

Arylation of Adamantanamines: IV.*

Palladium-Catalyzed Arylation of Amines of Adamantane Series with Isomeric Chloroquinolines

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Received February 22, 2012

Abstract—Palladium-catalyzed arylation of diverse amines of the adamantane series with isomeric chloroquinolines was investigated. The 2-chloroquinoline is the most reactive, however the best yields of the N-arylation products are most frequently obtained in the reaction with the less reactive 6-chloroquinoline. The applicability of the reaction is limited by the size of the substituent at the amino group. In some instances the noncatalytic amination of chloroquinolines was possible.

DOI: 10.1134/S1070428012110012

The pharmacological activity of adamantane derivatives is due to various factors, in particular, to the ability to interact with biological membranes containing a lipid layer, and also with the hydrophobic fragments of proteins owing to the presence of a bulky lipophilic cage structure [2]. A special place in the series of adamantane derivatives belongs to amines, among them to 1-adamantanamine hydrochloride (amantadine) [3, 4], 1-(1-adamantyl) ethanamine hydrochloride (rimantadine) [5], 1,3-dimethyladamantan-5-amine (memantine) [6]. Interesting results were obtained in the course of the examination of the pharmacological activity of more complex adamantanamine derivatives with heteroaromatic substituents. Adamantylpyridine derivatives possess a high psychotropic activity of the neurostimulating type and a sufficiently low toxicity like also the halopyridinyl derivatives of 1- and 2-adamantanamines [7]. The psychotropic activity was also studied of adamantane derivatives with the other nitrogen heterocycles: diphenylpyrazole [8], benzimidazole [9, 10], isoxazoles, isoxazolines, oxadiazoles, imidazolines [11]. However the information is scanty on the quinoline derivatives of adamantanamines: an article has been published on the synthesis of *N*-(quinolin-4-yl) derivatives of adamantan-1- and -2-amines [12], and also

two patents, one of which describes the synthesis of various adamantane derivatives of 4-aminoquinolines [13], and the second mentions the preparation of *N*-(quinolin-2-yl) derivative of 1,3-adamantanediamine [14] that has been obtained by noncatalytic procedure. The obtained quinolinyl derivatives of adamantanamines exhibited a high malaricidal activity like many among the other 4-aminoquinolines thus stimulating the synthesis and the study of the pharmacological activity of the other *N*-quinoline-substituted amines having in their structure the adamantane framework.

Many examples of 2-chloroquinoline amination were published, both noncatalytic and catalytic. The first type constitute the reactions with piperidine [15, 16], linear secondary amines [17], substituted benzotriazoles [18, 19], and the processes as a rule occur at high temperature (100–120°C) in the presence of a large excess of the amine. As solvents toluene [15], 2-propanol [16], and methanol (in the reactor at high pressure) [17] were used. A sufficiently large number of 2-chloroquinoline aminations was carried out in the presence of palladium catalysts. The following catalytic systems were mentioned: Pd₂(dba)₃/BINAP [20], Pd(OAc)₂ with donor ligands like 1-(dimethylamino)-2-(di-*tert*-butylphosphino) benzene, 1-(dimethylamino)-2-(diadamantylphosphino)

*For Communication III, see [1].

benzene [21], diadamantylbutylphosphine [22, 23], 2-(dicyclohexylphosphino)-*N*-phenylindole [24], 2-(dicyclohexylphosphino)biphenyl [23]. The amination of 2-chloroquinoline with cyclic secondary amines was also performed in the presence of cobalt complexes [25, 26].

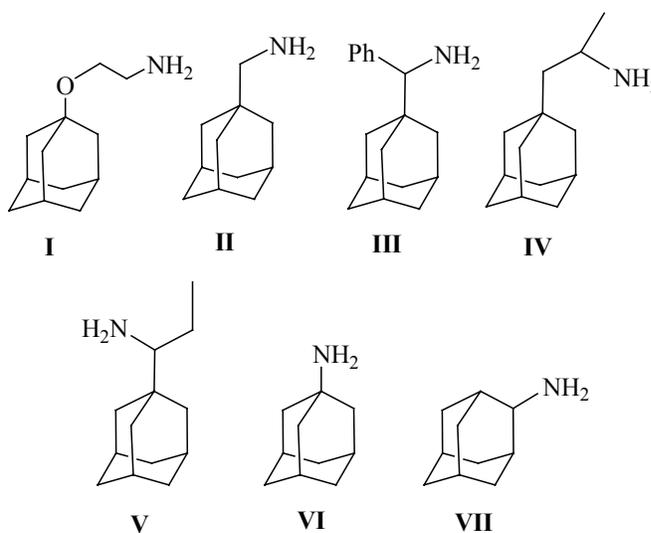
In the majority of papers dealing with the amination of the 4-chloroquinoline the process was carried out without catalyst. The reagents used were primary and secondary linear dialkylamines [17, 27, 28], aromatic amines [28, 29], cyclic secondary amines [30], some primary diamines [12, 31, 32], benzotriazole derivatives [18], and also adamantan-1- and -2-amines [12]. A multitude of solvents and bases was used in the amination of the 4-chloroquinoline: The reaction was carried out in *N*-methylpyrrolidinone at 135°C, in phenol at 180°C, in the boiling glacial acetic acid, in DMF, in pyridine (used simultaneously as a base), in methanol (in a steam reactor at 100–120°C). *N*-Methylmorpholine, NaOH, K₂CO₃, triethylamine, *N,N*-diisopropylethylamine, excess amine reagent were applied as bases. The catalytic arylation of amines with 4-chloroquinoline is far less investigated. The palladium-catalyzed arylation of aniline and pyrrolidine with 4-chloroquinoline in DMF at 135°C was described using potassium *tert*-butylate as a base and PdCl₂ complexes with di(*tert*-butyl)phosphinic acid as catalyst [33].

The amination of 6-haloquinoline is less understood. In all studies on this problem the palladium-catalyzed arylation of amines was performed. In the most cases secondary cyclic amines were used as reagents [34–36], some infrequent information concerned the reactions with aromatic amines. Often the amination of 6-bromoquinoline was performed since the catalytic amination occurred easier with bromo- than chloroderivatives. In a number of studies the selectivity of amination of 6-bromo-2-chloro- and 6-bromo-4-chloroquinolines was examined [36, 37]. In the amination of 6-chloroquinolines Pd₂(dba)₃-2-(di-*tert*-butylphosphino)-2',4',6'-triisopropyl-1,1'-biphenyl system was used as catalyst [38].

The analysis of these data led us to a conclusion that it was necessary to perform a systematic investigation of the amination of 2-, 4-, and 6-chloroquinolines with the amines of the adamantane series using two principal catalytic systems: Pd(dba)₂-BINAP and Pd(dba)₂-DavePhos comparing them if possible with noncatalytic reactions involving the more active 2- and 4-chloroquinolines. In the laboratory of organoelemental compounds of the Department of Chemistry of the Moscow State University up till now a certain experience existed concerning the

application of these catalytic systems in the adamantane amination with amines of isomeric bromochloro- and dibromobenzenes [1, 39, 40], of 2-bromopyridine [41], chloro- and bromo-substituted naphthalene, anthracene, and anthraquinone [42, 43].

The pharmacological activity of the amines of the adamantane series strongly depends on the position of the amino group with respect to the adamantane framework, and also on the presence of the other atoms between these two fragments of the molecule. We investigated in this research amines **I–VII** differing by the spatial surrounding of the amino group which was interesting for finding the rules of the course of catalytic arylation of these amines with isomeric chloroquinolines.



The synthesis of *N*-(quinolinyl)adamantanamines **VIII–XXVIII** is presented in Scheme 1. The data on the applied catalytic systems and the yields of the target products in the reactions with adamantanamines **I–V** are given in Table 1. The reactions were carried out under standard conditions using catalytic systems Pd(dba)₂-BINAP and Pd(dba)₂-DavePhos (4 mol%) at boiling in dioxane (*c* 0.1 mol l⁻¹) in the presence of a base (sodium *tert*-butylate). If necessary the amount of the catalyst was increased to 6–8 mol%. The reaction progress was monitored by the ¹H NMR spectroscopy, the reaction products were isolated by column chromatography on silica gel. The reaction of amine **I** with 2-chloroquinoline proceeded successfully, target amination product **VIII** was isolated by the chromatography on silica gel in 67% yield (Table 1, run no. 1). In this reaction we tested the phosphine ligand DavePhos, and it turned out according

to the data of ^1H NMR of the reaction mixture that the yield of compound **VIII** was approximately the same as at the use of the BINAP ligand, therefore in this case we did not perform the chromatography (run no. 2).

To prevent the formation of side product **XXIX** we decided to test a weaker base, cesium carbonate, incapable to react with 2-chloroquinoline, but the yield of the secondary amine **VIII** sharply decreased to 10–20%

Scheme 1.

