Adamantylation of *N*-aryl and *N*-arylalkyl acetamides in trifluoroacetic acid*

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Alkylation of *N*-aryl and *N*-arylalkyl acetamides with hydroxy adamantane derivatives in trifluoroacetic acid was studied. The differentiating effect of trifluoroacetic acid on the regioselectivity of adamantylation of *o*-alkyl-substituted acetanilides was established, leading to energetically more stable products of *para*-substitution with respect to the alkyl group (the content of *para*-alkyl isomers is 93—94%). This enabled the synthesis of adamantylaminoarenes in 83—99% yields and with 95—99% purity.

Key words: adamantylation, adamantan-1-ol, acetanilide, *N*-benzylacetamide, trifluoroacetic acid, density functional theory, Gasteiger—Marsili method.

Compounds containing adamantyl and aromatic moieties possess valuable properties,[1,2] which can be exemplified by the drug adapalene.[3,4] Adamantylated aromatic hydrocarbons appear to be convenient synthons for the search of compounds with this type of properties.[5,6] Sterically hindered phenols in which the functional group is surrounded by bulky adamantyl groups are active antioxidants.[7,8] They are mainly prepared by arylation of adamantane or adamantylation of arenes. Adamantane arylation did not gain popularity because of the necessity to maintain rather drastic conditions and high cost of the catalysts.[9—11] Therefore, aryladamantanes are synthesized most often by adamantylation of aromatic compounds with adamantane derivatives able to generate the adamantyl cation. Currently, there is no versatile procedure for adamantylation of aromatic compounds. The choice of the adamantylating reagent and catalyst is mainly determined by the nature of aromatic substrate. For example, adamantylation of phenols and naphthols with adamantan-1-ol in the presence of concentrated sulfuric acid[12,13] and with haloadamantane in the presence of various catalysts[14] were described in detail. The adamantylation of mono- and polyhydric phenols using trifluoroacetic acid (TFA) was reported.[15—18] It was noted that using hydroxyadamantanes and TFA allows conducting the alkylation of phenols and naphthalene derivatives under milder conditions and with lower amounts of by-products than in the presence of sulfuric acid.

Adamantylation of aromatic hydrocarbons with various catalysts was studied in detail, and results of quantum chemical studies of the mechanism and isomerization processes were reported.[19]

Despite the fact that adamantylation of phenols and naphthols[20] was studied very intensively, data on the adamantylation of aromatic amines are fragmentary. The adamantylation of nitroanilines in sulfuric, polyphosphoric, and trifluoroacetic acids was described;[21,22] under these conditions, only the nitrogen atom is adamantylated. Aminoaryladamantanes and unsymmetrical aryladamantyl diamines are of interest as promising starting compounds for the preparation of transparent and thermally stable polyimide films; therefore, the objective of our study is to develop methods for *C*-adamantylation of aromatic amines in order to prepare mono- and diaminoaryladamantanes.

Results and Discussion

We proposed a method for the synthesis of adamantylanilines by the reaction of aromatic compounds with hydroxyadamantanes in TFA (Scheme 1).

It is known[21] that, unlike phenols, which undergo only *C*-alkylation, the use of free amines results in *N*-alkylated products. Therefore, we used acetylated aniline derivatives and aminoadamantanol hydrogen sulfate derivatives. Note that in the TFA medium, the reaction proceeds without elevated pressure or long-term refluxing, and undesirable resinification of the reaction mixture can thus be avoided. After the reaction, excess TFA is easily distilled off and can be recovered and reused.

The acid hydrolysis of the synthesized compounds gave hydrochlorides, which were converted to free amines by treatment with alkaline solutions.

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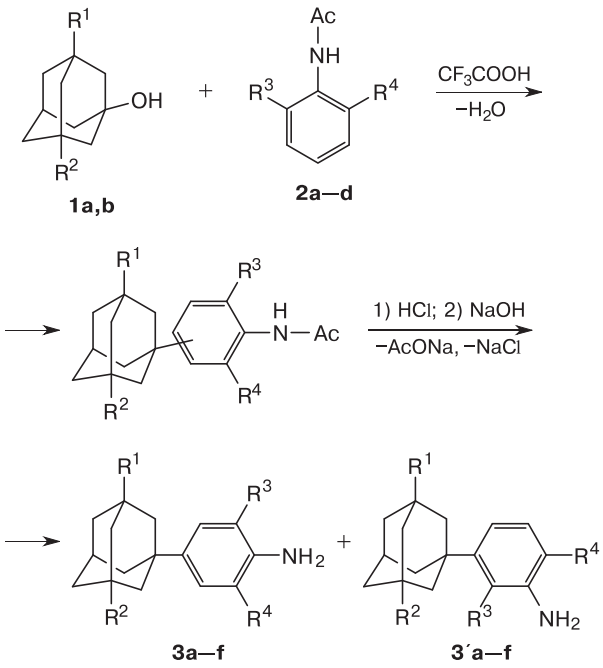
Scheme 1



