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Dedicated to Full Member of the Russian Academy of Sciences G.A. Tolstikov on his 75th anniversary

Design of Schiff Base-Like Postmetallocene Catalytic Systems for Polymerization of Olefins: IX.* Synthesis of Salicylaldehydes Containing an Isobornyl Substituent and Hydroxyphenyl Imine Ligands Based Thereon

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Abstract—Reactions of substituted 2-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenols with paraformaldehyde in the presence of tin(IV) chloride and 2,6-dimethylpyridine gave the corresponding salicylaldehydes which reacted with primary amines to produce a series of new Schiff bases as ligands for complex formation with transition metals.

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Hydroxyphenyl imine titanium and zirconium complexes attract attention due to their high catalytic activity in polymerization of olefins. In addition, catalytic systems based on such complexes ensure preparation of a broad spectrum of polyolefins with various parameters via variation of the ligand structure, which changes the polymerization mechanism [2, 3]. Substituents in the ligand affect the catalytic activity of the complexes derived therefrom in different modes, depending on the substituent nature and position. The catalytic activity sharply increases as the size of substituent in the 3-position of the ligand rises, while large substituents on the imino nitrogen atom reduce the catalytic activity [4]. The effect of substituent in the 5-position of the ligand on the catalytic activity remains unclear because of limited relevant experimental data.

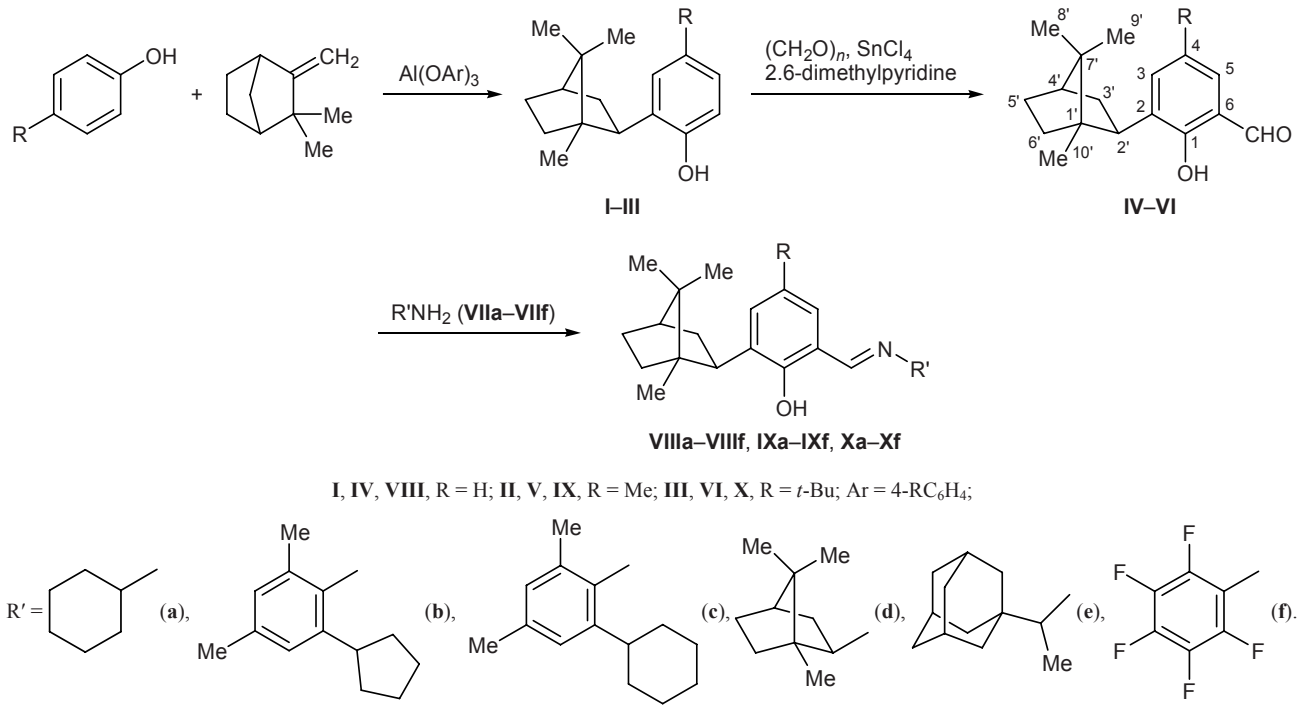
As shown in [3], zirconium complexes with salicylaldehyde imine ligands having a cage-like group, 1-adamantyl substituent, in the 3-position are active in the polymerization of ethylene promoted by methylalumoxane. However, these data give no grounds to predict how the catalytic activity of complexes will change upon variation of substituents in position *5* and on the imino nitrogen atom via replacement of the adamantyl fragment by other bulky groups.