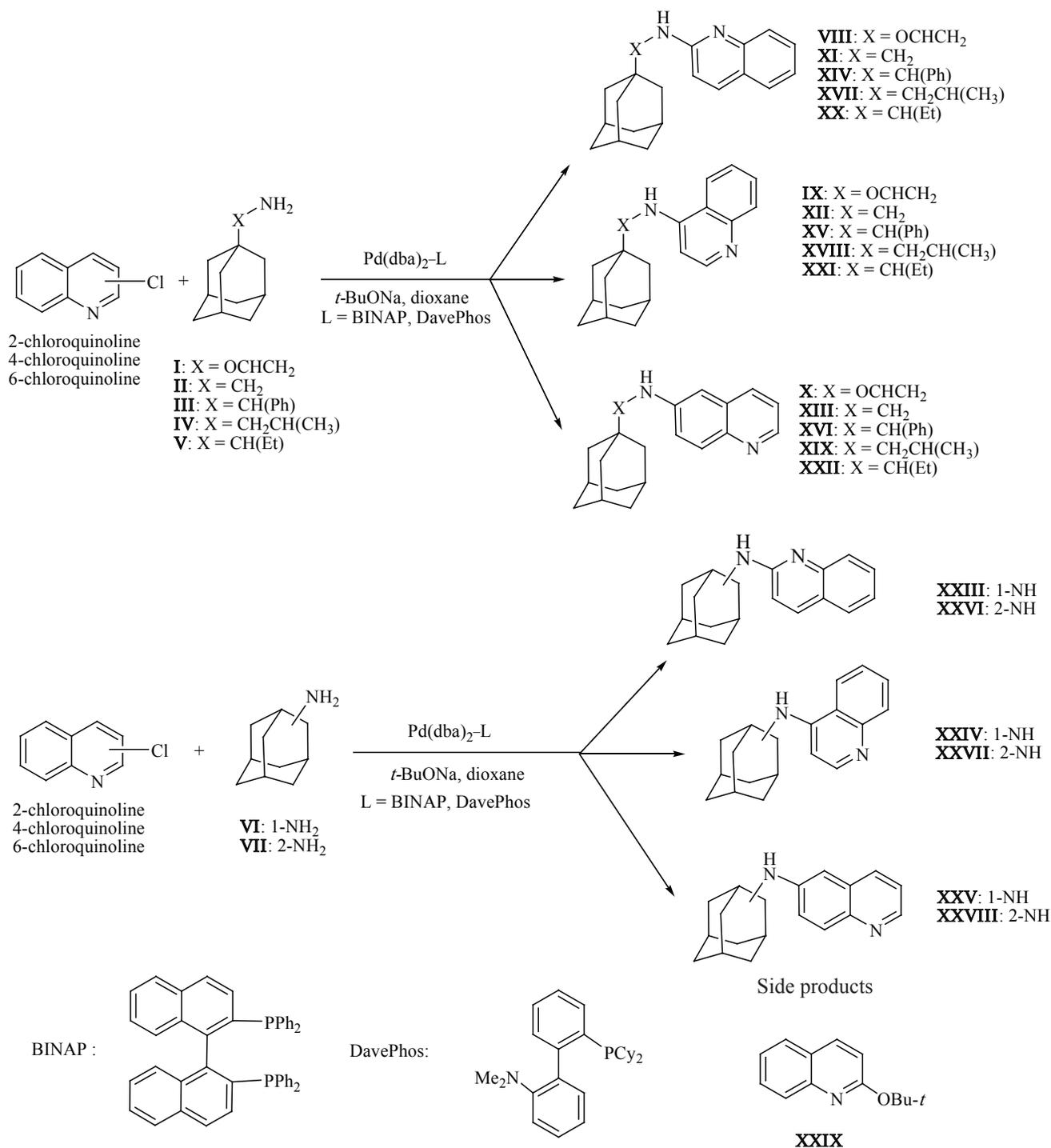


Table 1. Arylation of amines of adamantane series **I–V** with chloroquinolines

| Run no. | Chloroquinoline | Amine | Ligand L | Pd(dba) ₂ -L, mol% | Secondary amine | Yield, % ^a |
|-----------------|-------------------|------------|----------|----------------------------------|-----------------|-----------------------|
| 1 | 2-chloroquinoline | I | BINAP | 4/4.5 | VIII | 67 |
| 2 | 2-chloroquinoline | I | DavePhos | 4/4.5 | VIII | (65) |
| 3 ^b | 2-chloroquinoline | I | DavePhos | 4/4.5 | VIII | (10) |
| 4 ^b | 2-chloroquinoline | I | BINAP | 4/4.5 | VIII | (20) |
| 5 ^c | 2-chloroquinoline | I | – | – | VIII | (65) 42 |
| 6 ^d | 2-chloroquinoline | I | – | – | VIII | (15) 9 |
| 7 | 4-chloroquinoline | I | BINAP | 4/4.5 | IX | 78 |
| 8 ^c | 4-chloroquinoline | I | – | – | IX | (20) |
| 9 | 6-chloroquinoline | I | BINAP | 4/4.5 | X | 68 |
| 10 | 2-chloroquinoline | II | BINAP | 4/4.5 | XI | (48) 41 |
| 11 | 2-chloroquinoline | II | DavePhos | 8/9 | XI | (50) |
| 12 ^c | 2-chloroquinoline | II | – | – | XI | (48) 34 |
| 13 | 4-chloroquinoline | II | BINAP | 4/4.5 | XII | 52 |
| 14 | 6-chloroquinoline | II | BINAP | 4/4.5 | XIII | 64 |
| 15 | 2-chloroquinoline | III | BINAP | 4/4.5 | XIV | (41) 32 |
| 16 | 2-chloroquinoline | III | DavePhos | 8/9 | XIV | (50) |
| 17 ^c | 2-chloroquinoline | III | – | – | XIV | (11) |
| 18 | 4-chloroquinoline | III | BINAP | 4/4.5 | XV | 63 |
| 19 | 6-chloroquinoline | III | BINAP | 4/4.5 | XVI | 83 |
| 20 | 2-chloroquinoline | IV | BINAP | 4/4.5 | XVII | (24) |
| 21 | 2-chloroquinoline | IV | DavePhos | 8/9 | XVII | 38 |
| 22 ^c | 2-chloroquinoline | IV | – | – | XVII | 22 |
| 23 | 4-chloroquinoline | IV | BINAP | 4/4.5 | XVIII | 91 |
| 24 | 6-chloroquinoline | IV | BINAP | 4/4.5 | XIX | 88 |
| 25 | 2-chloroquinoline | V | DavePhos | 8/9 | XX | 0 ^e |
| 26 | 4-chloroquinoline | V | DavePhos | 8/9 | XXI | 56 |
| 27 | 6-chloroquinoline | V | DavePhos | 8/9 | XXII | 67 |

^a Yields of individual compounds after chromatography on silica gel; the yields of compounds in the reaction mixtures according to ¹H NMR data are given in parentheses.

^b Base Cs₂CO₃.

^c Solvent DMF, base K₂CO₃.

^d Solvent DMSO, base K₂CO₃.

^e 50% of compound **XXIX** has formed.

(runs nos. 3, 4). We also tested the noncatalytic procedures of the reaction. At boiling in DMF for 14 h using K₂CO₃ as a base we succeeded to obtain the secondary amine **VIII** whose yield in the reaction mixture was about 65% and 42% after chromatographing (run no. 5) Yet this yield was considerably lower than that obtained in the catalytic reaction (run no. 1). The attempt to raise the reaction temperature for the activation of the nucleophilic substitution by the replacement of DMF by DMSO was unsuccessful (run no. 6).

The use of the standard catalytic system in the reac-

tion of amine **I** with the isomeric 4-chloroquinoline resulted in a high preparative yield of secondary amine **IX** (78%, run no. 7), whereas the attempt at the noncatalytic reaction in DMF (run no. 8) was unsuccessful, and the yield of compound **IX** in the reaction mixture was only 20%. The reaction of amine **I** with 6-chloroquinoline proceeded cleanly at the use of 4 mol% of the catalyst, the preparative yield of compound **X** reached 68% (run no. 9). The reactions with the isomeric haloquinolines proceed with considerably different rates. The analysis of the ¹H NMR spectra of the reaction mixtures after equal

time intervals showed that the reaction of amine **I** with 2-chloroquinoline was completed within 15 min after the start of boiling, the reaction with 4-chloroquinoline required 1 h for the completion, and in the reaction with less active 6-chloroquinoline after 2 h the reaction mixture contained still 20% of the initial halide. All reactions were carried out in the presence of 4 mol% of the standard catalytic system. Thus it is possible to optimize the reaction time; however, the long boiling of the reaction mixtures after the completion of the reaction did not result in the decomposition of the products.

All compounds obtained were characterized by ^1H , ^{13}C NMR spectra and MALDI mass spectra of positive ions. In the ^1H NMR spectra a characteristic upfield shift is observed of the proton signals in the *ortho*-position with respect to the amino group, and this shift is considerably more pronounced in monoaryl derivatives **VIII–X** than in the *N,N*-diaryl derivatives, therefore the composition of the reaction mixtures is easily analyzed. In the ^{13}C NMR spectra also the analogous upfield shift of carbon atoms of the ring in the *ortho*-position with respect to amino group is observed. In the mass spectra alongside the signals of the pseudomolecular ions $[M + \text{H}]^+$ strong signals $[M - \text{H}]^+$ are present characteristic of arylalkylamines containing a fragment ArNHCHR indicating the formation of imines in the course of the sample irradiation with the laser and its reaction with the unsaturated matrix.

The reaction of more sterically hindered amine **II** with 2-chloroquinoline in the presence of 4 mol% of the standard catalytic system led to the formation of compound **XI** in 48% yield in the reaction system (41% after chromatography, run no. 10). The use of DavePhos as the ligand did not increase the yield of compound **XI** in the reaction mixture (50%, run no. 11). The formation of compound **XI** under noncatalytic conditions using DMF and potassium carbonate is of the similar efficiency (run no. 12), but like the case of compound **VIII**, the chromatographic separation is of low efficiency. A good yield of secondary amine **XII** was found in the reaction with the isomeric 4-chloroquinoline (52%, run no. 13), the 6-chloroquinoline reacted even better, and the yield of amine **XIII** after the chromatography reached 64% (run no. 14).

Amine **III** possesses even larger spatial hindrances at the amino group with the phenyl substituent in the α -position with respect to the amino group. In the reaction with the 2-chloroquinoline in the presence of the catalytic system $\text{Pd}(\text{dba})_2\text{-BINAP}$ (4 mol%) was found, firstly, a

lower yield of the secondary amine **XIV** in the reaction mixture compared to analogous compounds **VIII** and **XI**, secondly, **XI**, a large amount of the side product of alkoxylation **XXIX** was formed, and a half of the starting amine **III** was recovered by the chromatography (run no. 15) at the complete conversion of the 2-chloroquinoline. The application of the ligand DavePhos did not result in a significant increase in the yield of reaction product **XIV** (run no. 16). The attempt at the noncatalytic process was unsuccessful, and the yield of compound **XIV** in the reaction mixture was only 11% (run no. 17). In the presence of the standard catalytic system the total conversion of 2-chloroquinoline is attained in 30 min. The attempt to decrease the quantity of the base to 1 equiv to prevent the alkoxylation resulted in the smaller yield of secondary amine **XIV** in the reaction mixture.

In the reaction of amine **III** with 4-chloroquinoline the preparative yield of compound **XV** reached 63% (run no. 18), and the unreacted amine **III** was also partially recovered. Note that in the amination reaction the regeneration of pure initial amine is observed relatively seldom. The most successful reaction was with 6-chloroquinoline and compound **XVI** was obtained in a high yield (83%, run no. 19).

Amine **IV** at the first sight seems less spatially hindered than amine **III** since in this compound the adamantane moiety is farther from the amino group, and in the α -position to the NH_2 group a methyl substituent is located. Yet the reaction of amine **IV** with 2-chloroquinoline using the standard catalytic system led to the formation of the *tert*-butoxyderivative **XXIX** that even prevailed over secondary amine **XVII** in the reaction mixture (run no. 20). The application of the catalytic system $\text{Pd}(\text{dba})_2\text{-DavePhos}$ (8 mol%) proved to be more efficient apparently due to the acceleration of the catalytic amination compared to the noncatalytic alkoxylation, and compound **XVII** was isolated in 38% yield (run no. 21). The reaction with amine **IV** can occur also in noncatalytic conditions (run no. 22), but the yield of compound **XVII** is considerably lower (22%). Bringing into the reaction the 4- and 6-chloroquinolines possessing less labile chlorine atom resulted in very high yields of the amination products **XVIII** and **XIX**, ~90% (run no. 23, 24).

Isomeric amine **V**, the most sterically hindered among all studied since it contained an ethyl and an adamantyl substituents in the α -position to the amino group, proved to be the most problematic in the amination of the 2-chloroquinoline (run no. 25). Though the more ac-

tive catalytic system Pd(dba)₂–DavePhos (8 mol%) was used, in the reaction mixture about 50% of alkoxylation product **XXIX** was detected, and secondary amine **XX** was obtained in the trace amount. The amination of two other chloroquinolines proceeded more successfully: in the reaction with 4-chloroquinoline amine **XXI** was isolated in 56% yield, and in the reaction with 6-chloroquinoline, compound **XXII** was obtained in 67% yield (runs nos. 25, 26).

The research carried out formerly in the laboratory of organoelemental compounds showed that the use of 4 mol% of the standard catalytic system Pd(dba)₂–BINAP was insufficient for the amination of bromochloro- and dibromobenzenes with adamantan-1-amine. Therefore in the reaction of amine **VI** with chloroquinolines we increased the content of the catalyst to 6 mol% (Table 2). In these conditions the yield of the amination product of 2-chloroquinoline in the reaction mixture was small (run no. 1), whereas the main reaction product was compound **XXIX**. On increasing the catalyst amount to 8 mol% and replacing BINAP by DavePhos we succeeded to increase the yield of compound **XXIII** to 50% in the reaction mixture (isolated 24%), but compound **XXIX** was still formed in a large amount (run no. 2). The reaction in

the noncatalytic conditions resulted in an insignificant amount of amine **XXIII** (run no.3). In the reactions with 4-chloroquinoline the yields were also low both at the use as ligands of BINAP and DavePhos (runs nos. 4, 5) that may be ascribed to the steric influence of the hydrogen atom in the *peri*-position of the 4-chloroquinoline on the substitution with the bulky aminoadamantyl structure. The experiments with 6-chloroquinoline were far more satisfactory. In the reaction catalyzed with the complex with BINAP the yield of compound **XXV** in the reaction mixture attained 25% because of incomplete conversion of the initial 6-chloroquinoline (run no. 6), but at the use of 8 mol% of the catalyst and DavePhos as the ligand the yield of compound **XXV** grew to 82% (run no. 7). Thus again the 6-chloroquinoline was the most reactive substrate in the arylation.

The reaction with the isomeric adamantan-2-amine (**VII**) proceeded easier, apparently due to the weaker spatial hindrances at the nitrogen atom, therefore we used in all cases the catalytic system Pd(dba)₂–BINAP. Even at 4 mol% of the standard catalytic system we succeeded to obtain the product of 2-chloroquinoline amination **XXVI** in 49% yield (run no. 8); the application of the double amount of the same catalyst did not virtually increase

Table 2. Arylation of adamantanamines **VI**, **VII** with chloroquinolines

| Run no. | Chloroquinoline | Amine | Ligand L | Pd(dba) ₂ –L, mol% | Secondary amine | Yield, % ^a |
|-----------------|-------------------|------------|----------|-------------------------------|-----------------|-----------------------|
| 1 | 2-chloroquinoline | VI | BINAP | 6/7 | XXIII | (25) ^b |
| 2 | 2-chloroquinoline | VI | DavePhos | 8/9 | XXIII | (50) 24 |
| 3 ^c | 2-chloroquinoline | VI | – | – | XXIII | (22) |
| 4 | 4-chloroquinoline | VI | BINAP | 6/7 | XXIV | 30 |
| 5 | 4-chloroquinoline | VI | DavePhos | 8/9 | XXIV | 20 |
| 6 | 6-chloroquinoline | VI | BINAP | 6/7 | XXV | (25) |
| 7 | 6-chloroquinoline | VI | DavePhos | 8/9 | XXV | 82 |
| 8 | 2-chloroquinoline | VII | BINAP | 4/4.5 | XXVI | 49 |
| 9 | 2-chloroquinoline | VII | BINAP | 8/9 | XXVI | 52 |
| 10 ^c | 2-chloroquinoline | VII | – | – | XXVI | (15) |
| 11 | 4-chloroquinoline | VII | BINAP | 4/4.5 | XXVII | 89 |
| 12 | 4-chloroquinoline | VII | BINAP | 4/4.5 | XXVII | (55) |
| 13 | 6-chloroquinoline | VII | BINAP | 8/9 | XXVIII | (80) 56 |

^a Yields of individual compounds after chromatography on silica gel; the yields of compounds in the reaction mixtures according to ¹H NMR data are given in parentheses.

^b 70% of compound **XXIX** has formed.

^c Solvent DMF, base K₂CO₃.

the yield of compound **XXVI** (run no. 9). The reaction in the noncatalytic conditions gave a low yield of the secondary amine **XXVI** (run no. 10). 4-Chloroquinoline fairly well reacted with adamantan-2-amine giving compound **XXVII** in 89% yield (run no. 11) using only 4 mol% of the catalyst. The same amount of the catalyst proved to be insufficient for the complete conversion of 6-chloroquinoline (run no. 12); at the double quantity of the catalyst we succeeded to isolate 56% of the amination product **XXVIII** (run no. 13). The comparison of the obtained data shows that the chlorine atom in the position 4 of the quinoline structure is far more reactive than in the position 6 therefore in the absence of the sterical hindrances the successful amination of 4-chloroquinoline requires less catalyst.

