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Design of Postmetallocene Catalytic Systems of Arylimine Type for Olefin Polymerization:

XVII.* Synthesis of Methoxy-Substituted (*p*-Aryl)salicylaldimines Containing ω-Alkenyloxy Group, and Their Complexes with Titanium(IV) Dichloride

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Abstract—Reaction of 5-methoxy-substituted salicylic aldehydes containing in the position *3 tert*-butyl, 2-phenylpropan-2-yl, or 1-phenylethyl groups with *m*- and *p*-allyloxy-, (but-3-enyloxy)-, (pent-4-enyloxy)anilines without solvent in an open system at 130°C afforded a series of (*N*-aryl)salicylaldimines L that with $TiCl_2(OPr\text{-}i)_2$ formed complexes of titanium(IV) dichloride L_2TiCl_2.

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In the framework of the systematic research on the effect of structural modification of salicylaldarylimine complexes of titanium(IV) dichloride on their activity in ethylene polymerization and on the properties of the obtained polyethylene we found [2] that in catalytic system where the complexes contained an ω-alkenyloxyphenylimino group the catalyst in certain cases suffered a fast "self-immobilization" on polyethylene macromolecules. The homogenous catalytic system spontaneously transferred into a heterogenic state without adding an alien substance. These catalytic systems compared with homogeneous analogs show more stable activity in time and are capable of producing polyethylene of superhigh molecular weight and improved morphology of particles. The molecule of the complex is fixed on the polyethylene macromolecule at the expense of the ethylene fragment of the ω-alkenyl substituent acting as a comonomer in the course of ethylene polymerization [2–6]. Probably it indicates the potential ability of these complexes to perform the ethylene copolymerization with α-olefins. It is especially important considering that the known *N*-salicylaldarylimine catalysts characterized as a rule with high reactivity in ethylene homopolymerization usually show a low activity in the copolymerization: The formed polymer is of low comonomer content [7]. Apparently the α-olefin insertion into the $M–C_{macromol}$ bond occurs along the mechanism of 2,1-addition and consequently further monomer insertion is strongly hindered [8–11]. It was shown [11] that the increase in the rate of the monomer insertion by the 1,2-addition mechanism under the effect of the methoxy group in the ligand of the *N*-salicylaldarylimine complexes of zirconium(IV) dichloride resulted in the copolymerization in a larger content of the comonomer in the macromolecule at an insignificant reduction of the catalytic system activity compared to that in the ethylene homopolymerization. Deficit of data does not allow the evaluation of the generality of this phenolmenon and of the prospects of improving the catalytic systems of this type for ethylene copolymerization.

It is expectable that introducing the methoxy group into the ligand of salicylaldarylimine complexes of titanium(IV) dichloride would increase the catalytic

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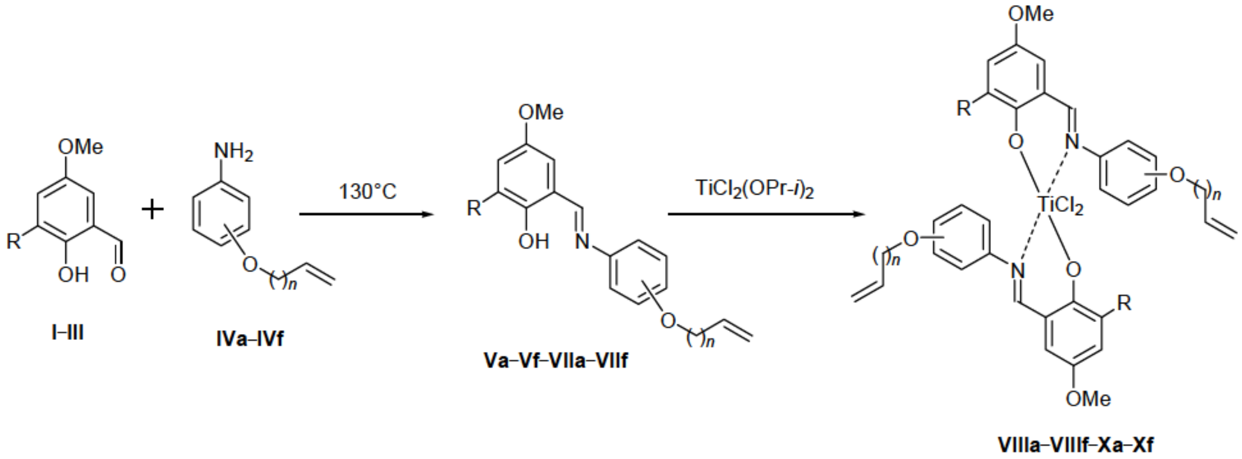
* For communication XVI, see [1].

† Deceased.

Scheme 1.



R = *t*-Bu (**I**, **V**, **VIII**), $CMe_2(Ph)$ (**II**, **VI**, **IX**), CHMe(Ph) (**III**, **VII**, **X**); **IV**–**X**, *m*-$OCH_2CH{=}CH_2$ (**a**), *m*-$O(CH_2)_2CH{=}CH_2$ (**b**), *m*-$O(CH_2)_3CH{=}CH_2$ (**c**), *p*-$OCH_2CH{=}CH_2$ (**d**), *p*-$O(CH_2)_2CH{=}CH_2$ (**e**), *p*-$O(CH_2)_3CH{=}CH_2$ (**f**).

ability of the complexes to copolymerize ethylene with α-olefins and in combination with the possibility to vary the number of methylene units in the alkenyl substituent and to alter its position in the phenyl ring would provide an opportunity of more effective control of the heterogenic catalyst activity, of the properties of polyolefin obtained, and of the process of the complex self-immobilization.

In this report a synthesis is described of (*N*-aryl) salicylaldimine ligands with a methoxy group in the salicylidene fragment and of their complexes with titanium(IV) dichloride. (*N*-Aryl)salicylaldimines were obtained by reacting 5-methoxy-substituted salicylic aldehydes with *m*- and *p*-isomers of anilines containing an ω-alkenyloxy group [1, 12, 13].

In the process of optimizing the synthesis conditions in order to simplify the procedure and to get the highest yield of Schiff's bases we established that the condensation of the substituted salicylic aldehydes **I**–**III** with an equimolar amount of *m*- and *p*-allyloxy-, (but-3-enyloxy)-, (pent-4-enyloxy)anilines **IVa**–**IVf** by melting the initial compounds in an open system at 130°C proceeded with virtually quantitative yields of imines **Va**–**Vf**–**VIIa**–**VIIf**.

