Photocatalytic tandem reaction of primary alcohols with arylamines in the synthesis of amides and alkylquinolines in the presence of a heterogeneous $Fe(CrO_2)_2$—TiO_2/X system under aerobic conditions

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A heterogeneous system $Fe(CrO_2)_2$—TiO_2/X (where X is promoter NiO, CuO, ZnO, Cr_2O_3, Fe_2O_3, PrOCl, TbOCl, LaOCl, or EuOCl) was prepared. The photocatalytic activity of the system was tested in the tandem reaction of primary alcohols (BnOH, EtOH) with arylamines aimed at synthesizing benzamides and substituted 2-methylquinolines under aerobic conditions at room temperature.

Key words: benzamides, alkylquinolines, benzyl alcohol, ethanol, arylamines, photocatalysis, iron chromite, titanium dioxide.

Photoactivation and photocatalysis provide new possibilities for enhancing selectivity and efficiency of the heterogeneous catalytic systems,[1—3] since organic compounds, in particular, nitrogen-containing organic substances, can be synthesized under milder conditions (aqueous medium, atmospheric pressure, room temperature) than in the presence of traditional catalysts.[4]

Nitrogen-containing functional groups, for example, amide group and quinolone cycle, are components of many synthetic and natural compounds applied in the pharmaceutical branch, oil-and-gas industry, agroindustrial complex, and nanoelectronics.[5,6]

Direct oxidative amidation from alcohols and amines is an attractive method for amide synthesis, which is consistent with the green chemistry concept.[7,8] The use of alcohols as reactants of the tandem synthesis is advantageous due to their availability, low storage expenses, and the possibility to reduce the number of synthesis steps.[9] The development of the nanocatalysis methods resulted in the preparation of efficient heterogeneous catalytic systems based on Pd (see Ref. 6) and Au (see Refs 10—13) nanoparticles on special supports, for example, on graphene oxide (GO).[6] These systems can perform the tandem synthesis of aliphatic, aromatic, and cyclic (lactam) amides of various classes directly from alcohols in the presence of H_2O_2 or under aerobic conditions. At the same time, the synthesis of these nanostructural catalysts is fraught with very high expenses. The ruthenium complexes[14] are alternative efficient catalytic systems for the synthesis of amides by the dehydrogenation of alcohols and hemiamines with hydrogen evolution. However, these complexes must be regenerated after the reaction completion.

The photocatalytic activity of heterogeneous chromite $Fe(CrO_2)_2$ in the oxidation of alcohols with H_2O_2 to the corresponding aldehydes followed by the condensation of aldehydes with arylamines to alkyl-substituted quinolones has recently been discovered.[15] The use of chromite can favor the development of the tandem synthesis of nitrogen-containing organic compounds of diverse types, including amides, by the reactions of alcohols with amines under mild environmentally friendly conditions. Unlike the nanocatalytic structures and ruthenium complexes, catalytically active chromite $Fe(CrO_2)_2$ can be obtained from available and abundant reagents by the photochemical reaction of $FeCl_3 \cdot 6H_2O$ and $K_2Cr_2O_7$ in an aqueous-alcohol medium.[4]

In this work, we describe the photochemical synthesis of the catalytic combined system $Fe(CrO_2)_2$—TiO_2/X (X is promoter NiO, CuO, ZnO, Cr_2O_3, Fe_2O_3, PrOCl, TbOCl, LaOCl, or EuOCl taken in an amount of 1.0 mol.% with respect to TiO_2). The results of testing the photocatalytic activity of $Fe(CrO_2)_2$—TiO_2/X in the tandem reaction of primary alcohols (BnOH, EtOH) with arylamines are also presented.

