

# Alkylation of Aromatic Compounds with Adamantan-1-ol

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**Abstract**—Reactions of substituted benzenes, naphthalenes, and 2- and 3-phenyl-1-benzofurans with adamantan-1-ol in trifluoroacetic acid lead to the formation of the corresponding mono- and diadamantyl-substituted aromatic compounds.

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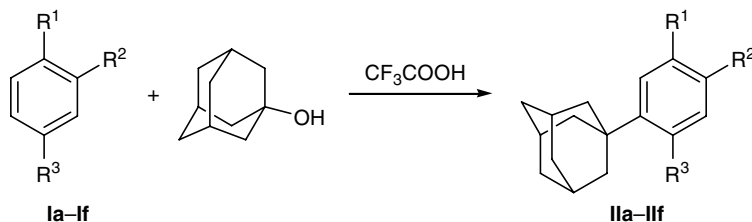
Extensive studies in the field of adamantane chemistry are related to wide prospects in using adamantane derivatives in the synthesis of biologically active compounds, heat-resistant polymers, and oil and fuel additives [1–3]. Adamantane derivatives are well known as antiviral and antimicrobial agents with a broad spectrum of activity [4–6]; some of these compounds can be used in the treatment of diseases of nervous system [7, 8]. Adamantylation of aromatic hydrocarbons leads to compounds that are convenient starting materials in target-oriented organic synthesis [9–11]. One of the main procedures for the introduction of an adamantyl group into an aromatic ring is based on reactions of halogenated adamantanes with arenes in the presence of Lewis acids [12–18]. The use of hydroxy-substituted adamantanes in the alkylation of aromatic hydrocarbons ensures the process to occur under milder conditions. These reactions are carried out in strong protic acids [19]; phosphoric anhydride was also used as catalyst [20]. Kovalev and Shokova [21] reported on the alkylation of aromatic hydrocarbons with 1-adamantyl trifluoroacetate prepared from 1-bromoadamantane and trifluoroacetic acid. Reactions of adamantan-1-ol with substituted olefins in trifluoroacetic acid

were shown to produce the corresponding 1-(1-adamantyl)alkan-1-ols [22]. Alkylation of calix[*n*]arenes (*n* = 4–6) with adamantan-1-ol in trifluoroacetic acid was also described [23].

In the present work we examined reactions of some benzene and naphthalene derivatives, as well as of 2- and 3-phenyl-1-benzofurans with adamantan-1-ol in trifluoroacetic acid. *o*-Xylene (**Ia**) and 1,2,3,4-tetrahydronaphthalene (**Ia**) reacted with adamantan-1-ol in trifluoroacetic acid at room temperature to give 1-(1-adamantyl)-3,4-dimethylbenzene (**IIa**) and 6-(1-adamantyl)-1,2,3,4-tetrahydronaphthalene (**IIb**) in 84 and 72% yield, respectively. The melting points and spectral parameters of compounds **IIa** and **IIb** coincided with those reported in [24, 25]. The alkylation of phenol (**Ic**), *o*-methylphenol (**Id**), resorcinol (**Ie**), and 4-chloro-3-methylphenol (**If**) under analogous conditions afforded the corresponding adamantyl-substituted phenols **IIc–IIf** in high yields (Scheme 1). The melting points and spectral parameters of compounds **IIc–IIe** coincided with published data [15, 16, 18], and the corresponding data for **IIf** are given in Experimental.

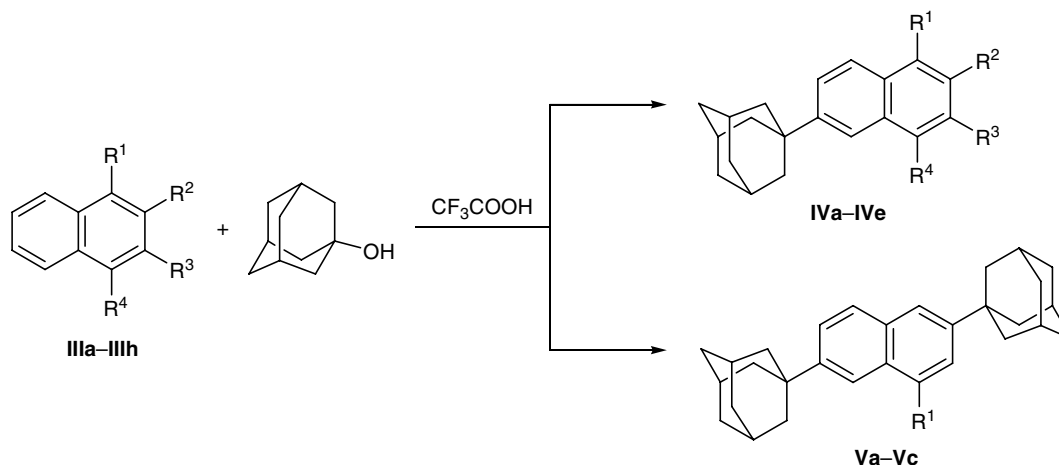
The reactions of 2-methyl-, 2-hydroxy-, 1,3-dimethyl-, 2,3-dihydroxy-, and 2-methoxynaphthalenes

