Part 7: Anti-Markovnikov Functionalizations of Unsaturated Compounds[+]

Amination of Aromatic Olefins with Anilines: A New Domino Synthesis of Quinolines

Matthias Beller,*[a] Oliver R. Thiel,[b] Harald Trauthwein,[b] and Christian G. Hartung[a]

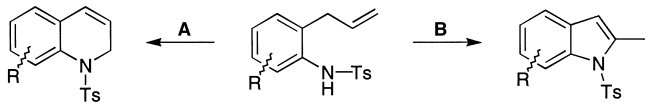
Dedicated to Professor Dr. Hartmut Oehme on the occasion of his 60th birthday

Abstract: A new catalytic amination of aromatic olefins with anilines is presented. In a domino reaction, substituted quinoline derivatives are obtained in the presence of cationic rhodium complexes, such as $[Rh(cod)_2]BF_4$, and PPh_3. Ethylbenzene is formed as a by-product in this new oxidative reaction. The first transition metal catalyzed anti-Markovnikov hydroamination of styrene with anilines occurs as a side reaction. Mechanistic investigations strongly support the regioselective oxidative amination of styrene as the key reaction step.

Keywords: anti-Markovnikov aminations · domino reactions · homogeneous catalysis · quinolines · rhodium

Introduction

The development of new methods for the synthesis of amines and nitrogen heterocycles is of fundamental importance in organic chemistry. In general, the direct amination of readily available olefins constitutes the most atom efficient way for the construction of carbon–nitrogen bonds in these products. Considerable efforts have been undertaken to develop catalytic amination processes.[2] So far amination of olefins has focussed mainly on the synthesis of simple amines and not on the synthesis of heterocycles. Pioneering work on the synthesis of heterocycles by amination of olefins was done by Hegedus et al, who used palladium complexes for the intramolecular oxidative amination of 2-aminostyrene derivatives, which led to *N*-heterocycles.[3] This work was continued by Larock et al, who showed that the intramolecular amination of allylanilines leads to 2,3-dihydroindoles or dihydroquinolines, according to the nature of the palladium catalyst (Scheme 1).[4]



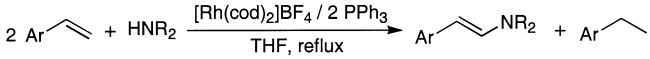
Ts = Tosylate

A: $Pd(OAc)_2$, NaOAc, O_2, DMSO

B: $PdCl_2(MeCN)_2$, benzoquinone, LiCl, THF

Scheme 1. Regioselective aminations of allylaniline derivatives.

Recently, Marks and co-workers have developed lanthanide catalysts for the hydroamination of olefins.[5] Lately, this methodology has been used for tandem C–N and C–C bond-forming processes, and this yields products with pyrrolizidine, indolizidine, pyrrole, and pyrazine skeletons.[6] Our approach to the catalytic amination of olefins[7] was based on the use of cationic rhodium complexes in order to enhance the reactivity of the known rhodium halide catalysts. Indeed, in the presence of catalytic amounts of $[Rh(cod)_2]^+BF_4^-/2\,PPh_3$, styrenes react with secondary amines to yield linear *N*-(2-arylethenyl)amines (Scheme 2).



Scheme 2. Rhodium-catalyzed oxidative anti-Markovnikov amination of styrenes.

In this paper, we describe the rhodium-catalyzed amination of styrenes with anilines that gives direct access to substituted quinolines produced in a new domino reaction.[8] Quinolines

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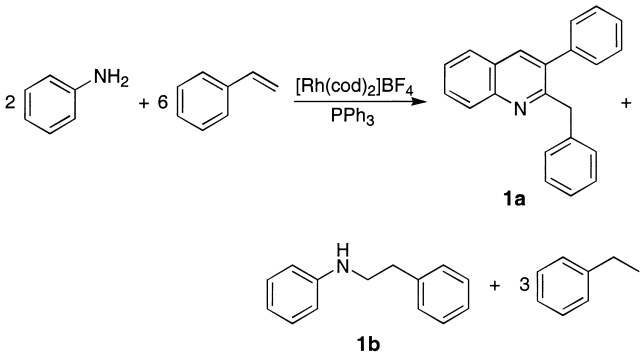
  0947-6539/00/0614-2513 $ 17.50+.50/0

are of importance as components of biologically active compounds, for example, the natural product quinine,[9] as well as synthetic pharmaceuticals, for example, primaquinine, chloroquine, and the antibacterial cloxyquine, which display anti-malaria activity.[10, 11] The synthesis of quinolines has been a focus of organic chemistry for more than 100 years. Classical routes for the synthesis of quinolines, such as the Skraup, Doebner – von Miller, Conrad – Limbach, Combes, Friedländer, and Pfitzinger quinoline syntheses,[12] mostly involve reactions of amines with carbonyl groups. Unfortunately, these routes are limited to certain substitution patterns, and due to the need for harsh reaction conditions, the yields obtained are low in most cases. A new approach was reported by Povarov et al, who utilized hetero-Diels – Alder reactions for the formation of quinoline derivatives for the first time.[13, 14]

Results

Domino reactions for the synthesis of quinoline derivatives: We have shown that cationic rhodium complexes catalyze the intermolecular oxidative amination of secondary amines and aromatic olefins to give terminal enamines.[7] With the use of primary amines as starting materials, the resulting enamines should tautomerize to the more stable imines. When aniline is used as the amine in the reaction with styrenes, the resulting imine, phenylethylideneaniline, provides a reactive intermediate, which can react with a further olefin in a formal hetero-Diels – Alder reaction. In fact, when we reacted aniline with styrene in the presence of the cationic rhodium complex $[Rh(cod)_2]BF_4$ (2.5 mol%) and PPh_3 (10 mol%) in a pressure tube, we obtained 2-benzyl-3-phenylquinoline (**1a**) in 20% yield (Scheme 3). Clearly, **1a** results from a formal hetero-Diels – Alder reaction of phenylethylideneaniline with styrene followed by dehydrogenation. Apart from 2-benzyl-3-phenylquinoline, whose structure was unambiguously determined by the ^{1}H NMR spectrum shown in Figure 1, no other substituted quinoline derivatives could be isolated.



Scheme 3. Rhodium-catalyzed reaction of aniline with styrene.

As a side reaction the anti-Markovnikov hydroamination of styrene yields *N*-(2-phenylethyl)aniline (**1b**) in 9% yield. In addition, the formation of ethylbenzene was detected. In order to increase the product yield of **1a**, we studied this new reaction under various conditions. The optimal reaction temperature was 140 °C in toluene. Lower yields of **1a** were obtained, when the reaction temperature was decreased to 120 °C or raised to 160 °C. Because of the relatively high reaction temperature, four equivalents of PPh_3 are needed for sufficient stabilization of the rhodium center. A broad number of solvents were tested for the reaction. Toluene, tetrahydrofuran, and di-*n*-butylether gave comparable yields of **1a**, whereas lower yields were obtained with dioxane, xylene, anisole, and *N*-methylpyrrolidone. Strongly coordinating solvents like diglyme or butyronitrile inhibit the reaction completely. Interestingly, the reaction could be performed with styrene as the solvent, but the formation of polystyrene leads to complications in the isolation of **1a**.

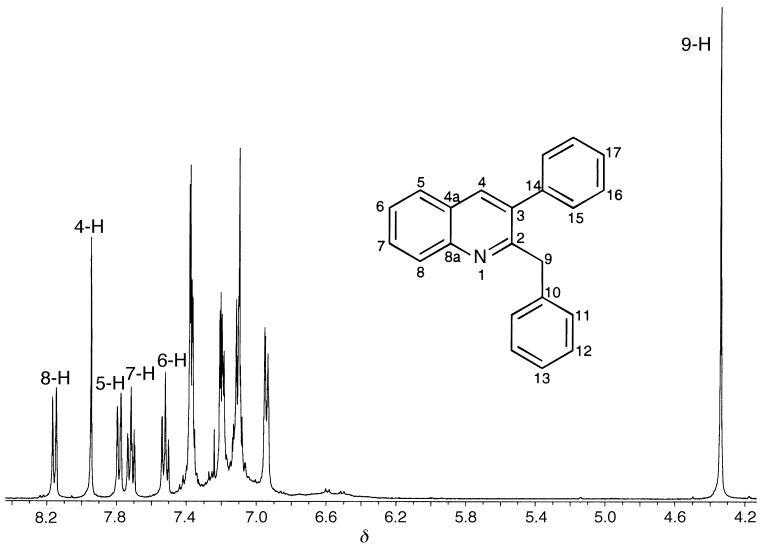


Figure 1. ^{1}H NMR spectrum of 2-benzyl-3-phenylquinoline (**1a**).

Abstract in German: *Eine neue katalytische Aminierungsreaktion von aromatischen Olefinen mit Anilinen wird beschrieben. Unter Einsatz von kationischen Rhodiumkomplexen wie $[Rh(cod)_2]BF_4/4PPh_3$ werden dabei direkt substituierte Chinolinderivate in einer Dominoreaktion erhalten. Als Nebenprodukt dieser neuen oxidativen Reaktion wird Ethylbenzol gebildet. Die erste übergangsmetallkatalysierte anti-Markownikow-Hydroaminierung von Styrol mit Anilin findet als Nebenreaktion statt. Mechanistische Untersuchungen dienen als Grundlage für einen Vorschlag zum Reaktionsablauf der Reaktion, der eine oxidative Aminierung von Styrol als Schlüsselschritt enthält.*

0947-6539/00/0614-2514 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 14

Table 1. Rhodium-catalyzed reaction of styrene with aniline.[a]

	styrene/aniline	$[Rh(cod)_2]BF_4$ [mol %]	PPh_3 [mol %]	additive [mol %]	quinoline (**1a**)	yield [%][b] ethylbenzene	alkylamine (**1b**)
1	5:1	2.5	10	–	20	89	9
2	1:1	2.5	10	–	11	34	7
3	10:1	2.5	10	–	18	99	9
4	5:1	10	40	–	40	134	8
5	5:1	10[c]	40	–	43	155	6
6	5:1	5	20	–	28	107	9
7	5:1	1	4	–	10	54	5
8	5:1	2.5	10	**1a** (20)	21 (=20+1)	13	3
9	5:1	2.5	10	quinoline (25)	6	27	4
10	5:1	2.5	10	DIPEA[d] (10)	3	27	5
11	5:1	2.5	10	$HBF_4 \cdot OEt_2$ (20)	< 0.1	< 0.1	< 0.1

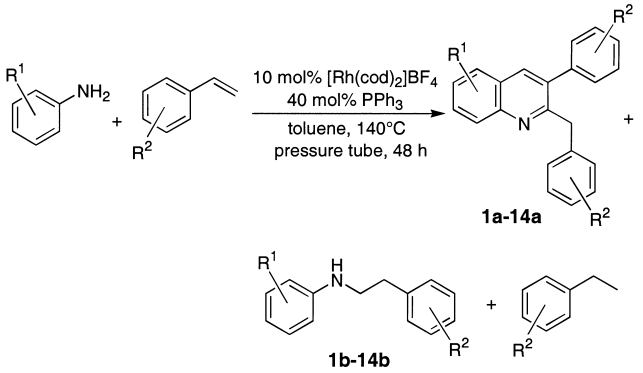
[a] $[Rh(cod)_2]BF_4$, PPh_3, and additives relative to aniline, 5 mL toluene, 140 °C, 20 h reaction time in a pressure tube. The yields are relative to aniline and were determined by gas chromatography with hexadecane as an internal standard. [b] Yields refer to aniline. [c] 48 h Reaction time. [d] DIPEA (diisopropylethylamine).

