ISSN 1070-3632, Russian Journal of General Chemistry, 2016, Vol. 86, No. 7, pp. 1613–1618. © Pleiades Publishing, Ltd., 2016.
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Quinolines Synthesis by Reacting 1,3-Butanediol with Anilines in the Presence of Iron Catalysts

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Received December 30, 2016

Abstract—2-, 4-, 6-, 7-, and 8-substituted quinolines were synthesized in 78–95% yield by the reaction of 1,3-butanediol with anilines in the presence of iron catalysts in carbon tetrachloride.

Keywords: cyclocondensation, anilines, 1,3-butanediol, carbon tetrachloride, quinolines, metal complex catalysis

DOI: 10.1134/S1070363216070136

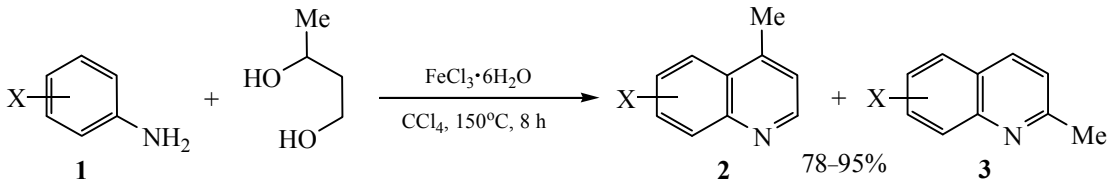
Quinoline and its derivatives are important synthons in the preparation of inhibitors of acid corrosion of metals, extractants, sorbents, and cyanine dyes. Some effective antimalarial, antibacterial, and anti-tremor medications consisted of quinoline derivatives. General methods for the synthesis of quinolines are based on cyclocondensation of anilines with oxygen-containing compounds like glycerol, α,β-unsaturated aldehydes, β-diketones, and β-ketoesters in the presence of mineral acids [1–4].

In recent years new methods of quinolines preparation in the absence of acids using metal complex catalysts were developed. They allowed a significant expansion of the range of C^3-substrates used for constructing quinoline ring involving anilines and 1,3-diols.

Synthesis of quinolines starting from anilines and 1,3-diols have been successfully carried out in the presence of ruthenium-containing catalysts $RuCl_3 \cdot nH_2O$–PBu_3 and $RuCl_3 \cdot nH_2O$–PEt_3 when refluxed in diglyme for 5 h [5, 6]. It should be noted that in the presence of ruthenium complexes the final stage of aromatization does not require the use of hydrogen acceptors, since the catalyst performs this role. Previously we have found that synthesis of quinolines can be carried out by reacting anilines with propane-1,3-diol in the presence of Fe-containing catalysts [7]. Here we report on the synthesis of quinolines by reacting 1,3-butanediol with anilines **1a**–**1j** in the presence of iron-containing catalysts like $FeCl_3 \cdot 6H_2O$, $FeCl_3$, $FeCl_2 \cdot 4H_2O$, $Fe(C_5H_5)_2$, $Fe(acac)_3$, $Fe(OAc)_2$, $Fe_2(CO)_9$, the best of which was $FeCl_3 \cdot 6H_2O$.

Thus, cyclocondensation of aniline **1a** with 1,3-butanediol produced a difficulty separable mixture of 4-methyl- (**2a**) and 2-methylquinolines (**3a**) with a predominance of the 4-substituted isomer. The reaction took place at 150°C in CCl_4 within 8 hours at a molar ratio $FeCl_3 \cdot 6H_2O$: **1a** : CCl_4 : 1,3-butanediol = 1 : 100 : 200 : 400. Substituted anilines **1b**–**1j** reacted with 1,3-butanediol similarly to form substituted quinolines **2** and **3** in 78–95% yields (see table, Scheme 1).

Scheme 1.