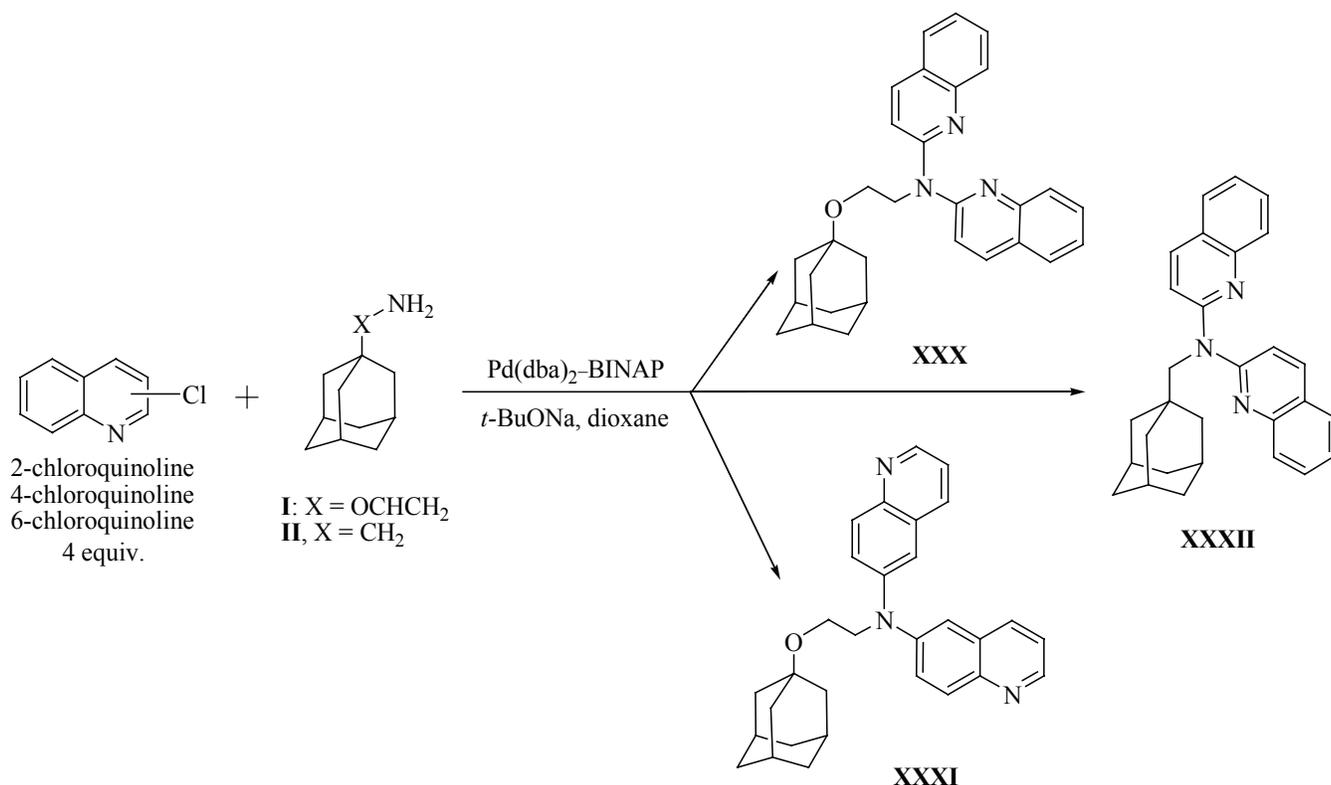
In some reactions involving 2-chloroquinoline *N,N*-diarylation products were detected, therefore we specially investigated the conditions of the formation of these compounds (Scheme 2). The reactions were carried out in the presence of the catalytic system Pd(dba)₂-BINAP (8 mol%) with 4 equiv of chloroquinoline at boiling for a longer time.

Even using 1 equiv of 2-chloroquinoline in the reac-

tion of amine **I** in the presence of 4 mol% of the catalyst the *N,N*-diarylation product **XXX** was isolated in 30% yield, and at the use of the double amount of the catalyst and 4 equiv of 2-chloroquinoline the yield of compound **XXX** increased to 78%. At the attempt to synthesize the *N,N*-diaryl derivative with the isomeric 4-chloroquinoline we obtained exclusively the monoarylation product **IX** apparently due to the steric factor. With the spatially unhindered 6-chloroquinoline at the use of 4 equiv of this compound and 8 mol% of the catalyst the *N,N*-diarylation product **XXXI** was obtained in 91% yield. In the reaction of more sterically hindered amine **II** with 1 equiv of 2-chloroquinoline the yield of the diarylation product **XXXII** was substantial (36%), and using the double quantity of the catalyst and 4 equiv of 2-chloroquinoline its yield grew to 62%. However in contrast to adamantan-1-amine (**I**) amine **II** did not form the diarylation product in the reaction with 6-chloroquinoline.

Thus in the course of experiments diverse *N*-quinolinyl derivatives of various amines of the adamantane series were synthesized. In the most cases the best yields were obtained using of the less reactive 6-chloroquinoline. The ligand DavePhos in more favorable than the ligand BINAP

Scheme 2.



in the reactions with the spatially hindered amines. In the case of amines with insignificant sterical hindrances the *N,N*-diarylation of the amino group is possible. In the amination of the more reactive 2-chloroquinoline the arising difficulty consists in the competing alkoxylation reaction. The obtained compounds will be tested for various kinds of the physiological, first of all psychotropic, activity.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance-400 (operating frequencies 400 and 100.6 MHz respectively) in CDCl_3 . Chloroform signals (δ_{H} 7.25, δ_{C} 77.00 ppm) served as internal references. Mass spectra MALDI-TOF of positive ions were obtained on an instrument Bruker Daltonics Autoflex II using 1,8,9-trihydroxyanthracene as a matrix and polyethylene glycols as internal references. UV spectra were recorded on a spectrophotometer Perkin Elmer Lambda 40. The preparative column chromatography was performed using silica gel Merck (40/60). Commercially available 2-, 4-, 6-chloroquinolines, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), 2-dicyclohexylphosphino-2'-dimethylaminobiphenyl (DavePhos), sodium *tert*-butylate, and cesium carbonate were used without additional purification. Amines I–V were synthesized by procedures [41, 44, 45], adamantan-1-amine (VI) was prepared by the method [46], adamantan-2-amine (VII), by the method [47]. Dioxane was distilled in succession over alkali and then over sodium metal; dichloromethane, petroleum ether, and methanol were distilled. The synthesis of $\text{Pd}(\text{dba})_2$ is described in [48].

***N*-Quinolinylamines of the amantane series.** In a flask filled with argon was placed 0.25 mmol (1 mmol at the synthesis of *N,N*-diaryl derivatives) 2-, 4-, or 6-chloroquinoline, 6–12 mg (4–8 mol%) of $\text{Pd}(\text{dba})_2$, 7–14 mg (4.5–9 mol%) of BINAP or 5–9 mg (4.5–9 mol%) of DavePhos, 2.5 ml of anhydrous dioxane, 0.25 mmol of an appropriate amine I–VII, 37–96 mg (1.5–3 equiv) of sodium *tert*-butylate, and the mixture was boiled for 7 h. The reaction mixture was filtered, dioxane was evaporated in a vacuum, the residue was chromatographed on silica gel.

***N*-[2-(Adamantan-1-yloxy)ethyl]quinolin-2-amine (VIII).** *a.* A mixture of 0.25 mmol (49 mg) of amine I, 0.25 mmol (41 mg) of 2-chloroquinoline, 6 mg (4 mol%) of $\text{Pd}(\text{dba})_2$, 7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate was boiled for 7 h in 2.5 ml of anhydrous dioxane. Yield after chromatography

(eluent CH_2Cl_2 –MeOH, 100 : 1) 54 mg (67%). With the same eluent 17 mg (30%) of diarylation product XXX was isolated.

b. With the same quantities of amine I and 2-chloroquinoline was used 6 mg (4 mol%) of $\text{Pd}(\text{dba})_2$, 5 mg (4.5 mol%) of DavePhos, and 36 mg (1.5 equiv) of sodium *tert*-butylate, the mixture was boiled for 7 h. According to ^1H NMR spectrum of the reaction mixture the ratio of the products of monoarylation (65%) and diarylation (35%) was similar to the data of the preceding experiment; the products were not subjected to chromatography.

c. With the same quantities of amine I and 2-chloroquinoline was used 6 mg (4 mol%) of $\text{Pd}(\text{dba})_2$, 5 mg (4.5 mol%) of DavePhos, and 163 mg (2 equiv) of cesium carbonate. According to ^1H NMR spectrum the reaction mixture contained 10% of compound VIII; the products were not subjected to chromatography.

d. With the same quantities of amine I and 2-chloroquinoline was used 6 mg (4 mol%) of $\text{Pd}(\text{dba})_2$, 7 mg (4.5 mol%) of BINAP, 163 mg (2 equiv) of cesium carbonate. According to ^1H NMR spectrum the reaction mixture contained 20% of secondary amine VIII; the products were not subjected to chromatography.

e. The reaction was carried out without catalyst: 0.2 mmol (39 mg) of amine I and 0.2 mmol (33 mg) of 2-chloroquinoline in the presence of 110 mg (4 equiv) of potassium carbonate was boiled for 14 h in 1 ml of DMF. Yield after chromatography (eluent CH_2Cl_2 –MeOH, 100:1) 27 mg (42%).

f. The reaction was carried out without catalyst: 0.2 mmol (39 mg) of amine I and 0.2 mmol (33 mg) of 2-chloroquinoline in the presence of 110 mg (4 equiv) of potassium carbonate was boiled for 14 h in 1 ml of DMSO. The reaction mixture was treated with water, the reaction products were extracted into dichloromethane, the extract was dried, evaporated, the residue was subjected to chromatography (eluent CH_2Cl_2 –MeOH, 100:1). Yield 6 mg (9%), light-yellow crystalline powder, mp 110–112°C. ^1H NMR spectrum, δ , ppm: 1.55–1.68 m (6H, $\text{CH}_{2\text{Ad}}$), 1.75 br.s (6H, $\text{CH}_{2\text{Ad}}$), 2.14 br.s (3H, CH_{Ad}), 3.65 br.s (4H, $\text{OCH}_2\text{CH}_2\text{N}$), 5.13 br.s (1H NH), 6.64 d (1H, H^3_{Q} , 3J 8.8 Hz), 7.18 t (1H, H^6_{Q} , 3J 7.4 Hz), 7.50 t (1H, H^7_{Q} , 3J 7.6 Hz), 7.56 d (1H, H^5_{Q} , 3J 7.8 Hz), 7.66 d (1H, H^8_{Q} , 3J 8.5 Hz), 7.78 d (1H, H^4_{Q} , 3J 8.9 Hz). ^{13}C NMR spectrum, δ , ppm: 30.5 (3C, CH_{Ad}), 39.4 (3C, $\text{CH}_{2\text{Ad}}$), 41.6 (3C, $\text{CH}_{2\text{Ad}}$), 42.0 (1C, CH_2N), 58.8 (1C, CH_2O), 72.4 (1C, C_{Ad}), 111.9 (1C, C^3_{Q}), 121.9 (1C, C_{Q}), 123.4 (1C, C_{Q}^{4a}), 126.1 (1C, C_{Q}), 127.4 (1C, C_{Q}), 129.4

(1C, C_Q), 137.1 (1C, C⁴_Q), 148.0 (1C, C_Q^{8a}), 156.9 (1C, C²_Q). Mass spectrum: *m/z* 323.210 [*M* + H]⁺. C₂₁H₂₇N₂O. Calculated (*M* + H) 323.212.

***N*-[2-(Adamantan-1-yloxy)ethyl]-*N*-(quinolin-2-yl)quinolin-2-amine (XXX).** A mixture of 0.25 mmol (49 mg) of amine **I**, 1 mmol (146 mg) of 2-chloroquinoline, 12 mg (8 mol%) of Pd(dba)₂, 14 mg (9 mol%) of BINAP, 144 mg (6 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. Yield after chromatography (eluent – CH₂Cl₂–MeOH, 200:1) 87 mg (78%), light-brown crystalline powder, mp 118–120°C. ¹H NMR spectrum, δ, ppm: 1.50–1.62 m (6H, CH_{2Ad}), 1.71 br.s (6H, CH_{2Ad}), 2.08 br.s (3H, CH_{Ad}), 3.89 t (2H, CH₂O, ³*J* 6.5 Hz), 4.60 t (2H, CH₂N, ³*J* 6.5 Hz), 7.38 t (2H, H⁶_Q, ³*J* 7.2 Hz), 7.46 d (2H, H³_Q, ³*J* 9.0 Hz), 7.61 t (2H, H⁷_Q, ³*J* 7.5 Hz), 7.70 d (2H, H⁵_Q, ³*J* 8.0 Hz), 7.84 d (2H, H⁸_Q, ³*J* 8.3 Hz), 7.96 d (2H, H_Q⁴, ³*J* 9.0 Hz). ¹³C NMR spectrum, δ, ppm: 30.4 (3C, CH_{Ad}), 36.4 (3C, CH_{2Ad}), 41.5 (3C, CH_{2Ad}), 49.7 (1C, CH₂N), 58.2 (1C, CH₂O), 72.4 (1C, C_{Ad}), 116.4 (2C, C³_Q), 124.2 (2C, C_Q), 125.1 (2C, C_Q^{4a}), 127.2 (2C, C_Q), 127.8 (2C, C_Q), 129.3 (2C, C_Q), 136.7 (2C, C_Q⁴), 147.4 (2C, C_Q^{8a}), 156.0 (2C, C²_Q). Mass spectrum: *m/z* 450.259 [*M* + H]⁺. C₃₀H₃₂N₃O. Calculated (*M*+H) 450.255.