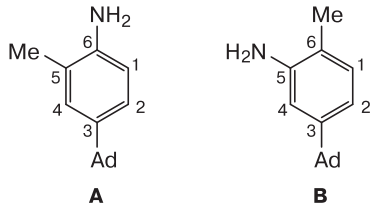
1: $R^1 = R^2 = H$ (**a**); $R^1 = R^2 = Me$ (**b**)
2: $R^3 = R^4 = H$ (**a**); $R^3 = H$, $R^4 = Me$ (**b**); $R^3 = H$, $R^4 = Et$ (**c**); $R^3 = R^4 = Me$ (**d**);

3, 3´	R^1	R^2	R^3	R^4	Content (%)	
					3	**3´**
a	H	H	H	H	100	0
b	H	H	H	Me	6	94
c	H	H	H	Et	7	90
d	H	H	Me	Me	100	0
e	Me	Me	H	H	100	0
f	Me	Me	Me	Me	100	0

Using TFA, the reaction can be accomplished selectively to give target products in high yields and with high purity. Trifluoroacetic acid[23] is an efficient medium for generating adamantyl cations from adamantanols, as it forms a bulky contact ion pair with the adamantyl cation, which prevents insertion of the cation into the *ortho*-position of the acetanilide benzene ring due to steric hindrance. Furthermore, with the formation of the adamantly cation—TFA ion pair, the reaction occurs under orbital control and involves the energetically most favorable *para*-position of the aromatic ring. The above factors make it possible to avoid the formation of a mixture of 2-, 3-, and 4-(1-adamantyl)anilines and *N*-(1-adamantyl)aniline. However, in the case of alkylation of aceto(2-alkylanilides) **2b,c**, the reaction gives a mixture of isomeric anilides with the predominant content of *para*-substituted product with respect to the alkyl group (93—94%) and a lower content of *meta*-substituted product (6—7%). In the alkylation of aceto(2,6-dimethylanilide) (**2d**), no isomer formation was detected.

This conclusion was confirmed by ^{13}C NMR spectroscopy data. As a result of comparison of experimental and simulated ^{13}C NMR spectra, the obtained compound was identified as the product of *para*-substitution with respect to the methyl group (Fig. 1).

The experimental ^{13}C NMR chemical shifts in low magnetic fields (aromatic region, CCl_4 as the solvent, 30 °C) and the calculated ^{13}C NMR chemical shifts for the two possible isomers **3b** and **3´b** are presented in Table 1. The structures **A** and **B** were recognized using additive schemes for calculation of ^{13}C chemical shifts, depending on the surrounding in substituted benzenes.[24]



