

Design of Schiff Base-Like Postmetallocene Catalytic Systems for Polymerization of Olefins: X.* Synthesis of Phenoxy Imino Ligands with Bulky Substituents

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Abstract—Reactions of primary amines with salicylaldehydes containing bulky substituents (*tert*-butyl, 2-phenylpropan-2-yl, triphenylmethyl) in positions 3 and 5 gave a number of new Schiff bases as ligands for complex formation with transition metals.

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Phenoxy imino titanium and zirconium complexes attract persistent attention due to their high catalytic activity in polymerization of olefins and the possibility for controlling the catalytic activity and structure of the resulting polymers by variation of the ligand structure [2, 3]. Advantages in using such complexes in catalytic systems for polymerization of olefins demonstrated their tremendous potential and indicated that synthesis of new phenoxy imino complexes and study on their properties are important problems. General concepts of the effect of substituents in the ligands on the catalytic activity of complexes derived therefrom were formulated in [3, 4]; these concepts make it possible to perform purposeful syntheses of highly effective catalysts.

In continuation of our systematic studies on structural modification of metal complexes and their catalytic activity [4, 5], we believed that an important aspect is the effect of bulky substituents and their different combinations in positions 3 and 5 of salicylaldehyde imine ligand on the catalytic activity of the corresponding transition metal complexes. Required salicylaldehydes having bulky substituents in positions 3 and 5 are accessible compounds [6].

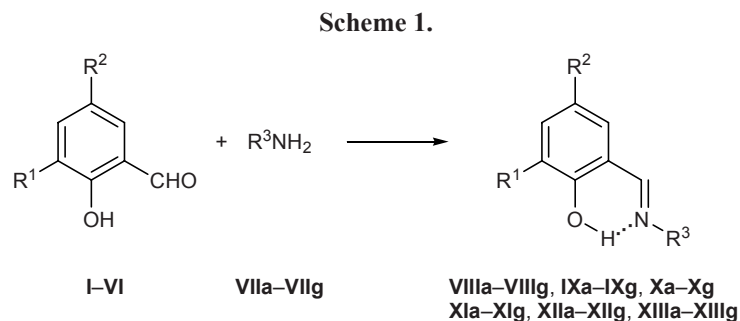
In the present article we describe the synthesis of a number of phenoxy imino ligands from salicylaldehydes **I–VI** containing *tert*-butyl, 2-phenylpropan-2-yl,

and triphenylmethyl substituents in positions 3 and 5. Analysis of published data on the catalytic activity of transition metal complexes in polymerization of olefins [3–5, 7] allowed us to select several most promising amines **VIIa–VIIg** as starting compounds for the synthesis of phenoxy imino ligands **VIII–XIII** from salicylaldehydes **I–VI**. Schiff base-like ligands are usually synthesized by heating a mixture of salicylaldehyde and amine in alcohol (methanol or ethanol) in the presence of a catalytic amount of an acid or dehydrating agent or by heating the reactants under reflux in an inert solvent with simultaneous removal of water as azeotrope or in the presence of *p*-toluenesulfonic acid.

Salicylaldehydes **I–VI** reacted with cyclohexylamine (**VIIa**), aniline (**VIIb**), 2-cyclopentyl-6-methylaniline (**VIIc**), 2-cyclopentyl-4,6-dimethylaniline (**VIIId**), and racemic 1,7,7-trimethylbicyclo[2.2.1]-heptan-*exo*-2-amine (**VIIe**) in boiling methanol in the presence of a catalytic amount of formic acid to give the corresponding Schiff bases **VIII–XIII (a–e)** in 64–98% yield (Scheme 1). Schiff bases **VIIIf–XIII f** were synthesized by heating aldehydes **I–VI** with 1-(1-adamantyl)ethanamine (**VIIIf**) hydrochloride and an equimolar amount of triethylamine in methanol, and the yields were 65–87%.

Less basic pentafluoroaniline (**VIIg**) reacted with aldehydes **I–VI** in methanol very slowly; therefore, the condensation was carried out by heating the reactants

* For communication IX, see [1].



I, VIII, $R^1 = \text{Me}_2\text{C}(\text{Ph})$, $R^2 = \text{Me}$; **II, IX**, $R^1 = \text{Me}_2\text{C}(\text{Ph})$, $R^2 = t\text{-Bu}$; **III, X**, $R^1 = R^2 = \text{Me}_2\text{C}(\text{Ph})$; **IV, XI**, $R^1 = \text{Me}_2\text{C}(\text{Ph})$, $R^2 = \text{Ph}_3\text{C}$; **V, XII**, $R^1 = t\text{-Bu}$, $R^2 = \text{Me}_2\text{C}(\text{Ph})$; **VI, XIII**, $R^1 = t\text{-Bu}$, $R^2 = \text{Ph}_3\text{C}$; **VII-XIII**, $R^3 = \text{cyclo-C}_6\text{H}_{11}$ (**a**), Ph (**b**), 2-cyclopentyl-6-methylphenyl (**c**), 2-cyclopentyl-4,6-dimethylphenyl (**d**), 1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl (**e**), 1-(1-adamantyl)ethyl (**f**), C_6F_5 (**g**).

in boiling toluene in the presence of *p*-toluenesulfonic acid and anhydrous calcium sulfate as dehydrating agent. In such a way we succeeded in isolating Schiff bases **VIIIg-XIIIg** in 59–73% yield.