After chromatography (eluent CH₂Cl₂) the yield of side product **2-*tert*-butoxyquinoline (XXIX)** 63 mg (31%). ¹H NMR spectrum, δ, ppm: 1.70 s (9H, CH₃), 6.79 d (1H, H³_Q, ³*J* 8.8 Hz), 7.33 t (1H, H⁶_Q, ³*J* 7.5 Hz), 7.57 t (1H, H⁷_Q, ³*J* 7.6 Hz), 7.66 d (1H, H⁵_Q, ³*J* 8.0 Hz), 7.79 d (1H, H⁸_Q, ³*J* 8.3 Hz), 7.91 d (1H, H_Q⁴, ³*J* 8.8 Hz). ¹³C NMR spectrum, δ, ppm: 28.6 (3C, CH₃), 80.1 (1C, CCH₃), 115.0 (1C, C³_Q), 123.6 (1C, C_Q), 124.5 (1C, C_Q^{4a}), 127.2 (1C, C_Q), 127.5 (1C, C_Q), 129.0 (1C, C_Q), 137.9 (1C, C_Q⁴), 146.5 (1C, C_Q⁸), 161.9 (1C, C²_Q). Mass spectrum: *m/z* 202.120 [*M* + H]⁺. C₁₃H₁₆NO. Calculated (*M* + H) 202.123.

***N*-[2-(Adamantan-1-yloxy)ethyl]quinoline-4-amine (IX).** *a.* A mixture of 0.25 mmol (49 mg) of amine **I**, 0.25 mmol (41 mg) of 4-chloroquinoline, 6 mg (4 mol%) of Pd(dba)₂, 7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate was boiled for 7 h in 2.5 ml of anhydrous dioxane. Yield after chromatography (eluent CH₂Cl₂–MeOH, 10:1) 63 mg (78%), light-yellow crystalline powder, mp 144–146°C.

b. The reaction was carried out without catalyst. A mixture of 0.25 mmol (49 mg) of amine **I**, 0.25 mmol (41 mg) of 4-chloroquinoline, 138 mg (4 equiv) of potassium carbonate, 1 ml of DMF was boiled for 5.5 h.

According to ¹H NMR spectrum of the reaction mixture the yield was 14%, the product was not chromatographed. ¹H NMR spectrum, δ, ppm: 1.56–1.68 m (6H, CH_{2Ad}), 1.77 br.s (6H, CH_{2Ad}), 2.16 br.s (3H, CH_{Ad}), 3.42 q (2H, CH₂N, ³*J* 4.9 Hz), 3.74 t (2H, CH₂O, ³*J* 5.1 Hz), 5.61 br.s (1H, NH), 6.42 d (1H, H³_Q, ³*J* 5.3 Hz), 7.42 t (1H, H⁶_Q, ³*J* 7.6 Hz), 7.61 t (1H, H⁷_Q, ³*J* 7.6 Hz), 7.74 d (1H, H⁵_Q, ³*J* 8.3 Hz), 7.97 d (1H, H⁸_Q, ³*J* 8.3 Hz), 8.52 d (1H, H²_Q, ³*J* 5.3 Hz). ¹³C NMR spectrum, δ, ppm: 30.4 (3C, CH_{Ad}), 36.3 (3C, CH_{2Ad}), 41.6 (3C, CH_{2Ad}), 43.4 (1C, CH₂N), 57.8 (1C, CH₂O), 72.8 (1C, C_{Ad}), 98.8 (1C, C³_Q), 118.7 (1C, C_Q^{4a}), 119.7 (1C, C_Q), 124.9 (1C, C_Q), 128.9 (1C, C_Q), 129.4 (1C, C_Q), 147.2 (1C, C_Q^{8a}), 149.9 (1C, C²_Q), 150.5 (1C, C_Q⁴). Mass spectrum: *m/z* 323.207 [*M* + H]⁺. C₂₁H₂₇N₂O. Calculated (*M* + H) 323.212.

***N*-[2-(Adamantan-1-yloxy)ethyl]quinolin-6-amine (X).** A mixture of 0.25 mmol (49 mg) of amine **I**, 0.25 mmol (41 mg) of 6-chloroquinoline, 6 mg (4 mol%) of Pd(dba)₂, 7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate was boiled for 7 h in 2.5 ml of anhydrous dioxane. Yield after chromatography (eluent CH₂Cl₂–MeOH, 100:1) 55 mg (68%), yellow oily substance, exhibits luminescence on dissolving in organic solvents. ¹H NMR spectrum, δ, ppm: 1.54–1.70 m (6H, CH_{2Ad}), 1.76 br.s (6H, CH_{2Ad}), 2.15 br.s (3H, CH_{Ad}), 3.33 q (2H, CH₂N, ³*J* 5.2 Hz), 3.68 t (2H, CH₂O, ³*J* 5.1 Hz), 4.39 br.s (1H, NH), 6.70 d (1H, H⁵_Q, ⁴*J* 2.3 Hz), 7.11 d.d (1H, H⁷_Q, ³*J* 8.8, ⁴*J* 2.5 Hz), 7.24 d.d (1H, H³_Q, ³*J* 8.3, 4.3 Hz), 7.85 d (1H, H⁸_Q, ³*J* 9.1 Hz), 7.89 d (1H, H_Q⁴, ³*J* 8.3 Hz), 8.59 d (1H, H²_Q, ³*J* 4.0 Hz). ¹³C NMR spectrum, δ, ppm: 30.5 (3C, CH_{Ad}), 36.4 (3C, CH_{2Ad}), 41.6 (3C, CH_{2Ad}), 44.3 (1C, CH₂N), 58.1 (1C, CH₂O), 72.5 (1C, C_{Ad}), 103.3 (1C, C⁷_Q), 121.3 (1C, C_Q), 121.8 (1C, C_Q), 130.1 (2C, C_Q, C_Q^{4a}), 133.8 (1C, C_Q), 143.2 (1C, C_Q^{8a}), 146.0 (1C, C²_Q), 146.4 (1C, C⁶_Q). Mass spectrum: *m/z* 323.208 [*M* + H]⁺. C₂₁H₂₇N₂O. Calculated (*M* + H) 323.212.

***N*-[2-(Adamantan-1-yloxy)ethyl]-*N*-(quinolin-6-yl)quinolin-6-amine (XXXI)** A mixture of 0.25 mmol (49 mg) of amine **I**, 1 mmol (146 mg) of 6-chloroquinoline, 12 mg (8 mol%) of Pd(dba)₂, 14 mg (9 mol%) of BINAP, 96 mg (4 equiv) of sodium *tert*-butylate was boiled for 7 h in 25 ml of anhydrous dioxane. Yield after chromatography (eluent CH₂Cl₂–MeOH, 50 : 1) 102 mg (91%), yellow thick oily substance, exhibits luminescence on dissolving in organic solvents. ¹H NMR spectrum, δ, ppm: 1.47–1.60 m (6H, CH_{2Ad}), 1.67 br.s (6H, CH_{2Ad}), 2.06 br.s (3H, CH_{Ad}), 3.71 t (2H, CH₂O, ³*J* 5.7 Hz), 4.13 t

(2H, CH₂N, ³J 5.7 Hz), 7.31 d.d (2H, H³_Q, ³J 8.2, 4.2 Hz), 7.47 d (2H, H⁵_Q, ⁴J 1.9 Hz), 7.54 d.d (2H, H⁷_Q, ³J 9.0, ⁴J 1.9 Hz), 7.95 d (2H, H⁸_Q, ³J 9.0 Hz), 7.96 d (2H, H_Q⁴, ³J 7.6 Hz), 8.74 d (2H, H²_Q, ³J 4.0 Hz). ¹³C NMR spectrum, δ, ppm: 30.3 (3C, CH_{Ad}), 36.3 (3C, CH_{2Ad}), 41.5 (3C, CH_{2Ad}), 53.2 (1C, CH₂N), 56.8 (1C, CH₂O), 72.6 (1C, C_{Ad}), 116.9 (2C, C⁷_Q), 121.4 (2C, C_Q), 126.0 (2C, C_Q), 129.4 (2C, C_Q^{4a}), 130.2 (2C, C_Q), 134.8 (2C, C_Q), 144.8 (2C, C_Q^{8a}), 145.5 (2C, C_Q⁶), 148.3 (2C, C_Q²). Mass spectrum: *m/z* 450.262 [*M* + H]⁺. C₃₀H₃₂N₃O. Calculated (*M* + H) 450.255.

***N*-[(Adamantan-1-yl)methyl]quinolin-2-amine (XI).** *a.* A mixture of 0.25 mmol (41 mg) of amine **II**, 0.25 mmol (41 mg) of 2-chloroquinoline, 6 mg (4 mol%) of Pd(dba)₂, 7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h, after chromatography (eluent CH₂Cl₂, CH₂Cl₂–MeOH, 200:1) we isolated 30 mg (41%) of compound **XI** and 19 mg (36%) of diarylation product **XXXII**.

b. A mixture of the same quantities of amine and 2-chloroquinoline, 12 mg (8 mol%) of Pd(dba)₂, 9 mg (9 mol%) of DavePhos, and 36 mg (1.5 equiv) of sodium *tert*-butylate was boiled for 7 h. According to ¹H NMR spectrum the reaction mixture contained 50% of secondary amine **XI**; the products were not subjected to chromatography.

c. The reaction was carried out without catalyst. A mixture of 0.2 mmol (33 mg) of amine **II**, 0.2 mmol (33 mg) of 2-chloroquinoline, 111 mg (4 equiv) of potassium carbonate, 1 ml of DMF was boiled for 14 h. Yield of compound **XI** after chromatography (eluent CH₂Cl₂–MeOH, 200:1) 20 mg (34%), light-yellow oily substance. UV spectrum (CH₂Cl₂): λ_{max} 343 nm (ε 6400). ¹H NMR spectrum, δ, ppm: 1.61–1.75 m (12H, CH_{2Ad}), 1.99 br.s (3H, CH_{Ad}), 3.19 d (2H, CH₂N, ³J 6.1 Hz), 4.82 br.s (1H, NH), 6.66 d (1H, H³_Q, ³J 8.8 Hz), 7.17 d.d.d (1H, H⁶_Q, ³J 8.0, 7.0, ⁴J 1.1 Hz), 7.50 d.d.d (1H, H⁷_Q, ³J 8.5, 7.0, ⁴J 1.5 Hz), 7.55 d.d (1H, H⁵_Q, ³J 8.0, ⁴J 1.1 Hz), 7.64 d (1H, H⁸_Q, ³J 8.5 Hz), 7.79 d (1H, H_Q⁴, ³J 8.8 Hz). ¹³C NMR spectrum, δ, ppm: 28.3 (3C, CH_{Ad}), 34.0 (1C, C_{Ad}), 37.0 (3C, CH_{2Ad}), 40.5 (3C, CH_{2Ad}), 53.6 (1C, CH₂N), 110.8 (1C, C³_Q), 121.7 (1C, C_Q), 123.3 (1C, C_Q^{4a}), 125.9 (1C, C_Q), 127.4 (1C, C_Q), 129.5 (1C, C_Q), 137.3 (1C, C_Q⁴), 148.1 (1C, C_Q^{8a}), 157.7 (1C, C_Q²). Mass spectrum: *m/z* 293.207 [*M* + H]⁺. C₂₀H₂₅N₂. Calculated (*M* + H) 293.202.

***N*-[(Adamantan-1-yl)methyl]-*N*-(quinolin-2-yl)-**

quinolin-2-amine (XXXII). A mixture of 0.25 mmol (41 mg) of amine **II**, 1 mmol (146 mg) of 2-chloroquinoline, 12 mg (8 mol%) of Pd(dba)₂, 14 mg (9 mol%) of BINAP, 96 mg (4 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. Yield after chromatography (eluent CH₂Cl₂) 70 mg (62%), light-brown oily substance. ¹H NMR spectrum, δ, ppm: 1.60–1.69 m (12H, CH_{2Ad}), 1.90 br.s (3H, CH_{Ad}), 4.45 s (2H, CH₂N), 7.31 d (2H, H³_Q, ³J 8.9 Hz), 7.38 d.d.d (2H, H⁶_Q, ³J 8.0, 7.0, ⁴J 1.0 Hz), 7.63 d.d.d (2H, ³J 8.4, H⁷_Q, ³J 7.0, ⁴J 1.4 Hz), 7.70 d.d (2H, H⁵_Q, ³J 8.0, ⁴J 1.0 Hz), 7.91 d (2H, H⁸_Q, ³J 8.5 Hz), 7.93 d (2H, H_Q⁴, ³J 8.9 Hz). ¹³C NMR spectrum, δ, ppm: 28.5 (3C, CH_{Ad}), 35.2 (1C, C_{Ad}), 36.9 (3C, CH_{2Ad}), 41.5 (3C, CH_{2Ad}), 59.2 (1C, CH₂N), 116.5 (2C, C³_Q), 124.2 (2C, C_Q), 125.0 (2C, C_Q^{4a}), 127.1 (2C, C_Q), 127.8 (2C, C_Q), 129.3 (2C, C_Q), 136.5 (2C, C_Q⁴), 147.4 (2C, C_Q^{8a}), 157.2 (2C, C_Q²). Mass spectrum: *m/z* 420.241 [*M* + H]⁺. C₂₉H₃₀N₃. Calculated (*M* + H) 420.244.

