Ruthenium-Catalyzed Synthesis of Quinolines from Anilines and *N*-Allylic Compounds by Cascade Amine Exchange Reaction-Heteroannulation

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Anilines react with *N*-allylic compounds such as triallylamine and *N,N*-diallylaniline in dioxane in the presence of a catalytic amount of ruthenium(III) chloride hydrate and bis(diphenylphosphino)methane and tin(II) chloride dihydrate to afford the corresponding quinolines in high yields. Several other phosphorus ligands are also effective, but bis(diphenylphosphino)methane is the ligand of choice. A reaction pathway involving cascade amine exchange reaction-heteroannulation is proposed for this catalytic process.

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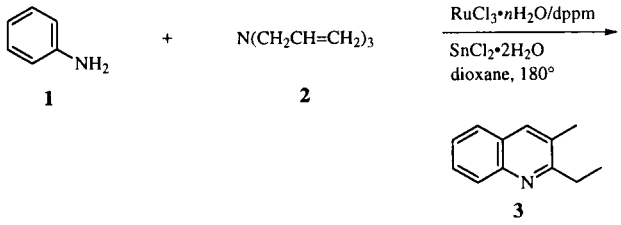
Introduction.

Transition metal-catalyzed heteroannulation process has been widely introduced for the formation of many heterocyclic compounds which play an important role as a basic skeleton for the design of many biologically active compounds [1]. The formation of the structural core of quinolines has also been attempted by a remarkable catalytic action of transition metal catalysts such as palladium [2-6], rhodium [7-12], ruthenium [13-18], and iron [19]. As part of our continuing studies on transition metal-catalyzed synthesis of *N*-heterocyclic compounds, we have recently developed and reported a new synthetic approach for the formation of indoles [20-22] and quinolines [23] from anilines and alkanolamines. It was suggested that all reactions proceed *via* amine exchange reactions [24-27] between anilines and alkanolamines. However, a clear-cut example for the synthesis of *N*-heterocyclic compounds using amine exchange reactions seems to be limited to palladium-catalyzed synthesis of pyrimidines and imidazoles [27] and ruthenium-catalyzed synthesis of indoles [20-22] and quinolines [23]. We now disclose another example for the synthesis of 2-ethyl-3-methylquinolines from anilines and *N*-allylic compounds through cascade amine exchange reaction-heteroannulation and report here the detailed results of this reaction from both synthetic and mechanistic viewpoints [28].

Results and Discussion.

We examined the heteroannulation between aniline (**1**) and triallylamine (**2**) in the presence of a ruthenium catalyst to optimize the reaction conditions using similar catalytic systems which were employed for the synthesis of indoles and quinolines by us [20-23]. Thus, treatment of aniline (**1**) with triallylamine (**2**) in dioxane under an argon atmosphere in the presence of a catalytic amount of ruthenium(III) chloride hydrate (4 mole% based on **2**) and a phosphorus ligand (in the case of monodentate phosphorus ligand: 3-fold molar amount to ruthenium(III) chloride hydrate; in the case of bidentate phosphorus ligand: 1.5-fold molar amount to ruthenium(III) chloride hydrate) together with tin(II) chloride dihydrate at 180° for 20 hours afforded 2-ethyl-3-methylquinoline (**3**) (Scheme 1). *N*-Propylaniline and *N*-allylaniline were obtained as by-products by an alkyl group transfer between aniline (**1**) and triallylamine (**2**) and by hydrogenation under the ruthenium catalyst (21% isolated yield under $RuCl_3 \cdot nH_2O/3PPh_3$ catalytic system; *N*-allylaniline/*N*-propylaniline = 2/5).