The structure of imines **Va**–**Vf**–**VIIa**–**VIIf** was established from the combination of analytic and spectral data. ^1H NMR spectra suggest that the obtained Schiff's bases are individual *E*-isomers. The ^1H NMR spectra of compounds **Va**–**Vf**–**VIIa**–**VIIf** along with the signals of the aromatic protons and the substituents in the aromatic fragments contain the singlets of the protons of N=CH groups in the region 8.48–8.58 ppm and singlets of the protons of OH groups in the region 12.97–13.66 ppm. ω-Alkenyloxy groups of imines **Va**–**Vf**–**VIIa**–**VIIf** give rise to characteristic sets of signals [1, 12, 13].

In the IR spectra of compounds **Va**–**Vf**–**VIIa**–**VIIf** a strong absorption band is observed in the region 1607–1622 cm^{-1} belonging to the stretching vibrations of the C=N bond of the imine group. The mass spectra of phenoxyimines **Va**–**Vf**–**VIIa**–**VIIf** contain intensive peaks of molecular ions.

In the synthesis of complexes a one-stage method was applied consisting in the reaction of the imine with $TiCl_2(OPr\text{-}i)_2$ [1, 12–14]. At the action of a solution of $TiCl_2(OPr\text{-}i)_2$ in toluene on imines **Va**–**Vf**–**VIIa**–**VIIf** at room temperature complexes titanium(IV) dichloride **VIIIa**–**VIIIf**–**Xa**–**Xf** formed that were isolated in 90–97% yields.

The composition of titanium(IV) dichloride complexes **VIIIa**–**VIIIf**–**Xa**–**Xf** was confirmed by the combination of analytic and spectral data. In the IR spectra of complexes absorption bands are observed in the regions 459–484 (Ti–N), 573–582 (Ti–O), and 1595–1611 cm^{-1} (N=CH). The complex formation results in the decrease in the frequency ν(N=CH). ^1H NMR spectra of the synthesized complexes along with the signals of the aromatic protons, of ω-alkenyloxy group and of the substituents in the aromatic fragments contain the peaks of the protons of group HC=N of the stereoisomeric forms [12] in the region 7.67–8.18 ppm, and the singlets of the OH group present in the spectra of initial imines **Va–Vf–VIIa–VIIf** are absent in the spectra of complexes **VIIIa–VIIIf–Xa–Xf**.

EXPERIMENTAL

Analytical and spectral measurements were carried out in the Chemical service center of joint usage of the Siberian Branch, Russian Academy of Sciences.

^{1}H NMR spectra of compounds solutions in $\mathrm{CDCl_3}$ were registered on a spectrometer Bruker AV-400 at operating frequency 400.13 MHz. IR spectra were recorded on a spectrophotometer Vector 22 from crystalline samples as pellets with KBr, from oily samples in pure state. The monitoring of reactions progress and checking the purity of compounds synthesized was done by TLC on Silufol UV-254 plates, eluent chloroform. Elemental analysis was carried out on a CHNS-analyzer Euro EA 3000. Elememtal formulas of compounds obtained were calculated from the data of high resolution mass spectra taken on a mass spectrometer DFS Thermo Electron Corporation. Melting points were measured on an instrument MettlerToledoFP90 in capillaries at a heating rate 1 deg/min.

m- and *p*-Allyloxyaniline [15], *m*- and *p*-(but-3-enyloxy)aniline [13], *p*- and *m*-(pent-4-enyloxy)-aniline [1, 16], $\mathrm{TiCl_2(OPr\text{-}\mathit{i})_2}$ [17] were prepared by known methods, salicylic aldehydes **I–III** were synthesized by the modified procedure [1]. The spectral and analytic characteristics of aldehyde **I** are in agreement with published data [11].

2-Hydroxy-5-methoxy-3-(2-phenylpropan-2-yl)-benzaldehyde (II). Yield 64%, mp 71°C. IR spectrum, ν, cm^{-1}: 1639 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.74 s [6H, $\mathrm{C(CH_3)_2}$], 3.86 s (3H, $\mathrm{OCH_3}$), 6.86 d (1H$_{\mathrm{Ar}}$, *J* 3.0 Hz), 7.10–7.27 m (5H$_{\mathrm{Ar}}$), 7.35 d (1H$_{\mathrm{Ar}}$, *J* 3.0 Hz), 9.80 s (1H, CH=O), 11.04 s (1H, OH). Found [*M*]$^+$ 270.1252. $\mathrm{C_{17}H_{18}O_3}$. Calculated *M* 270.1256.

2-Hydroxy-5-methoxy-3-(1-phenylethyl)benzaldehyde (III). Yield 67%, mp 56°C. IR spectrum, ν, cm^{-1}: 1652 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.62 d (3H, $\mathrm{CHC\underline{H}_3}$, *J* 7.3 Hz), 3.78 s (3H, $\mathrm{OCH_3}$), 4.62 q (1H,$\mathrm{C\underline{H}CH_3}$, *J* 7.3 Hz), 6.82 d (1H$_{\mathrm{Ar}}$, *J* 3.2 Hz), 7.03 d (1H$_{\mathrm{Ar}}$, *J* 3.2 Hz), 7.16–7.30 m (5H$_{\mathrm{Ar}}$), 9.83 s (1H, CH=O), 11.07 s (1H, OH). Found [*M*]$^+$ 256.1093. $\mathrm{C_{16}H_{16}O_3}$. Calculated *M* 256.1099.

(*N*-Aryl)salicylaldimines Va–Vf–VIIa–VIIf. To a heated at 130°C melt of 3 mmol of substituted salicylic aldehyde **I–III** was added at stirring 3 mmol of an appropriate ω-alkenyloxyaniline **IVa–IVf**, and the melt was stirred for 1 h. After cooling to room temperature the residue was purified by flash-chromatography on silica gel 2–25 μ, eluent $\mathrm{CHCl_3}$–hexane, 1 : 2, the first bright yellow fraction was collected. The solvent was distilled off, to obtain crystals the residue was triturated with 5 mL of methanol, the crystals were filtered off, washed with 3 mL of methanol, and dried in a vacuum-desiccator.