With a mixture of CH₂Cl₂–MeOH, 200:1 28 mg (35%) of monoarylation product **XI** was eluted.

***N*-[(Adamantane-1-yl)methyl]quinoline-4-amine (XII).** A mixture of 0.25 mmol (41 mg) of amine **II**, 0.25 mmol (41 mg) of 4-chloroquinoline, 6 mg (4 mol%) of Pd(dba)₂, 7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate was boiled for 7 h in 2.5 ml of anhydrous dioxane. Yield after chromatography (eluent CH₂Cl₂–MeOH, 50:1) 38 mg (52%), light-brown oily substance. UV spectrum (CH₂Cl₂): λ_{max} 321 nm (ε 11800). ¹H NMR spectrum, δ, ppm: 1.64 br.s (6H, CH_{2Ad}), 1.65–1.78 m (6H, CH_{2Ad}), 2.02 br.s (3H, CH_{Ad}), 2.99 d (2H, CH₂N, ³J 5.8 Hz), 5.12 br.s (1H, NH), 6.44 d (1H, H³_Q, ³J 5.4 Hz), 7.40 d.d.d (1H, H⁶_Q, ³J 8.4, 6.9, ⁴J 1.2 Hz), 7.60 t.d (1H, H⁷_Q, ³J 8.4, ⁴J 1.2 Hz), 7.73 d (1H, H⁵_Q, ³J 8.4 Hz), 7.96 d (1H, H⁸_Q, ³J 8.4 Hz), 8.51 d (1H, H_Q⁴, ³J 5.4 Hz). ¹³C NMR spectrum, δ, ppm: 28.2 (3C, CH_{Ad}), 34.1 (1C, C_{Ad}), 36.8 (3C, CH_{2Ad}), 40.7 (3C, CH_{2Ad}), 54.9 (1C, CH₂N), 98.6 (1C, C³_Q), 118.6 (1C, C_Q^{4a}), 119.1 (1C, C_Q), 124.5 (1C, C_Q), 129.0 (1C, C_Q), 129.7 (1C, C_Q), 148.1 (1C, C_Q^{8a}), 150.4 (1C, C_Q⁴), 150.7 (1C, C_Q²). Mass spectrum: *m/z* 293.197 [*M* + H]⁺. C₂₀H₂₅N₂. Calculated (*M* + H) 293.202.

***N*-[(Adamantan-1-yl)methyl]quinolin-6-amine (XIII).** A mixture of 0.25 mmol (41 mg) of amine **II**, 0.25 mmol (41 mg) of 6-chloroquinoline, 6 mg (4 mol%) of Pd(dba)₂, 7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate was boiled for 7 h in 2.5 ml of anhydrous dioxane. Yield after chromatography (eluent CH₂Cl₂–MeOH, 100:1) 47 mg (63%), light-green

viscous oily substance, exhibits luminescence on dissolving in organic solvents. UV spectrum (CH_2Cl_2): λ_{max} 361 nm (ϵ 7500). ^1H NMR spectrum, δ , ppm: 1.60 br.s (6H, $\text{CH}_{2\text{Ad}}$), 1.63–1.76 m (6H, $\text{CH}_{2\text{Ad}}$), 2.00 br.s (3H, CH_{Ad}), 2.88 d (2H, CH_2N , 3J 4.3 Hz), 4.01 br.s (1H, NH), 6.67 d (1H, H^5_{Q} , 4J 2.7 Hz), 7.08 d.d (1H, H^7_{Q} , 3J 9.0, 4J 2.7 Hz), 7.21 d.d (1H, H^3_{Q} , 3J 8.3, 4.2 Hz), 7.83 d (1H, H^8_{Q} , 3J 9.0 Hz), 7.87 d.d (1H, H^4_{Q} , 3J 8.5, 4J 1.0 Hz), 8.56 d.d (1H, H^2_{Q} , 3J 4.2, 4J 1.6 Hz). ^{13}C NMR spectrum, δ , ppm: 28.2 (3C, CH_{Ad}), 33.8 (1C, C_{Ad}), 36.9 (3C, $\text{CH}_{2\text{Ad}}$), 40.7 (3C, $\text{CH}_{2\text{Ad}}$), 56.0 (1C, CH_2N), 102.4 (1C, C^7_{Q}), 121.2 (1C, C_{Q}), 121.3 (1C, C_{Q}), 130.0 (1C, C_{Q}), 130.2 (1C, C_{Q}^{4a}), 133.5 (1C, C_{Q}), 142.9 (1C, C_{Q}^{8a}), 145.7 (1C, C^2_{Q}), 147.0 (1C, C^6_{Q}). Mass spectrum: m/z 293.206 [$M + \text{H}$] $^+$. $\text{C}_{20}\text{H}_{25}\text{N}_2$. Calculated ($M + \text{H}$) 293.202.

***N*–[(Adamantan-1-yl)(phenyl)methyl]quinolin-2-amine (XIV).** *a.* A mixture of 0.25 mmol (60 mg) of amine **III**, 0.25 mmol (41 mg) of 2-chloroquinoline, 6 mg (4 mol%) of $\text{Pd}(\text{dba})_2$, 7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h.

b. The same reaction mixture was boiled for 0.5 h to reduce the amount of the side product, 2-*tert*-butoxyquinoline (**XXIX**).

The reaction products were chromatographed (eluent petroleum ether– CH_2Cl_2 , 1:2) to obtain 58 mg (32%) of compound as light-yellow crystalline powder, mp 131–133°C; elution with dichloromethane provided 36% of 2-*tert*-butoxyquinoline (**XXIX**) and also 50% of initial amine **III**.

c. A mixture of the same amounts of amine **III** and 2-chloroquinoline, 12 mg (8 mol%) of $\text{Pd}(\text{dba})_2$, 9 mg (9 mol%) of DavePhos, and 36 mg (1.5 equiv) of sodium *tert*-butylate was boiled for 7 h. According to ^1H NMR spectrum of the reaction mixture the yield of compound **XIV** was 50%; the products were not subjected to chromatography.

d. The reaction was carried out in noncatalytic conditions. A mixture of 0.2 mmol (48 mg) of amine **III**, 0.2 mmol (33 mg) of 2-chloroquinoline, 111 mg (4 equiv) of potassium carbonate, 1 ml of DMF was boiled for 14 h. According to ^1H NMR spectrum of the reaction mixture the yield of compound **XIV** was 11%; the products were not subjected to chromatography. ^1H NMR spectrum, δ , ppm: 1.53–1.62 m (6H, $\text{CH}_{2\text{Ad}}$), 1.65–1.70 m (3H, $\text{CH}_{2\text{Ad}}$), 1.73–1.79 m (3H, $\text{CH}_{2\text{Ad}}$), 2.00 br.s (3H, CH_{Ad}), 4.36 d (1H, CHN, 3J 6.9 Hz), 5.63 d (1H, NH, 3J 6.9 Hz), 6.52 d (1H, H^3_{Q} , 3J 9.0 Hz), 7.14 d.d.d (1H, H, 3J 8.0, 7.0,

4J 1.1 Hz), 7.18–7.23 m (1H, H^4_{Ph}), 7.25–7.31 m (4H, H^2_{Ph} , H^3_{Ph}), 7.47–7.51 m (2H, H^7_{Q} , H^5_{Q}), 7.62 d (1H, H^8_{Q} , 3J 8.0 Hz), 7.70 d (1H, H^4_{Q} , 3J 9.0 Hz). ^{13}C NMR spectrum, δ , ppm: 28.4 (3C, CH_{Ad}), 36.5 (1C, C_{Ad}), 36.8 (3C, $\text{CH}_{2\text{Ad}}$), 39.1 (3C, $\text{CH}_{2\text{Ad}}$), 66.0 (1C, CHN), 109.8 (1C, C^3_{Q}), 121.8 (1C, C_{Q}), 123.4 (1C, C_{Q}^{4a}), 125.8 (1C, C_{Q}), 126.9 (1C, CH_{Ph}), 127.4 (1C, C_{Q}), 127.6 (2C, CH_{Ph}), 128.2 (2C, CH_{Ph}), 129.5 (1C, C_{Q}), 137.5 (1C, C_{Q}^{4f}), 139.8 (1C, C^1_{Ph}), 148.0 (1C, C_{Q}^{8a}), 157.1 (1C, C^2_{Q}). Mass spectrum: m/z 369.225 [$M + \text{H}$] $^+$. $\text{C}_{26}\text{H}_{29}\text{N}_2$. Calculated ($M + \text{H}$) 369.233.

***N*–[(Adamantan-1-yl)(phenyl)methyl]quinolin-4-amine (XV).** A mixture of 0.25 mmol (60 mg) of amine **III**, 0.25 mmol (41 mg) of 4-chloroquinoline, 6 mg (4 mol%) of $\text{Pd}(\text{dba})_2$, 7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. Yield after chromatography (eluent CH_2Cl_2 –MeOH, 25:1) 58 mg (63%), light-brown oily substance. Initial amine **III** (28%) was recovered by chromatography. ^1H NMR spectrum, δ , ppm: 1.55–1.65 m (6H, $\text{CH}_{2\text{Ad}}$), 1.68–1.80 m (6H, $\text{CH}_{2\text{Ad}}$), 2.03 br.s (3H, CH_{Ad}), 4.09 d (1H, CHN, 3J 6.3 Hz), 5.73 d (1H, NH, 3J 6.3 Hz), 6.13 d (1H, H^3_{Q} , 3J 5.3 Hz), 7.21–7.30 m (5H, Ph), 7.48 d.d.d (1H, H^6_{Q} , 3J 8.2, 7.0, 4J 1.0 Hz), 7.62 d.d.d (1H, H^7_{Q} , 3J 8.2, 7.0, 4J 1.1 Hz), 7.86 d (1H, H^5_{Q} , 3J 8.3 Hz), 7.95 d (1H, H^8_{Q} , 3J 8.5 Hz), 8.33 d (1H, H^2_{Q} , 3J 5.3 Hz). ^{13}C NMR spectrum, δ , ppm: 28.3 (3C, CH_{Ad}), 36.5 (1C, C_{Ad}), 36.8 (3C, $\text{CH}_{2\text{Ad}}$), 39.3 (3C, $\text{CH}_{2\text{Ad}}$), 67.0 (1C, CHN), 100.1 (1C, C^3_{Q}), 118.7 (1C, C_{Q}), 119.0 (1C, C_{Q}^{4a}), 124.6 (1C, C_{Q}), 127.3 (1C, C^4_{Ph}), 127.9 (2C, CH_{Ph}), 128.3 (2C, CH_{Ph}), 128.8 (1C, C_{Q}), 130.1 (1C, C_{Q}), 138.3 (1C, C^1_{Ph}), 148.2 (1C, C_{Q}^{8a}), 148.7 (1C, C_{Q}^{4f}), 150.9 (1C, C^2_{Q}). Mass spectrum: m/z 369.230 [$M + \text{H}$] $^+$. $\text{C}_{26}\text{H}_{29}\text{N}_2$. Calculated ($M + \text{H}$) 369.233.

***N*–[(Adamantan-1-yl)(phenyl)methyl]quinoline-6-amine (XVI).** A mixture of 0.25 mmol (60 mg) of amine **III**, 0.25 mmol (41 mg) of 6-chloroquinoline, 6 mg (4 mol%) of $\text{Pd}(\text{dba})_2$, 7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. Yield after chromatography (eluent CH_2Cl_2 –MeOH, 200:1) 77 mg (83%), yellow-green crystalline powder, mp 113–115°C. ^1H NMR spectrum, δ , ppm: 1.49–1.62 m (6H, $\text{CH}_{2\text{Ad}}$), 1.65–1.76 m (6H, $\text{CH}_{2\text{Ad}}$), 2.00 br.s (3H, CH_{Ad}), 4.00 d (1H, CHN, 3J 6.6 Hz), 4.70 d (1H, NH, 3J 6.6 Hz), 6.46 d (1H, H^5_{Q} , 4J 2.4 Hz), 7.11–7.15 m (2H, H^3_{Q} , H^7_{Q}), 7.18–7.23 m (1H, H^4_{Ph}), 7.26–7.33 m (4H, H^2_{Ph} , H^3_{Ph}), 7.71 d (1H, H^4_{Q} , 3J 7.8 Hz), 7.81 d (1H, H^8_{Q} , 3J 9.1 Hz), 8.53 d.d (1H,

H^2_Q , 3J 4.2, 4J 1.5 Hz). ^{13}C NMR spectrum, δ , ppm: 28.3 (3C, CH_{Ad}), 36.4 (1C, C_{Ad}), 36.8 (3C, CH_{2Ad}), 39.1 (3C, CH_{2Ad}), 67.9 (1C, CHN), 103.8 (1C, C^7_Q), 121.0 (1C, C_Q), 121.5 (1C, C_Q), 126.9 (1C, C^4_{Ph}), 127.6 (2C, CH_{Ph}), 128.5 (2C, CH_{Ph}), 129.9 (1C, C_Q), 133.7 (1C, C_Q), 139.5 (1C, C^1_{Ph}), 142.9 (1C, C_Q^{8a}), 145.5 (1C, C^2_Q), 145.8 (1C, C^6_Q), (quaternary atom C_Q^{4a} was not detected). Mass spectrum: m/z 369.238 [$M + H$] $^+$. $C_{26}H_{29}N_2$. Calculated ($M + H$) 369.233.