In order to investigate the influence of further reaction parameters, the stoichiometry of the reactants, the catalyst concentration, and additives were varied (Table 1). On analysis of the stoichiometry of the reaction, an optimal styrene/aniline ratio of 5:1 is expected, as two molecules of styrene are reduced to ethylbenzene when the aromatic quinoline system is formed. Indeed, the best results were obtained when a styrene/aniline ratio of 5:1 was used. At higher ratios, polystyrene is formed in significant amounts, and product isolation becomes difficult. Furthermore, the concentration of the reaction mixture is of great importance. A concentration of 1M aniline is optimal, whereas the reaction is very slow at lower concentrations. Despite considerable optimization, product yields (**1a**) above 25% were not realized with a catalyst amount of 2.5 mol%. Since *N*-heterocycles are known to act as strong coordinating ligands at the rhodium center,[15] we assumed that inhibition of the catalyst by the reaction products occurred. To prove this hypothesis 20 mol% of 2-benzyl-3-phenylquinoline (**1a**) was added to a reaction mixture at the beginning, and this resulted in a nearly complete deactivation of the catalyst. A similar result was obtained when we added 25 mol% quinoline to the reaction mixture.

In order to overcome the product inhibition, the use of a co-catalyst was tested in the reaction. We tried to influence the complexation behavior of the quinoline derivatives by the addition of small amounts of an inert acid or base (Table 1). However, a completely distinct reaction pathway was observed when $HBF_4 \cdot OEt_2$ was added as an acid, and the Markovnikov *N*-alkylation and *ortho*-C alkylation products of aniline were isolated.[16] Nevertheless, the product yield of **1a** can be increased by simply increasing the catalyst concentration. Thus, when the catalyst concentration was raised to 10 mol% $[Rh(cod)_2]BF_4/4\,PPh_3$, **1a** was obtained in 43% yield.

Next, we were interested in the application of the reaction to various aniline and styrene derivatives, and these results are summarized in Table 2. Except for the reaction of 3-fluoroaniline and 4-methylstyrene (Table 2, entry 14), the anti-Markovnikov hydroamination of styrene is a side reaction pathway, and hydroamination products in yields of 5–15% are obtained.

Table 2. Scope and limitations of the new domino quinoline synthesis.[a]



	aniline	styrene	quinoline **1–14a**	yield [%][b] ethyl-benzene	alkylamine **1–14b**
1	$R^1 = H$	$R^2 = H$	43 (40)	155	6
2	$R^1 = 4$-MeO	$R^2 = H$	42 (39)	138	7
3	$R^1 = 3$-MeO	$R^2 = H$	24 (19)	139	7
4	$R^1 = 4$-F	$R^2 = H$	30 (26)	115	12
5	$R^1 = 3$-F	$R^2 = H$	51 (48)	163	11
6	$R^1 = 4$-Ph	$R^2 = H$	32 (31)	126	10
7	$R^1 = 4$-Me	$R^2 = H$	33 (31)	141	10
8	$R^1 = H$	$R^2 = 4$-F	40 (35)	144	5
9	$R^1 = H$	$R^2 = 4$-MeO	40 (36)	129	10
10	$R^1 = H$	$R^2 = 3,4$-MeO	27 (23)	178	15
11	$R^1 = H$	$R^2 = 4$-Me	45 (44)	159	6
12	$R^1 = H$	$R^2 = 3$-CF_3	17 (16)	133	15
13	$R^1 = H$	2-vinylnaphthalene	35 (29)	177	12
14	$R^1 = 3$-F	$R^2 = 4$-Me	15 (13)	96	20

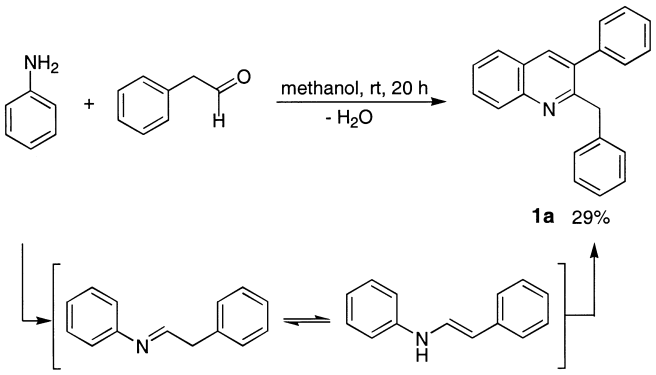
[a] Styrene:aniline 5:1, 10 mol% $[Rh(cod)_2]BF_4/4\,PPh_3$ relative to the amine, 5 mL toluene, 140 °C, 48 h reaction time in a pressure tube. The yields are relative to the amine and were determined by gas chromatography with hexadecane as an internal standard; isolated yields for compounds **1a–14a** are added in brackets. [b] Yields refer to the aniline.

Interestingly, the reaction of both *para*- and *meta*-substituted anilines leads regioselectively to the corresponding quinoline derivative, substituted in 6- or 7-position, respectively. No clear trend is observed with regard to the substituent influences in both the aniline or styrene rings. If a catalyst concentration of 10 mol% is used, in general, yields of 30–50% of the corresponding tri- or tetrasubstituted quinolines are obtained.

Mechanistic investigations: In order to shed some light on the mechanism of the domino reaction of styrene and aniline, the time-dependent conversion of the starting materials together with the product formation was studied. For this purpose, a reaction mixture of styrene and aniline in a ratio of 5:1, 5 mol% $[Rh(cod)_2]BF_4/4\,PPh_3$ (relative to aniline), and toluene as the solvent was equally distributed among eleven pressure tubes and heated to 140 °C. After a given reaction time, one of the pressure tubes was rapidly cooled to room temperature to stop any further reaction. The data obtained are shown in Figure 2.

The conversion of aniline and styrene is nearly parallel in the first 30 hours, however later on, only styrene is consumed, and polystyrene is formed. On the other hand, after 20 hours no further significant formation of **1a** and **1b** is observed. The formation of **1a** parallels the formation of ethylbenzene with a constant ratio of 1:4. In a stoichiometric reaction, only three equivalents of ethylbenzene should be formed per equivalent of quinoline. Hence, other oxidative side reactions that lead to oligomerization and polymerization products must also be considered. The main reaction products **1a** and **1b** are formed by independent pathways, no consecutive or decomposition reactions are involved. The first ten hours of the reaction are particularly interesting. A clear induction period was observed with the maximum rate of conversion after 1 hour. After this period, the reaction is slowed down as a result of the product inhibition of the catalyst. The induction period is explained by the slow formation of the active rhodium catalyst. Interestingly, $[Rh(cod)(PPh_3)_2]BF_4$ was isolated out of the reaction mixture in the form of orange crystals after a reaction time of 1 hour. However, this complex must also be a precursor of the active species, because of the lack of any styrene or aniline ligand. No other defined rhodium complexes could be isolated out of the reaction mixture after longer reaction times.

Based on our previous work, we proposed *N*-(2-phenylethenyl)aniline as the primary reaction intermediate of the domino reaction, which will tautomerize to the thermodynamically more stable *N*-(2-phenylethylidene)aniline. In order to study the following reaction steps, we tried to synthesize *N*-(2-phenylethylidene)aniline by condensation of aniline with phenylacetaldehyde. Surprisingly, the imine or enamine could not be isolated, instead 2-benzyl-3-phenylquinoline (**1a**) was formed in 29% yield (Scheme 4).



Scheme 4. Condensation of phenylacetaldehyde with aniline.

This condensation experiment showed that the presence of styrene is not a prerequisite for the formation of 2-benzyl-3-phenylquinoline (**1a**). We propose instead that the formation of the quinoline ring takes place by an attack of the enamine on the tautomeric imine followed by an electrophilic substitution in the *ortho*-position of the imine intermediate. This proposal is in agreement with the recently described condensation of aniline hydrochloride with phenylacetaldehyde in the presence of the reducing agent $NaBH_3CN$ that leads to 1,2,3,4-tetrahydro-2-benzyl-3-phenylquinoline.[17]

Nevertheless, the reactivity of styrene in an aza-Diels–Alder reaction with a stable imine (*N*-benzylideneaniline) in the presence of a rhodium catalyst (2.5 mol% $[Rh(cod)_2]BF_4/2\,PPh_3$) was tested. In the reaction, 2,4-diphenylquinoline was formed in 21% yield (Scheme 5). In addition, the imine is reduced instead of the styrene in this case, and no ethylbenzene is formed in the reaction. The observed 2,4-substitution pattern of the quinoline derivative is in good agreement with other catalyzed aza-Diels–Alder reactions,[14] and this shows that the 2,3-regiochemistry of the reported domino quinoline reaction can be ascribed to the reaction of *N*-(2-phenylethenyl)aniline with *N*-phenyl-*N*-phenylethylimine as dienophile instead of styrene.

