ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 12, pp. 1495–1508. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © O.K. Grigorova, A.D. Averin, A.S. Abel, O.A. Maloshitskaya, G.M. Butov, E.N. Savelyev, B.S. Orlinson, I.A. Novakov, I.P. Beletskaya, 2012, published in Zhurnal Organicheskoi Khimii, 2012, Vol. 48, No. 12, pp. 1525–1537.

Arylation of Adamantanamines: V.* Palladium-Catalyzed Amination of Isomeric Chloroquinolines with Diamines of the Adamantane Series

O. K. Grigorova[a], A. D. Averin[a], A. S. Abel[a], O. A. Maloshitskaya[a], G. M. Butov[b], E. N. Savelyev[c], B. S. Orlinson[c], I. A. Novakov[c], and I. P. Beletskaya[a]

[a] *Faculty of Chemistry, Moscow State University, Leninskie gory 1–3, Moscow, 119991 Russia*
e-mail: averin@org.chem.msu.ru

[b] *Volzhsky Polytechnical Institute, ul. Engel'sa 42a, Volzhsky, Volgograd oblast, 404121 Russia*

[c] *Volgograd State Technical University, pr. Lenina 28, Volgograd, 400005 Russia*

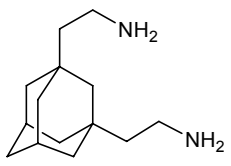
Received February 22, 2012

Abstract—Palladium-catalyzed arylation of diamines of the adamantane series with isomeric 2-, 4-, and 6-chloroquinoline was studied, and optimal conditions for the synthesis of the corresponding *N*,*N*′-diaryl derivatives were found. *N*,*N*-Diarylation products of primary amino groups in the diamines bearing 2-aminoethyl and 4-aminophenyl substituents were readily formed.

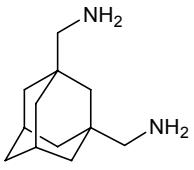
DOI: 10.1134/S1070428012120019

Diamines of the adamantane series, especially 2,2′-(adamantane-1,3-diyl)diethanamine (**I**), have found diverse applications. Compound **I** is incorporated into various polymers to enhance their heat resistance, hydrolytic stability [2], and mechanical strength [3], as well as to improve optical properties of epoxy resins [4]. Antiviral activity of 2,2′-(adamantane-1,3-diyl)diethanamine (**I**) and (adamantane-1,3-diyl)dimethanamine (**II**) was studied [5–7]. We previously described [8, 9] the use of 2,2′-(adamantane-1,3-diyl)-diethanamine (**I**) in the synthesis of nitrogen-containing macroheterocycles, and a detailed study on palladium-catalyzed arylation of adamantanediamines with isomeric bromochloro- and dibromobenzenes was performed [10]. In the preceding communication [1] we reported on the amination of isomeric chloroquinolines with amines of the adamantane series. In continuation of these studies, the present article reports on the palladium-catalyzed reactions of 2-, 4-, and 6-chloroquinolines with diamines **I**–**III** with different reactivities of the amino groups. Interest in such compounds is related to their potential physiological activity. For instance, *N*,*N*′-bis(pyridin-2-yl)-2,2′-(adamantane-1,3-diyl)diethanamine synthesized by us previously [11] showed psychotropic activity in mice.

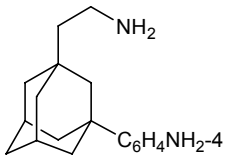
Initially, we examined the reaction of diamine **I** with 2 equiv of 2-chloroquinoline in the presence of a conventional (standard) catalytic system, $Pd(dba)_2$–BINAP (4 mol %), on heating in boiling dioxane (c = 0.1 mol/l) containing an equimolar amount of sodium *tert*-butoxide as a base to avoid noncatalytic formation of 2-*tert*-butoxyquinoline (Scheme 1). The reaction proceeded in a complicated manner, due primarily to extensive *N*,*N*-diarylation whose contribution was even larger than in the arylation of least sterically hindered adamantane monoamines [10]. Moreover, unlike monoamines, it was impossible to estimate the yield of one or another product in the reaction mixture with



I



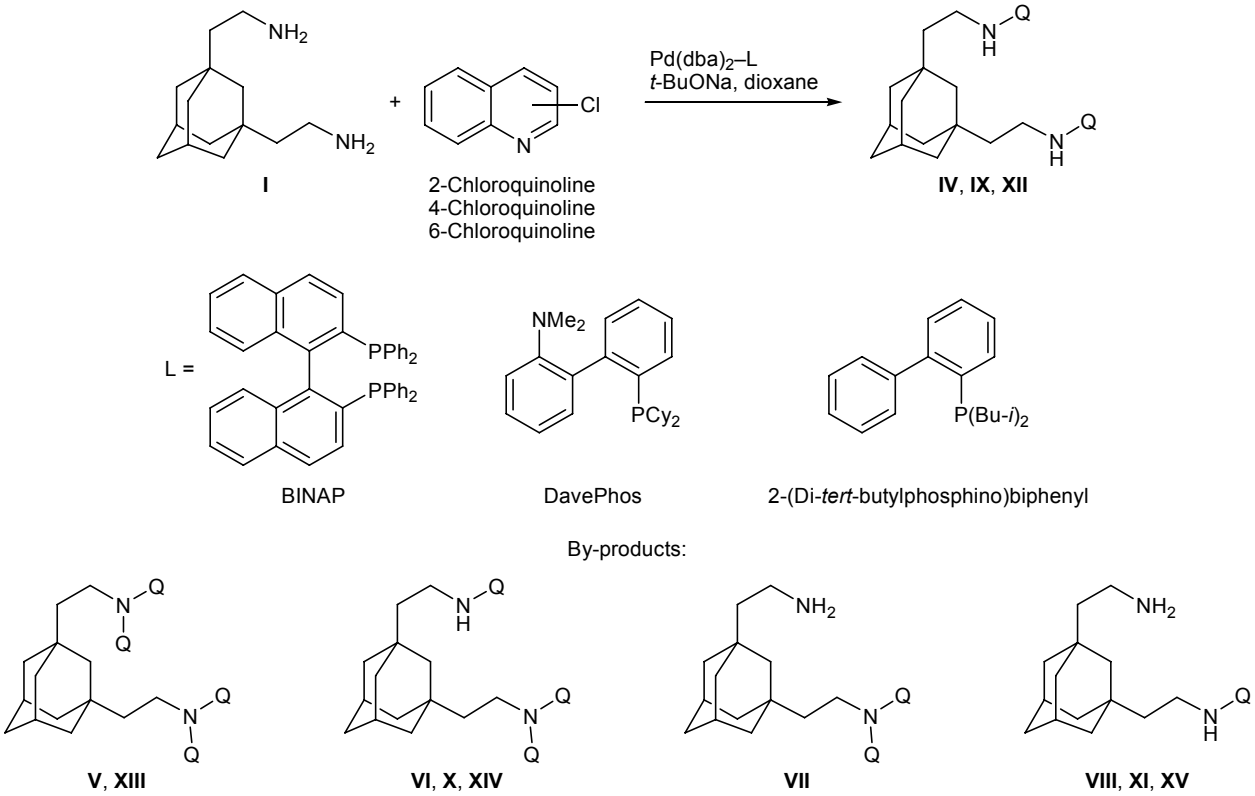
II



III

* For communication IV, see [1].

Scheme 1.



IV–**VIII**, Q = quinolin-2-yl; **IX**–**XI**, R = quinolin-4-yl; **XII**–**XV**, R = quinolin-6-yl.

diamines having two equivalent amino groups. This may be done only after complete chromatographic separation. The yield of target compound **IV** in the presence of the above catalytic system did not exceed 13%, while 8% of triaryl derivative **VI** and 33% of monoarylation product **VIII** were also obtained (Table 1, run no. 1). It is obvious that the *N*,*N*′-diarylation process was incomplete.

Replacement of BINAP as ligand by DavePhos and the use of 1.5 equiv of base per amino group (run no. 2) allowed us to raise the yield of **IV** to 26%; however, the amount of *N*,*N*-diarylation products also increased. In particular, we isolated *N*,*N*,*N*′,*N*′-tetraaryl derivative **V** and *N*,*N*-diaryl derivative **VII**. Therefore, another experiment (run no. 3) was performed again with 1 equiv of *t*-BuONa, and the yield of **IV** slightly increased (32%). The reactions with a larger amount of the ligand (8 mol % of BINAP and DavePhos) were even less selective, and the products were not separated. Good results were obtained when the donor DavePhos ligand was replaced by 2-(di-*tert*-butylphosphino)biphenyl which contains a sterically hindered phosphorus atom (run no. 4). In this case, target compound **IV** was isolated in 69% yield at the expense of the *N*,*N*-diaryl derivatives. Noncatalytic reaction with diamine **I** was also possible. The yield of **IV** in DMF (run no. 5) was 15%, and in boiling DMSO (run no. 6), 29%; these results are quite comparable with those obtained in the catalytic processes.

The reactions of diamine **I** with 4- and 6-chloroquinolines were more selective, though the main difficulty was also formation of tri- and tetraarylation products, which considerably reduced the yield of the target *N*,*N*′-diarylamines. In the reaction of **I** with 2 equiv of 4-chloroquinoline in the presence of standard catalytic system and 1.5 equiv of *t*-BuONa per amino group (run no. 7) we isolated 57% of **IX** and 33% of triaryl derivative **X**. This fact is quite interesting, for *N*,*N*-diarylation with 4-chloroquinoline has not been observed previously. An attempt to improve the yield of **IX** via reduction of the amount of the base (to suppress *N*,*N*-diarylation) resulted in sharp decrease of the yield of **IX** and formation of an appreciable amount of monoaryl derivative **XI** (run no. 8). Likewise, the use of 16 mol % of $Pd(dba)_2$/BINAP or 8 mol % of $Pd(dba)_2$/DavePhos was unsuccessful.

A different pattern was observed in analogous reaction of diamine **I** with 6-chloroquinoline. The reac-

tion in the presence of 1.5 equiv of *t*-BuONa afforded 16% of **XII** and 49% of triaryl derivative **XIV** (run no. 9), whereas the use of an equimolar amount of the base ensured a good yield of **XII** (52%), the only other product being monoaryl derivative **XV** (run no. 10). Replacement of BINAP by DavePhos resulted in sharp decrease of the yield of **XII** and formation of large amounts of polyaryl derivatives **XIII** and **XIV** (run no. 11), which is consistent with specific features of the arylation of **I** with 2-chloroquinoline.