1 **2** **3**

X = H (**a**), *o*-CH_3 (**b**), *m*-CH_3 (**c**), *p*-CH_3 (**d**), *o*-C_2H_5 (**e**), *o*-Cl (**f**), *m*-Cl (**g**), *p*-Cl (**h**), *p*-OCH_3 (**i**), *o*-OH (**j**).

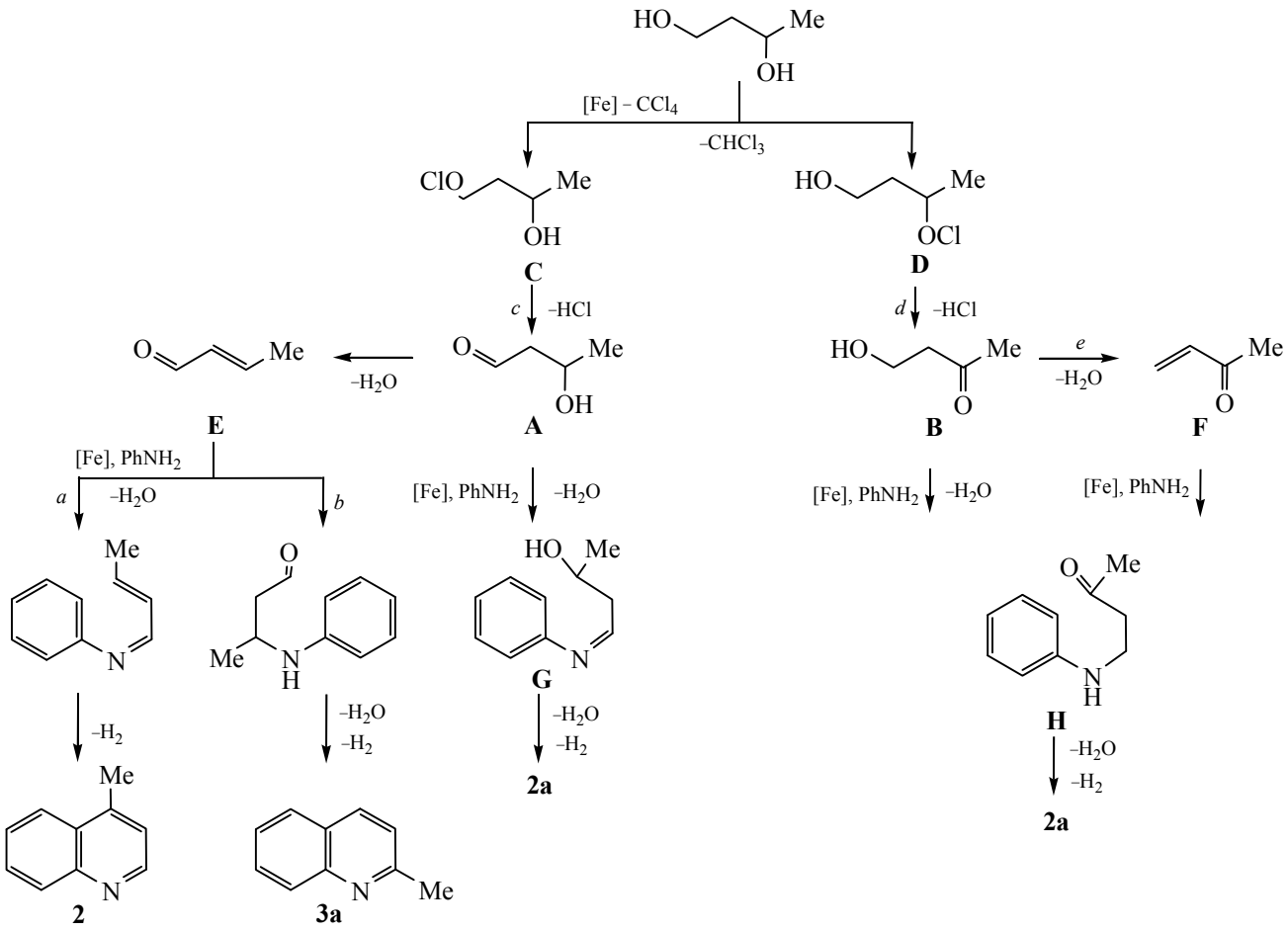
Synthesis of quinolines by reacting anilines with 1,3-butanediol in the presence of $FeCl_3 \cdot 6H_2O$[a]