While performing systematic studies in the field of structural modification of metal complexes and their catalytic activity [5], we believed it to be necessary to elucidate the effect of substituents in position *5* and on the imino nitrogen atom in salicylaldehyde imine ligands having a rigid cage-like substituent in the 3-position on the catalytic activity of complexes derived therefrom, as compared to analogous ligands containing such substituent as *tert*-butyl, 1-phenylethyl, 1-(4-*tert*-butylphenyl)ethyl, 1-phenyl-1-methylethyl, or triphenylmethyl groups in the 3-position.

In order to synthesize such complexes, a set of salicylaldehydes having cage-like substituents is required, for the corresponding hydroxyphenyl imine ligands are obtained by reaction of primary amines with aldehydes. On the basis of economy and accessibility considerations, we selected a cage-like isobornyl (1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl) substituent which can be readily introduced into the *ortho* position of

* For communication VIII, see [1].

Scheme 1.



I, **IV**, **VIII**, R = H; **II**, **V**, **IX**, R = Me; **III**, **VI**, **X**, R = *t*-Bu; Ar = 4-RC_6H_4;

phenol via reaction with camphene in the presence of a catalytic amount of aluminum phenoxide [6, 7]. A series of isobornyl-substituted phenols was obtained by alkylation of phenol, *p*-methylphenol, *p*-*tert*-butylphenol, and *p*-(1-methyl-1-phenylethyl)phenol with (–)-camphene in the presence of the corresponding aluminum phenoxides at 150–160°C according to the procedure described in [7]. We thus obtained racemic phenols **I**–**III** (Scheme 1), and the structure of the terpene substituent therein was confirmed by the ^{1}H NMR data. *p*-(1-Methyl-1-phenylethyl)phenol failed to react with camphene.

The most appropriate procedure for selective *ortho*-formylation of phenols having bulky substituents is based on the reaction with paraformaldehyde in the presence of tin(IV) chloride and 2,6-dimethylpyridine [8]. Using this procedure, from phenols **I**–**III** we synthesized the corresponding substituted salicylaldehydes **IV**–**VI** in 50–55% yield (Scheme 1); the structure of **IV**–**VI** was confirmed by the analytical and spectral data. In the ^{1}H NMR spectra of these compounds, the OH proton signal was displaced downfield (δ 11.33–11.51 ppm) relative to its position in the spectra of the initial phenols (δ 4.23–4.50 ppm) due to intramolecular hydrogen bonding.

Taking into account published data on the activity of transition metal complexes in catalytic systems for olefin polymerization [2, 3, 5, 9], we selected a set of most promising amines **VIIa**–**VIIf** for the synthesis of hydroxyphenyl imine ligands **VIII**–**X**. Schiff bases like **VIII**–**X** are usually prepared by heating initial salicylaldehydes and amines in alcohol (methanol or ethanol) in the presence of a catalytic amount of an acid or dehydrating agent or by heating in a boiling inert solvent with simultaneous removal of the liberated water as azeotrope or in the presence of *p*-toluenesulfonic acid.

By heating salicylaldehydes **IV**–**VI** with cyclohexylamine (**VIIa**), 2-cyclopentyl-4,6-dimethylaniline (**VIIb**), 2-cyclohexyl-4,6-dimethylaniline (**VIIc**), and racemic 1,7,7-trimethylbicyclo[2.2.1]heptan-*exo*-2-amine (**VIId**) in boiling methanol containing a catalytic amount of anhydrous formic acid we obtained the corresponding Schiff bases **VIIIa**–**VIIId**, **IXa**–**IXd**, and **Xa**–**Xd** (Scheme 1) which were isolated in 74–92% yield. Salicylaldehyde imines **VIIIe**, **IXe**, and **Xe** were synthesized by heating aldehydes **IV**–**VI** with racemic 1-(1-adamantyl)ethanamine (**VIIe**) and an equimolar amount of triethylamine in boiling methanol. Their yields were 72–92%. Aldehydes **IV**–**VI** reacted with less nucleophilic pentafluoroaniline (**VIIf**) in methanol very slowly; therefore, the condensation was carried out using toluene as solvent, *p*-toluenesulfonic acid as acid catalyst, and anhydrous $CaSO_4$ as dehydrating agent. Under these conditions, we succeeded in isolating 52–66% of fluorinated Schiff bases **VIIIf**, **IXf**, and **Xf**.

The structure of Schiff bases **VIII–X** was proved by their elemental compositions and spectral parameters. In the ^{1}H NMR spectra of **VIII–X**, the N=CH proton signal appeared as a singlet at δ 8.06–8.8 ppm, and the OH proton gave rise to a singlet at δ 12.26–13.60 ppm. The downfield shift of the latter signal relative to the corresponding signal of the initial phenol is likely to result from intramolecular hydrogen bonding (as in the spectra of salicylaldehydes **IV–VI**; see above). Schiff bases **VIIId**, **VIIIe**, **IXd**, **IXe**, **Xd**, and **Xe** having a chiral substituent on the imino nitrogen atom showed in the ^{1}H NMR spectra two OH signals due to the presence of diastereoisomers. The IR spectra of Schiff bases **VIII–X** contained an intense absorption band at 1614–1631 cm^{-1} due to stretching vibrations of the azomethine C=N bond, and strong molecular ion peaks were present in their mass spectra.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker WP-200SY spectrometer at 200.13 MHz from solutions in carbon tetrachloride using hexamethyldisiloxane as internal reference. The IR spectra were recorded in KBr or from thin films (neat) on a Vector 22 spectrometer. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using hexane as eluent. Flash chromatography [10] was performed on silica gel 5–40 μm using chloroform–hexane (1 : 2) as eluent. The elemental compositions were determined from the high-resolution mass spectra which were run on a Finnigan MAT-8200 mass spectrometer. The melting points were determined by heating samples placed between glass plates at a rate of 1 deg/min.