Scheme 1.



$R^1 = R^2 = \text{Me}, R^3 = \text{H}$  (a);  $R^1 R^2 = (\text{CH}_2)_4, R^3 = \text{H}$  (b);  $R^1 = R^3 = \text{H}, R^2 = \text{HO}$  (c);  $R^1 = \text{Me}, R^2 = \text{HO}, R^3 = \text{H}$  (d);  $R^1 = R^3 = \text{H}, R^2 = R^3 = \text{HO}$  (e);  $R^1 = \text{Cl}, R^2 = \text{Me}, R^3 = \text{HO}$  (f).

Scheme 2.



**III, IV**,  $R^1 = R^3 = R^4 = \text{H}$ ,  $R^2 = \text{Me}$  (a), HO (b);  $R^1 = R^3 = \text{H}$ ,  $R^2 = R^4 = \text{Me}$  (c);  $R^1 = R^4 = \text{H}$ ,  $R^2 = R^3 = \text{HO}$  (d);  $R^1 = R^3 = R^4 = \text{H}$ ,  $R^2 = \text{MeO}$  (e);  $R^1 = \text{HO}$ ,  $R^2 = R^3 = R^4 = \text{H}$  (f);  $R^1 = \text{MeO}$ ,  $R^2 = R^3 = R^4 = \text{H}$  (g);  $R^1 = \text{Me}$ ,  $R^2 = R^3 = R^4 = \text{H}$  (h); **V**,  $R^1 = \text{HO}$  (a), MeO (b), Me (c).

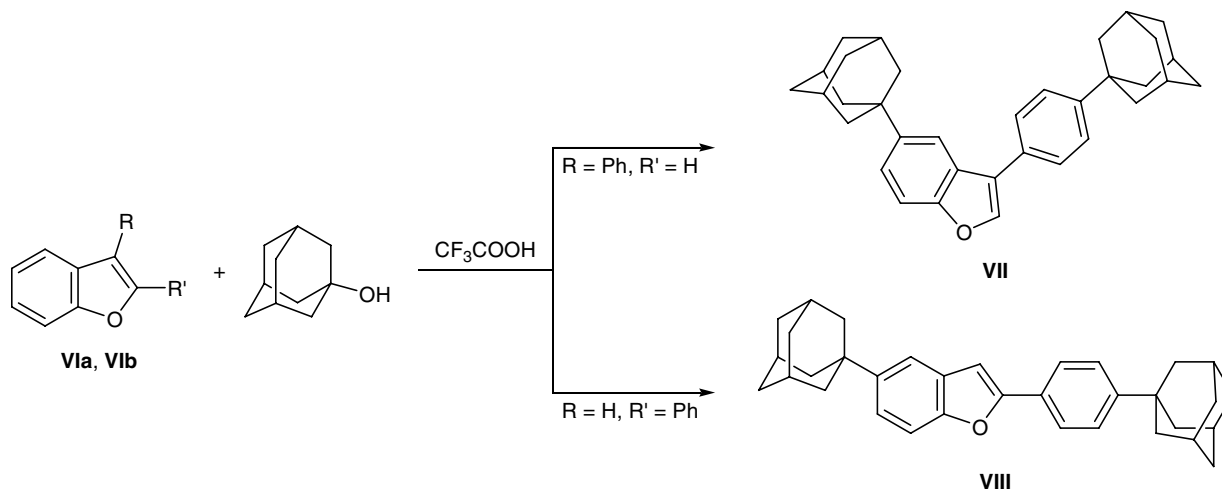
**IIIa-IIIe** with adamantan-1-ol in trifluoroacetic acid gave monoadamantyl-substituted naphthalenes **IVa-IVe** (Scheme 2). The new substituent entered the 6-position in **IIIa**, **IIIb**, **IIIc**, and **IIIe** and the 7-position in **IIIc**, as followed from the spectral parameters. The properties of compounds **IVa**, **IVb**, and **IVe** coincided with those reported in [18, 21, 26], and the melting points and spectral parameters of newly synthesized compounds **IVc** and **IVd** are given in Experimental.