Results and Discussion

The photocatalytic effect of chromite $Fe(CrO_2)_2$ in the synthesis of alkylquinolines becomes fully apparent only in the presence of an aqueous solution of H_2O_2.[15] As a rule, the work with media containing a strong oxidant requires special security measures, which considerably complicates the technology of synthesis and purification of reaction products thus increasing the risk of emergency

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 0068—0073, January, 2019.

conditions.[16] A combination of chromite $Fe(CrO_2)_2$ with the known semiconductor photocatalyst of alcohol oxidation by titanium dioxide[17] into a single system $Fe(CrO_2)_2$—TiO_2 makes it possible to avoid the application of such active oxidants as H_2O_2, NaClO, and others. Oxidizing power of air oxygen is sufficient to function efficiently as an oxidant of the $Fe(CrO_2)_2$—TiO_2 photocatalytic system.[18] A similar combination of the copper(II) complexes with the Schiff bases on TiO_2 led to the synthesis of hybrid systems of the complex—TiO_2 type, which are efficient photocatalysts of oxidation of the Cr^{IV} compounds in methanol.[19]

The combined $Fe(CrO_2)_2$—TiO_2 system was synthesized by the photochemical precipitation of chromite $Fe(CrO_2)_2$ from an aqueous-ethanol solution of $FeCl_3 \cdot 6H_2O$ and $K_2Cr_2O_7$ on the surface of a TiO_2 suspension under the irradiation with a Hg lamp at 25 °C for 200 min. The average particle size of the $Fe(CrO_2)_2$—TiO_2 system determined by the laser diffraction method is 1.8 μm. The crystals of chromite $Fe(CrO_2)_2$ obtained in the photochemical reaction in the absence of a TiO_2 suspension are larger: on the average 11.5 μm.

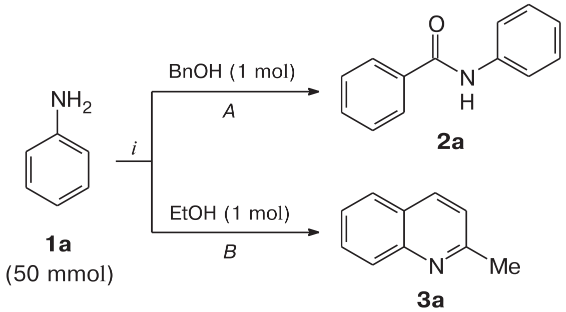
The photocatalytic activity of TiO_2 depends on the presence of modifying additives (promoters), in particular, the d- and f-metal compounds.[20—23] The d-metal oxides (NiO, CuO, ZnO, Cr_2O_3, Fe_2O_3) and f-metal oxychlorides (PrOCl, TbOCl, LaOCl, EuOCl) taken in an amount of 1.0 mol.% with respect to TiO_2 were used in this work as promoters (X) of the $Fe(CrO_2)_2$—TiO_2/X system. The procedure of catalyst preparation was described earlier.[24]

Samples of the $Fe(CrO_2)_2$—TiO_2/X system were used as photocatalysts of the tandem reaction for the synthesis of amides from benzyl alcohol (BnOH) and of alkylquinolines from ethanol (EtOH) with arylamines in the presence of atmospheric air oxygen under irradiation with a Hg lamp.

The main features of the photocatalytic synthesis of amides and alkylquinolines under the action of the $Fe(CrO_2)_2$—TiO_2/X system were studied on the model tandem reactions of BnOH and EtOH with aniline (**1a**). The model of photocatalytic synthesis of benzanilide (**2a**) and 2-methylquinoline (**3a**) under the action of the $Fe(CrO_2)_2$—TiO_2/X system is presented in Scheme 1.

The model process occurs in two different directions depending on the alcohol nature. The tandem reaction photooxidation—amidation occurs in the presence of aromatic alcohol BnOH (route *A*) to form benzanilide (**2a**) as the major product. The tandem reaction photooxidation—cyclocondensation is observed for aliphatic alcohol EtOH (route *B*), and the major product of the process is 2-methylquinoline (**3a**).

Scheme 1



i. 1 mol.% $Fe(CrO_2)_2$—TiO_2/X, oxidant, solvent, $\lambda < 400$ nm, 25 °C.