2-{[3-(Allyloxy)phenyl]iminomethyl}-6-*tert*-butyl-4-methoxyphenol (Va). Yield 95%. Oily substance. IR spectrum, ν, cm^{-1}: 1617 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.48 s [9H, $\mathrm{C(CH_3)_3}$], 3.80 s (3H, $\mathrm{OCH_3}$), 4.57 d.t (2H, $\mathrm{O\mathbf{C\underline{H}_2}CH{=}CH_2}$, *J* 5.3, 1.4 Hz), 5.31 d.q (1H, $\mathrm{OCH_2CH{=}\mathbf{C\underline{H}_2}}$, *J* 10.6, 1.4 Hz), 5.44 d.q (1H, $\mathrm{OCH_2CH{=}\mathbf{C\underline{H}_2}}$, *J* 17.3, 1.4 Hz), 6.07 d.d.t (1H, $\mathrm{OCH_2\mathbf{C\underline{H}}{=}CH_2}$, *J* 17.3, 10.6, 5.3 Hz), 6.70 d (1H$_{\mathrm{Ar}}$, *J* 2.9 Hz), 6.82–6.89 m (3H$_{\mathrm{Ar}}$), 7.05 d (1H$_{\mathrm{Ar}}$, *J* 2.9 Hz), 7.30 t.d (1H$_{\mathrm{Ar}}$, *J* 7.8, *0.9* Hz), 8.57 s (1H, CH=N), 13.47 s (1H, OH). Found [*M*]$^+$ 339.1832. $\mathrm{C_{21}H_{25}NO_3}$. Calculated *M* 339.1829.

2-{[3-(But-3-enyloxy)phenyl]iminomethyl}-6-*tert*-butyl-4-methoxyphenol (Vb). Yield 96%, mp 51°C. IR spectrum, ν, cm^{-1}: 1618 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.46 s [9H, $\mathrm{C(CH_3)_3}$], 2.56 m (2H, $\mathrm{O\mathbf{CH_2}C\underline{H}_2{\cdot}CH{=}CH_2}$), 3.79 s (3H, $\mathrm{OCH_3}$), 4.05 t (2H, $\mathrm{O\mathbf{C\underline{H}_2}{\cdot}CH_2CH{=}CH_2}$, *J* 6.7 Hz), 5.12 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2{\cdot}CH{=}C\underline{H}_2}$, *J* 10.3, 1.9, 1.1 Hz), 5.18 d.d.t (1H, $\mathrm{O\mathbf{CH_2}{\cdot}CH_2CH{=}C\underline{H}_2}$, *J* 17.2, 1.9, 1.5 Hz), 5.91 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2C\underline{H}{=}CH_2}$, *J* 17.2, 10.3, 6.9 Hz), 6.71 d (1H$_{\mathrm{Ar}}$, *J* 3.1 Hz), 6.80–6.88 m (3H$_{\mathrm{Ar}}$), 7.04 d (1H$_{\mathrm{Ar}}$, *J* 3.1 Hz), 7.29 t (1H$_{\mathrm{Ar}}$, *J* 7.9 Hz), 8.58 s (1H, CH=N), 13.49 s (1H, OH). Found [*M*]$^+$ 353.1989. $\mathrm{C_{22}H_{27}NO_3}$. Calculated *M* 353.1986.

2-*tert*-Butyl-4-methoxy-6-{[3-(pent-4-enyloxy)-phenyl]iminomethyl}phenol (Vc). Yield 99%. Oily substance. IR spectrum, ν, cm^{-1}: 1620 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.45 s [9H, $\mathrm{C(CH_3)_3}$], 1.89 t.t (2H, $\mathrm{O\mathbf{CH_2}C\underline{H}_2CH_2CH{=}CH_2}$, *J* 7.0, 6.4 Hz), 2.25 t.d (2H, $\mathrm{O\mathbf{CH_2}CH_2C\underline{H}_2CH{=}CH_2}$, *J* 7.0, 6.8 Hz), 3.79 s (3H, $\mathrm{OCH_3}$), 4.00 t (2H, $\mathrm{O\mathbf{C\underline{H}_2}CH_2CH_2CH{=}CH_2}$, *J* 6.4 Hz), 5.00 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2CH_2CH{=}C\underline{H}_2}$, *J* 10.2, 1.4, 1.2 Hz), 5.07 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2CH_2CH{=}C\underline{H}_2}$, *J* 17.2, 1.6, 1.4 Hz), 5.85 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2CH_2C\underline{H}{=}CH_2}$, *J* 17.2, 10.2, 6.8 Hz), 6.71 d (1H$_{\mathrm{Ar}}$, *J* 3.1 Hz), 6.79–6.87 m (3H$_{\mathrm{Ar}}$), 7.04 d (1H$_{\mathrm{Ar}}$, *J* 3.1 Hz), 7.26–7.31 m (1H$_{\mathrm{Ar}}$), 8.57 s (1H, CH=N), 13.49 s (1H, OH). Found [*M*]$^+$ 367.2144. $\mathrm{C_{23}H_{29}NO_3}$. Calculated *M* 367.2142.

2-{[4-(Allyloxy)phenyl]iminomethyl}-6-*tert*-butyl-4-methoxyphenol (Vd). Yield 98%, mp 60°C. IR spectrum, ν, cm^{-1}: 1617 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.46 s [9H, $\mathrm{C(CH_3)_3}$], 3.78 s (3H, $\mathrm{OCH_3}$), 4.54 d.t (2H, $\mathrm{O\mathbf{C\underline{H}_2}CH{=}CH_2}$, *J* 5.3, 1.4 Hz), 5.29 d.q (1H, $\mathrm{OCH_2CH{=}\mathbf{C\underline{H}_2}}$, *J* 10.5, 1.4 Hz), 5.41 d.q (1H, $\mathrm{OCH_2CH{=}\mathbf{C\underline{H}_2}}$, *J* 17.5, 1.4 Hz), 6.04 d.d.t (1H, $\mathrm{OCH_2\mathbf{C\underline{H}}{=}CH_2}$, *J* 17.5, 10.5, 5.3 Hz), 6.67 d (1$\mathrm{H_{Ar}}$, *J* 2.9 Hz), 6.92 d (1$\mathrm{H_{Ar}}$, *J* 8.8 Hz), 6.99 d (1$\mathrm{H_{Ar}}$, *J* 2.9 Hz), 7.23 d (1$\mathrm{H_{Ar}}$, *J* 8.8 Hz), 8.54 s (1H, CH=N), 13.57 s (1H, OH). Found $[M]^+$ 339.1823. $\mathrm{C_{21}H_{25}NO_3}$. Calculated *M* 339.1829.

