, Ser. Khim.* **2007**, 429.]
20. Bulgakov, R. G.; Kuleshov, S. P.; Makhmutov, A. R.; Dzhemilev, U. M. *Russ. J. Org. Chem.* **2006**, *42*, 1573. [*Zh. Org. Khim*. **2006**, 1583.]