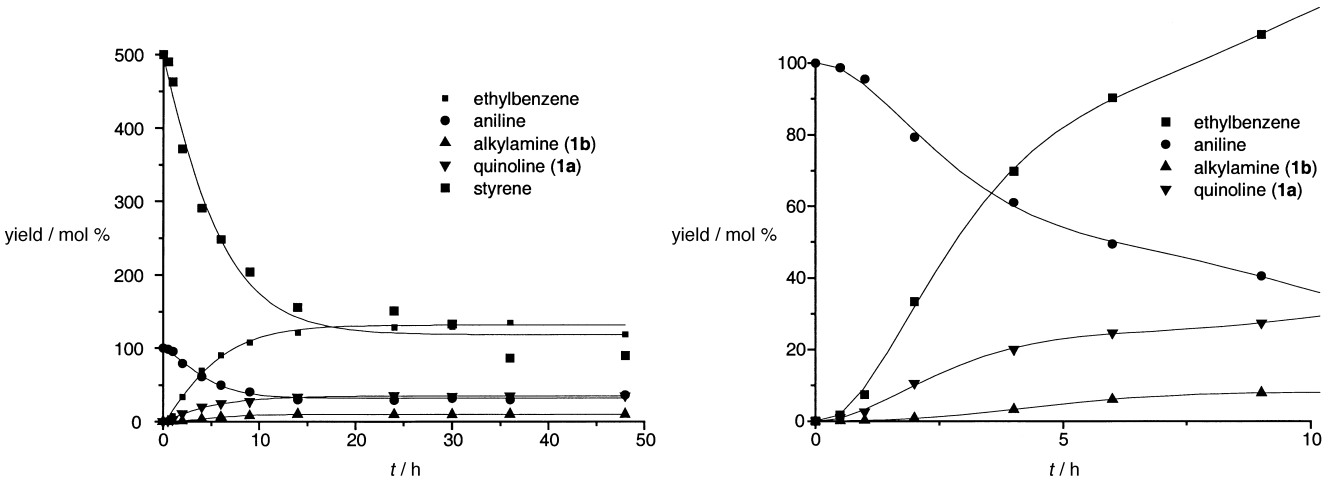


Figure 2. Time–yield diagram of the rhodium-catalyzed reaction of styrene with aniline.

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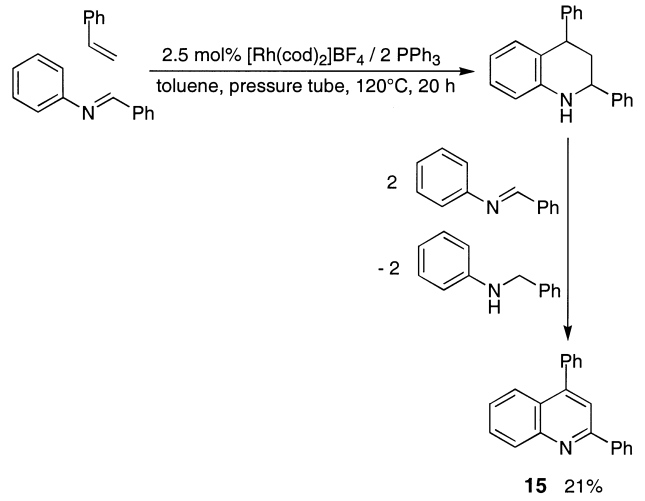


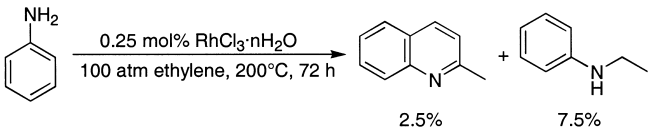
Scheme 5. aza-Diels–Alder reaction of styrene with *N*-benzylideneaniline.

Discussion

The rhodium-catalyzed domino reaction of styrene and aniline constitutes one of the very few amination reactions of olefins that provides access to heterocycles. As it starts from easily available reagents, this new reaction permits the direct synthesis of a variety of different di-, tri-, and tetrasubstituted quinolines. However, it is clear that this new reaction needs to be improved in order to be useful as a broad preparative method.

Interestingly, some time ago Brunet and co-workers demonstrated that a catalyst system of lithium anilide and rhodium bis(triethylphosphine)chloride $[Rh(PEt_3)_2Cl]_2$ led to a totally different outcome for the same reaction. In this case, both the oxidative amination and the hydroamination of styrene is observed with Markovnikov regioselectivity.[18]

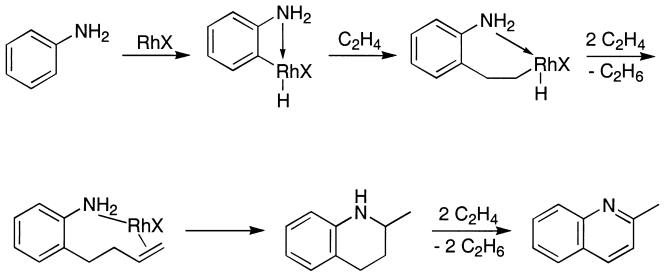
In 1979, Diamond and Mares et al. reported that the reaction of ethylene and aniline in the presence of $RhCl_3$ leads to the formation of 2-methylquinoline in 2.5% yield (Scheme 6).[19]



Scheme 6. Rhodium-catalyzed reaction of aniline with ethylene.

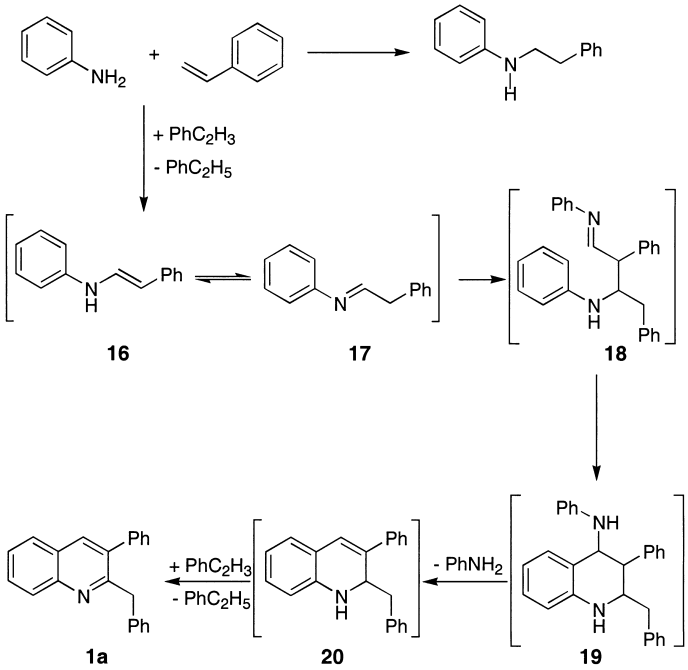
They postulated a mechanism (Scheme 7) for the formation of 2-methylquinoline that includes an *ortho*-metallation of aniline and subsequent ethylene insertion. After the second ethylene insertion step, a transfer hydrogenation would lead to an alkene–amine–rhodium complex, which could react in an intramolecular hydroamination reaction. Further hydrogen transfer to ethylene would yield 2-methylquinoline.

On consideration of our results for the rhodium-catalyzed oxidative amination of aromatic olefins with secondary amines as well as the results obtained in this work, the mechanistic proposal of Diamond and Mares et al. does not



Scheme 7. Mechanism proposed by Diamond, Mares et al.

seem very likely for the formation of 2-benzyl-3-arylquinoline. Based on the results for the formation of the anti-Markovnikov hydroamination product and the model reaction of phenylacetaldehyde with aniline, we propose the following mechanism (Scheme 8).



Scheme 8. Mechanism for the domino reaction of aniline with styrene.

The oxidative product *N*-(2-phenylethenyl)aniline **16**, which is intially formed, is in equilibrium with the corresponding imine *N*-(2-phenylethylidene)aniline **17**. The imine **17** reacts with the enamine **16** in a formal aza-Diels–Alder reaction. Similar aza-Diels–Alder reactions with substituted *N*-benzylideneanilines have been described in the literature.[13, 14, 20, 21] Mechanistic studies for this type of reaction have excluded a concerted [4+2] cycloaddition, and a stepwise mechanism has been proposed instead.[14f, 20b] Hence, we propose an attack of the enamine on the tautomeric imine followed by an electrophilic substitution in the *ortho*-position of the iminium intermediate **18**. Aniline is eliminated readily under the reaction conditions, and the dihydroquinoline **20** is formed. The oxidation to the aromatic system **1a** is performed by hydrogen transfer to styrene.

The comparison of the quinoline yields with different substituted anilines shows that the cyclization step is of great

influence. If 3-fluoroaniline is used, the cyclization occurs *para* to the fluoro substituent, whereas the ring closure with 4-fluoroaniline proceeds *meta* to the fluoro atom, although this should be disfavored. In agreement with this assumption, the yield of **4a** is lower compared with **5a**. In the case of substituted anisidines, the oxidative amination seems to determine the product yield. The more basic amine (4-anisidine) gives a better yield of **2a** compared with **3a**. The low yield of **6a** with 4-aminobiphenyl is explained by steric hinderance during the ring closure.

Conclusion

The rhodium-catalyzed amination of styrenes with anilines leads to the direct formation of substituted quinolines in yields of 30–50%; the yields mainly depend on the catalyst concentration. During the course of the reaction, one C–N and two C–C bonds are formed, and six hydrogen atoms are transferred. This new domino reaction represents one of the rare cases in heterocycle synthesis that involves an in situ amination of olefins. During the course of the reaction, styrene serves as the oxidizing agent and forms ethylbenzene. Side products *N*-(2-arylethyl)anilines are obtained, which result formally from the transition metal catalyzed anti-Markovnikov hydroamination of styrene with aniline.

Although it is clear that the reaction is not yet a complete preparative method for the synthesis of quinolines, the presented study offers interesting new aspects in the field of catalytic amination of unsaturated compounds to yield heterocycles. Further studies to enhance the yield of the products by means of an increase in catalyst concentration as well as the use of an additional partner for the "formal" Diels–Alder reaction are in progress.

Experimental Section

Materials and methods: All reactions with organometallic compounds were carried out with the use of vacuum line, Schlenk, and syringe techniques. The catalytic reactions were carried out in Ace pressure tubes (purchased from Aldrich). **Warning**: **the required safety measures should be taken when performing reactions under pressure.** All solvents were dried and distilled prior to use, according to standard procedures. Amines were distilled from CaH_2, and silver salts and other chemicals were purchased from Fluka and Aldrich and used as received. $[Rh(cod)Cl]_2$[22] and $[Rh(cod)_2]BF_4$[23] were prepared as described in the appropriate reference. *N*-benzylideneaniline[24] was prepared according to a literature procedure.

Physical and analytical methods: ^1H and ^{13}C NMR spectra were recorded on a JEOL-GX 400 spectrometer (^1H: 399.80 MHz; ^{13}C: 100.53 MHz). ^1H and ^{13}C chemical shifts have been reported in δ relative to tetramethylsilane. The elemental analyses were carried out by the Microanalytical Laboratory of the Technische Universität München. GC spectra for analysis of catalytic reactions were recorded on a HP 6890 gas chromatograph with a HP 1 capillary column. Yields were determined with hexadecane as the internal standard. GC/MS studies were conducted on a HP 5890 with EI electron impact ionization (detector: HP 5970 B, 70 eV).