***N*-[1-(Adamantan-1-yl)propan-2-yl]quinolin-2-amine (XVII).** *a.* A mixture of 0.25 mmol (48 mg) of amine **IV**, 0.25 mmol (41 mg) of 2-chloroquinoline, 6 mg (4 mol%) of $Pd(dba)_2$, 7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. According to 1H NMR spectrum of the reaction mixture the yield of reaction product **XVII** was 24%, of side compound **XXIX**, 27%; the products were not chromatographed.

b. A mixture of the same amounts of the amine and 2-chloroquinoline, 12 mg (8 mol%) of $Pd(dba)_2$, 9 mg (9 mol%) of DavePhos, and 36 mg (1.5 equiv) of sodium *tert*-butylate was boiled for 7 h. Yield after chromatography (eluent CH_2Cl_2 -MeOH, 200:1) 30 mg (38%).

c. The reaction was carried out without catalyst with 0.2 mmol (39 mg) of amine **IV**, 0.2 mmol (33 mg) of 2-chloroquinoline, 111 mg (4 equiv) of potassium carbonate, 1 ml of DMF; the mixture was boiled for 14 h. Yield after chromatography (eluent CH_2Cl_2 -MeOH, 100:1) 24 mg (22%), light-brown oily substance. 1H NMR spectrum, δ , ppm: 1.24 d (3H, CH_3 , 3J 6.5 Hz), 1.29 d.d (1H, CH_2 , 2J 14.5, 3J 4.2 Hz), 1.37 d.d (1H, CH_2 , 2J 14.5, 3J 7.5 Hz), 1.58 br.s (6H, CH_{2Ad}), 1.58–1.68 m (6H, CH_{2Ad}), 1.92 br.s (3H, CH_{Ad}), 4.15–4.28 m (1H, CHN), 4.49 d (1H, NH, 3J 7.0 Hz), 6.59 d (1H, H^3_Q , 3J 8.9 Hz), 7.17 d.d.d (1H, H^6_Q , 3J 8.0, 6.9, 4J 1.1 Hz), 7.50 d.d.d (1H, H^7_Q , 3J 8.3, 6.9, 4J 1.4 Hz), 7.55 d.d (1H, H^5_Q , 3J 8.0, 4J 1.3 Hz), 7.65 d (1H, H^8_Q , 3J 8.3 Hz), 7.79 d (1H, H^4_Q , 3J 8.9 Hz). ^{13}C NMR spectrum, δ , ppm: 23.9 (1C, CH_3), 28.7 (3C, CH_{Ad}), 32.7 (1C, C_{Ad}), 37.0 (3C, CH_{2Ad}), 42.8 (1C, CH_2), 43.0 (3C, CH_{2Ad}), 52.9 (1C, CHN), 111.0 (1C, C^3_Q), 121.6 (1C, C_Q), 123.3 (1C, C_Q^{4a}), 126.1 (1C, C_Q), 127.4 (1C, C_Q), 129.4 (1C, C_Q), 137.2 (1C, C_Q^4), 147.3 (1C, C_Q^{8a}), 156.0 (1C, C^2_Q). Mass spectrum: m/z 321.235 [$M + H$] $^+$. $C_{22}H_{29}N_2$. Calculated ($M + H$) 321.233.

***N*-[1-(Adamantan-1-yl)propan-2-yl]quinolin-4-amine (XVIII).** A mixture of 0.25 mmol (48 mg) of amine **IV**, 0.25 mmol (41 mg) of 4-chloroquinoline, 6 mg (4 mol%) of $Pd(dba)_2$, 7 mg (4.5 mol%) of BINAP, 36 mg

(1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. Yield after chromatography (eluent CH_2Cl_2 -MeOH, 50:1) 73 mg (91%), light-brown oily substance. 1H NMR spectrum, δ , ppm: 1.27 d (3H, CH_3 , 3J 6.4 Hz), 1.39 d.d (1H, CH_2 , 2J 14.7, 3J 3.6 Hz), 1.51–1.60 m (7H, CH_{2Ad} , CH_2), 1.63–1.68 m (6H, CH_{2Ad}), 1.90 br.s (3H, CH_{Ad}), 3.82–3.91 m (1H, CHN), 5.23 d (1H, NH, 3J 7.1 Hz), 6.44 d (1H, H^3_Q , 3J 5.6 Hz), 7.40 d.d.d (1H, H^6_Q , 3J 8.2, 3J 6.9, 4J 1.2 Hz), 7.59 d.d.d (1H, H^7_Q , 3J 8.2, 6.9, 4J 1.3 Hz), 7.79 d (1H, H^5_Q , 3J 8.5 Hz), 7.98 d (1H, H^8_Q , 3J 8.4 Hz), 8.49 d (1H, H^2_Q , 3J 5.6 Hz). ^{13}C NMR spectrum, δ , ppm: 22.4 (1C, CH_3), 28.4 (3C, CH_{Ad}), 32.5 (1C, C_{Ad}), 36.8 (3C, CH_{2Ad}), 42.9 (3C, CH_{2Ad}), 44.2 (1C, CH_2), 52.3 (1C, CHN), 98.2 (1C, C^3_Q), 118.5 (1C, C_Q^{4a}), 119.8 (1C, C_Q), 124.7 (1C, C_Q), 128.5 (1C, C_Q), 129.4 (1C, C_Q), 147.0 (1C, C_Q^{8a}), 149.1 (1C, C_Q^4), 149.5 (1C, C^2_Q). Mass spectrum: m/z 321.228 [$M + H$] $^+$. $C_{22}H_{29}N_2$. Calculated ($M + H$) 321.233.

***N*-[1-(Adamantan-1-yl)propan-2-yl]quinolin-6-amine (XIX).** A mixture of 0.25 mmol (48 mg) of amine **IV**, 0.25 mmol (41 mg) of 6-chloroquinoline, 6 mg (4 mol%) of $Pd(dba)_2$, 7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. Yield after chromatography (eluent CH_2Cl_2 -MeOH, 200:1) 71 mg (88%), yellow-green viscous oily substance, exhibits luminescence on dissolving in organic solvents. 1H NMR spectrum, δ , ppm: 1.21 d (3H, CH_3 , 3J 5.9 Hz), 1.28 d.d (1H, CH_2 , 2J 14.8, 3J 3.7 Hz), 1.35 d.d (1H, CH_2 , 2J 14.8, 3J 6.8 Hz), 1.54–1.57 m (6H, CH_{2Ad}), 1.57–1.68 m (6H, CH_{2Ad}), 1.92 br.s (3H, CH_{Ad}), 3.67–3.76 m (2H, CHN, NH), 6.65 d (1H, H^5_Q , 4J 2.6 Hz), 7.00 d.d (1H, H^7_Q , 3J 9.0, 4J 2.6 Hz), 7.22 d.d (1H, H^3_Q , 3J 8.3, 4.2 Hz), 7.48 d (1H, H^8_Q , 3J 9.0 Hz), 7.88 d.d (1H, H^4_Q , 3J 8.3, 4J 1.5 Hz), 8.57 d.d (1H, H^6_Q , 3J 4.2, 4J 1.6 Hz). ^{13}C NMR spectrum, δ , ppm: 22.8 (1C, CH_3), 28.6 (3C, CH_{Ad}), 32.5 (1C, C_{Ad}), 36.9 (3C, CH_{2Ad}), 43.0 (3C, CH_{2Ad}), 44.2 (1C, CH_2), 52.7 (1C, CHN), 102.5 (1C, C^7_Q), 121.2 (1C, C_Q), 121.6 (1C, C_Q), 130.2 (1C, C_Q), 130.3 (1C, C_Q^{4a}), 133.5 (1C, C_Q), 142.9 (1C, C_Q^{8a}), 145.0 (1C, C^6_Q), 145.6 (1C, C^2_Q). Mass spectrum: m/z 321.231 [$M + H$] $^+$. $C_{22}H_{29}N_2$. Calculated ($M + H$) 321.233.

***N*-[1-(Adamantan-1-yl)propyl]quinolin-4-amine (XXI).** A mixture of 0.25 mmol (48 mg) of amine **V**, 0.25 mmol (41 mg) of 4-chloroquinoline, 12 mg (8 mol%) of $Pd(dba)_2$, 9 mg (9 mol%) of DavePhos, 36 mg (1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. Yield after chromatography

(eluent CH_2Cl_2 -MeOH, 50:1-20:1) 45 mg (56%), light-brown oily substance. ^1H NMR spectrum, δ , ppm: 0.89 t (3H, CH_3 , 3J 7.3 Hz), 1.33 d.d.q (1H, CH_2 , 2J 14.5, 3J 11.0, 7.3 Hz), 1.57-1.72 m (12H, $\text{CH}_{2\text{Ad}}$), 1.90 d.q.d (1H, CH_2 , 2J 14.5, 3J 7.3, 2.7 Hz), 1.96 br.s (3H, CH_{Ad}), 3.18 t.d (1H, CHN, 3J 10.7, 2.4 Hz), 4.76 d (1H, NH, 3J 10.0 Hz), 6.48 d (1H, H^3_{Q} , 3J 5.6 Hz), 7.41 d.d.d (1H, H^6_{Q} , 3J 8.2, 6.9, 4J 1.3 Hz), 7.61 d.d.d (1H, H^7_{Q} , 3J 8.2, 6.9, 4J 1.1 Hz), 7.73 d (1H, H^5_{Q} , 3J 8.4 Hz), 7.96 d (1H, H^8_{Q} , 3J 8.4, 4J 1.3 Hz), 8.47 d (1H, H^2_{Q} , 3J 5.6 Hz). ^{13}C NMR spectrum, δ , ppm: 11.6 (1C, CH_3), 22.6 (1C, CH_2), 28.3 (3C, CH_{Ad}), 37.0 (3C, $\text{CH}_{2\text{Ad}}$), 37.9 (1C, C_{Ad}), 39.0 (3C, $\text{CH}_{2\text{Ad}}$), 63.7 (1C, CHN), 98.8 (1C, C^3_{Q}), 118.3 (1C, C_{Q}^{4a}), 118.8 (1C, C_{Q}), 124.3 (1C, C_{Q}), 128.9 (1C, C_{Q}), 130.0 (1C, C_{Q}), 148.6 (1C, C_{Q}^{8a}), 150.9 (1C, C^2_{Q}), 151.1 (1C, C_{Q}^4). Mass spectrum: m/z 321.239 [$M + \text{H}$] $^+$. $\text{C}_{22}\text{H}_{29}\text{N}_2$. Calculated ($M + \text{H}$) 321.233.

***N*-[1-(Adamantan-1-yl)propyl]quinolin-6-amine (XXII).** A mixture of 0.25 mmol (48 mg) of amine V, 0.25 mmol (41 mg) of 6-chloroquinoline, 12 mg (8 mol%) of $\text{Pd}(\text{dba})_2$, 9 mg (9 mol%) of DavePhos, 36 mg (1.5 equiv) of sodium *tert*-butylate was boiled for 7 h in 2.5 ml of anhydrous dioxane. Yield after chromatography (eluent CH_2Cl_2 -MeOH, 100:1) 54 mg (67%), yellow-green viscous oily substance, exhibits luminescence on dissolving in organic solvents. ^1H NMR spectrum, δ , ppm: 0.91 t (3H, CH_3 , 3J 7.3 Hz), 1.20 d.d.q (1H, CH_2 , 2J 14.6, 3J 11.0, 7.3 Hz), 1.54-1.70 m (12H, $\text{CH}_{2\text{Ad}}$), 1.83 d.q.d (1H, CH_2 , 2J 14.6, 3J 7.3, 2.6 Hz), 1.95 br.s (3H, CH_{Ad}), 2.96 t.d (1H, CHN, 3J 10.5, 2.6 Hz), 3.68 d (1H, NH, 3J 10.0 Hz), 6.67 d (1H, H^5_{Q} , 4J 2.6 Hz), 7.08 d.d (1H, H^7_{Q} , 3J 9.0, 4J 2.6 Hz), 7.19 d.d (1H, H^3_{Q} , 3J 8.3, 4.2 Hz), 7.81 d (1H, H^8_{Q} , 3J 8.9 Hz), 7.83 d (1H, H_{Q}^4 , 3J 8.1 Hz), 8.52 d.d (1H, H^2_{Q} , 3J 4.2, 4J 1.5 Hz). ^{13}C NMR spectrum, δ , ppm: 11.9 (1C, CH_3), 22.9 (1C, CH_2), 28.4 (3C, CH_{Ad}), 37.1 (3C, $\text{CH}_{2\text{Ad}}$), 37.9 (1C, C_{Ad}), 39.1 (3C, $\text{CH}_{2\text{Ad}}$), 64.4 (CHN), 102.2 (1C, C^7_{Q}), 121.1 (1C, C_{Q}), 121.2 (1C, C_{Q}), 130.1 (1C, C_{Q}), 130.3 (1C, C_{Q}^{4a}), 133.3 (1C, C_{Q}), 142.6 (1C, C_{Q}^{8a}), 145.4 (1C, C^2_{Q}), 148.2 (1C, C^6_{Q}). Mass spectrum: m/z 321.232 [$M + \text{H}$] $^+$. $\text{C}_{22}\text{H}_{29}\text{N}_2$. Calculated ($M + \text{H}$) 321.233.