Aniline	Isomer ratio **2** : **3**[b]	Yield, %
1a	2 : 1	95
1b	2 : 1	80
1c	3 : 2 : 1	78
1d	1 : 1	93
1e	2 : 1	87
1f	3 : 1	94
1g	3 : 2 : 1	79
1h	2 : 1	82
1i	1 : 1	89
1j	1 : 1	90

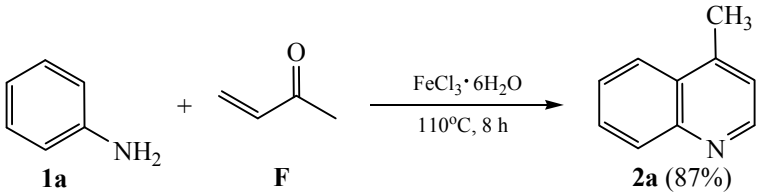
[a] Reaction conditions: 150°C, 8 h, $FeCl_3 \cdot 6H_2O$: **1** : CCl_4 : diol = 1 : 100 : 200 : 400. [b] The isomers ratio was determined by NMR spectroscopy.

It has been previously found [8] that the reaction of aniline with 1,3-diol in the presence of Ru-containing catalyst occurred via initial oxidation of diol into 3-hydroxybutanal **A**, which suffered a dehydrogenation to afford crotonaldehyde **E**. In our case, due to the known [7] ability of both hydroxy groups to be oxidized with CCl_4 by the action of iron compounds it was expectable to obtain 3-hydroxybutanal **A** and 4-hydroxybutane-2-one **B** through generating two alkylhypochlorites **C** and **D**. The degradation of hypochlorites **C** and **D** with the release of HCl yielded aldehydes **A** and **B**, which may undergo dehydration to form crotonaldehyde **E** and methyl vinyl ketone **F**. Compounds **A**, **B** and **F** reacted further with aniline to give the corresponding intermediates **G** and **H** [8]. Due to differences in the structure compounds **A**, **B** and **F** reacted with aniline in two directions: compound **A** provided a Schiff base, intermediate **B** alkylated aniline at the amino group, and compound **F** reacted

Scheme 2.



Scheme 3.



with aniline by Michael reaction. Intermediates **G** and **H** underwent heterocyclization, dehydration and dehydrogenation to give 4-methylquinoline **2a** (routes *c* and *d*) (Scheme 2).

The formation of 2-methylquinoline **3a** is only possible by Michael reaction (route *b*) involving crotonaldehyde **D**. The latter can react with aniline to form a Schiff base (route *a*) providing compound **2a**. The formation of 4-methylquinoline **2a** is possible by four pathways causing probably its prevalence in the reaction products.

Furthermore, the proposed mechanism is proved by the formation of stoichiometric amount of chloroform and HCl, which were detected by GLC and mercurimetric titration. A control experiment with methyl vinyl ketone **F** led to the selective production of 4-methylquinoline **2a**, which also confirms the proposed reaction mechanism, providing for the formation of intermediate **H**.

It should be noted that the reaction of aniline with methyl vinyl ketone was carried out at a lower temperature, since under standard conditions (150°C, 8.4 h) it underwent polymerization. It was found that in the absence of $FeCl_3 \cdot 6H_2O$ there was no reaction between aniline and methyl vinyl ketone. Apparently, a catalyst role in the quinolines formation from anilines and diols is not limited to the participation in 1,3-diols oxidation (Scheme 3).

