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Arylation of Adamantanamines: III.* Palladium-Catalyzed Arylation of Adamantane-1,3-diyldimethanamine and 2,2′-(Adamantane-1,3-diyl)diethanamine

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Abstract—Palladium-catalyzed arylation of adamantane-1,3-diyldimethanamine and 2,2′-(adamantane-1,3-diyl)diethanamine with isomeric bromochloro- and dibromobenzenes was studied. The yields of *N*,*N*′-diarylation products depend on the initial diamine and dihalobenzene structure. Side reactions were revealed, which reduced the yield of the target products. The arylation of 2,2′-(adamantane-1,3-diyl)diethanamine gives the corresponding *N*,*N*′-diaryl derivatives with better yield. The possibility for synthesizing unsymmetrical *N*,*N*′-diaryl derivatives of 2,2′-(adamantane-1,3-diyl)diethanamine was demonstrated.

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In the preceding communications [1, 2] we reported on the results of our studies on palladium-catalyzed arylation of adamantane-containing monoamines. The synthesis of nitrogen-containing macrocycles from 2,2′-(adamantane-1,3-diyl)diethanamine was described in [3, 4]. Insofar as catalytic amination with participation of adamantane-containing amines is largely determined by the amine structure, we believed it reasonable to perform systematic study on palladium-catalyzed arylation of diamines of the adamantane series, which could give rise to wider diversity of N-aryl derivatives. Adamantane-1,3-diyldimethanamine and 2,2′-(adamantane-1,3-diyl)diethanamine were synthesized from the corresponding dicarboxylic acids through their chlorides, amides, and nitriles; the latter were reduced with lithium tetrahydridoaluminate in tetrahydrofuran with a yield of up to 63% [5, 6]. Antiviral properties of adamantane-1,3-diyldimethanamine and 2,2′-(adamantan-1,3-diyl)diethanamine hydrochlorides were examined in [6], and the latter turned out to be active against bird influenza viruses.

The applications of these amines are quite versatile. New carbocyclic Schiff bases were synthesized via reactions with aromatic aldehydes, and their biological activity was studied [7]. Stroganov et al. [8] studied specificity of vitrification of polymers upon hardening with diaminoadamantanes. Khardin and Pershin [9] proposed a procedure for the synthesis of diisocyanates by treatment of adamantane-containing diamine dihydrochlorides with phosgene. Diisocyanates are introduced into polymeric chain of polyurethanes to enhance their chemical resistance and photostability. Diamines of the adamantane series were used to synthesize polyamides that are characterized by higher heat resistance and hydrolytic stability than polymers based on adamantane-1,3-dicarboxylic acid [10]; moreover, polymers obtained from adamantane-1,3-diyldimethanamine showed a higher heat resistance than those derived from 2,2′-(adamantane-1,3-diyl)diethanamine. These diamines were also used to modify aromatic polyimides [11–13]. Polyimides containing adamantane fragments are more hydrolytically and thermally stable. Highly efficient rubber stabilizers were obtained on the basis of 2,2′-(adamantane-1,3-diyl)diethanamine [14, 15]. For example, doping with such its derivatives as 1,3-bis[2-(*m*-fluorobenzylideneamino)ethyl]adamantane and 1,3-bis[2-(*p*-methoxybenzylideneamino)ethyl]adamantane considerably im-

* For communication II, see [1].

proves mechanical properties of rubber, whereas 1,3-bis[2-(*p*-nitrobenzylideneamino)ethyl]adamantane possesses a high reactivity and probably antibacterial properties [16]. 2,2′-(Adamantane-1,3-diyl)diethanamine is also added to epoxy resins to improve their optical properties and durability [17].

Antiviral activity of various adamantane-containing amines was studied [18]. 2,2′-(Adamantane-1,3-diyl)-diethanamine turned out to be less active than adamantane-1,3-diyldimethanamine at a minimal inhibitory concentration. On the other hand, adamantane-1,3-diyldimethanamine dihydrochloride was patented as antiviral agent for pets [19, 20].

Development of a convenient procedure for the synthesis of *N*,*N*′-bis(haloaryl) derivatives of adamantane-containing diamines is important from the viewpoint of their potential physiological activity, as well as of their possible application as intermediate products for the preparation of complex macrocyclic compounds containing adamantane fragments via palladium-catalyzed amination.

Arylation of adamantane-1,3-diyldimethanamine. Initially, palladium-catalyzed arylation of adamantane-1,3-diyldimethanamine (**I**) was studied with the use of isomeric bromochlorobenzenes in the presence of fairly universal catalytic system $Pd(dba)_2$–BINAP [21] and sodium *tert*-butoxide as base. The reactions were carried out in boiling dioxane at a diamine concentration of 0.1 M and a diamine–dihalobenzene ratio of 1:2.2. The products were isolated by column chromatography on silica gel. Unexpectedly, diamine **I** showed unpredictable reactivity, as compared to the reactivity of analogous monoamines. The reaction of diamine **I** with bromobenzene gave a complex mixture of products, from which *N*,*N*′-diaryl derivative **II** was isolated in a relatively poor yield (29%); in addition, amino aldehyde **IX** and imine **X** were formed (Table 1, run no. 1). In the reaction with more sterically hindered *o*-bromochlorobenzene the corresponding diaryl derivative **III** was obtained in almost quantitative yield (Table 1, run no. 2). On the other hand, *meta*- and *para*-isomeric bromochlorobenzenes gave rise to compounds **IV** and **V** in moderate yield (31%; Table 1, run nos. 3, 4). The reaction of diamine **I** with *m*-bromochlorobenzene was accompanied by formation of various by-products, including those resulting from reduction of the C–Cl bond and oxidation of the initial diamine (compounds **II** and **IX**–**XIV**); in the reaction with *p*-bromochlorobenzene a considerable amount of aldehyde **XV** was isolated (Scheme 1).

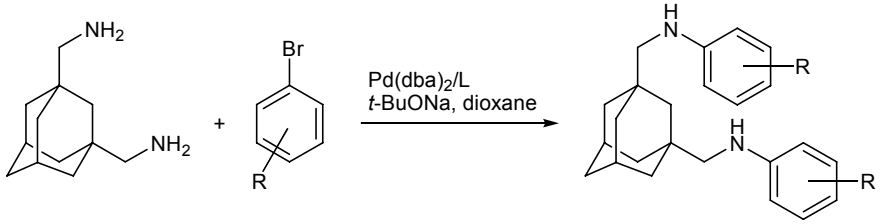
By-product mixtures (Table 1, run no. 3) were analyzed by NMR spectroscopy and MALDI-TOF mass spectrometry. However, it was almost impossible to estimate their composition, for different components contained similar molecular fragments. For example, a fraction isolated by elution with petroleum ether–methylene chloride (1:1) contained compound **IV**, reduction product **XI** (one C–Cl bond was reduced; *m*/*z* 380 $[M]^+$), aldehyde **XII** (*m*/*z* 303 $[M]^+$), and Schiff base **XIII** (*m*/*z* 412 $[M]^+$). Another fraction (eluent methylene chloride) was a mixture of compound **XII** with aldehyde **IX** (*m*/*z* 269 $[M]^+$) and Schiff bases **X** (*m*/*z* 344 $[M]^+$) and **XIV** (*m*/*z* 378 $[M]^+$). The reaction with *o*-dibromobenzene was much less successful than with *o*-bromochlorobenzene. Diarylation product **VI** was isolated in 30% yield, and a mixture of