The structure of Schiff bases **VIII-XIII** was confirmed by analytical and spectral data. These compounds displayed in the ^1H NMR spectra a singlet at δ 7.93–8.72 ppm from the $\text{N}=\text{CH}$ proton and a singlet at δ 12.03–13.80 ppm from the hydroxy proton. The downfield position of the latter signal indicates formation of intramolecular hydrogen bond which is possible for the *E* isomers with respect to the $\text{C}=\text{N}$ bond. In fact, we observed nuclear Overhauser effect in the ^1H NMR spectrum of Schiff base **Xd** in CDCl_3 ; therefore, it may be assumed that compounds **VIII-XIII** in solution exist exclusively as *E* isomers. The IR spectra of **VIII-XIII** contained a strong absorption band in the region 1613–1630 cm^{-1} , which corresponds to stretching vibrations of the $\text{C}=\text{N}$ bond. Schiff bases **VIII-XIII** showed strong molecular ion peaks in the mass spectra.

EXPERIMENTAL

The ^1H NMR spectra were recorded from solutions in carbon tetrachloride on a Bruker WP-200 SY spectrometer (200.13 MHz) using hexamethyldisiloxane as internal reference. The IR spectra were recorded from samples prepared as KBr pellets or neat substances on a Bruker Vector 22 instrument. The elemental compositions were calculated from the high-resolution mass spectra which were obtained on a Finnigan MAT-8200 instrument. The melting points were determined by heating samples placed between glass plates at a rate of 1 deg/min. The progress of reactions and the purity of products were monitored by thin-layer chromatography on Silufol UV-254 plates using chloroform as eluent. Flash chromatography [8] was

performed on silica gel (grain size 5–40 μm , eluent chloroform–hexane, 2:1).

Substituted salicylaldehydes **I-VI** were synthesized according to the procedure reported in [6], 2-cyclopentyl-6-methyl- and 2-cyclopentyl-4,6-dimethylanilines were prepared as described in [9], 1-(1-adamantyl)ethanamine hydrochloride was isolated from Remantadin by extraction with chloroform, and racemic 1,7,7-trimethylbicyclo[2.2.1]heptan-*exo*-2-amine was synthesized according to [10].

Schiff bases VIII-XIII (a-e) (general procedure). A mixture of 1 mmol of substituted salicylaldehyde **I-VI**, 10 ml of methanol, 1 mmol of amine **VIIa-VIIg**, 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 and washed with 5 ml of methanol. Oily compounds were isolated by removal of the solvent, followed by flash chromatography.

2-[(Cyclohexylimino)methyl]-4-methyl-6-(2-phenylpropan-2-yl)phenol (VIIIa). Yield 91%, mp 107–108°C. IR spectrum: ν 1630 cm^{-1} ($\text{N}=\text{CH}$). ^1H NMR spectrum, δ , ppm: 1.05–1.62 m and 1.72–1.93 m (10H, CH_2), 1.67 s (6H, CMe_2), 2.29 s (3H, 4-Me), 2.98–3.19 m (1H, CHN), 6.78 d (1H, 3-H, $J = 2.0$ Hz), 6.95–7.23 m (6H, H_{arom}), 8.20 s (1H, $\text{CH}=\text{N}$), 13.03 s (1H, OH). Found: $[M]^+$ 335.22536. $\text{C}_{23}\text{H}_{29}\text{NO}$. Calculated: M 335.22490.

4-Methyl-2-[(phenylimino)methyl]-2-(2-phenylpropan-2-yl)phenol (VIIIb). Yield 87%, mp 92–93°C. IR spectrum: ν 1619 cm^{-1} ($\text{N}=\text{CH}$). ^1H NMR spectrum, δ , ppm: 1.71 s (6H, CMe_2), 2.34 s (3H, 4-Me), 6.95–7.35 m (12H, H_{arom}), 8.46 s (1H, $\text{CH}=\text{N}$), 12.92 s (1H, OH). Found: $[M]^+$ 329.17780. $\text{C}_{23}\text{H}_{23}\text{NO}$. Calculated: M 329.17795.

2-[(2-Cyclopentyl-6-methylphenylimino)methyl]-4-methyl-6-(2-phenylpropan-2-yl)phenol (VIIIc). Yield 88%, mp 104–105°C. IR spectrum: ν 1622 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.15–1.65 and 1.78–1.90 m (8H, CH_2), 1.74 s (6H, CMe_2), 2.10 s and 2.33 s (3H each, 4-Me, 6'-Me), 2.78–2.96 m (1H, CH), 6.89 d (1H, 3-H, $J = 2.0$ Hz), 6.95–7.25 m (9H, H_{arom}), 8.16 s (1H, CH=N), 12.80 s (1H, OH). Found: $[M]^+$ 411.2558. $\text{C}_{29}\text{H}_{33}\text{NO}$. Calculated: M 411.2562.

2-[(2-Cyclopentyl-4,6-dimethylphenylimino)methyl]-4-methyl-6-(2-phenylpropan-2-yl)phenol (VIIIId). Yield 94%, mp 98–100°C. IR spectrum: ν 1622 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.27–1.65 m and 1.78–1.94 m (8H, CH_2); 1.74 s (6H, CMe_2); 2.05 s, 2.23 s, and 2.32 s (3H each, 4-Me, 4'-Me, 6'-Me); 2.77–2.89 m (1H, CH); 6.68–7.30 m (9H, H_{arom}); 8.13 s (1H, CH=N); 12.88 s (1H, OH). Found: $[M]^+$ 425.27344. $\text{C}_{30}\text{H}_{35}\text{NO}$. Calculated: M 425.27185.

4-Methyl-2-(2-phenylpropan-2-yl)-6-[(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-ylimino)methyl]phenol (VIIIe). Yield 92%, oily substance. IR spectrum: ν 1627 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 0.66 s, 0.84 s, and 0.99 s (3H each, 1'-Me, 7'-Me); 1.03–1.60 m and 1.78–2.12 m (7H, 3'-H, 4'-H, 5'-H, 6'-H); 1.70 s (6H, CMe_2); 2.27 s (3H, 4-Me); 3.06 t (1H, 2'-H, $J = 9$ Hz); 6.79 s (1H, 5-H); 6.96–7.23 m (6H, H_{arom}); 8.01 s (1H, CH=N); 12.78 s (1H, OH). Found: $[M]^+$ 389.2723. $\text{C}_{27}\text{H}_{35}\text{NO}$. Calculated: M 389.2718.