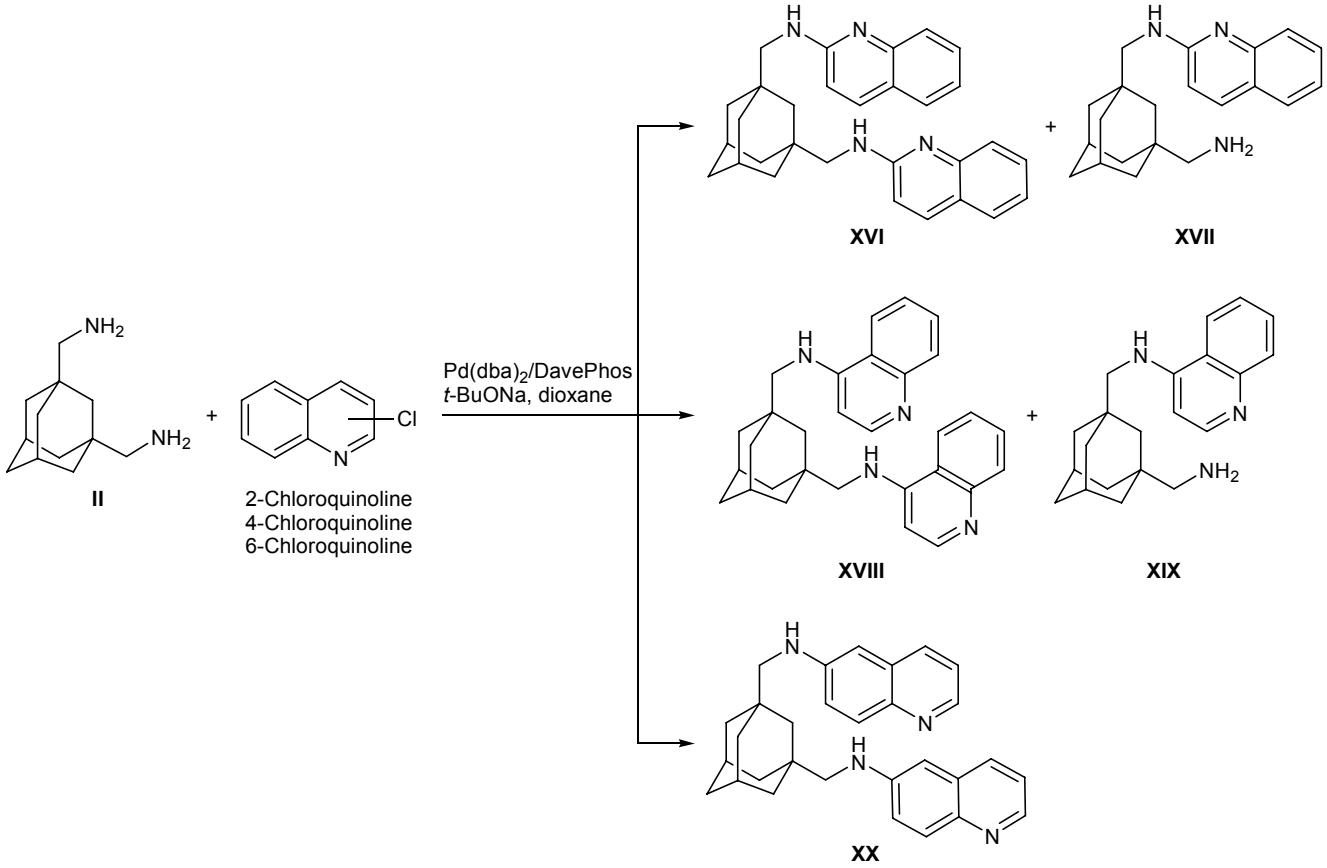
Chloroquinolines reacted with (adamantane-1,3-diyl)dimethanamine (**II**) in a more selective fashion (Scheme 2). Taking into account numerous examples of successful arylation of diamine **II** only in the presence of $Pd(dba)_2$–DavePhos (8 mol %), just the same catalytic conditions were applied. The reactions with

Table 1. Arylation of 2,2′-(adamantane-1,3-diyl)diethanamine (**I**) with chloroquinolines

Run no.	Chloroquinoline	Ligand L	$Pd(dba)_2$–L, mol %	Product	Yield, %
1[a]	2-Chloroquinoline	BINAP	4/4.5	**IV**	13
				VI	8
				VIII	33
2[b]	2-Chloroquinoline	DavePhos	8/9	**IV**	26
				VI	38
				VII	11
				VIII	23
3[a]	2-Chloroquinoline	DavePhos	4/4.5	**IV**	32
				V	8
				VII	11
				VII	21
				VIII	24
4[b]	2-Chloroquinoline	2-(Di-*tert*-butylphosphino)biphenyl	4/4.5	**IV**	69
				VI	27
5[c]	2-Chloroquinoline	–	–	**IV**	15
				VIII	20
6[d]	2-Chloroquinoline	–	–	**IV**	29
				VIII	11
7	4-Chloroquinoline	BINAP	8/9	**IX**	57
				X	33
				XI	9
8[a]	4-Chloroquinoline	BINAP	8/9	**IX**	24
				XI	12
9	6-Chloroquinoline	BINAP	8/9	**XII**	16
				XIV	49
10[a]	6-Chloroquinoline	BINAP	8/9	**XII**	52
				XV	48
11[a]	6-Chloroquinoline	DavePhos	8/9	**XII**	12
				XIII	17
				XIV	32

[a] 1 equiv. of sodium *tert*-butoxide per amino group.
[b] 1.5 equiv. of sodium *tert*-butoxide per amino group.
[c] Solvent DMF, base K_2CO_3.
[d] Solvent DMSO, base K_2CO_3.

Scheme 2.

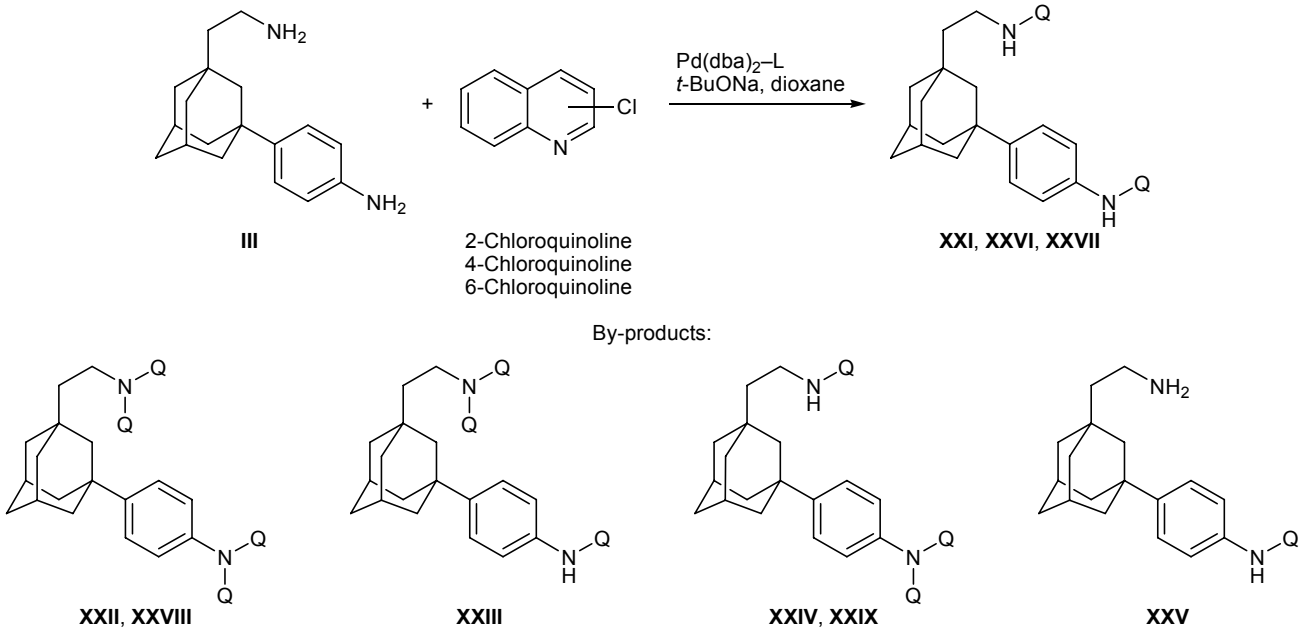


2- and 4-chloroquinolines gave approximately similar results: the yield of *N*,*N*′-diaryl derivatives **XVI** and **XVIII** was 31 and 33%, respectively, whereas the major products were monoaryl-substituted diamines **XVII** (64%) and **XIX** (50%). In the reaction of **II** with 6-chloroquinoline the yield of *N*,*N*′-diaryl derivative **XX** was much better, 89%. In no case *N*,*N*-diarylation products were detected, which may be due to considerable steric hindrances in starting diamine **II** where the reaction centers are located closely to the adamantane core.

Having obtained the data on the reactivity of symmetric diamines of the adamantane series, we proceeded with reactions of isomeric chloroquinolines with unsymmetrical diamine **III** possessing chemically nonequivalent amino groups. Our recent studies [12] have shown that diamine **III** reacts with isomeric bromofluorobenzenes and 3-bromopyridine quite successfully to afford the corresponding *N*,*N*′-diarylation products despite different reactivities of the amino groups. However, the reaction of **III** with 2-chloroquinoline (Scheme 3, Table 2) gave a large number of products, including target *N*,*N*′-diaryl derivative **XXI**. We failed to isolate it as individual substance, but only chromatographically inseparable mixture of **XXI** with triaryl-substituted diamine **XXIV** was obtained, regardless of the ligand used (run nos. 1, 2). The main problem was active *N*,*N*-diarylation of the aniline nitrogen atom. Although DavePhos was less favorable for that reaction, it did not ensure formation of compound **XXI** in an amount sufficient for its isolation in pure form. We tried 2-(di-*tert*-butylphosphino)biphenyl which turned out to be efficient in the synthesis of the *N*,*N*′-diaryl derivative of diamine **IV**; however, the reaction mixture contained mainly *N*,*N*-diarylaminophenyl derivatives **XXII** and **XXIV**, so that the mixture was not subjected to chromatographic separation.

The reactions of diamine **III** with 4- and 6-chloroquinolines in the presence of DavePhos were more selective. In the reaction with 4-chloroquinoline (run no. 3) the yield of *N*,*N*′-diarylation product **XXVI** was 37%, and no other individual compounds were isolated. The reaction with 6-chloroquinoline gave 43% of *N*,*N*′-diaryl diamine **XXVII** in addition to 41% of tetraaryl derivative **XXVIII** and 15% of triaryl derivative **XXIX** (run no. 4).

Scheme 3.



XXI–**XXV**, Q = quinolin-2-yl; **XXVI**, R = quinolin-4-yl; **XXVII**–**XXIX**, R = quinolin-6-yl.

Taking into account easy diarylation of the aniline nitrogen atom in diamine **III**, we specially studied the activity of different ligands used in palladium-catalyzed amination and ensuring formation of *N*,*N*-diarylation products of primary diamines (Scheme 4). As model compound we selected *p*-toluidine, and the reactions were carried out with equimolar amounts of chloroquinolines and the same amount of the catalyst as in the diarylation reactions (Table 3).

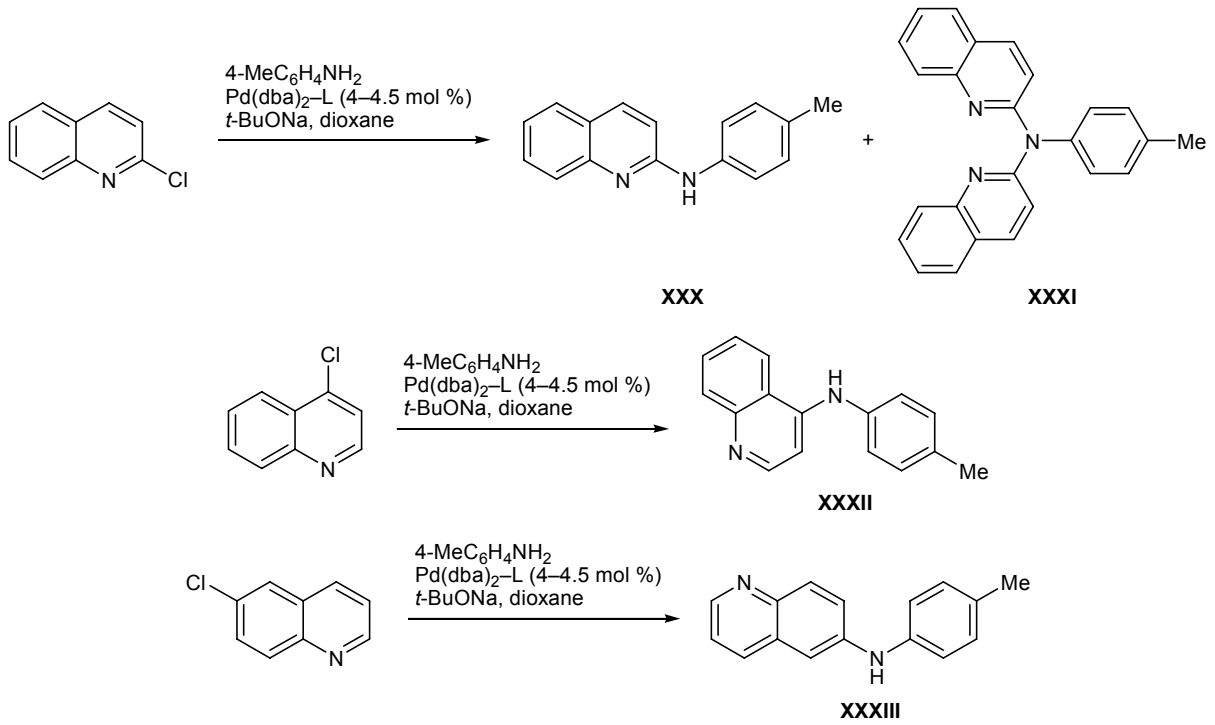
As follows from Scheme 4 and Table 3, in the reaction of *p*-toluidine with 2-chloroquinoline diarylation product **XXXI** dominates over monoaryl derivative **XXX** to a lesser or greater extent, whereas the former is almost the only product in the presence of BINAP. The use of the same ligand ensures formation of 4- and 6-aminoquinoline derivatives **XXXII** and **XXXIII** in 85 and 88% yield, respectively, while no diaryl derivatives are obtained. These findings suggest the necessity

Table 2. Arylation of 4-[3-(2-aminoethyl)adamantan-1-yl]aniline (**III**) with chloroquinolines

Run no.	Chloroquinoline	Ligand L	Arylation products	Yield, %
1	2-Chloroquinoline	BINAP	**XXI** + **XXIV**	50[a]
			XXII	29
			XXIII	11
			XXV	10
2	2-Chloroquinoline	DavePhos	**XXI** + **XXIV**	35[a]
			XXII	27
			XXIII	16
3	4-Chloroquinoline	DavePhos	**XXVI**	37
4	6-Chloroquinoline	DavePhos	**XXVII**	43
			XXVIII	41
			XXIX	15

[a] Chromatographically inseparable mixture.