2-{[4-(But-3-enyloxy)phenyl]iminomethyl}-6-*tert*-butyl-4-methoxyphenol (Ve). Yield 98%. Oily substance. IR spectrum, ν, cm^{-1}: 1618 (C=N). ^{1}H NMR spec-trum, δ, ppm: 1.46 s [9H, $\mathrm{C(CH_3)_3}$], 2.55 m (2H, $\mathrm{O\mathbf{CH_2}C\underline{H}_2CH{=}CH_2}$), 3.79 s (3H, $\mathrm{OCH_3}$), 4.02 t (2H, $\mathrm{O\mathbf{C\underline{H}_2}CH_2CH{=}CH_2}$, *J* 6.7 Hz), 5.12 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2CH{=}C\underline{H}_2}$, *J* 10.3, 1.8, 1.1 Hz), 5.18 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2CH{=}C\underline{H}_2}$, *J* 17.1, 1.8, 1.5 Hz), 5.91 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2C\underline{H}{=}CH_2}$, *J* 17.1, 10.3, 6.8 Hz), 6.70 d (1$\mathrm{H_{Ar}}$, *J* 3.0 Hz), 6.91 d (2$\mathrm{H_{Ar}}$, *J* 9.0 Hz), 7.01 d (1$\mathrm{H_{Ar}}$, *J* 3.0 Hz), 7.25 d (2$\mathrm{H_{Ar}}$, *J* 9.0 Hz), 8.56 s (1H, CH=N), 13.66 s (1H, OH). Found $[M]^+$ 353.1989. $\mathrm{C_{22}H_{27}NO_3}$. Calculated *M* 353.1986.

2-*tert*-Butyl-4-methoxy-6-{[4-(pent-4-enyloxy)phenyl]iminomethyl}phenol (Vf). Yield 97%. Oily substance. IR spectrum, ν, cm^{-1}: 1619 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.47 s [9H, $\mathrm{C(CH_3)_3}$], 1.92 t.t (2H, $\mathrm{O\mathbf{CH_2}C\underline{H}_2CH_2CH{=}CH_2}$, *J* 7.1, 6.6 Hz), 2.27 t.d (2H, $\mathrm{O\mathbf{CH_2}CH_2C\underline{H}_2CH{=}CH_2}$, *J* 7.1, 6.8 Hz), 3.80 s (3H, $\mathrm{OCH_3}$), 4.00 t (2H, $\mathrm{O\mathbf{C\underline{H}_2}CH_2CH_2CH{=}CH_2}$, *J* 6.6 Hz), 5.02 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2CH_2CH{=}C\underline{H}_2}$, *J* 10.3, 1.4, 1.2 Hz), 5.08 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2CH_2CH{=}C\underline{H}_2}$, *J* 7.1, 1.6, 1.4 Hz), 5.86 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2CH_2C\underline{H}{=}CH_2}$, *J* 17.1, 10.3, 6.8 Hz), 6.68 d (1$\mathrm{H_{Ar}}$, *J* 2.9 Hz), 6.89–7.28 m (4$\mathrm{H_{Ar}}$), 6.99 d (1$\mathrm{H_{Ar}}$, *J* 2.9 Hz), 8.57 s (1H, CH=N), 13.57 s (1H, OH). Found $[M]^+$ 367.2144. $\mathrm{C_{23}H_{29}NO_3}$. Calculated *M* 367.2142.

2-{[3-(Allyloxy)phenyl]iminomethyl}-4-methoxy-6-(2-phenylpropan-2-yl)phenol (VIa). Yield 96%, mp 142°C. IR spectrum, ν, cm^{-1}: 1619 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.75 s [6H, $\mathrm{C(CH_3)_2}$], 3.85 s (3H, $\mathrm{OCH_3}$), 4.52 d.t (2H, $\mathrm{O\mathbf{C\underline{H}_2}CH{=}CH_2}$, *J* 5.3, *1.5* Hz), 5.28 d.q (1H, $\mathrm{OCH_2CH{=}\mathbf{C\underline{H}_2}}$, *J* 10.5, *1.2* Hz), 5.40 d.q (1H, $\mathrm{OCH_2CH{=}\mathbf{C\underline{H}_2}}$, *J* 17.2, *1.5* Hz), 6.04 d.d.t (1H, $\mathrm{OCH_2\mathbf{C\underline{H}}{=}CH_2}$, *J* 17.2, 10.5, 5.3 Hz), 6.72–6.81 m (4$\mathrm{H_{Ar}}$), 7.08–7.28 m (7$\mathrm{H_{Ar}}$), 8.51 s (1H, CH=N), 12.97 s (1H, OH). Found $[M]^+$ 401.1981. $\mathrm{C_{26}H_{27}NO_3}$. Calculated *M* 401.1986.

2-{[3-(But-3-enyloxy)phenyl]iminomethyl}-4-methoxy-6-(2-phenylpropan-2-yl)phenol (VIb). Yield 90%, mp 98°C. IR spectrum, ν, cm^{-1}: 1616 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.75 s (6H, $\mathrm{CH_3}$), 2.55 m (2H, $\mathrm{O\mathbf{CH_2}C\underline{H}_2CH{=}CH_2}$), 3.84 s (3H, $\mathrm{OCH_3}$), 4.00 t (2H, $\mathrm{O\mathbf{C\underline{H}_2}CH_2CH{=}CH_2}$, *J* 6.7 Hz), 5.10 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2CH{=}C\underline{H}_2}$, *J* 10.4, 1.8, 1.1 Hz), 5.16 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2CH{=}C\underline{H}_2}$, *J* 17.1, 1.8, 1.4 Hz), 5.89 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2C\underline{H}{=}CH_2}$, *J* 17.1, 10.4, 6.8 Hz), 6.72–6.80 m (4$\mathrm{H_{Ar}}$), 7.12–7.28 m (7$\mathrm{H_{Ar}}$), 8.52 s (1H, CH=N), 13.00 s (1H, OH). Found $[M]^+$ 415.2138. $\mathrm{C_{25}H_{29}NO_3}$. Calcu-lated *M* 415.2142.

