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New Tertiary Aminomethylphenols Having an Isobornyl Substituent

E. V. Buravlev[a], I. Yu. Chukicheva[a], K. Yu. Suponitskii[b], and A. V. Kuchin[a]

[a] *Institute of Chemistry, Komi Research Center, Ural Division, Russian Academy of Sciences, ul. Pervomaiskaya 48, Syktyvkar, 167982 Russia*
e-mail: chukicheva-iy@chemi.komisc.ru

[b] *Nesmeyanov Institute of Organometallic Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*

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Abstract—New tertiary aminomethylphenols having an isobornyl fragment in the *ortho* position with respect to the phenolic hydroxy group were synthesized by the Mannich reaction.

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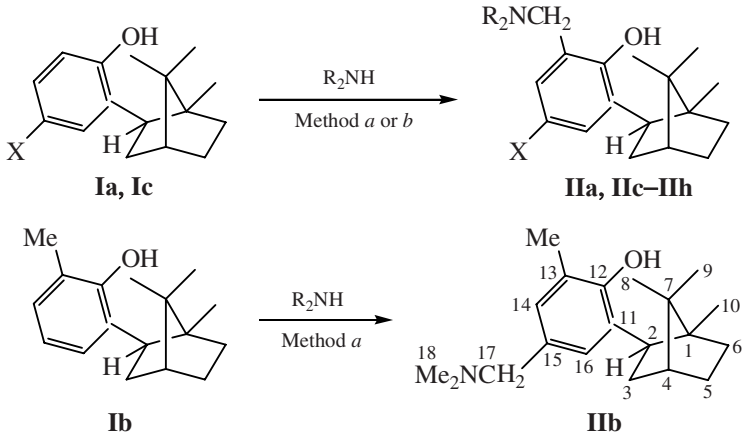
We previously performed a series of studies on the synthesis of terpenophenols with an isobornyl substituent. Naturally occurring analogs of these compounds are known to exhibit a broad spectrum of biological activity toward warm-blooded animals [1]. Introduction of additional functional groups (e.g., amino group) into molecules of alkylphenols considerably extends the spectrum of their biological activity, as well as their synthetic potential. Aminomethylation of aromatic compounds having a labile hydrogen atom (Mannich reaction) is an important method for the synthesis and modification of natural compounds and pharmacological agents. In addition, the Mannich reaction ensures a convenient synthetic approach to many building blocks, for the amino group can be readily converted into other functional groups [2–3].

In the present article we report on the synthesis of tertiary aminomethylphenols having an isobornyl fragment in the *ortho* position with respect to the hydroxy group (Scheme 1). Amines **IIa–IIc** were synthesized in 59–83% yield by heating the corresponding phenol **Ia–Ic** with *N*,*N*,*N*′,*N*′-tetramethylmethane-

Scheme 1.



I, X = H (**a**), CH_3 (**c**); **II**, X = H (**a**), Me (**c**–**h**), R = Me (**a**, **c**), *n*-C_4H_9 (**d**), *n*-C_6H_{13} (**e**), *n*-C_8H_{17} (**f**), R_2N = morpholino (**g**), piperidino (**h**).

