Ruthenium-Catalyzed Formal Alkyl Group Transfer: Synthesis of Quinolines from Nitroarenes and Alkylammonium Halides

Chan Sik Cho*

Research Institute of Industrial Technology, Kyungpook National University, Daegu 702-701, Korea

Na Young Lee, Tae-Jeong Kim and Sang Chul Shim*

Department of Applied Chemistry, College of Engineering, Kyungpook National University, Daegu 702-701, Korea

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Nitroarenes are reductively cyclized with an array of tetraalkylammonium halides and trialkylammonium chlorides in the presence of a catalytic amount of a ruthenium catalyst along with tin(II) chloride dihydrate at 180° to afford the corresponding quinolines in moderate to good yields. The addition of tin(II) chloride dihydrate is necessary for the effective formation of quinolines and toluene is the solvent of choice. A reaction pathway involving initial reduction of nitroarenes to anilines and conversion of alkylammonium halides to alkylamines, alkyl group transfer from alkylamines to anilines to form an imine, dimerization of imine, and heteroannulation is proposed for this catalytic process.

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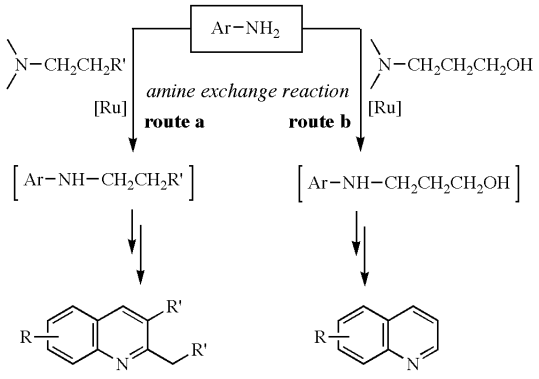
Introduction.

It is known that many quinoline containing compounds exhibit a wide spectrum of pharmacological and biological activities [1]. Thus, besides conventional named routes such as Skraup, Döbner-von Miller, Conrad-Limpach, Friedländer and Pfitzinger syntheses [2], homogeneous transition metal-catalyzed synthetic methods have been attempted for the construction of quinoline framework because of the facility and efficiency of reaction and wide availability of substrate [3]. In connection with this report, during the course of our ongoing studies on homogeneous ruthenium catalysis [4-10], we have also reported on construction of quinolines *via* ruthenium-catalyzed alkyl group transfer from alkylamines (Scheme 1, route a) [3a,5a-5c] and alkanolamines (Scheme 1, route b) [5d,5e] to N-atom of anilines (amine exchange reaction [11]) and oxidative cyclization of 2-aminobenzyl alcohol with ketones [12] and secondary alcohols [13] (modified Friedländer quinoline synthesis [14]). The amine exchange reaction has been used for the synthesis of unsymmetrical amines and N-heterocycles and the study of the metabolism of amines [11]. However, except for our findings, a clear-cut example for the synthesis of N-heterocycles using amine exchange reaction as yet seems to be limited to palladium-catalyzed synthesis of hydropyrimidines, imidazolidines and imidazoles [15]. Prompted by these circumstances, we also reported the direct use of nitroarenes instead of anilines for such heterocycles since nitroarenes are precursors of anilines from the viewpoint of industrial organic chemistry [16,17]. Herein, as another example for the synthesis of N-heterocycles using amine exchange reaction and nitroarenes, we report a ruthenium-catalyzed *in situ* reduction of nitroarenes to anilines and cyclization of anilines with alkylammonium halides leading to quinolines *via* an intrinsic amine exchange reaction.

Scheme 1

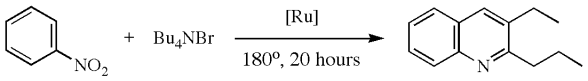


Results and Discussion.