General procedure for the synthesis of substituted quinolines by a domino reaction: $[Rh(cod)_2]BF_4$ (90 mg, 0.22 mmol) and PPh_3 (232 mg, 0.88 mmol) were suspended in a pressure tube (15 mL) in toluene (2.5 mL) under an argon atmosphere. A dark yellow solution and an orange precipitate were formed. The solution cleared slightly during addition of the aromatic amine (2.2 mmol). Afterwards the aromatic olefin (11 mmol) and hexadecane (100 μL) were added. The reaction vessel was closed cautiously and placed in an oil bath (140 °C). The reaction mixture was stirred for 48 h, and a brown to black solution was produced. The solvent was evaporated in vacuo. The crude product was separated by column chromatography with a given eluent.

2-Benzyl-3-phenylquinoline (1a): According to the general procedure, aniline (0.20 mL, 2.2 mmol) was treated with styrene (1.26 mL, 11 mmol). After purification by column chromatography (hexane/ethylacetate 10:1), **1a** was obtained as a yellow oil. Compound **1b** was isolated as the by-product. Yield of **1a**: 43% (GC); 260 mg, 40% (isolated); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 8.08$ (d, $^3J(H,H) = 8.0$ Hz, 1H; CH), 7.84 (s, 1H; CH), 7.67 (d, $^3J(H,H) = 8.0$ Hz, 1H; CH), 7.61 (dd, $^3J(H,H) = 8.0$, $^3J(H,H) = 7.0$ Hz, 1H; CH), 7.41 (dd, $^3J(H,H) = 8.0$, $^3J(H,H) = 7.0$ Hz, 1H; CH), 7.28–7.26 (m, 2H; CH), 7.10–7.07 (m, 2H; CH), 7.02–6.98 (m, 4H; CH), 6.86–6.83 (m, 2H; CH), 4.25 (s, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 159.5$, 147.5, 139.9, 139.6, 137.4, 136.5, 129.9, 129.8, 129.3, 129.2, 128.6, 128.5, 128.0, 127.9, 127.3, 126.8, 126.3, 43.2; MS (70 eV, EI): *m*/*z* (%): 294 [$M^+ - H$], 218 [$M^+ - C_6H_5$], 204 [$M^+ - CH_2 - C_6H_5$], 189, 176, 146, 134, 108, 91, 77; $C_{22}H_{17}N$ (295.38): calcd C 89.46, H 5.80, N 4.74; found C 89.38, H 6.12, N 4.43.

***N*-(2-Phenylethyl)aniline (1b)**: Yield of **1b**: 6% (GC); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.34–7.15$ (m, 7H; CH), 6.71 (t, $^3J(H,H) = 7.0$ Hz, 1H; CH), 6.62 (d, $^3J(H,H) = 8.1$ Hz, 2H; CH), 3.69 (s, 1H; NH), 3.42 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2), 2.93 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 148.0$, 139.3, 129.4, 128.8, 128.6, 126.4, 117.4, 113.0, 45.0, 35.5; MS (70 eV, EI): *m*/*z* (%): 197 [M^+], 106 [$M^+ - CH_2 - C_6H_5$], 91, 77, 65.

2-Benzyl-3-phenyl-6-methoxyquinoline (2a): According to the general procedure, 4-anisidine (271 mg, 2.2 mmol) was treated with styrene (1.26 mL, 11 mmol). After purification by column chromatography (hexane/ethylacetate 20:1), **2a** was obtained as an orange oil. Compound **2b** was isolated as the by-product. Yield of **2a**: 42% (GC); 279 mg, 39% (isolated); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 8.00$ (d, $^3J(H,H) = 8.9$ Hz, 1H; CH), 7.74 (s, 1H; CH), 7.25–7.21 (m, 2H; CH), 7.17 (d, $^3J(H,H) = 8.9$ Hz, 1H; CH), 7.11 (s, 1H; CH), 7.05–7.03 (m, 2H; CH), 6.97–6.91 (m, 4H; CH), 6.79 (d, $^3J(H,H) = 7.5$ Hz, 2H; CH), 4.19 (s, 2H; CH_2), 3.78 (s, 3H; CH_3); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 157.8$, 156.2, 139.8, 139.7, 139.6, 136.3, 136.0, 129.4, 129.3, 128.8, 128.2, 128.0, 127.9, 127.6, 125.8, 114.9, 112.5, 55.5, 42.8; MS (70 eV, EI): *m*/*z* (%): 324 [$M^+ - H$], 310 [$M^+ - CH_3$], 281, 248 [$M^+ - C_6H_5$], 232, 204, 191, 163, 139, 91, 77; $C_{23}H_{19}NO$ (325.41): calcd C 84.89, H 5.88, N 4.30; found C 84.69, H 6.03, N 4.35.

***N*-(2-Phenylethyl)-(4-methoxy)aniline (2b)**: Yield of **2b**: 7% (GC); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.39–7.13$ (m, 5H; CH), 6.77 (d, $^3J(H,H) = 8.8$ Hz, 2H; CH), 6.53 (d, $^3J(H,H) = 8.8$ Hz, 2H; CH), 3.76 (s, 3H; CH_3), 3.71 (s, 1H; NH), 3.39 (t, $^3J(H,H) = 7.1$ Hz, 2H; CH_2), 2.95 (t, $^3J(H,H) = 7.1$ Hz, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 148.6$, 142.0, 139.2, 128.7, 128.3, 127.9, 114.9, 114.5, 55.7, 46.5, 35.8; MS (70 eV, EI): *m*/*z* (%): 227 [M^+], 162, 136 [$M^+ - CH_2 - C_6H_5$], 108, 91, 77, 65.

2-Benzyl-3-phenyl-7-methoxyquinoline (3a): According to the general procedure, 3-anisidine (0.25 mL, 2.2 mmol) was treated with styrene (1.26 mL, 11 mmol). After purification by column chromatography (hexane/ethylacetate 20:1), **3a** was obtained as an orange oil. Compound **3b** was isolated as the by-product. Yield of **3a**: 24% (GC); 136 mg, 19% (isolated); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.77$ (s, 1H; CH), 7.54 (d, $^3J(H,H) = 8.8$ Hz, 1H; CH), 7.40 (d, $^4J(H,H) = 2.2$ Hz, 1H; CH), 7.25–7.23 (m, 2H; CH), 7.12–6.98 (m, 7H; CH), 6.84 (dd, $^3J(H,H) = 7.4$, $^4J(H,H) = 1.5$ Hz, 2H; CH), 4.20 (s, 2H; CH_2), 3.86 (s, 3H; CH_3); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 160.8$, 159.0, 148.3, 139.6, 139.3, 136.8, 133.9, 129.5, 128.8, 128.4, 128.1, 128.0, 127.4, 125.8, 122.0, 119.6, 106.7, 55.6, 42.5; MS (70 eV, EI): *m*/*z* (%): 324 [$M^+ - H$], 310 [$M^+ - CH_3$], 281, 248 [$M^+ - C_6H_5$], 232, 204, 191, 163, 139, 102, 91; $C_{23}H_{19}NO$ (325.41): calcd C 84.89, H 5.88, N 4.30; found C 84.74, H 6.18, N 4.15.

***N*-(2-Phenylethyl)-(3-methoxy)aniline (3b)**: Yield of **3b**: 7% (GC); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.36–7.08$ (m, 6H; CH), 6.31 (m, 1H; CH), 6.29 (m, 1H; CH), 6.21 (dd, $^4J(H,H) = 2.3$, $^4J(H,H) = 2.2$ Hz, 1H; CH), 3.82 (s, 1H; NH), 3.79 (s, 3H; CH_3), 3.42 (t, $^3J(H,H) =$

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7.0 Hz, 2H; CH_2), 2.94 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 160.8$, 149.1, 138.5, 129.9, 128.8, 128.6, 126.4, 106.2, 102.7, 99.0, 55.0, 45.1, 35.4; MS (70 eV, EI): *m/z* (%): 227 [M^+], 136 [$M^+ - CH_2 - C_6H_5$], 91, 77.

2-Benzyl-3-phenyl-6-fluoroquinoline (4a): According to the general procedure, 4-fluoroaniline (0.21 mL, 2.2 mmol) was treated with styrene (1.26 mL, 11 mmol). After purification by column chromatography (hexane/ethylacetate 10:1), **4a** was obtained as an orange oil. Compound **4b** was isolated as the by-product. Yield of **4a**: 24% (GC); 136 mg, 19% (isolated); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 8.06$ (dd, $^3J(H,H) = 8.6$ Hz, $^4J(H,F) = 5.5$ Hz, 1H; CH), 7.79 (s, 1H; CH), 7.37 (ddd, $^3J(H,F) = 9.0$, $^3J(H,H) = 8.6$, $^4J(H,H) = 3.0$ Hz, 1H; CH), 7.29–7.21 (m, 3H; CH), 7.11–7.08 (m, 2H; CH), 7.03–7.01 (m, 4H; CH), 6.84 (dd, $^3J(H,H) = 7.0$, $^4J(H,H) = 2.0$, 2H; CH), 4.23 (s, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 160.9$ (d, $^1J(C,F) = 247.8$ Hz), 158.9, 144.6 (d, $^4J(C,F) = 2.9$ Hz), 139.6, 139.5, 136.6, 131.8 (d, $^3J(C,F) = 9.7$ Hz), 129.8, 129.3, 128.7, 128.5, 127.9 (d, $^3J(C,F) = 9.7$ Hz), 128.2, 126.4, 119.9 (d, $^2J(C,F) = 25.3$ Hz), 110.9 (d, $^2J(C,F) = 21.4$ Hz), 43.0; MS (70 eV, EI): *m/z* (%): 312 [$M^+ - H$], 298, 277, 236 [$M^+ - C_6H_5$], 207, 174, 142, 129, 105, 96; $C_{22}H_{18}FN$ (313.37): calcd C 84.32, H 5.79, N 4.46; found C 84.45, H 5.85, N 4.37.

***N*-(2-Phenylethyl)-(4-fluoro)aniline (4b)**: Yield of **4b**: 12% (GC); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.30–7.27$ (m, 2H; CH), 7.14–7.09 (m, 3H; CH), 6.79 (dd, $^3J(H,F) = 9.0$, $^3J(H,H) = 8.0$ Hz, 2H; CH), 6.45–6.42 (m, 2H; CH), 3.42 (s, 1H; NH), 3.26 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2), 2.80 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 156.3$ (d, $^1J(C,F) = 235.0$ Hz), 144.7 (d, $^4J(C,F) = 3.0$ Hz), 137.4, 129.2, 129.0, 126.9, 116.0 (d, $^2J(C,F) = 22.4$ Hz), 114.2 (d, $^3J(C,F) = 7.8$ Hz), 46.1, 35.8; MS (70 eV, EI): *m/z* (%): 215 [M^+], 124 [$M^+ - CH_2 - C_6H_5$], 91, 75, 65.