Table 1. Palladium-catalyzed arylation of adamantane-1,3-diyldimethanamine (**I**); diamine–dihalobenzene ratio 1:2.2

Run no.	Dihalobenzene	Pd/L, molar ratio	Product (yield, %)
1	Bromobenzene	$Pd(dba)_2$/BINAP, 8:9	**II** (29), **IX** (19), **X** (12)
2	*o*-Bromochlorobenzene	$Pd(dba)_2$/BINAP, 4:4.5	**III** (95)
3[a]	*m*-Bromochlorobenzene	$Pd(dba)_2$/BINAP, 4:4.5	**IV** (31)
4[b]	*p*-Bromochlorobenzene	$Pd(dba)_2$/BINAP, 4:4.5	**V** (31), **XV** (25)
5	*o*-Dibromobenzene	$Pd(dba)_2$/BINAP, 4:4.5	**VI** (30), **XVI** (4), **XVII** (14)
6	*m*-Dibromobenzene	$Pd(dba)_2$/BINAP, 2:2.5	**VII** (0)
7	*m*-Dibromobenzene	$Pd(dba)_2$/Xantphos, 4:5	**VII** (0)
8[c]	*p*-Dibromobenzene	$Pd(dba)_2$/BINAP, 2:2.5	**VIII** (traces)
9	*p*-Dibromobenzene	$Pd(dba)_2$/Xantphos, 4:5	**VIII** (0)

[a] Some fractions contained mixtures of compounds **II**, **IV**, and **XI** and of **IX**, **X**, and **XII**–**XIV**.
[b] *p*-Chloroaniline (18%) and benzidine (7%) were also isolated.
[c] *p*-Bromoaniline (5%) and benzidine (5%) were also isolated.

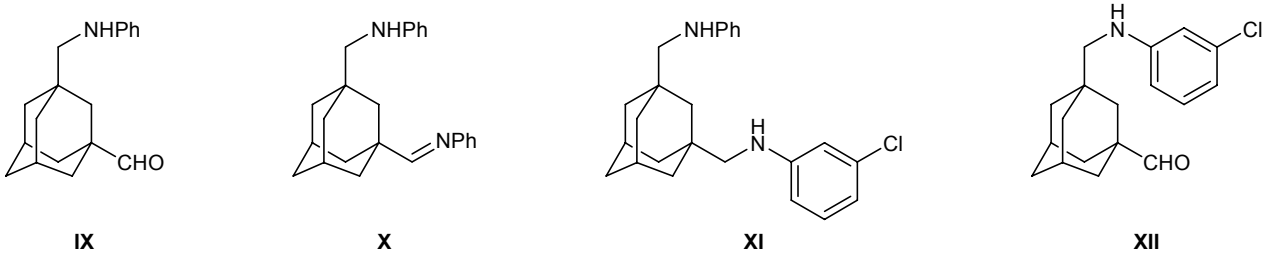
Scheme 1.



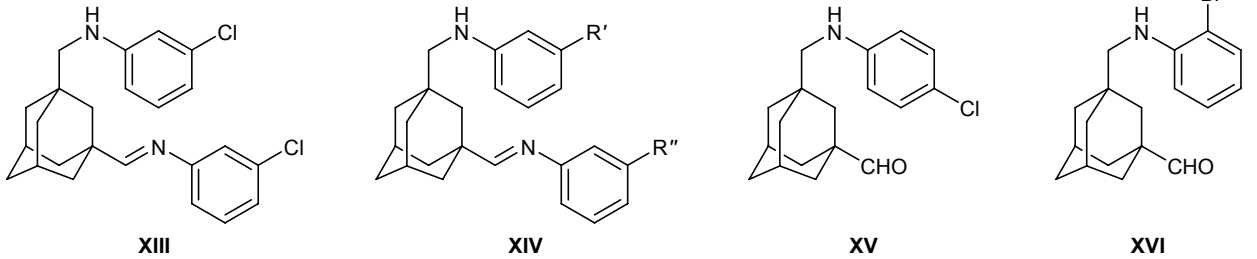
I **II–VIII**

II, R = H; **III**, R = *o*-Cl; **IV**, R = *m*-Cl; **V**, R = *p*-Cl; **VI**, R = *o*-Br; **VII**, R = *m*-Br; **VIII**, R = *p*-Br.

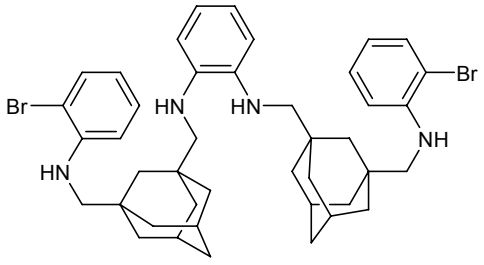
By-products:



IX **X** **XI** **XII**



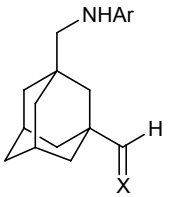
XIII **XIV** **XV** **XVI**



XVII

XIV, R′ = Cl or H, R″ = H or Br.

aldehyde **XVI** (yield 4%; (*m*/*z* 347 $[M]^+$) with linear oligomer **XVII** (14%; (*m*/*z* 770 $[M]^+$) was obtained; oligomer **XVII** was formed as a result of *ortho*-diamination of dibromobenzene (Table 1, run no. 5). The most complex pattern was observed in the reactions of diamine **I** with *m*- and *p*-dibromobenzenes. In the first case (Table 1, run no. 6), the ^{1}H NMR spectrum of the reaction mixture contained very weak signals from diarylation product **VII** at δ 2.12 (adamantane fragment) and 2.81 ppm (CH_2N). Signals at δ 2.20, 2.28 and 2.86, 2.90 ppm from the corresponding protons in compounds like **A** (X = O, NH, NR) were much more intense.



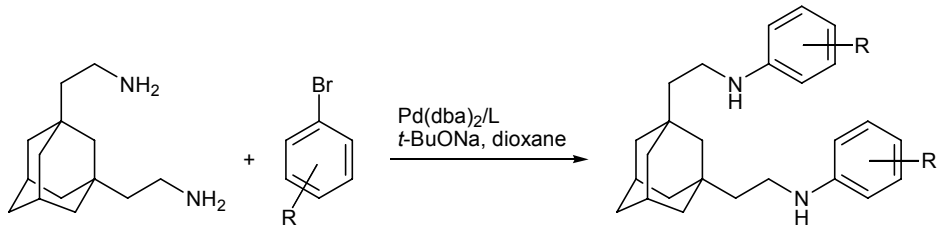
A

Numerous singlets in the region δ 7.54–7.61 ppm are typical of azomethine protons (CH=N). Signals in the aromatic region, assignable to *m*-bromoaniline derivatives, were very weak, indicating predominant contribution of processes involving reduction of

bromoarenes and oxidation of the initial amine. Insofar as the product mixture was very complex, it was unreasonable to separate it by chromatography. The selectivity of the reaction was not improved when less active ligand (Xantphos) was used (Table 1, run no. 7). Likewise, low selectivity was observed in the reaction of *p*-dibromobenzene with diamine **I** (Table 1, run no. 8). By column chromatography we isolated very small amounts of bromoaniline and biphenyl-4,4′-diamine (as a single fraction), but we failed to separate target compound **VIII** from other (unidentified) products. In the MALDI-TOF mass spectrum of that mixture we observed a ion peak with *m*/*z* 502, which corresponds to the molecular ion of compound **VIII**.