Scheme 4.



of searching for other catalytic systems for successful *N*,*N*′-diarylation of diamine **III** with 2-chloroquinoline; efforts must be focused primarily on copper-containing catalysts.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400 and 100.6 MHz, respectively, using $CDCl_3$ as solvent and reference ($CHCl_3$, δ 7.25 ppm; $CDCl_3$, δ_C 77.00 ppm). The mass spectra (MALDI-TOF, positive ion detection) were obtained on a Bruker Daltonics Autoflex II instrument using 1,8,9-trihydroxyanthracene as matrix and polyethylene glycols as references. The UV spectra were measured on a Perkin Elmer Lambda 40 spectrophotometer. Silica gel 40/60 (Merck) was used for preparative column chromatography. Commercially available 2-, 4-, and 6-chloroquinolines, *p*-toluidine, 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (BINAP), 2-dicyclohexylphosphino-2′-dimethylaminobiphenyl (DavePhos), 2-di-*tert*-butylphosphinobiphenyl, 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (XantPhos), bis(2-diphenylphosphinophenyl) ether (DPEPhos), and 1,1′-bis(diphenylphosphino)ferrocene (dppf) were used without additional purification. Adamantane diamines **I**–**III** were synthesized as described in [13]. Dioxane was distilled first over alkali and then over metallic sodium; methylene chloride, petroleum ether, and methanol were distilled prior to use; $Pd(dba)_2$ was prepared according to the procedure reported in [14].

Table 3. Arylation of *p*-toluidine with 2-chloroquinoline

Run no.	Ligand L	Molar ratio **XXX**/**XXXI**
1	BINAP	0.1 : 1
2	XantPhos	0.8 : 1
3	DPEPhos	0.4 : 1
4	dppf	0.6 : 1

***N*-Quinolinyl-substituted diamines of the adamantane series (*general procedure*).** A flask was filled with argon and charged with required amounts of 2-, 4-, or 6-chloroquinoline, $Pd(dba)_2$, BINAP or DavePhos, anhydrous dioxane, diamine **I**–**III**, and sodium *tert*-butoxide. The mixture was heated under reflux and filtered, the filtrate was evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel.

***N*,*N*′-[2,2′-(Adamantane-1,3-diyl)bis(ethane-2,1-diyl)]diquinolin-2-amine (IV).** *a*. A mixture of 0.25 mmol (55 mg) of diamine **I**, 0.5 mmol (82 mg) of 2-chloroquinoline, 6 mg (4 mol %) of $Pd(dba)_2$, 7 mg (4.5 mol %) of BINAP, 48 mg (1 equiv) of sodium

tert-butoxide, and 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic separation (CH_2Cl_2–MeOH, 25:1) gave 15 mg (13%) of **IV**.

b. A mixture of the same amounts of diamine **I** and 2-chloroquinoline, 6 mg (4 mol %) of $Pd(dba)_2$, 5 mg (4.5 mol %) of DavePhos, and 72 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic separation (CH_2Cl_2–MeOH, 50:1) gave 29 mg (26%) of **IV**.

c. A mixture of the same amounts of diamine **I** and 2-chloroquinoline, 6 mg (4 mol %) of $Pd(dba)_2$, 5 mg (4.5 mol %) of DavePhos, and 48 mg (1 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic separation (CH_2Cl_2–MeOH, 50:1) gave 35 mg (32%) of **IV**.

d. The reaction was carried out using the same amounts of diamine **I** and 2-chloroquinoline and 4 mg (5 mol %) of 2-(di-*tert*-butylphosphino)biphenyl as ligand. Yield 83 mg (69%) (CH_2Cl_2–MeOH, 100:1 to 50:1).

e. The reaction was carried out in the absence of catalyst. A mixture of 0.2 mmol (44 mg) of diamine **I**, 0.45 mmol (74 mg) of 2-chloroquinoline, and 220 mg (8 equiv) of potassium carbonate in 1 ml of DMF was heated for 14 h under reflux. Chromatographic separation (CH_2Cl_2–MeOH, 50:1) gave 15 mg (15%) of **IV**.

f. A mixture of 0.2 mmol (44 mg) of diamine **I**, 0.4 mmol (66 mg) of 2-chloroquinoline, and 220 mg (8 equiv) of potassium carbonate in 1 ml of DMSO was heated for 14 h under reflux. The mixture was treated with water and extracted with methylene chloride, the extract was dried and evaporated, and the residue was subjected to chromatography using CH_2Cl_2–MeOH (50:1) as eluent. Yield 27 mg (29%), light yellow crystals, mp 110–112°C. UV spectrum (CH_2Cl_2): λ_{max} 341 nm (ε = 8000). ^{1}H NMR spectrum,** δ, ppm: 1.36 br.s (2H, Ad), 1.41–1.61 m (14H, Ad, AdC**H**$_2$CH), 2.04 br.s (2H, 2-H, Ad), 3.44–3.49 m (4H, CH_2N), 4.72 br.s (2H, NH), 6.62 d (2H, 3′-H, ^3J = 8.8 Hz), 7.18 d.d.d (2H, 6′-H, ^3J = 8.0, 7.1, ^4J = 1.0 Hz), 7.51 d.d.d (2H, 7′-H, ^3J = 8.5, 7.2, ^4J = 1.5 Hz), 7.56 d.d (2H, 5′-H, ^3J = 8.0, ^4J = 1.0 Hz), 7.69 d (2H, 8′-H, ^3J = 8.3 Hz), 7.78 d (2H, 4′-H, ^3J = 8.8, ^4J = 1.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.0 (2C, CH_{Ad}), 32.8 (2C, C_{Ad}), 36.5 (1C, CH_{2Ad}), 36.8 (2C, Ad**C**H_2), 42.0 (4C, CH_{2Ad}), 43.8 (2C, CH_2N), 47.6 (1C, CH_{2Ad}), 111.1 (2C, C$^{3'}$), 121.9 (2C, Q), 123.3 (2C, C$^{4a'}$), 125.9 (2C, Q), 127.4 (2C, Q), 129.6 (2C, Q), 137.4 (2C, C$^{4'}$), 148.0 (2C, C$^{8a'}$), 157.0 (2C, C$^{2'}$). Mass spectrum: *m*/*z* 477.305 [*M* + H]$^+$. $C_{21}H_{27}N_2O$. Calculated: (*M* + H) 477.302.

***N*,*N*′-[2,2′-(Adamantane-1,3-diyl)bis(ethane-2,1-diyl)]bis[*N*-(quinolin-2-yl)quinolin-2-amine] (V)** was isolated as by-product in the synthesis of compound **IV** according to *c*. Yield 7 mg (8%; after chromatography, CH_2Cl_2–MeOH, 200:1), yellow amorphous substance. ^{1}H NMR spectrum, δ, ppm: 1.56–1.70 m (16H, Ad, AdC**H**$_2$), 2.04 br.s (2H, 2-H, Ad), 4.53–4.59 m (4H, CH_2N), 7.34 d (4H, 3′-H, ^3J = 9.0 Hz), 7.35 d.d.d (4H, 6′-H, ^3J = 8.1, 7.0, ^4J = 1.1 Hz), 7.56 d.d.d (4H, 7′-H, ^3J = 8.5, 7.0, ^4J = 1.5 Hz), 7.68 d.d (4H, 5′-H, ^3J = 7.8, ^4J = 1.3 Hz), 7.86 d (4H, 8′-H, ^3J = 8.5 Hz), 7.94 d (4H, 4′-H, ^3J = 8.9 Hz). Mass spectrum: *m*/*z* 731.391 [*M* + H]$^+$. $C_{50}H_{47}N_6$. Calculated: (*M* + H) 731.386.

***N*-[2-(3-{2-[Di(quinolin-2-yl)amino]ethyl}adamantan-1-yl)ethyl]quinolin-2-amine (VI)** was isolated as by-product in the synthesis of compound **IV**. Yield (after chromatographic separation, CH_2Cl_2–MeOH, 100:1) 7 mg (13%) (*a*), 52 mg (38%) (*b*), 16 mg (11%) (*c*), 27 mg (27%) (*d*). Yellow amorphous substance. ^{1}H NMR spectrum, δ, ppm: 1.47–1.69 m (16H, Ad, AdC**H**$_2$), 2.09 br.s (2H, 2-H), 3.48–3.52 m (2H, 1-CH_2C**H**$_2$), 4.52–4.57 m (2H, 3-CH_2C**H**$_2$), 4.67 br.s (1H, NH), 6.61 d (1H, 3′-H, ^3J = 9.0 Hz), 7.18 t (1H, 6′-H, ^3J = 7.5 Hz), 7.33 d (2H, 3″-H, ^3J = 9.0 Hz), 7.36 t (2H, 6″-H, ^3J = 7.7 Hz), 7.50 t (1H, 7′-H, ^3J = 7.5 Hz), 7.56 d (1H, 5′-H, ^3J = 8.3 Hz), 7.60 t (2H, 7″-H, ^3J = 7.7 Hz), 7.67 d (1H, 8′-H, ^3J = 8.5 Hz), 7.70 d (2H, 5″-H, ^3J = 8.2 Hz), 7.80 d (1H, 4′-H, ^3J = 8.8 Hz), 7.87 d (2H, 8″-H, ^3J = 8.5 Hz), 7.95 d (2H, 4″-H, ^3J = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.1 (2C, CH_{Ad}), 32.8 (1C, C_{Ad}), 33.1 (1C, C_{Ad}), 36.6 (1C, CH_{2Ad}), 36.9 and 41.6 (1C each, Ad**C**H_2), 41.7 (2C, CH_{2Ad}), 42.1 (2C, CH_{2Ad}), 44.0 and 44.1 (1C each, CH_2N), 47.4 (1C, CH_{2Ad}), 111.0 (1C, C$^{3'}$), 116.0 (2C, C$^{3''}$), 121.9 (1C, C′), 123.3 (1C, C$^{4a'}$), 124.2 (2C, C″), 125.0 (2C, C$^{4a''}$), 126.0 (1C, C′), 127.2 (2C, C″), 127.4 (1C, C′), 127.8 (2C, C″), 129.5 (2C, C″), 129.5 (1C, C′), 136.8 (2C, C″), 137.4 (1C, C′), 147.7 (2C, C$^{8a'}$), 149.0 (1C, C$^{8a''}$), 155.7 (2C, C$^{2''}$), 157.0 (1C, C$^{2'}$).