Reaction of amine V with 2-chloroquinoline. The reaction product of amine V and 2-chloroquinoline obtained in the presence of 12 mg (8 mol%) of $\text{Pd}(\text{dba})_2$, 9 mg (9 mol%) of DavePhos, 36 mg (1.5 equiv) of sodium *tert*-butylate after boiling for 7 h in 2.5 ml of dioxane was not isolated in the pure state. In the ^1H NMR spectrum of the reaction mixture a small amount of compound XX

was detected and 50% of 2-*tert*-butoxyquinoline XXIX.

***N*-(Adamantan-1-yl)quinolin-2-amine (XXIII).** *a.* A mixture of 0.25 mmol (38 mg) of amine VI, 0.25 mmol (41 mg) of 2-chloroquinoline, 8.5 mg (6 mol%) of $\text{Pd}(\text{dba})_2$, 10 mg (7 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. According to ^1H NMR spectrum of the reaction mixture the yield of reaction product XXIII was 25%, of side compound XXIX, 70%; the products were not chromatographed.

b. The same amounts of amine and 2-chloroquinoline, 12 mg (8 mol%) of $\text{Pd}(\text{dba})_2$, 9 mg (9 mol%) of DavePhos, and 36 mg (1.5 equiv) of sodium *tert*-butylate were boiled for 7 h. Yield of compound XXIII after chromatography (eluent CH_2Cl_2 -MeOH, 200:1) 17 mg (24%), light-yellow crystalline substance, mp 131-133°C. By elution with CH_2Cl_2 50 mg (33%) of compound XXIX was isolated.

c. The reaction was carried out without catalyst. A mixture of 0.2 mmol (30 mg) of amine VI and 0.2 mmol (33 mg) of 2-chloroquinoline, 111 mg (4 equiv) of potassium carbonate, 1 ml DMF was boiled for 14 h. According to ^1H NMR spectrum of the reaction mixture the yield of reaction product XXIII was 22%, the products were not chromatographed. ^1H NMR spectrum, δ , ppm: 1.74 br.s (6H, $\text{CH}_{2\text{Ad}}$), 2.14 br.s (3H, CH_{Ad}), 2.18 br.s (6H, $\text{CH}_{2\text{Ad}}$), 4.57 br.s (1H, NH), 6.62 d (1H, H^3_{Q} , 3J 9.0 Hz), 7.16 t (1H, H^6_{Q} , 3J 7.4 Hz), 7.48 t (1H, H^7_{Q} , 3J 7.6 Hz), 7.53 d (1H, H^5_{Q} , 3J 8.0 Hz), 7.63 d (1H, H^8_{Q} , 3J 8.3 Hz), 7.73 d (1H, H_{Q}^4 , 3J 8.8 Hz). ^{13}C NMR spectrum, δ , ppm: 29.7 (3C, CH_{Ad}), 36.6 (3C, $\text{CH}_{2\text{Ad}}$), 42.4 (3C, $\text{CH}_{2\text{Ad}}$), 52.0 (1C, C_{Ad}), 113.0 (1C, C^3_{Q}), 121.7 (1C, C_{Q}), 122.9 (1C, C_{Q}^{4a}), 126.3 (1C, C_{Q}), 127.2 (1C, C_{Q}), 129.2 (1C, C_{Q}), 136.5 (1C, C_{Q}), 148.0 (1C, C_{Q}^{8a}), 156.4 (1C, C^2_{Q}). Mass spectrum: m/z 279.180 [$M + \text{H}$] $^+$. $\text{C}_{19}\text{H}_{23}\text{N}_2$. Calculated ($M + \text{H}$) 279.186.

***N*-(Adamantan-1-yl)quinolin-4-amine (XXIV).** *a.* A mixture of 0.25 mmol (38 mg) of amine VI, 0.25 mmol (41 mg) of 4-chloroquinoline, 8.5 mg (6 mol%) of $\text{Pd}(\text{dba})_2$, 10 mg (7 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. Yield after chromatography (eluent CH_2Cl_2 -MeOH, 25:1) 21 mg (30%).

b. A mixture of the same quantities of the amine and 4-chloroquinoline, 12 mg (8 mol%) of $\text{Pd}(\text{dba})_2$, 9 mg (9 mol%) of DavePhos, and 36 mg (1.5 equiv) of sodium *tert*-butylate was boiled for 7 h. Yield after chromatography (eluent CH_2Cl_2 -MeOH, 25:1) 14 mg (20%), yellow-

brown crystalline powder, mp 134–136°C. ¹H NMR spectrum, δ, ppm: 1.75 br.s (6H, CH_{2Ad}), 2.12 br.s (6H, CH_{2Ad}), 2.20 br.s (3H, CH_{Ad}), 5.02 br.s (1H, NH), 6.75 d (1H, H³_Q, ³J 5.6 Hz), 7.40 t (1H, H⁶_Q, ³J 7.6 Hz), 7.59 t (1H, H⁷_Q, ³J 7.6 Hz), 7.70 d (1H, H⁵_Q, ³J 8.5 Hz), 7.96 d (1H, H⁸_Q, ³J 8.2 Hz), 8.45 d (1H, H²_Q, ³J 5.5 Hz). ¹³C NMR spectrum, δ, ppm: 29.5 (3C, CH_{Ad}), 36.3 (3C, CH_{2Ad}), 41.9 (3C, CH_{2Ad}), 52.6 (1C, C_{Ad}), 101.6 (1C, C³_Q), 119.2 (1C, C_Q), 124.7 (1C, C_Q), 129.2 (1C, C_Q), 129.3 (1C, C_Q), 147.6 (1C, C_Q^{8a}), 148.2 (1C, C_Q⁴), 149.2 (1C, C_Q²), the quaternary atom C^{4a} was not detected. Mass spectrum: *m/z* 279.184 [*M* + H]⁺. C₁₉H₂₃N₂. Calculated (*M* + H) 279.186.

***N*-(Adamantan-1-yl)quinolin-6-amine (XXV).** *a.* A mixture of 0.25 mmol (38 mg) of amine VI, 0.25 mmol (41 mg) of 6-chloroquinoline, 8.5 mg (6 mol%) of Pd(dba)₂, 10 mg (7 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. According to ¹H NMR spectrum of the reaction mixture the yield of reaction product was 25%, the conversion of 6-chloroquinoline was incomplete.

b. The same quantities of the amine and 2-chloroquinoline, 12 mg (8 mol%) of Pd(dba)₂, 9 mg (9 mol%) of DavePhos, and 36 mg (1.5 equiv) of sodium *tert*-butylate were boiled for 7 h. Yield after chromatography (eluent CH₂Cl₂–MeOH, 100:1) 57 mg (82%), yellow oily substance, exhibits luminescence on dissolving in organic solvents. ¹H NMR spectrum, δ, ppm: 1.69 br.s (6H, CH_{2Ad}), 1.97 br.s (6H, CH_{2Ad}), 2.12 br.s (3H, CH_{Ad}), 3.72 br.s (1H, NH), 6.95 d (1H, H⁵_Q, ⁴J 2.5 Hz), 7.10 d.d (1H, H⁷_Q, ³J 9.1, ⁴J 2.5 Hz), 7.22 d.d (1H, H³_Q, ³J 8.2, ⁴J 2 Hz), 7.82 d (1H, H⁸_Q, ³J 9.1 Hz), 7.88 d (1H, H_Q⁴, ³J 7.8 Hz), 8.59 d.d (1H, H²_Q, ³J 4.2, ⁴J 1.5 Hz). ¹³C NMR spectrum, δ, ppm: 29.6 (3C, CH_{Ad}), 36.4 (3C, CH_{2Ad}), 42.9 (3C, CH_{2Ad}), 52.2 (1C, C_{Ad}), 108.4 (1C, C⁷_Q), 121.1 (1C, C_Q), 124.5 (1C, C_Q), 129.6 (1C, C_Q^{4a}), 129.8 (1C, C_Q), 133.8 (1C, C_Q), 143.2 (1C, C_Q^{8a}), 144.2 (1C, C_Q⁶), 146.4 (C_Q²). Mass spectrum: *m/z* 279.191 [*M* + H]⁺. C₁₉H₂₃N₂. Calculated (*M* + H) 279.186.

***N*-(Adamantan-2-yl)quinolin-2-amine (XXVI).** *a.* A mixture of 0.25 mmol (38 mg) of amine VII, 0.25 mmol (41 mg) of 2-chloroquinoline, 6 mg (4 mol%) of Pd(dba)₂, 7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. Yield after chromatography (eluent CH₂Cl–MeOH, 200:1) 34 mg (49%), light-yellow crystalline substance, mp 115–117°C.

b. A mixture of the same amounts of the amine and

2-chloroquinoline, 12 mg (8 mol%) of Pd(dba)₂, 14 mg (9 mol%) of BINAP, and 36 mg (1.5 equiv) of sodium *tert*-butylate was boiled for 7 h. Yield after chromatography (eluent CH₂Cl₂–MeOH, 100:1) 36 mg (52%).

c. The reaction was carried out without catalyst. A mixture of 0.2 mmol (30 mg) of amine VIII and 0.2 mmol (33 mg) of 2-chloroquinoline, 111 mg (4 equiv) of potassium carbonate, 1 ml of DMF was boiled for 14 h. According to ¹H NMR spectrum of the reaction mixture the yield of reaction product was 15%; the product was not subjected to chromatography. ¹H NMR spectrum, δ, ppm: 1.60–1.66 m (2H, CH_{2Ad}), 1.77 br.s (2H, CH_{Ad}), 1.84–2.00 m (8H, CH_{2Ad}), 2.09 br.s (2H, CH_{Ad}), 4.05 d (1H, CHN, ³J 7.4 Hz), 5.19 d (1H, NH, ³J 6.6 Hz), 6.65 d (1H, H³_Q, ³J 9.0 Hz), 7.17 t (1H, H⁶_Q, ³J 7.4 Hz), 7.50 d.d.d (1H, H⁷_Q, ³J 8.3, 7.1, ⁴J 1.3 Hz), 7.56 d (1H, H⁵_Q, ³J 8.1 Hz), 7.63 d (1H, H⁸_Q, ³J 8.3 Hz), 7.81 d (1H, H_Q⁴, ³J 9.0 Hz). ¹³C NMR spectrum, δ, ppm: 27.2 (1C, C_{Ad}), 27.3 (1C, C_{Ad}), 31.7 (2C, C_{Ad}), 32.0 (2C, C_{Ad}), 37.3 (2C, C_{Ad}), 37.7 (1C, C_{Ad}), 56.2 (1C, CHN), 110.6 (1C, C_Q), 121.7 (1C, C_Q), 123.3 (1C, C_Q^{4a}), 125.9 (1C, C_Q), 127.4 (1C, C_Q), 129.5 (1C, C_Q), 137.4 (1C, C_Q⁴), 148.3 (1C, C_Q^{8a}), 156.4 (1C, C_Q²). Mass spectrum: *m/z* 279.184 [*M* + H]⁺. C₁₉H₂₃N₂. Calculated (*M* + H) 279.186.

***N*-(Adamantane-2-yl)quinoline-4-amine (XXVII).** A mixture of 0.25 mmol (38 mg) of amine VII, 0.25 mmol (41 mg) of 4-chloroquinoline, 6 mg (4 mol%) of Pd(dba)₂, 7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. Yield after chromatography (eluent CH₂Cl₂–MeOH, 10:1) 62 mg (89%), light-brown crystalline powder, mp 143–145°C. ¹H NMR spectrum, δ, ppm: 1.66–1.73 m (2H, CH_{2Ad}), 1.79 br.s (2H, CH_{Ad}), 1.85–1.97 m (8H, CH_{2Ad}), 2.08 br.s (2H, CH_{Ad}), 3.75–3.79 m (1H, CHN), 5.32 d (1H, NH, ³J 6.6 Hz), 6.39 d (1H, H³_Q, ³J 5.5 Hz), 7.41 d.d.d (1H, H⁶_Q, ³J 8.3, 6.9, ⁴J 1.3 Hz), 7.60 d.d.d (1H, H⁷_Q, ³J 8.3, 6.9, ⁴J 1.3 Hz), 7.75 d.d (1H, H⁵_Q, ³J 8.3, ⁴J 1.1 Hz), 7.96 d.d (1H, H_Q⁸, ³J 8.4, ⁴J 1.2 Hz), 8.51 d (1H, H²_Q, ³J 5.5 Hz). ¹³C NMR spectrum, δ, ppm: 27.0 (1C, C_{Ad}), 27.1 (1C, C_{Ad}), 31.1 (2C, C_{Ad}), 31.8 (2C, C_{Ad}), 37.0 (2C, C_{Ad}), 37.3 (1C, C_{Ad}), 56.3 (1C, CHN), 98.9 (1C, C³_Q), 118.6 (1C, C_Q^{4a}), 119.1 (1C, C_Q), 124.7 (1C, C_Q), 129.1 (1C, C_Q), 129.3 (1C, C_Q), 147.5 (1C, C_Q^{8a}), 148.9 (1C, C_Q⁴), 150.0 (1C, C_Q²). Mass spectrum: *m/z* 279.182 [*M* + H]⁺. C₁₉H₂₃N₂. Calculated (*M* + H) 279.186.