The effects of the oxidant and solvent and the duration of the tandem process on the conversion of the initial compound **1a** and the yields of the reaction products **2a** and **3a** are shown in Table 1.

Table 1. Influence of the nature of the oxidant and solvent and process time on the photocatalytic activity of the $Fe(CrO_2)_2$—TiO_2 system in the model reactions[a]

Oxidant	Solvent[b]	τ/h	Route *A*		Route *B*	
			Conversion of arylamine **1a**	Yield of benzamide **2a**	Conversion of arylamine **1a**	Yield of 2-methylquinoline **3a**
$O_{2(air)}$	—	6	11	5	14	8
	H_2O	6	14	9	17	13
	DMSO	6	18	15	17	11
	MeCN	6	12	6	14	6
	Dioxane	6	11	7	15	7
	Toluene	6	10	7	9	3
	H_2O	24	15	13	29	22
	DMSO	24	27	25	23	18
H_2O_2[d]	(H_2O)	6	>99	86	>99	92
NaClO[d]	(H_2O)	6	>99	57	>99	73

[a] Here and in Tables 2 and 3, the conversion of the initial compound and yields of the product are given in %.
[b] Solvent content 1.5 mol; (H_2O) is an aqueous solution of oxidants.
[c] Bubbling with atmospheric air.
[d] Weight content of the active substance is 10%.

Oxygen of atmospheric air is inferior to active oxidants H_2O_2 and NaClO in oxidation activity. However, the elongation of the time of the model process under aerobic conditions to 24 h allows one to increase the conversion of compound **1a** and yields of products **2a** and **3a**.

The influence of the solvents was observed for aqueous solutions and DMSO. The effect of DMSO is most favorable for the synthesis of product **2a**, *i.e.*, it facilitates the tandem reaction photooxidation—amidation (route *A*). No influence of other solvents, acetonitrile, dioxane, and toluene, on the conversion of compound **1a** and the yields of the products of the model reactions was recorded. The parameters in the presence of these solvents were close to those in the absence of solvent.

The influence of the nature of the promoter (X) of the photocatalytic system $Fe(CrO_2)_2$—TiO_2/X on the conversion of compound **1a** and the yield of the products of the model reactions under the action of $O_{2(air)}$ in a medium of DMSO and H_2O for 24 h is presented in Table 2.

The maximum conversion of compound **1a** and high yields of products **2a** and **3a** are observed only for the NiO and CuO promoters, *i.e.*, for the $Fe(CrO_2)_2$—TiO_2/NiO and $Fe(CrO_2)_2$—TiO_2/CuO systems (see Table 2). This is probably related to the reduction of modifying oxides NiO and CuO to the corresponding metals Ni^0 and Cu^0 under the photocatalytic conditions, which exerts a positive effect on the tandem reaction as a whole. For example, it is known that nickel as a cocatalyst (promoter, modifier) of TiO_2 enhances the oxidation rate of isopropyl alcohol with gaseous hydrogen evolution.[24]

The conversion of compound **1a** and the yields of target products **2a** and **3a** in the model reactions using promoters ZnO, Cr_2O_3, and Fe_2O_3 are comparable with the parameters found for the initial system $Fe(CrO_2)_2$—TiO_2 without a promoter. Probably, this is caused by the absence of an efficient route of charge separation in the indicated photocatalytic systems and low reduction potentials of oxides that prevent their reduction to metals under the photocatalytic conditions.[24]

A specific feature of the photochemical behavior of the TiO_2 composites containing iron oxides as modifiers, which were prepared by thermal sintering or iron nitrate decomposition on the TiO_2 surface, is the initiation of the chain reaction

$$Fe^{3+} + e^- \rightarrow Fe^{2+};\ Fe^{2+} + h^+ \rightarrow Fe^{3+}.$$

This reaction opposes an efficient charge separation and substantially diminishes the photocatalytic activity of TiO_2.[23] Nevertheless, some data indicate quite opposite, favorable effect of doping TiO_2 with iron ions in the case of the photocatalytic processes.[21,22] The phenomenon is explained by the ability of iron ions to capture and transfer photogenerated electrons and holes. However, we did not observe any appreciable influence of Fe_2O_3 as a promoter in the studied $Fe(CrO_2)_2$—TiO_2 system on the model reaction (see Scheme 1).