** Hereinafter, in the description of NMR spectra primed locants refer to the quinoline fragments. If nonequivalent quinoline fragments are present, as in triaryl derivatives of diamines **I** and **II** and derivatives of diamine **III**, primed locants correspond to the quinoline ring attached to NH group (or the aminoethyl nitrogen atom in **III**), and double primed, to the two quinoline rings at the same nitrogen atom (or aniline nitrogen atom in **III**).

Mass spectrum: *m/z* 604.355 $[M + H]^+$. $C_{41}H_{42}N_5$. Calculated: (*M* + H) 604.344.

***N*-{2-[3-(2-Aminoethyl)adamantan-1-yl]ethyl}-*N*-(quinolin-2-yl)quinolin-2-amine (VII)** was isolated as by-product in the synthesis of compound **IV**. Yield 13 mg (11%) (*b*; CH_2Cl_2–MeOH, 10:1); 24 mg (21%) (*c*; CH_2Cl_2–MeOH, 25:1); yellow viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 1.31–1.67 m (16H, H_{Ad}, AdC**H**$_2$), 1.99 br.s (2H, 2-H, Ad), 2.90–3.00 m (2H, C**H**$_2$NH$_2$), 4.44–4.48 m (2H, 1-CH$_2$C**H**$_2$), 7.28 d (2H, 3′-H, ^3J = 8.8 Hz), 7.34 t (2H, 6′-H, ^3J = 7.4 Hz), 7.61 d.d.d (2H, 7′-H, ^3J = 8.2, 7.1, ^4J = 1.1 Hz), 7.66 d (2H, 5′-H, ^3J = 8.0 Hz), 7.84 d (2H, 8′-H, ^3J = 8.3 Hz), 7.91 d (2H, 4′-H, ^3J = 9.0 Hz); signals from NH protons were not identified. ^{13}C NMR spectrum, δ_C, ppm: 28.7 (2C, CH_{Ad}), 32.4 (1C, C_{Ad}), 32.9 (1C, C_{Ad}), 35.5 and 36.3 (1C each, CH_{2Ad}), 41.3–41.7 m (6C, CH_{2Ad}, Ad**C**H$_2$, **C**H$_2$NH$_2$), 43.9 (1C, 2′-NCH$_2$), 47.1 (1C, CH_{2Ad}), 115.9 (2C, C$^{3'}$), 124.2 (2C, C′), 125.0 (2C, C$^{4a'}$), 127.2 (2C, C′), 127.8 (2C, C′), 129.5 (2C, C′), 136.8 (2C, C$^{4'}$), 147.6 (2C, C$^{8a'}$), 155.6 (2C, C$^{2'}$). Mass spectrum: *m/z* 477.299 $[M + H]^+$. $C_{32}H_{37}N_4$. Calculated: (*M* + H) 477.302.

***N*-{2-[3-(2-Aminoethyl)adamantan-1-yl]ethyl}-quinolin-2-amine (VIII)** was isolated as by-product in the synthesis of compound **IV**. Yield (after chromatographic separation, CH_2Cl_2–MeOH, 3:1) 29 mg (33%) (*a*), 20 mg (23%) (*b*), 21 mg (24%) (*c*), 14 mg (20%) (*e*), 8 mg (11%) (*f*). Light yellow crystalline substance, mp 143–145°C. ^{1}H NMR spectrum, δ, ppm: 1.23 br.s (2H, Ad), 1.30–1.51 m (14H, Ad, AdC**H**$_2$), 1.93 br.s (2H, 2-H, Ad), 2.91–2.95 m (2H, C**H**$_2$NH$_2$), 3.34–3.38 m (2H, 2′-NCH$_2$), 6.69 d (1H, 3′-H, ^3J = 9.0 Hz), 7.16 t (1H, 6′-H, ^3J = 7.4 Hz), 7.48 d.d.d (1H, 7′-H, ^3J = 8.5, 7.2, ^4J = 1.3 Hz), 7.53 d (1H, 5′-H, ^3J = 7.8 Hz), 7.67 d (1H, 8′-H, ^3J = 8.3 Hz), 7.78 d (1H, 4′-H, ^3J = 9.0 Hz); signals from NH protons were not identified. ^{13}C NMR spectrum, δ_C, ppm: 28.6 (2C, CH_{Ad}), 32.4 (1C, C_{Ad}), 32.5 (1C, C_{Ad}), 35.5 and 36.1 (1C each, Ad**C**H$_2$), 36.9 (1C, CH_{2Ad}), 41.4 (2C, CH_{2Ad}), 41.6 (3C, CH_{2Ad}, CH_2NH_2), 43.2 (1C, 2′-NCH$_2$), 46.7 (1C, CH_{2Ad}), 111.4 (1C, C$^{3'}$), 122.2 (1C, C′), 123.0 (1C, C$^{4a'}$), 124.7 (1C, C′), 127.5 (1C, C′), 129.9 (1C, C′), 137.9 (1C, C$^{4'}$), 146.7 (1C, C$^{8a'}$), 156.7 (1C, C$^{2'}$). Mass spectrum: *m/z* 350.261 $[M + H]^+$. $C_{23}H_{32}N_3$. Calculated: (*M* + H) 350.260.

***N*,*N*′-[2,2′-(Adamantane-1,3-diyl)bis(ethane-2,1-diyl)]diquinolin-4-amine (IX).** *a*. A mixture of 0.25 mmol (55 mg) of diamine **I**, 0.5 mmol (82 mg) of 4-chloroquinoline, 12 mg (8 mol %) of Pd(dba)$_2$, 14 mg (9 mol %) of BINAP, and 72 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic separation (CH_2Cl_2–MeOH, 3:1) gave 68 mg (57%) of **IX**.

b. A mixture of the same amounts of diamine **I** and 4-chloroquinoline, 12 mg (8 mol %) of Pd(dba)$_2$, 14 mg (9 mol %) of BINAP, and 48 mg (1 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic separation (CH_2Cl_2–MeOH, 3:1) gave 29 mg (24%) of **IX** as a light yellow crystalline powder, mp 153–155°C. UV spectrum (CH_2Cl_2), λ_{max} 321 nm (ε = 7400). ^{1}H NMR spectrum, δ, ppm: 1.38 br.s (2H, Ad), 1.50–1.67 m (14H, Ad, AdC**H**$_2$), 2.11 br.s (2H, 2-H, Ad), 3.32–3.37 m (4H, 4′-NCH$_2$), 5.20 br.s (2H, NH), 6.40 d (2H, 3′-H, ^3J = 5.4 Hz), 7.42 d.d.d (2H, 6′-H, ^3J = 8.1, 7.0, ^4J = 1.0 Hz), 7.62 d.d.d (2H, 7′-H, ^3J = 8.1, 7.0, ^4J = 1.0 Hz), 7.77 d (2H, 3′-H, ^3J = 8.2 Hz), 7.97 d (2H, 5′-H, ^3J = 8.3 Hz), 8.52 d (2H, 2′-H, ^3J = 5.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.8 (2C, CH_{Ad}), 32.8 (2C, C_{Ad}), 36.2 (1C, CH_{2Ad}), 38.1 (2C, Ad**C**H$_2$), 41.8 (4C, CH_{2Ad}), 42.8 (2C, 4′-NCH$_2$), 47.7 (1C, CH_{2Ad}), 98.6 (2C, C$^{3'}$), 118.9 (2C, C$^{4a'}$), 119.4 (2C, C′), 124.7 (2C, C′), 129.1 (2C, C′), 129.5 (2C, C′), 148.0 (2C, C$^{8a'}$), 149.9 (2C, C$^{4'}$), 150.6 (2C, C$^{2'}$). Mass spectrum: *m/z* 477.306 $[M + H]^+$. $C_{32}H_{37}N_4$. Calculated: (*M* + H) 477.302.

***N*-[2-(3-{2-[Di(quinolin-4-yl)amino]ethyl}adamantan-1-yl)ethyl]quinolin-4-amine (X)** was isolated as by-product in the synthesis of compound **IX** according to *a*. Yield 34 mg (33%; after chromatography, CH_2Cl_2–MeOH, 10:1), yellow amorphous substance. ^{1}H NMR spectrum, δ, ppm: 1.32 br.s (2H, Ad), 1.44–1.73 m (14H, Ad, AdC**H**$_2$), 2.12 br.s (2H, 2-H, Ad), 3.25–3.32 m (2H, 4′-NHC**H**$_2$), 3.90–3.94 m (2H, 4″-NCH$_2$), 5.50 br.s (1H, NH), 6.34 d (1H, 3′-H, ^3J = 5.4 Hz), 6.87 d (2H, 3″-H, ^3J = 4.9 Hz), 7.36 t (1H, 6′-H, ^3J = 7.5 Hz), 7.56 t (2H, 6″-H, ^3J = 7.2 Hz), 7.63 t (3H, 7′-H, 7″-H, ^3J = 7.8 Hz), 7.77 d (1H, 8′-H, ^3J = 8.5 Hz), 7.80 d (2H, 8″-H, ^3J = 8.5 Hz), 7.92 d (1H, 5′-H, ^3J = 8.5 Hz), 8.09 d (2H, 5″-H, ^3J = 8.5 Hz), 8.43 d (1H, 2′-H, ^3J = 4.9 Hz), 8.72 d (2H, 2″-H, ^3J = 4.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.6 (2C, CH_{Ad}), 32.6 (1C, C_{Ad}), 32.7 (1C, C_{Ad}), 36.2 (1C, CH_{2Ad}), 38.0 and 48.0 (1C each, Ad**C**H$_2$), 41.4 (2C, CH_{2Ad}), 41.7 (2C, CH_{2Ad}), 42.6 (1C, 4′-NHCH$_2$), 47.4 (1C, CH_{2Ad}), 49.2 (1C, 4″-NCH$_2$), 96.4 (1C, C$^{3'}$), 114.1 (2C, C$^{3''}$), 118.5 (1C, C$^{4a'}$), 119.7 (1C, C′), 123.4 (2C, C″), 124.1 (2C, C$^{4a''}$), 124.7 (1C, C′), 126.3 (2C, C″), 129.3 (1C, C′), 128.5 (2C, C″), 129.7 (1C, C′), 130.2 (2C, C″), 147.2 (1C, C$^{8a'}$), 149.8 (2C, C$^{8a''}$), 150.1 (2C, C$^{4''}$), 150.2 (1C, C$^{4'}$), 150.6 (3C, C$^{2'}$, C$^{2''}$). Mass

spectrum: *m*/*z* 604.352 $[M + H]^+$. $C_{41}H_{42}N_5$. Calculated: (*M* + H) 604.344.

***N*-{2-[3-(2-Aminoethyl)adamantan-1-yl]ethyl}-quinolin-4-amine (XI)** was isolated as by-product in the synthesis of **IX**. Yield (after chromatography, CH_2Cl_2–MeOH–aq. NH_3, 100:20:1) 8 mg (9%) (*a*), 10 mg (12%) (*b*); yellow crystalline substance, mp 125–127°C. ^{1}H NMR spectrum, δ, ppm: 1.31 br.s (2H, H_{Ad}), 1.39–1.66 m (14H, Ad, Ad**CH**$_2$), 2.04 br.s (2H, 2-H, Ad), 2.67–2.72 m (2H, **CH**$_2$NH$_2$), 3.28–3.35 m (2H, 4′-NH**CH**$_2$), 4.92 br.s (1H, NH), 6.41 d (1H, 3′-H, ^3J = 5.3 Hz), 7.40 t (1H, 6′-H, ^3J = 7.5 Hz), 7.61 t (1H, 7′-H, ^3J = 7.6 Hz), 7.70 d (1H, 8′-H, ^3J = 7.7 Hz), 7.96 d (1H, 5′-H, ^3J = 8.3 Hz), 8.55 d (1H, 2′-H, ^3J = 5.3 Hz); signals from the NH_2 protons were not identified. ^{13}C NMR spectrum, δ_C, ppm: 28.9 (2C, CH_{Ad}), 32.8 (2C, C_{Ad}), 36.4 (1C, CH_{2Ad}), 38.1 (2C, Ad**C**H$_2$), 41.9 (2C, CH_{2Ad}), 42.0 (2C, CH_{2Ad}), 42.9 and 43.0 (1C each, CH_2N), 47.8 (1C, CH_{2Ad}), 98.7 (1C, $C^{3'}$), 118.7 (1C, $C^{4a'}$), 119.2 (1C, C′), 124.6 (1C, C′), 129.0 (1C, C′), 129.9 (1C, C′), 148.3 (1C, $C^{8a'}$), 149.7 (1C, $C^{4'}$), 150.9 (1C, $C^{2'}$). Mass spectrum: *m*/*z* 350.263 $[M + H]^+$. $C_{23}H_{32}N_3$. Calculated: (*M* + H) 350.260.