Arylation of 2,2′-(adamantane-1,3-diyl)diethanamine. 2,2′-(Adamantane-1,3-diyl)diethanamine (**XVIII**) reacted with dihaloarenes more selectively than did diamine **I**. The reaction of **XVIII** with 2.2 equiv of bromobenzene gave 75% of diarylation product **XIX** (Scheme 2; Table 2, run no. 1). In the reaction with *o*-bromochlorobenzene the yield of diaryl derivative **XX** reached 92% (Table 2, run no. 2). Although the reactions of **XVIII** with *m*- and *p*-bromochlorobenzenes were characterized by lower yields of *N*,*N*′-diaryl derivatives **XXI** and **XXII** (61 and 70%, respectively), the yields were much higher than those in analogous reactions of adamantane-1,3-diyldimethanamine (**I**) (cf. Table 1; run nos. 3, 4). However, diamine **XVIII** reacted with *o*-dibromobenzene fairly difficultly: in the presence of $Pd(dba)_2$–BINAP as catalytic system (regardless of its amount, 4–16 mol %) the yield of diarylation product **XXIII** was very poor, but a considerable amount of monoarylation product **XXVI** was formed (Table 2; run nos. 5, 6). An attempt to improve the results using DavePHOS as donor ligand was unsuccessful (Table 2, run no. 7). Compound **XXIV** (arylation product at both amino groups with *m*-dibromobenzene) was obtained in a higher yield in the presence of 2–4 mol % of the catalyst containing BINAP as ligand (Table 2; run nos. 8, 10); in all cases, an appreciable amount of linear oligomer **XXVII** was formed as a result of facile diamination of *m*-dibromobenzene. A mixture of compound **XXIV** with reduction product **XXVIII** and

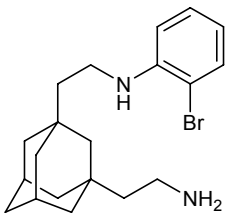
Scheme 2.



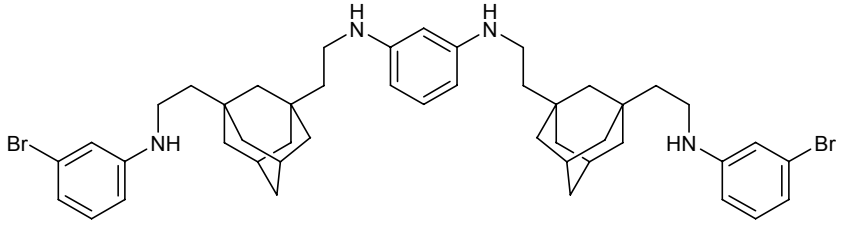
XVIII **XIX–XXV**

XIX, R = H; **XX**, R = *o*-Cl; **XXI**, R = *m*-Cl; **XXII**, R = *p*-Cl; **XXIII**, R = *o*-Br; **XXIV**, R = *m*-Br; **XXV**, R = *p*-Br.

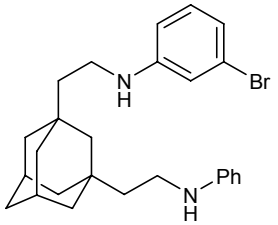
By-products:



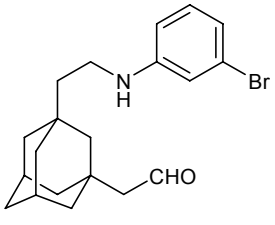
XXVI



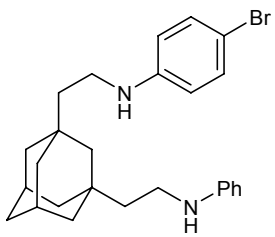
XXVII



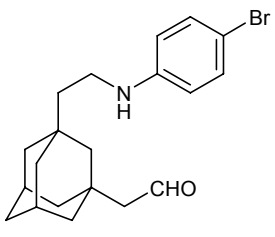
XXVIII



XXIX



XXX



XXXI

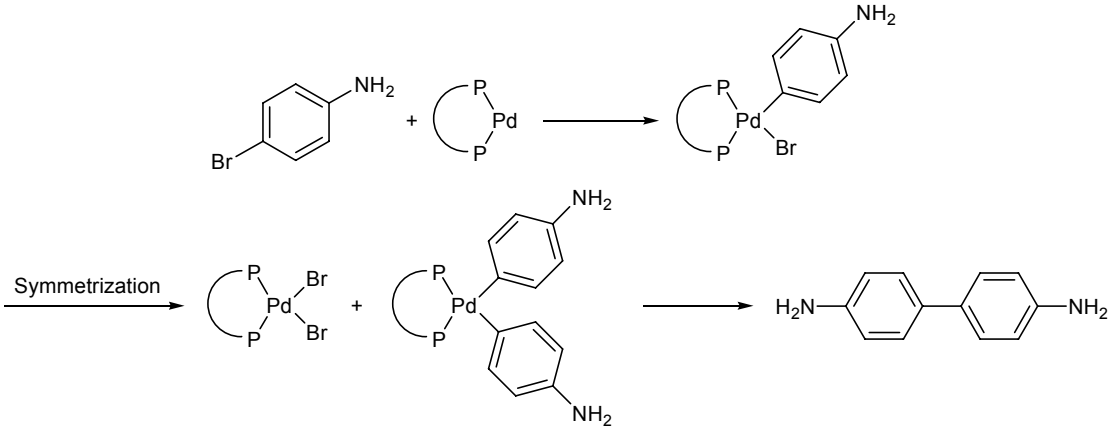
Table 2. Palladium-catalyzed arylation of 2,2′-(adamantane-1,3-diyl)diethanamine; ratio diamine–dihalobenzene 1 : 2.2