2-Cyclopentyl- and 2-cyclohexyl-4,6-dimethylanilines were synthesized according to the procedure described in [11]; 1-(1-adamantyl)ethanamine hydrochloride was isolated by chloroform extraction of the active substance from commercial drug Rimantadine, and racemic 1,7,7-trimethylbicyclo[2.2.1]heptan-*exo*-2-amine was prepared as reported in [12]. 2-(1,7,7-Trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (**I**) was synthesized as described in [7], and *para*-substituted derivatives **II** and **III** were prepared according to a modified procedure (see below).

4-Substituted 2-(1,7,7-trimethylbicyclo[2.2.1]-hept-*exo*-2-yl)phenols II and III (*general procedure***).** *p*-Methylphenol or *p*-*tert*-butylphenol, 0.4 mol, was heated to 210–220°C, and 0.8 g (0.03 mol) of aluminum powder was added under vigorous stirring. When the mixture became homogeneous, it was cooled to 130°C, 27.2 g (0.2 mol) of (–)-camphene was added, and the mixture was stirred for 8 h at 150–160°C, cooled to room temperature, and treated with 5 ml of concentrated hydrochloric acid, 45 ml of water, and 100 ml of diethyl ether. The organic phase was separated, the aqueous phase was extracted with diethyl ether (3×50 ml), the extracts were combined with the organic phase, washed with water until neutral reaction and with a saturated aqueous solution of sodium chloride, and dried over anhydrous sodium sulfate, the solvent was distilled off, and the residue was subjected to distillation under reduced pressure. Compounds **II** and **III** were additionally purified by recrystallization from hexane.

4-Methyl-2-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (II). Yield 67%, bp 146–148°C (2 mm). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.74 s (3H, 10′-Me), 0.82 s and 0.87 s (3H each, 8′-Me, 9′-Me), 1.21–1.39 m (1H, 5′-H), 1.42–1.63 m (3H, 3′-H, 6′-H), 1.76–1.88 m (2H, 4′-H, 5′-H), 2.09–2.19 m (1H, 3′-H), 2.23 s (3H, 4-Me), 3.06 br.t (1H, 2′-H, *J* = 8.8), 4.23 s (1H, OH), 6.48 d (1H, 6-H, *J* = 8.1), 6.71 d.d (1H, 5-H, *J* = 8.1, 1.2), 6.96 d (1H, 3-H, *J* = 1.2) (cf. [13]).

4-*tert*-Butyl-2-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (III). Yield 62%, bp 152–155°C (1 mm). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.71 s (3H, 10′-Me), 0.76 s and 0.84 s (3H each, 8′-Me, 9′-Me), 1.18 s (9H, *t*-Bu), 1.21–1.39 m (1H, 5′-H), 1.44–1.67 m (3H, 3′-H, 6′-H), 1.79–1.91 m (2H, 4′-H, 5′-H), 2.05–2.16 m (1H, 3′-H), 3.2 t (1H, 2′-H, *J* = 8.7), 4.5 s (1H, OH), 6.55 d (1H, 6-H, *J* = 8.2), 6.94 d.d (1H, 5-H, *J* = 8.2, 1.2), 7.26 d (1H, 3-H, *J* = 1.2). Found: $[M]^+$ 286.22947. $C_{20}H_{30}O$. Calculated: *M* 286.22967.

Salicylaldehydes IV–VI (*general procedure***).** Tin(IV) chloride, 0.47 ml (0.004 mol), was added to a mixture of 0.04 mol of phenol **I–III**, 40 ml of toluene, and 1.87 ml (0.016 mol) of 2,6-dimethylpyridine under stirring in an argon atmosphere. The suspension was stirred for 1 h at room temperature, 2.64 g (0.088 mol) of paraformaldehyde was added, and the mixture was heated for 10 h under reflux at a bath temperature of 115–125°C. The mixture was then cooled to room temperature, diluted with 20 ml of diethyl ether, and treated with 2 N hydrochloric acid to pH 2. The organic phase was separated, the aqueous phase was extracted with diethyl ether (3×20 ml), the extracts were combined with the organic phase, washed with water until neutral reaction and with a saturated

aqueous solution of sodium chloride, and dried over anhydrous sodium sulfate, the solvent was distilled off, and the residue was distilled under reduced pressure. The product was additionally purified by recrystallization from methanol.