In summary, a convenient method for the synthesis of 2-, 4-, 6-, 7-, and 8-substituted quinolines was developed based on the reaction of aniline and its derivatives with 1,3-butanediol catalyzed with $FeCl_3 \cdot 6H_2O$ in the presence of CCl_4. The latter takes part in 1,3-butanediol oxidation, converting it into a carbonyl compound.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer (400.13 and 100.62 MHz, respectively) in $CDCl_3$, internal reference TMS. Mass spectra were obtained on a Shimadzu GCMS-QP2010Plus spectrometer (capillary column SPB-5, 30 mm × 0.25 mm, carrier gas helium, programming temperature from 40 to 300°C at a rate of 8 deg/min, evaporation temperature 280°C, temperature of ion source 200°C, ionization energy 70 eV). GLC analysis was performed on Shimadzu GC-9A, GC-2014 instruments [column 2 m × 3 mm, stationary phase Silicone SE-30 (5%) on Chromaton N-AW-HMDS, ramp from 50 to 270°C C, heating rate 8 deg/min, carrier gas helium (47 mL/min)]. High performance liquid chromatographic analysis was carried out under the following conditions: column 250 mm × 10 mm, Zorbax ODS, 5 μm, eluent CH_3CN : H_2O = 70 : 30, 0.1% $(C_2H_5)_3N$, 3 mL/min, detector SPD-20A, λ = 265 nm.

Commercially available anilines, 1,3-butanediol, and carbon tetrachloride were distilled before use. Iron catalysts [$FeCl_3 \cdot 6H_2O$, $FeCl_3$, $FeCl_2 \cdot 4H_2O$, $Fe(C_5H_5)_2$, $Fe(acac)_3$, $Fe(OAc)_2$, $Fe_2(CO)_9$] were used as purchased without further purification.

General procedure for preparation of substituted quinolines 2 and 3. A vial charged with 0.02 mmol of $FeCl_3 \cdot 6H_2O$ [$FeCl_3$, $FeCl_2 \cdot 4H_2O$, $Fe(C_5H_5)_2$, $Fe(acac)_3$, $Fe(OAc)_2$, $Fe_2(CO)_9$], 2 mmol of aniline **1**, 4 mmol of carbon tetrachloride and 8 mmol of 1,3-diol under argon was sealed, placed into a pressure reactor, and heated at 150°C with stirring for 8 h. After the reaction completed the mixture was dissolved in hydrochloric acid, and separated. The aqueous layer was neutralized with 10% sodium hydroxide and extracted with methylene chloride. The organic layer was filtered and evaporated. The residue was distilled in a vacuum. Analytically pure samples were isolated by semi-preparative HPLC. Physical and chemical constants and spectral characteristics corresponded to those reported in [5, 6, 8–22].

4-Methylquinoline (2a). bp 80–81°C (2 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.68 s (3H, CH_3), 7.18 d (1H, C^3H, J = 8.0 Hz), 7.53 t (1H, C^6H, J = 7.6 Hz), 7.68 t (1H, C^7H, J = 7.6 Hz), 7.95 d (1H, C^5H, J = 9.2 Hz), 8.09 d (1H, C^8H, J = 8.4 Hz), 8.73 d (1H,

C^2H, J = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.40 (CH_3), 121.87 (C^3), 123.85 (C^5), 126.33 (C^6), 127.99 (C^{4a}), 128.95 (C^7), 129.76 (C^8), 144.50 (C^4), 147.76 (C^{8a}), 150.01 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 143.18 (100) $[M - H]^+$, 128 (34), 115 (19), 101 (8), 89 (5), 75 (4), 51(4).

4,8-Dimethylquinoline (2b). bp 65–66°C (0.3 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.79 s (3H, CH_3), 2.89 s (3H, CH_3), 7.15–7.30 m (1H, C^3H), 7.47 t (1H, C^6H, J = 7.2 Hz), 7.50–7.65 m (1H, C^7), 7.86 d (1H, C^5H, J = 8.4 Hz), 8.84 d (1H, C^2H, J = 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.91 (CH_3), 18.94 (CH_3), 121.79 (C^3), 125.55 (C^6), 126.07 (C^5), 129.42 (C^7), 136.26 (C^8), 139.45 (C^{4a}), 148.84 (C^4), 147.00 (C^{8a}), 148.94 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 157.00 (100) $[M - H]^+$, 156 (31), 143 (10), 115 (8), 71 (4), 65 (2), 52 (2).