Run no.	Dihalobenzene	Pd/L, molar ratio	Product (yield, %)
1	Bromobenzene	$Pd(dba)_2$/BINAP, 8 : 9	**XIX** (75)
2	*o*-Bromochlorobenzene	$Pd(dba)_2$/BINAP, 4 : 4.5	**XX** (92)
3	*m*-Bromochlorobenzene	$Pd(dba)_2$/BINAP, 4 : 4.5	**XXI** (61)
4	*p*-Bromochlorobenzene	$Pd(dba)_2$/BINAP, 4 : 4.5	**XXII** (70)
5[a]	*o*-Dibromobenzene	$Pd(dba)_2$/BINAP, 4 : 4.5	**XXIII** (6), **XXVI** (20)
6[a]	*o*-Dibromobenzene	$Pd(dba)_2$/BINAP, 16 : 18	
7	*o*-Dibromobenzene	$Pd(dba)_2$/DavePHOS, 8 : 9	**XXVI** (15)
8	*m*-Dibromobenzene	$Pd(dba)_2$/BINAP, 4 : 4.5	**XXIV** (39), **XXVII** (19)
9[b]	*m*-Dibromobenzene	$Pd(dba)_2$/BINAP, 2 : 2.5	**XXIV** (26), **XXVII** (11)
10	*m*-Dibromobenzene	$Pd(dba)_2$/BINAP, 2 : 2.5	**XXIV** (27), **XXVII** (18)
11	*m*-Dibromobenzene	$Pd(dba)_2$/Xantphos, 8 : 9	**XXIV** (26), **XXVIII** (13)
12[c]	*p*-Dibromobenzene	$Pd(dba)_2$/BINAP, 4 : 4.5	**XXV** (11)

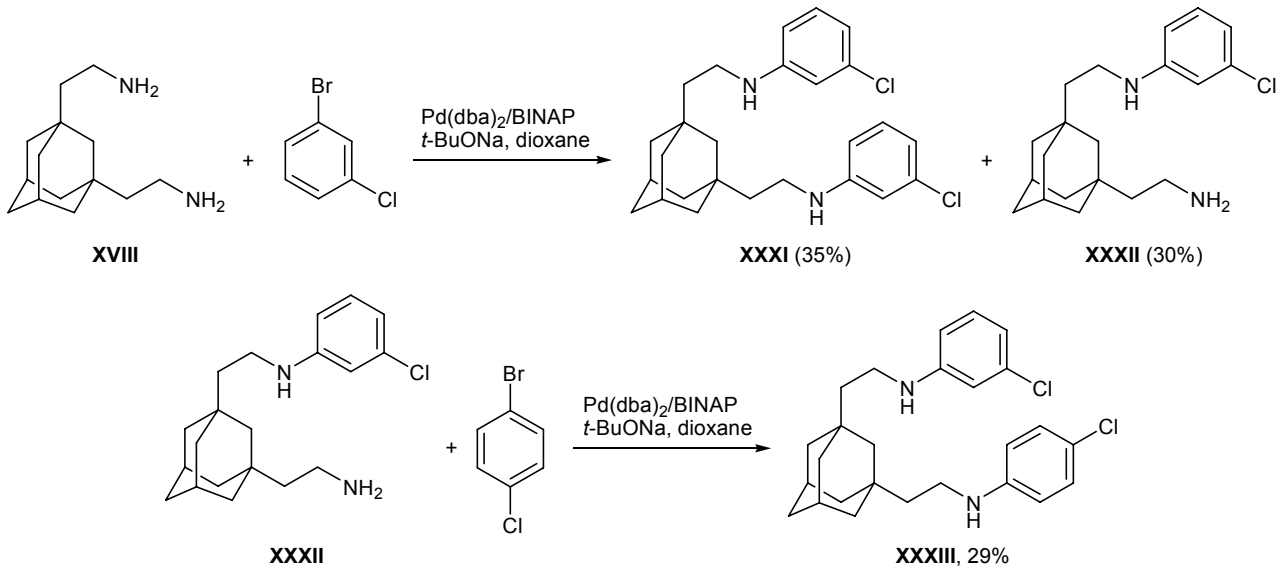
[a] Joint chromatographic separation of the product mixture isolated in two experiments.
[b] A separate fraction contained compounds **XXIV**, **XXVIII**, and **XXIX**.
[c] Benzidine (9%) was also isolated; a separate fraction contained compounds **XXV**, **XXX**, and **XXXI**.

partial oxidation product of diamine **XVIII** (aldehyde **XXIX**) was isolated as a separate fraction (Table 2, run no. 9). The N-substituted aniline fragment (reduction product) in diamine **XXVIII** gave rise to the following signals in the ^{1}H NMR spectrum, δ, ppm: 6.59 d (2H, ^3J = 8.6 Hz), 6.68 t (1H, ^3J = 7.4 Hz), 7.16 d.d (2H, ^3J = 8.5, 7.3 Hz); the CH_2CHO fragment in **XXIX** was characterized by signals at δ, ppm: 9.86 t (1H, ^3J = 3.3 Hz), 2.17 d (2H, ^3J = 3.3 Hz). The use of Xantphos to minimize diamination process completely suppressed the formation of compound **XXVII**; however, the yield of target product **XXIV** decreased, and compound **XXVIII** was formed (Table 2, run no. 11). *N*,*N*′-Bis(4-bromophenyl)-substituted diamine **XXV** was formed in a fairly good yield (47% in the reaction mixture), but chromatographic isolation of this compound was not complete (Table 2, run no. 12. In addition, benzidine was isolated as by-product (9%), and a separate fraction contained a mixture of diarylation product **XXV**, reduction product of one C–Br bond (**XXX**; *m*/z 452 $[M]^+$), and partial oxidation product **XXXI** (*m*/z 375 $[M]^+$). The N-substituted aniline fragment in diamine **XXX** was characterized by the following signals in the ^{1}H NMR spectrum, δ, ppm: 6.59 d (2H, ^3J = 7.6 Hz), 6.68 t (1H, ^3J = 7.3 Hz), 7.17 t (2H, ^3J = 7.9 Hz) (cf. the corresponding data for **XXVIII**); the corresponding carbon signals appeared in the ^{13}C NMR spectrum at δ_C 112.7 (2C), 117.1 (1C), and 129.2 ppm (2C). Protons in the CH_2CHO fragment of aldehyde **XXXI** resonated in the ^{1}H NMR spectrum

Scheme 3.



Scheme 4.



at δ, ppm: 9.86 t (1H, ^3J = 3.2 Hz), 2.16 d (2H, ^3J = 3.2 Hz); δ_C 203.3 (1C), 56.8 ppm (1C).

The formation of benzidine in the reaction of diamine **XVIII** with *p*-dibromobenzene may be rationalized as shown in Scheme 3. Initially, *p*-bromoaniline is formed according to the catalytic mechanism proposed in [1]. *p*-Bromoaniline is capable of reacting with palladium complex to give oxidative addition product which may undergo so-called symmetrization [22], so that benzidine is formed from two aminophenyl fragments. Analogous ligand exchange at the palladium atom could give rise to other products which were neither isolated as individual substances nor identified, but their formation could reduce the yield of the target product and make the product mixture more complex.