2-Hydroxy-3-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)benzaldehyde (IV). Yield 55%, bp 140–142°C (1 mm), mp 75–78°C. IR spectrum: ν 1658 cm^{-1} (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.75 s (3H, 10′-Me), 0.83 s and 0.86 s (3H each, 8′-Me, 9′-Me), 1.29–1.41 m (1H, 5′-H), 1.49–1.67 m (3H, 3′-H, 6′-H), 1.79–1.91 m (2H, 4′-H, 5′-H), 2.08–2.17 m (1H, 3′-H), 3.33 br.t (1H, 2′-H, *J* = 9), 6.96 t (1H, 4-H, *J* = 8.2), 7.35 d (1H, 5-H, *J* = 8.2), 7.56 d (1H, 3-H, *J* = 8.2), 9.86 s (1H, CHO), 11.51 s (1H, OH). Found: $[M]^+$ 258.16185. $C_{17}H_{22}O_2$. Calculated: *M* 258.16198.

2-Hydroxy-5-methyl-3-(1,7,7-trimethylbicyclo-[2.2.1]hept-*exo*-2-yl)benzaldehyde (V). Yield 52%, bp 158–160°C (3 mm), mp 82–84°C. IR spectrum: ν 1652 cm^{-1} (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.73 s (3H, 10′-Me), 0.84 s and 0.86 s (3H each, 8′-Me, 9′-Me), 1.22–1.41 m (1H, 5′-H), 1.48–1.65 m (3H, 3′-H, 6′-H), 1.72–1.88 m (2H, 4′-H, 5′-H), 2.02–2.19 m (1H, 3′-H), 2.31 s (3H, 4-Me), 3.28 br.t (1H, 2′-H, *J* = 9), 7.06 s (1H, 5-H), 7.27 s (1H, 3-H), 9.78 s (1H, CHO), 11.33 s (1H, OH) (cf. [13]).

5-*tert*-Butyl-2-hydroxy-3-(1,7,7-trimethylbicyclo-[2.2.1]hept-*exo*-2-yl)benzaldehyde (VI). Yield 55%, bp 146–148°C (1 mm), mp 93–95°C. IR spectrum: ν 1646 cm^{-1} (C=O). ^{1}H NMR spectrum, δ, ppm: 0.75 s (3H, 10′-Me), 0.84 s and 0.87 s (3H each, 8′-Me, 9′-Me), 1.29 s (9H, *t*-Bu), 1.30–1.43 m (1H, 5′-H), 1.49–1.68 m (3H, 3′-H, 6′-H), 1.75–1.87 m (2H, 4′-H, 5′-H), 2.03–2.15 m (1H, 3′-H), 3.31 t (1H, 2′-H, *J* = 8.6 Hz), 7.21 s (1H, 5-H), 7.55 s (1H, 3-H), 9.81 s (1H, CHO), 11.36 s (1H, OH). Found: $[M]^+$ 314.22447. $C_{21}H_{30}O_2$. Calculated: *M* 314.22457.

Salicylaldehyde imines VIIIa–VIIId, IXa–IXd, and Xa–Xd (*general procedure*). A mixture of 1 mmol of aldehyde **IV**–**VI**, 10 ml of methanol, 1 mmol of amine **VIIa**–**VIId**, and 10 mg of 99% formic acid was heated for 6–12 h under reflux with stirring until the initial compounds disappeared according to the TLC data. The mixture was cooled, and the light yellow precipitate was filtered off, washed with 5 ml of methanol, and dried in air.

2-Cyclohexyliminomethyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (VIIIa). Yield 76%, mp 91–93°C. IR spectrum: ν 1628 cm^{-1} (N=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.75 s (3H, 10′-Me), 0.83 s and 0.88 s (3H each, 8′-Me, 9′-Me), 1.21–1.42 m (3H, 5′-H, CH_2, cyclohexyl), 1.48–1.63 m (7H, 3′-H, 6′-H, CH_2, cyclohexyl), 1.72–1.88 m (6H, 4′-H, 5′-H, CH_2, cyclohexyl), 2.00–2.17 m (1H, 3′-H), 3.11–3.24 m (1H, CHN), 3.33 t (1H, 2′-H, *J* = 9), 6.69 t (1H, 4-H, *J* = 8.5), 6.92 d (1H, 5-H, *J* = 8.5), 7.23 d (1H, 3-H, *J* = 8.5), 8.30 s (1H, CH=N), 13.51 br.s (1H, OH). Found: $[M]^+$ 339.25656. $C_{23}H_{33}NO$. Calculated: *M* 339.25620.