The alkylation of 1-substituted naphthalenes **IIIf-IIIh** with adamantan-1-ol resulted in the formation of the corresponding 3,7-diadamantyl derivatives **Va-Vc** (Scheme 2). The  $^1\text{H}$  NMR spectra of **Va-Vc** contained

signals in the region  $\delta$  1.5–2.2 ppm (30H) from protons in the adamantyl substituents and signals from aromatic protons,  $\delta$ , ppm: **Va**: 6.94 s, 7.18 s, 7.97 s, 7.51 d, 7.71 d ( $J = 8.2$  Hz); **Vb**: 6.90 s, 7.31 s, 8.11 s, 7.57 d, 7.74 d ( $J = 8.4$  Hz); **Vc**: 7.57 s, 7.78 s, 8.07 s, 7.67 d, 7.99 d ( $J = 9.7$  Hz).

We also examined alkylation of 2- and 3-phenyl-1-benzofurans **VIa** and **VIb** with 1-adamantan-1-ol in trifluoroacetic acid. The reaction involved both aromatic rings in molecules **VIa** and **VIb** and gave diadamantyl-substituted derivatives **VII** and **VIII** (Scheme 3). The alkylation of 3-phenyl-1-benzofuran (**VIa**) was accompanied by considerable tarring of the reaction mixture, and adamantyl-substituted benzo-

Scheme 3.



$R = \text{Ph}$ ,  $R' = \text{H}$  (a);  $R = \text{H}$ ,  $R' = \text{Ph}$  (b).

furan **VII** was isolated in 22% yield by treatment of the mixture with methanol–acetone. Compound **VII** displayed in the  $^1\text{H}$  NMR spectrum signals at  $\delta$  1.7–2.0 ppm (30H) from protons in the adamantyl fragments, a singlet at  $\delta$  7.5 ppm from 2-H, signals at  $\delta$  7.2 and 7.1 ppm (d,  $J = 7.9$  Hz) from 7-H and 6-H, respectively, and signals from the *para*-substituted benzene ring at  $\delta$  7.38 and 7.42 ppm (d,  $J = 8.2$  Hz). In the  $^{13}\text{C}$  NMR spectrum of **VII**, strong signals at  $\delta_{\text{C}}$  128.3 and 131.3 ppm were observed due to equivalent carbon nuclei in the *para*-substituted benzene ring.

The alkylation of 2-phenyl-1-benzofuran (**VIb**) led to a product (yield 56%) which was assigned the structure of 5-(1-adamantyl)-2-[4-(1-adamantylphenyl)]-1-benzofuran (**VIII**) on the basis of its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The  $^1\text{H}$  NMR spectrum of **VIII** contained signals from adamantane protons ( $\delta$  1.8–2.2 ppm, 30H), 3-H ( $\delta$  7.2 ppm, s), 7-H and 6-H ( $\delta$  7.4 and 7.3 ppm, d, respectively,  $J = 7.7$  Hz), and aromatic protons ( $\delta$  7.46 and 7.90 ppm, d,  $J = 8.0$  Hz). Equivalent carbon atoms in the *para*-substituted benzene ring gave strong peaks at  $\delta_{\text{C}}$  125.1 and 129.2 ppm.

Thus our results demonstrated that the reaction of adamantan-1-ol with aromatic compounds in trifluoroacetic acid provides a convenient procedure for the synthesis of adamantyl-substituted derivatives.

## EXPERIMENTAL

The elemental compositions were determined on a Hewlett–Packard 185-B CHN analyzer. The melting points were determined on a Boetius melting point apparatus. The IR spectra were recorded from 2% solutions in chloroform on a UR-20 spectrometer. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker DPX-300 instrument (300 and 75 MHz, respectively) from 2% solutions in  $\text{CDCl}_3$  (compounds **IVa**, **IVc–IVe**, **Vb**, **VII**, **VIII**),  $\text{DMSO}-d_6$  (**IIc–IIf**, **IVb**, **Va**), or benzene- $d_6$  (**IIa**, **IIb**, **Vc**). The UV spectra were obtained in dichloroethane on a Specord UV-Vis spectrophotometer. The purity of the products was checked, and the progress of reactions was monitored, by TLC on Silufol UV-254 plates. Adamantan-1-ol was synthesized by the procedure described in [21].