2-Benzyl-3-phenyl-7-fluoroquinoline (5a): According to the general procedure, 3-fluoroaniline (0.21 mL, 2.2 mmol) was treated with styrene (1.26 mL, 11 mmol). After purification by column chromatography (hexane/ethylacetate 10:1), **5a** was obtained as a pale brown oil. Compound **5b** was isolated as the by-product. Yield of **5a**: 51% (GC); 331 mg, 48% (isolated); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.81$ (s, 1H; CH), 7.68 (dd, $^3J(H,F) = 10.0$, $^4J(H,H) = 2.5$ Hz, 1H; CH), 7.63 (dd, $^3J(H,H) = 9.0$, $^4J(H,F) = 6.0$ Hz, 1H; CH), 7.04–7.02 (m, 1H; CH), 7.28–7.26 (m, 2H; CH), 7.11–7.08 (m, 2H; CH), 7.01–6.95 (m, 4H; CH), 6.86–6.83 (m, 2H; CH), 4.21 (s, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 163.5$ (d, $^1J(C,F) = 249.0$ Hz), 160.7, 148.4 (d, $^3J(C,F) = 12.6$ Hz), 139.7, 139.5, 137.2, 135.8, 130.7 (d, $^3J(C,F) = 9.7$ Hz), 129.9, 129.3, 128.6, 128.5, 128.1, 126.5, 124.3 (d, $^4J(C,F) = 2.0$ Hz), 117.2 (d, $^2J(C,F) = 25.3$ Hz), 113.0 (d, $^2J(C,F) = 19.4$ Hz), 43.1; MS (70 eV, EI): *m/z* (%): 312 [$M^+ - H$], 234 [$M^+ - C_6H_5$], 221, 207, 155, 142, 119, 91; $C_{22}H_{18}FN$ (313.37): calcd C 84.32, H 5.79, N 4.46; found C 84.03, H 6.15, N 4.34.

***N*-(2-Phenylethyl)-(3-fluoro)aniline (5b)**: Yield of **5b**: 11% (GC); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.27–7.16$ (m, 6H; CH), 6.29–6.04 (m, 3H; CH), 3.24 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2), 3.79 (s, 1H; NH), 2.78 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 164.6$ (d, $^1J(C,F) = 243.0$ Hz), 150.2 (d, $^3J(C,F) = 10.7$ Hz), 139.4, 129.9, 129.3, 129.1 (d, $^3J(C,F) = 9.7$ Hz), 128.7, 109.2 (d, $^4J(C,F) = 1.9$ Hz), 104.1 (d, $^2J(C,F) = 22.4$ Hz), 99.9 (d, $^2J(C,F) = 25.3$ Hz), 45.3, 35.7; MS (70 eV, EI): *m/z* (%): 215 [M^+], 124 [$M^+ - CH_2 - C_6H_5$], 95, 77, 65.

2-Benzyl-3-phenyl-6-phenylquinoline (6a): According to the general procedure, 4-aminobiphenyl (372 mg, 2.2 mmol) was treated with styrene (1.26 mL, 11 mmol). After purification by column chromatography (hexane/ethylacetate 10:1), **6a** was obtained as an orange oil. By-product **6b** could not be isolated. Yield of **6a**: 32% (GC); 253 mg, 31% (isolated); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 8.11$ (d, $^3J(H,H) = 8.6$ Hz, 1H; CH), 7.87–7.83 (m, 3H; CH), 7.58 (d, $^3J(H,H) = 7.0$ Hz, 2H; CH), 7.36 (t, $^3J(H,H) = 7.5$ Hz, 1H; CH), 7.28–7.24 (m, 4H; CH), 7.11–7.08 (m, 2H; CH), 7.01–6.97 (m, 4H; CH), 6.85 (dd, $^3J(H,H) = 7.0$, $^4J(H,H) = 2.0$ Hz, 2H; CH), 4.24 (s, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 159.6$, 147.0, 140.9, 140.0, 139.8, 139.6, 137.5, 136.9, 129.9, 129.8, 129.6, 129.4, 129.3, 128.7, 128.6, 128.1, 128.0, 127.8, 127.5, 126.4, 125.6, 43.2; MS (70 eV, EI): *m/z* (%): 370 [$M^+ - H$], 281, 207, 168, 150, 131, 96; $C_{28}H_{21}N$ (371.48): calcd C 90.53, H 5.70, N 3.77; found C 90.50, H 5.96, N 3.39.

***N*-(2-Phenylethyl)-(4-phenyl)aniline (6b)**: Yield of **6b**: 10% (GC); MS (70 eV, EI): *m/z* (%): 273 [M^+], 207, 182 [$M^+ - CH_2 - C_6H_5$], 152, 133, 110, 96.

2-Benzyl-3-phenyl-6-methylquinoline (7a): According to the general procedure, 4-toluidine (236 mg, 2.2 mmol) was treated with styrene (1.26 mL, 11 mmol). After purification by column chromatography (hexane/ethylacetate 15:1), **7a** was obtained as a yellow solid. Compound **7b** was isolated as the by-product. Yield of **7a**: 33% (GC); 210 mg, 31% (isolated); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 8.03$ (d, $^3J(H,H) = 8.1$ Hz, 1H; CH), 7.82 (s, 1H; CH), 7.51 (d, $^3J(H,H) = 8.1$ Hz, 1H; CH), 7.50 (s, 1H; CH), 7.33 (m, 3H; CH), 7.16 (m, 2H; CH), 7.07 (m, 3H; CH), 6.91 (m, 2H; CH), 4.30 (s, 2H; CH_2), 2.49 (s, 3H; CH_3); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 158.0$, 145.7, 139.7, 139.4, 136.1, 136.1, 136.0, 131.6, 129.4, 128.8, 128.6, 128.1, 127.9, 127.4, 126.9, 126.2, 125.8, 42.7, 21.5; MS (70 eV, EI): *m/z* (%): 308 [$M^+ - H$], 232 [$M^+ - C_6H_5$], 230, 217, 154, 146, 91; $C_{23}H_{19}N$ (309.41): calcd C 89.28, H 6.19, N 4.53; found C 88.71, H 6.34, N 4.95.

***N*-(2-Phenylethyl)-(4-methyl)aniline (7b)**: Yield of **7b**: 10% (GC); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.35–7.20$ (m, 5H; CH), 7.00 (d, $^3J(H,H) = 8.4$ Hz, 2H; CH), 6.55 (d, $^3J(H,H) = 8.4$ Hz, 2H; CH), 3.38 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2), 2.91 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2), 2.24 (s, 3H; CH_3); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 145.7$, 139.4, 129.7, 128.8, 128.5, 128.3, 126.3, 113.2, 45.4, 35.5, 20.4; MS (70 eV, EI): *m/z* (%): 211 [M^+], 120 [$M^+ - CH_2 - C_6H_5$], 91, 77, 65.

2-(4-Fluorophenylmethyl)-3-(4-fluorophenyl)quinoline (8a): According to the general procedure, aniline (0.20 mL, 2.2 mmol) was treated with 4-fluorostyrene (1.31 mL, 11 mmol). After purification by column chromatography (hexane/ethylacetate 10:1), **8a** was obtained as a dark yellow oil. Compound **8b** was isolated as the by-product. Yield of **8a**: 40% (GC); 255 mg, 35% (isolated); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 8.06$ (d, $^3J(H,H) = 8.5$ Hz, 1H; CH), 7.82 (s, 1H; CH), 7.67 (d, $^3J(H,H) = 8.0$ Hz, 1H; CH), 7.62 (ddd, $^3J(H,H) = 8.5$, $^3J(H,H) = 8.0$, $^4J(H,H) = 1.6$ Hz, 1H; CH), 7.43 (ddd, $^3J(H,H) = 8.0$, $^3J(H,H) = 8.0$, $^4J(H,H) = 1.0$ Hz, 1H; CH), 7.01 (dd, $^3J(H,H) = 8.5$, $^4J(H,F) = 6.0$ Hz, 2H; CH), 6.95 (dd, $^3J(H,F) = 9.0$, $^3J(H,H) = 8.5$ Hz, 2H; CH), 6.77 (dd, $^3J(H,H) = 8.5$, $^4J(H,F) = 6.0$ Hz, 2H; CH), 6.69 (dd, $^3J(H,F) = 9.0$, $^3J(H,H) = 8.5$ Hz, 2H; CH), 4.18 (s, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 161.4$ (d, $^1J(C,F) = 246.9$ Hz), 160.3 (d, $^1J(C,F) = 243.9$ Hz), 157.8, 145.9, 136.3, 134.2 (d, $^4J(C,F) = 3.9$ Hz), 133.9, 133.5 (d, $^4J(C,F) = 2.9$ Hz), 130.0 (d, $^3J(C,F) = 7.8$ Hz), 129.1 (d, $^3J(C,F) = 7.8$ Hz), 128.7, 127.7, 126.4, 125.8, 125.6, 114.1 (d, $^2J(C,F) = 21.4$ Hz), 113.8 (d, $^2J(C,F) = 21.4$ Hz), 40.9; MS (70 eV, EI): *m/z* (%): 330 [$M^+ - H$], 236 [$M^+ - C_6H_4F$], 207, 166, 133, 109, 83, 75; $C_{22}H_{15}F_2N$ (331.36): calcd C 79.74, H 4.56, N 4.23; found C 79.41, H 4.89, N 4.05.

***N*-(2-(4-Fluorophenyl)ethyl)aniline (8b)**: Yield of **8b**: 5% (GC); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.25–7.05$ (m, 4H; CH), 6.91–6.87 (m, 2H; CH), 6.62 (t, $^3J(H,H) = 7.5$ Hz, 1H; CH), 6.52 (d, $^3J(H,H) = 8.4$ Hz, 2H; CH), 3.60 (s, 1H; NH), 3.27 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2), 2.78 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 160.6$ (d, $^1J(C,F) = 244.9$ Hz), 146.8, 133.9 (d, $^4J(C,F) = 2.7$ Hz), 129.1 (d, $^3J(C,F) = 7.8$ Hz), 128.3, 116.6, 114.3 (d, $^2J(C,F) = 21.4$ Hz), 112.0, 44.1, 33.6; MS (70 eV, EI): *m/z* (%): 215 [M^+], 201, 148, 107.