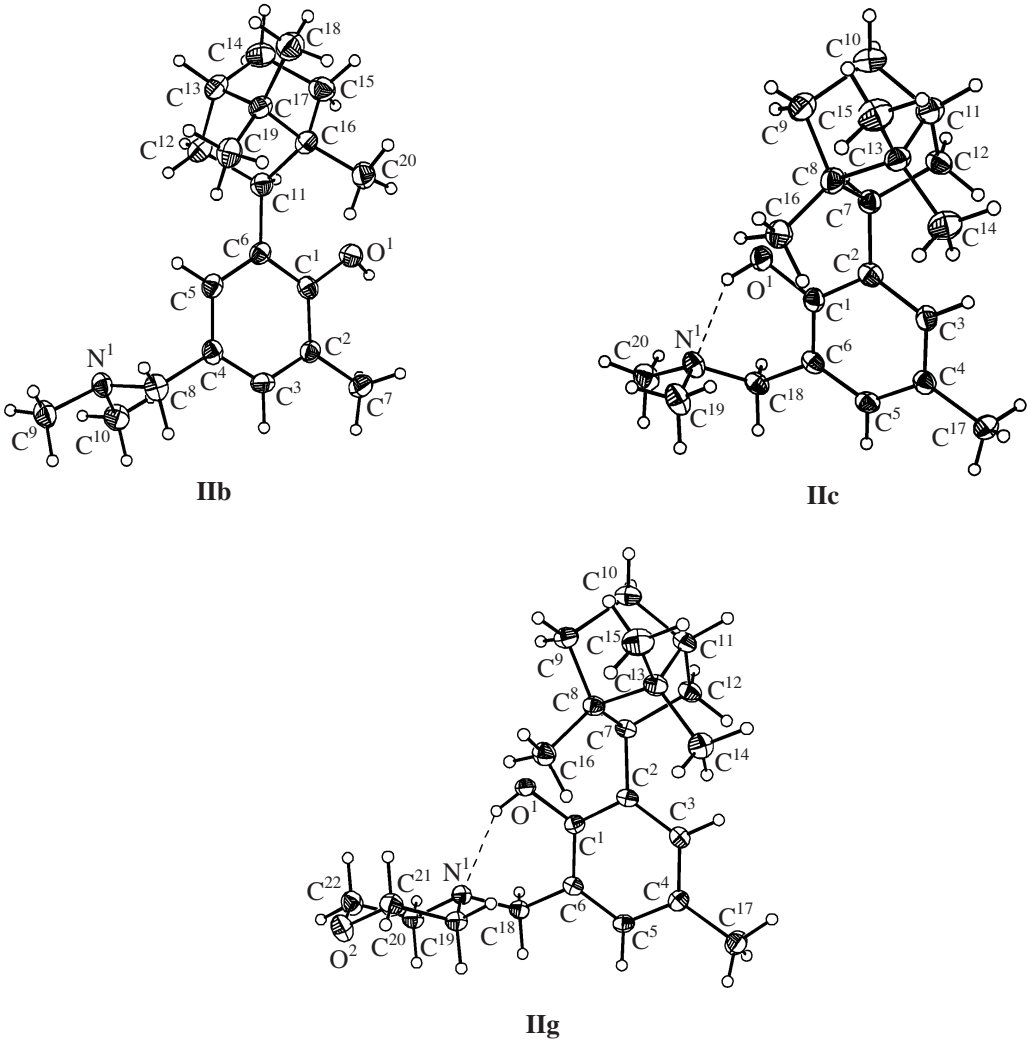


Fig. 1. Structures of molecules **IIb**, **IIc**, and **IIg** according to the X-ray diffraction data. Atoms are shown as thermal ellipsoids with a probability of 50%.

diamine in boiling anhydrous methanol (method *a*); the reactions were selective, and no other products were formed. Amines **IId–IIh** were obtained in 91–98% yield by the Mannich reaction of 2-isobornyl-4-methylphenol (**Ic**) (method *b*) [2]. In addition, amines **IIe** and **IIf** were converted into the corresponding hydrochlorides **IIe**·HCl and **IIf**·HCl (yield 85–87%).

The structure of newly synthesized compounds **IIa–IIh** was confirmed by the IR and ^{1}H and ^{13}C NMR spectra and elemental analyses. In the aromatic region of their ^{13}C NMR spectra we observed signals from quaternary carbon atoms linked to OH and CH_3 groups (except for **IIa**), terpene fragment, and aminomethyl group. The hydroxy proton in amines **IIa** and **IIc–IIh** resonated in the ^{1}H NMR spectrum as a broadened singlet at δ 10.5–11.5 ppm. The IR spectra of **IIa–IIh** lacked absorption in the region 3400–3600 cm^{-1}, which is typical of phenolic hydroxy group.

The structure of compounds **IIb**, **IIc**, and **IIg** was also proved by X-ray analysis (Fig. 1). The crystalline structures of **IIb** and **IIc** include one crystallographically independent molecule, while structure **IIg** is composed of two independent molecules A and A' with almost identical structures; therefore, only molecule A is shown in Fig. 1 and is considered below.