**1-(1-Adamantyl)-3,4-dimethylbenzene (IIa).** Adamantan-1-ol, 0.72 g (4.7 mmol), was added under stirring to a solution of 0.5 g (4.7 mmol) of *o*-xylene (**Ia**) in 5 ml of trifluoroacetic acid, and a solid material began to separate from the solution almost immediately. The mixture was diluted with 30 ml of water,

and the precipitate was filtered off, washed with a solution of sodium carbonate, dried, and recrystallized from ethanol. Yield 0.95 g (84%), mp 110–112°C; published data [13]: mp 99–112°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1110, 1140, 1240, 1320, 1340, 1460, 1520, 1610, 2910 s.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.77–2.11 (15H, Ad), 2.21 s (3H, Me), 2.25 s (3H, Me), 7.20 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.24 s (1H,  $\text{H}_{\text{arom}}$ ), 7.27 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ).

Compounds **IIb–IIf** were synthesized in a similar way.

**6-(1-Adamantyl)-1,2,3,4-tetrahydronaphthalene (IIb)** was obtained from 0.17 g (1.3 mmol) of 1,2,3,4-tetrahydronaphthalene (**Ib**) and 0.2 g (1.3 mmol) of adamantan-1-ol in 4 ml of trifluoroacetic acid. Yield 0.26 g (72%), mp 76–78°C (from MeOH); published data [25]: mp 78–80°C. UV spectrum (ethanol):  $\lambda_{\text{max}}$  279 nm ( $\log \epsilon$  3.78). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 970, 990, 1040, 1110, 1240, 1320, 1350, 1460, 1540, 1620, 2920 s.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.66–2.11 (19H, Ad,  $\text{CH}_2$ ), 2.71–2.82 m (4H,  $\text{CH}_2$ ), 7.15 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.23 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.30 s (1H,  $\text{H}_{\text{arom}}$ ).

**4-(1-Adamantyl)phenol (IIc)** was obtained from 0.12 g (1.3 mmol) of phenol (**Ic**) and 0.2 g (1.3 mmol) of adamantan-1-ol in 4 ml of trifluoroacetic acid. Yield 0.23 g (79%), mp 180–182°C (from EtOH); published data [16]: mp 181–183°C.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.17–2.03 (15H, Ad), 6.98 d (2H,  $\text{H}_{\text{arom}}$ ,  $J = 7.2$ ), 7.12 d (2H,  $\text{H}_{\text{arom}}$ ,  $J = 7.2$ ), 9.11 br.s (1H, OH).

**4-(1-Adamantyl)-2-methylphenol (IId)** was obtained from 0.2 g (1.8 mmol) of 2-methylphenol (**Id**) and 0.27 g (1.8 mmol) of adamantan-1-ol in 4 ml of trifluoroacetic acid. Yield 0.35 g (81%), mp 138–139°C (from EtOH); published data [18]: mp 138–139°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1120, 1240, 1320, 1340, 1460, 1520, 1600, 2920 s, 3590.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.17–2.02 (15H, Ad), 2.10 s (3H, Me), 6.68 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 6.93 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.01 s (1H,  $\text{H}_{\text{arom}}$ ), 8.97 br.s (1H, OH).

**4-(1-Adamantyl)benzene-1,3-diol (IIe)** was obtained from 0.2 g (1.8 mmol) of resorcinol (**Ie**) and 0.27 g (1.8 mmol) of adamantan-1-ol in 4 ml of trifluoroacetic acid. Yield 0.34 g (76%), mp 233–235°C (from EtOH); published data [15]: mp 235–236°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 970, 1120, 1240, 1340, 1450, 1510, 2920, 3600.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.70–2.00 (15H, Ad), 6.12 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.3$ ), 6.22 s (1H,  $\text{H}_{\text{arom}}$ ), 6.80 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.3$ ), 8.92 s (1H, OH), 9.01 s (1H, OH).

**2-(1-Adamantyl)-3-chloro-4-methylphenol (IIc)** was obtained from 0.09 g (0.63 mmol) of 3-chloro-4-methylphenol (**If**) and 0.1 g (0.66 mmol) of adamantan-1-ol in 3 ml of trifluoroacetic acid. Yield 0.1 g (59%), mp 153–155°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 890, 980, 1060, 1110, 1150, 1240, 1320, 1350, 1390, 1460, 1510, 1610, 2930 s, 3590.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.71–2.02 (15H, Ad), 2.31 s (3H, Me), 6.70 s (1H,  $\text{H}_{\text{arom}}$ ), 6.96 s (1H,  $\text{H}_{\text{arom}}$ ), 9.39 br.s (1H, OH). Found, %: C 73.35; H 7.53.  $\text{C}_{17}\text{H}_{21}\text{ClO}$ . Calculated, %: C 73.77; H 7.65.