4-*tert*-Butyl-2-[(cyclohexylimino)methyl]-6-(2-phenylpropan-2-yl)phenol (IXa). Yield 96%, oily substance. IR spectrum: ν 1630 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.08–1.23 m and 1.38–1.67 m (10H, CH_2), 1.32 s (9H, *t*-Bu), 1.71 s (6H, CMe_2), 3.05–3.15 m (1H, CHN), 6.99–7.34 m (7H, H_{arom}), 8.27 s (1H, CH=N), 13.17 s (1H, OH). Found: $[M]^+$ 377.27236. $\text{C}_{26}\text{H}_{35}\text{NO}$. Calculated: M 377.27185.

4-*tert*-Butyl-2-[(phenylimino)methyl]-6-(2-phenylpropan-2-yl)phenol (IXb). Yield 79%, oily substance. IR spectrum: ν 1618 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.33 s (9H, *t*-Bu), 1.74 s (6H, CMe_2), 6.98–7.45 m (12H, H_{arom}), 8.54 s (1H, CH=N), 12.94 s (1H, OH). Found: $[M]^+$ 371.22494. $\text{C}_{26}\text{H}_{29}\text{NO}$. Calculated: M 371.22490.

4-*tert*-Butyl-2-[(2-cyclopentyl-6-methylphenylimino)methyl]-6-(2-phenylpropan-2-yl)phenol (IXc). Yield 92%, oily substance. IR spectrum: ν 1622 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.12–1.25 m and 1.35–1.70 m (8H, CH_2), 1.31 s (9H,

t-Bu), 1.74 s (6H, CMe_2), 2.12 s (3H, 6'-Me), 2.81–2.95 m (1H, CH), 6.83–7.42 m (10H, H_{arom}), 8.22 s (1H, CH=N), 12.87 s (1H, OH). Found: $[M]^+$ 453.30309. $\text{C}_{32}\text{H}_{39}\text{NO}$. Calculated: M 453.30315.

4-*tert*-Butyl-2-[(2-cyclopentyl-4,6-dimethylphenylimino)methyl]-6-(2-phenylpropan-2-yl)phenol (IXd). Yield 87%, mp 119–121°C. IR spectrum: ν 1620 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.31 s (9H, *t*-Bu), 1.42–1.69 m (8H, CH_2), 1.77 s (6H, CMe_2), 2.08 s and 2.24 s (3H each, 4'-Me, 6'-Me), 2.82–2.95 m (1H, CH), 6.73 s and 6.80 s (1H each, 3'-H, 5'-H), 7.00–7.19 m (6H, H_{arom}), 7.39 s (1H, 5-H), 8.19 s (1H, CH=N), 12.95 s (1H, OH). Found: $[M]^+$ 467.31817. $\text{C}_{33}\text{H}_{41}\text{NO}$. Calculated: M 467.31880.

4-*tert*-Butyl-2-(2-phenylpropan-2-yl)-6-[(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-ylimino)methyl]phenol (IXe). Yield 87%, mp 130–132°C. IR spectrum: ν 1624 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 0.69 s, 0.85 s, and 1.01 s (3H each, 1'-Me, 7'-Me); 1.06–1.20 m and 1.35–1.67 m (7H, 3'-H, 4'-H, 5'-H, 6'-H); 1.27 s (9H, *t*-Bu); 1.70 s (6H, CMe_2); 3.05 t (1H, 2'-H, $J = 9.0$ Hz); 6.95–7.25 m (7H, H_{arom}); 8.09 s (1H, CH=N); 12.85 s (1H, OH). Found: $[M]^+$ 431.31908. $\text{C}_{30}\text{H}_{41}\text{NO}$. Calculated: M 431.31880.

2-[(Cyclohexylimino)methyl]-4,6-bis(2-phenylpropan-2-yl)phenol (Xa). Yield 96%, oily substance. IR spectrum: ν 1629 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.05–1.56 m and 1.67–1.89 m (10H, CH_2), 1.63 s (12H, CMe_2), 2.96–3.15 m (1H, CHN), 6.81 d (1H, 3-H, $J = 2.0$ Hz), 7.00–7.26 m (11H, H_{arom}), 8.19 s (1H, CH=N), 13.15 s (1H, OH). Found: $[M]^+$ 439.28828. $\text{C}_{31}\text{H}_{37}\text{NO}$. Calculated: M 439.28750.

6-[(Phenylimino)methyl]-4,6-bis(2-phenylpropan-2-yl)phenol (Xb). Yield 89%, mp 117–118°C. IR spectrum: ν 1616 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.66 s and 1.68 s (6H each, CMe_2), 6.97–7.35 m (17H, H_{arom}), 8.46 s (1H, CH=N), 12.99 s (1H, OH). Found: $[M]^+$ 433.24213. $\text{C}_{31}\text{H}_{31}\text{NO}$. Calculated: M 433.24055.

2-[(2-Cyclopentyl-6-methylphenylimino)methyl]-4,6-bis(2-phenylpropan-2-yl)phenol (Xc). Yield 69%, mp 147–148°C. IR spectrum: ν 1623 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.05–1.56 m and 1.70–1.91 m (8H, CH_2), 1.66 s and 1.68 s (6H each, CMe_2); 2.11 s (3H, 6'-Me), 2.85–2.96 m (1H, CH), 6.86–7.22 m (15H, H_{arom}), 8.16 s (1H, CH=N), 12.94 s (1H, OH). Found: $[M]^+$ 515.31958. $\text{C}_{37}\text{H}_{41}\text{NO}$. Calculated: M 515.31880.