We also tried to obtain diarylation products of 2,2′-(adamantane-1,3-diyl)diethanamine (**XVIII**) with different aryl substituents on the nitrogen atoms (Scheme 4). For this purpose, diamine **XVIII** was brought into reaction with an equimolar amount of *m*-bromochlorobenzene. We thus isolated 30% of monoaryl derivative **XXXII** and 35% (calculated on the initial diamine) of diarylation product **XXI**. By reaction of compound **XXXII** with *p*-bromochlorobenzene we obtained 29% of unsymmetrically substituted diaryl derivative **XXXIII**.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker Avance-400 spectrometer at 400 and 100.6 MHz, respectively, using the residual proton and carbon signals of the solvent as reference ($CHCl_3$, δ 7.25 ppm; $CDCl_3$, δ_C 77.00 ppm). The MALDI-TOF mass spectra (positive ion detection) were obtained on a Bruker Daltonics Ultraflex instrument using 1,8,9-trihydroxyanthracene as matrix and polyethylene glycols as internal standards. Silica gel (Merck, 40–60 μm) was used for preparative column chromatography. Commercially available isomeric bromochloro- and dibromobenzenes, sodium *tert*-butoxide, and phosphine ligands were used without additional purification. Adamantane-1,3-diyldimethanamine (**I**) and 2,2′-(adamantane-1,3-diyl)diethanamine (**XVIII**) were synthesized as described in [23], and $Pd(dba)_2$ was prepared according to the procedure reported in [24] and used without additional recrystallization. Dioxane was distilled first over alkali and then over metallic sodium; methylene chloride, petroleum ether, and methanol were distilled prior to use.

***N*,*N*′-Diaryl-substituted diamines II–VIII, XIX–XXV, and XXXIII (*general procedure*).** A two-necked flask was charged under argon with the corresponding dihaloarene (0.2–0.25 mmol), $Pd(dba)_2$ (2–8 mol %), and phosphine ligand (2.5–9 mol %), 2 ml of anhydrous dioxane, 0.44–0.55 mmol of diamine **I** or **XVIII**, and 1.5–2 equiv of sodium *tert*-butoxide were added, and the mixture was heated for 7 h under reflux. The mixture was cooled, the precipitate was filtered off, the organic phase was evaporated under reduced pressure, the solid residue was dissolved in methylene chloride, the solution was washed with water, and the organic phase was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was

separated by chromatography on silica gel using the following solvent systems as eluents (in succession): petroleum ether–methylene chloride (4:1 to 1:4), methylene chloride, methylene chloride–methanol (500:1 to 100:1).

***N*-[3-(Phenylaminomethyl)adamantan-1-ylmethyl]aniline (II)** was synthesized from 0.25 mmol (48.5 mg) of diamine **I** and 0.55 mmol (86 mg) of bromobenzene in the presence of 11.5 mg (8 mol %) of $Pd(dba)_2$, 14 mg (9 mol %) of BINAP, and 80 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane. Yield (after chromatography; petroleum ether–CH_2Cl_2, 1:1) 25 mg (29%), colorless crystals, mp 101–103°C. ^{1}H NMR spectrum, δ, ppm: 1.41 s (2H), 1.50–1.64 m (8H), 1.66 br.s (2H), 2.12 br.s (2H), 2.85 s (4H), 3.64 br.s (2H), 6.61 d (4H, ^3J = 8.6 Hz), 6.66 t (2H, ^3J = 7.3 Hz), 7.15 d.d (4H, ^3J = 7.3, 8.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.5 (2C), 34.6 (2C), 36.5 (1C), 40.3 (4C), 43.8 (1C), 56.0 (2C), 112.6 (4C), 116.9 (2C), 129.2 (4C), 149.1 (2C). Mass spectrum: *m*/*z* 346.2390 $[M]^+$. $C_{24}H_{30}N_2$. Calculated: *M* 346.2409.

Elution with methylene chloride gave 9 mg (10%) of compound **II**, 14 mg (19%) of **IX**, and 10 mg (12%) of **X**.

3-(Phenylaminomethyl)adamantane-1-carbaldehyde (IX). ^{1}H NMR spectrum, δ, ppm: 1.48–1.84 m (12H), 2.19 br.s (2H), 2.89 s (2H), 3.65 br.s (1H), 6.61 d (2H, ^3J = 7.7 Hz), 6.67 t (1H, ^3J = 7.3 Hz), 7.15 t (2H, ^3J = 7.4 Hz), 9.36 s (1H). Mass spectrum: *m*/*z* 269.21 $[M]^+$.

***N*-[3-(Phenylaminomethyl)adamantan-1-ylmethylidene]aniline (X).** ^{1}H NMR spectrum, δ, ppm: 1.48–1.84 m (12H), 2.28 br.s (2H), 2.90 s (2H), 3.65 br.s (1H), 6.61 d (2H, ^3J = 7.7 Hz), 6.67 t (1H, ^3J = 7.3 Hz), 6.98 d (2H, ^3J = 8.2 Hz), 7.15 t (2H, ^3J = 7.4 Hz), 7.31 t (2H, ^3J = 7.8 Hz), 7.57 s (1H); signal from one proton was not assigned unambiguously. Mass spectrum: *m*/*z* 344.25 $[M]^+$.

2-Chloro-*N*-[3-(2-chlorophenylaminomethyl)-adamantan-1-ylmethyl]aniline (III) was synthesized from 0.2 mmol (39 mg) of diamine **I** and 0.44 mmol (84 mg) of *o*-bromochlorobenzene in the presence of 4.5 mg (4 mol %) of $Pd(dba)_2$, 5.5 mg (4.5 mol %) of BINAP, and 80 mg (2 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane. Yield 79 mg (95%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.44 s (2H), 1.50–1.66 m (8H), 1.67 s (2H), 2.14 br.s (2H), 2.91 d (4H, ^3J = 5.9 Hz), 4.37 br.s (2H), 6.59 t (2H, ^3J = 7.6 Hz), 6.67 d (2H, ^3J = 8.1 Hz), 7.11 t (2H, ^3J = 7.8 Hz), 7.24 d (2H, ^3J = 8.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.3 (2C), 34.7 (2C), 36.3 (1C), 40.1 (4C), 43.8 (1C), 55.4 (2C), 111.1 (2C), 116.6 (2C), 118.9 (2C), 127.7 (2C), 129.0 (2C), 144.6 (2C). Mass spectrum: *m*/*z* 414.1603 $[M]^+$. $C_{24}H_{28}Cl_2N_2$. Calculated: *M* 414.1630.

3-Chloro-*N*-[3-(3-chlorophenylaminomethyl)-adamantan-1-ylmethyl]aniline (IV) was synthesized from 0.2 mmol (39 mg) of diamine **I** and 0.44 mmol (84 mg) of *m*-bromochlorobenzene in the presence of 4.5 mg (4 mol %) of $Pd(dba)_2$, 5.5 mg (4.5 mol %) of BINAP, and 80 mg (2 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane. Yield (after chromatography; petroleum ether–CH_2Cl_2, 2:1) 26 mg (31%), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.36 s (2H), 1.45–1.58 m (8H), 1.64 s (2H), 2.12 br.s (2H), 2.82 d (4H, ^3J = 5.5 Hz), 3.73 br.s (2H), 6.46 d.d.d (2H, ^3J = 8.3, ^4J = 2.2, 0.7 Hz), 6.57 t (2H, ^4J = 2.1 Hz), 6.61 d.d.d (2H, ^3J = 7.8, ^4J = 1.9, 0.8 Hz), 7.03 t (2H, ^3J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.3 (2C), 34.7 (2C), 36.3 (1C), 40.1 (4C), 43.6 (1C), 55.6 (2C), 111.10 (2C), 112.1 (2C), 116.7 (2C), 130.1 (2C), 135.0 (2C), 150.1 (2C). Mass spectrum: *m*/*z* 414.1699 $[M]^+$. $C_{24}H_{28}Cl_2N_2$. Calculated: *M* 414.1630. Elution with petroleum ether–CH_2Cl_2 (1:1) gave a mixture of compound **IV**, partial reduction product **XI**, and compounds **XII** and **XIII**. Elution with methylene chloride gave a mixture of compounds **IX**, **X**, **XIII**, and **XIV**.