2-(4-Methoxyphenylmethyl)-3-(4-methoxyphenyl)quinoline (9a): According to the general procedure, aniline (0.20 mL, 2.2 mmol) was treated with 4-methoxystyrene (1.46 mL, 11 mmol). After purification by column chromatography (hexane/ethylacetate 10:1), **9a** was obtained as a yellow oil. Compound **9b** was isolated as the by-product. Yield of **9a**: 40% (GC); 281 mg, 36% (isolated); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 8.06$ (d, $^3J(H,H) = 8.1$ Hz, 1H; CH), 7.81 (s, 1H; CH), 7.65 (d, $^3J(H,H) = 7.9$ Hz, 1H; CH), 7.57 (dd, $^3J(H,H) = 8.1$, $^3J(H,H) = 7.0$ Hz, 1H; CH), 7.40 (dd, $^3J(H,H) = 7.9$, $^3J(H,H) = 7.0$ Hz, 1H; CH), 7.14 (d, $^3J(H,H) = 8.5$ Hz, 2H; CH), 6.74 (d, $^3J(H,H) = 8.6$ Hz, 2H; CH), 6.58 (d, $^3J(H,H) = 8.5$ Hz, 2H; CH), 6.49 (d, $^3J(H,H) = 8.6$ Hz, 2H; CH), 4.20 (s, 2H; CH_2), 3.73 (s, 3H; CH_3), 3.70 (s, 3H; CH_3); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 157.3$, 157.2, 156.7, 143.5, 138.5, 136.7, 131.0, 129.5, 129.4, 129.2, 128.5, 128.3, 127.6, 127.0, 126.1, 113.4, 113.0, 54.2, 54.1, 42.5; MS (70 eV, EI): *m/z* (%): 354 [$M^+ - H$], 310, 248 [$M^+ - C_6H_4OCH_3$], 234 [$M^+ - CH_2 - C_6H_4OCH_3$], 229, 176, 138, 121, 107, 77; $C_{24}H_{21}NO_2$ (355.43): calcd C 81.10, H 5.96, N 3.94; found C 80.93, H 6.31, N 3.76.

***N*-(2-(4-Methoxyphenyl)ethyl)aniline (9b)**: Yield of **9b**: 10% (GC); ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.35-7.15$ (m, 4H; CH), 6.90 (d, $^3J(H,H) = 8.4$ Hz, 2H; CH), 6.79 (t, $^3J(H,H) = 7.5$ Hz, 1H; CH), 6.70 (d, $^3J(H,H) = 7.5$ Hz, 2H; CH), 3.84 (s, 3H; CH_3), 3.75 (s, 1H; NH), 3.41 (t, $^3J(H,H) = 7.1$ Hz, 2H; CH_2), 2.91 (t, $^3J(H,H) = 7.1$ Hz, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 158.2$, 147.3, 131.0, 129.6, 129.3, 118.0, 114.0, 113.4, 55.2, 45.6, 34.3; MS (70 eV, EI): *m*/*z* (%): 227 [M^+], 207, 167, 134, 106, 77, 51.

2-(3,4-Dimethoxyphenylmethyl)-3-(3,4-dimethoxyphenyl)quinoline (10a): According to the general procedure, aniline (0.20 mL, 2.2 mmol) was treated with 3,4-dimethoxystyrene (1.63 mL, 11 mmol). After purification by column chromatography (hexane/ethylacetate gradient 10:1 to 2:1), **10a** was obtained as a yellow oil. Compound **10b** was isolated as the by-product. Yield of **10a**: 27% (GC); 210 mg, 23% (isolated); ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 8.04$ (d, $^3J(H,H) = 8.1$ Hz, 1H; CH), 7.84 (s, 1H; CH), 7.65 (d, $^3J(H,H) = 8.0$ Hz, 1H; CH), 7.55 (dd, $^3J(H,H) = 8.1$, $^3J(H,H) = 7.2$ Hz, 1H; CH), 7.39 (dd, $^3J(H,H) = 8.0$, $^3J(H,H) = 7.2$ Hz, 1H; CH), 6.74 (d, $^3J(H,H) = 8.0$ Hz, 1H; CH), 6.70 (s, 1H; CH), 6.54 (d, $^3J(H,H) = 8.0$ Hz, 1H; CH), 6.42 (d, $^3J(H,H) = 8.0$ Hz, 1H; CH), 6.30 (d, $^3J(H,H) = 8.0$ Hz, 1H; CH), 6.25 (s, 1H; CH), 4.25 (s, 2H; CH_2), 3.77 (s, 3H; CH_3), 3.71 (s, 3H; CH_3), 3.70 (s, 3H; CH_3), 3.58 (s, 3H; CH_3); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 166.7$, 147.5, 146.4, 146.2, 143.8, 141.4, 139.6, 137.6, 132.8, 129.9, 129.6, 129.3, 127.7, 126.7, 126.2, 121.1, 120.8, 111.3, 110.2, 110.0, 109.8, 55.0, 54.9, 54.7, 54.5, 48.6; MS (70 eV, EI): *m*/*z* (%): 414 [$M^+ - H$], 370, 278 [$M^+ - C_6H_4(OCH_3)_2$], 264 [$M^+ - CH_2 - C_6H_3(OCH_3)_2$], 259, 206, 168, 151, 137, 121, 107, 77; $C_{26}H_{25}NO_4$ (415.49): calcd C 75.16, H 6.06, N 3.37; found C 74.97, H 6.36, N 3.26.

***N*-(2-(3,4-Dimethoxyphenyl)ethyl)aniline (10b)**: Yield of **10b**: 15% (GC); ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.05$ (m, 2H; CH), 6.70 (t, $^3J(H,H) = 8.0$ Hz, 1H; CH), 6.62 (m, 3H; CH), 6.55 (dd, $^3J(H,H) = 8.5$, $^4J(H,H) = 2.0$ Hz, 1H; CH), 6.50 (dd, $^3J(H,H) = 8.5$, $^4J(H,H) = 1.0$ Hz, 1H; CH), 3.74 (s, 3H; CH_3), 3.73 (s, 3H; CH_3), 3.42 (s, 1H; NH), 3.25 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2), 2.91 (t, $^3J(H,H) = 7.1$ Hz, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 148.0$, 147.0, 146.6, 130.8, 128.2, 119.6, 117.4, 116.4, 114.0, 112.0, 54.8, 54.7, 44.1, 34.0; MS (70 eV, EI): *m*/*z* (%): 257 [M^+], 152, 106 [$M^+ - CH_2 - C_6H_3(OCH_3)_2$], 91, 77, 65, 51.

2-(4-Methylphenylmethyl)-3-(4-methylphenyl)quinoline (11a): According to the general procedure, aniline (0.20 mL, 2.2 mmol) was treated with 4-methylstyrene (1.45 mL, 11 mmol). After purification by column chromatography (hexane/ethylacetate 10:1), **11a** was obtained as an orange oil. Compound **11b** was isolated as the by-product. Yield of **11a**: 45% (GC); 313 mg, 44% (isolated); ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 8.04$ (d, $^3J(H,H) = 8.5$ Hz, 1H; CH), 7.81 (s, 1H; CH), 7.65 (d, $^3J(H,H) = 8.0$ Hz, 1H; CH), 7.57 (ddd, $^3J(H,H) = 8.5$, $^3J(H,H) = 8.0$, $^4J(H,H) = 1.0$ Hz, 1H; CH), 7.37 (dd, $^3J(H,H) = 8.0$, $^3J(H,H) = 8.0$ Hz, 1H; CH), 7.08 (d, $^3J(H,H) = 8.0$ Hz, 2H; CH), 7.01 (d, $^3J(H,H) = 8.0$ Hz, 2H; CH), 6.84 (d, $^3J(H,H) = 8.0$ Hz, 2H; CH), 6.78 (d, $^3J(H,H) = 8.0$ Hz, 2H; CH), 4.20 (s, 2H; CH_2), 2.31 (s, 3H; CH_3), 2.13 (s, 3H; CH_3); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 159.4$, 147.1, 137.2, 136.8, 136.6, 136.4, 136.0, 135.2, 129.3, 129.1, 128.8, 128.7, 128.6, 128.5, 127.4, 126.9, 126.2, 42.2, 21.2, 20.9; MS (70 eV, EI): *m*/*z* (%): 322 [$M^+ - H$], 307, 278, 264, 230, 217, 189, 160, 145, 105, 77, 65; $C_{24}H_{21}N$ (323.44): calcd C 89.12, H 6.54, N 4.33; found C 89.49, H 6.57, N 3.95.

***N*-(2-(4-Methylphenyl)ethyl)aniline (11b)**: Yield of **11b**: 6% (GC); ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.29-7.08$ (m, 6H; CH), 6.77 (t, $^3J(H,H) = 7.0$ Hz, 1H; CH), 6.68 (d, $^3J(H,H) = 8.0$ Hz, 2H; CH), 3.72 (s, 1H; NH), 3.43 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2), 2.94 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2), 2.39 (s, 3H; CH_3); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 148.5$, 138.5, 136.6, 130.0, 129.3, 128.1, 117.9, 113.4, 45.6, 35.5, 21.5; MS (70 eV, EI): *m*/*z* (%): 211 [M^+], 106 [$M^+ - CH_2 - C_6H_4CH_3$], 77, 65.

2-(3-Trifluoromethylphenylmethyl)-3-(3-trifluoromethylphenyl)quinoline (12a): According to the general procedure, aniline (0.20 mL, 2.2 mmol) was treated with 3-trifluoromethylstyrene (1.63 mL, 11 mmol). After purification by column chromatography (hexane/ethylacetate 12:1), **12a** was obtained as an orange oil. Compound **12b** was isolated as the by-product. Yield of **12a**: 17% (GC); 152 mg, 16% (isolated); ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 8.17$ (d, $^3J(H,H) = 8.5$ Hz, 1H; CH), 7.96 (s, 1H; CH), 7.81 (d, $^3J(H,H) = 8.1$ Hz, 1H; CH), 7.76 (dd, $^3J(H,H) = 8.5$, $^3J(H,H) = 7.9$ Hz, 1H; CH), 7.63 (d, $^3J(H,H) = 7.7$ Hz, 1H; CH), 7.57 (dd, $^3J(H,H) = 8.1$, $^3J(H,H) = 7.9$ Hz, 1H; CH), 7.48 (t, $^3J(H,H) = 7.7$ Hz, 1H; CH), 7.37–7.30 (m, 3H; CH), 7.20 (t, $^3J(H,H) = 7.7$ Hz, 1H; CH), 7.10 (d, $^3J(H,H) = 7.7$ Hz, 1H; CH), 7.05 (s, 1H; CH), 4.35 (s, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 157.7$, 147.3, 140.0, 139.6, 137.3, 134.3, 132.5, 132.0, 130.9 (q, $^2J(C,F) = 32.4$ Hz), 130.4 (q, $^2J(C,F) = 32.4$ Hz), 130.0, 129.0, 128.8, 128.6, 127.5, 126.9, 126.8, 126.0 (q, $^3J(C,F) = 3.8$ Hz), 125.4 (q, $^3J(C,F) = 3.8$ Hz), 124.6 (q, $^3J(C,F) = 3.8$ Hz), 123.0 (q, $^3J(C,F) = 3.8$ Hz), 43.0; MS (70 eV, EI): *m*/*z* (%): 430 [$M^+ - H$], 390, 361, 286 [$M^+ - C_6H_4CF_3$], 266, 217, 170, 146, 75; $C_{24}H_{15}F_6N$ (431.38): calcd C 66.82, H 3.50, N 3.25; found C 66.70, H 3.66, N 3.26.