***N*,*N*′-[2,2′-(Adamantane-1,3-diyl)bis(ethane-2,1-diyl)]diquinolin-6-amine (XII).** *a*. A mixture of 0.25 mmol (55 mg) of diamine **I**, 0.5 mmol (82 mg) of 6-chloroquinoline, 12 mg (9 mol %) of $Pd(dba)_2$, 14 mg (9 mol %) of BINAP, and 72 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic separation (CH_2Cl_2–MeOH, 50:1) gave 19 mg (16%) of **XII**.

b. A mixture of the same amounts of diamine **I** and 6-chloroquinoline, 12 mg (8 mol %) of $Pd(dba)_2$, 9 mg (9 mol %) of DavePhos, and 48 mg (1 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic separation (CH_2Cl_2–MeOH, 25:1) gave 14 mg (12%) of **XII**.

c. A mixture of the same amounts of diamine **I** and 6-chloroquinoline, 12 mg (8 mol %) of $Pd(dba)_2$, 14 mg (9 mol %) of BINAP, and 48 mg (1 equiv) of sodium *tert*-butoxide in 2.5 ml in anhydrous dioxane was heated for 7 h under reflux. Chromatographic separation (CH_2Cl_2–MeOH, 50:1) gave 62 mg (52%) of **XII** as a yellow–green amorphous substance. UV spectrum (CH_2Cl_2): λ_{max} 360 nm (ε = 7000). ^{1}H NMR spectrum, δ, ppm: 1.34 br.s (2H, Ad), 1.43–1.50 m (8H, Ad, Ad**CH**$_2$), 1.53–1.58 m (4H, Ad), 1.62 br.s (2H, Ad), 2.06 br.s (2H, 2-H, Ad), 3.15–3.20 m (4H, CH_2N), 3.94 br.s (2H, NH), 6.64 br.s (2H, 5′-H), 7.03 d.d (2H, 7′-H, ^3J = 9.1, ^4J = 2.3 Hz), 7.21 d.d (2H, 3′-H, ^3J = 8.1, 4.1 Hz), 7.83 d (2H, 8′-H, ^3J = 9.0 Hz), 7.88 d (2H, 4′-H, ^3J = 8.2 Hz), 8.58 d (2H, 2′-H, ^3J = 4.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.8 (2C, CH_{Ad}), 32.6 (2C, C_{Ad}), 36.3 (1C, CH_{2Ad}), 38.5 (2C, AdCH_2), 41.8 (4C, CH_{2Ad}), 43.2 (2C, CH_2N), 47.7 (1C, CH_{2Ad}), 102.5 (2C, $C^{7'}$), 121.2 (2C, C′), 121.4 (2C, C′), 130.0 (2C, C′), 130.1 (2C, $C^{4a'}$), 133.5 (2C, C′), 143.0 (2C, $C^{8a'}$), 145.8 (2C, $C^{2'}$), 146.3 (2C, $C^{6'}$). Mass spectrum: *m*/*z* 477.304 $[M + H]^+$. $C_{32}H_{37}N_4$. Calculated: (*M* + H) 477.302.

***N*,*N*′-[2,2′-(Adamantane-1,3-diyl)bis(ethane-2,1-diyl)]bis[*N*-(quinolin-6-yl)quinolin-6-amine] (XIII)** was isolated as by-product in the synthesis of **XII** according to *b*. Yield 16 mg (17%; CH_2Cl_2–MeOH, 25:1 to 10:1), yellow amorphous substance. ^{1}H NMR spectrum, δ, ppm: 1.39 br.s (2H, Ad), 1.50–1.66 m (14H, Ad, Ad**CH**$_2$), 2.11 br.s (2H, 2-H, Ad), 3.97–4.01 m (4H, CH_2N), 7.29–7.32 m (8H, quinoline), 7.47 d.d (4H, 7′-H, ^3J = 9.1, ^4J = 2.5 Hz), 7.95 d (4H, quinoline, ^3J = 7.8 Hz), 7.98 d (4H, 8′-H, ^3J = 9.1 Hz), 8.76 d.d (4H, 2′-H, ^3J = 4.3, ^4J = 1.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.8 (2C, CH_{Ad}), 32.7 (2C, C_{Ad}), 36.3 (1C, CH_{2Ad}), 40.3 (2C, Ad**C**H$_2$), 41.6 (4C, CH_{2Ad}), 47.6 (3C, CH_{2Ad}, CH_2N), 115.4 (4C, $C^{7'}$), 121.4 (4C, C′), 125.7 (4C, C′), 129.4 (4C, $C^{4a'}$), 130.5 (4C, C′), 134.7 (4C, C′), 144.8 (4C, $C^{8a'}$), 145.4 (4C, $C^{6'}$), 148.4 (4C, $C^{2'}$). Mass spectrum: *m*/*z* 731.382 $[M + H]^+$. $C_{50}H_{47}N_6$. Calculated: (*M* + H) 731.386.

***N*-[2-(3-{2-[Di(quinolin-6-yl)amino]ethyl}adamantan-1-yl)ethyl]quinolin-6-amine (XIV)** was isolated as by-product in the synthesis of **XII**. Yield (CH_2Cl_2–MeOH, 25:1), 50 mg (49%) (*a*), 33 mg (32%) (*b*); yellow amorphous substance. ^{1}H NMR spectrum, δ, ppm: 1.38 br.s (2H, Ad), 1.47–1.67 m (14H, Ad, Ad**CH**$_2$), 2.09 br.s (2H, 2-H, Ad), 3.16–3.22 m (2H, 6′-NH**CH**$_2$), 3.78 br.s (1H, NH), 3.96–4.00 m (2H, 6″-NCH_2), 6.65 d (1H, 5′-H, ^4J = 2.5 Hz), 7.04 d.d (1H, 7′-H, ^3J = 9.1, ^4J = 2.5 Hz), 7.22 d.d (1H, 3′-H, ^3J = 8.2, 4.2 Hz), 7.28–7.31 m (4H, H″),7.47 d.d (2H, 7″-H, ^3J = 9.2, ^4J = 2.5 Hz), 7.83 d (1H, 8′-H, ^3J = 9.0 Hz), 7.89 t (1H, 4′-H, ^3J = 7.3 Hz), 7.96 br.d (2H, H″, ^3J = 6.1 Hz), 7.97 br.d (2H, H″, ^3J = 7.5 Hz), 8.58 d.d (1H, 2′-H, ^3J = 4.3, ^4J = 1.5 Hz), 8.74 d.d (2H, 2″-H, ^3J = 4.2, ^4J = 1.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.2 (2C, CH_{Ad}), 32.7 (1C, C_{Ad}), 32.8 (1C, C_{Ad}), 36.3 (1C, CH_{2Ad}), 38.6 and 40.3 (1C each, AdCH_2), 41.6 (2C, CH_{2Ad}), 41.9 (2C, CH_{2Ad}), 43.3 (1C, 6′-$NHCH_2$), 47.6 (2C, 6″-NCH_2, CH_{2Ad}), 102.6 (1C, $C^{7'}$), 115.4 (2C, $C^{7''}$), 121.3 (1C, C′), 121.4 (1C, C′),

121.5 (2C, C″), 125.7 (2C, C″), 129.4 (2C, $C^{4a''}$), 130.1 (2C, $C^{4a'}$, C′), 130.5 (2C, C″), 133.6 (1C, C′), 134.7 (2C, C″), 143.1 (1C, $C^{8a'}$), 144.7 (2C, $C^{8a''}$), 145.4 (2C, $C^{6''}$), 145.9 (1C, $C^{2'}$), 146.3 (1C, $C^{6'}$), 148.4 (2C, $C^{2''}$). Mass spectrum: *m*/*z* 604.338 $[M + H]^+$. $C_{41}H_{42}N_5$. Calculated: (*M* + H) 604.344.

***N*-{2-[3-(2-Aminoethyl)adamantan-1-yl]ethyl}-quinolin-6-amine (XV)** was isolated as by-product in the synthesis of **XII** according to *c*. Yield 42 mg (48%; CH_2Cl_2–MeOH–aq. NH_3, 100:20:1), light yellow crystalline substance, mp 141–143°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.29 br.s (2H, Ad), 1.37–1.58 m (14H, Ad, AdC**H**$_2$), 2.01 br.s (2H, 2-H, Ad), 2.74–2.79 m (2H, C**H**$_2$NH$_2$), 3.05–3.10 m (2H, C**H**$_2$NH), 5.99 t (1H, NH, ^3J = 4.7 Hz), 6.62 d (1H, 5′-H, ^4J = 2.4 Hz), 7.17 d.d (1H, 7′-H, ^3J = 9.1, ^4J = 2.3 Hz), 7.26 d.d (1H, 3′-H, ^3J = 8.2, 4.2 Hz), 7.65 d (1H, 8′-H, ^3J = 9.1 Hz), 7.95 d (1H, 4′-H, ^3J = 8.3 Hz), 8.44 d (1H, 2′-H, ^3J = 4.2 Hz); signals from the NH_2 protons were not identified. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 28.3 (2C, CH_{Ad}), 32.1 (1C, C_{Ad}), 32.2 (1C, C_{Ad}), 34.2 (1C, CH_{2Ad}), 35.8 and 37.6 (1C each, Ad**C**H$_2$), 40.7 (1C, CH_2NH_2), 41.0 (2C, CH_{2Ad}), 41.2 (2C, CH_{2Ad}), 42.2 (1C, CH_2NH), 46.4 (1C, CH_{2Ad}), 100.7 (1C, $C^{7'}$), 121.1 (1C, C′), 121.6 (1C, C′), 129.2 (1C, C′), 130.0 (1C, $C^{4a'}$), 132.9 (1C, C′), 144.7 (1C, $C^{2'}$), 146.8 (1C, $C^{8a'}$), 146.9 (1C, $C^{6'}$). Mass spectrum: *m*/*z* 350.259 $[M + H]^+$. $C_{23}H_{32}N_3$. Calculated: (*M* + H) 350.260.

***N*,*N*′-[(Adamantane-1,3-diyl)bismethylene]diquinolin-2-amine (XVI).** A mixture of 0.25 mmol (48 mg) of diamine **II**, 0.5 mmol (82 mg) of 2-chloroquinoline, 12 mg (8 mol %) of $Pd(dba)_2$, 9 mg (9 mol %) of DavePhos, and 48 mg (1 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic separation (CH_2Cl_2–MeOH, 25:1) gave 35 mg (31%) of **XVI** as a yellow viscous oily material. ^{1}H NMR spectrum, δ, ppm: 1.43 br.s (2H, Ad), 1.49–1.62 m (10H, Ad), 2.08 br.s (2H, 2-H, Ad), 3.23 d (4H, C**H**$_2$NH, ^3J = 5.9 Hz), 4.49 br.s (2H, NH), 6.49 d (2H, 3′-H, ^3J = 9.0 Hz), 7.17 d.d (2H, 6′-H, ^3J = 7.4, ^3J = 7.1 Hz), 7.50 d.d.d (2H, 7′-H, ^3J = 8.5, 7.2, ^4J = 1.4 Hz), 7.54 d (2H, 5′-H, ^3J = 7.8 Hz), 7.63 d (2H, 8′-H, ^3J = 8.2 Hz), 7.73 d (2H, 4′-H, ^3J = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.4 (2C, CH_{Ad}), 34.7 (2C, C_{Ad}), 36.4 (1C, CH_{2Ad}), 39.9 (4C, CH_{2Ad}), 43.1 (1C, CH_{2Ad}), 53.0 (2C, CH_2N), 110.9 (2C, $C^{3'}$), 121.8 (2C, C′), 123.3 (2C, $C^{4a'}$), 125.8 (2C, C′), 127.4 (2C, C′), 129.5 (2C, C′), 137.3 (2C, $C^{4'}$), 147.9 (2C, $C^{8a'}$), 157.5 (2C, $C^{2'}$). Mass spectrum: *m*/*z* 449.269 $[M + H]^+$. $C_{30}H_{33}N_4$. Calculated: (*M* + H) 449.271.

