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Palladium-Catalyzed Amination of Isomeric Dihalobenzenes with 1- and 2-Aminoadamantanes

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Abstract—Palladium-catalyzed amination of isomeric bromochloro- and dibromobenzenes with 1- and 2-aminoadamantanes was studied. The best yields of the corresponding monoamination products were obtained in the reactions of 2-aminoadamantane with bromochlorobenzenes. The arylation of 1-aminoadamantane was successful in the presence of donor phosphine ligand. The amination of *o*- and *m*-dibromobenzenes was strongly complicated by formation of diamination products. Conditions ensuring predominant formation of the latter were found. The arylation of 2-aminoadamantane was accompanied by oxidation of the initial amine and reduction of aryl halide.

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Adamantane is one of the simplest cage-like hydrocarbons, which attracts researchers' attention over a period of more than 50 years. Up to now, thousands compounds containing an adamantane fragment have been synthesized and studied, and many of them have found applications in various fields of practice, primarily as physiologically active substances. Aminoadamantanes and their derivatives are especially interesting as potential medicines; for example, adamantan-1-amine hydrochloride (amantadine) turned out to be effective in the treatment of Parkinson's disease [1, 2] and was also used in the treatment of hepatitis C [3]. 1-(1-Adamantyl)ethanamine (rimantadine) [4] is widely used as antiviral agent, memantine (derivative with two amino groups) [5] is an *N*-methyl D-aspartate receptor antagonist; many other drugs have more complex structures and often contain aromatic fragments; examples are chlodantane (immunostimulant) [6], ladasten (neurostimulator) [7], etc. Most publications deal with adamantan-1- and -2-amine derivatives possessing an amide group; many hundreds of such compounds have already been reported. In the recent years, successful biological tests have been performed with various *N*-aryl- and *N*-hetarylaminoadamantanes, including those containing halogen atoms (fluorine, chlorine, bromine) in the aromatic substituent. Therefore, we set ourselves the task of developing a convenient procedure for the synthesis of a new family of *N*-haloaryl-substituted adamantanamines with a view to subsequently test them for biological activity.

There are hundreds publications on the synthesis and applications of adamantan-1-amine; however, published data on the synthesis of its *N*-aryl derivatives are very scanty. Olifirov et al. [8] synthesized *N*-phenyladamantan-1-amine in 51% yield from adamantan-1-ol and aniline in the presence of aniline hydrochloride or aluminum anilide hydrochloride. In the early publication by Kogay and Sokolenko [9], the use of 1,3-dehydroadamantane was described: this compound reacted with aniline in the presence of aniline hydrochloride to produce a mixture of aniline alkylation products at the nitrogen atom and at the *para*-position at a ratio of 4:1. *N*-(1-Adamantyl)aniline was isolated in 55% yield. Stepanov and Stolyarov [10] synthesized *N*-(1-adamantyl)aniline by alkylation of aniline with 1-bromoadamantane. The reaction occurred under severe conditions and involved the nitrogen atom (yield 20%) and benzene ring (yield 7%). When the reaction was carried out in 10 equiv of aniline or in the presence of an equivalent amount of K_2CO_3, the yield

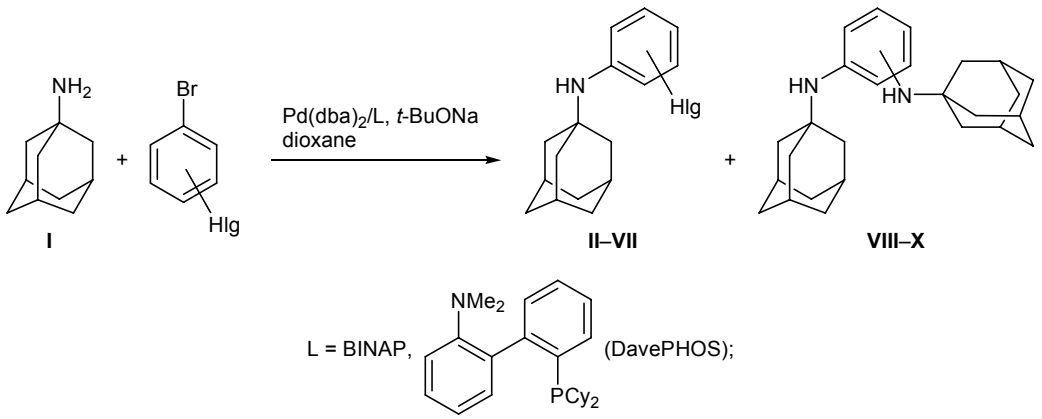
of *N*-(1-adamantyl)aniline increased to 40–53%, while the yield of the corresponding *C*-adamantyl derivative decreased to 1.5–2.3%. More recently [11], *N*-(1-adamantyl)aniline was synthesized via oxidative coupling catalyzed by copper(II). The yield was 57% in the presence of potassium trifluoro(phenyl)borate and 67% in the presence of phenylboronic acid. The synthesis of *N*-(1-adamantyl)pyridin-2-amine in 44% yield from pyridin-2-amine and hydroxylamine in the presence of trifluoroacetic acid was described in [12]. As shown in [13], *N*-(1-adamantylamino)pyridin-2-amine is a potent TNF-α inducer in cancer cells in mice. The only example of the use of palladium catalyst was described in [14]: *N*-(1-adamantyl)pyridin-2-amine was synthesized in 60% yield by cross coupling of adamantan-1-amine with 2-bromopyridine in the presence of $Pd(dba)_2$/dppp as catalyst.