4-Chloro-*N*-[3-(4-chlorophenylaminomethyl)-adamantan-1-ylmethyl]aniline (V) was synthesized from 0.2 mmol (39 mg) of diamine **I** and 0.44 mmol (84 mg) of *p*-bromochlorobenzene in the presence of 4.5 mg (4 mol %) of $Pd(dba)_2$, 5.5 mg (4.5 mol%) of BINAP, and 80 mg (2 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane. Yield (after chromatography; petroleum ether–CH_2Cl_2, 2:1, 1:1) 26 mg (31%), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.37 s (2H), 1.47–1.59 m (8H), 1.64 br.s (2H), 2.12 br.s (2H), 2.80 s (4H), 3.68 br.s (2H), 6.52 d (4H, ^3J = 8.8 Hz), 7.08 d (4H, ^3J = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.4 (2C), 34.7 (2C), 36.4 (1C), 40.1 (4C), 43.6 (1C), 56.1 (2C), 113.7 (4C), 121.4 (2C), 129.0 (4C), 147.6 (2C). Mass spectrum: *m*/*z* 414.1596 $[M]^+$. $C_{24}H_{28}Cl_2N_2$. Calculated: *M* 414.1630. Elution with methylene chloride gave 15 mg (25%) of compound **XV** containing *p*-chloroaniline (18 mol %) and benzidine (7 mol %) as impurities.

3-(4-Chlorophenylaminomethyl)adamantane-1-carbaldehyde (XV). ^{1}H NMR spectrum, δ, ppm: 1.50–

1.85 m (12H), 2.19 br.s (2H), 2.85 s (2H), 3.69 br.s (1H), 6.52 d (2H, ^3J = 8.7 Hz), 7.08 d (2H, ^3J = 8.7 Hz), 9.35 s (1H). ^{13}C NMR spectrum, δ_C, ppm: 27.5 (2C), 35.2 (1C), 35.5 (2C), 35.9 (1C), 38.8 (1C), 39.8 (2C), 45.5 (1C) 55.7 (1C), 113.76 (2C), 120.5 (1C), 129.0 (2C), 147.5 (1C), 205.3 (1C). Mass spectrum: *m*/*z* 303.1388 $[M]^+$. $C_{18}H_{22}ClNO$. Calculated: *M* 303.1390.

2-Bromo-*N*-[3-(2-bromophenylaminomethyl)-adamantan-1-ylmethyl]aniline (VI) was synthesized from 0.2 mmol (39 mg) of diamine **I** and 0.44 mmol (104 mg) of *o*-dibromobenzene in the presence of 4.5 mg (4 mol %) of $Pd(dba)_2$, 5.5 mg (4.5 mol %) of BINAP, and 80 mg (2 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane. Yield (after chromatography; petroleum ether–CH_2Cl_2, 2:1) 30 mg (30%), colorless crystals, mp 135–137°C. ^{1}H NMR spectrum, δ, ppm: 1.44 s (2H), 1.50–1.65 m (8H), 1.67 s (2H), 2.14 br.s (2H), 2.90 d (4H, ^3J = 5.8 Hz), 4.37 t (2H, ^3J = 4.6 Hz), 6.52 t.d (2H, ^3J = 7.6, ^4J = 1.4 Hz), 6.64 d (2H, ^3J = 8.2 Hz), 7.14 t.d (2H, ^3J = 7.8, ^4J = 1.2 Hz), 7.39 d.d (2H, ^3J = 7.9, ^4J = 1.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.4 (2C), 34.7 (2C), 36.3 (1C), 40.2 (4C), 43.8 (1C), 55.6 (2C), 109.8 (2C), 111.2 (2C), 117.2 (2C), 128.4 (2C), 132.3 (2C), 145.6 (2C). Mass spectrum: *m*/*z* 502.11 $[M]^+$. Using the same eluent, a mixture of compounds **XVI** and **XVII** was isolated.

***N*-{2-[3-(2-Phenylaminoethyl)adamantan-1-yl]-ethyl}aniline (XIX)** was synthesized from 0.25 mmol (56 mg) of diamine **XVIII** and 0.55 mmol (86 mg) of bromobenzene in the presence of 11.5 mg (8 mol %) of $Pd(dba)_2$, 14 mg (9 mol %) of BINAP, and 80 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane. Yield 70 mg (75%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.37 s (2H), 1.46 t (4H, ^3J = 8.1 Hz), 1.48–1.61 m (8H), 1.67 s (2H), 2.10 br.s (2H), 3.15 t (4H, ^3J = 7.9 Hz), 3.51 br.s (2H), 6.64 d (4H, ^3J = 7.6 Hz), 6.73 t (2H, ^3J = 7.3 Hz), 7.21 d.d (4H, ^3J = 8.5, 7.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.8 (2C), 32.6 (2C), 36.4 (1C), 38.5 (2C), 41.9 (4C), 43.6 (2C), 47.7 (1C), 112.6 (4C), 117.0 (2C), 129.1 (4C), 148.4 (2C). Mass spectrum: *m*/*z* 374.2790 $[M]^+$. $C_{26}H_{34}N_2$. Calculated: *M* 374.2722.

2-Chloro-*N*-(2-{3-[2-(2-chlorophenylamino)-ethyl]adamantan-1-yl}ethyl)aniline (XX) was synthesized from 0.25 mmol (56 mg) of diamine **XVIII** and 0.55 mmol (105 mg) of *o*-bromochlorobenzene in the presence of 5.5 mg (4 mol %) of $Pd(dba)_2$, 7 mg (4.5 mol %) of BINAP, and 80 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane. Yield 86 mg (92%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.38 s (2H), 1.48–1.62 m (12H), 1.66 br.s (2H), 2.10 br.s (2H), 3.18 t (4H, ^3J = 8.0 Hz), 4.16 t (2H, ^3J = 4.7 Hz), 6.63 t.d (2H, ^3J = 7.6, ^4J = 1.4 Hz), 6.67 d (2H, ^3J = 8.1 Hz), 7.16 t.d (2H, ^3J = 7.8, ^4J = 1.4 Hz), 7.26 d.d (2H, ^3J = 7.6, ^4J = 1.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.9 (2C), 32.7 (2C), 36.4 (1C), 38.2 (2C), 41.9 (4C), 43.3 (2C), 47.6 (1C), 111.0 (2C), 116.8 (2C), 118.9 (2C), 127.7 (2C), 129.0 (2C), 144.1 (2C). Mass spectrum: *m*/*z* 442.2002 $[M]^+$. $C_{26}H_{32}Cl_2N_2$. Calculated: *M* 442.1943.