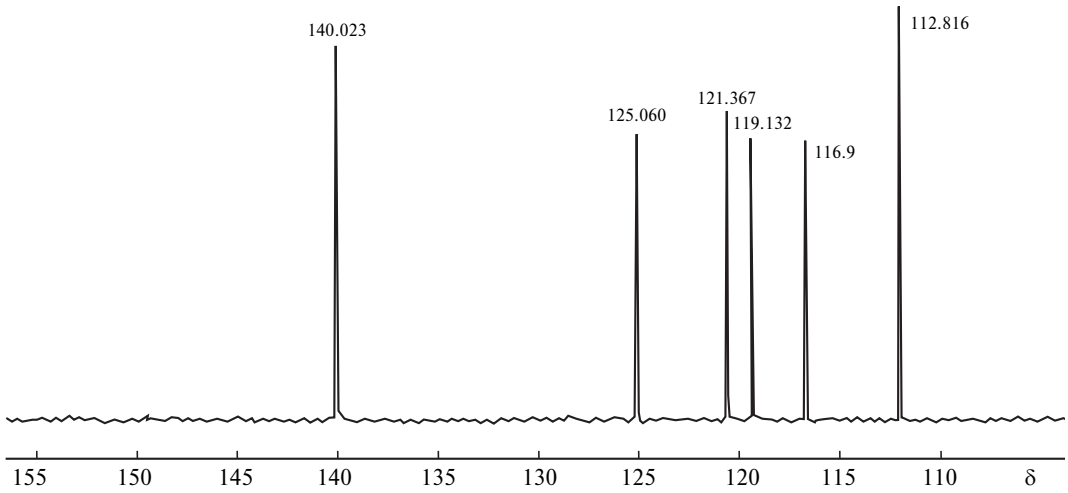


Fig. 1. ^{13}C NMR spectra of the aromatic cores of compound **3´b**.

Table 1. Experimental and simulated ^{13}C NMR data for two possible isomers **3b** and **3′b**

Number of atom*	$\delta_{^{13}C}$		
	Experiment	Simulation	
		A	**B**
1	121	115	116
2	119	148	115
3	140	130	149
4	112	159	112
5	117	124	117
6	125	144	121

* Does not correspond to IUPAC numbering.

A comparison of the experimental and simulated spectra for structure **A** shows no correlation, while coincidence of structure **B** with experimental data for carbon atoms 4, 1, 2, and 5 are close to 95%, and the average is 80%. Incomplete coincidence is, most likely, due to the solvent effect, as the solvents can change ^{13}C chemical shifts for aromatic compounds by up to 10%. In total, the ^{13}C NMR spectrum corresponds to structure **B** (see Table 1).

In order to gain additional information and to predict the possibility of synthesizing some other compounds, we carried out quantum chemical calculations of the energies of possible structures resulting from reaction of hydroxyadamantane with aceto(2-methylanilide) (**2b**) and aceto(2,6-dimethylanilide) (**2d**). The calculations were carried out by density functional theory method with the hybrid B3LYP/6-31G(d) functional and preliminary optimization of the molecular geometry by semiempirical quantum chemical PM3 method. All calculations were carried out using the GAMESS (US) software.

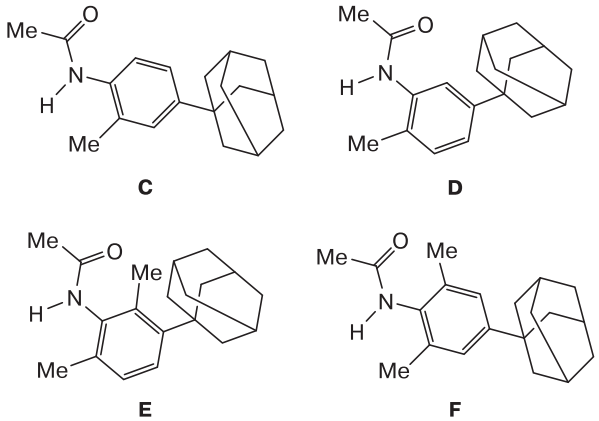
The calculation was carried out for structures **C**—**F**. The above-described procedure gave the following ground state energies: 868.5244874614, 868.5250500892, 907.8097647119, and 907.8237399584 eV for structures **C**—**F**, respectively.

The obtained ground state energies account for the unexpected substitution particularly into the *para*-position with respect to the alkyl substituent rather than to the acetamide substituent, as expected, and substitution exclusively into the *para*-position with respect to the acetamide group in the case of aceto(2,6-dimethylanilide) (**2d**).

In the case of adamantylation of *N*-arylalkyl acetamides, the idea of using acyl amino derivatives for the formation of exactly *C*-alkylated products proved to be inefficient. The adamantylation of *N*-benzylacetamide in trifluoroacetic acid gave a complex mixture of products (Scheme 2).

According to gas chromatography—mass spectrometry data, the reaction products included both *C*- and *N*-adamantylated compounds and *N*-benzylacetamide self-alkylation products. Chromatographic analysis of the reaction mixture (after evaporation of TFA) demonstrated that at 94% conversion of adamantanol, the content of the *C*-alkylated product is only 25.6%, with the content of the *N*-alkylated product being 43.0%. Among by-products, dibenzylacetamide (15.5%), adamantylacetamide (6.3%), and tribenzylamine (3.4%) predominated. The presence of these by-products indicated that the electrophilic attack is directed, first of all, to *N*-benzylacetamide nitrogen.