The central aromatic ring in all molecules **IIb**, **IIc**, and **IIg** is planar. The orientation of the isobornyl substituent, which is determined by torsional angles (Table 1) is similar for all molecules **IIb**, **IIc**, and **IIg**. The aminomethyl groups in *ortho*-aminomethylphenols **IIc** and **IIg** are also oriented similarly, and

Table 1. Torsion angles defining orientation of substituents in the central aromatic ring in molecules **IIb**, **IIc**, and **IIg**

Torsion angle[a]	**IIb**	**IIc**	**IIg** (A)	**IIg** (A')
$C^1C^2C^7C^8$ ($C^1C^6C^{11}C^{16}$)	78.6(2)	81.6(3)	82.6(3)	82.2(2)
$C^3C^2C^7C^{12}$ ($C^5C^6C^{11}C^{12}$)	19.3(2)	22.3(4)	23.5(2)	25.7(2)
$C^5C^6C^{18}N^1$ ($C^3C^4C^8N^1$)	106.4(2)	143.3(3)	132.43(13)	128.87(14)
$C^6C^{18}N^1C^{19}$ ($C^4C^8N^1C^{10}$)	–65.3(2)	–65.7(3)	–58.6(2)	–59.6(2)
$C^6C^{18}N^1C^{20}$ ($C^4C^8N^1C^9$)	173.3(2)	171.1(3)	179.99(12)	178.64(12)

[a] In parentheses are given the corresponding torsion angles in molecule **IIb**.

Table 2. Hydrogen-bond parameters in the crystal structure of compounds **IIb**, **IIc**, and **IIg**

Comp. no.	Bond	O···N, Å	H···N, Å	∠OHN, deg
IIb	O^1–H^1···N^1(x, $-y + 0.5$, $z - 0.5$)	2.750(2)	1.99	148
IIc	O^1–H^1···N^1	2.683(3)	1.95	144
IIg (A)	O^1–H^1···N^1	2.749(2)	1.99	148
IIg (A')	$O^{1'}$–$H^{1'}$···$N^{1'}$	2.766(2)	1.99	152

intramolecular hydrogen bond is formed in crystal [4] (Table 2). The $CH_2N(CH_3)_2$ group in molecule **IIb** is oriented slightly differently (Table 1), presumably due to participation of the N^1 atom in intermolecular hydrogen bond which gives rise to chains along the crystallographic *c* axis (Fig. 2). Crystal packings of **IIc** and **IIg** are formed via common van der Waals interactions. Thus, in the crystalline structures of all the examined compounds, the hydroxy group is involved in hydrogen bonding, which is reflected in their IR and ^{1}H NMR spectra.

Initial phenols **Ia**–**Ic**, amines **IIa**–**IIh**, and hydrochlorides **IId**·HCl and **IIe**·HCl are racemates. The structure of the terpene fragment did not change in the course of the examined transformations.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer from KBr pellets (solid samples) or thin films (liquids). The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX-400 spectrometer at 400 and 100 MHz, respectively, using $CDCl_3$ as solvent. The melting points were determined on a Kofler hot stage. The progress of reactions was monitored by TLC on Sorbfil plates; spots were detected by

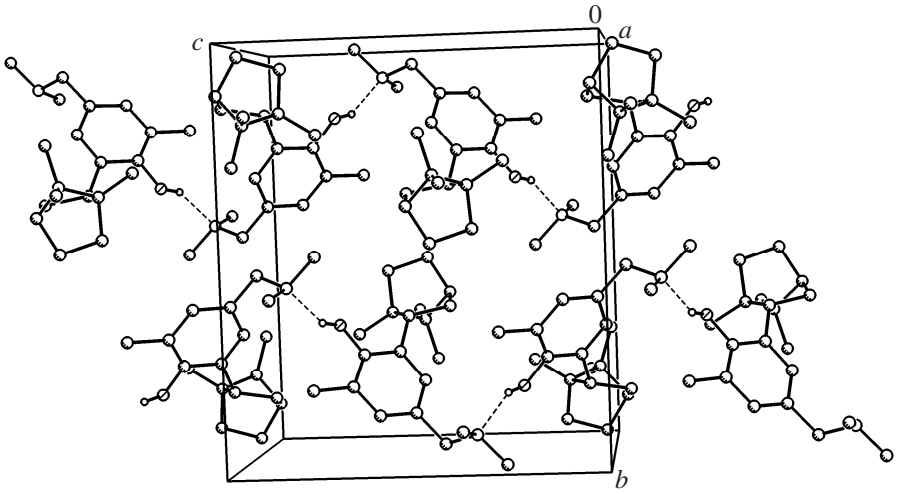


Fig. 2. A fragment of the crystal packing of compound **IIb**; hydrogen-bond system responsible for the formation of bands along the crystallographic *c* axis is shown.

treatment with a solution of $KMnO_4$ (15 g of $KMnO_4$, 300 ml of H_2O, and 0.5 ml of concentrated sulfuric acid). Amines were detected by treatment with a 0.5% solution of ninhydrin in ethanol containing glacial acetic acid (3 vol %), followed by heating to 100–120°C. Benzene was dried over $CaCl_2$ and then distilled over metallic sodium. Petroleum ether boiling at 65–70°C was used. *N*,*N*,*N*′,*N*′-Tetramethylmethanediamine, di-*n*-butylamine, di-*n*-hexylamine, di-*n*-octylamine, morpholine, and piperidine were distilled just before use. Methanol was refluxed over magnesium methoxide and then distilled. Silica gel (Alfa Aesar, 70–230 μm) was used for column chromatography (wet packing). *o*-Isobornylphenols **Ia**–**Ic** were synthesized by the procedures described in [1].