4-Methoxy-2-{[3-(pent-4-enyloxy)phenyl]iminomethyl}-6-(2-phenylpropan-2-yl)phenol (VIc). Yield 95%, mp 92°C. IR spectrum, ν, cm^{-1}: 1611 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.75 s [6H, $\mathrm{C(CH_3)_2}$], 1.87 t.t (2H, $\mathrm{O\mathbf{CH_2}C\underline{H}_2CH_2CH{=}CH_2}$, *J* 7.1, 6.8 Hz), 2.23 t.d (2H, $\mathrm{O\mathbf{CH_2}CH_2C\underline{H}_2CH{=}CH_2}$, *J* 7.1, 6.8 Hz), 3.84 s (3H, $\mathrm{OCH_3}$), 3.95 t (2H, $\mathrm{O\mathbf{C\underline{H}_2}CH_2CH_2CH{=}CH_2}$, *J* 6.8 Hz), 4.89–5.16 m (2H, $\mathrm{O\mathbf{CH_2}CH_2CH_2CH{=}C\underline{H}_2}$), 5.84 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2CH_2C\underline{H}{=}CH_2}$, *J* 17.1, 10.3, 6.8 Hz), 6.71–6.76 m (4$\mathrm{H_{Ar}}$), 7.13–7.26 m (7$\mathrm{H_{Ar}}$), 8.52 s (1H, CH=N), 12.99 s (1H, OH). Found $[M]^+$ 429.2296. $\mathrm{C_{28}H_{31}NO_3}$. Calculated *M* 429.2299.

2-{[4-(Allyloxy)phenyl]iminomethyl}-4-methoxy-6-(2-phenylpropan-2-yl)phenol (VId). Yield 95%, mp 111°C. IR spectrum, ν, cm^{-1}: 1618 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.76 s [6H, $\mathrm{C(CH_3)_2}$], 3.84 s (3H, $\mathrm{OCH_3}$), 4.52 d.t (2H, $\mathrm{O\mathbf{C\underline{H}_2}CH{=}CH_2}$, *J* 5.3, *1.5* Hz), 5.29 d.q (1H, $\mathrm{OCH_2CH{=}\mathbf{C\underline{H}_2}}$, *J* 10.5, *1.3* Hz), 5.40 d.q (1H, $\mathrm{OCH_2CH{=}\mathbf{C\underline{H}_2}}$, *J* 17.2, *1.5* Hz), 6.04 d.d.t (1H, $\mathrm{OCH_2\mathbf{C\underline{H}}{=}CH_2}$, *J* 17.2, 10.5, 5.3 Hz), 6.76 d (1$\mathrm{H_{Ar}}$, *J* 3.2 Hz), 6.89 d (2$\mathrm{H_{Ar}}$, *J* 9.1 Hz), 7.13–7.27 m (8$\mathrm{H_{Ar}}$), 8.50 s (1H, CH=N), 13.12 s (1H, OH). Found $[M]^+$ 401.1987. $\mathrm{C_{26}H_{27}NO_3}$. Calculated *M* 401.1986.

2-{[4-(But-3-enyloxy)phenyl]iminomethyl}-4-methoxy-6-(2-phenylpropan-2-yl)phenol (VIe). Yield 92%, mp 88°C. IR spectrum, ν, cm^{-1}: 1617 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.77 s (6H, $\mathrm{CH_3}$), 2.54 m (2H, $\mathrm{OCH_2C\underline{H}_2CH{=}CH_2}$), 3.84 s (3H, $\mathrm{OCH_3}$), 4.00 t (2H, $\mathrm{OC\underline{H}_2CH_2CH{=}CH_2}$, *J* 6.7 Hz), 5.12 d.d.t (1H, $\mathrm{O\mathbf{CH_2}CH_2CH{=}C\underline{H}_2}$, *J* 10.3, 1.8, 1.2 Hz), 5.17 d.d.t (1H, $\mathrm{OCH_2CH_2CH{=}C\underline{H}_2}$, *J* 17.2, 1.8, 1.4 Hz), 5.90 d.d.t (1H, $\mathrm{OCH_2CH_2C\underline{H}{=}CH_2}$, *J* 17.2, 10.3, 6.8 Hz), 6.77 d (1$\mathrm{H_{Ar}}$, *J* 3.1 Hz), 6.88 d (2$\mathrm{H_{Ar}}$, *J* 8.9 Hz), 7.21–7.33 m (8$\mathrm{H_{Ar}}$), 8.50 s (1H, CH=N), 13.14 s (1H, OH). Found $[M]^+$ 415.2139. $\mathrm{C_{25}H_{29}NO_3}$. Calculated *M* 415.2142.

4-Methoxy-2-{[4-(pent-4-enyloxy)phenyl]iminomethyl}-6-(2-phenylpropan-2-yl)phenol (VIf). Yield 97%, mp 100°C. IR spectrum, ν, cm^{-1}: 1613 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.75 s [6H, $C(CH_3)_2$], 1.89 t.t (2H, $O\mathbf{CH_2}C\underline{H}_2CH_2CH{=}CH_2$, *J* 7.0, 6.8 Hz), 2.25 t.d (2H, $O\mathbf{CH_2}CH_2C\underline{H}_2CH{=}CH_2$, *J* 7.0, 6.8 Hz), 3.82 s (3H, OCH_3), 3.94 t (2H, $OC\underline{\mathbf{H}}_2CH_2CH_2CH{=}CH_2$, *J* 6.8 Hz), 4.89–5.16 m (2H, $O\mathbf{CH_2}CH_2CH_2CH{=}C\underline{H}_2$), 5.83 d.d.t (1H, $O\mathbf{CH_2}CH_2CH_2C\underline{H}{=}CH_2$, *J* 17.2, 10.2, 6.8 Hz), 6.73 d ($1H_{Ar}$, *J* 2.0 Hz), 6.82–6.86 m ($2H_{Ar}$), 7.12–7.34 m ($8H_{Ar}$), 8.48 s (1H, CH=N), 13.08 s (1H, OH). Found $[M]^+$ 429.2296. $C_{28}H_{31}NO_3$. Calculated *M* 429.2299.

2-{[3-(Allyloxy)phenyl]iminomethyl}-4-methoxy-6-(1-phenylethyl)phenol (VIIa). Yield 99%, mp 57°C. IR spectrum, ν, cm^{-1}: 1620 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.63 d (3H, CH_3, *J* 7.2 Hz), 3.76 s (3H, OCH_3), 4.56 d.t (2H, $OC\underline{\mathbf{H}}_2CH{=}CH_2$, *J* 5.3, *1.5* Hz), 4.67 q (1H, CH, *J* 7.2 Hz), 5.29 d.q (1H, $OCH_2 \cdot CH{=}\mathbf{C\underline{H}_2}$, *J* 10.4, *1.5* Hz), 5.38 d.q (1H, $OCH_2 \cdot CH{=}\mathbf{C\underline{H}_2}$, *J* 17.3, *1.5* Hz), 6.06 d.d.t (1H, $OCH_2 \cdot \mathbf{C\underline{H}}{=}CH_2$, *J* 17.3, 10.4, 5.3 Hz), 6.73 d ($1H_{Ar}$, *J* 3.0 Hz), 6.80–6.86 m ($3H_{Ar}$), 6.92 d ($1H_{Ar}$, *J* 3.0 Hz), 7.15–7.33 m ($6H_{Ar}$), 8.55 s (1H, CH=N), 13.17 s (1H, OH). Found $[M]^+$ 387.1826. $C_{25}H_{25}NO_3$. Calculated *M* 387.1829.