The experimental data suggest that the adamantyl cation formed under the action of TFA attacks the *N*-benzylacetamide molecule to both the aromatic ring and the nitrogen atom. The product of *N*-adamantylation is then protonated, thus generating *N*-acetylaminoadamantane and benzyl cation. The benzyl cation, in turn, attacks the nitrogen atom of *N*-benzylacetamide, which results in the formation of dibenzyl- and tribenzylamines. The predominance of *N*-alkylated products attests to a considerable difference between the reactivities of the aromatic ring and the nitrogen atom in aromatic and fatty aromatic amides. The charges in acetanilide and *N*-benzylacetamide calculated by the Gasteiger—Marsili method clearly demonstrates different charges on nitrogen. With the charges on aromatic carbon atoms being virtually equal, the charge on nitrogen is almost three times higher for benzylacetamide than for acetanilide (Fig. 2, Table 2);



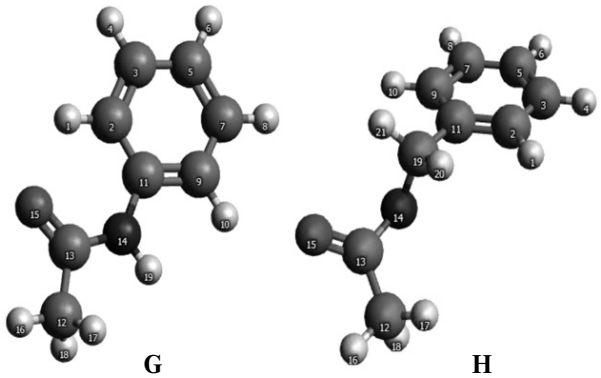
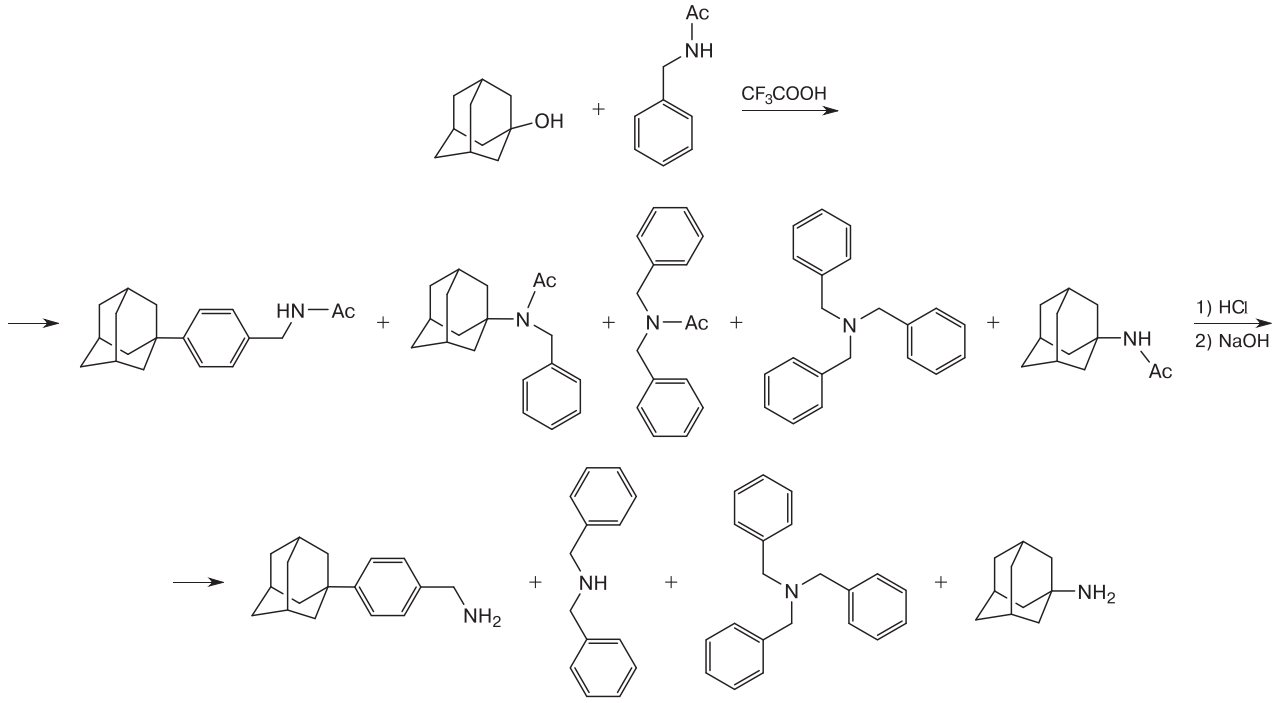


Fig. 2. Structures of acetanilide (**G**) and *N*-benzylacetamide (**H**).