***N*-(2-(3-Trifluoromethylphenyl)ethyl)aniline (12b)**: Yield of **12b**: 15% (GC); ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.53-7.37$ (m, 4H; CH), 7.19 (dd, $^3J(H,H) = 8.0$, $^3J(H,H) = 7.3$ Hz, 2H; CH), 6.73 (tt, $^3J(H,H) = 7.3$, $^4J(H,H) = 1.0$ Hz, 1H; CH), 6.62 (dt, $^3J(H,H) = 8.0$, $^4J(H,H) = 1.0$ Hz, 2H; CH), 3.42 (t, $^3J(H,H) = 7.1$ Hz, 2H; CH_2), 2.97 (t, $^3J(H,H) = 7.1$ Hz, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 147.6$, 140.3, 132.2, 130.9 (q, $^2J(C,F) = 32.4$ Hz), 129.4, 129.0, 125.5 (q, $^3J(C,F) = 3.8$ Hz), 123.3 (q, $^3J(C,F) = 3.8$ Hz), 119.5 (q, $^1J(C,F) = 112.5$ Hz), 117.7, 113.0, 44.8, 35.3; MS (70 eV, EI): *m*/*z* (%): 265 [M^+], 219, 159, 106 [$M^+ - CH_2 - C_6H_4CF_3$], 51.

2-(2-Naphthylmethyl)-3-(2-naphthyl)quinoline (13a): According to the general procedure, aniline (0.20 mL, 2.2 mmol) was treated with 2-vinylnaphthalene (1.70 g, 11 mmol). After purification by column chromatography (hexane), **13a** was obtained as a colorless oil. Compound **13b** was isolated as the by-product. Yield of **13a**: 35% (GC); 260 mg, 29% (isolated); ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.98-7.10$ (m, 21H; CH), 4.88 (s, 1H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 158.7$, 143.5, 139.5, 138.7, 134.6, 132.3, 131.6, 131.4, 131.2, 130.9, 129.7, 129.2, 127.3, 127.1, 126.9, 126.7, 126.5, 126.2, 126.1, 125.9, 125.7, 125.0, 124.8, 124.7, 124.1, 123.5, 123.3, 123.2, 40.0; MS (70 eV, EI): *m*/*z* (%): 406 [$M^+ - H$], 279 [$M^+ - C_{10}H_7$], 265 [$M^+ - CH_2 - C_{10}H_7$], 141, 137, 127; $C_{31}H_{21}N$ (407.51): calcd C 91.36, H 5.19, N 3.44; found C 91.56, H 5.37, N 3.07.

***N*-(2-(2-Naphthyl)ethyl)aniline (13b)**: Yield of **13b**: 12% (GC); ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.73-7.61$ (m, 3H; CH), 7.55 (s, 1H; CH), 7.36–7.32 (m, 2H; CH), 7.23 (dd, $^3J(H,H) = 8.5$, $^4J(H,H) = 2.0$ Hz, 1H; CH), 7.11–7.07 (m, 2H; CH), 6.63 (t, $^3J(H,H) = 7.0$ Hz, 1H; CH), 6.54 (d, $^3J(H,H) = 8.0$ Hz, 2H; CH), 3.64 (s, 1H; NH), 3.37 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2), 2.96 (t, $^3J(H,H) = 7.0$ Hz, 2H; CH_2); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 148.3$, 139.6, 137.2, 134.0, 129.8, 128.7, 128.1, 127.8, 127.7, 127.6, 126.7, 125.9, 118.1, 113.6, 45.4, 36.0; MS (70 eV, EI): *m*/*z* (%): 247 [M^+], 154, 141, 106, 77, 65.

2-(4-Methylphenylmethyl)-3-(4-methylphenyl)-7-fluoroquinoline (14a): According to the general procedure, 3-fluoroaniline (0.21 mL, 2.2 mmol) was treated with 4-methylstyrene (1.45 mL, 11 mmol). After purification by column chromatography (hexane/ethylacetate 20:1), **14a** was obtained as a yellow oil. Compound **14b** was isolated as the by-product. Yield of **14a**: 15% (GC); 97 mg, 13% (isolated); ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.91$ (s, 1H; CH), 7.77 (dd, $^3J(H,F) = 10.3$, $^4J(H,H) = 2.7$ Hz, 1H; CH), 7.74 (dd, $^4J(H,F) = 5.9$, $^3J(H,H) = 8.9$ Hz, 1H; CH), 7.29 (td, $^3J(H,F) = {}^3J(H,H) = 8.9$, $^4J(H,H) = 2.7$ Hz, 1H; CH), 7.21 (d, $^3J(H,H) = 8.0$ Hz, 2H; CH), 7.12 (d, $^3J(H,H) = 8.0$ Hz, 2H; CH), 6.96 (d, $^3J(H,H) = 8.0$ Hz, 2H; CH), 6.90 (d, $^3J(H,H) = 8.0$ Hz, 2H; CH), 4.27 (s, 2H; CH_2), 2.43 (s, 3H; CH_3), 2.26 (s, 3H; CH_3); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 162.9$ (d, $^1J(C,F) = 248.9$ Hz), 160.6, 148.0 (d, $^3J(C,F) = 12.4$ Hz), 137.4, 136.6, 136.4, 136.1, 135.4, 135.3 (d, $^4J(C,F) = 2.9$ Hz), 129.3, 129.3 (d, $^3J(C,F) = 9.5$ Hz), 128.9, 128.8, 128.7, 123.8, 116.6 (d, $^2J(C,F) = 25.8$ Hz), 112.5 (d, $^2J(C,F) = 20.0$ Hz), 42.1, 21.2, 21.0; MS (70 eV, EI): *m*/*z* (%): 340 [$M^+ - H$], 325, 309, 248, 235, 170, 155, 105, 77; $C_{24}H_{20}FN$ (341.43): calcd C 84.43, H 5.90, N 4.10; found C 84.20, H 6.01, N 3.95.

***N*-(2-(4-Methylphenyl)ethyl)-(3-fluoro)aniline (14b)**: Yield of **14b**: 20% (GC); ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.17-7.04$ (m, 5H; CH), 6.41–6.27 (m, 3H; CH), 3.80 (s, 1H; NH), 3.35 (t, $^3J(H,H) = 6.9$ Hz, 2H; CH_2), 2.87 (t, $^3J(H,H) = 6.9$ Hz, 2H; CH_2), 2.34 (s, 3H; CH_3); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 164.1$ (d, $^1J(C,F) = 243.2$ Hz), 149.8 (d, $^3J(C,F) = 10.5$ Hz), 136.1, 135.8, 130.2 (d, $^3J(C,F) = 10.5$ Hz), 129.3, 128.6, 108.8 (d, $^4J(C,F) = 1.9$ Hz), 103.7 (d, $^2J(C,F) = 21.9$ Hz), 99.5 (d, $^2J(C,F) = 25.8$ Hz), 44.9, 34.8, 21.0; MS (70 eV, EI): *m*/*z* (%): 229 [M^+], 124 [$M^+ - CH_2 - C_6H_4CH_3$], 95.

Time-dependent formation of 1a and 1b: The model reaction of styrene with aniline was performed in eleven independent Ace pressure tubes.

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$[Rh(cod)_2]BF_4$ (45 mg, 0.11 mmol) and PPh_3 (116 mg, 0.44 mmol) were added to each tube. Toluene (27.50 mL), styrene (13.86 mL, 121 mmol), aniline (2.20 mL, 24.2 mmol), and hexadecane (0.55 mL) were mixed in a separate Schlenk vessel. The solution was distributed to the pressure tubes under an inert atmosphere, and the catalyst concentration was 5 mol% $[Rh(cod)_2]BF_4/4\,PPh_3$. All reaction mixtures were stirred at 140 °C. After 30 min and 1, 2, 4, 6, 9, 14, 24, 30, 36, and 48 hours, the corresponding reaction was stopped by cooling the pressure tube to room temperature. Each mixture was then analyzed by gas chromatography.

When a reaction mixture, that had been heated for 1 hour, was cooled to room temperature $[Rh(cod)(PPh_3)_2]BF_4$ precipitated. The compound was characterized with ^1H, ^{13}C, and ^{31}P NMR spectroscopy.

Reaction of phenylacetaldehyde with aniline: Aniline (1.00 mL, 11 mmol) and phenylacetaldehyde (1.30 mL, 11 mmol) were dissolved in methanol (10 mL). The reaction mixture was stirred for 20 h in air. The gas chromatographic analysis after the reaction showed the selective formation of 2-benzyl-3-phenylquinoline (**1a**). Yield of **1a**: 29% (GC).

2,4-Diphenylquinoline (15): With the aid of a pressure tube (35 mL), $[Rh(cod)_2]BF_4$ (45 mg, 0.11 mmol), PPh_3 (58 mg, 0.22 mmol), and *N*-benzylidenaniline (798 mg, 4.4 mmol) were suspended in toluene (10 mL) under an argon atmosphere. A dark yellow solution and a white precipitate were formed. Styrene (2.00 mL, 17.6 mmol) and hexadecane (100 μL) were added. The reaction vessel was closed cautiously and placed in an oil bath (120 °C). The reaction mixture was stirred for 28 h, and a bright yellow solution was produced. The solvent was removed in vacuo. The crude product was purified by column chromatography with hexane/ethylacetate (50:1) as the eluent. Compound **15** was isolated as a yellow oil. Yield of **15**: 21% (GC); 247 mg, 20% (isolated); ^1H NMR (400 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 7.98$ (d, $^3J(H,H) = 8.4$ Hz, 1H; CH), 7.92 (m, 2H; CH), 7.63 (d, $^3J(H,H) = 8.4$ Hz, 1H; CH), 7.54 (s, 1H; CH), 7.45 (m, 1H; CH), 7.27–6.87 (m, 9H; CH); ^{13}C NMR (101 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 156.8$, 149.2, 148.8, 139.6, 138.4, 130.7, 130.1, 129.6, 129.5, 129.3, 128.6, 128.4, 127.6, 126.3, 125.0, 119.3; MS (70 eV, EI): *m*/*z* (%): 280 $[M^+ - H]$, 204 $[M^+ - C_6H_5]$, 139.