Adamantan-2-amine and its derivatives also attract much interest. Among them, the most studied is *N*-(2-adamantyl)-4-bromoaniline which is more widely known as ladasten (bromantane, a very potent psychostimulant [7, 15]). Ladasten was synthesized in 96% yield by the Leuckart reaction [16], and its stimulant-like psychotropic activity was noted. The effect of different doses of ladasten on the behavior and fertility of rats was studied in [17–22]. Ladasten was also found to stimulate expression of genes responsible for biosynthesis of dopamine in different brain areas in rats [23]. The action of ladasten on blood pressure and vasoconstrictive effect of adrenaline and noradrenaline [24] was studied, and its specific effect on blood tissue was described [25]. Ladasten is also used as immunostimulant [26]; it partially prevents development of immune disorders in immune-deficient mice and coordinates cellular immune reactions [27].

The above data indicate exceptional practical importance of N-aryl-substituted aminoadamantanes. We have accumulated much experience related to the synthesis of various arylamines via palladium-catalyzed amination of aryl halides [28–31]. We have also studied catalytic arylation of various adamantane derivatives with 2-bromopyridine [32] and tried to synthesize polyaza macrocycles with the use of 1,3-bis(2-aminoethyladamantane) [33]. In the present work we examined palladium-catalyzed arylation of adamantan-1- and -2-amines with isomeric dihalobenzenes with a view to find out how the reactant structure affects the reaction course and outcome.

Adamantan-1-amine (**I**) was subjected to arylation with *p*-, *m*-, and *o*-bromochlorobenzenes and *p*-, *m*-, and *o*-dibromobenzenes. The reactions were carried out using 4–8 mol% of $Pd(dba)_2$ as catalyst and BINAP [34] or DavePHOS [35] as phosphine ligand; the initial reactants were taken in equimolar amounts, and their concentration was 0.1 M in anhydrous dioxane as solvent (Scheme 1). The reaction of adamantan-1-amine (**I**) with *p*-bromochlorobenzene in the presence of $Pd(dba)_2$/BINAP gave only 50% of the corresponding substituted *p*-chloroamine **II** (Table 1, run no. 1), while in the presence of a donor phosphine ligand, 2′-(dicyclohexylphosphanyl)-*N*,*N*-dimethylbiphenyl-2-amine (DavePHOS), the yield of **II** increased to 78% (Table 1, run no. 2). Using the same ligand, *m*- and *o*-derivatives **III** and **IV** were obtained in 75 and 62% yield, respectively, and in both cases the reaction was accompanied by formation of diamination products. The yield of diamine **IX** in the reaction with *m*-bromochlorobenzene was 7%, and the yield of analogous diamination product **X** in the reaction with *o*-bromochlorobenzene was 25% (Table 1; run nos. 1,

Scheme 1.



II, Hlg = *p*-Cl; **III**, Hlg = *m*-Cl; **IV**, Hlg = *o*-Cl; **V**, Hlg = *p*-Br; **VI**, Hlg = *m*-Br; **VII**, Hlg = *o*-Br; **VIII**, *para* isomer; **IX**, *meta* isomer; **X**, *ortho* isomer.

Table 1. Synthesis of *N*-aryl-substituted adamantan-1-amines **II**–**X**[a]

Run no.	Dihalobenzene	Amine–dihalobenzene ratio	Pd–L, mol %	Product (yield, %)
1	1-Br-4-ClC_6H_4	1:1	$Pd(dba)_2$–BINAP, 5:6	**II** (50)
2	1-Br-4-ClC_6H_4	1:1	$Pd(dba)_2$–DavePHOS, 5:6	**II** (78)
3	1-Br-3-ClC_6H_4	1:1	$Pd(dba)_2$–DavePHOS, 5:6	**III** (75), **IX** (7)
4	1-Br-2-ClC_6H_4	1:1	$Pd(dba)_2$–DavePHOS, 5:6	**IV** (62, 57[a]), **X** (25, 24[a])
5	1,4-$Br_2C_6H_4$	1:1	$Pd(dba)_2$–BINAP, 10.5:11	**V** (72)
6[b]	1,3-$Br_2C_6H_4$	1:1	$Pd(dba)_2$–BINAP, 10.5:11	**VI** (56, 23[a]), **IX** (11)
7[c]	1,3-$Br_2C_6H_4$	1:1	$Pd(dba)_2$–DavePHOS, 5:6	**VI** (15), **IX** (60)
8[d]	1,2-$Br_2C_6H_4$	1:1	$Pd(dba)_2$–BINAP, 5:6	**VII** (48)
9[e]	1,2-$Br_2C_6H_4$	1:1	$Pd(dba)_2$–BINAP, 10.5:11	**VII** (50, 16[a])
10	1,4-$Br_2C_6H_4$	2:1	$Pd(dba)_2$–DavePHOS, 10.5:11	**VIII** (45, –[a])
11[f]	1,3-$Br_2C_6H_4$	2:1	$Pd(dba)_2$–DavePHOS, 10:11.5	**IX** (69)
12[f]	1,3-$Br_2C_6H_4$	6:1	$Pd(dba)_2$–DavePHOS, 10.5:11	**IX** (54)
13	1,2-$Br_2C_6H_4$	2:1	$Pd(dba)_2$–DavePHOS, 10.5:11	**X** (60, 58[a]) **VII** (20)

[a] After chromatographic separation.
[b] Conversion of *m*-dibromobenzene 80%.
[c] Conversion of *m*-dibromobenzene 95%.
[d] Conversion of *o*-dibromobenzene 48%.
[e] Conversion of *o*-dibromobenzene 67%.
[f] Joint chromatographic separation: yield of **IX** 27%.