Scheme 1



1 **2** **3**

Several representative results were summarized in Table 1. The yield of 2-ethyl-3-methylquinoline (**3**) was considerably affected by the molar ratio of aniline (**1**) to triallylamine (**2**) as has been observed in our recent report (runs 1-5) [20-23]. Table 1 shows that the optimum yield was obtained at the molar ratio of 6. The existence of tin(II) chloride dihydrate was essential for the effective formation of **3**, since the yield of **3** was only 4% in the absence of tin(II) chloride dihydrate (run 6). When a variety of phosphorus chelating ligands such as bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp) and

Table 1

Ruthenium-Catalyzed Synthesis of 2-Ethyl-3-methylquinoline (**3**) from Aniline (**1**) and Triallylamine (**2**) Under Various Conditions [a]

Run	Molar Ratio of **1**/**2**	Catalyst	GLC Yield [b]
1	2	$RuCl_3 \cdot nH_2O/3PPh_3/SnCl_2 \cdot 2H_2O$	43
2	4	$RuCl_3 \cdot nH_2O/3PPh_3/SnCl_2 \cdot 2H_2O$	57
3	6	$RuCl_3 \cdot nH_2O/3PPh_3/SnCl_2 \cdot 2H_2O$	60
4	8	$RuCl_3 \cdot nH_2O/3PPh_3/SnCl_2 \cdot 2H_2O$	64
5	10	$RuCl_3 \cdot nH_2O/3PPh_3/SnCl_2 \cdot 2H_2O$	63
6	10	$RuCl_3 \cdot nH_2O/3PPh_3$	4
7	6	$RuCl_3 \cdot nH_2O$/1.5dppm/$SnCl_2 \cdot 2H_2O$	82 (71)
8	6	$RuCl_3 \cdot nH_2O$/1.5dppe/$SnCl_2 \cdot 2H_2O$	78
9	6	$RuCl_3 \cdot nH_2O$/1.5dppp/$SnCl_2 \cdot 2H_2O$	76
10	6	$RuCl_3 \cdot nH_2O$/1.5dppf/$SnCl_2 \cdot 2H_2O$	56
11	6	$RuCl_3 \cdot nH_2O/3P(OEt)_3/SnCl_2 \cdot 2H_2O$	67
12	6	$RuCl_3 \cdot nH_2O/3P(OPh)_3/SnCl_2 \cdot 2H_2O$	48
13	6	$RuCl_2(PPh_3)_3/SnCl_2 \cdot 2H_2O$	66
14	6	$Ru_3(CO)_{12}/SnCl_2 \cdot 2H_2O$	0

[a] All reactions were carried out with aniline (**1**), triallylamine (**2**) (1 mmole), ruthenium catalyst (0.04 mmole), $SnCl_2 \cdot 2H_2O$ (1 mmole) in dioxane (10 ml) at 180° for 20 hours unless othewise stated; [b] Isolated yield is shown in parenthesis.

Table 2

Ruthenium-Catalyzed Synthesis of 2-Ethyl-3-methylquinolines from Anilines and Triallylamine (**2**) [a]

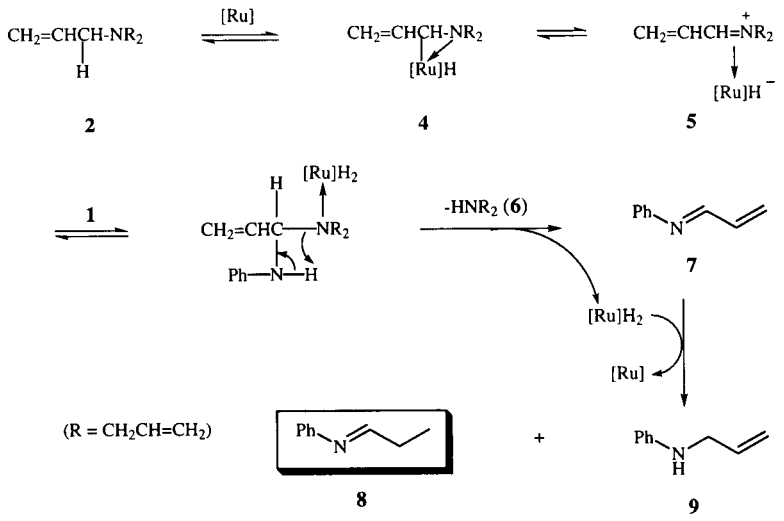
Run	Aniline Derivative	Product	Isolated Yield [b]
1	aniline	2-ethyl-3-methylquinoline	71 (51)
2	*p*-toluidine	2-ethyl-3,6-dimethylquinoline	74 (61)
3	*m*-toluidine	[c]	65 (56)
4	*o*-toluidine	*N*-allyl-*o*-toluidine	(37)
5	*p*-anisidine	2-ethyl-6-methoxy-3-methylquinoline	73 (55)
6	*m*-anisidine	2-ethyl-7-methoxy-3-methylquinoline	61 (50)
7	*p*-chloroaniline	6-chloro-2-ethyl-3-methylquinoline	29 (24)
8	*m*-chloroaniline	7-chloro-2-ethyl-3-methylquinoline	(28)
9	*p*-ethylaniline	2,6-diethyl-3-methylquinoline	65
10	*p*-butylaniline	6-butyl-2-ethyl-3-methylquinoline	66 (55)
11	*p*-*sec*-butylaniline	6-(*sec*-butyl)-2-ethyl-3-methylquinoline	67 (61)
12	3,5-dimethylaniline	2-ethyl-3,5,7-trimethylquinoline	76 (59)