**6-(1-Adamantyl)-2-methylnaphthalene (IVa)**. Adamantan-1-ol, 0.32 g (2.1 mmol), was added under stirring to a solution of 0.3 g (2.1 mmol) of 2-methylnaphthalene (**IIIa**) in 6 ml of trifluoroacetic acid. The mixture was kept for 12 h at room temperature and diluted with water, and the precipitate was filtered off, washed with a solution of sodium carbonate, dried, and recrystallized from ethanol. Yield 0.56 g (82%). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 880, 980, 1040, 1110, 1114, 1240, 1320, 1450, 1530, 1610, 2910 s.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.84–2.17 (15H, Ad), 2.52 s (3H, Me), 7.31 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.4$ ), 7.56 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.4$ ), 7.59 s (1H,  $\text{H}_{\text{arom}}$ ), 7.70 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.4$ ), 7.72 s (1H,  $\text{H}_{\text{arom}}$ ), 7.75 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.4$ ). Found, %: C 91.18; H 8.77.  $\text{C}_{21}\text{H}_{24}$ . Calculated, %: C 91.25; H 8.75.

Compounds **IVb–IVe** were synthesized in a similar way.

**6-(1-Adamantyl)naphthalen-2-ol (IVb)** was obtained from 0.3 g (2.1 mmol) of naphthalen-2-ol (**IIIb**) and 0.32 g (2.1 mmol) of adamantan-1-ol in 6 ml of trifluoroacetic acid. Yield 0.43 g (73%), mp 193–195°C (from EtOH); published data [18]: mp 194–195°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1150, 1240, 1320, 1450, 1540, 1620, 2920 s, 3590.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.76–2.08 (15H, Ad), 7.04 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.06 s (1H,  $\text{H}_{\text{arom}}$ ), 7.48 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.60 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.63 s (1H,  $\text{H}_{\text{arom}}$ ), 7.72 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 9.56 br.s (1H, OH).

**7-(1-Adamantyl)-1,3-dimethylnaphthalene (IVc)** was obtained from 0.4 g (2.56 mmol) of 1,3-dimethylnaphthalene (**IIIc**) and 0.39 g (2.56 mmol) of adamantan-1-ol in 7 ml of trifluoroacetic acid. Yield 0.64 g  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ): 283 (3.79), 312 (2.97), 320 (2.72), 326 (2.92). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 880, 980, 1040, 1110, 1240, 1320, 1450, 1540, 1620, 2990 s.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.85–2.18 (15H, Ad), 2.48 s (3H, Me), 2.70 s (3H, Me), 7.17 s (1H,  $\text{H}_{\text{arom}}$ ), 7.47 s (1H,  $\text{H}_{\text{arom}}$ ), 7.57 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.9$ ), 7.76 d (1H,  $\text{H}_{\text{arom}}$ ,

$J = 8.9$ ), 7.83 s (1H,  $\text{H}_{\text{arom}}$ ). Found, %: C 90.74; H 8.96.  $\text{C}_{22}\text{H}_{26}$ . Calculated, %: C 90.98; H 9.02.

**6-(1-Adamantyl)naphthalene-2,3-diol (IVd)** was obtained from 0.21 g (1.3 mmol) of naphthalene-2,3-diol (**IIIId**) and 0.2 g (1.3 mmol) of adamantan-1-ol in 6 ml of trifluoroacetic acid. Yield 0.3 g (78%), mp 210–212°C (from EtOH– $\text{H}_2\text{O}$ ). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 870, 890, 1120, 1250, 1270, 1320, 1350, 1460, 1520, 1630, 2920 s, 3550, 3590.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.83–2.15 (15H, Ad), 5.62 br.s (2H, OH), 7.19 s (1H,  $\text{H}_{\text{arom}}$ ), 7.21 s (1H,  $\text{H}_{\text{arom}}$ ), 7.42 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 9.1$ ), 7.53 s (1H,  $\text{H}_{\text{arom}}$ ), 7.61 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 9.1$ ). Found, %: C 81.23; H 7.47.  $\text{C}_{20}\text{H}_{22}\text{O}_2$ . Calculated, %: C 81.60; H 7.53.