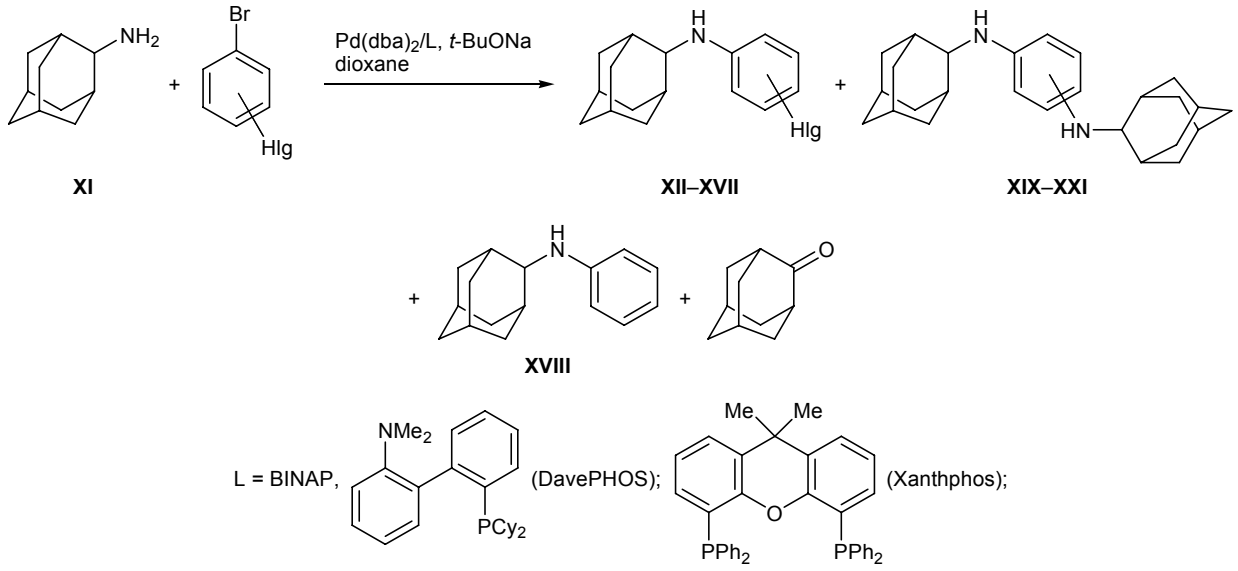
3, 4). The amination of *p*-dibromobenzene in the presence of 10.5 mol % of $Pd(dba)_2$/BINAP resulted in the formation of target compound **V**) in a high yield (72%; Table 1; run no. 5). Compound **I** reacted with *m*-dibromobenzene under analogous conditions to give 56% of monoamination product **VI**, while the yield of diamine **IX** was 11%, the overall conversion of initial *m*-dibromobenzene being 80% (Table 1; run no. 6). The use of donor DavePHOS in the synthesis of compound **VI** was poorly effective: the yield of diamination product **IX** sharply increased (60%), while the yield of **VI** decreased almost 4-fold; the overall conversion of *m*-dibromobenzene was almost quantitative (Table 1; run no. 7).

We did not use DavePHOS as ligand in the reaction with *o*-dibromobenzene, for in this case the yield of the corresponding diamination product would be even larger. The yield of target product **VII** in the reaction with standard amount of $Pd(dba)_2$–BINAP (5/6 mol %) was 48%, the conversion of *o*-dibromobenzene being appropriate (Table 1, run no. 8). Raising the amount of the catalyst to 10.5 mol % increased the conversion of *o*-dibromobenzene to 67%, but the yield of **VII** remained almost unchanged (Table 1, run no. 9). These data indicated that palladium-catalyzed amination involves concurrent processes which do not result in the formation of C–N bond but consume the initial aryl halide.

Taking into account that the reactions of equimolar amounts of adamantan-1-amine (**I**) with *o*- and *m*-dibromobenzenes were accompanied by formation of considerable amounts of diamination products, we tried to obtain the latter as major products by using 2 equiv of amine **I**. In the reaction with *o*-dibromobenzene we succeeded in increasing the yield of diamino derivative **X** to 60% (Table 1, run no. 13), while the yield of **IX** in the reaction with *m*-dibromobenzene increased from 56 to only 69% (Table 1, run no. 11). The use of a larger excess (6 equiv) of the amine led to even lower yield of **IX** (Table 1, run. no. 12). However, the most difficult was to obtain diamination product from *p*-dibromobenzene. Although compound **VIII** was formed in 45% yield (in the reaction mixture), all attempts to isolate it by chromatography were unsuccessful (Table 1, run no. 10).

Isomeric adamantan-2-amine (**XI**) is characterized by lesser steric hindrances at the nitrogen atom, and it turned out to be much more reactive than adamantan-1-amine (**I**) (Scheme 2). The yields of compounds **XII**–**XIV** in the reactions with isomeric bromochlorobenzenes were 80–83% (Table 2, run nos. 1–3), and the reaction with *o*-bromochlorobenzene was accom-

Scheme 2.



XII, Hlg = *p*-Cl; **XIII**, Hlg = *m*-Cl; **XIV**, Hlg = *o*-Cl; **XV**, Hlg = *p*-Br; **XVI**, Hlg = *m*-Br; **XVII**, Hlg = *o*-Br; **XIX**, *para* isomer; **XX**, *meta* isomer; **XXI**, *ortho* isomer.

panied by formation of an appreciable amount of the diamination product (Table 2, run no. 3). The yield of *o*-diamino derivative **XXI** in the reaction with *o*-dibromobenzene was comparable with that of monoamination product **XVII** (Table 2, run no. 7); an attempt to raise the yield of the latter using less active catalytic system $Pd(dba)_2$/Xanthphos was unsuccessful: the yield of **XVII** fell down to 25%, but the formation of *o*-phenylenediamine derivative **XXI** was not suppressed completely (7%), and the major product

Table 2. Synthesis of *N*-aryl-substituted adamantan-2-amines **XII**–**XXI**[a]