2-[(2-Cyclopentyl-4,6-dimethylphenylimino)methyl]-4,6-bis(2-phenylpropan-2-yl)phenol (Xd).

Yield 82%, mp 158–160°C. IR spectrum: ν 1623 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.15–1.61 m and 1.70–1.90 m (8H, CH_2), 1.66 s and 1.67 s (6H each, CMe_2), 2.07 s and 2.23 s (3H each, 4'-Me, 6'-Me), 2.78–2.94 m (1H, CH), 6.71 s and 6.78 s (1H each, 3'-H, 5'-H), 6.92 d (1H, 3-H, $J = 2.0$ Hz), 6.95–7.23 m (11H, H_{arom}), 8.14 s (1H, CH=N), 13.03 s (1H, OH). Found: $[M]^+$ 529.33469. $\text{C}_{38}\text{H}_{43}\text{NO}$. Calculated: M 529.33445.

2,4-Bis(2-phenylpropan-2-yl)-6-[(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-ylimino)methyl]phenol (Xe). Yield 93%, mp 59–60°C. IR spectrum: ν 1625 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 0.68 s, 0.84 s, and 1.00 s (3H each, 1'-Me, 7'-Me); 0.88–0.98 m, 1.12–1.58 m, and 1.69–1.96 m (7H, 3'-H, 4'-H, 5'-H, 6'-H); 1.61 s and 1.66 s (6H each, CMe_2); 3.04 t (1H, 2'-H, $J = 9$ Hz); 6.82 d (1H, 5-H, $J = 2.0$ Hz); 6.96–7.20 m (11H, H_{arom}); 8.02 s (1H, CH=N); 12.92 s (1H, OH). Found: $[M]^+$ 493.33577. $\text{C}_{35}\text{H}_{43}\text{NO}$. Calculated: M 493.33445.

2-[(Cyclohexylimino)methyl]-6-(2-phenylpropan-2-yl)-4-(triphenylmethyl)phenol (XIa). Yield 82%, mp 199–201°C. IR spectrum: ν 1626 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.10–1.45 m and 1.55–1.90 m (10H, CH_2), 1.52 s (6H, CMe_2), 2.97–3.15 m (1H, CHN), 6.82 d (1H, 3-H, $J = 2.0$ Hz), 6.95–7.27 m (21H, H_{arom}), 8.12 s (1H, CH=N), 13.37 s (1H, OH). Found: $[M]^+$ 563.31840. $\text{C}_{41}\text{H}_{41}\text{NO}$. Calculated: M 563.31880.

2-[(Phenylimino)methyl]-6-(2-phenylpropan-2-yl)-4-(triphenylmethyl)phenol (XIb). Yield 84%, mp 131–133°C. IR spectrum: ν 1616 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.55 s (6H, CMe_2), 6.85–7.30 m (27H, H_{arom}), 8.36 s (1H, CH=N), 13.20 s (1H, OH). Found: $[M]^+$ 557.27213. $\text{C}_{41}\text{H}_{35}\text{NO}$. Calculated: M 557.27185.

2-[(2-Cyclopentyl-6-methylphenylimino)methyl]-6-(2-phenylpropan-2-yl)-4-triphenylmethylphenol (XIc). Yield 72%, mp 212–214°C. IR spectrum: ν 1620 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.25–1.58 m and 1.65–1.89 m (8H, CH_2), 1.61 s (6H, CMe_2), 2.11 s (3H, 6'-Me), 2.85–3.01 m (1H, CH), 6.86–7.28 m (25H, H_{arom}), 8.08 s (1H, CH=N), 13.16 s (1H, OH). Found: $[M]^+$ 639.34933. $\text{C}_{47}\text{H}_{45}\text{NO}$. Calculated: M 639.35009.

2-[(2-Cyclopentyl-4,6-dimethylphenylimino)methyl]-6-(2-phenylpropan-2-yl)-4-(triphenylmethyl)phenol (XIId). Yield 71%, mp 88–89°C. IR spectrum: ν 1620 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.20–1.52 m and 1.63–1.97 m (8H, CH_2), 1.58 s

(6H, CMe_2), 2.06 s and 2.22 s (3H each, 4'-Me, 6'-Me), 2.72–2.95 m (1H, CH), 6.68 s and 6.76 s (1H each, 3'-H, 5'-H), 6.91 d (1H, 3-H, $J = 2.0$ Hz), 6.95–7.23 m (21H, H_{arom}), 8.04 s (1H, CH=N), 13.25 s (1H, OH). Found: $[M]^+$ 653.36852. $\text{C}_{48}\text{H}_{47}\text{NO}$. Calculated: M 653.36574.

2-(2-Phenylpropan-2-yl)-6-[(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-ylimino)methyl]-4-(triphenylmethyl)phenol (XIe). Yield 85%, mp 188–189°C. IR spectrum: ν 1626 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 0.69 s, 0.84 s, and 1.01 s (3H each, 1'-Me, 7'-Me); 1.05–1.48 m and 1.60–1.92 m (7H, 3'-H, 4'-H, 5'-H, 6'-H); 1.51 s and 1.57 s (3H each, CMe_2); 3.04 t (1H, 2'-H, $J = 9.0$ Hz); 6.82 d (1H, 5-H, $J = 2.0$ Hz); 6.96–7.20 m (21H, H_{arom}); 7.93 s (1H, CH=N); 13.15 s (1H, OH). Found: $[M]^+$ 617.36489. $\text{C}_{45}\text{H}_{47}\text{NO}$. Calculated: M 617.36574.