Amines IIa-IIc *(general procedure, method a).* A mixture of 4.0 mmol of phenol **Ia**–**Ic** and 4.4 mmol of *N*,*N*,*N*′,*N*′-tetramethylmethanediamine in 20 ml of anhydrous methanol was stirred at room temperature and was then heated for 14 h under reflux, the progress of the reaction being monitored by TLC using petroleum ether–diethyl ether (3:1) as eluent. When the reaction was complete, the mixture was cooled to room temperature, and the precipitate was filtered off, washed with methanol (20 ml), and recrystallized from methanol.

2-(Dimethylaminomethyl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (IIa). Yield 59%. Colorless crystals, mp 92–94°C (from methanol). IR spectrum, ν, cm^{-1}: 2990, 2950, 2878, 1453, 1375 (Me, CH_2), 1595 (C=C), 1250 (C–O), 1215 (C–N), 851, 784 (=C–H). ^{1}H NMR spectrum, δ, ppm: 0.78 s (3H, $C^{10}H_3$), 0.84 s (3H, C^9H_3), 0.91 s (3H, C^8H_3), 1.33–1.40 m (1H, 3-H), 1.50–1.65 m (3H, 4-H, 5-H), 1.81–1.90 m (2H, 6-H), 2.14–2.21 m (1H, 3-H), 2.31 s (6H, NCH_3), 3.32 t (1H, 2-H, *J* 9.0 Hz), 3.62 s (2H, NCH_2), 6.73 t (1H, 15-H, *J* 7.4 Hz), 6.80 d and 7.23 d (1H each, 14-H, 16-H, *J* 7.2, 7.6 Hz), 11.20 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 157.16 (C^{12}), 130.54 (C^{11}), 127.08 (C^{15}), 125.59 (C^{14}), 121.06 (C^{13}), 117.74 (C^{16}), 62.96 (NCH_2), 49.81 (C^1), 47.85 (C^7), 45.72 (C^4), 44.72 (C^2), 44.19 (NCH_3), 39.65 (C^6), 33.86 (C^3), 27.56 (C^5), 21.48 (C^8), 20.31 (C^9), 12.09 (C^{10}). Found, %: C.47; H 10.11; N 4.89. $C_{19}H_{29}NO$. Calculated, %: C 79.39; H 10.17; N 4.87.

4-(Dimethylaminomethyl)-2-methyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (IIb). Yield 73%. Colorless crystals, mp 135–137°C (from methanol). IR spectrum, ν, cm^{-1}: 2951, 2940, 2874, 1456, 1362 (Me, CH_2), 1593 (C=C), 1194 (C–O), 1177 (C–N), 884, 893 (=C–H). ^{1}H NMR spectrum, δ, ppm: 0.77 s (3H, $C^{10}H_3$), 0.84 s (3H, C^9H_3), 0.89 s (3H, C^8H_3), 1.32–1.47 m (2H, 3-H, 4-H), 1.57–1.67 m (2H, 5-H), 1.84–1.90 m (2H, 6-H), 2.20 s (6H, NCH_3), 2.21 s (3H, $C^{17}H_3$), 2.23–2.26 m (1H, 3-H), 3.09 t (1H, 2-H, *J* 8.8 Hz), 3.28 d and 3.38 d (1H each, NCH_2, *J* 12.4 Hz), 5.02 br.s (1H, OH), 6.91 d and 7.04 d (1H each, 14-H, 16-H, *J* 1.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 152.20 (C^{12}), 129.09 (C^{11}), 128.89 (C^{14}), 128.52 (C^{15}), 126.96 (C^{16}), 122.60 (C^{13}), 64.26 (NCH_2), 49.68 (C^1), 48.02 (C^7), 45.72 (C^4), 45.53 (C^2), 45.09 (NCH_3), 40.04 (C^6), 34.16(C^3), 27.54 (C^5), 21.42 (C^8), 20.18 (C^9), 16.21 (C^{17}), 12.37 (C^{10}). Found, %: C 79.75; H 10.29; N.68. $C_{20}H_{31}NO$. Calculated, %: C 79.68; H 10.36; N 4.65.