***N*-{[3-(Aminomethyl)adamantan-1-yl]methyl}-quinolin-2-amine (XVII)** was isolated as by-product in the synthesis of **XVI**. Yield 52 mg (64%; CH_2Cl_2–MeOH, 3:1), light yellow viscous oily material. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.34–1.59 m (12H, Ad), 2.02 br.s (2H, 2-H, Ad), 2.41 s (2H, C**H**$_2$NH$_2$), 3.20 d (2H, C**H**$_2$NH, ^3J = 5.3 Hz), 5.68 t (1H, NH, ^3J = 5.5 Hz), 6.89 d (1H, 3′-H, ^3J = 9.0 Hz), 7.08 d.d.d (1H, 6′-H, ^3J = 7.8, 6.3, ^4J = 1.6 Hz), 7.40 t.d (1H, 7′-H, ^3J = 8.3, ^4J = 1.3 Hz), 7.46 d (1H, 5′-H, ^3J = 8.0 Hz), 7.55 d (1H, 8′-H, ^3J = 7.7 Hz), 7.77 d (1H, 4′-H, ^3J = 9.0 Hz); signals from protons in the NH_2 group were not identified. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 28.8 (2C, CH_{Ad}), 32.9 (1C, C_{Ad}), 34.3 (1C, C_{Ad}), 35.8 (1C, CH_{2Ad}), 37.8 (2C, CH_{2Ad}), 39.4 (2C, CH_{2Ad}), 42.3 (1C, CH_{2Ad}), 51.0 (1C, CH_2NH_2), 51.7 (1C, CH_2NH), 113.4 (1C, $C^{3'}$), 120.9 (1C, C′), 122.9 (1C, $C^{4a'}$), 125.5 (1C, C′), 127.4 (1C, C′), 128.9 (1C, C′), 135.9 (1C, $C^{4'}$), 147.8 (1C, $C^{8a'}$), 157.7 (1C, $C^{2'}$). Mass spectrum: *m*/*z* 322.231 $[M + H]^+$. $C_{21}H_{28}N_3$. Calculated: (*M* + H) 322.228.

***N*,*N*′-[(Adamantane-1,3-diyl)bismethylene]diquinolin-4-amine (XVIII).** A mixture of 0.25 mmol (48 mg) of diamine **II**, 0.5 mmol (82 mg) of 4-chloroquinoline, 12 mg (8 mol %) of $Pd(dba)_2$, 9 mg (9 mol %) of DavePhos, and 48 mg (1 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic separation (CH_2Cl_2–MeOH, 10:1) gave 37 mg (33%) of **XVIII** as a yellow viscous oily material. ^{1}H NMR spectrum, δ, ppm: 1.51–1.64 m (12H, Ad), 2.13 br.s (2H, 2-H, Ad), 3.06 d (4H, CH_2N, ^3J = 5.1 Hz), 5.55 br.s (2H, NH), 6.41 d (2H, 3′-H, ^3J = 5.5 Hz), 7.37 d.d.d (2H, 6′-H, ^3J = 8.0, 7.1, ^4J = 1.0 Hz), 7.58 d.d.d (2H, 7′-H, ^3J = 7.9, 7.0, ^4J = 1.0 Hz), 7.84 d (2H, 8′-H, ^3J = 8.3 Hz), 7.94 d (2H, 5′-H, ^3J = 8.3 Hz), 8.44 d (2H, 2′-H, ^3J = 5.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.2 (2C, CH_{Ad}), 35.2 (2C, C_{Ad}), 36.0 (1C, CH_{2Ad}), 40.0 (4C, CH_{2Ad}), 43.8 (1C, CH_{2Ad}), 54.4 (2C, CH_2N), 98.6 (2C, $C^{3'}$), 118.6 (2C, $C^{4a'}$), 119.6 (2C, C′), 124.7 (2C, C′), 129.1 (2C, C′), 129.2 (2C, C′), 147.6 (2C, $C^{8a'}$), 150.1 (2C, $C^{2'}$), 150.8 (2C, $C^{4'}$). Mass spectrum: *m*/*z* 449.262 $[M + H]^+$. $C_{30}H_{33}N_4$. Calculated: (*M* + H) 449.271.

***N*-{[3-(Aminomethyl)adamantan-1-yl]methyl}-quinolin-4-amine (XIX)** was isolated as by-product in the synthesis of compound **XVIII**. Yield 40 mg (50%; CH_2Cl_2–MeOH, 3:1), light yellow oily substance.

^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.39 br.s (2H, Ad), 1.45–1.56 m (10H, Ad), 1.99 br.s (2H, 2-H, Ad), 2.41 s (2H, C**H**$_2$NH$_2$), 3.02 br.s (2H, C**H**$_2$NH), 6.51 d (1H, 3′-H, ^3J = 5.7 Hz), 6.97 br.s (1H, NH), 7.37 t (1H, 6′-H, ^3J = 7.5 Hz), 7.57 t (1H, 7′-H, ^3J = 7.6 Hz), 7.75 d (1H, 8′-H, ^3J = 8.3 Hz), 7.83 d (1H, 5-H, ^3J = 8.5 Hz), 8.33 d (1H, 2′-H, ^3J = 5.7 Hz); signals from the NH$_2$ protons were not identified. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 27.7 (2C, CH$_{Ad}$), 32.8 (1C, C$_{Ad}$), 35.5 (1C, C$_{Ad}$), 35.6 (1C, CH$_{2Ad}$), 38.5 (2C, CH$_{2Ad}$), 39.4 (2C, CH$_{2Ad}$), 42.3 (1C, CH$_{2Ad}$), 50.6 (1C, CH$_2$NH$_2$), 53.6 (1C, CH$_2$NH), 98.5 (1C, C$^{3'}$), 118.8 (1C, C$^{4a'}$), 122.1 (1C, C′), 123.6 (1C, C′), 128.8 (2C, C′), 148.2 (1C, C$^{8a'}$), 150.5 (1C, C$^{2'}$), 151.1 (1C, C$^{4'}$). Mass spectrum: *m*/*z* 322.226 [*M* + H]$^+$. $C_{21}H_{28}N_3$. Calculated: (*M* + H) 322.228.

***N*,*N*′-[(Adamantane-1,3-diyl)bismethylene]diquinolin-6-amine (XX).** A mixture of 0.25 mmol (48 mg) of diamine **II**, 0.5 mmol (82 mg) of 6-chloroquinoline, 12 mg (8 mol %) of Pd(dba)$_2$, 9 mg (9 mol %) of DavePhos, and 72 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic separation (CH$_2$Cl$_2$–MeOH, 50:1) gave 100 mg (89%) of **XX** as a light green viscous oily material which showed luminescence when dissolved in organic solvents. ^{1}H NMR spectrum, δ, ppm: 1.46 br.s (2H, Ad), 1.50–1.63 m (8H, Ad), 1.63–1.67 m (2H, Ad), 2.12 br.s (2H, 2-H, Ad), 2.92 br.s (4H, CH$_2$N), 4.10 br.s (2H, NH), 6.66 d (2H, 5′-H, ^4J = 2.5 Hz), 7.06 d.d (2H, 7′-H, ^3J = 9.1, ^4J = 2.5 Hz), 7.19 d.d (2H, 3′-H, ^3J = 8.3, 4.3 Hz), 7.82 d (2H, 8′-H, ^3J = 8.8 Hz), 7.83 d.d (2H, 4′-H, ^3J = 8.1, ^4J = 1.5 Hz), 8.56 d.d (2H, 2′-H, ^3J = 4.3, ^4J = 1.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.3 (2C, CH$_{Ad}$), 34.6 (2C, C$_{Ad}$), 36.3 (1C, CH$_{2Ad}$), 40.1 (4C, CH$_{2Ad}$), 43.6 (1C, CH$_{2Ad}$), 55.6 (2C, CH$_2$N), 102.5 (2C, C$^{7'}$), 121.2 (2C, C′), 121.3 (2C, C′), 130.0 (2C, C′), 130.1 (2C, C$^{4a'}$), 133.5 (2C, C′), 142.9 (2C, C$^{8a'}$), 145.8 (2C, C$^{2'}$), 146.9 (2C, C$^{6'}$). Mass spectrum: *m*/*z* 449.274 [*M* + H]$^+$. $C_{30}H_{33}N_4$. Calculated: (*M* + H) 449.271.

***N*-(4-{3-[2-(Quinolin-2-ylamino)ethyl]adamantan-1-yl}phenyl)quinolin-2-amine (XXI) and *N*-[2-(3-{4-[di(quinolin-2-yl)amino]phenyl}adamantan-1-yl)ethyl]quinolin-2-amine (XXIV).** *a*. A mixture of 0.25 mmol (68 mg) of diamine **III**, 0.5 mmol (82 mg) of 2-chloroquinoline, 12 mg (9 mol %) of Pd(dba)$_2$, 14 mg (9 mol %) of BINAP, and 72 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic treatment (CH$_2$Cl$_2$–MeOH, 100:1) gave 60 mg (50%) of an inseparable mixture of di- and triaryl derivatives **XXI** and **XXIV**. Elution with CH$_2$Cl$_2$–MeOH (200:1) afforded 10 mg (11%) of pure triaryl derivative **XXIV** as a yellow amorphous substance.

b. A mixture of the same amounts of diamine **III** and 2-chloroquinoline, 12 mg (8 mol %) of Pd(dba)$_2$, 9 mg (9 mol %) of DavePhos, and 72 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic treatment (CH$_2$Cl$_2$–MeOH, 100:1) gave 42 mg (35%) of an inseparable mixture of compounds **XXI** and **XXIV**.

Compound **XXI**. ^{1}H NMR spectrum, δ, ppm: 1.51–1.55 m (2H, AdC**H**$_2$), 1.58–1.67 m (4H, Ad), 1.72 br.s (4H, Ad), 1.88 br.s (4H, Ad), 2.19 br.s (2H, 2-H, Ad), 3.50–3.55 m (2H, CH$_2$N), 4.64 br.s (1H, CH$_2$N**H**), 6.61 d (1H, 3′-H, ^3J = 8.9 Hz), 6.94 br.s (1H, C$_6$H$_4$N**H**), 6.96 d (1H, 3″-H, ^3J = 9.0 Hz), 7.14–7.29 m (4H, *m*-H, 6′-H, 6″-H), 7.48–7.53 m (3H, *o*-H, 7′-H), 7.56–7.59 m (2H, 5′-H, 7″-H), 7.62 d (1H, 5″-H, ^3J = 8.0 Hz), 7.68 d (1H, 8′-H, ^3J = 7.8 Hz), 7.76 d (1H, 8″-H, ^3J = 8.8 Hz), 7.79 d (1H, 4′-H, ^3J = 8.7 Hz), 7.87 d (1H, 4″-H, ^3J = 8.8 Hz). Mass spectrum: *m*/*z* 525.297 [*M* + H]$^+$. $C_{36}H_{37}N_4$. Calculated: (*M* + H) 525.302.