4,7-Dimethylquinoline (2c). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.54 s (3H, CH_3), 2.64 s (3H, CH_3), 7.14 d (1H, C^3H, J = 7.2 Hz), 7.38 d (1H, C^8H, J = 6.8 Hz), 7.85–7.95 m (1H, $C^{5,6}H$), 8.71 d (1H, C^2H, J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.61 (CH_3), 21.72 (CH_3), 121.13 (C^3), 123.56 (C^6), 126.34 (C^5), 128.56 (C^{4a}), 128.82 (C^8), 139.3 (C^7), 144.15 (C^4), 148.10 (C^{8a}), 150.04 (C^2).

4,6-Dimethylquinoline (2d). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.59 s (3H, CH_3), 2.69 s (3H, CH_3), 7.16 d (1H, C^3H, J = 8.0 Hz), 7.52 d (1H, C^7H, J = 8.4 Hz), 7.72 s (1H, C^5H), 7.99 d (1H, C^8H, J = 8.4 Hz), 8.69 d (1H, C^2H, J = 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.61 (CH_3), 21.80 (CH_3), 121.81 (C^3), 122.75 (C^5), 128.20 (C^{4a}), 129.60 (C^8), 131.34 (C^7), 136.02 (C^4), 143.53 (C^6), 146.46 (C^{8a}), 149.21 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 158.00 (100) $[M - H]^+$.

4-Methyl-8-ethylquinoline (2e). bp 73–74°C (0.2 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.30–1.60 m (3H, CH_3), 2.68 s (3H, CH_3), 3.30–3.50 m (2H, CH_2), 7.51 t (1H, C^6H, J = 7.6 Hz), 7.60 d (1H, C^7H, J = 7.6 Hz), 7.86 d (1H, C^5H, J = 8.4 Hz), 7.99 s (1H, C^4H). ^{13}C NMR spectrum, δ_C, ppm: 15.22 ($CH_2\underline{C}H_3$), 25.00 ($\underline{C}H_2CH_3$), 18.97 (CH_3), 121.79 (C^3), 125.39 (C^5), 126.03 (C^6), 126.43 (C^{4a}), 127.67 (C^7), 136.22 (C^8), 143.40 (C^4), 144.36 (C^{8a}), 148.91 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 170.10 (100) $[M - H]^+$, 171 (83), 143 (63), 128 (16), 115 (36), 63 (40), 51 (50).

4-Methyl-8-chloroquinoline (2f). bp 87–89°C (0.2 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.68 s (3H, CH_3), 7.20–7.40 m (1H, C^3H), 7.45–7.60 m (1H, C^6H), 7.58 d (1H, C^7H, J = 7.6 Hz), 7.84 d (1H, C^5H, J = 8.4 Hz), 8.80 m (1H, C^2H). ^{13}C NMR spectrum, δ_C, ppm: 18.98 (CH_3), 121.68 (C^3), 125.41 (C^6), 126.41 (C^{4a}), 127.71 (C^7), 127.65 (C^5), 142.30 (C^8), 143.28 (C^4), 144.53 (C^{8a}), 148.84 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 177. 1 $[M - H]^+$, 142 (14), 115 (15), 76 (7).