3-Chloro-*N*-(2-{3-[2-(3-chlorophenylamino)-ethyl]adamantan-1-yl}ethyl)aniline (XXI) was synthesized from 0.25 mmol (56 mg) of diamine **XVIII** and 0.55 mmol (105 mg) of *m*-bromochlorobenzene in the presence of 5.5 mg (4 mol %) of $Pd(dba)_2$, 7 mg (4.5 mol %) of BINAP, and 80 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane. Yield 57 mg (61%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.32 s (2H), 1.41 t (4H, ^3J = 8.0 Hz), 1.43–1.58 m (8H), 1.63 br.s (2H), 2.07 br.s (2H), 3.04–3.11 m (4H), 3.57 t (2H, ^3J = 4.6 Hz), 6.44 d (2H, ^3J = 8.1 Hz), 6.56 t (2H, ^4J = 1.9 Hz), 6.64 d (2H, ^3J = 7.7 Hz), 7.06 t (2H, ^3J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.8 (2C), 32.7 (2C), 36.3 (1C), 38.4 (2C), 41.9 (4C), 43.4 (2C), 47.7 (1C), 111.0 (2C), 112.1 (2C), 116.8 (2C), 130.1 (2C), 134.9 (2C), 149.6 (2C). Mass spectrum: *m*/*z* 442.1919 $[M]^+$. $C_{26}H_{32}Cl_2N_2$. Calculated: *M* 442.1943.

4-Chloro-*N*-(2-{3-[2-(4-chlorophenylamino)-ethyl]adamantan-1-yl}ethyl)aniline (XXII) was synthesized from 0.25 mmol (56 mg) of diamine **XVIII** and 0.55 mmol (105 mg) of *p*-bromochlorobenzene in the presence of 5.5 mg (4 mol %) of $Pd(dba)_2$, 7 mg (4.5 mol %) of BINAP, and 80 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane. Yield 65 mg (70%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.31 s (2H), 1.40 t (4H, ^3J = 8.0 Hz), 1.42–1.58 m (8H), 1.63 br.s (2H), 2.06 br.s (2H), 3.02–3.10 m (4H), 3.51 t (2H, ^3J = 4.8 Hz), 6.50 d (4H, ^3J = 8.8 Hz), 7.11 d (4H, ^3J = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.8 (2C), 32.6 (2C), 36.3 (1C), 38.6 (2C), 41.8 (4C), 43.4 (2C), 47.7 (1C), 113.6 (4C), 121.9 (2C), 128.9 (4C), 147.0 (2C). Mass spectrum: *m*/*z* 442.1887 $[M]^+$. $C_{26}H_{32}Cl_2N_2$. Calculated: *M* 442.1943.

2-Bromo-*N*-(2-{3-[2-(2-bromophenylamino)-ethyl]adamantan-1-yl}ethyl)aniline (XXIII). *a*. Compound **XXIII** was synthesized from 0.25 mmol (56 mg) of diamine **XVIII** and 0.55 mmol (130 mg) of *o*-dibrombenzene in the presence of 5.5 mg (4 mol %) of $Pd(dba)_2$, 7 mg (4.5 mol %) of BINAP, and 80 mg

(1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane.

b. The synthesis was performed in the presence of 23 mg (16 mol %) of $Pd(dba)_2$ and 28 mg (18 mol %) of BINAP.

The products obtained in the two experiments were combined and subjected to chromatography using petroleum ether–CH_2Cl_2 (2:1) as eluent. Yield 15 mg (6%), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.38 s (2H), 1.47–1.58 m (12H), 1.63 br.s (2H), 2.08 br.s (2H), 3.16 t (4H, ^3J = 7.9 Hz), 4.15 br.s (2H), 6.55 t.d (2H, ^3J = 7.6, ^4J = 1.0 Hz), 6.62 d.d (2H, ^3J = 8.2, ^4J = 1.0 Hz), 7.17 t.d (2H, ^3J = 7.8, ^4J = 1.0 Hz), 7.40 d.d (2H, ^3J = 7.8, ^4J = 1.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.9 (2C), 32.8 (2C), 36.4 (1C), 38.6 (2C), 42.0 (4C), 43.3 (2C), 47.7 (1C), 109.6 (2C), 111.1 (2C), 117.4 (2C), 128.5 (2C), 132.3 (2C), 145.1 (2C). Mass spectrum: *m*/*z* 530.01 $[M]^+$.

Elution with CH_2Cl_2–MeOH (3:1) gave 37 mg (20%) of monoarylation product **XXVI**.

2-Bromo-*N*-{2-[3-(2-aminoethyl)adamantan-1-yl]ethyl}aniline (XXVI). ^{1}H NMR spectrum, δ, ppm: 1.36–1.63 m (16H), 2.01 br.s (2H), 2.96–3.03 m (2H), 3.09 t (2H, ^3J = 7.2 Hz), 4.10 br.s (1H), 6.52 t.d (1H, ^3J = 7.6, ^4J = 1.4 Hz), 6.60 d.d (1H, ^3J = 8.2, ^4J = 1.1 Hz), 7.15 t.d (1H, ^3J = 7.7, ^4J = 1.4 Hz), 7.37 d.d (1H, ^3J = 7.8, ^4J = 1.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.7 (2C), 32.5 (1C), 32.6 (1C), 35.5 (1C), 36.1 (1C), 38.4 (1C), 41.1 (1C), 41.4 (2C), 41.7 (2C), 43.1 (1C), 47.2 (1C), 109.5 (1C), 111.2 (1C), 117.4 (1C), 128.5 (1C), 132.2 (1C), 145.0 (1C). Mass spectrum: *m*/*z* 376.20 $[M]^+$.

3-Bromo-*N*-(2-{3-[2-(3-Bromophenylamino)-ethyl]adamantan-1-yl}ethyl)aniline (XXIV). *a*. Compound **XXIV** was synthesized from 0.25 mmol (56 mg) of diamine **XVIII** and 0.55 mmol (130 mg) of *m*-dibromobenzene in the presence of 3 mg (2 mol %) of $Pd(dba)_2$, 4 mg (2.5 mol %) of BINAP, and 80 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane. Yield (after chromatography; petroleum ether–CH_2Cl_2, 1:1) 34 mg (26%), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.32 s (2H), 1.41 t (4H, ^3J = 8.0 Hz), 1.44–1.56 m (8H), 1.62 br.s (2H), 2.06 br.s (2H), 3.07 t (4H, ^3J = 8.0 Hz), 6.48 d.d.d (2H, ^3J = 8.2, ^4J = 2.2, 0.9 Hz), 6.71 t (2H, ^4J = 2.0 Hz), 6.78 d.d.d (2H, ^3J = 7.8, ^4J = 1.8, 0.9 Hz), 6.99 t (2H, ^3J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.9 (2C), 32.7 (2C), 36.4 (1C), 38.5 (2C), 41.9 (4C), 43.5 (2C), 47.7 (1C), 111.5 (2C), 115.0 (2C), 119.8 (2C), 123.3 (2C), 130.4 (2C), 149.7 (2C). Mass spectrum: *m*/*z* 530.08 $[M]^+$. Elution with methylene chloride gave a mixture of compound **XXIV**, reduction product **XXVIII**, and aldehyde **XXIX**.

b. The synthesis was performed using double amounts of the reactants and catalyst. Elution with methylene chloride gave 73 mg (27%) of compound **XXIV**; the subsequent elution with the same eluent afforded 38 mg (18%) of oligomer **XXVII**.