The results of several attempted reductive cyclizations between nitrobenzene (**1a**) and tetrabutylammonium bromide (**2a**) under various conditions to achieve effective formation of 3-ethyl-2-propylquinoline (**3a**) are listed in Table 1 (Scheme 2). Generally, **1a** was subjected to react with **2a** in the presence of a catalytic amount of a ruthenium catalyst (2-3 mol% based on **2a**) at 180° for 20 hours to afford **3a**. The molar ratio of [**1a**]/[**2a**] = 2 was the choice of preference for the effective formation of **3a**. The addition of an appropriate amount of $SnCl_2 \cdot 2H_2O$ was necessary for the effective formation of **3a** (runs 1-4). The absence of $SnCl_2 \cdot 2H_2O$ resulted in incomplete conversion of **1a** to aniline (run 4). This result indicates that $SnCl_2 \cdot 2H_2O$ plays a role for the reduction of **1a** to aniline. It is known that

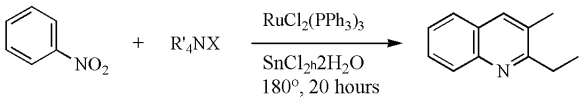
nitroarenes can be easily converted into anilines in the presence of $SnCl_2•2H_2O$ under nonacidic and nonaqueous media [18]. However, as has been observed in our recent report on the synthesis of indoles and quinolines from anilines and alkylamines, another feature of $SnCl_2•2H_2O$ seems to play a decisive role in either alkyl group transfer or heteroannulation step [4,5]. As shown in Table 1, among the activity of various ruthenium precursors examined $RuCl_2(PPh_3)_3$, $RuCl_3•nH_2O$ combined with PPh_3, $RuH_2(PPh_3)_4$, and $Cp^*RuCl_2(CO)$ revealed to be effective toward the formation of **3a** (runs 5-10). Finally, among solvents examined toluene turned out to be the most effective for the formation of **3a** (runs 11-14). Interestingly, much more *N*-butylaniline (54%) was formed under the employment of dioxane/H_2O (9 mL/1 mL) compared to that of other solvents (3-29%) (run 12).

Scheme 2



1a **2a** **3a**

Scheme 3



1a **2** **3b**

	Isolated yield (%)	
2	in dioxane	in toluene
2b Pr_4NCl	19	19
2c Pr_4NBr	40	58
2d Pr_4NI	35	56

The present reductive heteroannulation could also be applied to many nitroarenes **1** as well as tetraalkylammonium bromides **2** under two sets of reaction conditions, and several representative results are summarized in Table 2. In all cases, as is the solvent for the reaction of **1a** with **2a**, toluene was suitable for the formation of quinolines. Table 2 shows that the quinoline yield was considerably affected by the position of the substituent on the nitroarene, whereas the electronic nature of that had no relevance to the product yield. With *para*- and *meta*-substituted nitroarenes (**1b** and **1c**), the quinoline yield was higher than that when *ortho*-substituted nitroarene **1d** was used. In the case of 3-nitrotoluene (**1c**), the corresponding quinolines **3d** were obtained as a regioisomeric mixture, favoring the 7-methyl isomer which was formed *via* the less sterically hindered position on **1c**. Furthermore, although product yield in toluene was superior to that in dioxane, regioisomers were obtained with the same molar distribution. From the reaction of various nitroarenes bearing electron donating (**1e**

Table 1
Optimization of Conditions for Reductive Cyclization of **1a** with **2a** Leading to **3a** [a]

Run	Ruthenium catalysts (mmol)	$SnCl_2•2H_2O$ (mmol)	Solvents	Conv. (%) of **1a**	GLC yield (%) [b]
1	$RuCl_2(PPh_3)_3$ (0.02)	1	dioxane	100	50
2	$RuCl_2(PPh_3)_3$ (0.02)	0.2	dioxane	65	23
3	$RuCl_2(PPh_3)_3$ (0.02)	2	dioxane	100	35
4	$RuCl_2(PPh_3)_3$ (0.02)	-	dioxane	51	24
5	$RuCl_3•nH_2O$ (0.02)/3PPh_3	1	dioxane	100	48
6	$RuCl_3•nH_2O$ (0.02)/1.5dppm [c]	1	dioxane	100	38
7	$RuH_2(PPh_3)_4$ (0.02)	1	dioxane	100	48
8	$RuCl_2(=CHPh)(PCy_3)_2$ (0.02)	1	dioxane	100	13
9	$Cp^*RuCl_2(CO)$ [d] (0.02)	1	dioxane	66	48
10	$Ru_3(CO)_{12}$ (0.02)	1	dioxane	100	37
11	$RuCl_2(PPh_3)_3$ (0.03)	1	dioxane	100	67
12	$RuCl_2(PPh_3)_3$ (0.03)	1	dioxane/H_2O [e]	100	24
13	$RuCl_2(PPh_3)_3$ (0.03)	1	THF	100	50
14	$RuCl_2(PPh_3)_3$ (0.03)	1	toluene	100	88

[a] Reaction conditions: **1a** (2 mmol), **2a** (1 mmol), solvent (10 mL), 180°, for 20 hours, under Ar; [b] Based on **2a**. [c] Bis(diphenylphosphino)methane. [d] Cp* = pentamethylcyclopentadienyl. [e] Dioxane/H_2O = 9 mL/1 mL.