Run no.	Dihalobenzene	Amine–dihalobenzene ratio	Pd–L, mol %	Product (yield, %)
1	1-Br-4-ClC_6H_4	1:1	$Pd(dba)_2$–BINAP, 5:5.5	**XII** (83)
2	1-Br-3-ClC_6H_4	1:1	$Pd(dba)_2$–BINAP, 4:5	**XIII** (80)
3	1-Br-2-ClC_6H_4	1:1	$Pd(dba)_2$–BINAP, 5:5.5	**XIV** (82), **XXI** (18)
4	1,4-$Br_2C_6H_4$	1:1	$Pd(dba)_2$–BINAP, 4:5	**XV** (57)
5[b]	1,4-$Br_2C_6H_4$	1:1	$Pd(dba)_2$–Xanthphos, 4:4.5	**XV** (28, 7[a])
6	1,3-$Br_2C_6H_4$	1:1	$Pd(dba)_2$–BINAP, 4:5	**XVI** (63), **XVIII** (7), **XX** (5)
7[c]	1,2-$Br_2C_6H_4$	1:1	$Pd(dba)_2$–BINAP, 4:5	**XVII** (53), **XXI** (42)
8[d]	1,2-$Br_2C_6H_4$	1:1	$Pd(dba)_2$–Xanthphos, 4:4.5	**XVII** (25, 25[a]), **XVIII** (10, 7[a]), **XXI** (7)
9	1,4-$Br_2C_6H_4$	2:1	$Pd(dba)_2$–BINAP, 10.5:11	**XVIII** (31, 31[a])
10	1,4-$Br_2C_6H_4$	3:1	$Pd(dba)_2$–DavePHOS, 8:9	**XV** (17), **XVIII** (22), **XIX** (5)
11	1,3-$Br_2C_6H_4$	2:1	$Pd(dba)_2$–BINAP, 8:9	**XVI** (54), **XVIII** (16), **XX** (6)
12	1,2-$Br_2C_6H_4$	2:1	$Pd(dba)_2$–BINAP, 4:4.5	**XXI** (70), **XVIII** (18)
13[c]	1,2-$Br_2C_6H_4$	3:1	$Pd(dba)_2$–BINAP, 8:9	**XXI** (59), **XVIII** (13)

[a] After chromatographic separation.
[b] Adamantan-2-one (55%), *p*-bromoaniline (13%).
[c] Joint chromatographic separation: **XVII** (35%), **XXI** (35%).
[d] Adamantan-2-one (60%), *o*-bromoaniline (25%).

was adamantan-2-one resulting from oxidation of amine **XI** (60%; Table 2, run no. 8). The reaction of adamantan-2-amine with *m*-dibromobenzene gave much better results: target product **XVI** was formed in 63% yield, and insignificant amounts of reduction product **XVIII** and *m*-phenylenediamine derivative **XX** were obtained (Table 2, run no. 6). In the reaction of **XI** with *p*-dibromobenzene, BINAP also turned out to be much more effective than Xanthphos. In the latter case, a large amount of adamantan-2-one was isolated (Table 2, run nos. 4, 5). Presumably, Xanthphos favors oxidation of adamantan-2-amine to adamantanone through the corresponding imine and reduction of the initial dibromobenzenes to bromobenzene (the latter was almost undetectable in the NMR spectra of the product mixtures, for it was removed together with dioxane by distillation under reduced pressure). The other reduction product, compound **XVIII**, was not formed at all (Table 2, run no. 5) or its yield was several times lower than the yield of adamantan-2-one (Table 2, run no. 8). The results of our attempts to obtain *o*-diamine **XXI** as the major product showed that (as in the reaction with adamantan-1-amine) increase of the amount of the initial amine did not improve the yield of **XXI**; by contrast, its yield slightly decreased (Table 2, run nos. 12, 13). Unfortunately, we failed to obtain *m*-diamino derivative **XX**; instead, 54% of monoamination product **XVI** was formed (Table 2, run no. 11). The reason for such behavior remains unclear. Likewise, the yield of *p*-diamino derivative **XIX** did not exceed a few percent (Table 2, run no. 10); therefore, we succeeded in isolating by chromatography only reduction product **XVIII**. *p*- and *m*-Diamino-substituted adamantanes **XIX** and **XX** were identified only by spectral methods in the reaction mixtures. Compound **XIX** displayed in the ^{1}H NMR spectrum a signal at δ 6.53 ppm (s, 4H) from aromatic protons, and in the mass spectrum (MALDI) of the reaction mixture we observed a peak with *m*/*z* 376.35 $[M]^+$. Compound **XX** was identified by ^{1}H NMR signals at δ 5.85 (t, 1H) and 5.96 ppm (d.d, 2H).

To conclude, we have studied palladium-catalyzed amination of 1- and 2-aminoadamantanes with isomeric bromochloro- and dibromobenzenes, optimized conditions for the synthesis of *N*-(halophenyl)adamantanamines and *N*,*N*′-diadamantylbenzenediamines, and revealed unusually facile formation of *N*,*N*′-diadamantylbenzene-1,2-diamines and catalytic reduction of bromine in the initial haloarene.

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 solvent signals (δ 7.25, δ_C 77.00 ppm) as reference. The mass spectra (MALDI-TOF, positive ion detection) were obtained on a Bruker Daltonics Ultrafex instrument using 1,8,9-trihydroxyanthracene as matrix. Silica gel (Merck, 40–60 μm) was used for preparative column chromatography. Commercially available isomeric bromochloro- and dibromobenzenes, sodium *tert*-butoxide, BINAP, DavePHOS, and Xanthphos were used without additional purification. Adamantan-1-amine (**I**) [36], adamantan-2-amine (**XI**) [37], and $Pd(dba)_2$ [38] were synthesized according to known methods (the latter was not recrystallized). Dioxane was distilled first over alkali and then over metallic sodium; CH_2Cl_2 and MeOH were distilled.