***N*-(Adamantan-2-yl)quinolin-6-amine (XXVIII).** *a.* A mixture of 0.25 mmol (38 mg) of amine VII, 0.25 mmol (41 mg) of 6-chloroquinoline, 6 mg (4 mol%) of Pd(dba)₂,

7 mg (4.5 mol%) of BINAP, 36 mg (1.5 equiv) of sodium *tert*-butylate, 2.5 ml of anhydrous dioxane was boiled for 7 h. According to ^1H NMR spectrum of the reaction mixture the yield of reaction product was 55%, the conversion of the initial 6-chloroquinoline was 60%; the product was not subjected to chromatography.

b. A mixture of the same quantities of the amine and 6-chloroquinoline, 12 mg (8 mol%) of $\text{Pd}(\text{dba})_2$, 14 mg (9 mol%) of BINAP, and 36 mg (1.5 equiv) of sodium *tert*-butylate was boiled for 7 h. Yield after chromatography (eluent CH_2Cl_2 -MeOH, 200:1) 39 mg (56%), light-green crystalline powder, mp 128–130°C, the substance exhibits luminescence on dissolving in organic solvents. ^1H NMR spectrum, δ , ppm: 1.57–1.64 m (2H, $\text{CH}_{2\text{Ad}}$), 1.75 br.s (2H, CH_{Ad}), 1.83–1.96 m (8H, $\text{CH}_{2\text{Ad}}$), 2.09 br.s (2H, CH_{Ad}), 3.64 br.s (1H, CHN), 4.30 br.s (1H, NH), 6.63 d (1H, H^5_{Q} , 4J 2.6 Hz), 7.08 d.d (1H, H^7_{Q} , 3J 9.1, 4J 2.6 Hz), 7.20 d.d (1H, H^3_{Q} , 3J 8.3, 4.2 Hz), 7.84 d (1H, H^8_{Q} , 3J 9.0 Hz), 7.85 d (1H, H^4_{Q} , 3J 8.2 Hz), 8.56 d.d (1H, H^2_{Q} , 3J 4.2, 4J 1.5 Hz). ^{13}C NMR spectrum, δ , ppm: 27.2 (1C, C_{Ad}), 27.3 (1C, C_{Ad}), 31.3 (2C, C_{Ad}), 31.6 (2C, C_{Ad}), 37.2 (2C, C_{Ad}), 37.5 (1C, C_{Ad}), 56.8 (1C, CHN), 102.9 (1C, C^7_{Q}), 121.2 (1C, C_{Q}), 121.5 (1C, C_{Q}), 130.2 (2C, C_{Q} , C_{Q}^{4a}), 133.4 (1C, C_{Q}), 142.8 (1C, $\text{C}_{\text{Q}}^{\delta a}$), 145.1 (1C, C^6_{Q}), 145.7 (1C, C^2_{Q}). Mass spectrum: m/z 279.193 [$M + \text{H}$] $^+$. $\text{C}_{19}\text{H}_{23}\text{N}_2$. Calculated ($M + \text{H}$) 279.186.

ACKNOWLEDGMENTS

The study was carried out under the financial support of the Russian Academy of Sciences (program P-8 “Development of the methods of organic synthesis and creation of compounds with valuable applied properties”) and the Russian Foundation for Basic Research (grant no. 10-03-01108).

REFERENCES

- Averin, A.D., Ulanovskaya, M.A., Buryak, A.K., Savel'ev, E.N., Orlinson, B.S., Novakov, I.A., and Beletskaya, I.P., *Zh. Org. Khim.*, 2011, vol. 47, p. 35.
- Bagrii, E.I., *Adamantany: poluchenie, svoistva, primenenie* (Adamantanes: Synthesis, Properties, Application), Moscow: Nauka, 1989.
- Kamyranov, I.M., Polis, Ya. Yu. and Kupisk, A.G., *Midantan i ego primenenie v terapii i profilaktike neirolepticheskogo sindroma* (Amantadine and Its Application in Treatment and Prevention of Neuroleptic Syndrome), Riga: Zinatne, 1973.
- Gilligan, B.S., Veale, J., and Wodak, J., *Med. J. Austral.*, 1970, vol. 2, p. 634.
- Dolin, R. and Bentley, D.W., *Options Contr. Influenza. Proc. Viratek-Ucla, Symp., Keystone. Apr., 20–25, 1985*, New York: 1986.
- Svenson, T.N., *Eur. J. Pharm.*, 1973, vol. 34, p. 232.
- Klimova, N.V., Zaitseva, N.M., Avdyunina, N.I., Pyatin, B.M., Morozov, I.S., Bykov, N.P., and Kuz'min, V.I., *Khim.-Farm. Zh.*, 1990, p. 26.
- Morozov, I.S., Petrov, V.I., and Sergeeva, S.A., *Farmakologiya adamantanov* (Pharmacology of Adamantanes), Volgograd: Izd. Volgograd. Med. Akad., 2001.
- Avdyunina, N.I., Morozov, I.S., Bol'shakova, R.F., Militareva, N.A., Klimova, N.A., Pyatin, B.M., Khranilov, A.A., and Dvalishvili, E.G., *Khim.-Farm. Zh.*, 1988, 819.
- Da Settimo, A., Marini, A.M., Primofiore, G., and da Settimo, F., *Farmacology*, 1995, vol. 50, p. 321.
- Ficarra, R., Ficarra, P., Tommasini, A., Fenech, G., Pizzementi, F.C., and Bisignano, G., *Bull. Chim. Farm.*, 1984, vol. 123, p. 317.
- Ismail, F.M.D., Dascombe, M.I., Carrand, P., and North, S.E., *J. Pharm. Pharmacol.*, 1996, vol. 48, p. 841.
- Gerzon, K., US Patent 3730956, 1971; *Chem. Abstr.*, 1973, vol. 79, P18597r.
- Aranyi, P., Bata, I., Batory, S., Boronkay, E., Bovy, P., Kapui, Z., Edit, S., Szabo, T., Urban-Szabo, K., and Varga, M., WO Patent WO2005021536, 2003; *Chem. Abstr.*, 2005, vol. 142, 298122.
- Abdulqader, A., Alhaider, M., Abdelkader, A., and Lien, E.J., *J. Med. Chem.*, 1985, vol. 28, p. 1394.
- Asagarasu, A., Matsui, T., Hayashi, H., Tamaoki, S., Yamachi, Y., Minato, K., and Sato, M., *J. Med. Chem.*, 2010, vol. 53, p. 7549.
- Nasr, M., Drach, J., Smith, S., Shipman, C. Jr., and Burckhalter, J.H., *J. Med. Chem.*, 1988, vol. 31, p. 1347.
- Beauchard, A., Jaunet, A., Murillo, L., Baldeyrou, B., Lansiaux, A., Cherrouvri, J., Domona, L., Picot, L., Bailly, C., Besson, T., and Thierry, V., *Eur. J. Med. Chem.*, 2009, vol. 44, p. 3858.
- Sayed, I., van der Veken, P., Steert, K., Dhooghe, L., Hostyn, S., V. Baelen, G., Lemiere, G., Bert, U., Maes, W., Cos, P., Maes, L., Joossens, J., Haemers, A., Pieters, L., and Augustyns, K., *J. Med. Chem.*, 2009, vol. 52, p. 2979.
- Deraeve, C., Maraval, A., Vendier, L., Faugoux, V., Pitié, M., and Meunier, B., *Eur. J. Inorg. Chem.*, 2008, p. 5622.
- Lundgren, R.J., Sapping-Kumankumah, A., and Stradiotto, M., *Chem. Eur. J.*, 2010, vol. 16, p. 1983.

22. Michalik, D., Kumar, K., Zapf, A., Tillack, A., Arlt, M., Heinrich, T., and Beller, M., *Tetrahedron Lett.*, 2004, vol. 45, p. 2057.
23. Knight, R., Allen, D., Birch, H., Chapman, G., Galvin, F., Jopling, L., Lock, C., Meissner, W. G.J., Owen, D., Raphy, G., Watson, R.J., and Williams, S., *Bioorg. Med. Chem. Lett.*, 2008, p. 629.
24. Rataboul, F., Zapf, A., Jackstell, R., Harkal, S., Riermeier, T., Monsees, A., Dingerdissen, U., and Beller, M., *Chem. Eur. J.*, 2004, vol. 10, p. 2983.
25. Toma, G., Fujita, K., and Yamaguchi, R., *Eur. J. Org. Chem.*, 2009, p. 4586.
26. Manolikakes, G., Gavryushin, A., and Knochel, P., *J. Org. Chem.*, 2008, vol. 73, p. 1429.
27. Musonda, C.C., Whitlock, G.A., Witty, M. J., Brun, R., and Kaiser, M., *Bioorg. Med. Chem. Lett.*, 2009, p. 481.
28. Sanchez-Martin, R., Campos, M.J., Conejo-Garcia, A., Cruz-Lopez, O., Banez-Coronel, M., Rodriguez-Gonzalez, A., Gallo, A.M., Lacal, C.J., and Espinosa, A., *J. Med. Chem.*, 2005, vol. 48, p. 3354.
29. Pinard, E., Alanine, A., Bourson, A., Buttelmann, B., Heitz, M.-P., Mutel, V., Gill, R., Trube, T., and Pharma, R., *Bioorg. Med. Chem. Lett.*, 2002, p. 2615.
30. Ghosh, B., Antonio, T., Reith, E.A.M., and Dutta, K.A., *J. Med. Chem.*, 2010, vol. 53, p. 2114.
31. Girault, S., Grellier, P., Berecibar, A., Maes, L., Lemiere, P., Mouray, E., Davioud-Charvet, E., and Sergheraert, C., *J. Med. Chem.*, 2001, vol. 44, p. 1658.
32. Abeywickrama, S., Rotenberg, A.S., and Baker, A.D., *Bioorg. Med. Chem. Lett.*, 2006, p. 7796.
33. Wolf, C. and Lerebours, R., *J. Org. Chem.*, 2003, vol. 68, p. 7077.
34. Scott, D.A., Bell, J.K., Campbell, T.C., Cook, J.D., Dakin, A.L., Valle, J.D., Drew, L., Gero, W.T., Hattersley, M.M., Omer, C.A., Tyurin, B., and Zheng, X., *Bioorg. Med. Chem. Lett.*, 2009, p. 701.
35. Zhu, C., Hansen, R.A., Bateman, T., Chen, Z., Holt, G.T., Hubert, A.J., Karanam, V.B., Lee, J.S., Pan, J., Su, Qian, Reddy, B.G.V., Reitman, L.M., Strack, M.A., Tong, V., Weingarth, T.D., Wolff, M.S., McNeil, J.D., Weber, E.A., Duffy, L.J., and Edmondson, D.S., *Bioorg. Med. Chem. Lett.*, 2008, p. 4393.
36. Beletskaya, I.P., Tsvetkov, A.V., Tsvetkov, P.V., Latyshev, G.V., and Lukashov, N.V., *Izv. Akad. Nauk, Ser. Khim.*, 2005, vol. 54, p. 210.
37. Smith, A.J., Jones, K.R., Booker, W.G., and Pyke, M.S., *J. Org. Chem.*, 2008, vol. 73, p. 8880.
38. Anderson, W.K., Tundel, E.R., Ikawa, T., Altman, A.R., and Buchwald, S.L., *Angew. Chem., Int. Ed.*, 2006, vol. 45, p. 6523.
39. Averin, A.D., Ulanovskaya, M.A., Kovalev, V.V., Buryak, A.K., Orlinson, B.S., Novakov, I.A., and Beletskaya, I.P., *Zh. Org. Khim.*, 2010, vol. 46, p. 64.
40. Averin, A.D., Ulanovskaya, M.A., Buryak, A.K., Savel'ev, E.N., Orlinson, B.S., Novakov, I.A., and Beletskaya, I.P., *Zh. Org. Khim.*, 2010, vol. 46, p. 1779.
41. Averin, A.D., Ranyuk, E.R., Golub, S.L., Buryak, A.K., Savelyev, E.N., Orlinson, B.S., Novakov, I.A., Beletskaya, I.P., *Synthesis*, 2007, p. 2215.
42. Ranyuk, E.R., Averin, A.D., Buryak, A.K., Savel'ev, E.N., Orlinson, B.S., Novakov, I.A., and Beletskaya, I.P., *Zh. Org. Khim.*, 2009, vol. 45, p. 1569.
43. Averin, A.D., Ranyuk, E.R., Buryak, A.K., Savelyev, E.N., Orlinson, B.S., Novakov, I.A., and Beletskaya, I.P., *Mendeleeev Commun.*, 2009, vol. 19, p. 136.
44. Gopalan, B., Thomas, A., and Shah, D.M., PCT Int. Appl. WO 2006090244, 2006; *Chem. Abstr.*, 2006, vol. 145, 292604.
45. Novakov, I.A., Kulev, I.A., Radchenko, S.S., Birznieks, K.A., Boreko, E.I., Vladyko, G.V., and Korobchenko, L.V., *Pharm. Chem. J.*, 1987, vol. 21, p. 454.
46. Jirgensons, A., Kaus, V., Kalvinsh, I., and Gold, M., *Synthesis*, 2000, 1709.
47. Lavrova, L.N., Klimova, N.V., Shmar'yan, M.I., Ul'yanova, O.V., Vikhlyaev, Yu.I., and Skoldinov, A.P., *Zh. Org. Khim.*, 1974, vol. 10, p. 761.
48. Ukai, T., Kawazura, H., Ishii, Y., Bonnet, J.J., and Ibers, J.A., *J. Organometal. Chem.*, 1974, vol. 65, p. 253.