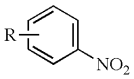
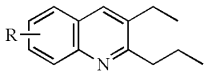
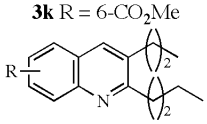
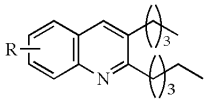
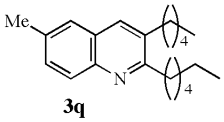
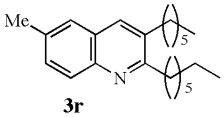
First, given these results, the reactions of **1a** with tetrapropylammonium halides (**2b**-**2d**) were screened in order to compare the reactivity of halides analogues under two sets of reaction conditions shown in entries 11 and 14 of Table 1 (Scheme 3). Much more 2-ethyl-3-methylquinoline (**3b**) was formed with the employment of tetrapropylammonium bromides (**2c**) and iodide (**2d**) compared to that of chloride analogue **2b**.

and **1f**) and withdrawing (**1g**-**1j**) substituents with **2a**, the corresponding quinolines (**3f**-**3k**) were also formed in moderate to good yields. Nitroarenes also reacted with an array of tetraalkylammonium bromides (**2e**-**2h**) and the corresponding quinolines (**3l**-**3r**) were obtained in similar yields irrespective of the alkyl chain length on **2e**-**2h**. As has been observed in our recent reports on ruthenium-catalyzed synthesis of indoles and quinolines [4,5], in the reactions of two-methyl substituted nitroarene **1f** with tetraalkylammonium bromides (**2a**, **2e**, and **2f**), much more product yield was observed when compared with mono-substituted nitroarenes.

Next, we examined a similar reductive heteroannulation of nitroarenes **1** with trialkylammonium chlorides **4** under $RuCl_2(PPh_3)_3/SnCl_2•2H_2O$/toluene conditions. Several representative results were summarized in Table 3. The reactions of **1a** with several trialkylammonium chlorides (**4a**-**4e**) proceed to afford the corresponding quinolines (**3a** and **3s**-**3v**) with concomitant formation of aniline and N-alkylanilines. Here, in contrast to the reaction of **1** with **2**, the product yield decreased with the increase of the alkyl chain length on **4a**-**4d**. Lower yield was observed with triamylammonium chloride (**4e**) having branched alkyl chain when compared to that with straight trialkylammonium

Table 2

Ruthenium-Catalyzed Synthesis of Quinolines **3** from Nitroarenes **1** and Tetraalkylammonium Bromides **2** [a]

Nitroarenes **1**	R'_4NX **2**	Quinolines **3**	Yield (%) [b] A	B
				
1a R = H	**2a** Bu_4NBr	**3a** R = H	44	62
1b R = 4-Me	**2a** Bu_4NBr	**3c** R = 6-Me	46	63
1c R = 3-Me	**2a** Bu_4NBr	**3d** R = 7- and 5-Me	47 [c]	81 [c]
1d R = 2-Me	**2a** Bu_4NBr	**3e** R = 8-Me	20	34
1e R = 4-OMe	**2a** Bu_4NBr	**3f** R = 6-OMe	32	43
1f R = 3,5-Me_2	**2a** Bu_4NBr	**3g** R = 5,7-Me_2	50	81
1g R = 4-Cl	**2a** Bu_4NBr	**3h** R = 6-Cl	11	43
1h R = 4-acetyl	**2a** Bu_4NBr	**3i** R = 6-acetyl	33	44
1i R = 4-benzoyl	**2a** Bu_4NBr	**3j** R = 6-benzoyl	23	47
1j R = 4-CO_2Me	**2a** Bu_4NBr	**3k** R = 6-CO_2Me	10	23
				