Compound **XXIV**. ^{1}H NMR spectrum, δ, ppm: 1.50–1.54 m (2H, AdC**H**$_2$), 1.58–1.89 m (12H, Ad), 2.19 br.s (2H, 2-H, Ad), 3.50–3.55 m (2H, CH$_2$N), 4.64 br.s (1H, CH$_2$N**H**), 6.65 d (1H, 3′-H, ^3J = 8.5 Hz), 7.14–7.29 m (7H, 6′-H, Ph, 3″-H), 7.39 t (2H, 6″-H, ^3J = 7.4 Hz), 7.50–7.59 m (3H, 7′-H, 7″-H), 7.62 d (1H, 5′-H, ^3J = 8.0 Hz), 7.69 d (1H, 8′-H, ^3J = 8.5 Hz), 7.71 d (2H, 5″-H, ^3J = 8.5 Hz), 7.78 d (1H, 4′-H, ^3J = 8.5 Hz), 7.79 d (2H, 8″-H, ^3J = 8.6 Hz), 7.97 d (2H, 4″-H, ^3J = 8.8 Hz). Mass spectrum: *m*/*z* 652.347 [*M* + H]$^+$. $C_{45}H_{42}N_5$. Calculated: (*M* + H) 652.344.

***N*-[4-(3-{2-Di(quinolin-2-yl)amino]ethyl}adamantan-1-yl)phenyl]-*N*-(quinolin-2-yl)quinolin-2-amine (XXII)** was isolated as by-product in the synthesis of **XXI**. Yield (CH$_2$Cl$_2$–MeOH, 200:1) 40 mg (29%) (*a*), 37 mg (27%) (*b*); yellow viscous oily material. ^{1}H NMR spectrum, δ, ppm: 1.65–1.93 m (14H, Ad, AdC**H**$_2$), 2.22 br.s (2H, 2-H, Ad), 4.57–4.62 m (2H, CH$_2$N), 7.22–7.29 m (6H, Ph, 3″-H), 7.34 d (2H, 3′-H, ^3J = 9.0 Hz), 7.35–7.40 m (4H, 6′-H, 6″-H), 7.54–7.60 m (4H, 7′-H, 7″-H), 7.70 d (2H, 5′-H, ^3J = 7.5 Hz), 7.71 d (2H, 5″-H, ^3J = 7.5 Hz), 7.77 d (2H, 8″-H, ^3J = 8.2 Hz), 7.85 d (2H, 8′-H, ^3J = 8.3 Hz), 7.95 d (2H, 4′-H, ^3J = 8.1 Hz), 7.97 d (2H, 4″-H, ^3J = 8.3 Hz). Mass spectrum: *m*/*z* 779.382 [*M* + H]$^+$. $C_{54}H_{47}N_6$. Calculated: (*M* + H) 779.386.

***N*-[4-(3-{2-[Di(quinolin-2-yl)amino]ethyl}adamantan-1-yl)phenyl]quinolin-2-amine (XXIII)** was isolated as by-product in the synthesis of **XXI** according to *b*. Yield 18 mg (16%; CH_2Cl_2–MeOH, 200:1), yellow amorphous material. ^{1}H NMR spectrum, δ, ppm: 1.68–1.93 m (14H, Ad, AdC**H**$_2$), 2.22 br.s (2H, 2-H, Ad), 4.59–4.63 m (2H, CH_2N), 6.89 br.s (1H, C_6H_4N**H**), 6.97 d (1H, 3″-H, ^3J = 8.8 Hz), 7.23–7.29 m (3H, 6″-H, *m*-H), 7.32–7.36 m (4H, 3′-H, 6′-H), 7.50 d (2H, *o*-H, ^3J = 8.7 Hz), 7.54–7.64 m (3H, 7′-H, 7″-H), 7.61 d (1H, 5″-H, ^3J = 8.2 Hz), 7.70 d (2H, 5′-H, ^3J = 7.8 Hz), 7.78 d (1H, 8″-H, ^3J = 8.1 Hz), 7.79 d (1H, 4″-H, ^3J = 8.2 Hz), 7.86 d (2H, 8′-H, ^3J = 8.5 Hz), 7.95 d (2H, 4′-H, ^3J = 8.8 Hz). Mass spectrum: *m*/*z* 652.340 $[M + H]^+$. $C_{45}H_{42}N_5$. Calculated: (*M* + H) 652.344.

***N*-(4-{3-[2-(Quinolin-4-ylamino)ethyl]adamantan-1-yl}phenyl)quinolin-4-amine (XXVI).** A mixture of 0.25 mmol (68 mg) of diamine **III**, 0.5 mmol (82 mg) of 4-chloroquinoline, 12 mg (8 mol %) of $Pd(dba)_2$, 9 mg (9 mol %) of DavePhos, and 72 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic separation (CH_2Cl_2–MeOH, 3:1) gave 32 mg (37%) of **XXVI** as a yellow viscous oily material. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.56–1.60 m (2H, AdC**H**$_2$), 1.61 br.s (4H, Ad), 1.68 br.s (2H, Ad), 1.72 br.s (2H, Ad), 1.83 br.s (4H, Ad), 2.14 br.s (2H, 2-H, Ad), 3.34–3.40 m (2H, CH_2N), 6.50 d (1H, 3′-H, ^3J = 5.7 Hz), 6.86 d (1H, 3″-H, ^3J = 5.3 Hz), 7.30 d (2H, *m*-H, ^3J = 8.6 Hz), 7.41 d (2H, *o*-H, ^3J = 8.6 Hz), 7.44 t (1H, quinoline, ^3J = 7.7 Hz), 7.49–7.53 m (2H, quinoline, PhN**H**); 7.64 t (1H, ^3J = 7.7 Hz), 7.68 t (1H, ^3J = 7.6 Hz), 7.79 d (1H, ^3J = 8.5 Hz), 7.86 d (1H, ^3J = 8.5 Hz), 8.29 d (1H, ^3J = 8.5 Hz), 8.39–8.43 m (3H) (quinoline). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 28.7 (2C, CH_{Ad}), 32.6 (1C, C_{Ad}), 35.6 (1C, CH_{2Ad}), 36.3 (1C, C_{Ad}), 37.5 (1C, Ad**C**H_2), 40.8 (2C, CH_{2Ad}), 41.5 (1C, CH_{2Ad}), 42.2 (2C, CH_{2Ad}), 47.4 (1C, CH_2N), 98.0 (1C, $C^{3'}$), 101.1 (1C, $C^{3''}$), 118.5 (1C, $C^{4a'}$), 119.6 (1C, $C^{4a''}$), 122.5 (2C, C^m); 122.0 (1C), 122.1 (1C), 124.2 (1C), 124.5 (1C) (quinoline); 125.7 (2C, C^o); 127.3 (1C), 128.9 (1C), 129.2 (1C), 129.5 (1C) (quinoline); 137.9 (1C, C^i), 146.2 (1C, C^p), 146.3 (1C, $C^{8a'}$), 148.1 (1C, $C^{4'}$), 148.7 (1C, $C^{8a''}$), 149.1 (1C, $C^{2'}$), 150.4 (1C, $C^{2''}$), 150.8 (1C, $C^{4''}$). Mass spectrum: *m*/*z* 525.295 $[M + H]^+$. $C_{36}H_{37}N_4$. Calculated: (*M* + H) 525.302.

***N*-(4-{3-[2-(Quinolin-6-ylamino)ethyl]adamantan-1-yl}phenyl)quinolin-6-amine (XXVII).** A mixture of 0.25 mmol (68 mg) of diamine **III**, 0.5 mmol (82 mg) of 6-chloroquinoline, 12 mg (8 mol %) of $Pd(dba)_2$, 9 mg (9 mol %) of DavePhos, and 72 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. Chromatographic separation (CH_2Cl_2–MeOH, 50:1) gave 57 mg (43%) of **XXVII** as a green–yellow viscous oily material. ^{1}H NMR spectrum, δ, ppm: 1.53–1.57 m (2H, AdC**H**$_2$), 1.60–1.65 m (4H, Ad), 1.72 br.s (4H, Ad), 1,89 br.s (4H, Ad), 2.21 br.s (2H, 2-H, Ad), 3.22–3.26 m (2H, CH_2N), 3.90 br.s (1H, CH_2N**H**), 6.60 br.s (1H, C_6H_4N**H**), 6.68 d (1H, 5′-H, ^4J = 2.4 Hz), 7.06 d.d (1H, 7′-H, ^3J = 9.0, ^4J = 2.5 Hz), 7.18 d (2H, *m*-H, ^3J = 8.6 Hz), 7.22–7.27 m (2H, 3′-H, 3″-H), 7.30 d (1H, 5″-H, ^4J = 2.4 Hz), 7.33 d (2H, *o*-H, ^3J = 8.6 Hz), 7.39 d.d (1H, 7″-H, ^3J = 9.1, ^4J = 2.5 Hz), 7.86 d (1H, 8′-H, ^3J = 9.1 Hz), 7.88 d (1H, 4′-H, ^3J = 8.1 Hz), 7.90 d (1H, 4″-H, ^3J = 7.6 Hz), 7.95 d (1H, 8″-H, ^3J = 9.0 Hz), 8.59 d.d (1H, 2′-H, ^3J = 4.3, ^4J = 1.6 Hz), 8.68 d.d (1H, 2″-H, ^3J = 4.2, ^4J = 1.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.1 (2C, CH_{Ad}), 32.1 (1C, C_{Ad}), 36.0 (1C, CH_{2Ad}), 36.4 (1C, C_{Ad}), 38.5 (1C, Ad**C**H_2), 41.6 (2C, CH_{2Ad}), 42.5 (2C, CH_{2Ad}), 43.4 (1C, CH_2N), 48.5 (1C, CH_{2Ad}), 102.5 (1C, $C^{7'}$), 108.4 (1C, $C^{7''}$), 119.2 (2C, C^m); 121.3 (1C), 121.4 (2C), 122.8 (1C) (quinoline); 125.8 (2C, C^o), 129.6 (1C, $C^{4a''}$), 130.0 (1C, quinoline), 130.1 (1C, $C^{4a'}$); 130.3 (1C), 133.6 (1C), 134.1 (1C) (quinoline); 139.6 (1C, C^i), 142.1 (1C, C^p), 143.0 (1C, $C^{8a'}$), 144.0 (1C, $C^{8a''}$), 144.7 (1C, $C^{6''}$), 145.8 (1C, $C^{2'}$), 146.3 (1C, $C^{6'}$), 147.2 (1C, $C^{2''}$). Mass spectrum: *m*/*z* 525.298 $[M + H]^+$. $C_{36}H_{37}N_4$. Calculated: (*M* + H) 525.302.

***N*-[4-(3-{2-[Di(quinolin-6-yl)amino]ethyl}adamantan-1-yl)phenyl]-*N*-(quinolin-6-yl)quinolin-6-amine (XXVIII)** was isolated as by-product in the synthesis of **XXVII**. Yield 40 mg (41%; CH_2Cl_2–MeOH, 25:1), green–yellow viscous oily material. ^{1}H NMR spectrum, δ, ppm: 1.60–1.75 m (10H, Ad, AdC**H**$_2$), 1.90 br.s (4H, Ad), 2.23 br.s (2H, 2-HAd), 4.01–4.06 m (2H, CH_2N), 7.13 d (2H, *m*-H, ^3J = 8.7 Hz), 7.29 d (2H, 5′-H, ^4J = 2.0 Hz), 7.30–7.34 m (6H, quinoline, *o*-H), 7.37–7.40 m (2H, quinoline), 7.48 d.d (2H, 7′-H, ^3J = 9.2, ^4J = 2.5 Hz), 7.35 d.d (2H, 7″-H, ^3J = 9.1, ^4J = 2.4 Hz), 7.89 d (2H, 4′-H, ^3J = 8.2 Hz), 7.96–7.80 m (6H, 4″-H, 8′-H, 8″-H), 8.76 d.d (2H, 2′-H, ^3J = 4.0, ^4J = 1.6 Hz), 8.78 d.d (2H, 2″-H, ^3J = 4.2, ^4J = 1.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.1 (2C, CH_{Ad}), 32.1 (1C, C_{Ad}), 36.1 (1C, CH_{2Ad}), 36.7 (1C, C_{Ad}), 40.5 (1C, Ad**C**H_2), 41.3 (1C, CH_{2Ad}), 41.4 (1C, CH_{2Ad}), 42.5 (2C, CH_{2Ad}), 47.6 (1C, CH_2N), 48.3 (1C, CH_{2Ad}), 111.5 (2C, $C^{7'}$), 119.1 (2C, $C^{7''}$), 121.5 (4C, C^m, quinoline); 125.0 (2C), 125.8 (2C),

126.1 (2C), 127.6 (2C) (quinoline); 129.3 and 129.5 (2C each, $C^{4a'}$, $C^{4a''}$), 130.5 (4C, C^o, quinoline); 134.8 (2C), 134.9 (2C), 145.3 (2C), 145.5 (2C), 145.7 (2C), 147.3 (2C) (quinoline); 148.4 (2C, $C^{2'}$), 148.9 (2C, $C^{2''}$); signals from two quaternary carbon atoms were not identified. Mass spectrum: *m*/*z* 779.383 $[M + H]^+$. $C_{54}H_{47}N_6$. Calculated: (*M* + H) 779.386.