2-(Dimethylaminomethyl)-4-methyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (IIc). Yield 83%. Colorless crystals, mp 123–124°C (from methanol). IR spectrum, ν, cm^{-1}: 2996, 2960, 2884, 1464, 1390 (Me, CH_2), 1616 (C=C), 1256 (C–O), 1232 (C–N), 846, 784 (=C–H). ^{1}H NMR spectrum, δ, ppm: 0.78 s (3H, $C^{10}H_3$), 0.84 s (3H, C^9H_3), 0.91 s (3H, C^8H_3), 1.32–1.39 m (1H, 3-H), 1.50–1.65 m (3H, 4-H, 5-H), 1.82–1.89 m (2H, 6-H), 2.12–2.21 m (1H, 3-H), 2.25 s (3H, $C^{17}H_3$), 2.30 s (6H, NCH_3), 3.30 t (1H, 2-H, *J* 9.0 Hz), 3.58 s (2H, NCH_2), 6.61 d and 7.02 d (1H each, 14-H, 16-H), 11.15 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 154.73 (C^{12}), 130.22 (C^{11}), 127.73 (C^{14}), 126.49 (C^{15}), 126.12 (C^{16}), 120.78 (C^{13}), 62.99 (NCH_2), 49.80 (C^1), 47.87 (C^7), 45.74 (C^4), 44.70 (C^2), 44.23 (NCH_3), 39.63 (C^6), 33.81 (C^3), 27.56 (C^5), 21.49 (C^{17}), 20.91 (C^8), 20.33 (C^9), 12.08 (C^{10}). Found, %: C.74; H 10.31; N 4.70. $C_{20}H_{31}NO$. Calculated, %: C 79.68; H 10.36; N 4.65.

Amines IId–IIh *(general procedure, method b).* Phenol **Ic**, 4.0 mmol, and paraformaldehyde, 4.8 mmol, were dissolved in 20 ml of anhydrous benzene at 20°C, the corresponding amine was added, and the mixture was heated for 6 h under reflux, the progress of the reaction being monitored by TLC using petroleum ether–diethyl ether (5:1) as eluent. When the reaction was complete, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel using petroleum ether–diethyl ether (gradient elution). Amines **IIg** and **IIh** were additionally recrystallized from pentane.

2-(Dibutylaminomethyl)-4-methyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (IId). Yield 95%. Colorless oil. IR spectrum, ν, cm^{-1}: 2955, 2928, 2874, 1460, 1368 (Me, CH_2), 1613 (C=C), 1283 (C–

O), 1231 (C–N), 862, 781 (=C–H). ^{1}H NMR spectrum, δ, ppm: 0.77 s (3H, $C^{10}H_3$), 0.83 s (3H, C^9H_3), 0.89 t (6H, $C^{22}H_3$, $C^{22'}H_3$, *J* 7.4 Hz), 0.90 s (3H, C^8H_3), 1.21–1.38 m (5H, 3-H, 21-H, 21'-H), 1.43–1.61 m (7H, 4-H, 5-H, 20-H, 20'-H), 1.78–1.87 m (2H, 6-H), 2.11–2.19 m (1H, 3-H), 2.23 s (3H, $C^{17}H_3$), 2.36–2.45 m (2H, 19-H, 19'-H), 2.50–2.59 m (2H, 19-H, 19'-H), 3.28 t (1H, 2-H, *J* 9.0 Hz), 3.54 d and 3.79 d (1H each, NCH_2, *J* 14.0 Hz), 6.59 d and 7.00 d (1H each, 14-H, 16-H, *J* 1.2 Hz), 11.34 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 154.86 (C^{12}), 130.17 (C^{11}), 127.56 (C^{14}), 126.35 (C^{15}), 126.22 (C^{16}), 121.13 (C^{13}), 58.29 (NCH_2), 53.00 (C^{19}, $C^{19'}$), 49.78 (C^1), 47.88 (C^7), 45.78 (C^4), 44.63 (C^2), 39.63 (C^6), 33.81 (C^3), 28.50 (C^{20}, $C^{20'}$), 27.56 (C^5), 21.51 (C^{17}), 20.94 (C^8), 20.66 (C^{21}, $C^{21'}$), 20.37 (C^9), 14.02 (C^{22}, $C^{22'}$), 12.10 (C^{10}). Found, %: C 80.90; H 11.31; N 3.64. $C_{26}H_{43}NO$. Calculated, %: C 80.98; H 11.24; N 3.63.