Scheme 2



therefore, in the case of *N*-benzylacetamide, it is impossible to obtain only the *C*-alkylated product.

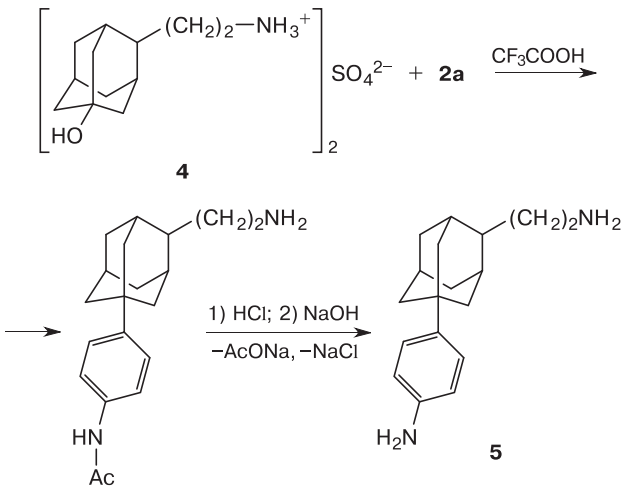
Table 2. Atomic charges according to the Gasteiger—Marsili method in acetanilide (**G**) and *N*-benzylacetamide (**H**) molecules (see Fig. 2)

Number of atom (**G**)	Atom	Charge	Number of atom (**H**)	Atom	Charge
1	H	0.064	1	H	0.062
2	C	−0.040	2	C	−0.060
3	C	−0.060	3	C	−0.062
4	H	0.062	4	H	0.062
5	C	−0.062	5	C	−0.062
6	H	0.062	6	H	0.062
7	C	−0.060	7	C	−0.062
8	H	0.062	8	H	0.062
9	C	−0.040	9	C	−0.060
10	H	0.064	10	H	0.062
11	C	0.033	11	C	−0.065
12	C	0.012	12	C	−0.024
13	C	0.214	13	C	0.043
14	N	−0.286	14	N	−0.639
15	O	−0.276	15	O	−0.319
16	H	0.032	16	H	0.029
17	H	0.032	17	H	0.029
18	H	0.032	18	H	0.029
19	H	0.155	19	C	−0.108
—	—	—	20	H	0.010
—	—	—	21	H	0.010

Apart from the above factors, adamantylation of benzylacetamide is complicated by parallel self-alkylation giving di- and tribenzylamines because of easy generation of the benzyl cation from benzylacetamide in TFA.

The method we developed can also be applied for the synthesis of aryladamantyl-containing diamines, which, in turn, can serve as monomers for polycondensation polymers. Therefore, we synthesized a representative of this class in TFA using hydrogen sulfate of amino adamantanol derivative **4** and acetanilide (**2a**) (Scheme 3).

Scheme 3



The target diamine **5** is formed in high yield (90%), with minimized amounts of acidic waste and by-products.

Thus, we studied adamantylation of aromatic amino derivatives and ascertained that TFA is an efficient medium for the preparation of the desired compounds. Adamantylaminoarenes were synthesized in high yields (83—99%) and with high purity (95—99%), according to X-ray diffraction data. TFA was found to have a differentiating effect on the regioselectivity of adamantylation of *o*-alkyl-substituted acetanilides, resulting in the formation of energetically more favorable *para*-substituted products with respect to the alkyl group. The use of *N*-benzylacetamide as the aromatic compound leads to *C*- and *N*-adamantylation and self-alkylation products formed as a mixture difficult to separate. The predominance of *N*-alkylation over *C*-alkylation is due to higher charge on the nitrogen atom in *N*-benzylacetamide compared to acetanilide and the ease of fragmentation of benzylacetamide in TFA, which results in dibenzyl- and tribenzylamines.

Experimental

Mass spectra were measured on a Saturn-2100 gas chromatograph—mass spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Mercury 300 plus BB instrument (Varian) (HMDS as the internal standard; DMSO-d_6, $CDCl_3$, and CCl_4 as solvents). The ^{13}C nuclei were identified using partial or complete proton decoupling. The proton decoupled spectra were obtained using DEPT procedure. The IR spectra were measured on a Nicolet-6700 FT IR spectrometer (ATR).