Lanthanide oxychlorides were also tested as promoters of the $Fe(CrO_2)_2$—TiO_2 system (see Table 2). The efficiency of the lanthanide promoters is lower than that of the d-metal oxides and decreases in the following series: PrOCl > TbOCl > LaOCl > EuOCl. For the first time, the dependence of the photocatalytic activity of titanium dioxide on the nature of the doped lanthanide ion was observed in nitrite ion oxidation.[23]

The influence of functional groups (R) of arylamines (**1b—f**) on the efficiency of the photocatalytic tandem reaction aimed at synthesizing the corresponding benzamides (**2b—f**) and 2-methylquinolines (**3b—f**) under the action of $O_{2(air)}$ was studied for the $Fe(CrO_2)_2$—TiO_2/CuO photocatalytic system as an example (Scheme 2).

Table 2. Effect of the promoter (X) on the photocatalytic activity of the $Fe(CrO_2)_2$—TiO_2/X system in the model reactions under aerobic conditions

Promoter[a]	Route *A*		Route *B*	
	Conversion of arylamine **1a**	Yield of benzamide **2a**[b]	Conversion of arylamine **1a**	Yield of 2-methylquinoline **3a**[c]
Without promoter	27	25	29	22
NiO	>99	89	>99	76
CuO	>99	81	>99	82
ZnO	29	27	33	21
Cr_2O_3	27	22	31	24
Fe_2O_3	25	19	27	24
LaOCl	28	23	35	28
PrOCl	42	41	49	37
EuOCl	27	23	29	21
TbOCl	29	25	42	33

[a] The modifier content is 1.0 mol.% based on TiO_2.

[b] Solvent DMSO (1.5 mol).

[c] Solvent H_2O (1.5 mol).

Table 3. Influence of the nature of arylamines on the photocatalytic activity of the $Fe(CrO_2)_2$—TiO_2/CuO system in the syntheses of benzamides and 2-methylquinolines[a]

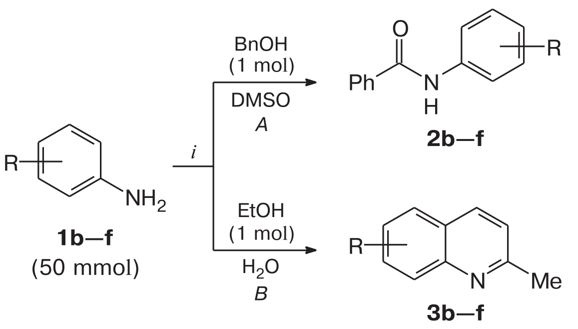
Arylamine	Route *A*		Route *B*	
	Conversion of arylamine **1a—f**	Yield of benzamide **2a—f**[b]	Conversion of arylamine **1a—f**	Yield of 2-methylquinoline **3a—f**[c]
1a	>99	81	>99	82
1b	>99	78	>99	85
1c	89	86	86	83
1d	65	60	67	64
1e	76	72	59	55
1f	68	62	77	73

[a] Atmospheric air oxygen as an oxidant.

[b] Solvent DMSO (1.5 mol).

[c] Solvent H_2O (1.5 mol).