***N*-Aryladamantanamines II–VII and XII–XVIII (*general procedure*).** A two-necked flask was filled with argon and charged with required reactants, solvent, and catalyst. The mixture was heated under reflux, cooled, and filtered, the filtrate 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 sodium sulfate and evaporated under reduced pressure. The product mixtures were separated by chromatography on silica gel using (in succession) petroleum ether–methylene chloride (4 : 1 to 1 : 4) and methylene chloride as eluent.

***N*,*N*′-Diadamantylbenzenediamines VIII–X and XIX–XXI (*general procedure*).** A two-necked flask was filled with argon and charged with required reactants, solvent, and catalyst. The mixture was heated under reflux, cooled, and filtered, the filtrate 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 sodium sulfate and evaporated under reduced pressure. The product mixtures were separated by chromatography on silica gel using (in succession) petroleum ether–methylene chloride (4 : 1 to 1 : 4), methylene chloride, and methylene chloride–methanol (100 : 1) as eluent.

***N*-(4-Chlorophenyl)adamantan-1-amine (II)** was synthesized from 0.2 mmol (30 mg) of adamantan-1-amine and 0.2 mmol (38 mg) of *p*-bromochlorobenzene in the presence of 6 mg (5 mol %) of $Pd(dba)_2$,

4.5 mg (6 mol %) of DavePHOS, and 37 mg (0.39 mmol) of sodium *tert*-butoxide in 2 ml of anhydrous dioxane. The reaction mixture was heated for 7 h. Yield 41 mg (78%), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.60–1.71 m (6H), 1.83 br.s (6H), 2.09 br.s (3H), 3.28 br.s (1H), 6.70 d (2H, ^3J = 8.6 Hz), 7.08 d (2H, ^3J = 8.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.6 (3C), 36.3 (3C), 43.3 (3C), 52.3 (1C), 120.0 (2C), 123.8 (1C), 128.6 (2C), 144.6 (1C).

Compounds **III** and **IV** were synthesized in a similar way.

***N*-(3-Chlorophenyl)adamantan-1-amine (III).** Yield 39 mg (75%), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.66 br.s (6H), 1.87 br.s (6H), 2.10 br.s (3H), 3.43 br.s (1H), 6.60 d.d (1H, ^3J = 8.2, ^4J = 1.2 Hz), 6.68 d (1H, ^3J = 7.9 Hz), 6.73 t (1H, ^4J = 2.0 Hz), 7.01 t (1H, ^3J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.6 (3C), 36.3 (3C), 43.1(3C), 52.1 (1C), 115.9 (1C), 117.3 (1C), 118.0 (1C), 129.7 (1C), 134.3 (1C), 147.5 (1C). Mass spectrum (MALDI-TOF): *m*/*z* 260.96 $[M]^+$.

***N*-(2-Chlorophenyl)adamantan-1-amine (IV).** Yield 30 mg (57%); eluent petroleum ether–methylene chloride (4:1); colorless oily substance. Elution with petroleum ether–methylene chloride (1:1) and then with methylene chloride gave 9 mg (24%) of compound **X**. ^{1}H NMR spectrum, δ, ppm: 1.70 br.s (6H), 1.96 br.s (6H), 2.13 br.s (3H), 4.15 br.s (1H), 6.60–6.65 m (1H), 7.02–7.08 m (2H), 7.22–7.26 m (1H). ^{13}C NMR spectrum, δ_C, ppm: 29.7 (3C), 36.4 (3C), 43.1 (3C), 52.4 (1C), 116.9 (1C), 117.9 (1C), 121.7 (1C), 127.0 (1C), 129.3 (1C), 142.5 (1C). Mass spectrum (MALDI-TOF): *m*/*z* 261.1350 $[M]^+$. $C_{16}H_{20}ClN$. Calculated: *M* 261.1284.

***N*-(4-Bromophenyl)adamantan-1-amine (V)** was synthesized from 0.2 mmol (30 mg) of adamantan-1-amine and 0.2 mmol (47 mg) of *p*-dibromobenzene using 12 mg (10.5 mol %) of $Pd(dba)_2$, 14 mg (11 mol%) of BINAP, and 37 mg (0.39 mmol) of sodium *tert*-butoxide in 2 ml of anhydrous dioxane (reaction time 7 h). Yield 44 mg (72%), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.63–1.71 m (6H), 1.83–1.85 m (6H), 2.10 br.s (3H), 3.32 br.s (1H), 6.65 d (2H, ^3J = 8.6 Hz), 7.22 d (2H, ^3J = 8.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.6 (3C), 36.4 (3C), 43.3 (3C), 52.2 (1C), 110.8 (1C), 120.2 (2C), 131.5 (2C), 145.1 (1C). Mass spectrum (MALDI-TOF): *m*/*z* 305.04 $[M]^+$.

Compounds **VI** and **VII** were synthesized in a similar way.

***N*-(3-Bromophenyl)adamantan-1-amine (VI).** Yield 14 mg (23%); eluent petroleum ether–methylene chloride (2:1); colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.67 br.s (6H), 1.87 br.s (6H), 2.11 br.s (3H), 3.40 br.s (1H), 6.65 d.d.d (1H, ^3J = 8.1, ^4J = 2.3, 0.9 Hz), 6.83 d.d.d (1H, ^3J = 7.8, ^4J = 1.8, 0.9 Hz), 6.89 t (1H, ^4J = 2.0 Hz), 6.97 t (1H, ^3J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.6 (3C), 36.3 (3C), 43.1 (3C), 52.1 (1C), 116.4 (1C), 120.3 (1C), 121.0 (1C), 122.5 (1C), 129.9 (1C), 147.6 (1C). Mass spectrum (MALDI-TOF): *m*/*z* 305.0800 $[M]^+$. $C_{16}H_{20}BrN$. Calculated: *M* 305.0779.