1a	**2e** $[CH_3(CH_2)_4]_4NBr$	**3l** R = H	46	
1b	**2e**	**3m** R = 6-Me	49	62
1f	**2e**	**3n** R = 5,7-Me_2	61	
				
1b	**2f** $[CH_3(CH_2)_5]_4NBr$	**3o** R = 6-Me	46	58
1f	**2f**	**3p** R = 5,7-Me_2	61	
1b	**2g** $[CH_3(CH_2)_6]_4NBr$	 **3q**	52	63
1b	**2h** $[CH_3(CH_2)_7]_4NBr$	 **3r**	48	60

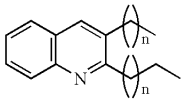
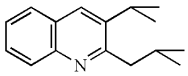
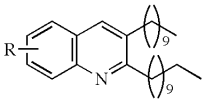
[a] Reaction conditions: **1** (2 mmol), **2** (1 mmol), $RuCl_2(PPh_3)_3$ (0.03 mmol), $SnCl_2h2H_2O$ (1 mmol), solvent (10 mL), 180°, for 20 hours, under argon. [b] Isolated yield based on **2**. A: in dioxane; B: in toluene. [c] Regioisomeric distribution was calculated by ^1H NMR (400 MHz): 5-methyl/7-methyl=1/6.

chlorides (**4a** and **4b**) having similar chain length. Nitroarenes such as **1b** and **1f** were also reacted with trialkylammonium chlorides (**4b** and **4d**) to give the corresponding quinolines (**3o**, **3w**, and **3x**).

Markovnikov hydroamination to form an enamine, isomerization of enamine to tautomeric imine, and imine dimerization [22]. A similar catalytic cycle has also been made by others [23] and in our recent report [5c].

Table 3

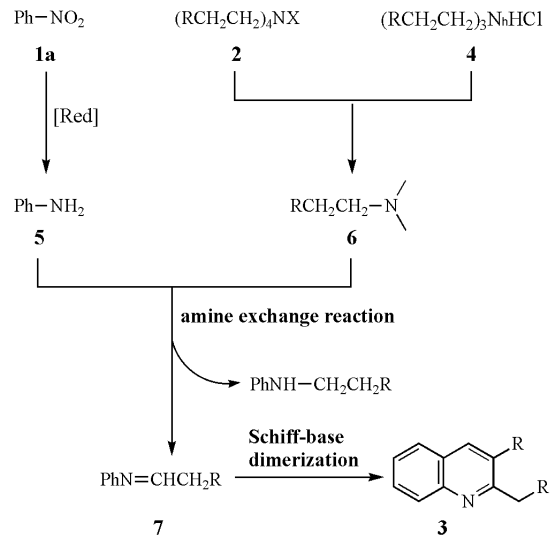
Ruthenium-Catalyzed Synthesis of Quinolines **3** from Nitroarenes **1** and Trialkylammonium Chlorides **4** [a]

Nitroarenes **1**	R_3N•HCl **4**	Quinolines **3**	Yield (%) [b]
			
1a	**4a** Bu_3N•HCl	**3a** n = 1	56
1a	**4b** $[CH_3(CH_2)_5]_3NhHCl$	**3s** n = 3	51
1a	**4c** $[CH_3(CH_2)_7]_3NhHCl$	**3t** n = 5	40
1a	**4d** $[CH_3(CH_2)_{11}]_3NhHCl$	**3u** n = 9	22
1a	**4e** $[(CH_3)_2CH(CH_2)_2]_3NhHCl$	 **3v**	32
1b	**4b**	**3o** 	51
1b	**4d**	**3w** R = 6-Me	38
1f	**4d**	**3x** R = 5,7-Me_2	24

[a] Reaction conditions: **1** (2 mmol), **4** (1 mmol), $RuCl_2(PPh_3)_3$ (0.03 mmol), $SnCl_2$•$2H_2O$ (1 mmol), toluene (10 mL), 180°, for 20 hours, under argon. [b] Isolated yield based on **4**.