4-Methyl-7-chloroquinoline (2g). bp 92–93°C (0.3 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.75 s (3H, CH_3), 7.10–7.20 m (1H, C^3H), 7.30–7.55 m (1H, C^6H), 7.70–8.00 m (1H, C^5H), 8.07 s (1H, C^8H), 8.60–8.78 m (1H, C^2H). ^{13}C NMR spectrum, δ_C, ppm: 18.55 (CH_3), 122.04 (C^3), 125.23 (C^6), 127.82 (C^{4a}), 130.25 (C^5), 127.16 (C^8), 134.90 (C^7), 144.40 (C^4), 150.19 (C^{8a}), 151.14 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 177 (100) $[M - H]^+$, 179 (34), 178 (10), 143 (12), 115 (19), 76 (9).

4-Methyl-6-chloroquinoline (2h). bp 100–101°C (0.5 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.69 s (3H, CH_3), 7.25 d (1H, C^3H, J = 7.6 Hz), 7.72 d (1H, C^7H, J = 7.6 Hz), 7.72 s (1H, C^5H), 8.10 d (1H, C^8H, J = 8.4 Hz), 8.76 d (1H, C^2H, J = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.57 (CH_3), 122.85 (C^3), 135.10 (C^6), 127.05 (C^{4a}), 126.11 (C^5), 122.85 (C^8), 130.26 (C^7), 143.93 (C^4), 145.86 (C^{8a}), 150.07 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 177 (100) $[M - H]^+$, 179 (42), 142 (51), 116 (27), 99 (14), 51 (27).

4-Methyl-6-methoxyquinoline (2i). mp 26–29°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.63 s (3H, CH_3), 3.94 s (3H, OCH_3), 7.15–7.18 m (2H, $C^{3,5}H$), 7.35 d (1H, C^7H, J = 7.6 Hz), 8.00 d (1H, C^8H, J = 8.4 Hz), 8.61 d (1H, C^2H, J = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.80 (CH_3), 55.53 (OCH_3), 101.9 (C^5), 121.47 (C^7), 122.15 (C^3), 129.25 (C^{4a}), 131.46 (C^4), 142.73 (C^8), 144.01 (C^{8a}), 147.67 (C^2), 157.60 (C^6).

4-Methyl-8-hydroxyquinoline (2j). bp 65–66°C (0.2 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.68 s (3H, CH_3), 7.12–7.28 m (2H, $C^{3,5}H$), 7.43–7.45 m (2H, $C^{6,7}H$), 8.61 d (1H, C^2H, J = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.72 (CH_3), 109.68 (C^7), 114.87 (C^5), 122.46 (C^3), 127.2 (C^{4a}), 128.41 (C^6), 138.04 (C^4), 145.00 (C^{8a}), 147.30 (C^8), 152.57 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 159 (100) $[M - H]^+$, 160 (12), 131 (77).

2-Methylquinoline (3a). bp 80–81°C (2 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.78 s (3H, CH_3), 7.22 d (1H, C^3H, J = 8.0 Hz), 7.68 t (1H, C^7H, J = 4.0 Hz), 7.46 t (1H, C^6H, J = 6.4 Hz), 7.73 d (1H, C^5H, J = 9.2 Hz), 7.91 d (1H, C^4H, J = 9.2 Hz), 7.91 d (1H,

C^8H, J = 9.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 25.12 (CH_3), 121.74 (C^3), 125.45 (C^6), 126.32 (C^{4a}), 127.37 (C^5), 128.80 (C^8), 129.19 (C^7), 135.84 (C^4), 147.76 (C^{8a}), 158.67 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 143.18 (100) $[M - H]^+$, 128 (20), 115 (22), 101 (5), 89 (4), 75 (5), 51(4).

2,8-Dimethylquinoline (3b). bp 65–66°C (0.3 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.65 s (3H, CH_3), 2.87 s (3H, CH_3), 6.98 d (1H, C^5H, J = 8.0 Hz), 7.24 d (1H, C^3H, J = 8.4 Hz), 7.38 t (1H, C^6H, J = 8.0 Hz), 7.65 d (1H, C^7H, J = 8.0 Hz), 7.89 d (1H, C^4H, J = 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.56 (CH_3), 25.67 (CH_3), 121.63 (C^3), 125.29 (C^5), 126.98 (C^6), 127.33 (C^{4a}), 128.26 (C^7), 136.50 (C^8), 137.49 (C^4), 144.67 (C^{8a}), 157.85 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 157.00 (100) $[M - H]^+$, 156 (31), 143 (10), 115 (8), 71 (4), 65 (2), 52 (2).