2-Cyclohexyliminomethyl-4-methyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (IXa). Yield 74%, mp 122–123°C. IR spectrum: ν 1630 cm^{-1} (N=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.74 s (3H, 10′-Me), 0.82 s and 0.87 s (3H each, 8′-Me, 9′-Me), 1.23–1.41 m (3H, 5′-H, CH_2, cyclohexyl), 1.47–1.68 m (7H, 3′-H, 6′-H, CH_2, cyclohexyl), 1.71–1.91 m (6H, 4′-H, 5′-H, CH_2, cyclohexyl), 2.01–2.18 m (1H, 3′-H), 2.25 s (3H, 4-Me), 3.05–3.16 m (1H, CHN), 3.30 t (1H, 2′-H, *J* = 9), 6.72 s (1H, 5-H), 7.02 s (1H, 3-H), 8.24 s (1H, CH=N), 13.25 br.s (1H, OH). Found: $[M]^+$ 353.27256. $C_{24}H_{35}NO$. Calculated: *M* 353.27185.

4-*tert*-Butyl-2-cyclohexyliminomethyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (Xa). Yield 78%, mp 73–75°C. IR spectrum: ν 1631 cm^{-1} (N=C). ^{1}H NMR spectrum, δ, ppm: 0.75 s (3H, 10′-Me), 0.83 s and 0.89 s (3H each, 8′-Me, 9′-Me), 1.26 s (9H, *t*-Bu), 1.23–1.41 m (3H, 5′-H, CH_2, cyclohexyl), 1.48–1.68 m (7H, 3′-H, 6′-H, CH_2, cyclohexyl), 1.72–1.89 m (6H, 4′-H, 5′-H, CH_2, cyclohexyl), 2.01–2.19 m (1H, 3′-H), 3.08–3.21 m (1H, CHN), 3.32 t (1H, 2′-H, *J* = 9 Hz), 6.85 s (1H, 5-H), 7.29 s (1H, 3-H), 8.31 s (1H, CH=N), 13.26 br.s (1H, OH). Found: $[M]^+$ 395.31910. $C_{27}H_{41}NO$. Calculated: *M* 395.31880.

2-(2-Cyclopentyl-4,6-dimethylphenyliminomethyl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)-phenol (VIIIb). Yield 88%, mp 98–100°C. IR spectrum: ν 1621 cm^{-1} (N=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.81 s (3H, 10′-Me), 0.84 s and 0.90 s (3H each, 8′-Me, 9′-Me), 1.20–1.40 m (1H, 5′-H), 1.51–1.68 m (7H, 3′-H, 6′-H, CH_2, cyclopentyl), 1.71–1.95 m (6H, 4′-H, 5′-H, CH_2, cyclopentyl), 2.13 s and 2.27 s (3H each, 4″-Me, 6″-Me), 2.15–2.23 m (1H, 3′-H), 2.88–3.16 m (1H, CHN), 3.42 t (1H, 2′-H, *J* = 9), 6.73–6.88 m (3H, 4-H, 3″-H, 5″-H), 7.03 d (1H, 5-H, *J* = 8.5), 7.35 d (1H, 3-H, *J* = 8.5), 8.23 s (1H, CH=N), 13.33 s (1H, OH). Found: $[M]^+$ 429.30201. $C_{30}H_{39}NO$. Calculated: *M* 429.30205.

2-(2-Cyclopentyl-4,6-dimethylphenyliminomethyl)-4-methyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (IXb). Yield 81%, mp 134–136°C. IR

spectrum: ν 1624 cm^{-1} (N=C). ^1H NMR spectrum, δ, ppm: 0.79 s (3H, 10′-Me); 0.84 s and 0.89 s (3H each, 8′-Me, 9′-Me); 1.24–1.81 m (14H, 3′-H, 4′-H, 5′-H, 6′-H, CH_2, cyclopentyl); 2.14–2.23 m (1H, 3′-H); 2.11 s, 2.27 s, and 2.29 s (3H each, 4-Me, 4″-Me, 6″-Me); 2.85–3.02 m (1H, CHN); 3.45 t (1H, 2′-H, *J* = 9 Hz); 6.76 s (1H, 5-H); 6.81 s and 6.84 s (1H each, 3′-H, 5′-H); 7.13 s (1H, 3-H); 8.17 s (1H, CH=N); 13.07 s (1H, OH). Found: $[M]^+$ 443.31871. $C_{31}H_{41}NO$. Calculated: *M* 443.31880.

4-*tert*-Butyl-2-(2-cyclopentyl-4,6-dimethylphenyliminomethyl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (Xb). Yield 87%, mp 48–50°C. IR spectrum: ν 1622 cm^{-1} (N=C). ^1H NMR spectrum, δ, ppm: 0.82 s (3H, 10′-Me), 0.85 s and 0.91 s (3H each, 8′-Me, 9′-Me), 1.29 s (9H, *t*-Bu), 1.30–1.92 m (14H, 3′-H, 4′-H, 5′-H, 6′-H, CH_2, cyclopentyl), 2.02–2.09 m (1H, 3′-H), 2.13 s and 2.27 s (3H each, 4″-Me, 6″-Me), 2.85–3.08 m (1H, CHN), 3.39 t (1H, 2′-H, *J* = 9 Hz), 6.77 s (1H, 5-H), 6.84 s and 6.95 s (1H each, 3′-H, 5′-H), 7.41 s (1H, 3-H), 8.22 s (1H, CH=N), 13.1 s (1H, OH). Found: $[M]^+$ 485.36574. $C_{34}H_{47}NO$. Calculated: *M* 485.36617.