[a] All reactions were carried out with aniline (6 mmoles), triallylamine (**2**) (1 mmole), $RuCl_3 \cdot nH_2O$ (0.04 mmole), bis(diphenylphosphino)methane (0.06 mmole), $SnCl_2 \cdot 2H_2O$ (1 mmole) in dioxane (10 ml) at 180° for 20 hours; [b] The yield using triphenylphosphine as ligand is shown in parentheses; [c] 2-Ethyl-3,5-dimethylquinoline and 2-ethyl-3,7-dimethylquinoline were obtained as a mixture (2-ethyl-3,7-dimethylquinoline/2-ethyl-3,5-dimethylquinoline = 93/7).

1,1'-bis(diphenylphosphino)ferrocene (dppf) combined with ruthenium(III) chloride hydrate were used alternatively in place of triphenylphosphine, the yield of 2-ethyl-3-methylquinoline (**3**) was generally improved (runs 7-10). Other monodentate phosphorus ligands such as triethyl phosphite and triphenyl phosphite combined with ruthenium(III) chloride hydrate (runs 11-12) and other catalyst precursor dichlorotris(triphenylphophine)ruthenium(II) (run 13) were as effective as tripenylphosphine for the present heteroannulation. However, when dodecacarbonyltriruthenium(0) was used as catalyst precursor, the quinoline **3** was not detected at all on GLC analysis and the starting aniline was recovered almost completely (run 14).

The present cyclization could also be applied to many primary aromatic amines, and several representative results are summarized in Table 2. The reaction under ruthenium(III) chloride hydrate-bis(diphenylphosphino)-methane catalytic system proved to be more effective toward quinoline formation than the reaction under ruthenium(III) chloride hydrate-triphenylphosphine system as observed in previous section. All reactions were accompanied by the formation of *N*-propylanilines and *N*-allylanilines as side products. The quinoline yield was considerably affected by the substituent effect in the aniline derivatives. The product yield was generally lower in the use of anilines with an electron-withdrawing group (runs 7, 8) than in the employment of anilines having an