2-*tert*-Butyl-6-[(cyclohexylimino)methyl]-4-(2-phenylpropan-2-yl)phenol (XIIa). Yield 98%, oily substance. IR spectrum: ν 1630 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.38–1.60 m and 1.70–1.95 m (10H, CH_2), 1.34 s (9H, *t*-Bu), 1.65 s (6H, CMe_2), 3.05–3.20 m (1H, CHN), 6.77 d (1H, 5-H, $J = 2.0$ Hz), 7.03–7.23 m (6H, H_{arom}), 8.24 s (1H, CH=N), 13.50 br.s (1H, OH). Found: $[M]^+$ 377.27234. $\text{C}_{26}\text{H}_{35}\text{NO}$. Calculated: M 377.27185.

2-*tert*-Butyl-6-[(phenylimino)methyl]-4-(2-phenylpropan-2-yl)phenol (XIIb). Yield 81%, oily substance. IR spectrum: ν 1618 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.38 s (9H, *t*-Bu), 1.65 s (6H, CMe_2), 6.94 d (1H, 5-H, $J = 2.0$ Hz), 6.99–7.38 m (11H, H_{arom}), 8.50 s (1H, CH=N), 13.41 s (1H, OH). Found: $[M]^+$ 371.22494. $\text{C}_{26}\text{H}_{29}\text{NO}$. Calculated: M 371.22490.

2-*tert*-Butyl-6-[(2-cyclopentyl-6-methylphenylimino)methyl]-4-(2-phenylpropan-2-yl)phenol (XIIc). Yield 75%, mp 145–147°C. IR spectrum: ν 1624 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.15–1.32 m, 1.40–1.61 m, and 1.85–2.09 m (8H, CH_2); 1.38 s (9H, *t*-Bu); 1.65 s (6H, CMe_2); 2.18 s (3H, 2'-Me); 2.95–3.12 m (1H, CH); 6.85–7.28 m (10H, H_{arom}); 8.20 s (1H, CH=N); 13.28 s (1H, OH). Found: $[M]^+$ 453.30266. $\text{C}_{32}\text{H}_{39}\text{NO}$. Calculated: M 453.30315.

2-*tert*-Butyl-6-[(2-cyclopentyl-4,6-dimethylphenylimino)methyl]-4-(2-phenylpropan-2-yl)phenol (XIId). Yield 89%, mp 89–91°C. IR spectrum: ν 1624 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.38 s (9H, *t*-Bu), 1.40–1.62 m and 1.70–2.03 m (8H, CH_2), 1.65 s (6H, CMe_2), 2.14 s and 2.27 s (3H each,

4'-Me, 6'-Me), 2.90–3.10 m (1H, CH), 6.75 s and 6.83 s (1H, 3'-H, 5'-H), 6.87 d (1H, 5-H, $J = 2.0$ Hz), 7.00–7.29 m (6H, H_{arom}), 8.18 s (1H, CH=N), 13.38 s (1H, OH). Found: $[M]^+$ 467.31956. $C_{33}H_{41}NO$. Calculated: M 467.31880.

2-tert-Butyl-4-(2-phenylpropan-2-yl)-6-[(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl-imino)methyl]phenol (XIIE). Yield 80%, mp 98–99°C. IR spectrum: ν 1626 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 0.78 s, 0.90 s, and 1.16 s (3H each, 1'-Me, 7'-Me); 0.95–1.12 m, 1.42–1.60 m, and 1.69–1.95 m (7H, 3'-H, 4'-H, 5'-H, 6'-H); 1.33 s (9H, *t*-Bu); 1.62 s (6H, CMe_2); 3.10 t (1H, 2'-H, $J = 9.0$ Hz); 6.78 d (1H, 5-H, $J = 2.0$ Hz); 7.02–7.25 m (6H, H_{arom}); 8.06 s (1H, CH=N); 13.32 s (1H, OH). Found: $[M]^+$ 431.31865. $C_{30}H_{41}NO$. Calculated: M 431.31880.

2-tert-Butyl-6-[(cyclohexylimino)methyl]-4-(triphenylmethyl)phenol (XIIIa). Yield 74%, mp 182–183°C. IR spectrum: ν 1627 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.24 s (9H, *t*-Bu), 1.28–1.90 m (10H, CH_2), 3.02–3.18 m (1H, CHN), 6.78 d (1H, 5-H, $J = 2.0$ Hz), 6.95–7.27 m (16H, H_{arom}), 8.17 s (1H, CH=N), 13.77 s (1H, OH). Found: $[M]^+$ 501.30288. $C_{36}H_{39}NO$. Calculated: M 501.30315.

2-tert-Butyl-6-[(phenylimino)methyl]-4-(triphenylmethyl)phenol (XIIIb). Yield 68%, mp 157–159°C. IR spectrum: ν 1614 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.28 s (9H, *t*-Bu), 6.95–7.35 m (22H, H_{arom}), 8.41 s (1H, CH=N), 13.62 s (1H, OH). Found: $[M]^+$ 495.25653. $C_{36}H_{33}NO$. Calculated: M 495.25620.

2-tert-Butyl-6-[(2-cyclopentyl-6-methylphenylimino)methyl]-4-(triphenylmethyl)phenol (XIIIc). Yield 64%, mp 208–210°C. IR spectrum: ν 1622 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.31 s (9H, *t*-Bu), 1.38–2.05 m (8H, CH_2), 2.18 s (3H, 2'-Me), 2.92–3.13 m (1H, CH), 6.90 d (1H, 5-H, $J = 2.0$ Hz), 6.98–7.27 m (19H, H_{arom}), 8.11 s (1H, CH=N), 13.47 s (1H, OH). Found: $[M]^+$ 577.33433. $C_{42}H_{43}NO$. Calculated: M 577.33445.