2,7-Dimethylquinoline (3c). bp 53–54°C (0.25 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.40 s (3H, CH_3), 2.64 s (3H, CH_3), 7.00 d (1H, C^5H, J = 8.0 Hz), 7.03 d (1H, C^6H, J = 8.0 Hz), 7.47 d (1H, C^4H, J = 7.6 Hz), 7.78 d (1H, C^3H, J = 8.4 Hz), 7.79 s (1H, C^8H). ^{13}C NMR spectrum, δ_C, ppm: 21.78 (CH_3), 25.29 (CH_3), 121.00 (C^3), 124.48 (C^5), 127.03 (C^{4a}), 127.78 (C^8), 127.81 (C^7), 135.65 (C^6), 139.40 (C^4), 148.26 (C^{8a}), 158.71 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 157.00 (100) $[M - H]^+$, 156 (28), 142 (11), 115 (11), 89 (4), 65 (4), 51 (4).

2,6-Dimethylquinoline (3e). bp 75–76°C (0.4 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.54 s (3H, CH_3), 2.72 s (CH_3), 7.21 d (1H, C^3H, J = 8.0 Hz), 7.59 d (1H, C^7H, J = 8.4 Hz), 7.73 s (1H, C^5H), 7.95 d (1H, C^4H, J = 7.2 Hz), 7.93 d (1H, C^8H, J = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.36 (CH_3), 25.13 (CH_3), 121.78 (C^3), 126.37 (C^5), 126.42 (C^{4a}), 128.35 (C^8), 131.50 (C^7), 135.19 (C^6), 135.41 (C^4), 146.76 (C^{8a}), 157.84 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 157.00 (100) $[M - H]^+$, 156 (32), 142 (8), 115 (8), 89 (3), 77 (3), 65 (3).

2-Methyl-8-ethylquinoline (3f). bp 73–74°C (0.2 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.30–1.60 m (3H, CH_3), 2.78 s (3H, CH_3), 3.30–3.50 m (2H, CH_2), 7.43 t (1H, C^6H, J = 7.2 Hz), 7.56 d (1H, C^7H, J = 6.8 Hz), 7.55–7.68 m (1H, C^5H), 7.99 s (1H, C^4H). ^{13}C NMR spectrum, δ_C, ppm: 15.15 ($CH_2\underline{C}H_3$), 24.34 ($\underline{C}H_2CH_3$), 25.68 (CH_3), 121.82 (C^3), 125.43 (C^5), 126.07 (C^6), 126.24 (C^{4a}), 128.34 (C^7), 136.15 (C^8), 142.38 (C^4), 146.47 (C^{8a}), 157.65 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 170.10 (100) $[M - H]^+$, 171 (83), 143 (63), 128 (16), 115 (36), 63 (40), 51 (50).

2-Methyl-8-chloroquinoline (3g). mp 65–68°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.84 s (3H, CH_3), 7.38–7.50 m (1H, $C^{3,6}H$), 7.82 d (1H, C^7H, J = 7.6 Hz), 8.00 d (1H, C^4H, J = 8.4 Hz), 8.03 d (1H, C^5H, J = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 25.19 (CH_3), 122.84 (C^3), 125.45(C^6), 126.32 (C^{4a}), 127.37 (C^5), 128.80 (C^7), 130.13 (C^8), 137.89 (C^4), 148.56 (C^{8a}), 161.87 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 177. 1 $[M - H]^+$.