Scheme 2

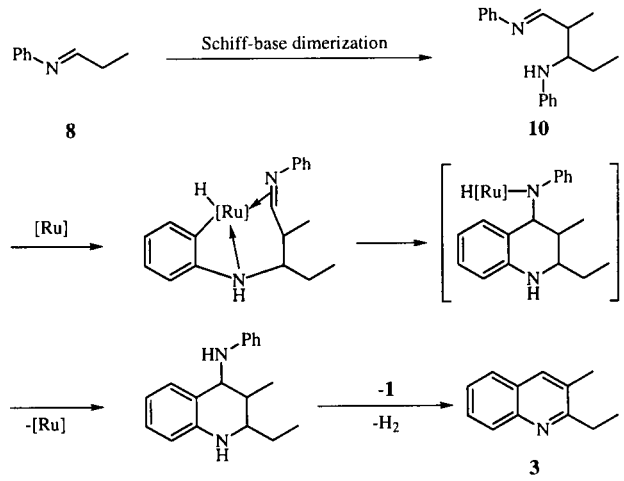


electron-donating group (runs 5, 6). In the case of *o*-toluidine, the reaction did not proceed at all toward quinoline formation, and *N*-allyl-*o*-toluidine was only detectable product (run 4). In the cases of *meta*-substituted anilines such as *m*-toluidine, *m*-anisidine and *m*-chloroaniline, the corresponding quinolines were obtained as a regioisomeric mixture in good yields, favoring predominantly the formation of 7-substituted isomers (runs 3, 6, 8). However, in the reaction with *m*-anisidine and *m*-chloroaniline, even if 5-substituted isomers were present, these were only a trace amount on the analysis of ^{1}H nmr and gas chromatography (runs 6, 8). In the cases of other alkylanilines such as *p*-ethylaniline, *p*-butylaniline, *p-sec*-butylaniline, and 3,5-dimethylaniline, the corresponding quinolines were also obtained in good yields (runs 9-11).

Although the details of the present heteroannulation pathway are not yet fully understood, a possible pathway is presented in Schemes 2 and 3 by choosing aniline (**1**) and triallylamine (**2**) as an example. The reaction seems to proceed *via* an initial formation of phenylpropylideneamine (**8**) shown in Scheme 2. It is well-known that the intermolecular alkyl group transfer between alkylamines proceeds through iminium ion complex under transition metals such as palladium and ruthenium [24-27,29]. Thus, the transfer of allylic moiety from **2** to **1** can be rationalized by Scheme 2. The initial coordination of triallylamine (**2**) to ruthenium followed by oxidative insertion of ruthenium in the adjacent C-H bond forms an alkylruthenium complex **4**, which rapidly equilibrates with an iminium ion complex **5**. Nucleophilic attack of the aniline (**1**) to the complex **5** gives allylidenephenylamine (**7**) along with diallylamine (**6**) and dihydridoruthenium. This is followed by selective reduction of **7** by dihydridoruthenium to afford phenylpropylideneamine (**8**) as well as *N*-allylaniline (**9**).

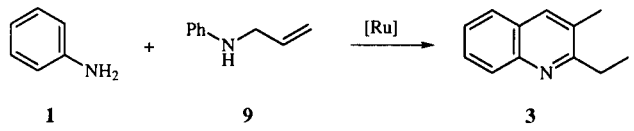
In the next heteroannulation stage, the reaction seems to proceed *via* Schiff-base dimer (**10**) as shown in Scheme 3. It is known that anilines react with aliphatic aldehyde to give Schiff-base dimer on simple mixing at room temperature [30]. Watanabe and co-workers reported that the Schiff-base dimer (**10**) was cyclized to give quinolines under ruthenium catalyst through subsequent organometallic actions such as oxidative addition of the *ortho* carbon-hydrogen bond of Schiff-base dimer to low valent ruthenium *via* orthometallation, insertion of the carbon-nitrogen double bond into the ruthenium-carbon bond, reductive elimination of ruthenium, and elimination of aniline and hydrogen [15].

Scheme 3



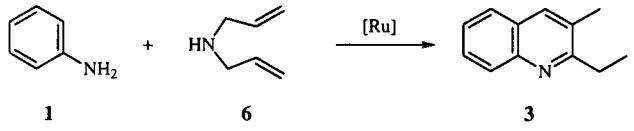
The following experimental observations are worth noting as evidence for phenylpropylideneamine (**8**) as a key intermediate in our catalytic system. Similar treatment of aniline (**1**) with *N*-allylaniline (**9**), which can be alternatively formed by reduction of allylidenephenylamine (**7**), afforded 2-ethyl-3-methylquinoline (**3**) in only 10% yield ($RuCl_3 \cdot nH_2O$-$3PPh_3$ system) (Scheme 4). Actually, *N*-allylaniline (**9**) was obtained along with *N*-propylaniline from the reaction of aniline (**1**) and triallylamine (**2**) under the ruthenium catalyst system as describe above. However, *N*-allylaniline (**9**) itself was not reacted toward quinoline under the ruthenium catalyst system. These results indicate that phenylpropylideneamine (**8**) formed in the course of amine exchange reaction is a key intermediate under the present reaction. In a separate experiment, we also observed that a similar reaction of aniline (**1**) with diallylamine (**6**) gave the same quinoline **3** in 33% yield ($RuCl_3 \cdot nH_2O$-$3PPh_3$ system) (Scheme 5). This result indicates that at least two allyl groups out of three in triallylamine (**2**) are available for alkyl group transfer.