2-(Dihexylaminomethyl)-4-methyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (IIe). Yield 91%. Colorless oil. IR spectrum, ν, cm^{-1}: 2936, 2884, 1468, 1376 (Me, CH_2), 1614 (C=C), 1282 (C–O), 1232 (C–N), 868, 784 (=C–H). ^{1}H NMR spectrum, δ, ppm: 0.78 s (3H, $C^{10}H_3$), 0.84 s (3H, C^9H_3), 0.88 t (6H, $C^{24}H_3$, $C^{24'}H_3$, *J* 6.8 Hz), 0.91 s (3H, C^8H_3), 1.22–1.39 m (13H, 3-H, 21-H, 21'-H, 22-H, 22'-H, 23-H, 23'-H), 1.45–1.62 m (7H, 4-H, 5-H, 20-H, 20'-H), 1.79–1.88 m (2H, 6-H), 2.13–2.20 m (1H, 3-H), 2.24 s (3H, $C^{17}H_3$), 2.37–2.58 m (4H, 19-H, 19'-H), 3.29 t (1H, 2-H, *J* 9.0 Hz), 3.57 d and 3.78 d (1H each, 18-H, *J* 14.0, 14.0 Hz), 6.60 br.d and 7.01 br.d (1H each, 14-H, 16-H), 11.30 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 154.88 (C^{12}), 130.17 (C^{11}), 127.54 (C^{14}), 126.33 (C^{15}), 126.22 (C^{16}), 121.14 (C^{13}), 58.29 (NCH_2), 53.22 (C^{19}, $C^{19'}$), 49.78 (C^1), 47.87 (C^7), 45.78 (C^4), 44.63 (C^2), 39.60 (C^6), 33.81 (C^3), 31.70 (C^{22}, $C^{22'}$), 27.56 (C^5), 27.11 (C^{20}, $C^{20'}$), 26.59 (C^{21}, $C^{21'}$), 22.57 (C^{23}, $C^{23'}$), 21.51 (C^{17}), 20.94 (C^8), 20.36 (C^9), 14.01 (C^{24}, $C^{24'}$), 12.11 (C^{10}). Found, %: C 81.67; H 11.52; N 3.15. $C_{30}H_{51}NO$. Calculated, %: C 81.57; H 11.64; N 3.17.

2-(Dioctylaminomethyl)-4-methyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (IIf). Yield 91%. Light yellow oil. IR spectrum, ν, cm^{-1}: 2932, 2864, 1468, 1376 (Me, CH_2), 1616 (C=C), 1282 (C–O), 1234 (C–N), 866, 784 (=C–H). ^{1}H NMR spectrum, δ, ppm: 0.78 s (3H, $C^{10}H_3$), 0.84 s (3H, C^9H_3), 0.88 t (6H, $C^{26}H_3$, $C^{26'}H_3$, *J* 6.8 Hz), 0.91 s (3H, C^8H_3), 1.18–1.39 m (21H, 3-H, 21-H, 21'-H, 22-H, 22'-H, 23-H, 23'-H, 24-H, 24′-H, 25-H, 25'-H), 1.45–1.64 m (7H, 4-H, 5-H, 20-H, 20'-H), 1.78–1.88 m (2H, 6-H), 2.13–2.21 m (1H, 3-H), 2.24 s (3H, $C^{17}H_3$), 2.36–2.53 m (4H, 19-H, 19'-H), 3.29 t (1H, 2-H, *J* 9.0 Hz), 3.56 d and 3.78 d (1H each, NCH_2, *J* 14.0, 14.0 Hz), 6.59 d and 7.00 d (1H, 14-H, 16-H, *J* 1.2, 1.2 Hz), 11.33 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 154.88 (C^{12}), 130.17 (C^{11}), 127.54 (C^{14}), 126.33 (C^{15}), 126.22 (C^{16}), 121.15 (C^{13}), 58.29 (NCH_2), 53.21 (C^{19}, $C^{19'}$), 49.78 (C^1), 47.88 (C^7), 45.78 (C^4), 44.64 (C^2), 39.61 (C^6), 33.80 (C^3), 31.80 (C^{24},$C^{24'}$), 29.45 (C^{22}, $C^{22'}$), 29.21 (C^{23}, $C^{23'}$), 27.56 (C^5), 27.43 (C^{20}, $C^{20'}$), 26.28 (C^{21}, $C^{21'}$), 22.64 (C^{25}, $C^{25'}$), 21.51 (C^{17}), 20.94 (C^8), 20.36 (C^9), 14.09 (C^{26}, $C^{26'}$), 12.14 (C^{10}). Found, %: C 81.89; H 12.07; N.78. $C_{34}H_{59}NO$. Calculated, %: C 82.03; H 11.95; N 2.81.