Scheme 2



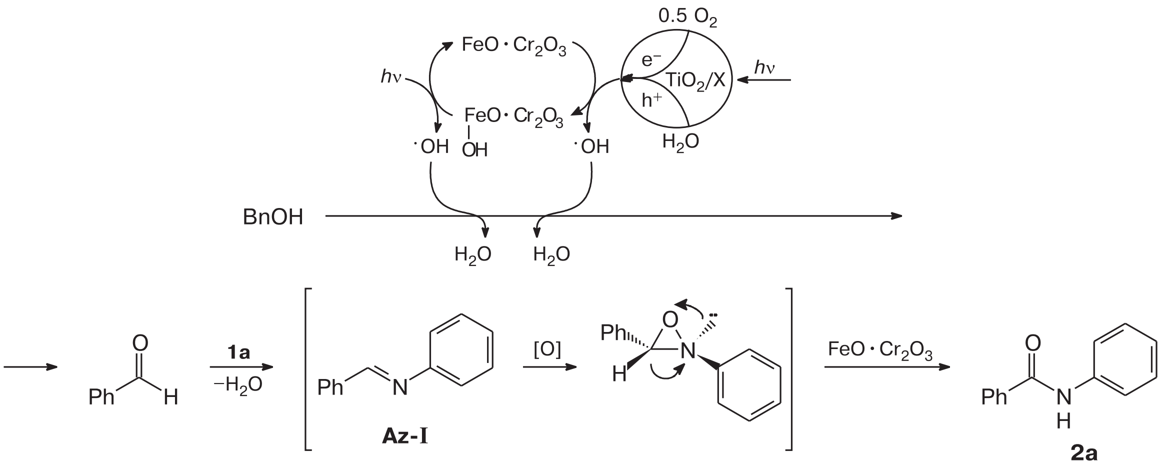
R = *o*-Me (**b**), *p*-Me (**c**), *p*-Cl (**d**), *p*-Br (**e**), *p*-OH (**f**)

i. 1 mol.% $Fe(CrO_2)_2$—TiO_2/CuO, $O_{2(air)}$, $\lambda < 400$ nm, 25 °C.

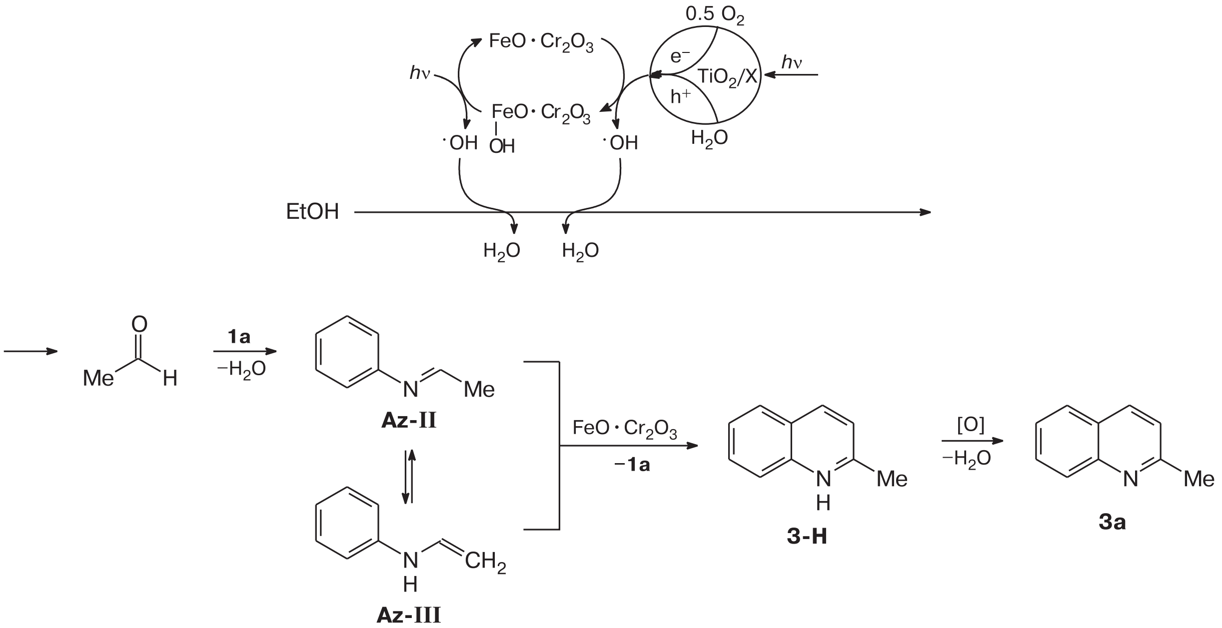
Since arylamines **1a** and **1b** have no substituents in the *para*-position relative to the amino group, they are completely converted in the photocatalytic processes (Table 3). However, the yield of the target products **2a**,**b** and **3a**,**b** is somewhat lower than the conversion value, because some portion of arylamine is consumed to photo polymerization with the formation of polyanilines and to photodestruction. The yields of reaction products **2c—f** and **3c—f** and the conversion value of arylamines with the substituents in the *para*-position **1c—f** are close, indicating insignificant contribution of processes of arylamine photodestruction under UV irradiation with no photopolymerization. The minimum photocatalytic effect of the $Fe(CrO_2)_2$—TiO_2/CuO system is observed for halosubstituted arylamines.