2-tert-Butyl-6-[(2-cyclopentyl-4,6-dimethylphenylimino)methyl]-4-(triphenylmethyl)phenol (XIII d). Yield 68%, mp 200–202°C. IR spectrum: ν 1618 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.22 s (9H, *t*-Bu), 1.28–1.95 m (8H, CH_2), 2.06 s and 2.17 s (3H each, 4'-Me, 6'-Me), 2.82–3.03 m (1H, CH), 6.65 s and 6.74 s (1H each, 3'-H, 5'-H), 6.80 d (1H, 5-H, $J = 2.0$ Hz), 7.00–7.23 m (16H, H_{arom}), 8.00 s (1H, CH=N), 13.49 s (1H, OH). Found: $[M]^+$ 591.35054. $C_{43}H_{45}NO$. Calculated: M 591.35009.

2-tert-Butyl-6-[(1,7,7-trimethylbicyclo[2.2.1]hept-*exo*-2-yl-imino)methyl]-4-triphenylmethylphenol (XIIIe). Yield 96%, mp 240–242°C. IR spectrum: ν 1623 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 0.78 s, 0.89 s, and 1.16 s (3H each, 1'-H, 7'-Me); 1.24 s (9H, *t*-Bu); 0.95–1.13 m and 1.32–1.97 m (7H, 3'-H, 4'-H, 5'-H, 6'-H); 3.04 t (1H, 2'-H, $J = 9.0$ Hz); 6.80 d (1H, 5-H, $J = 2.0$ Hz); 6.96–7.25 m (16H, H_{arom}); 7.98 s (1H, CH=N); 13.54 s (1H, OH). Found: $[M]^+$ 555.34964. $C_{40}H_{45}NO$. Calculated: M 555.35009.

Schiff bases VIII f–XIII f (general procedure). Triethylamine, 0.14 ml (1 mmol), was added to a mixture of 1 mmol of aldehyde I–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 (TLC). The solvent was distilled off, the residue was dissolved in chloroform, the solution was washed with water, dried over Na_2SO_4 , and evaporated, and the residue was subjected to flash chromatography. The eluate was evaporated, and the solid residue was recrystallized from methanol.

2-[[1-(1-Adamantyl)ethylimino]methyl]-4-methyl-6-(2-phenylpropan-2-yl)phenol (VIII f). Yield 79%, mp 153–154°C. IR spectrum: ν 1630 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.10 d (3H, 1'-Me, $J = 7.2$ Hz), 1.15–1.69 m and 1.77–2.20 m (15H, H_{Ad}), 1.68 s and 1.73 s (3H each, CMe_2), 2.28 s (3H, 4-Me), 2.67 q (1H, CHN, $J = 7.2$ Hz), 6.79 d (1H, 3-H, $J = 2.0$ Hz), 6.95–7.25 m (6H, H_{arom}), 8.09 s (1H, CH=N), 13.02 s (1H, OH). Found: $[M]^+$ 415.28745. $C_{29}H_{37}NO$. Calculated: M 415.28750.

2-[[1-(1-Adamantyl)ethylimino]methyl]-4-tert-butyl-6-(2-phenylpropan-2-yl)phenol (IX f). Yield 81%, oily substance. IR spectrum: ν 1630 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.12 d (3H, 1'-Me, $J = 7.2$ Hz), 1.27 s (9H, *t*-Bu), 1.30–1.95 m (15H, H_{Ad}), 1.71 s and 1.76 s (3H each, CMe_2), 2.69 q (1H, CHN, $J = 7.2$ Hz), 6.97 d (1H, 3-H, $J = 2.0$ Hz), 7.00–7.28 m (6H, H_{arom}), 8.15 s (1H, CH=N), 12.31 s (1H, OH). Found: $[M]^+$ 457.33427. $C_{32}H_{43}NO$. Calculated: M 457.33445.

2-[[1-(1-Adamantyl)ethylimino]methyl]-4,6-bis-(2-phenylpropan-2-yl)phenol (X f). Yield 82%, mp 104–106°C. IR spectrum: ν 1629 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.09 d (3H, 1'-Me, $J = 7.2$ Hz), 1.12–1.55 m and 1.68–1.99 m (15H, H_{Ad}), 1.62 s (12H, CMe_2), 2.64 q (1H, CHN, $J = 7.2$ Hz), 6.84 d (1H, 3-H, $J = 2.0$ Hz), 6.95–7.29 m (11H, H_{arom}), 8.10 s (1H, CH=N), 13.15 s (1H, OH). Found: $[M]^+$ 519.34924. $C_{37}H_{45}NO$. Calculated: M 519.35009.

2-{[1-(1-Adamantyl)ethylimino]methyl}-6-(2-phenylpropan-2-yl)-4-(triphenylmethyl)phenol (XIIf). Yield 65%, mp 216–217°C. IR spectrum: ν 1628 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.08 d (3H, 1'-Me, $J = 7.2$ Hz), 1.25–1.55 m and 1.69–1.98 m (15H, H_{Ad}), 1.61 s (6H, CMe_2), 2.66 q (1H, CHN, $J = 7.2$ Hz), 6.84 d (1H, 3-H, $J = 2.0$ Hz), 6.95–7.29 m (21H, H_{arom}), 7.99 s (1H, CH=N), 13.43 s (1H, OH). Found: $[M]^+$ 643.38051. $\text{C}_{47}\text{H}_{49}\text{NO}$. Calculated: M 643.38139.

2-{[1-(1-Adamantyl)ethylimino]methyl}-6-tert-butyl-4-(2-phenylpropan-2-yl)phenol (XIIf). Yield 87%, mp 126–128°C. IR spectrum: ν 1628 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.16 d (3H, 1'-Me, $J = 7.2$ Hz), 1.35 s (9H, t -Bu), 1.41–1.59 m and 1.68–2.03 m (15H, H_{Ad}), 1.62 s (6H, CMe_2), 2.71 q (1H, CHN, $J = 7.2$ Hz), 6.79 d (1H, 3-H, $J = 2.0$ Hz), 7.02–7.20 m (6H, H_{arom}), 8.14 s (1H, CH=N), 13.58 s (1H, OH). Found: $[M]^+$ 457.33608. $\text{C}_{32}\text{H}_{43}\text{NO}$. Calculated: M 457.33445.