***N*-(4-Methylphenyl)quinolin-2-amine (XXX) and *N*-(4-methylphenyl)-*N*-(quinolin-2-yl)quinolin-2-amine (XXXI)** [15]**.** *a*. A mixture of 0.25 mmol (27 mg) of *p*-toluidine, 0.25 mmol (41 mg) of 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*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. According to the ^{1}H NMR data, the mixture contained compounds **XXX** and **XXXI** at a ratio of 0.1 : 1.

b. The conditions were the same as in *a*, but 6 mg (4 mol %) of $Pd(dba)_2$ and 7 mg (4.5 mol %) of XantPhos were used. According to the ^{1}H NMR data, the ratio **XXX**/**XXXI** was 0.8 : 1.

c. The conditions were the same as in *b*, but 7 mg (4.5 mol %) of DPEPhos was used as ligand. The ratio **XXX**/**XXXI** was 0.4 : 1.

d. The conditions were the same as in *b*, but 7 mg (4.5 mol %) of dppf was used as ligand. The ratio **XXX**/**XXXI** was 0.6 : 1.

Compound **XXX**. ^{1}H NMR spectrum, δ, ppm: 2.35 s (3H, CH_3), 6.92 d (1H, 3′-H, ^3J = 8.8 Hz), 6.97 d (2H, *o*-H, ^3J = 8.1 Hz), 7.25 t (1H, 6′-H, ^3J = 7.6 Hz), 7.46 d (2H, *m*-H, ^3J = 8.1 Hz), 7.57 t (1H, 7′-H, ^3J = 7.6 Hz), 7.61 d (1H, 5′-H, ^3J = 8.1 Hz), 7.78 d (1H, 8′-H, ^3J = 8.7 Hz), 7.83 d (1H, 4′-H, ^3J = 9.0 Hz); signal from the NH proton was not identified. ^{13}C NMR spectrum, δ_C, ppm: 20.8 (1C, CH_3), 111.6 (1C, $C^{3'}$), 120.8 (2C, C^o), 122.8 (1C, quinoline), 124.0 (1C, $C^{4a'}$), 129.6 (2C, C^m); 126.6 (1C), 127.3 (1C), 129.7 (1C), 137.4 (1C) (quinoline); 147.7 (1C, $C^{8a'}$), 156.6 (1C, $C^{2'}$); signals from two quaternary atoms were not identified.

Compound **XXXI**. ^{1}H NMR spectrum, δ, ppm: 2.40 s (3H, CH_3), 7.19–7.23 m (4H, C_6H_4), 7.29 d (2H, 3′-H, ^3J = 9.0 Hz), 7.39 t (2H, 6′-H, ^3J = 7.6 Hz), 7.57 t (2H, 7′-H, ^3J = 7.9 Hz), 7.71 d (2H, 5′-H, ^3J = 8.0 Hz), 7.79 d (2H, 8′-H, ^3J = 8.5 Hz), 7.97 d (2H, 4′-H, ^3J = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.1 (1C, CH_3), 117.7 (2C, CH_{Ph}), 124.7 (2C, C_{Ar}), 125.6 (2C, $C^{4a'}$), 127.1 (2C, C_{Ar}), 128.7 (2C, C_{Ar}), 128.0 (2C, C_{Ar}), 129.3 (2C, C_{Ar}), 130.2 (2C, C_{Ar}), 136.7 (1C, C^p), 136.9 (2C, $C^{4'}$), 141.8 (1C, C^i), 147.3 (2C, $C^{8a'}$), 156.6 (2C, $C^{2'}$).

***N*-(4-Methylphenyl)quinolin-4-amine (XXXII)** [16]**.** A mixture of 0.25 mmol (27 mg) of *p*-toluidine, 0.25 mmol (41 mg) of 4-chloroquinoline, 6 mg (4 mol %) of $Pd(dba)_2$, 7 mg (4.5 mol %) of BINAP, and 36 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. According to the ^{1}H NMR data, the yield of **XXXII** was 85%. ^{1}H NMR spectrum, δ, ppm: 2.36 s (3H, CH_3), 6.88 d (1H, 3′-H, ^3J = 5.3 Hz), 7.16–7.21 m (4H, C_6H_4), 7.43 t (1H, 6′-H, ^3J = 7.7 Hz), 7.64 t (1H, 7′-H, ^3J = 7.6 Hz), 7.96 d (1H, 8′-H, ^3J = 8.5 Hz), 8.02 d (1H, 5′-H, ^3J = 3.5 Hz), 8.52 d (1H, 2′-H, ^3J = 5.3 Hz); signal from the NH proton was not identified. ^{13}C NMR spectrum, δ_C, ppm: 20.9 (1C, CH_3), 101.6 (1C, $C^{3'}$), 119.5 (1C, $C^{4a'}$), 119.8 (1C, quinoline), 123.2 (2C, C^o); 125.0 (1C), 129.2 (1C), 129.9 (1C) (quinoline); 130.1 (2C, C^m), 134.5 (1C, C^p), 137.1 (1C, C^i), 148.1 (1C, $C^{8a'}$), 149.0 (1C, $C^{4'}$), 150.8 (1C, $C^{2'}$).

***N*-(4-Methylphenyl)quinolin-6-amine (XXXIII)** [17]**.** A mixture of 0.25 mmol (27 mg) of *p*-toluidine, 0.25 mmol (41 mg) of 6-chloroquinoline, 6 mg (4 mol %) of $Pd(dba)_2$, 7 mg (4.5 mol %) of BINAP, and 36 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane was heated for 7 h under reflux. According to the ^{1}H NMR data, the yield of **XXXIII** was 88%. ^{1}H NMR spectrum, δ, ppm: 2.34 s (3H, CH_3), 7.10–7.15 m (4H, C_6H_4), 7.24–7.27 m (2H, 5′-H, 3′-H), 7.35 d.d (1H, 7′-H, ^3J = 9.1, ^4J = 2.5 Hz), 7.87 d (1H, 4′-H, ^3J = 8.3 Hz), 7.95 d (1H, 8′-H, ^3J = 9.0 Hz), 8.68 d.d (1H, 2′-H, ^3J = 4.0, ^4J = 1.4 Hz); signal from the NH proton was not identified. ^{13}C NMR spectrum, δ_C, ppm: 20.7 (1C, CH_3), 107.9 (1C, $C^{7'}$), 119.9 (2C, C^o); 121.3 (1C), 122.6 (1C) (quinoline); 129.6 (1C, $C^{4a'}$), 129.9 (2C, C^m), 130.3 (1C, quinoline), 131.9 (1C, C^p), 134.1 (1C, quinoline), 139.3 (1C, C^i), 142.4 (1C, $C^{8a'}$), 144.0 (1C, $C^{6'}$), 147.1 (1C, $C^{2'}$).

This study was performed under financial support by the Russian Academy of Sciences (program no. P-8 “Development of Methodology of Organic Synthesis and Design of Compounds Possessing Valuable Practical Properties”) and by the Russian Foundation for Basic Research (project no. 10-03-01108).

REFERENCES

1. Grigorova, O.K., Averin, A.D., Abel’, A.S., Maloshitskaya, O.A., Kovalev, V.V., Savel’ev, E.N., Orlinson, B.S., Novakov, I.A., and Beletskaya, I.P., *Russ. J. Org. Chem*., 2012, vol. 48, p. 1391.

2. Khardin, A.P., Novakov, I.A, Radchenko, S.S., Brel', N.A., Kuznechikov, O.A., and Vygodskii, Ya.S., *Vysokomol. Soedin., Ser. B*, 1983, vol. 25, p. 433.
3. Popov, Yu.V., Korchagina, T.K., Chicherina, G.V., and Ermakova, T.A., *Russ. J. Org. Chem*., 2000, vol. 36, p. 601.
4. Sidorenko, E.V., Stroganov, V.F., Mikhal'chuk, V.M., Bondar', V.G., Kocherovskaya, E.S., Kretsul, I.I., Dorfman, G.A., and Kulagin, E.F., Russian Patent no. 1735329, 1992; *Chem. Abstr*., 1993, vol. 119, no. P118741w.
5. Aigami, K., Inamoto, Y., Takaishi, N., Hattori, K., Takatsuki, A., and Tamura, G., *J. Med. Chem*., 1975, vol. 18, p. 713.
6. Inamoto, Y., Aigami, K., and Kadono, T., JPN Patent Appl. no. 50-108252, 1975; *Chem. Abstr*., 1976, vol. 84, no. 58783.
7. Inamoto, Y., Aigami, K., Hattori, K., and Kakuno, T., JPN Patent Appl. no. 50-111218, 1975; *Chem. Abstr*., 1975, vol. 83, no. 188517.
8. Averin, A.D., Ranyuk, E.R., Buryak, A.K., Savelyev, E.N., Orlinson, B.S., Novakov, I.A., and Beletskaya, I.P., *Mendeleev Commun*. 2009, vol. 19, p. 136.
9. Ranyuk, E.R., Averin, A.D., Buryak, A.K., Savel'ev, E.N., Orlinson, B.S., Novakov, I.A., and Beletskaya, I.P., *Russ. J. Org. Chem*., 2009, vol. 45, p. 1555.
10. Averin, A.D., Ulanovskaya, M.A., Buryak, A.K., Savel'ev, E.N., Orlinson, B.S., Novakov, I.A., and Beletskaya, I.P., *Russ. J. Org. Chem*., 2011, vol. 47, p. 30.
11. Averin, A.D., Ranyuk, E.R., Golub, S.L., Buryak, A.K., Savelyev, E.N., Orlinson, B.S., Novakov, I.A., and Beletskaya, I.P., *Synthesis*, 2007, p. 2215.
12. Baranova, T.Yu., Abel', A.S., Averin, A.D., Savel'ev, E.N., Orlinson, B.S., Novakov, I.A., and Beletskaya, I.P., Abstracts of Papers, *2 Mezhdunarodnaya nauchnaya konferentsiya "Novye napravleniya v khimii geterotsiklicheskikh soedinenii"* (2nd Int. Scientific Conf. "New Lines in the Chemistry of Heterocyclic Compoundi"), Zheleznovodsk, April 25–30, 2011, p. 95.
13. Novikov, S.S., Khardin, A.P., Radchenko, S.S., Novakov, I.A., Orlinson, B.S., Blinov, V.F., Gorelov, V.I., and Zamakh, V.P., USSR Inventor's Certificate no. 682507, 1979; *Chem. Abstr*., 1979, vol. 91, no. P193887e.
14. Ukai, T., Kawazura, H., Ishii, Y., Bonnet, J.J., and Ibers, J.A., *J. Organomet. Chem*., 1974, vol. 65, p. 253.
15. Desmarets, S., Schneider, R., and Fort, Y., *J. Org. Chem*., 2002, vol. 67, p. 3029.
16. Katritzky, A.R., Huang, T.B., and Voronkov, M.V., *J. Org. Chem*., 2001, vol. 66, p. 1043.
17. Ogata, T. and Hartwig, J.F., *J. Am. Chem. Soc*., 2008, vol. 130, p. 13848.