Commercial chemicals were used as received.

Quantum chemical calculations were carried out using the GAMESS (US) software program. The calculations were performed by the density functional theory method using the B3LYP/6-31G(d) hybrid functional and preliminary geometry optimization by semiempirical quantum chemical PM3 method.

Synthesis of amines 3a—f (general procedure). Compound **1a,b** (0.15 mol), the specified acetanilide (**2a—d**) (0.21 mol), and TFA (0.9 mol) were charged into a flat-bottom flask equipped with a reflux condenser and electromagnetic stirrer (the reactant molar ratio **1a,b** : **2a—d** : TFA = 1 : 1.4 : 6). The reaction mixture was stirred for 3 h at 80 °C. After completion of the reaction, TFA was distilled off, the residue was hydrolyzed with 10% hydrochloric acid and filtered. A 20% sodium hydroxide solution was added to the filtrate with cooling (up to highly alkaline medium). The precipitate was collected on a filter and dried *in vacuo*.

4-(Tricyclo[3.3.1.1^{3,7}]dec-1-yl)aniline (3a). Yield 96%, main component content 99%, m.p. 105—106 °C. IR, ν/cm^{-1}: 3360 (NH_2), 2896, 2846, 2646 (CH), 1685 (NH_2), 1620 (C—C_{Ar}), 1451 (CH_2), 1305, 1282 (C—N), 1256, 1183, 1005, 965, 881, 742, 674. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 228 [M + 1]$^+$ (33.4), 227 [M]$^+$ (100), 185 [M – C_3H_6(Ad)] (1.2), 184 (5.4), 170 [M – C_3H_6(Ad) – CH_3] (75), 168 [M – C_3H_6(Ad) – CH_3 – 2 H] (1.2), 133 (disubstituted Ad) (10.6), 130 (2.4), 119 (1.2), 106 (6.2), 91 (4), 77 (4.0). ^{1}H NMR (300 MHz, CCl_4, δ): 1.74 (s, 6 H, H(δ)); 1.87 (s, 6 H, H(β)); 2.04 (s, 3 H, H(γ)); 3.68 (s, 2 H, NH_2); 6.44 (s, 2 H, H(2), H(6)); 7.18 (s, 2 H, H(3), H(5)).

2-Methyl-5-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)aniline (3′b). Yield 86%, main component content 94%, m.p. 138—140 °C. IR, ν/cm^{-1}: 3365 (NH_2), 3264, 3037, 2963, 2868 (CH), 1647 (NH_2), 1587 (C—C_{Ar}), 1463, 1445 (CH_2), 1370 (CH_3), 1293 (C—N), 1052, 1010, 970, 747. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 242 [M + 1]$^+$ (30.1), 241 [M]$^+$ (100), 226 [M – CH_3(Ar)] (1.8), 198 [M – – C_2H_4(Ad) – CH_3(Ar)] (1.2); 185 [M – C_2H_4 – CH(Ad) – – CH_3(Ar)] (3.0), 184 (10.0), 170 [M – C_2H_4 – CH – CH_3(Ad) – – CH_3(Ar)] (1.0), 169 (1.0), 147 (1.7), 135 (disubstituted Ad) (1.1), 130 (1.5), 120 (1.7), 106 (16.1), 77 (1.0). ^{1}H NMR (300 MHz, CCl_4, δ): 1.57 (s, 6 H, H(δ)); 1.87 (s, 6 H, H(β)); 2.02 (s, 3 H, H(γ)); 2.02 (s, 3 H, 2-Me); 3.20 (s, 2 H, NH_2); 6.33—6.81 (m, 3 H, Ar). ^{13}C NMR (300 MHz, CCl_4, δ): 15.92 (s, C(18)); 27.23 (s, C(3), C(5), C(8)); 33.40 (s, C (1)); 35.23 (all s, C (4), C(9), C(10)); 41.56—41.90 (all s, C(2), C(6), C(7)); 112.82 (s, C(12)); 116.90 (s, C(13)); 119.13 (s, C(16)); 121.37 (s, C(15)); 125.06 (s, C(14)); 140.02 (s, C(11)).