***N*-(2-Bromophenyl)adamantan-1-amine (VII).** Yield 10 mg (16%); eluent petroleum ether–methylene chloride (5:1); colorless crystals, mp 110–112°C. ^{1}H NMR spectrum, δ, ppm: 1.69 br.s (6H), 1.96 br.s (6H), 2.12 br.s (3H), 4.16 br.s (1H), 6.55 t.d (1H, ^3J = 7.5, ^4J = 1.6 Hz), 7.03 d.d (1H, ^3J = 8.2, ^4J = 1.5 Hz), 7.10 t.d (1H, ^3J = 7.6, ^4J = 1.5 Hz), 7.41 d.d (1H, ^3J = 8.0, ^4J = 1.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.7 (3C), 36.5 (3C), 43.1 (3C), 52.6 (1C), 113.0 (1C), 116.8 (1C), 118.4 (1C), 127.7 (1C), 132.7 (1C), 143.6 (1C). Mass spectrum (MALDI-TOF): *m*/*z* 305.0773 $[M]^+$. $C_{16}H_{20}BrN$. Calculated: *M* 305.0779.

***N*,*N*′-Bis(1-adamantyl)benzene-1,4-diamine (VIII).** *a*. The reaction of 0.2 mmol (30 mg) of adamantan-1-amine with 0.1 mmol (24 mg) of *p*-dibromobenzene in the presence of 6 mg (10 mol%) of $Pd(dba)_2$, 4.5 mg (11.5 mol %) of DavePHOS, and 37 mg (0.39 mmol) of sodium *tert*-butoxide in 2 ml of anhydrous dioxane (reaction time 7 h) gave 45% of compound **VIII** (identified in the reaction mixture by NMR spectra). We failed to isolate the product by chromatography. ^{1}H NMR spectrum, δ, ppm: 1.58–1.68 m (12H), 1.75 br.s (12H), 2.06 br.s (6H), 2.89 br.s (2H), 6.68 s (4H). ^{13}C NMR spectrum, δ_C, ppm: 29.7 (6C), 36.5 (6C), 43.7 (6C), 52.3 (2C), 122.5 (4C), 139.0 (2C). Mass spectrum (MALDI-TOF): *m*/*z* 376.25 $[M]^+$.

Compounds **IX** and **X** were obtained in a similar way.

b. Compound **VIII** was obtained from 0.6 mmol (91 mg) of adamantan-1-amine and 0.1 mmol (24 mg) of *m*-dibromobenzene in the presence of 6 mg (10 mol %) of $Pd(dba)_2$, 4.5 mg (11.5 mol%) of DavePHOS, and 70 mg (0.73 mmol) of sodium *tert*-butoxide in 2 ml of anhydrous dioxane (reaction time 7 h). Yield 20 mg (27%; *a*, *b*); eluent methylene chloride–methanol (100:1); colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.65 br.s (12H), 1.86 br.s

(12H), 2.09 br.s (6H), 3.18 br.s (2H), 6.25 d.d (2H, ^3J = 8.0, ^4J = 2.1 Hz), 6.30 t (1H, ^4J = 2.1 Hz), 6.90 t (1H, ^3J = 7.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.8 (6C), 36.5 (6C), 43.6 (6C), 52.2 (2C), 110.1 (1C), 110.8 (2C), 128.8 (1C), 146.5 (2C). Mass spectrum (MALDI-TOF): *m*/*z* 376.21 $[M]^+$.

***N*,*N*′-Bis(1-adamantyl)benzene-1,2-diamine (X).** Yield 22 mg (58%); eluent petroleum ether–methylene chloride (1:1), methylene chloride; colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.64 br.s (12H), 1.84 br.s (12H), 2.07 br.s (6H), 3.06 br.s (2H), 6.70–6.75 m (2H), 6.88–6.93 m (2H). ^{13}C NMR spectrum, δ_C, ppm: 29.8 (6C), 38.6 (6C), 43.4 (6C), 52.6 (2C), 120.2 (2C), 121.9 (2C), 138.1 (2C). Mass spectrum (MALDI-TOF): *m*/*z* 376.2800 $[M]^+$. $C_{26}H_{36}N_2$. Calculated: *M* 376.2878.

***N*-(4-Chlorophenyl)adamantan-2-amine (XII)** was synthesized from 0.2 mmol (30 mg) of adamantan-2-amine and 0.2 mmol (38 mg) of *p*-bromochlorobenzene in the presence of 6 mg (5 mol %) of $Pd(dba)_2$, 7 mg (5.5 mol %) of BINAP, and 37 mg (0.39 mmol) of sodium *tert*-butoxide in 2 ml of anhydrous dioxane (reaction time 7 h). Yield 43 mg (83%), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.60 d (2H, ^3J = 12.6 Hz), 1.76 br.s (2H), 1.78–1.94 m (8H), 2.00 br.s (2H), 3.48 br.s (1H), 3.98 d (1H, ^3J = 6.8 Hz), 6.51 d (2H, ^3J = 8.2 Hz), 7.09 d (2H, ^3J = 8.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 27.2 (1C), 27.3 (1C), 31.4 (2C), 31.5 (2C), 37.3 (2C), 37.6 (1C), 56.8 (1C), 114.0 (2C), 121.0 (1C), 129.0 (2C), 145.8 (1C). Mass spectrum (MALDI-TOF): *m*/*z* 261.08 $[M]^+$.