***N*,*N*′-Bis(2-{3-[2-(3-bromophenylamino)ethyl]-adamantan-1-yl}ethyl)benzene-1,3-diamine (XXVII).** ^{1}H NMR spectrum, δ, ppm: 1.31 s (4H), 1.38–1.57 m (24H), 1.61 br.s (4H), 2.05 br.s (4H), 3.02–3.12 m (8H), 3.48 br.s (2H), 3.65 br.s (2H), 5.85 br.s (1H), 5.99 d.d (2H, ^3J = 8.1, ^4J = 2.1 Hz), 6.48 d.d (2H, ^3J = 8.2, ^4J = 2.1 Hz), 6.70 t (2H, ^4J = 1.8 Hz), 6.77 d (2H, ^3J = 7.9 Hz), 6.97 t (1H, ^3J = 8.2 Hz), 6.99 t (2H, ^3J = 8.1 Hz).

4-Bromo-*N*-(2-{3-[2-(4-bromophenylamino)-ethyl]adamantan-1-yl}ethyl)aniline (XXV) was synthesized from 0.25 mmol (56 mg) of diamine **XVIII** and 0.55 mmol (130 mg) of *p*-dibromobenzene in the presence of 5.5 mg (4 mol %) of $Pd(dba)_2$, 7 mg (4.5 mol %) of BINAP, and 80 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane. Yield (after chromatographic separation; petroleum ether–CH_2Cl_2, 1:1) 14 mg (11%), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.31 s (2H), 1.40 t (4H, ^3J = 8.1 Hz), 1.42–1.56 m (8H) 1.61 br.s (2H), 2.06 br.s (2H), 3.06 t (4H, ^3J = 8.0 Hz), 3.56 br.s (2H), 6.45 d (4H, ^3J = 8.9 Hz), 7.23 d (4H, ^3J = 8.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.9 (2C), 32.7 (2C), 36.4 (1C), 38.7 (2C), 41.9 (4C), 43.5 (2C), 47.8 (1C), 108.6 (2C), 114.2 (4C), 131.9 (4C), 147.4 (2C). Mass spectrum: *m*/*z* 530.0880 $[M]^+$. $C_{26}H_{32}Br_2N_2$. Calculated: *M* 530.0932. Elution with petroleum ether–CH_2Cl_2 (4:1) gave 4 mg (9%) of benzidine, elution with petroleum ether–CH_2Cl_2 (1:1) gave 3 mg (7%) of *p*-bromoaniline, and a mixture of compound **XXV**, reduction product **XXX**, and aldehyde **XXXI** was isolated by elution with methylene chloride.

***N*-{2-[3-(2-Aminoethyl)adamantan-1-yl]ethyl}-3-chloroaniline (XXXII)** was synthesized from 0.625 mmol (139 mg) of diamine **XVIII** and 0.625 mmol (120 mg) of *m*-bromochlorobenzene in the presence of 7 mg (2 mol %) of $Pd(dba)_2$, 10 mg (2.5 mol %) of BINAP, and 100 mg (1.5 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane. By chromatography using petroleum ether–CH_2Cl_2 (1:1) as eluent we isolated 48 mg (35%) of diarylation product **XXI**, and elution with CH_2Cl_2–MeOH (first

5:1 and then 2.5:1) gave 62 mg (30%) of compound **XXXII** as a colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.25 s (2H), 1.32–1.51 m (12H), 1.57 br.s (2H), 2.01 br.s (2H), 2.76 t (2H, ^3J = 8.3 Hz), 3.04 t (2H, ^3J = 7.8 Hz), 3.58 br.s (1H), 3.72 br.s (2H), 6.42 d.d (1H, ^3J = 8.2, ^4J = 1.4 Hz), 6.53 br.s (1H), 6.61 d (1H, ^3J = 7.7 Hz), 7.03 t (1H, ^3J = 8.0 Hz). ^{13}C NMR spectrum, δ, ppm: 28.8 (2C), 32.6 (2C), 36.1 (1C), 36.3 (1C), 38.4 (1C), 41.7 (2C), 41.8 (2C), 43.4 (1C), 46.2 (1C), 47.6 (1C), 111.0 (1C), 112.1 (1C), 116.8 (1C), 130.1 (1C), 134.9 (1C), 149.6 (1C). Mass spectrum: *m*/*z* 332.2040 $[M]^+$. $C_{20}H_{29}ClN_2$. Calculated *M* 332.2019.

3-Chloro-*N*-(2-{3-[2-(4-chlorophenylamino)-ethyl]adamantan-1-yl}ethyl)aniline (XXXIII) was synthesized from 0.186 mmol (62 mg) of compound **XXXII** and 0.209 mmol (40 mg) of *p*-bromochlorobenzene in the presence of 4.5 mg (4 mol %) of $Pd(dba)_2$, 6 mg (4.5 mol %) of BINAP, and 40 mg (2 equiv) of sodium *tert*-butoxide in 2.5 ml of anhydrous dioxane. By chromatography using petroleum ether–CH_2Cl_2 (1:1) as eluent we isolated 24 mg (29%) of compound **XXXIII** as a colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.32 s (2H), 1.41 t (4H, ^3J = 8.1 Hz), 1.43–1.57 m (8H) 1.62 br.s (2H), 2.06 br.s (2H), 3.07 t (4H, ^3J = 8.1 Hz), 3.51 br.s (2H), 6.44 d.d.d (1H, ^3J = 8.2, ^4J = 2.1, 0.8 Hz), 6.50 d (2H, ^3J = 8.8 Hz), 6.55 t (1H, ^3J = 2.0 Hz), 6.64 d.d.d (1H, ^3J = 7.9, ^4J = 1.8, 0.8 Hz), 7.05 t (1H, ^3J = 8.0 Hz), 7.10 d (2H, ^3J = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.9 (2C), 32.7 (2C), 36.4 (1C), 38.5 (1C), 38.8 (1C), 41.9 (4C), 43.5 (2C), 47.8 (1C), 111.1 (1C), 112.1 (1C), 113.7 (2C), 116.9 (1C), 121.6 (1C), 129.0 (2C), 130.1 (1C), 135.0 (1C), 147.0 (1C), 149.6 (1C). Mass spectrum: *m*/*z* 442.1958 $[M]^+$. $C_{26}H_{32}Cl_2N_2$. Calculated *M* 442.1943.

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