2-(2-Cyclohexyl-4,6-dimethylphenyliminomethyl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)-phenol (VIIIc). Yield 92%, mp 154–156°C. IR spectrum: ν 1619 cm^{-1} (N=C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.81 s (3H, 10′-Me), 0.84 s and 0.90 s (3H each, 8′-Me, 9′-Me), 1.20–1.41 m (5H, 5′-H, CH_2, cyclohexyl), 1.51–1.68 m (5H, 3′-H, 6′-H, CH_2, cyclohexyl), 1.71–1.93 m (6H, 4′-H, 5′-H, CH_2, cyclohexyl), 1.98–2.09 m (1H, 3′-H), 2.13 s and 2.28 s (3H each, 4″-Me, 6″-Me), 2.48–2.63 m (1H, CHN), 3.43 t (1H, 2′-H, *J* = 9), 6.73–6.85 m (3H, 4-H, 3″-H, 5″-H), 7.06 d (1H, 5-H, *J* = 8.5), 7.37 d (1H, 3-H, *J* = 8.5), 8.23 s (1H, CH=N), 13.34 s (1H, OH). Found: $[M]^+$ 443.31880. $C_{31}H_{41}NO$. Calculated: *M* 443.31880.

2-(2-Cyclohexyl-4,6-dimethylphenyliminomethyl)-4-methyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (IXc). Yield 82%, mp 186–187°C. IR spectrum: ν 1625 cm^{-1} (N=C). ^1H NMR spectrum, δ, ppm: 0.80 s (3H, 10′-Me); 0.84 s and 0.89 s (3H each, 8′-Me, 9′-Me); 1.18–1.43 m (5H, 5′-H, CH_2, cyclohexyl); 1.52–1.67 m (5H, 3′-H, 6′-H, CH_2, cyclohexyl); 1.69–1.88 m (6H, 4′-H, 5′-H, CH_2, cyclohexyl); 2.01–2.09 m (1H, 3′-H); 2.11 s, 2.27 s, and 2.29 s (3H each, 4-Me, 4″-Me, 6″-Me); 2.43–2.65 m (1H, CHN); 3.43 t (1H, 2′-H, *J* = 9 Hz); 6.74–6.84 m (3H, 5-H, 3″-H, 5″-H); 7.04 s (1H, 3-H); 8.16 s (1H, CH=N); 13.07 s (1H, OH). Found: $[M]^+$ 457.33586. $C_{32}H_{43}NO$. Calculated: *M* 457.33445.

4-*tert*-Butyl-2-(2-cyclohexyl-4,6-dimethylphenyliminomethyl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (Xc). Yield 77%, mp 66–68°C. IR spectrum: ν 1622 cm^{-1} (N=C). ^1H NMR spectrum, δ, ppm: 0.82 s (3H, 10′-Me), 0.85 s and 0.91 s (3H each, 8′-Me, 9′-Me), 1.3 s (9H, *t*-Bu), 1.32–2.07 m (17H, 3′-H, 4′-H, 5′-H, 6′-H, CH_2, cyclohexyl), 2.14 s and 2.27 s (3H each, 4″-Me, 6″-Me), 2.47–2.65 m (1H, CHN), 3.42 t (1H, 2′-H, *J* = 9 Hz), 6.78 s and 6.81 s (1H each, 3′-H, 5″-H), 6.97 d (1H, 5-H, *J* = 1.2 Hz), 7.42 d (1H, 3-H, *J* = 1.2 Hz), 8.22 s (1H, CH=N), 13.12 br.s (1H, OH). Found: $[M]^+$ 499.38139. $C_{35}H_{49}NO$. Calculated: *M* 499.38233.

2-(1,7,7-Trimethylbicyclo[2.2.1]hept-*exo*-2-yl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yliminomethyl)phenol (VIIId). Yield 88%, mp 157–159°C. IR spectrum: ν 1623 cm^{-1} (N=C). ^1H NMR spectrum, δ, ppm: 0.72 s and 0.74 s (3H each, 10′-Me, 10″-Me), 0.77 s and 0.82 s (3H each, 9′-Me, 9″-Me), 0.88 s and 0.90 s (3H each, 8′-Me, 8″-Me), 1.15–1.42 m (2H, 5′-H, 5″-H), 1.48–1.65 m (6H, 3′-H, 6′-H, 3″-H, 6″-H), 1.71–1.93 m (4H, 4′-H, 5′-H, 4″-H, 5″-H), 1.93–2.16 m (2H, 3′-H, 3″-H), 3.13 d.d (1H, 2″-H, *J* = 9, 8 Hz), 3.33 t (1H, 2′-H, *J* = 9 Hz), 6.69 t (1H, 4-H, *J* = 8.5 Hz), 6.93 d (1H, 5-H, *J* = 8.5 Hz), 7.23 d (1H, 3-H, *J* = 8.5 Hz), 8.12 s (1H, CH=N), 13.26 s and 13.31 s (1H, OH). Found: $[M]^+$ 393.30315. $C_{27}H_{39}NO$. Calculated: *M* 393.30315.