The mechanism of action of various forms of TiO_2 during the photogenerated oxidation of alcohols with air oxygen *via* photogeneration of active radical species ($^{\bullet}OH$, $^{\bullet}O_2^{-}$, and others) has been described.[17] It was also proved that hydroxyl particles ($^{\bullet}OH$) were selectively formed on the TiO_2 in aqueous-alcohol systems.[25] We found a similar selective photogeneration of $^{\bullet}OH$ particles in an aqueous-alcohol system for the oxidation of alcohols to aldehydes under the action of chromite $Fe(CrO_2)_2$.[4] Thus, the initial step of the photocatalytic synthesis of amides and alkylquinolines from primary alcohols BnOH and EtOH in the presence of the $Fe(CrO_2)_2$—TiO_2/X system under irradiation with a Hg lamp starts, most probably, with the generation of hydroxyl particles $^{\bullet}OH$ (Schemes 3 and 4, respectively).

Scheme 3



Scheme 4



Hydroxyl radicals are active oxidation species and convert alcohols to aldehydes. Then azomethine (**Az-I**) is formed from benzaldehyde in the presence of aniline (**1a**), and the oxidation of **Az-I** leads to benzanilide (**2a**)[5] (see Scheme 3). The photocatalytic oxidation of EtOH to acetaldehyde in the presence of aniline (**1a**) (see Scheme 4) affords the Schiff base in two isomeric forms: aldimine (**Az-II**) and enamine (**Az-III**). The reaction of the azomethine forms **Az-II** and **Az-III** under the action of the catalytic system (chromite moiety) results in 1,2-dihydroquinaldine (**3-H**).[4] The final target product 2-methylquinoline (**3a**) is formed due to the oxidation of compound **3-H**.

To conclude, the photocatalytic activity of the combined system $Fe(CrO_2)_2$—TiO_2/X (X is promoter NiO, CuO, ZnO, Cr_2O_3, Fe_2O_3, PrOCl, TbOCl, LaOCl, or EuOCl) was studied in the tandem reaction aimed at synthesizing benzamides and substituted 2-methylquinolines. The optimum conditions of the reaction were determined including the promoter, oxidant, solvent, and process time. The maximum efficiency with respect to the yield of the target products under mold aerobic conditions was observed for the photocatalytic system $Fe(CrO_2)_2$—TiO_2/CuO. The probable mechanism was proposed for the tandem photocatalytic synthesis of benzanilide and 2-methylquinoline.