4-Methyl-2-(morpholinomethyl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (IIg). Yield 98%. Colorless crystals, mp 95–97°C (from pentane). IR spectrum, ν, cm^{-1}: 2960, 2884, 1466, 1376 (Me, CH_2), 1618 (C=C), 1258 (C–O), 1236 (C–N), 870, 784 (=C–H). ^{1}H NMR spectrum, ppm: 0.75s (3H, $C^{10}H_3$), 0.83 s (3H, C^9H_3), 0.89 s (3H, C^8H_3), 1.32–1.39 m (1H, H^3), 1.50–1.64 m (3H, 4-H, 5-H), 1.81–1.89 m (2H, 6-H), 2.13–2.20 m (1H, 3-H), 2.24 s (3H, $C^{17}H_3$), 2.46–2.62 br.m (4H, 19-H, 19'-H), 3.28 t (1H, 2-H, *J* 9.0 Hz), 3.64 s (2H, NCH_2), 3.69–3.81 m (4H, 20-H, 20'-H), 6.63 d and 7.03 d (1H each, 14-H, 16-H, *J* 1.6, 1.6 Hz), 10.45 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 154.18 (C^{12}), 130.41 (C^{11}), 128.07 (C^{14}), 126.96 (C^{15}), 126.68 (C^{16}), 119.62 (C^{13}), 66.74 (C^{20}, $C^{20'}$), 62.00 (NCH_2), 52.76 (C^{19}, $C^{19'}$), 49.83 (C^1), 47.91 (C^7), 45.73 (C^4), 44.71 (C^2), 39.61 (C^6), 33.73 (C^3), 27.56 (C^5), 21.49 (C^{17}), 20.89 (C^8), 20.30 (C^9), 12.05 (C^{10}). Found, %: C 77.12; H 9.55; N 4.10. $C_{23}H_{33}NO_2$. Calculated, %: C 76.92; H 9.68; N 4.08.

4-Methyl-2-(piperidinomethyl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (IIh). Yield 97%. Colorless crystals, mp 96–98°C (from pentane). IR spectrum, ν, cm^{-1}: 2956, 2884, 1472, 1376 (Me, CH_2), 1616 (C=C), 1250 (C–O), 1234 (C–N), 1122 (C–O–C), 864, 782 (=C–H). ^{1}H NMR spectrum, δ, ppm: 0.78 s (3H, $C^{10}H_3$), 0.84 s (3H, C^9H_3), 0.86 s (3H, C^8H_3), 1.26–1.68 m (10H, 3-H, 4-H, 5-H, 20-H, 20'-H, 21'-H), 1.80–1.90 m (2H, 6-H), 2.14–2.22 m (1H, 3-H), 2.25 s (3H, $C^{17}H_3$), 2.30–2.73 m (4H, 19-H, 19'-H), 3.30 t (1H, 2-H, *J* 9.2 Hz), 3.56 d and 3.63 d (1H each, CH_2N, *J* 13.6, 13.6 Hz), 6.61 d and 7.02 d (1H each, 14-H, 16-H, *J* 0.8, 1.2 Hz), 11.20 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 154.74 (C^{12}), 130.19 (C^{11}), 127.58 (C^{14}), 126.42 (C^{15}), 126.31 (C^{16}), 120.62 (C^{13}), 62.28 (C^{19}, $C^{19'}$), 53.68 (NCH_2), 49.79 (C^1), 47.89 (C^7),

45.76 (C^4), 44.68 (C^2), 39.61 (C^6), 33.73 (C^3), 27.58 (C^5), 25.75, 25.76 (C^{20}, $C^{20'}$), 24.08 (C^{21}), 21.51 (C^{17}), 20.91 (C^8), 20.32 (C^9), 11.99 (C^{10}). Found, %: C 80.65; H.28; N 4.13. $C_{23}H_{35}NO$. Calculated, %: C 80.88; H 10.33; N 4.10.