**6-(1-Adamantyl)-2-methoxynaphthalene (IVe)** was obtained from 0.5 g (3.16 mmol) of 2-methoxynaphthalene (**IIIe**) and 0.48 g (3.16 mmol) of adamantan-1-ol in 8 ml of trifluoroacetic acid. Yield 0.71 g (77%), mp 143–145°C; published data [21]: mp 143–144.5°C. UV spectrum (dichloroethane),  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ): 263 (3.82), 272 (3.81), 320 (3.29), 333 (3.40). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 860, 890, 930, 980, 1040, 1130, 1170, 1270, 1340, 1390, 1460, 1490, 1510, 1620, 2920 s.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.84–2.16 (15H, Ad), 3.94 s (3H, OMe), 7.13 s (1H,  $\text{H}_{\text{arom}}$ ), 7.15 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.57 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.68 s (1H,  $\text{H}_{\text{arom}}$ ), 7.72 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.75 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ).

**3,7-Bis(1-adamantyl)naphthalen-1-ol (Va)**. A solution of 0.12 g (0.83 mmol) of naphthalen-1-ol (**IIIIf**) in 4 ml of trifluoroacetic acid was added under stirring to a solution of 0.3 g (1.97 mmol) of adamantan-1-ol in 2 ml of trifluoroacetic acid. A solid began to separate from the resulting solution in a few minutes. The mixture was kept for 16 h at room temperature and diluted with 30 ml of water, and the precipitate was filtered off, washed with a solution of sodium carbonate, dried, and recrystallized from isopropyl alcohol. Yield 0.23 g (67%), mp 345–350°C.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.76–2.12 (30H, Ad), 6.94 s (1H,  $\text{H}_{\text{arom}}$ ), 7.18 s (1H,  $\text{H}_{\text{arom}}$ ), 7.51 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.71 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.97 s (1H,  $\text{H}_{\text{arom}}$ ), 9.53 br.s (1H, OH). Found, %: C 87.52; H 8.60.  $\text{C}_{30}\text{H}_{36}\text{O}$ . Calculated, %: C 87.33; H 8.79.

Compounds **Vb** and **Vc** were synthesized in a similar way.

**3,7-Bis(1-adamantyl)-1-methoxynaphthalene (Vb)** was obtained from 0.2 g (1.3 mmol) of adamantan-1-ol and 0.1 g (0.63 mmol) of 1-methoxynaphthalene (**IIIg**) in 7 ml of trifluoroacetic acid. Yield 0.22 g

(81%), mp 293–295°C (from octane). UV spectrum (dichloroethane),  $\lambda_{\max}$ , nm (log  $\epsilon$ ): 293 (3.70), 312 (3.47), 323 (3.30). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 880, 980, 1010, 1120, 1290, 1320, 1400, 1460, 1580, 1600, 2910 s.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.84–2.16 (30H, Ad), 4.05 s (3H, OMe), 6.90 s (1H,  $\text{H}_{\text{arom}}$ ), 7.31 s (1H,  $\text{H}_{\text{arom}}$ ), 7.57 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.4$ ), 7.74 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 8.4$ ), 8.11 s (1H,  $\text{H}_{\text{arom}}$ ). Found, %: C 87.41; H 8.71.  $\text{C}_{31}\text{H}_{38}\text{O}$ . Calculated, %: C 87.27; H 8.98.

**3,7-Bis(1-adamantyl)-1-methylnaphthalene (Vc)** was obtained from 0.3 g (1.97 mmol) of adamantan-1-ol and 0.12 g (0.84 mmol) of 1-methylnaphthalene (**IIIh**) in 6 ml of trifluoroacetic acid. Yield 0.32 g (92%), mp 302–303°C (from toluene). UV spectrum (dichloroethane):  $\lambda_{\max}$  280 nm (log  $\epsilon$  3.79).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.86–2.16 (30H, Ad), 2.77 s (3H, Me), 7.57 s (1H,  $\text{H}_{\text{arom}}$ ), 7.67 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 9.7$ ), 7.78 s (1H,  $\text{H}_{\text{arom}}$ ), 7.99 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 9.7$ ), 8.07 s (1H,  $\text{H}_{\text{arom}}$ ). Found, %: C 90.58; H 9.21.  $\text{C}_{31}\text{H}_{38}$ . Calculated, %: C 90.67; H 9.33.