Scheme 4



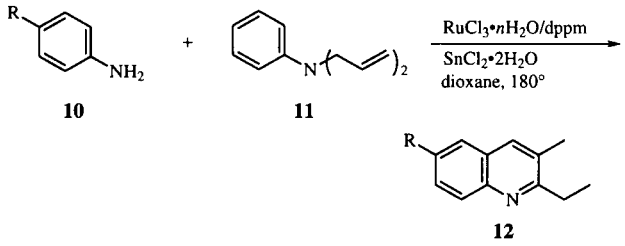
1 9 3

Scheme 5



1 6 3

Scheme 6



10 11 12

We then examined the heteroannulation between aniline **10** and *N*,*N*-diallylaniline (**11**) as cyclization counterpart under similar catalytic system as described above (Scheme 6). Several representative results were summarized in Table 3. Treatment of equimolar amount of *p*-toluidine (**10**, R = Me) with *N*,*N*-diallylaniline (**11**) in dioxane under an argon atmosphere in the presence of a catalytic amount of ruthenium(III) chloride hydrate (4 mole%) and bis(diphenylphosphino)methane (6 mole%) and tin(II) chloride dihydrate (1 equivalent) at 180° for 20 hours afforded 2-ethyl-3,6-dimethylquinoline (**12**, R = Me, 20%) and 2-ethyl-3-methylquinoline (**3**, 3%) along with aniline (**1**, 25%), *N*-allylaniline (**9**, 7%), *N*-propylaniline (9%), and *N*-propyl-*p*-toluidine (14%). This result indicates that *N*,*N*-diallylaniline (**11**) can be used as a cyclization counterpart. On the other hand, similar treatment of excess *p*-toluidine (**10**, R = Me) with *N*,*N*-diallylaniline (**11**) (the molar ratio of *p*-toluidine to **11** = 6) afforded 2-ethyl-3,6-dimethylquinoline (39%) as the sole cyclized product along with aniline (**1**, 53%), *N*-allylaniline (**9**, 14%), *N*-propylaniline (5%), and *N*-propyl-*p*-toluidine (13%). From other easily available anilines **10** the corresponding quinolines **12** were also formed in good yields without the formation of 2-ethyl-3-methylquinoline (runs 4-6).

Table 3

Ruthenium-Catalyzed Synthesis of Quinolines **12** from **10** and *N*,*N*-Diallylaniline (**11**) [a]

Run	Aniline Derivative	Product	Yield [b]
1 [c]	*p*-toluidine	2-ethyl-3,6-dimethylquinoline	20 [d]
2	*p*-toluidine	2-ethyl-3,6-dimethylquinoline	39
3	**1**	2-ethyl-3-methylquinoline	40
4	*p*-anisidine	2-ethyl-6-methoxy-3-methylquinoline	46
5	*p*-butylaniline	6-butyl-1-ethyl-3-methylquinoline	51
6	*p*-*sec*-butylaniline	6-(*sec*-butyl)-2-ethyl-3-methylquinoline	54

[a] All reactions were carried out with aniline (6 mmoles), *N*,*N*-diallylaniline (**11**) (1 mmole), $RuCl_3 \cdot nH_2O$ (0.04 mmole), bis(diphenylphosphino)-methane (0.06 mmole), $SnCl_2 \cdot 2H_2O$ (1 mmole) in dioxane (10 ml) at 180° for 20 hours unless otherwise stated; [b] Determined by gas chromatography using undecane as an internal standard; [c] 1 Mmole of *p*-toluidine was used; [d] 2-Ethyl-3-methylquinoline (**3**) was formed in 3% yield.