***N*-(3-Chlorophenyl)adamantan-2-amine (XIII)** was synthesized from 0.15 mmol (23 mg) of adamantan-2-amine and 0.15 mmol (29 mg) of *m*-bromochlorobenzene in the presence of 4 mg (4 mol %) of $Pd(dba)_2$, 4.5 mg (5 mol %) of BINAP, and 23 mg (0.24 mmol) of sodium *tert*-butoxide in 1.5 ml of anhydrous dioxane (reaction time 7 h). Yield 31 mg (80%), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.61 d (2H, ^3J = 12.6 Hz), 1.75 br.s (2H), 1.79–1.94 m (8H), 2.00 br.s (2H), 3.50 br.s (1H), 4.05 d (1H, ^3J = 7.0 Hz), 6.45 d.d.d (1H, ^3J = 8.2, ^4J = 2.2, 0.8 Hz), 6.55 t (1H, ^4J = 2.1 Hz), 6.60 d.d.d (1H, ^3J = 7.8, ^4J = 1.9, 0.7 Hz), 7.04 t (1H, ^3J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 27.2 (1C), 27.3 (1C), 31.4 (2C), 31.5 (2C), 37.3 (2C), 37.6 (1C), 56.6 (1C), 111.3 (1C), 112.4 (1C), 116.4 (1C), 130.1 (1C), 135.0 (1C), 148.5 (1C).

***N*-(2-Chlorophenyl)adamantan-2-amine (XIV)** was synthesized from 0.2 mmol (30 mg) of adamantan-2-amine and 0.2 mmol (38 mg) of *o*-bromochlorobenzene in the presence of 6 mg (5 mol %) of $Pd(dba)_2$, 7 mg (5.5 mol %) of BINAP, and 37 mg (0.39 mmol) of sodium *tert*-butoxide in 2 ml of anhydrous dioxane (reaction time 7 h). Yield 42 mg (82%), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.64 d (2H, ^3J = 12.8 Hz), 1.78 br.s (2H), 1.81–2.01 m (8H), 2.05 br.s (2H), 3.62 d (1H, ^3J = 7.3 Hz), 4.72 d (1H, ^3J = 6.7 Hz), 6.58 t.d (1H, ^3J = 7.6, ^4J = 1.3 Hz), 6.64 d (1H, ^3J = 8.4 Hz), 7.11 t.d (1H, ^3J = 7.8, ^4J = 1.2 Hz), 7.26 d.d (1H, ^3J = 7.8, ^4J = 1.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 27.2 (1C), 27.4 (1C), 31.5 (2C), 31.6 (2C), 37.3 (2C), 37.6 (1C), 56.5 (1C), 111.6 (1C), 116.4 (1C), 118.8 (1C), 127.7 (1C), 129.2 (1C), 143.0 (1C). Mass spectrum (MALDI-TOF): *m*/*z* 261.11 $[M]^+$.

***N*-(4-Bromophenyl)adamantan-2-amine (XV).** *a*. Compound **XV** was synthesized from 0.15 mmol (23 mg) of adamantan-2-amine and 0.15 mmol (35 mg) of *p*-dibromobenzene in the presence of 4 mg (4 mol %) of $Pd(dba)_2$, 4.5 mg (5 mol%) of BINAP, and 23 mg (0.24 mmol) of sodium *tert*-butoxide in 1.5 ml of anhydrous dioxane (reaction time 7 h). Yield 26 mg (57%).

b. The reaction of 0.18 mmol (27 mg) of adamantan-2-amine with 0.18 mmol (43 mg) of *p*-dibromobenzene in the presence of 4 mg (4 mol %) of $Pd(dba)_2$, 5 mg (4.5 mol %) of Xanthphos, and 30 mg (0.31 mmol) of sodium *tert*-butoxide in 2 ml of anhydrous dioxane (reaction time 7 h) gave 4 mg (7%) of **XV** as a colorless oily substance (eluent petroleum ether–methylene chloride, 4:1). Elution with petroleum ether–methylene chloride (1:1) gave 4 mg (13%) of *p*-bromoaniline, and elution with methylene chloride gave 15 mg (55%) of adamantan-2-one. ^{1}H NMR spectrum of **XV**, δ, ppm: 1.60 d (2H, ^3J = 12.0 Hz), 1.74 br.s (2H), 1.79–1.92 m (8H), 1.99 br.s (2H), 3.47 br.s (1H), 3.98 d (1H, ^3J = 7.0 Hz), 6.46 d (2H, ^3J = 8.8 Hz), 7.21 d (2H, ^3J = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 27.2 (1C), 27.3 (1C), 31.4 (2C), 31.5 (2C), 37.3 (2C), 37.6 (1C), 56.7 (1C), 108.0 (1C), 114.5 (2C), 131.9 (2C), 146.3 (1C).

***N*-(3-Bromophenyl)adamantan-2-amine (XVI)** was synthesized from 0.15 mmol (23 mg) of adamantan-2-amine and 0.15 mmol (35 mg) of *m*-dibromobenzene in the presence of 4 mg (4 mol%) of $Pd(dba)_2$, 4.5 mg (5 mol %) of BINAP, and 23 mg (0.24 mmol) of sodium *tert*-butoxide in 1.5 ml of anhydrous dioxane (reaction time 7 h). yield 29 mg (63%), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.60 d (2H, ^3J = 12.0 Hz), 1.75 br.s (2H), 1.80–1.94 m (8H), 2.00 br.s (2H), 3.49 br.s (1H), 4.04 br.s (1H, ^3J =

7.2 Hz), 6.49 d.d (1H, ^3J = 8.1, ^4J = 1.5 Hz), 6.71 br.s (1H), 6.74 d (1H, ^3J = 7.8 Hz), 6.98 t (1H, ^3J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 27.2 (1C), 27.3 (1C), 31.4 (2C), 31.5 (2C), 37.3 (2C), 37.6 (1C), 56.6 (1C), 111.7 (1C), 115.3 (1C), 119.3 (1C), 123.3 (1C), 130.5 (1C), 148.7 (1C). Mass spectrum (MALDI-TOF): *m*/*z* 305.12 $[M]^+$.