**5-(1-Adamantyl)-3-[4-(1-adamantyl)phenyl]-1-benzofuran (VII)**. A solution of 0.22 g (1.13 mmol) of 3-phenyl-1-benzofuran (**VIa**) in 4 ml of trifluoroacetic acid was added under stirring to a solution of 0.4 g (2.63 mmol) of adamantan-1-ol in 4 ml of trifluoroacetic acid. After several minutes, an oily substance separated and solidified on storage (for about 12 h) to form a dense amorphous material. The product was crushed into small pieces, filtered off, washed with a solution of sodium carbonate, and dried. It was then treated with methanol, the mixture was heated to the boiling point, and acetone was added dropwise until a crystalline material separated. Yield 0.1 g (22%), mp 222–224°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 910, 980, 1060, 1110, 1170, 1240, 1320, 1360, 1470, 1490, 1610, 2910 s.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.68–2.12 (30H, Ad), 7.09 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 7.9$ ), 7.22 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 7.9$ ), 7.38 d (2H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.42 d (2H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ), 7.43 s (1H,  $\text{H}_{\text{arom}}$ ), 7.49 s (1H, 2-H).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 28.7, 29.5, 36.8, 37.1, 37.3, 41.9, 44.1 (Ad); 107.3, 115.7, 119.2, 119.8 ( $\text{C}_{\text{arom}}$ ); 127.5 ( $\text{C}^3$ ); 128.3, 129.9, 131.3, 134.8 ( $\text{C}_{\text{arom}}$ ); 148.2 ( $\text{C}^2$ ); 153.3, 160.6 ( $\text{C}_{\text{arom}}$ ). Found, %: C 88.14; H 8.29.  $\text{C}_{34}\text{H}_{38}\text{O}$ . Calculated, %: C 88.26; H 8.28.

**5-(1-Adamantyl)-2-[4-(1-adamantyl)phenyl]-1-benzofuran (VIII)**. A solution of 0.17 g (0.87 mmol) of 2-phenyl-1-benzofuran (**VIb**) in 4 ml of trifluoroacetic acid was added under stirring to a solution of 0.3 g (1.97 mmol) of adamantan-1-ol in 3 ml of trifluoroacetic acid. After several minutes, a solid began

to separate from the solution. The mixture was kept for 8 h at room temperature and diluted with water, and the precipitate was filtered off, washed with a solution of sodium carbonate, dried, and recrystallized twice from ethanol–ethyl acetate. Yield 0.23 g (56%). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 990, 1030, 1050, 1110, 1240, 1320, 1350, 1400, 1450, 1490, 1610, 2910 s.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 1.83–2.20 (30H, Ad), 7.20 s (1H, 3-H), 7.29 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 7.7$ ), 7.31 s (1H,  $\text{H}_{\text{arom}}$ ), 7.36 d (1H,  $\text{H}_{\text{arom}}$ ,  $J = 7.7$ ), 7.46 d (2H,  $\text{H}_{\text{arom}}$ ,  $J = 8.0$ ), 7.90 d (2H,  $\text{H}_{\text{arom}}$ ,  $J = 8.2$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 29.5, 29.6, 37.2, 37.3, 37.5, 38.3, 42.8, 44.0 (Ad); 102.6 ( $\text{C}^3$ ); 106.0, 116.4, 124.0, 125.1, 128.5, 129.2, 131.3, 144.0, 148.6, 154.3 ( $\text{C}_{\text{arom}}$ ); 156.6 ( $\text{C}^2$ ). Found, %: C 88.22; H 8.13.  $\text{C}_{34}\text{H}_{38}\text{O}$ . Calculated, %: C 88.26; H 8.28.