EXPERIMENTAL

The ^1H (300 MHz) and ^{13}C (75.5 MHz) nmr spectra were recorded on a Varian Unity Plus 300 spectrometer using tetramethylsilane as an internal standard. Chemical shifts are reported in δ units downfield from tetramethylsilane. Electron impact mass spectra were obtained on a Shimadzu QP-1000 spectrometer. The GLC analyses were carried out with Shimadzu GC-17A equipped with CBP10-S25-050 column (Shimadzu, fused silica capillary column, 0.33 mm x 25 m, 0.25 μm film thickness) using nitrogen as the carrier gas. All GLC yields were determined using undecane as an internal standard. The isolation of pure products was carried out *via* column chromatography (silica gel 60 HF_{254}, Merck) and thin layer chromatography. Commercially available organic and inorganic compounds were used without further purification. Both *N,N*-diallylaniline and *N*-allylaniline were prepared by the reaction of aniline with allyl chloride under potassium carbonate [31]. Ruthenium catalysts such as dichlorotris(triphenylphosphine)-ruthenium(II) [32] and dodecacarbonyltriruthenium(0) [33] were prepared by the reported method.

General Procedure for Ruthenium-Catalyzed Synthesis of 2-Ethyl-3-methylquinolines from Anilines and Triallylamine (**2**).

A mixture of aniline (6 mmoles), triallylamine (137 mg, 1 mmole), ruthenium(III) chloride hydrate (10 mg, 0.04 mmole), bis(diphenylphosphino)methane (23 mg, 0.06 mmole), and tin(II) chloride dihydrate (226 mg, 1 mmole) in dioxane (10 ml) was placed in a stainless steel pressure vessel. After the system was flushed with argon, the mixture was stirred at 180° for 20 hours. The reaction mixture was filtered through a short column (silica gel, chloroform/ethyl acetate = 1/3) to eliminate inorganic compounds and poured into brine. The organic layer was dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left an oil which was separated by column chromatography using an ethyl acetate-hexane mixture as the eluent to give the corresponding pure 2-ethyl-3-methylquinolines. The products obtained by the above procedure were characterized spectroscopically as shown below. All compounds are known except for 2,6-diethyl-3-methylquinoline, 6-butyl-2-ethyl-3-methylquinoline, 6-(*sec*-butyl)-2-ethyl-3-methylquinoline and 2-ethyl-3,5,7-trimethylquinoline [10].

2-Ethyl-3-methylquinoline.

This compound was obtained as pale yellow oil; ir (neat): ν 3058, 2973, 1614, 1498, 1452, 749 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.36 (t, J = 7.5 Hz, 3H), 2.44 (s, 3H), 2.97 (q, J = 7.5 Hz, 2H), 7.39-7.44 (m, 1H), 7.56-7.68 (m, 2H), 7.78 (s, 1H), 8.02 (d, J = 8.4 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 12.7, 19.0, 29.4, 125.5, 126.6, 127.2, 128.2, 128.4, 129.3, 135.6, 146.6, 163.2; ms: m/z (%) 171 (M^+, 78), 170 (100), 143 (45), 128 (8), 115 (33), 77 (13).

2-Ethyl-3,6-dimethylquinoline.

This compound was obtained as pale yellow oil; ir (neat): ν 2971, 2934, 1611, 1495, 1452, 826, 795 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.33 (t, J = 7.5 Hz, 3H), 2.35 (s, 3H), 2.42 (s, 3H), 2.91 (q, J = 7.5 Hz, 2H), 7.34-7.39 (m, 2H), 7.59 (s, 1H), 7.91 (d, J = 8.4 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 12.6, 18.8, 21.2, 29.1, 125.3, 127.1, 127.9, 129.0, 130.2, 134.9 (x2), 145.0, 161.9; ms: m/z (%) 185 (M^+, 49), 184 (100), 157 (23), 128 (12), 115 (9), 91 (7), 77 (9).

2-Ethyl-3,7-dimethylquinoline.

This compound was obtained as pale yellow oil; ^1H nmr (deuteriochloroform): δ 1.35 (t, J = 7.5 Hz, 3H), 2.41 (s, 3H), 2.50 (s, 3H), 2.95 (q, J = 7.5 Hz, 2H), 7.24 (d, J = 8.1 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.72 (s, 1H), 7.80 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 12.7, 18.9, 21.6, 29.3, 125.2, 126.2, 127.5, 127.6, 128.3, 135.4, 138.2, 146.7, 163.0; ms: m/z (%) 185 (M^+, 58), 184 (100), 157 (26), 128 (13), 115 (10), 91 (10), 77 (11). Representative ^1H nmr data of regioisomeric 2-ethyl-3,5-dimethylquinoline is as follows; ^1H nmr (deuteriochloroform): δ 1.36 (t, J = 7.5 Hz, 3H), 2.47 (s, 3H), 2.60 (s, 3H).