Experimental

A GCMS-QP2010S Ultra GC-MS spectrometer (Shimadzu, column Restek Rtx-5MS, 30 mS0.25 mm, 0.25 μm) was used for the identification of the reaction products. The quantitative content of the reaction products was analyzed with an apparatus program complex based on Khromatek-Kristall 5000.1 and 5000.2 chromatographs (columns Agilent Technologies 19091F-413 HP-FFAP, 30 mS0.32 mm, 0.25 μm; Analytical Science, 30 m×0.32 mm, 0.5 μm).

^1H and ^{13}C NMR spectra were recorded on the equipment of the Center for Collective Use "Chemistry" of the Ufa Institute of Chemistry (Russian Academy of Sciences): Bruker Avance III pulse spectrometers with the working frequencies 500.13 (^1H) and 125.47 (^{13}C) MHz relative to the signal from Me_4Si as an internal standard.

Prior to experiments, the initial reagents, namely, benzyl alcohol (BnOH, analytical pure grade, AO Reakhim), ethanol (EtOH, reagent grade, AO EKOS-1), aniline (analytical pure grade, AO Reakhim), dimethyl sulfoxide (DMSO, reagent grade, AO Reakhim), acetonitrile (CH_3CN, special pure grade, OOO NPK KRIOKhROM), dioxane (reagent grade, AO EKOS-1), toluene (reagent grade, AO EKOS-1), and diethyl ether (analytical pure grade, AO Reakhim), were distilled according to described procedures.[26]

The reagents for the synthesis of the photocatalysts, namely, $FeCl_3 \cdot 6H_2O$ (pure grade, OAO Brom), $K_2Cr_2O_7$ (reagent grade, ZAO Russkii Khrom), TiO_2 (special pure grade, ZAO Promkhimperm), $Fe(NO_3)_3 \cdot 9H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot$ $\cdot 6H_2O$ (pure, AO LenReaktiv), $Cu(NO_3)_2 \cdot 3H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$ (analytical pure grade, AO LenReaktiv), and $LaCl_3 \cdot 6H_2O$, $PrCl_3 \cdot 6H_2O$, $EuCl_3 \cdot 6H_2O$, and $TbCl_3 \cdot 6H_2O$ (Alfa Aesar GmbH & Co KG, Reacton*, 99.9% REO) were used as received.

The oxidants were an aqueous solution of H_2O_2 (10 wt.%) prepared from a commercial 30% solution of hydrogen peroxide (special pure grade, OOO Lega) and an aqueous solution of hypochlorite NaOCl (10 wt.%) prepared from chloride of lime (trade mark A, ZAO Vekton) as described previously.[27]

Aerobic photocatalytic tandem synthesis of amides and alkylquinolines (general procedure). The photocatalytic synthesis of amides and alkylquinolines from primary alcohols was carried out in a Photo Catalytic Reactor Lelesil Innovative Systems photocatalytic system with a 250-mL quartz reactor (photoreactor of Stromeyer´s type with magnetic stir bar). The photoreactor flask was loaded with a photocatalyst paste (5.0 g corresponding to 1 mol.% with respect to alcohol), alcohol (BnOH or EtOH, 1.0 mol), the corresponding arylamine (0.05 mol), and a solvent (1.5 mol). The loaded reactor was attached to the system (according to the producer´s instruction) equipped with a reverse condenser and a bubbler for passing atmospheric air through the reaction medium. A medium-pressure Hg lamp (power 250 W) served as a radiation source. The spectral composition of the radiation by energy was as follows: UV range 48%, visible range 43%, and IR range 9%. The spectral range was 222—1368 nm. The luminous flux reached the reaction system after passing through an aqueous layer maintained at 25 °C. The irradiation time was 6—24 h. After the reaction completion, a precipitate of the photocatalyst was separated and fractionation *in vacuo* was conducted.

The physicochemical parameters and spectroscopic characteristics of the tandem reaction products **2a**,**e**,**f** (see Ref. 5) and **3a—d** (see Ref. 28) are consistent with the literature data.