2-{[1-(1-Adamantyl)ethylimino]methyl}-6-tert-butyl-4-(triphenylmethyl)phenol (XIIf). Yield 70%, mp 243–244°C. IR spectrum: ν 1630 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.13 d (3H, 1'-Me, $J = 7.2$ Hz), 1.25 s (9H, t -Bu), 1.45–2.04 m (15H, H_{Ad}), 2.71 q (1H, CHN, $J = 7.2$ Hz), 6.80 d (1H, 3-H, $J = 2.0$ Hz), 7.00 d (1H, 5-H, $J = 2.0$ Hz), 7.05–7.22 m (15H, H_{arom}), 8.04 s (1H, CH=N), 13.80 s (1H, OH). Found: $[M]^+$ 581.36684. $\text{C}_{42}\text{H}_{47}\text{NO}$. Calculated: M 581.36574.

Schiff bases VIIIg–XIIIg (general procedure). A mixture of 1 mmol of aldehyde I–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 20–30 h under reflux with stirring until the initial compounds disappeared (TLC). The solvent was distilled off, and the residue was subjected to flash chromatography. The eluate was evaporated, and the solid residue was recrystallized from methanol.

4-Methyl-2-[(pentafluorophenylimino)methyl]-6-(2-phenylpropan-2-yl)phenol (VIIIg). Yield 66%, mp 97–98°C. IR spectrum: ν 1613 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.72 s (6H, CMe_2), 2.34 s (3H, 4-Me), 6.92–7.41 m (7H, H_{arom}), 8.67 s (1H, CH=N), 12.03 s (1H, OH). Found: $[M]^+$ 419.12886. $\text{C}_{23}\text{H}_{18}\text{F}_5\text{NO}$. Calculated: M 419.13084.

4-tert-Butyl-2-[(pentafluorophenylimino)methyl]-6-(2-phenylpropan-2-yl)phenol (IXg). Yield 70%, mp 80–83°C. IR spectrum: ν 1615 cm^{-1} (N=CH).

^1H NMR spectrum, δ , ppm: 1.32 s (9H, t -Bu), 1.72 s (6H, CMe_2), 7.00–7.53 m (7H, H_{arom}), 8.72 s (1H, CH=N), 12.09 s (1H, OH). Found: $[M]^+$ 461.17859. $\text{C}_{26}\text{H}_{24}\text{F}_5\text{NO}$. Calculated: M 461.17779.

2-[(Pentafluorophenylimino)methyl]-4,6-bis(2-phenylpropan-2-yl)phenol (Xg). Yield 60%, mp 145–146°C. IR spectrum: ν 1616 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.65 s and 1.68 s (6H each, CMe_2), 7.00–7.30 m (11H, H_{arom}), 7.33 d (1H, 5-H, $J = 2.0$ Hz), 8.67 s (1H, CH=N), 12.13 s (1H, ON). Found: $[M]^+$ 523.19292. $\text{C}_{31}\text{H}_{26}\text{F}_5\text{NO}$. Calculated: M 523.19344.

2-[(Pentafluorophenylimino)methyl]-6-(2-phenylpropan-2-yl)-4-(triphenylmethyl)phenol (XIg). Yield 59%, oily substance. IR spectrum: ν 1613 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.55 s (6H, CMe_2), 6.90–7.33 m (22H, H_{arom}), 8.64 s (1H, CH=N), 12.28 s (1H, OH). Found: $[M]^+$ 647.22541. $\text{C}_{41}\text{H}_{30}\text{F}_5\text{NO}$. Calculated: M 647.22475.

2-tert-Butyl-6-[(pentafluorophenylimino)methyl]-4-(2-phenylpropan-2-yl)phenol (XIIf). Yield 73%, mp 141–143°C. IR spectrum: ν 1618 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.37 s (9H, t -Bu), 1.66 s (6H, CMe_2), 6.98 d (1H, 5-H, $J = 2.0$ Hz), 7.05–7.28 m (6H, H_{arom}), 8.71 s (1H, CH=N), 12.57 s (1H, OH). Found: $[M]^+$ 461.17677. $\text{C}_{26}\text{H}_{24}\text{F}_5\text{NO}$. Calculated: M 461.17779.

2-tert-Butyl-6-[(pentafluorophenylimino)methyl]-4-(triphenylmethyl)phenol (XIIIg). Yield 62%, mp 188–189°C. IR spectrum: ν 1614 cm^{-1} (N=CH). ^1H NMR spectrum, δ , ppm: 1.24 s (9H, t -Bu), 7.00–7.30 m (17H, H_{arom}), 8.62 s (1H, CH=N), 12.42 s (1H, OH). Found: $[M]^+$ 585.20887. $\text{C}_{36}\text{H}_{28}\text{F}_5\text{NO}$. Calculated: M 585.20909.