2-Ethyl-5-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)aniline (3′c). Yield 83%, main component content 93%, m.p. 108—110 °C. IR, ν/cm^{-1}: 3375 (NH_2), 3298, 2959, 2896, 2844 (CH), 1621 (NH_2), 1620 (C—C_{Ar}), 1503 (CH_2), 1416, 1315, 1272 (C—N), 1161, 1101, 933, 807, 753 (C_2H_5). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 257 [M + 2] (2.8), 256 [M + 1]$^+$ (22.1), 255 [M]$^+$ (100), 240 [M – – CH_3(Ar)] (1.6), 226 [M – C_2H_5(Ar)] (1.4), 213 [M – CH(Ad) – – C_2H_5(Ar)] (3.3), 200 [M – C_2H_2(Ad) – C_2H_5(Ar)] (1.4), 199 (8.8), 198 (46.3), 186 (1.9), 185 [M – C_2H_2 – CH_3(Ad) – – C_2H_5(Ar)] (1.6), 184 (1.5), 170 [M – C_2H_2 – CH_3 – CH_3(Ad) – – C_2H_5(Ar)] (12.0), 169 (3.3), 146 (2.3), 135 (disubstituted Ad) (2.9), 130 (3.0), 119 (1.4), 118 (1.8), 117 (1.2), 106 (1.6), 77 (1.0). ^{1}H NMR (300 MHz, CCl_4, δ): 1.23 (s, 3 H, $CH_2C\underline{H}_3$); 1.74 (s, 6 H, H(δ)); 1.86 (s, 6 H, H(β)); 2.02 (s, 3 H, H(γ)); 2.74 (s, 2 H, $C\underline{H}_2CH_3$); 3.20 (s, 2 H, NH_2); 6.22—6.73 (m, 3 H, Ar).

2,6-Dimethyl-4-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)aniline (3d). Yield 88%, main component content 97%, m.p. 125—127 °C. IR, ν/cm^{-1}: 3381 (NH_2), 3050, 2899, 2846, 2390 (CH), 1620 (NH_2), 1616 (C—C_{Ar}), 1591, 1519, 1490, 1477 (CH_2), 1379 (CH_3), 1321, 1249 (C—N), 1180, 924, 867, 716. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 256 [M + 1]$^+$ (20.1), 255 [M]$^+$ (100), 227 [M – – C_2H_4(Ar)] (5.1), 212 [M – CH_3(Ad) – C_2H_4(Ar)] (1.9), 199 [M – C_2H_4(Ad) – C_2H_4(Ar)] (3.9), 198 (19.1), 185 [M – C_2H_4 – – CH_3(Ad) – C_2H_4(Ar)] (1.1), 184 (3.8), 170 [M – C_2H_4 – CH_3 – – CH_3(Ad) – C_2H_4(Ar)] (1.8), 160 (2.0), 159 (1.9), 146 (2.3), 135 (disubstituted Ad) (45.8), 130 (4.1), 119 (1.0), 117 (1.2), 106 (2.6), 93 (5.8), 91 (5.9), 79 (6.2), 77 (1.0). ^{1}H NMR (300 MHz, CCl_4, δ): 1.79 (s, 6 H, H(δ)); 1.87 (s, 6 H, H(β)); 2.02 (s, 3 H, H(γ)); 2.04 (s, 6 H, 2-Me, 6-Me); 3.18 (s, 2 H, NH_2); 6.31—6.73 (m, 3 H, Ar).

4-(3,5-Dimethyltricyclo[3.3.1.1^{3,7}]dec-1-yl)aniline (3e). Yield 90%, main component content 95%, m.p. 90—91 °C. IR, ν/cm^{-1}: 3365 (NH_2 stretch.), 2898, 2845, 2641 (CH stretch.), 1681 (NH_2), 1622 (C—C_{Ar}), 1450 (CH_2), 1375 (CH_3), 1305, 1280 (C—N), 1228, 1182, 1003, 963, 863, 740, 674. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 256 [M + 1]$^+$ (30.1), 255 [M]$^+$ (100), 226 [M – C_2H_5 (Me groups of Ad)] (1.8), 198 [M – C_2H_4(Ad) – – C_2H_5 (Me groups of Ad)] (1.2), 185 [M – C_2H_4 – CH(Ad) – – C_2H_5 (Me groups of Ad)] (3.0), 184 (10.0), 170 [M – C_2H_4 – – CH – CH_3(Ad) – C_2H_5 (Me groups of Ad)] (1.0), 169 (1.0), 147 (1.7), 135 (disubstituted Ad) (1.1), 130 (1.5), 120 (1.7), 106 (16.1), 77 (1.0). ^{1}H NMR (300 MHz, CCl_4, δ): 0.79 (s, 6 H, Me(Ad)); 1.52—2.42 (m, 13 H, H(Ad)); 3.21 (s, 2 H, H(NH_2)); 6.48—6.97 (m, 4 H, H(Ar)).