2-{[3-(But-3-enyloxy)phenyl]iminomethyl}-4-methoxy-6-(1-phenylethyl)phenol (VIIb). Yield 94%, mp 59.5°C. IR spectrum, ν, cm^{-1}: 1618 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.63 d (3H, CH_3, *J* 7.2 Hz), 2.55 m (2H, $O\mathbf{CH_2}C\underline{H}_2CH{=}CH_2$), 3.76 s (3H, OCH_3), 4.03 t (2H, $OC\underline{\mathbf{H}}_2CH_2CH{=}CH_2$, *J* 6.7 Hz), 5.12 d.d.t (1H, $O\mathbf{CH_2}CH_2CH{=}C\underline{H}_2$, *J* 10.3, 1.8, 1.1 Hz), 5.18 d.d.t (1H, $O\mathbf{CH_2}CH_2CH{=}C\underline{H}_2$, *J* 17.3, 1.8, 1.5 Hz), 5.91 d.d.t (1H, $O\mathbf{CH_2}CH_2C\underline{H}{=}CH_2$, *J* 17.3, 10.3, 6.8 Hz), 6.73 d ($1H_{Ar}$, *J* 3.0 Hz), 6.79–6.85 m ($3H_{Ar}$), 6.92 d ($1H_{Ar}$, *J* 3.0 Hz), 7.26–7.32 m ($6H_{Ar}$), 8.55 s (1H, CH=N), 13.20 s (1H, OH). Found $[M]^+$ 401.1990. $C_{26}H_{27}NO_3$. Calculated *M* 401.1986.

4-Methoxy-2-{[3-(pent-4-enyloxy)phenyl]iminomethyl}-6-(1-phenylethyl)phenol (VIIc). Yield 96%. Oily substance. IR spectrum, ν, cm^{-1}: 1622 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.65 d (3H, $CH \cdot C\underline{H}_3$, *J* 7.2 Hz), 1.91 t.t (2H, $O\mathbf{CH_2}C\underline{H}_2CH_2CH{=}CH_2$, *J* 7.1, 6.8 Hz), 2.26 t.d (2H, $O\mathbf{CH_2}CH_2C\underline{H}_2CH{=}CH_2$, *J* 7.1, 6.8 Hz), 3.77 s (3H, OCH_3), 4.00 t (2H, $OC\underline{\mathbf{H}}_2 \cdot CH_2CH_2CH{=}CH_2$, *J* 6.8 Hz), 4.69 q (1H, $C\underline{H}CH_3$, *J* 7.2 Hz), 5.03 d.d.t (1H, $O\mathbf{CH_2}CH_2CH_2CH{=}C\underline{H}_2$, *J* 10.2, 1.4, 1.2 Hz), 5.09 d.d.t (1H, $O\mathbf{CH_2}CH_2CH_2 \cdot CH{=}C\underline{H}_2$, *J* 17.1, 1.7, 1.4 Hz), 5.88 d.d.t (1H, $O\mathbf{CH_2} \cdot CH_2CH_2C\underline{H}{=}CH_2$, *J* 17.1, 10.2, 6.8 Hz), 6.74 d ($1H_{Ar}$, *J* 3.0 Hz), 6.80–6.86 m ($3H_{Ar}$), 6.94 d ($1H_{Ar}$, *J* 3.0 Hz), 7.18–7.35 m ($6H_{Ar}$), 8.56 s (1H, CH=N), 13.24 s (1H, OH). Found $[M]^+$ 415.2140. $C_{27}H_{29}NO_3$. Calculated *M* 415.2142.

2-{[4-(Allyloxy)phenyl]iminomethyl}-4-methoxy-6-(1-phenylethyl)phenol (VIId). Yield 99%, mp 93°C. IR spectrum, ν, cm^{-1}: 1620 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.63 d (3H, CH_3, *J* 7.2 Hz), 3.76 s (3H, OCH_3), 4.55 d.t (2H, $OC\underline{\mathbf{H}}_2CH{=}CH_2$, *J* 5.3, *1.5* Hz), 4.69 q (1H, CH, *J* 7.2 Hz), 5.31 d.q (1H, $OCH_2 \cdot CH{=}\mathbf{C\underline{H}_2}$, *J* 10.5, *1.4* Hz), 5.43 d.q (1H, $OCH_2 \cdot CH{=}\mathbf{C\underline{H}_2}$, *J* 17.3, *1.6* Hz), 6.06 d.d.t (1H, $OCH_2 \cdot \mathbf{C\underline{H}}{=}CH_2$, *J* 17.3, 10.5, 5.3 Hz), 6.72 d ($1H_{Ar}$, *J* 3.0 Hz), 6.89 d ($1H_{Ar}$, *J* 3.0 Hz), 6.95 d ($2H_{Ar}$, *J* 9.1 Hz), 7.21–7.33 m ($7H_{Ar}$), 8.54 s (1H, CH=N), 13.36 s (1H, OH). Found $[M]^+$ 387.1829. $C_{25}H_{25}NO_3$. Calculated *M* 387.1828.

2-{[4-(But-3-enyloxy)phenyl]iminomethyl}-4-methoxy-6-(1-phenylethyl)phenol (VIIe). Yield 94%, mp 64°C. IR spectrum, ν, cm^{-1}: 1620 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.64 d (3H, CH_3, *J* 7.3 Hz), 2.56 m (2H, $O\mathbf{CH_2}C\underline{H}_2CH{=}CH_2$), 3.76 s (3H, OCH_3), 4.03 t (2H, $OC\underline{\mathbf{H}}_2CH_2CH{=}CH_2$, *J* 6.7 Hz), 5.13 d.d.t (1H, $O\mathbf{CH_2}CH_2CH{=}C\underline{H}_2$, *J* 10.3, 1.8, 1.2 Hz), 5.19 d.d.t (1H, $O\mathbf{CH_2}CH_2CH{=}C\underline{H}_2$, *J* 17.2, 1.8, 1.5 Hz), 5.92 d.d.t (1H, $O\mathbf{CH_2}CH_2C\underline{H}{=}CH_2$, *J* 17.2, 10.3, 6.9 Hz), 6.72 d ($1H_{Ar}$, *J* 3.0 Hz), 6.90 d ($1H_{Ar}$, *J* 3.0 Hz), 6.93 d ($2H_{Ar}$, *J* 8.8 Hz), 7.25–7.34 m ($7H_{Ar}$), 8.54 s (1H, CH=N), 13.39 s (1H, OH). Found $[M]^+$ 401.1987. $C_{26}H_{27}NO_3$. Calculated *M* 401.1986.