***N*-(2-Bromophenyl)adamantan-2-amine (XVII).** *a*. Compound **XVII** was synthesized from 0.15 mmol (23 mg) of adamantan-2-amine and 0.15 mmol (35 mg) of *o*-dibromobenzene in the presence of 4 mg (4 mol %) of $Pd(dba)_2$, 4.5 mg (5 mol %) of BINAP, and 23 mg (0.24 mmol) of sodium *tert*-butoxide in 5 ml of anhydrous dioxane (reaction time 7 h). The product was isolated by chromatography together with those obtained in the synthesis of compound **XXI**; eluent petroleum ether–methylene chloride (10:1). Yield 16 mg (35%), colorless oily substance.

b. The reaction of 0.18 mmol (27 mg) of adamantan-2-amine with 0.18 mmol (43 mg) of *o*-dibromobenzene in the presence of 4 mg (4 mol %) of $Pd(dba)_2$, 5 mg (4.5 mol %) of Xanthphos, and 30 mg (0.31 mmol) of sodium *tert*-butoxide in 2 ml of anhydrous dioxane (reaction time 7 h) gave 14 mg (25%) of compound **XVII** (eluent petroleum ether–methylene chloride, 4:1). Elution with petroleum ether–methylene chloride (2:1) gave 2.5 mg (7%) of compound **XXI** and 3 mg (7%) of **XVIII**, and subsequent elution with methylene chloride gave 8 mg (25%) of *o*-bromoaniline and 16 mg (60%) of adamantan-2-one. ^{1}H NMR spectrum, δ, ppm: 1.62 d (2H, ^3J = 12.7 Hz), 1.76 br.s (2H), 1.79–1.99 m (8H), 2.03 br.s (2H), 3.60 d (1H, ^3J = 7.3 Hz), 4.71 d (1H, ^3J = 6.4 Hz), 6.50 t (1H, ^3J = 7.6 Hz), 6.60 d (1H, ^3J = 8.1 Hz), 7.13 t (1H, ^3J = 7.7 Hz), 7.40 d (1H, ^3J = 7.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 27.3 (1C), 27.4 (1C), 31.4 (2C), 31.7 (2C), 37.3 (2C), 37.7 (1C), 56.7 (1C), 111.7 (1C), 117.0 (1C), 124.5 (1C), 128.4 (1C), 132.5 (1C), 144.0 (1C). Mass spectrum (MALDI-TOF): *m*/*z* 305.0800 $[M]^+$. $C_{16}H_{20}BrN$. Calculated: *M* 305.0779.

***N*-Phenyladamantan-2-amine (XVIII)** was synthesized from 0.2 mmol (30 mg) of adamantan-2-amine and 0.1 mmol (24 mg) of *p*-dibromobenzene in the presence of 6 mg (10.5 mol %) of $Pd(dba)_2$, 7 mg (11 mol %) of BINAP, and 37 mg (0.39 mmol) of sodium *tert*-butoxide in 1 ml of anhydrous dioxane (reaction time 7 h). Yield 7 mg (31%); eluent petroleum ether–methylene chloride (2:1), colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.60 d (2H, ^3J = 12.8 Hz), 1.75 br.s (2H), 1.78–1.95 m (8H), 2.02 br.s (2H), 3.54 br.s (1H), 3.96 br.s (1H), 6.59 d (2H, ^3J = 7.8 Hz), 6.64 t (1H, ^3J = 7.4 Hz), 7.15 t (2H, ^3J = 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 27.3 (1C), 27.5 (1C), 31.6 (4C), 37.4 (2C), 37.7 (1C), 56.8 (1C), 113.0 (2C), 116.7 (1C), 129.3 (2C), 147.4 (1C). Mass spectrum (MALDI-TOF): *m*/*z* 227.1620 $[M]^+$. $C_{16}H_{21}N$. Calculated: *M* 227.1674.

***N*,*N*′-Bis(2-adamantyl)benzene-1,2-diamine (XXI)** was obtained from 0.45 mmol (68 mg) of adamantan-2-amine and 0.15 mmol (35 mg) of *o*-dibromobenzene in the presence of 7 mg (8 mol %) of $Pd(dba)_2$, 8.5 mg (9 mol %) of BINAP, and 45 mg (0.47 mmol) of sodium *tert*-butoxide in 1.5 ml of anhydrous dioxane (reaction time 7 h). The product was isolated by chromatography together with those obtained in the synthesis of compound **XVII** according to method *a*. Yield 39 mg (35%); eluent petroleum ether–methylene chloride (4:1, 2:1). Elution with petroleum ether–methylene chloride (4:1) gave 4.5 mg (13%) of compound **XVIII**. ^{1}H NMR spectrum of **XXI**, δ, ppm: 1.61 d (4H, ^3J = 12.4 Hz), 1.76 br.s (4H), 1.78–1.92 m (16H), 2.03 br.s (4H), 3.50 br.s (2H), 3.66 br.s (2H), 6.64–6.68 m (2H), 6.70–6.74 m (2H). ^{13}C NMR spectrum, δ_C, ppm: 27.5 (2C), 27.6 (2C), 31.9 (4C), 32.0 (4C), 37.4 (4C), 37.8 (2C), 56.9 (2C), 113.6 (2C), 118.8 (2C), 136.8 (2C). Mass spectrum (MALDI-TOF): *m*/*z* 376.2880 $[M]^+$. $C_{26}H_{36}N_2$. Calculated: *M* 376.2878.

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