4-(3,5-Dimethyltricyclo[3.3.1.1^{3,7}]dec-1-yl)-2,6-dimethylaniline (3f). Yield 89%, main component content 94%, m.p. 94—97 °C. IR, ν/cm^{-1}: 3380 (NH_2), 3051, 2895, 2844, 2391

(CH), 1620 (NH_2), 1615 (C—C_{Ar}), 1592, 1518, 1491, 1475 (CH_2), 1378 (CH_3), 1321, 1245 (C—N), 1180, 925, 865, 717. MS (EI, 70 eV), m/z (I_{rel} (%)): 284 $[M + 1]^+$ (21), 283 $[M]^+$ (100), 255 [M – C_2H_4 (Me groups of Ad)] (2.4), 227 [M – – C_2H_4(Ar) – C_2H_5 (Me groups of Ad)] (5.2), 212 [M – – CH_3(Ad) – C_2H_4(Ar) – C_2H_4 (Me groups of Ad)] (1.7), 199 [M – C_2H_4(Ad) – C_2H_4(Ar) – C_2H_4 (Me groups of Ad)] (4.8), 198 (19.1), 185 [M – C_2H_4 – CH_3(Ad) – C_2H_4(Ar) – C_2H_4 (Me groups of Ad)] (1.5), 184 (3.8), 170 [M – C_2H_4 – CH_3 – CH_3(Ad) – – C_2H_4(Ar) – C_2H_4 (Me groups of Ad)] (1.6), 160 (2.0), 159 (1.9), 146 (2.3), 135 (disubstituted Ad) (45.8), 130 (4.1), 119 (1.0), 117 (1.2), 106 (2.6), 93 (5.8), 91 (5.9), 79 (6.2), 77 (1.0). ^{1}H NMR (300 MHz, CCl_4, δ): 0.78 (s, 6 H, Me(Ad)); 1.51—2.46 (m, 13 H, H(Ad), 6 H, 2-Me, 6-Me)); 3.18 (s, 2 H, H(NH_2)); 6.59 (s, 2 H, H(Ar)).

4-[4-(2-Aminoethyl)tricyclo[3.3.1.1^{3,7}]dec-1-yl]aniline (5). 4-(2-Amino)ethyladamantan-2-ol hydrogen sulfate (**4**) (9.08 g, 0.02 mol), acetanilide (7.56 g, 0.056 mol), and trifluoroacetic acid (46 g, 0.4 mol) were allowed to react in a similar way. The reaction mixture was heated for 2 h at 80 °C. Yield 92%, main component content 99%, m.p. 91—93 °C. IR, ν/cm^{-1} : 3373 (NH_2), 2905, 2854 (CH), 1674 (NH_2), 1613 (C—C_{Ar}), 1453 (CH_2), 1313, 1264 (C—N), 1139, 1009, 961, 838, 744, 722. MS (EI, 70 eV), m/z (I_{rel} (%)): 271 [M + 1] (30.7), 270 $[M]^+$ (100), 253 [M – NH_3] (60.8), 227 [M – C_2H_2 – NH_3] (3.4), 183 [M – C_2H_5 – CH_3(Ad) – C_2H_2 – NH_3] (3.2), 170 [M – CH_3 – – C_2H_5 – CH_3(Ad) – C_2H_2 – NH_3] (9.8), 133 (disubstituted Ad) (20), 106 (16.1), 77 (3.5). ^{1}H NMR (300 MHz, CCl_4, δ): 0.78 (s, 2 H, Ad$CH_2CH_2N\underline{H}_2$); 1.20 (s, 2 H, Ad$C\underline{H}_2CH_2NH_2$); 1.43—2.00 (m, 14 H, H(Ad)); 2.40 (t, 2 H, Ad$CH_2C\underline{H}_2NH_2$, J = 7.1 Hz, J = 0.9 Hz); 3.68 (s, 2 H, Ar$N\underline{H}_2$); 6.70 (s, 2 H, H(2), H(6)); 7.02 (s, 2 H, H(3), H(5)).

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