4-Methoxy-2-{[4-(pent-4-enyloxy)phenylimino]methyl}-6-(1-phenylethyl)phenol (VIIf). Yield 95%, mp 65°C. IR spectrum, ν, cm^{-1}: 1619 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.65 d (3H, $CHC\underline{H}_3$, *J* 7.3 Hz), 1.91 t.t (2H, $O\mathbf{CH_2}C\underline{H}_2CH_2CH{=}CH_2$, *J* 7.1, 6.8 Hz), 2.27 t.d (2H, $O\mathbf{CH_2}CH_2C\underline{H}_2CH{=}CH_2$, *J* 7.1, 6.8 Hz), 3.77 s (3H, OCH_3), 3.99 t (2H, $OC\underline{H}_2CH_2CH_2CH{=}CH_2$, *J* 6.8 Hz), 4.69 q (1H, $C\underline{H}CH_3$, *J* 7.3 Hz), 5.02 d.d.t (1H, $O\mathbf{CH_2}CH_2CH_2CH{=}C\underline{H}_2$, *J* 10.2, 1.4, 1.2 Hz), 5.09 d.d.t (1H, $O\mathbf{CH_2}CH_2CH_2CH{=}C\underline{H}_2$, *J* 17.1, 1.7, 1.4 Hz), 5.87 d.d.t (1H, $O\mathbf{CH_2}CH_2CH_2C\underline{H}{=}CH_2$, *J* 17.1, 10.2, 6.8 Hz), 6.71 d ($1H_{Ar}$, *J* 3.0 Hz), 6.87 d ($1H_{Ar}$, *J* 3.0 Hz), 6.89–6.93 m ($2H_{Ar}$), 7.18 t.t ($1H_{Ar}$, *J* 6.9, 1.8 Hz), 7.21–7.34 m ($6H_{Ar}$), 8.55 s (1H, CH=N), 13.38 s (1H, OH). Found $[M]^+$ 415.2143. $C_{27}H_{29}NO_3$. Calculated *M* 415.2142.

Complexes VIIIa–VIIIf–Xa–Xf. A mixture of 1.4 mmol of imine **Va–Vf–VIIa–VIIf**, 15 mL of anhydrous dichloromethane, 2.39 g of toluene solution containing 0.166 g (0.7 mmol) of $TiCl_2(OPr\text{-}i)_2$ was stirred at room temperature in an argon atmosphere for 24 h. The solvents were distilled off from the formed dark-red solution in a vacuum of the water-jet pump. The residue was washed on the filter with hexane (2 × 2 mL) and dried in a vacuum of an oil pump at 100°C for 1 h to obtain complexes **VIIIa–VIIIf–Xa–Xf** as red-brown powders.

Bis(2-{[3-(allyloxy)phenyl]iminomethyl}-6-*tert*-butyl-4-methoxyphenoxy)titanium(IV) dichloride (VIIIa). Yield 95%. IR spectrum, ν, cm^{-1}: 1597 (C=N), 573 (Ti–O), 482 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.30–1.61 m [18H, $C(CH_3)_3$], 3.75–3.83 m (6H, OCH_3), 4.17–4.52 m (4H, $O\mathbf{C\underline{H}_2}CH=CH_2$), 5.26–5.45 m (4H, $OCH_2CH=\mathbf{C\underline{H}_2}$), 5.87–6.10 m (2H, $OCH_2\mathbf{C\underline{H}}=CH_2$), 6.57–7.28 m ($12H_{Ar}$), 7.93–8.10 m (2H, CH=N). Found, %: C 63.30; H 6.30; Cl 8.50; N 3.49. $C_{42}H_{48}Cl_2N_2O_6Ti$. Calculated, %: C 63.40; H 6.08; Cl 8.91; N 3.52.

Bis(2-{[3-(but-3-enyloxy)phenyl]iminomethyl}-6-*tert*-butyl-4-methoxyphenoxy)titanium(IV) dichloride (VIIIb). Yield 92%. IR spectrum, ν, cm^{-1}: 1597 (C=N), 573 (Ti–O), 482 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.27–1.59 m [18H, $C(CH_3)_3$], 2.36–2.57 m (4H, $O\mathbf{CH_2}C\underline{H}_2CH=CH_2$), 3.73–3.81 m (6H, OCH_3), 3.94–4.06 m (4H, $O\mathbf{C\underline{H}_2}CH_2CH=CH_2$), 5.05–5.19 m (4H, $O\mathbf{CH_2}CH_2CH=C\underline{H}_2$), 5.72–5.95 m (2H, $O\mathbf{CH_2}CH_2C\underline{H}=CH_2$), 6.54–7.33 m ($12H_{Ar}$), 7.90–8.17 m (2H, CH=N). Found, %: C 64.23; H 6.35; Cl 8.66; N 3.39. $C_{44}H_{52}Cl_2N_2O_6Ti$. Calculated, %: C 64.16; H 6.36; Cl 8.61; N 3.40.

Bis(2-*tert*-butyl-4-methoxy-6-{[3-(pent-4-enyloxy)phenyl]iminomethyl}phenoxy)titanium(IV) dichloride (VIIIc). Yield 95%. IR spectrum, ν, cm^{-1}: 1597 (C=N), 573 (Ti–O), 484 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.27–1.59 m [18H, $C(CH_3)_3$], 1.70–1.92 m (4H, $O\mathbf{CH_2}C\underline{H}_2CH_2CH=CH_2$), 2.09–2.27 m (4H, $O\mathbf{CH_2}CH_2C\underline{H}_2CH=CH_2$), 3.71–3.79 m (6H, OCH_3), 3.86–4.00 m (4H, $O\mathbf{C\underline{H}_2}CH_2CH_2CH=CH_2$), 4.94–5.12 m (4H, $O\mathbf{CH_2}CH_2CH_2CH=C\underline{H}_2$), 5.74–5.90 m (2H, $O\mathbf{CH_2}CH_2CH_2C\underline{H}=CH_2$), 6.52–7.29 m ($12H_{Ar}$), 7.91–8.18 m (2H, CH=N). Found, %: C 64.94; H 6.66; Cl 8.34; N 3.21. $C_{46}H_{56}Cl_2N_2O_6Ti$. Calculated, %: C 64.87; H 6.63; Cl 8.33; N 3.29.