4-Methyl-2-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yliminomethyl)phenol (IXd). Yield 84%, mp 154–156°C. IR spectrum: ν 1627 cm^{-1} (N=C). ^1H NMR spectrum, δ, ppm: 0.76 s and 0.83 s (3H each, 10′-Me, 10″-Me), 0.88 s and 0.9 s (3H each, 9′-Me, 9″-Me), 0.93 s and 0.97 s (3H each, 8′-Me, 8″-Me), 1.13–1.41 m (2H, 5′-H, 5″-H), 1.47–1.68 m (6H, 3′-H, 6′-H, 3″-H, 6″-H), 1.75–1.89 m (4H, 4′-H, 5′-H, 4″-H, 5″-H), 1.96–2.12 m (2H, 3′-H, 3″-H), 2.25 s (3H, 4-Me), 3.11 d.d (1H, 2″-H, *J* = 9, 8 Hz), 3.3 t (1H, 2′-H, *J* = 8.5 Hz), 6.72 s (1H, 5-H), 7.03 s (1H, 3-H), 8.06 s (1H, CH=N), 12.98 s and 13.03 s (1H, OH). Found: $[M]^+$ 407.31922. $C_{28}H_{41}NO$. Calculated: *M* 407.31880.

4-*tert*-Butyl-2-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yliminomethyl)phenol (Xd). Yield 90%, mp 88–90°C. IR spectrum: ν 1628 cm^{-1} (N=C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.74 s and 0.76 s (3H each, 10′-Me, 10″-Me), 0.77 s and 0.79 s (3H each, 9′-Me, 9″-Me), 0.85 s and 0.91 s (3H each, 8′-Me, 8″-Me), 1.26 s (9H, *t*-Bu), 1.3–1.42 m (2H, 5′-H, 5″-H), 1.54–1.69 m (6H, 3′-H, 6′-H, 3″-H, 6″-H), 1.71–1.87 m (4H, 4′-H, 5′-H,

4″-H, 5″-H), 1.91–2.12 m (2H, 3′-H, 3″-H), 3.12 d.d (1H, 2″-H, J = 9, 8 Hz), 3.33 t (1H, 2′-H, J = 8.5 Hz), 6.89 s (1H, 5-H), 7.32 s (1H, 3-H), 8.12 s (1H, CH=N), 13.01 s and 13.05 s (1H, OH). Found: $[M]^+$ 449.36574. $C_{31}4$-H_7NO. Calculated: M 449.36671.

Salicylaldehyde imines VIIIe, IXe, and Xe (*general procedure*). Triethylamine, 0.14 ml (1 mmol), was added to a mixture of 1 mmol of salicylaldehyde **IV**–**VI**, 10 ml of methanol, and 0.216 g (1 mmol) of 1-(1-adamantyl)ethanamine hydrochloride, and the mixture was heated for 12 h under reflux with stirring (until the initial compounds disappeared according to the TLC data). The solvent was distilled off, the residue was dissolved in chloroform, the solution was washed with water, dried over sodium sulfate, and evaporated, and the residue was subjected to flash chromatography. The eluate was evaporated, and the bright yellow solid residue was recrystallized from methanol.

2-[1-(1-Adamantyl)ethyliminomethyl]-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (VIIIe). Yield 72%, mp 192–194°C. IR spectrum: ν 1630 cm^{-1} (N=C). ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.74 s and 0.79 s (3H, 10′-Me), 0.83 s and 0.89 s (3H each, 8′-Me, 9′-Me), 1.12–1.89 m (21H, 3′-H, 4′-H, 5′-H, 6′-H, H_{Ad}), 1.99 br.s (3H, 1″-Me), 2.07–2.19 m (1H, 3′-H), 2.68–2.83 m (1H, CHN), 3.37 t (1H, 2′-H, J = 9), 6.73 t (1H, 4-H, J = 8.5), 6.91 d (1H, 5-H, J = 8.5), 7.25 d (1H, 3-H, J = 8.5), 8.18 s (1H, CH=N), 13.58 s and 13.60 s (1H, OH). Found: $[M]^+$ 419.31900. $C_{29}H_{41}NO$. Calculated: M 419.31880.

2-[1-(1-Adamantyl)ethyliminomethyl]-4-methyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (IXe). Yield 92%, mp 215–217°C. IR spectrum: ν 1631 cm^{-1} (N=C). ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.74 s and 0.78 s (3H, 10′-Me), 0.83 s and 0.89 s (3H each, 8′-Me, 9′-Me), 1.07–1.98 m (21H, 3′-H, 4′-H, 5′-H, 6′-H, H_{Ad}), 1.99 s (3H, 1″-Me), 2.03–2.15 m (1H, 3′-H), 2.25 s (3H, 4-Me), 2.69–2.78 m (1H, CHN), 3.35 t (1H, 2′-H, J = 9), 6.73 s (1H, 5-H), 7.04 s (1H, 3-H), 8.13 s (1H, CH=N), 13.25 s and 13.30 s (1H, OH). Found: $[M]^+$ 433.33485. $C_{30}H_{43}NO$. Calculated: M 433.33445.