2-Ethyl-6-methoxy-3-methylquinoline.

This compound was obtained as pale yellow oil; ^1H nmr (deuteriochloroform): δ 1.33 (t, J = 7.5 Hz, 3H), 2.38 (s, 3H), 2.91 (q, J = 7.5 Hz, 2H), 3.83 (s, 3H), 6.90 (d, J = 2.7 Hz, 1H), 7.24 (dd, J = 2.7 and 9.3 Hz, 1H), 7.64 (s, 1H), 7.91 (d, J = 9.3 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 12.7, 18.8, 29.0, 55.1, 104.3, 120.5, 127.9, 129.4, 129.7, 134.6, 142.4, 156.9, 160.4; ms: m/z (%) 201 (M^+, 64), 200 (100), 186 (21), 157 (20), 143 (9), 130 (14), 115 (11), 102 (7), 77 (10).

2-Ethyl-7-methoxy-3-methylquinoline.

This compound was obtained as pale yellow oil; ^1H nmr (deuteriochloroform): δ 1.35 (t, J = 7.5 Hz, 3H), 2.41 (s, 3H), 2.95 (q, J = 7.5 Hz, 2H), 3.91 (s, 3H), 7.09 (dd, J = 2.7 and 8.7 Hz, 1H), 7.36 (d, J = 2.7 Hz, 1H), 7.54 (d, J = 8.7 Hz, 1H), 7.71 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 12.8, 18.6, 29.3, 55.2, 106.5, 118.4, 122.2, 126.7, 127.5, 135.5, 147.9, 159.7, 163.2; ms: m/z (%) 201 (M^+, 67), 200 (100), 173 (13), 158 (26), 115 (8), 102 (9), 77 (12).

6-Chloro-2-ethyl-3-methylquinoline.

This compound was obtained as white solid, mp 46-48° (ethyl acetate-hexane) (lit [10] bp 101-102°/0.35 torr); ^1H nmr (deuteriochloroform): δ 1.36 (t, J = 7.5 Hz, 3H), 2.47 (s, 3H), 2.97 (q, J = 7.5 Hz, 2H), 7.53 (dd, J = 2.4 and 9.0 Hz, 1H), 7.66 (d, J = 2.4 Hz, 1H), 7.72 (s, 1H), 7.94 (d, J = 9.0 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 12.5, 19.0, 29.3, 125.2, 127.8, 129.0, 130.1, 130.5, 131.0, 134.6, 144.9, 163.5; ms: m/z (%) 207 (M^++2, 21), 205 (M^+, 66), 204 (100), 177 (17), 140 (6), 114 (6), 84 (6).

7-Chloro-2-ethyl-3-methylquinoline.

This compound was obtained as pale yellow solid, mp 52-54° (ethyl acetate-hexane) (lit [10] mp 54-56°); ^1H nmr (deuteriochloroform): δ 1.36 (t, J = 7.5 Hz, 3H), 2.45 (s, 3H), 2.96 (q, J = 7.5 Hz, 2H), 7.37 (dd, J = 2.1 and 8.7 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.77 (s, 1H), 8.02 (d, J = 2.1 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 12.5, 19.0 29.4, 125.6, 126.5, 127.6, 127.8, 129.7, 133.8, 135.3, 146.9, 164.3; ms: m/z (%) 207 (M^++2, 21), 205 (M^+, 69), 204 (100), 177 (29), 154 (7), 140 (21), 115 (23), 99 (7), 84 (28), 75 (14), 63 (24), 51 (11).

2,6-Diethyl-3-methylquinoline.

This compound was obtained as pale yellow oil; ^1H nmr (deuteriochloroform): δ 1.28 (t, J = 7.5 Hz, 3H), 1.34 (t, J = 7.5 Hz, 3H), 2.37 (s, 3H), 2.75 (q, J = 7.5 Hz, 2H), 2.93 (q, J = 7.5 Hz, 2H), 7.40-7.45 (m, 2H), 7.66 (s, 1H), 7.95 (d, J = 8.7 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 12.7, 15.2, 18.8, 28.6, 29.1, 124.0, 127.1, 128.1, 128.9, 129.2, 135.1, 141.2, 162.0.