2-(Dibutylaminomethyl)-4-methyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol hydrochloride (IId·HCl). A 2 N alcoholic solution of hydrogen chloride was added dropwise under stirring at room temperature to a solution of amine **IId** in diethyl ether until pH 6. The precipitate of **IId**·HCl was filtered off, washed with diethyl ether, and dried under reduced pressure. Yield 87%. Colorless powder, mp 70–72°C (from Et_2O). Found, %: C 74.11; H 10.41; N 3.30. $C_{26}H_{43}NO·HCl$. Calculated, %: C 73.98; H 10.51; N 3.32.

2-(Dihexylaminomethyl)-4-methyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol hydrochloride (IIe·HCl) was synthesized in a similar way. Yield 85%. Colorless powder, mp 144–146°C (Et_2O). Found, %: C 75.19; H 11.09; N 2.94. $C_{30}H_{51}NO·HCl$. Calculated, %: C.35; H 10.96; N 2.93.

X-Ray analysis of compounds IIb, IIc, and IIg. Single crystals of compounds **IIb**, **IIc**, and **IIg**, suitable for X-ray analysis, were ontained by slow evaporation of solutions in methanol (**IIb**, **IIc**) or pentane (**IIg**). Experimental reflection intensities were measured on SMART 1000 CCD and SMART APEX2 CCD diffractometers (λMoK$_\alpha$, 0.71073 Å, graphite monochromator, ω-scanning). The reflections intensity arrays were processed using SAINT Plus [5], SADABS [6], and APEX2 programs [7]. The structures were solved by the direct method and were refined with respect to F^2_{hkl} by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms (except for the hydrogen atoms in the hydroxy groups) were calculated from the geometry considerations and were refined using the riding model [$U_{iso}(H) = nU_{eq}(C)$, where $n = 1.2$]; the hydrogen atoms in the hydroxy groups were localized by difference syntheses of electron density, and their positions were refined using the riding model [$U_{iso}(H) = nU_{eq}(O)$, where $n = 1.5$]. The structures were solved and refined using SHELXTL software package [8]. The principal crystallographic data and parameters of X-ray diffraction experiments are collected in Table 3.

Table 3. Crystallographic data for compounds **IIb**, **IIc**, and **IIg** and parameters of X-ray diffraction experiment

Parameter	**IIb**	**IIc**	**IIg**
Formula	$C_{20}H_{31}NO$	$C_{20}H_{31}NO$	$C_{22}H_{33}NO_2$
Molecular weight	301.46	301.46	343.50
Color	Colorless	Colorless	Colorless
Shape	Plates	Plates	Plates
Habit, mm	0.15×0.10×0.02	0.20×0.15×0.15	0.20×0.15×0.15
Temperature, K	120(2)	100(2)	100(2)
Crystal system	Monoclinic	Rhombic	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2/c$
a, Å	9.3212(17)	7.7876(11)	17.7041(10)
b, Å	14.753(3)	13.9974(15)	10.7854(6)
c, Å	12.953(2)	16.047(2)	21.0086(12)
β, deg	93.662(4)	90	106.2350(10)
V, Å^3	1777.7(6)	1749.2(4)	3851.5(4)
Z	4	4	8
d_{calc}, g/cm^3	1.126	1.145	1.185
Absorption coefficient μ, mm^{-1}	0.068	0.069	0.074
F(000)	664	664	1504
Scan range (θ), deg	2.09–27.00	2.91–27.00	2.02–29.00
Total number of reflections	9451	10172	45835
Number of unique reflections	3858	2143	10191
R_{int}	0.0513	0.0478	0.0587
Number of refined parameters	205	205	459
Number of reflections with $I \geq 2\sigma(I)$	1960	1832	7060

Table 3. (Contd.)

Parameter	IIb	IIc	IIg
Completeness of reflections array, %	99.5	98.0	99.4
Goodness of fit	0.970	1.048	1.032
Divergence factor $R_1(F)$[a] (reflections with $I \geq 2\sigma(I)$	0.0485	0.0541	0.0476
Divergence factor $wR_2(F^2)$[b] (all reflections)	0.0802	0.1043	0.0985
Residual electron density, min/max, $e/Å^3$	0.208/–0.201	0.375/–0.186	0.319/–0.259

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma(F_0)$. [b] $wR_2 = \Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]^{1/2}$.

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