Although the present reaction pathway including the exact role of $SnCl_2$•$2H_2O$ is not yet fully understood [19], the outline of the reaction scheme, consistent with the product and by-product formed, is shown in Scheme 4. The starting nitrobenzene **1a** and alkylammonium halides (**2** and **4**) seem initially to be converted into aniline **5** and alkylamine **6**, respectively. It appears that the latter transformation occurs for easy coordination of tertiary amine to catalyst ruthenium [20]. An alkyl group transfer from **6** to N-atom of **5** gives an imine **7** with concomitant formation of N-alkylaniline through several known mechanistic sequences, which is described in our recent report [5b,5c]. This alkyl group transfer is known as an amine exchange reaction (amine scrambling reaction) [11]. Although we have no evidence for the generation of **7**, the formation of N-alkylaniline in all cases shown in Table 2 supports the presence of **7** in the reaction course as an intermediate. It is well known that the intermolecular alkyl group transfer between alkylamines proceeds through an imine or iminium ion complex under transition metals [11]. Subsequent step seems to proceed *via* the known Schiff-base dimerization [21] to form quinoline **3**. It was reported by Beller *et al.* that anilines react with styrenes to give quinolines *via* initial *anti-*

Scheme 4



Conclusion.

We have demonstrated that nitroarenes can be reductively cyclized with tetraalkylammonium halides as well as trialkylammonium chlorides in the presence of a ruthe-

nium catalyst and $SnCl_2•2H_2O$ to afford quinolines in moderate to good yields. The present reaction is another example for the synthesis of N-heterocycles using amine exchange reaction by the direct use of nitroarenes.

EXPERIMENTAL

^1H- and ^{13}C-NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance Digital 400 spectrometer using TMS as an internal standard. Infrared spectra were obtained on a Mattson Galaxy 7020A spectrophotometer. The GLC analyses were carried out with Shimadzu GC-17A (FID) equipped with CBP10-S25-050 column (Shimadzu, a silica fused capillary column, 0.33 mm x 25 m, 0.25 μm film thickness) using N_2 as carrier gas. Mass spectra were obtained using EI ionization at 70 eV. The isolation of pure products was carried out *via* column chromatography (silica gel 60, 70-230 mesh, Merck) and thin layer chromatography (silica gel 60 GF_{254}, Merck). Commercially available organic and inorganic compounds were used without further purification. $Cp^*RuCl_2(CO)$ [24] and $RuCl_2(PPh_3)_3$ [25] were prepared by the reported methods.

General Procedure for Ruthenium-Catalyzed Reactions between **1a** and **2a** (for GLC Analysis).

A mixture of **1a** (246 mg, 2 mmol), **2a** (322 mg, 1 mmol), ruthenium catalyst (0.02-0.03 mmol), $SnCl_2•2H_2O$ (0-1 mmol) in solvent (10 mL) was charged in 50 mL stainless steel autoclave. After the system was flushed with argon, the resulting mixture was stirred at 180° for 20 hours. The reaction mixture was filtered through a short silica gel column (ethyl acetate-chloroform mixture) to eliminate inorganic salts. To the extract was added appropriate amount of internal standard and analyzed by GLC.

General Procedure for Ruthenium-Catalyzed Synthesis of **3** from **1** and **2** (or **4**) (for Isolation).

A mixture of **1** (2 mmol), **2** or **4** (1 mmol), $RuCl_2(PPh_3)_3$ (29 mg, 0.03 mmol), and $SnCl_2•2H_2O$ (226 mg, 1 mmol) in dioxane or toluene was charged in 50 mL stainless steel autoclave. After the system was flushed with argon, the reaction mixture was stirred at 180° for 20 hours. The reaction mixture was filtered through a short silica gel column (ethyl acetate-chloroform mixture) to eliminate inorganic salts and the filtrate was concentrated under reduced pressure. The residual mixture was separated by TLC or column chromatography to give quinolines. All products prepared by this procedure, except for the following compounds, were noted in our recent reports [3a,13,16c].

Methyl 3-Ethyl-2-propylquinoline-6-carboxylate (**3k**).

This compound was obtained as a pale yellow oil; ir (neat): ν 1717 (C=O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.08 (t, J = 7.5 Hz, 3H), 1.35 (t, J = 7.5 Hz, 3H), 1.81-1.90 (m, 2H), 2.85 (q, J = 7.5 Hz, 2H), 2.97 (t, J = 8.0 Hz, 2H), 3.98 (s, 3H), 7.94 (s, 1H), 8.03 (d, J = 9.0 Hz, 1H), 8.20 (dd, J = 9.0 and 2.0 Hz, 1H), 8.50 (d, J = 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.16, 14.31, 22.57, 25.07, 37.86, 52.23, 126.40, 127.00, 127.87, 128.69, 130.19, 134.78, 136.27, 148.27, 164.59, 166.91; ms: m/z (%) 257 (M^+, 39), 229 (100).

Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.34; H, 7.40; N, 5.62.

2-Butyl-3-propylquinoline (**3l**) [26].

This compound was obtained as a pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 0.98 (t, J = 7.0 Hz, 3H), 1.04 (t, J = 7.0 Hz, 3H), 1.45-1.54 (m, 2H), 1.67-1.82 (m, 4H), 2.75 (t, J = 7.5 Hz, 2H), 2.98 (t, J = 8.0 Hz, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.70 (d, J = 8.7 Hz, 1H), 7.82 (s, 1H), 8.01 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.07, 14.09, 23.07, 23.60, 31.91, 34.42, 35.67, 125.51, 126.88, 127.20, 128.32, 128.46, 133.86, 134.85, 146.51, 162.31; ms: m/z (%) 228 (M^+, 25), 157 (100).

2-Butyl-6-methyl-3-propylquinoline (**3m**).

This compound was obtained as a pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 0.96-1.03 (m, 6H), 1.44-1.53 (m, 2H), 1.64-1.71 (m, 2H), 1.73-1.81 (m, 2H), 2.45 (s, 3H), 2.71 (t, J = 7.5 Hz, 2H), 2.94 (t, J = 8.0 Hz, 2H), 7.38-7.42 (m, 2H), 7.69 (s, 1H), 7.91 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.07 (x2), 21.47, 23.08, 23.61, 31.91, 34.44, 35.56, 125.77, 127.23, 128.19, 130.53, 133.74, 134.25, 135.11, 145.14, 161.23; ms: m/z (%) 241 (M^+, 25), 171 (100).

Anal. Calcd. for $C_{17}H_{23}N$: C, 84.59; H, 9.60; N, 5.80. Found: C, 84.28; H, 9.68; N, 5.63.

2-Butyl-5,7-dimethyl-3-propylquinoline (**3n**).

This compound was obtained as a pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, J = 7.5 Hz, 3H), 1.04 (t, J = 7.5 Hz, 3H), 1.44-1.53 (m, 2H), 1.66-1.81 (m, 4H), 2.47 (s, 3H), 2.60 (s, 3H), 2.76 (t, J = 8.0, 2H), 2.94 (t, J = 7.8 Hz, 2H), 7.10 (s, 1H), 7.66 (s, 1H), 7.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.08, 14.13, 18.51, 21.72, 23.08, 24.02, 31.98, 34.79, 35.54, 124.46, 125.82, 128.34, 131.37, 132.49, 133.26, 137.96, 147.05, 161.59; ms: m/z (%) 255 (M^+, 8), 185 (100).

Anal. Calcd. for $C_{18}H_{25}N$: C, 84.65; H, 9.87; N, 5.48. Found: C, 84.43; H, 9.71; N, 5.65.

2-Hexyl-6-methyl-3-pentylquinoline (**3q**).

This compound was obtained as a pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88-0.94 (m, 6H), 1.32-1.48 (m, 10H), 1.64-1.70 (m, 2H), 1.94-1.98 (m, 2H), 2.48 (s, 3H), 2.75 (t, J = 7.5 Hz, 2H), 2.94 (t, J = 7.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 1H), 7.46 (s, 1H), 7.73 (s, 1H), 7.90 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.05, 14.11, 21.51, 22.58, 22.65, 29.66, 29.80, 30.26, 31.79, 31.82, 32.39, 35.91, 125.76, 127.25, 128.18, 130.53, 134.05, 134.22, 135.14, 145.11, 161.30; ms: m/z (%) 297 (M^+, 6), 171 (100).

Anal. Calcd. for $C_{21}H_{31}N$: C, 84.79; H, 10.50; N, 4.71. Found: C, 84.63; H, 10.44; N, 4.81.

2-Heptyl-3-hexylquinoline (**3t**).