## REFERENCES

1. Newkome, G.R., Narayana, V.V., Patri, A.K., Grob, J., Moorefield, C.N., and Baker, G.R., *Polym. Mater. Sci. Eng.*, 1995, vol. 737, p. 222.
2. Chen, S.H., Mastrangelo, J.C., Shi, H., Bashir-Hashemi, A., Li, J., and Gelber, N., *Macromolecules*, 1995, vol. 28, p. 7775.
3. Ishizone, T., Matsuoka, S., Sakai, S., Harada, W., and Tajima, H., *Macromolecules*, 2004, vol. 37, p. 7069.
4. Zoidis, G., Papanastasiou, I., Dotsikas, I., Sandoval, A., Gouvea Dos Santos, R., Papadopoulou-Daifoti, Z., Vamvakides, A., Kolocouris, N., and Felix, R., *Bioorg. Med. Chem.*, 2005, vol. 13, p. 2791.
5. Baxter, A., Bent, J., Bowers, K., Braddock, M., Brough, S., Fagura, M., Lawson, M., McInally, T., Mortimore, M., Robertson, M., Weaver, R., and Webborn, P., *Bioorg. Med. Chem. Lett.*, 2003, vol. 13, p. 4047.
6. Gandhi, C.S., Shuck, K., Lear, J.D., Dieckmann, G.R., DeGrado, W.F., Lamb, R.A., and Pinto, L.H., *J. Biol. Chem.*, 1999, vol. 274, p. 5474.
7. Henkel, J.G., Hane, J.T., and Gianutsos, G., *J. Med. Chem.*, 1982, vol. 25, p. 51.
8. Skolimowski, J., Kochmann, A., Gebicka, L., and Metodieva, D., *Bioorg. Med. Chem.*, 2003, vol. 11, p. 3529.
9. Li, Q., Rukavishnikov, A.V., Petukhov, P.A., Zaikova, T.O., and Keana, J.F.W., *Org. Lett.*, 2002, vol. 4, p. 3631.
10. Li, Q., Jin, C., Petukhov, P.A., Rukavishnikov, A.V., Zaikova, T.O., Phadke, A., LaMunyon, D.H., Lee, M.D., and Keana, J.F.W., *J. Org. Chem.*, 2004, vol. 69, p. 1010.
11. Li, Q., Rukavishnikov, A.V., Petukhov, P.A., Zaikova, T.O., Jin, C., and Keana, J.F.W., *J. Org. Chem.*, 2003, vol. 68, p. 4862.

12. No, B.I., Buteev, G.M., and Ledenev, S.M., *Zh. Org. Khim.*, 1994, vol. 30, p. 315; Rundel, W., *Chem. Ber.*, 1966, vol. 99, p. 2707.
13. Voronenkov, A.V., Aliev, A.A., Kuttrakov, A.A., and Voronenkov, V.V., *Russ. J. Org. Chem.*, 1999, vol. 35, p. 305.
14. Stetter, H., Weber, J., and Wulf, C., *Chem. Ber.*, 1964, vol. 97, p. 3488.
15. Shvedov, V.I., Safonova, O.A., Korsakova, I.A., Bogdanova, N.S., Nikolaeva, I.S., and Peters, V.V., *Khim.-Farm. Zh.*, 1980, vol. 14, no. 2, p. 54.
16. Stepanov, F.N., Srebrodol'skii, Yu.I., Dikolenko, E.I., and Ziborova, I.F., *Zh. Org. Khim.*, 1970, vol. 6, p. 1619.
17. More, R.E., US Patent no. 3594427, 1971; *Chem. Abstr.*, 1971, vol. 75, no. 118780f.
18. Yoshiaki, J., Masaaki, T., Hirokazu, N., and Morimasa, T., US Patent no. 3883603, 1971; *Ref. Zh., Khim.*, 1976, no. 7N245P.
19. Tsy-pin, V.G. and Golod, E.L., *Russ. J. Org. Chem.*, 1998, vol. 34, p. 1059.
20. Zosin, L.A. and Yurchenko, A.G., *Zh. Org. Khim.*, 1980, vol. 16, p. 887.
21. Kovalev, V.V. and Shokova, E.A., *Zh. Org. Khim.*, 1985, vol. 21, p. 2085.
22. Kovalev, V.V. and Shokova, E.A., *Zh. Org. Khim.*, 1981, vol. 17, p. 109.
23. Khomich, A.N., Shokova, E.A., and Kovalev, V.V., *Synlett*, 1994, vol. 12, p. 1027; Shokova, E.A., Khomich, A.N., and Kovalev, V.V., *Tetrahedron Lett.*, 1996, p. 543; Kovalev, V.V., Shokova, E.A., and Paraskevov, Ya.V., *Russ. J. Org. Chem.*, 1999, vol. 35, p. 1464; Shokova, E.A., Khomich, A.N., and Kovalev, V.V., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 612; Shokova, E.A., Khomich, A.N., Akhmetov, N.N., Vatsuro, I.M., Luzikov, Yu.N., and Kovalev, V.V., *Russ. J. Org. Chem.*, 2003, vol. 39, p. 368.
24. Sharbat'yan, T.A., Terent'ev, P.B., Kovalev, V.V., and Shokova, E.A., *Zh. Org. Khim.*, 1980, vol. 16, p. 308.
25. Kovalev, V.V., Vasil'eva, M.A., and Shokova, E.A., *Neftekhimiya*, 1978, vol. 18, no. 1, p. 17.
26. Luzikov, Yu.I., Kovalev, V.V., and Shokova, E.A., *Neftekhimiya*, 1978, vol. 18, no. 3, p. 345.