2-Methyl-7-chloroquinoline (3h). bp 70–71°C (0.2 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.63 s (3H, CH_3), 7.12 d (1H, C^3H, J = 7.6 Hz), 7.25 d (1H, C^6H, J = 7.6 Hz), 7.48 d (1H, C^5H, J = 9.2 Hz), 7.84 d (1H, C^4H, J = 8.4 Hz), 7.93 s (1H, C^8H). ^{13}C NMR spectrum, δ_C, ppm: 25.38 (CH_3), 122.17 (C^3), 124.89 (C^6), 126.69 (C^{4a}), 124.86 (C^5), 127.85 (C^8), 135.11 (C^7), 135.84 (C^4), 148.36 (C^{8a}), 159.99 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 177 (100) $[M - H]^+$, 179 (32), 178 (12), 142 (16), 115 (15), 76 (6).

2-Methyl-5-chloroquinoline (3i). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.66 s (3H, CH_3), 7.11 d (1H, C^3H, J = 7.6 Hz), 7.24 d (1H, C^6H, J = 7.6 Hz), 7.45 t (1H, C^7H, J = 8.4 Hz), 7.84 d (1H, C^4H, J = 8 Hz), 8.20 d (1H, C^8H, J = 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 25.38 (CH_3), 122.82 (C^3), 124.96 (C^6), 126.63 (C^8), 126.69 (C^{4a}), 130.08 (C^7), 132.85 (C^4), 134.88 (C^5), 148.14 (C^{8a}), 159.80 (C^2).

2-Methyl-6-chloroquinoline (3j). mp 94–96°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.69 s (3H,CH_3), 7.28 d (1H, C^3H, J = 7.6 Hz), 7.60 d (1H, C^7H, J = 7.6 Hz), 7.73 s (1H, C^5H), 7.91 d (1H, C^8H, J = 8.4 Hz) 8.03 d (1H, C^4H, J = 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 25.30 (CH_3), 122.89 (C^3), 135.21 (C^6), 128.99 (C^{4a}), 126.41 (C^5), 122.89 (C^8), 130.16 (C^7), 135.21 (C^4), 145.55 (C^{8a}), 159.01 (C^2). Mass spectrum, *m/z* (I_{rel}, %): 177 (100) $[M - H]^+$, 179 (47), 142 (48), 116 (27), 99 (24), 51 (23).

2-Methyl-6-methoxyquinoline (3k). bp 95–96°C (0.4 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.69 s (3H, CH_3), 3.76 s (3H, OCH_3), 6.89 d (1H, C^3H, J = 8.0 Hz), 7.48 d (1H, C^7H, J = 7.6 Hz), 7.63 s (1H, C^5H), 7.71 d (1H, C^4H, J = 8.4 Hz), 7.91 d (1H, C^8H, J = 9.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 24.85 (CH_3), 55.42 (OCH_3), 121.71 (C^3), 122.01 (C^6), 127.32 (C^{4a}), 129.89 (C^7), 134.78 (C^4), 143.67 (C^5), 155.49 (C^{8a}), 157.45(C^2). Mass spectrum, *m/z* (I_{rel}, %): 173 (100) $[M - H]^+$, 158 (38), 130 (80), 103 (23), 77 (23).

2-Methyl-8-hydroxyquinoline (3l). bp 64–65°C (0.2 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.72

s (3H, CH_3), 7.14 d (1H, C^7H, J = 7.6 Hz), 7.27 d (1H, C^5H, J = 4.4 Hz), 7.29 d (1H, C^3H, J = 8.4 Hz), 7.38 t (1H, C^6H, J = 7.6 Hz), 8.02 d (1H, C^4H, J = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 24.82 (CH_3), 110.32 (C^7), 117.37 (C^5), 122.57 (C^3), 126.59 (C^6), 127.98 (C^{4a}), 136.04 (C^4), 138.65 (C^{8a}), 151.80 (C^8), 156.77 (C^2). Mass spectrum, m/z (I_{rel}, %): 159 (100) $[M - H]^+$, 160 (12), 131 (53), 130 (24), 89 (4), 77 (7).

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