Acknowledgements

We thank Dr. A. Tillack (IfOK, Rostock) for general discussions and Dr. M. Hateley (IfOK, Rostock) for helpful comments on the manuscript. Degussa AG, Hoechst AG, and Heraeus AG are thanked for the loan of precious metals. H.T. acknowledges funding from the Fonds der Chemischen Industrie. We also thank the Deutsche Forschungsgemeinschaft (BE 1931/3-1) for financial support.

[1] H. Trauthwein, A. Tillack, M. Beller, *Chem. Commun.* **1999**, 2029.

[2] Reviews: a) M. Beller, T. E. Müller, *Chem. Rev.* **1998**, *98*, 675; b) M. Beller, T. E. Müller in *Transition Metals for Organic Synthesis* (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **1998**; c) R. Taube in *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**, p. 507; d) D. M. Roundhill, *Chem. Rev.* **1992**, *92*, 1; e) J.-J. Brunet, D. Neibecker, F. Niedercorn, *J. Mol. Catal.* **1989**, *49*, 235; f) M. B. Gasc, A. Lattes, J. J. Perie, *Tetrahedron* **1983**, *39*, 703; g) J.-E. Bäckvall, *Acc. Chem. Res.* **1983**, *16*, 335; h) V. Jäger, H. G. Viehe, *Houben-Weyl*, *Methoden der Organischen Chemie*, *Vol. 5/2a*, Thieme, Stuttgart, **1977**, p. 713.

[3] a) L. S. Hegedus, J. M. McKearin, *J. Am. Chem. Soc.* **1982**, *104*, 2444; b) L. S. Hegedus, G. F. Allen, J. J. Bozell, E. L. Waterman, *J. Am. Chem. Soc.* **1978**, *100*, 5800; c) B. Åkermark, J. E. Bäckvall, L. S. Hegedus, K. Zetterberg, K. Siirala-Hansén, K. Sjöberg, *J. Organomet. Chem.* **1974**, *72*, 127; d) L. S. Hegedus, *Angew. Chem.* **1988**, *100*, 1147; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1113.

[4] R. C. Larock, T. R. Hightower, L. A. Hasvold, K. P. Peterson, *J. Org. Chem.* **1996**, *61*, 3584.

[5] For hydroamination catalyzed by lanthanide complexes see: a) M. R. Bürgstein, H. Berbeich, P. W. Roesky, *Organometallics* **1998**, *17*, 1452; b) Y. Li, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 9295; c) Y. Li, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 707; d) Y. Li, T. J. Marks, *Organometallics* **1996**, *15*, 3770; e) C. M. Haar, C. L. Stern, T. J. Marks, *Organometallics* **1996**, *15*, 1765; f) E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, *11.3c*, Wiley, New York, **1994**, 682; g) M. A. Giardell, V. P. Conticello, L. Brard, M. R. Gagné, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10241; h) M. A. Giardello, V. P. Conticello, L. Brard, M. Sabat, A. L. Rheingold, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10212; i) Y. Li, P. F. Fu, T. J. Marks, *Organometallics* **1994**, *13*, 439; j) M. R. Gagné, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 275; k) M. R. Gagné, S. P. Nolan, T. J. Marks, *Organometallics* **1990**, *9*, 1716; l) M. R. Gagné, T. J. Marks, *J. Am. Chem. Soc.* **1989**, *111*, 4108.

[6] Y. Li, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 1757.

[7] a) M. Beller, M. Eichberger, H. Trauthwein, *Angew. Chem.* **1997**, *109*, 2306; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2225; b) M. Beller, H. Trauthwein, M. Eichberger, C. Breindl, J. Herwig, T. E. Müller, O. R. Thiel, *Chem. Eur. J.* **1999**, *5*, 1304.

[8] For domino reactions in organic synthesis see: a) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115; b) L. F. Tietze, U. Beifuß, *Angew. Chem.* **1993**, *105*, 137; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131.

[9] G. Habermehl, P. E. Hammann, *Naturstoffchemie*, Springer, Berlin, **1992**, p. 192.

[10] M. Balasubramanian, J. G. Keay in *Comprehensive Heterocyclic Chemistry II*, *Vol. 5* (Ed.: A. McKillop), Elsevier, **1996**, p. 245.

[11] a) H. Auterhoff, J. Knabe, H.-D. Höltje, *Lehrbuch der Pharmazeutischen Chemie*, 12. Aufl., Wissenschaftliche Verlagsgesellschaft, Stuttgart, **1991**; b) E. Mutschler, *Arzneimittelwirkungen*, 6. Aufl., Wissenschaftliche Verlagsgesellschaft, Stuttgart, **1991**.

[12] a) G. Jones, *The Chemistry of Heterocyclic Compounds*, *Vol. 32*, *Quinolines*, Wiley, London, **1977**; b) Z. H. Skraup, *Monatsh. Chem.* **1880**, *1*, 316; c) O. Doebner, W. von Miller, *Ber.* **1881**, *14*, 2812; d) M. Conrad, L. Limbach, *Ber.* **1887**, *20*, 944; e) A. Combes, *Compt. Rend.* **1888**, *106*, 142; e) P. Friedländer, *Ber.* **1882**, *15*, 2572; f) W. Pfitzinger, *J. Prakt. Chem.* **1886**, *33*, 100.

[13] a) L. S. Povarov, B. M. Mikhailov, *Izv. Akad. Nauk SSSR Ser. Khim.* **1963**, 955; b) L. S. Povarov, V. I. Grigos, B. M. Mikhailov, *Izv. Akad. Nauk SSSR Ser. Khim.* **1963**, 2039; c) L. S. Povarov, V. I. Grigos, R. A. Karakhanov, B. M. Mikhailov, *Izv. Akad. Nauk SSSR Ser. Khim.* **1964**, 179; d) L. S. Povarov, V. I. Grigos, R. A. Karakhanov, B. M. Mikhailov, *Izv. Akad. Nauk SSSR Ser. Khim.* **1965**, 365; e) V. I. Grigos, L. S. Povarov, B. M. Mikhailov, *Izv. Akad. Nauk SSSR Ser. Khim.* **1965**, 2163.

[14] For further examples of hetero-Diels–Alder reactions see: a) C. K. Bradsher in *Advances in Heterocyclic Chemistry*, *Vol. 16* (Eds.: A. K. Katritzky, A. J. Bouilon), **1974**, p. 289; b) N. S. Kozlov, L. Yu, *Zh. Obshch. Khim.* **1963**, *33*, 1079; c) T. Joh, N. Hagihara, *Tetrahedron Lett.* **1967**, 4199; d) T. Joh, N. Hagihara, *Nippon Kagaku Kaishi* **1970**, *91*, 378; e) T. Joh, N. Hagihara, *Nippon Kagaku Kaishi* **1970**, *91*, 383; f) Y. Nomura, M. Kimura, Y. Takeuchi, S. Tomoda, *Chem. Lett.* **1978**, 267; g) S. Miyajima, K. Ito, I. Kashiwagura, C. Kitamura, *Nippon Kagaku Kaishi* **1979**, *11*, 1514; h) T. Kametami, H. Takeda, Y. Suzuki, T. Honda, *Heterocycles* **1984**, *22*, 275; i) T. Kametami, H. Takeda, Y. Suzuki, T. Honda, *Synth. Commun.* **1985**, *15*, 499.

[15] For rhodium complexes with pyridine and quinoline ligands see: a) T. Masahiko, Y. Hiroshi, N. Hagihara, *Nipon Kagaku Zasshi* **1968**, *89*, 1121; b) B. Denise, G. Pannetier, *J. Organomet. Chem.* **1973**, *63*, 423; c) R. Usón, L. A. Oro, C. Claver, M. A. A. Garralda, *J. Organomet. Chem.* **1976**, *105*, 365; d) R. Usón, L. A. Oro, J. A. Cuchi, M. A. A. Garralda, *J. Organomet. Chem.* **1976**, *116*, C35; e) R. Usón, L. A. Oro, R. Sariego, M. A. Esteruelas, *J. Organomet. Chem.* **1981**, *214*, 399; f) R. H. Fish, J. L. Tan, A. D. Thormodsen, *J. Org. Chem.* **1984**, *49*, 4500; g) R. H. Fish, H.-S. Kim, J. E. Babin, R. D. Adams, *Organometallics* **1988**, *7*, 2250.

[16] M. Beller, O. R. Thiel, H. Trauthwein, *Synlett.* **1999**, *2*, 243.

[17] G. Lewin, C. Schaeffer, *Heterocycles* **1998**, *48*, 171.

[18] a) J.-J. Brunet, D. Neibecker, K. Philippot, *J. Chem. Soc. Chem. Commun.* **1992**, 1215; b) J.-J. Brunet, D. Neibecker, K. Philippot, *Tetrahedron Lett.* **1993**, *34*, 3877; c) J.-J. Brunet, G. Commenges, D. Neibecker, K. Philippot, *J. Organomet. Chem.* **1994**, *469*, 221.

[19] a) S. E. Diamond, G. F. Allen, E. L. Waterman, *J. Am. Chem. Soc.* **1979**, *101*, 490; b) S. E. Diamond, F. Mares, (Allied Chemical Corp.), US 4215218, **1980**; [*Chem. Abstr.* **1980**, *93*, 185931].

[20] a) Y. Makioka, T. Shindo, Y. Taniguchi, K. Takaki, Y. Fujiwara, *Synthesis* **1995**, 801; b) S. Kobayashi, H. Ishitani, S. Nagayama, *Synthesis* **1995**, 1195; c) S. Kobayashi, H. Ishitani, S. Nagayama, *Chem. Lett.* **1995**, 423.
[21] H. Ishitani, S. Kobayashi, *Tetrahedron Lett.* **1996**, *37*, 7357.
[22] G. Giordano, R. H. Crabtree, *Inorg. Synth.* **1979**, *19*, 218.
[23] R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1971**, *93*, 3089.
[24] D. Hunter, D. G. Neilson, T. J. R. Weakly, *J. Chem. Soc. Perkin Trans 1* **1985**, 2709.

Received: September 21, 1999 [F2046]

  0947-6539/00/0614-2522 $ 17.50+.50/0