2-[1-(1-Adamantyl)ethyliminomethyl]-4-*tert*-butyl-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)-phenol (Xe). Yield 81%, mp 76–78°C. IR spectrum: ν 1630 cm^{-1} (N=C). ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.75 s and 0.81 s (3H, 10′-Me), 0.83 s and 0.90 s (3H each, 8′-Me, 9′-Me), 1.03–1.21 m and 1.31–1.88 m (21H, 3′-H, 4′-H, 5′-H, 6′-H, H_{Ad}), 1.26 s (9H, *t*-Bu), 2.02–2.18 m (1H, 3′-H), 2.0 s (3H, 1″-Me), 2.76–2.81 m (1H, CHN), 3.34 t (1H, 2′-H, J = 9), 6.89 s (1H, 5-H), 7.32 s (1H, 3-H), 8.19 s (1H, CH=N), 13.32 s and 13.35 s (1H, OH). Found: $[M]^+$ 475.38139. $C_{33}H_{49}NO$. Calculated: M 475.37945.

Salicylaldehyde imines VIIIf, IXf, and Xf (*general procedure*). A mixture of 1 mmol of salicylaldehyde **IV**–**VI**, 10 ml of toluene, 0.18 g (1 mmol) of pentafluoroaniline, 10 mg of *p*-toluenesulfonic acid, and 0.27 g (2 mmol) of anhydrous $CaSO_4$ was heated for 30 h under reflux with stirring (until the initial compounds disappeared according to the TLC data). The solvent was distilled off, and the residue was subjected to flash chromatography. The eluate was evaporated, and the bright yellow solid product was recrystallized from methanol.

2-(Pentafluorophenyliminomethyl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (VIIIf). Yield 52%, mp 134–136°C. IR spectrum: ν 1616 cm^{-1} (N=H). ^{1}H NMR spectrum, δ, ppm: 0.8 s (3H, 10′-Me), 0.85 s and 0.89 s (3H each, 8′-Me, 9′-Me), 1.32–1.41 m (1H, 5′-H), 1.52–1.67 m (3H, 3′-H, 6′-H), 1.81–1.91 m (2H, 4′-H, 5′-H), 2.09–2.18 m (1H, 3′-H), 3.41 t (1H, 2′-H, J = 9 Hz), 6.91 t (1H, 4-H, J = 8.6 Hz), 7.21 d (1H, 5-H, J = 8.6 Hz), 7.51 d (1H, 3-H, J = 8.6 Hz), 8.8 s (1H, CH=N), 12.65 s (1H, OH). Found: $[M]^+$ 423.16212. $C_{23}H_{22}F_5NO$. Calculated: M 423.16221.

4-Methyl-2-(pentafluorophenyliminomethyl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (IXf). Yield 54%, mp 142–144°C. IR spectrum: ν 1615 cm^{-1} (N=C). ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.75 s (3H, 10′-Me), 0.83 s and 0.86 s (3H each, 8′-Me, 9′-Me), 1.29–1.39 m (1H, 5′-H), 1.49–1.65 m (3H, 3′-H, 6′-H), 1.79–1.88 m (2H, 4′-H, 5′-H), 2.08–2.17 m (1H, 3′-H), 2.31 s (3H, 4-Me), 3.3 t (1H, 2′-H, J = 9), 7.13 d (1H, 5-H, J = 1.2), 7.37 d (1H, 3-H, J = 1.2), 8.72 s (1H, CH=N), 12.42 s (1H, OH). Found: $[M]^+$ 437.17812. $C_{24}H_{24}F_5NO$. Calculated: M 437.17823.

4-*tert*-Butyl-2-(pentafluorophenyliminomethyl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)phenol (Xf). Yield 66%, mp 98–100°C. IR spectrum: ν 1614 cm^{-1} (N=C). ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.79 s (3H, 10′-Me), 0.86 s and 0.91 s (3H each, 8′-Me, 9′-Me), 1.3 s (9H, *t*-Bu), 1.32–1.46 m (1H, 5′-H), 1.52–1.69 m (3H, 3′-H, 6′-H), 1.77–1.91 m (2H, 4′-H, 5′-H), 2.05–2.14 m (1H, 3′-H), 3.38 t (1H, 2′-H, J = 9), 7.05 d (1H, 5-H, J = 1.2), 7.52 d (1H, 3-H, J = 1.2), 8.77 s (1H, CH=N), 12.26 s (1H, OH). Found: $[M]^+$ 479.22474. $C_{27}H_{30}F_5NO$. Calculated: M 479.22383.

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