***N*-(2´-Methylphenyl)benzamide (2b)**. M.p. 145—146 °C. ^{1}H NMR (DMSO-d$_6$), δ: 2.32 (s, 3 H, C(2)Me); 7.09—7.80 (m, 9 H, 2 Ph); 7.85 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d$_6$), δ: 19.37 (Me), 125.53 (C(6´)), 125.81 (C(5´)), 126.76 (C(4´)), 127.27 (C(2), C(6)), 128.09 (C(3), C(5)), 130.04 (C(3´)), 133.65 (C(2´)), 131.24 (C(4)), 134.56 (C(1)), 136.82 (C(1´)), 165.23 (C=O). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 212 (6), 211 [M]$^+$ (42), 106 (12), 105 (100), 77 (37).

***N*-(4´- Methylphenyl)benzamide (2c).** M.p. 158—159 °C. ^{1}H NMR (DMSO-d$_6$), δ: 2.35 (s, 3 H, C(2)Me); 7.08—7.90 (m, 9 H, 2 Ph); 8.04 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d$_6$), δ: 20.77 (Me), 122.51 (C(2´), C(6´)), 128.57 (C(2), C(6)), 129.62 (C(3), C(5)), 130.38 (C(3´), C(5´)), 132.42 (C(4)), 135.16 (C(4´)), 136.18 (C(1)), 137.26 (C(1´)), 165.11 (C=O). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 211 [M]$^+$ (41), 106 (10), 105 (100), 77 (45), 51 (9).

***N*-(4´-Chlorophenyl)benzamide (2d).** M.p. 154—156 °C. ^{1}H NMR (DMSO-d$_6$), δ: 7.26—7.90 (m, 9 H, 2 Ph); 8.15 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d$_6$), δ: 121.82 (C(2´), C(6´)), 127.75 (C(2), C(6)), 128.16 (C(4´)), 128.91 (C(3), C(5)), 129.07 (C(3´), C(5´)), 131.19 (C(4)), 135.15 (C(1)), 138.41 (C(1´)), 165.86 (C=O). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 231 [M]$^+$ (20), 106 (8), 105 (100), 77 (58), 51 (22).

6-Bromo-2-methylquinoline (3e). M.p. 102—104 °C. ^{1}H NMR (CDCl$_3$), δ: 2.76 (s, 3 H, C(2)Me); 7.49, 7.64 (both d, 1 H each, H(3), H(7), J = 7.6 Hz); 7.76 (s, 1 H, H(5)); 7.94 (d, 1 H, H(4), J = 7.6 Hz); 8.10 (d, 1 H, H(8), J = 8.4 Hz). ^{13}C NMR, δ: 28.57 (Me), 129.18 (C(3)), 134.49 (C(4a)), 136.39 (C(5)), 139.81 (C(8)), 140.26 (C(7)), 140.72 (C(4)), 149.48 (C(6)), 155.36 (C(8a)), 158.65 (C(2)). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 223 (100), 222 [M]$^+$ (17), 221 (97), 142 (40), 115 (52).

6-Hydroxy-2-methylquinoline (3f). M.p. 214—218 °C. ^{1}H NMR (CDCl$_3$), δ: 2.52 (s, 3 H, C(2)Me); 7.03 (d, 1 H, H(5), J = 2.6 Hz); 7.18, 7.72 (both d, 1 H each, H(7), H(8), J = 8.3 Hz); 7.21, 7.96 (both d, 1 H each, H(3), H(4), J = 8.1 Hz); 9.83 (s, 1 H, OH). ^{13}C NMR, δ: 24.80 (Me), 108.54 (C(5)), 121.36 (C(7)), 122.83 (C(3)), 127.08 (C(4a)), 129.97 (C(8)), 134.49 (C(4)), 142.54 (C(8a)), 155.69 (C(6)), 156.19 (C(2)). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 160 (11), 159 [M]$^+$ (100), 131 (32), 130 (79), 103 (9).

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Received July 16, 2018;
in revised form October 4, 2018;
accepted November 15, 2018