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.21; H, 8.48; N, 7.01.

6-Butyl-2-ethyl-3-methylquinoline.

This compound was obtained as pale yellow oil; ^{1}H nmr (deuteriochloroform): δ 0.93 (t, J = 7.5 Hz, 3H), 1.32-1.40 (m, 5H), 1.66-1.71 (m, 2H), 2.42 (s, 3H), 2.73 (t, J = 7.5 Hz, 2H), 2.95 (q, J = 7.5 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.71 (s, 1H), 7.94 (d, J = 8.7 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 12.8, 13.8, 18.9, 22.2, 29.3, 33.3, 35.4, 124.9, 127.2, 128.1, 129.1, 129.7, 135.2, 140.1, 145.3, 162.2; ms: m/z (%) 227 (M^+, 94), 214 (9), 200 (16), 184 (100), 169 (16), 157 (17), 142 (10), 128 (14), 115 (14), 106 (13), 91 (5), 77 (9), 41 (21).

Anal. Calcd. for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16. Found: C, 84.40; H, 9.18; N, 6.10.

6-(*sec*-Butyl)-2-ethyl-3-methylquinoline.

This compound was obtained as pale yellow oil; ^{1}H nmr (deuteriochloroform): δ 0.82 (t, J = 7.5 Hz, 3H), 1.29 (d, J = 6.9 Hz, 3H), 1.35 (t, J = 7.5 Hz, 3H), 1.61-1.71 (m, 2H), 2.42 (s, 3H), 2.68-2.79 (m, 1H), 2.96 (q, J = 7.5 Hz, 2H), 7.44-7.48 (m, 2H), 7.74 (s, 1H), 7.97 (d, J = 8.4 Hz, 1H); ^{13}C nmr (deuteriochloroform): δ 12.1, 12.9, 18.9, 21.7, 29.3, 30.9, 41.5, 123.8, 127.2, 128.1, 128.2, 129.0, 135.4, 144.7, 145.5, 162.2; ms: m/z (%) 227 (M^+, 71), 213 (11), 198 (100), 184 (17), 170 (8), 154 (4), 141 (3), 91 (1).

Anal. Calcd. for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16. Found: C, 84.35; H, 9.11; N, 6.08.

2-Ethyl-3,5,7-trimethylquinoline.

This compound was obtained as pale yellow solid, mp 60-62° (ethyl acetate-hexane); ^{1}H nmr (deuteriochloroform): δ 1.35 (t, J = 7.5 Hz, 3H), 2.47 (s, 6H), 2.59 (s, 3H), 2.96 (q, J = 7.5 Hz, 2H), 7.10 (s, 1H), 7.66 (s, 1H), 7.91 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 12.8, 18.3, 19.1, 21.6, 29.2, 124.4, 125.7, 127.8, 128.2, 132.0, 133.0, 137.7, 147.0, 162.4; ms: m/z (%) 199 (M^+, 62), 198 (100), 171 (15), 156 (4), 115 (3), 91 (2), 77 (2).

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.22; H, 8.58; N, 6.99.

Typical Procedure for Ruthenium-Catalyzed Heteroannulation Between Anilines and *N,N*-Diallylaniline (**11**).

A mixture of *p*-toluidine (643 mg, 6 mmoles), *N,N*-diallylaniline (173 mg, 1 mmole), ruthenium(III) chloride hydrate (10 mg, 0.04 mmole), bis(diphenylphosphino)methane (23 mg, 0.06 mmole), and tin(II) chloride dihydrate (226 mg, 1 mmole) in dioxane (10 ml) was placed in a stainless steel autoclave. After the system was flushed with argon, the mixture was stirred at 180° for 20 hours. The reaction mixture was filtered through a short column (silica gel, chloroform/ethyl acetate = 1/3) to eliminate inorganic compounds. To the filtrate was added undecane as an internal standard and the mixture was analyzed by gas chromatography.

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