REFERENCES

- Oleinik, I.I., Romanov, V.E., Oleinik, I.V., and Ivanchev, S.S., *Russ. J. Org. Chem.*, 2008, vol. 44, p. 107.
- Ivanchev, S.S., *Usp. Khim.*, 2007, vol. 76, p. 669.
- Matsui, S., Mitani, M., Saito, J., Tohi, Y., Makio, H., Tanaka, H., and Fujita, T., *Chem. Lett.*, 1999, vol. 28, p. 1263; Matsui, S., Mitani, M., Saito, J., Matsukawa, N., Tanaka, H., Nakano, T., and Fujita, T., *Chem. Lett.*, 2000, vol. 29, p. 554; Matsui, S. and Fujita, T., *Catal. Today.*, 2001, vol. 66, p. 61; Saito, J., Mitani, M., Mohri, J., Yoshida, Y., Matsui, S., Ishii, S., Kojoh, S., Kashiwa, N., and Fujita, T., *Angew. Chem., Int. Ed.*, 2001, vol. 40, p. 2918; Matsui, S., Mitani, M., Saito, J., Tohi, Y., Makio, H., Matsukawa, N., Takagi, Y., Tsuru, K., Nitabar, M., Nakano, T., Tanaka, H., Kashiwa, N., and Fujita, T., *J. Am. Chem. Soc.*, 2001, vol. 123, p. 6847;

- Makio, H., Kashiwa, N., and Fujita, T., *Adv. Synth. Catal.*, 2002, vol. 344, p. 477; Mitani, M., Mohri, J., Yoshida, Y., Saito, J., Ishii, S., Tsuru, K., Matsui, S., Furuyama, R., Nakano, T., Tanaka, H., Kojoh, S., Matsugi, T., Kashiwa, N., and Fujita, T., *J. Am. Chem. Soc.*, 2002, vol. 124, p. 3327; Furuyama, R., Saito, J., Ishii, S., Mitani, M., Matsui, S., Tohi, Y., Makio, H., Tanaka, N., and Fujita, T., *J. Mol. Catal. A: Chem.*, 2003, vol. 200, p. 31; Ivanchev, S.S., Badaev, V.K., Ivancheva, N.I., and Khaikin, S.Ya., *Dokl. Ross. Akad. Nauk*, 2004, vol. 394, p. 639; Parssinen, A., Luhtanen, T., Klinga, M., Pakkanen, T., Leskela, M., and Repo, T., *Eur. J. Inorg. Chem.*, 2005, p. 2100; Ivanchev, S.S., Trunov, V.A., Rybakov, V.B., Al'bov, D.V., and Rogozin, D.G., *Dokl. Ross. Akad. Nauk*, 2005, vol. 404, p. 57; Gagieva, S.Ch., Sukhova, T.A., Savinov, D.V., Tuskaev, V.A., Lysenko, K.A., Bravaya, N.M., Belokon', Yu.N., and Bulychev, B.M., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2006, p. 1730.
- Ivancheva, N.I., Malinskaya, M.Yu., Ivanchev, S.S., Oleinik, I.I., Kochnev, A.I., and Tolstikov, G.A., *Kinet. Katal.*, 2007, vol. 48, p. 887; Malinskaya, M.Yu., Ivancheva, N.I., Oleinik, I.I., Tolstikov, G.A., and Ivanchev, S.S., *Zh. Prikl. Khim.*, 2007, vol. 80, p. 1479.
 - Ivancheva, N.I., Badaev, V.K., Oleinik, I.I., Ivanchev, S.S., and Tolstikov, G.A., *Dokl. Ross. Akad. Nauk*, 2000, vol. 374, p. 648; Ivanchev, S.S., Tolstikov, G.A., Badaev, V.K., Ivancheva, N.I., Oleinik, I.I., Serushkin, M.I., and Oleinik, I.V., *Vysokomol. Soedin.*, 2000, vol. 43, p. 2053; Ivanchev, S.S., Tolstikov, G.A., Badaev, V.K., Ivancheva, N.I., Oleinik, I.I., Khaikin, S.Ya., and Oleinik, I.V., *Vysokomol. Soedin.*, 2002, vol. 44, p. 1478; Ivanchev, S.S., Tolstikov, G.A., Badaev, V.K., Oleinik, I.I., Ivancheva, N.I., Rogozin, D.G., Oleinik, I.V., and Myakin, S.V., *Kinet. Katal.*, 2004, vol. 45, p. 192; Ivanchev, S.S., Badaev, V.K., Ivancheva, N.I., Sviridova, E.V., Khaikin, S.Ya., Rogozin, D.G., and Abakunchik, A.S., *Vysokomol. Soedin.*, 2005, vol. 47, p. 934; Tolstikov, G.A., Ivanchev, S.S., Oleinik, I.I., Ivancheva, N.I., and Oleinik, I.V., *Dokl. Ross. Akad. Nauk*, 2005, vol. 404, p. 208.
 - Kochnev, A.I., Oleinik, I.I., Oleinik, I.V., Ivanchev, S.S., and Tolstikov, G.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2007, p. 1084.
 - Ivanchev, S.S., Tolstikov, G.A., Gabutdinov, M.S., Kudryashov, V.N., Oleinik, I.I., Ivancheva, N.I., Badaev, V.K., and Oleinik, I.V., Russian Patent no. 2194056, 2002; *Byull. Izobret.*, 2002, no. 34; Ivanchev, S.S., Tolstikov, G.A., Kudryashov, V.N., Ivancheva, N.I., Oleinik, I.I., Gabutdinov, M.S., Badaev, V.K., Oleinik, I.V., Rogozin, D.G., Tikhonov, M.V., Vakhbreit, A.Z., Khasanshin, R.A., and Balabueva, G.Ch., Russian Patent no. 2202559, 2003; *Byull. Izobret.*, 2003, no. 11; Fujita, T., Tohi, Y., Mitani, M., Matsui, S., Saito, J., Nitabaru, M., Sugi, K., Makio, H., and Tsutsui, T., US Patent no. 6875718, 2005.
 - Still, W.C., Kahn, M., and Mitra, A., *J. Org. Chem.*, 1978, vol. 43, p. 2923.
 - Oleinik, I.I., Oleinik, I.V., Abdrakhmanov, I.B., Ivanchev, S.S., and Tolstikov, G.A., *Russ. J. Gen. Chem.*, 2004, vol. 74, p. 1423.
 - Ipaktschi, J., *Chem. Ber.*, 1984, vol. 117, p. 856.