This compound was obtained as a pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 0.87-0.92 (m, 6H), 1.25-1.48 (m, 14H), 1.64-1.71 (m, 2H), 1.75-1.83 (m, 2H), 2.77 (t, J = 7.5 Hz, 2H), 2.97 (t, J = 8.0 Hz, 2H), 7.40-7.44 (m, 1H), 7.57-7.61 (m, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.82 (s, 1H), 8.01 (d, J = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.11 (x2), 22.63, 22.68, 29.26, 29.31, 29.82, 29.94, 30.53, 31.73, 31.85, 32.41, 35.96, 125.51, 126.86, 127.25, 128.30, 128.45, 134.15, 134.80, 146.50, 162.32.

Anal. Calcd. for $C_{22}H_{33}N$: C, 84.83; H, 10.68; N, 4.50. Found: C, 84.70; H, 10.74; N, 4.67.

3-Decyl-2-undecylquinoline (**3u**).

This compound was obtained as a yellowish brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86-0.89 (m, 6H), 1.26-1.48 (m, 30H), 1.65-1.72 (m, 2H), 1.74-1.82 (m, 2H), 2.78 (t, J = 8.0 Hz, 2H), 2.97 (t, J = 8.0 Hz, 2H), 7.42-7.45 (m, 1H), 7.58-7.62 (m, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.84 (s, 1H), 8.01 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.12, 22.70, 29.37, 29.52, 29.63, 29.66, 29.69, 29.81, 29.98, 30.57, 31.94, 32.42, 35.97, 125.52, 126.87, 127.25, 128.31, 128.47, 134.18, 134.83, 162.35. Several peaks are eclipsed.

Anal. Calcd. for $C_{30}H_{49}N$: C, 85.04; H, 11.66; N, 3.31. Found: C, 85.17; H, 11.75; N, 3.22.

2-iso-Butyl-3-iso-propylquinoline (**3v**) [27].

This compound was obtained as a pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (d, J = 6.5 Hz, 6H), 1.33 (d, J = 6.5 Hz, 6H), 2.21-2.32 (m, 1H), 2.92 (d, J = 7.5 Hz, 2H), 3.32 (sept, J = 6.5 Hz, 1H), 7.42-7.46 (m, 1H), 7.58-7.62 (m, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.94 (s, 1H), 8.02 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.63, 23.87, 28.81, 29.40, 44.12, 125.50, 127.03, 127.29, 128.33, 128.52, 131.53, 140.75, 146.17, 160.77.

3-Decyl-6-methyl-2-undecylquinoline (**3w**).

This compound was obtained as a yellowish brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86-0.89 (m, 6H), 1.26-1.45 (m, 30H), 1.62-1.70 (m, 2H), 1.74-1.82 (m, 2H), 2.48 (s, 3H), 2.74 (t, J = 8.0 Hz, 2H), 2.94 (t, J = 8.0 Hz, 2H), 7.40-7.45 (m, 2H), 7.72 (s, 1H), 7.90 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.13, 21.50, 22.72, 29.38, 29.40, 29.55, 29.63, 29.66, 29.69, 29.72, 29.84, 30.00, 30.59, 31.96, 32.44, 125.75, 127.26, 128.20, 130.52, 134.04, 134.21, 135.11, 145.12, 161.28. Several peaks are eclipsed.

Anal. Calcd. for $C_{31}H_{51}N$: C, 85.06; H, 11.74; N, 3.20. Found: C, 85.26; H, 11.80; N, 3.29.

3-Decyl-5,7-dimethyl-2-undecylquinoline (**3x**).

This compound was obtained as a yellowish brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86-0.89 (m, 6H), 1.26-1.48 (m, 30H), 1.63-1.71 (m, 2H), 1.73-1.81 (m, 2H), 2.47 (s, 3H), 2.60 (s, 3H), 2.77 (t, J = 8.0 Hz, 2H), 2.94 (t, J = 8.0 Hz, 2H), 7.10 (s, 1H), 7.66 (s, 1H), 7.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.12, 18.50, 21.72, 22.71, 29.37, 29.39, 29.54, 29.62, 29.66, 29.71, 29.86, 29.98, 30.96, 31.93, 31.96, 32.75, 35.81, 114.67, 118.99, 124.51, 125.82, 128.34, 131.32, 132.77, 133.22, 137.93, 147.02, 161.59. Several peaks are eclipsed.

Anal. Calcd. for $C_{32}H_{53}N$: C, 85.07; H, 11.82; N, 3.10. Found: C, 85.19; H, 11.91; N, 3.24.

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