Bis(2-{[4-(allyloxy)phenyl]iminomethyl}-6-*tert*-butyl-4-methoxyphenoxy)titanium(IV) dichloride (VIIId). Yield 94%. IR spectrum, ν, cm^{-1}: 1611 (C=N), 580 (Ti–O), 476 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.31–1.56 m [18H, $C(CH_3)_3$], 3.75–3.82 m (6H, OCH_3), 4.34–4.57 m (4H, $O\mathbf{C\underline{H}_2}CH=CH_2$), 5.25–5.47 m (4H, $OCH_2CH=\mathbf{C\underline{H}_2}$), 5.90–6.12 m (2H, $OCH_2\mathbf{C\underline{H}}=CH_2$), 6.51–7.29 m ($12H_{Ar}$), 7.90–8.09 m (2H, CH=N). Found, %: C 63.33; H 6.25; Cl 8.80; N 3.46. $C_{42}H_{48}Cl_2N_2O_6Ti$. Calculated, %: C 63.40; H 6.14; Cl 8.93; N 3.52.

Bis(2-{[4-(but-3-enyloxy)phenyl]iminomethyl}-6-*tert*-butyl-4-methoxyphenoxy)titanium(IV) dichloride (VIIIe). Yield 96%. IR spectrum, ν, cm^{-1}: 1609 (C=N), 582 (Ti–O), 478 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.35–1.57 m [18H, $C(CH_3)_3$], 2.40–2.58 m (4H, $O\mathbf{CH_2}C\underline{H}_2CH=CH_2$), 3.73–3.85 m (6H, OCH_3), 3.91–3.98 m (4H, $O\mathbf{C\underline{H}_2}CH_2CH=CH_2$), 5.07–5.21 m (4H, $O\mathbf{CH_2}CH_2CH=C\underline{H}_2$), 5.77–5.96 m (2H, $O\mathbf{CH_2}CH_2C\underline{H}=CH_2$), 6.51–7.26 m ($12H_{Ar}$), 7.88–8.13 m (2H, CH=N). Found, %: C 64.43; H 6.50; Cl 8.58; N 3.21. $C_{44}H_{52}Cl_2N_2O_6Ti$. Calculated, %: C 64.16; H 6.36; Cl 8.61; N 3.40.

Bis(2-*tert*-butyl-4-methoxy-6-{[4-(pent-4-enyloxy)phenyl]iminomethyl}phenoxy)titanium(IV) dichloride (VIIIf). Yield 97%. IR spectrum, ν, cm^{-1}: 1609 (C=N), 579 (Ti–O), 476 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.31–1.58 m [18H, $C(CH_3)_3$], 1.74–1.94 m (4H, $O\mathbf{CH_2}C\underline{H}_2CH_2CH=CH_2$), 2.14–2.28 m (4H, $O\mathbf{CH_2}CH_2C\underline{H}_2CH=CH_2$), 3.73–3.78 m (6H, OCH_3), 3.80–4.00 m (4H, $O\mathbf{C\underline{H}_2}CH_2CH_2CH=CH_2$), 4.96–5.09 m (4H, $O\mathbf{CH_2}CH_2CH_2CH=C\underline{H}_2$), 5.76–5.90 m (2H, $O\mathbf{CH_2}CH_2CH_2C\underline{H}=CH_2$), 6.51–7.28 m ($12H_{Ar}$), 7.87–8.00 m (2H, CH=N). Found, %: C 65.12; H 6.56; Cl 8.18; N 3.24. $C_{46}H_{56}Cl_2N_2O_6Ti$. Calculated, %: C 64.87; H 6.63; Cl 8.33; N 3.29.

Bis[2-{[3-(allyloxy)phenyl]iminomethyl}-4-methoxy-6-(2-phenylpropan-2-yl)phenoxy]titanium (IV) dichloride (IXa). Yield 91%. IR spectrum, ν, cm^{-1}: 1597 (C=N), 575 (Ti–O), 471 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.38–2.05 m [12H, $C(CH_3)_2$], 3.64–3.77 m (6H, OCH_3), 4.31–4.42 m (4H, $O\mathbf{C\underline{H}_2}CH=CH_2$), 5.10–5.31 m (4H, $OCH_2CH=\mathbf{C\underline{H}_2}$), 5.72–5.97 m (2H, $OCH_2\mathbf{C\underline{H}}=CH_2$), 6.35–6.86 m ($12H_{Ar}$), 7.10–7.48 m ($10H_{Ar}$), 7.67–7.89 m (2H, CH=N). Found, %: C 67.56; H 5.94; Cl 7.70; N 2.94. $C_{52}H_{52}Cl_2N_2O_6Ti$. Calculated, %: C 67.90; H 5.70; Cl 7.71; N 3.05.

Bis[2-{[3-(but-3-enyloxy)phenyl]iminomethyl}-4-methoxy-6-(2-phenylpropan-2-yl)phenoxy]-titanium(IV) dichloride (IXb). Yield 90%. IR spectrum, ν, cm^{-1}: 1597 (C=N), 575 (Ti–O), 471 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.44–2.11 m [12H, $C(CH_3)_2$], 2.31–2.51 m (4H, $O\mathbf{CH_2}C\underline{H}_2CH=CH_2$), 3.71–3.83 m

(6H, $\mathrm{OCH_3}$), 3.87–3.97 m (4H, $\mathbf{OC\underline{H}_2}\mathrm{CH_2CH{=}CH_2}$), 5.01–5.13 m (4H, $\mathbf{OCH_2}\mathrm{CH_2CH{=}C\underline{H}_2}$), 5.68–5.89 m (2H, $\mathbf{OCH_2}\mathrm{CH_2C\underline{H}{=}CH_2}$), 6.38–7.44 m ($\mathrm{22H_{Ar}}$), 7.73–7.96 m (2H, CH=N). Found, %: C 68.63; H 6.02; Cl 7.35; N 3.05. $\mathrm{C_{54}H_{56}Cl_2N_2O_6Ti}$. Calculated, %: C 68.43; H 5.96; Cl 7.48; N 2.96.

Bis[4-methoxy-2-{[3-(pent-4-enyloxy)phenyl]iminomethyl}-6-(2-phenylpropan-2-yl)phenoxy]titanium(IV) dichloride (IXc). Yield 93%. IR spectrum, ν, cm^{-1}: 1597 (C=N), 575 (Ti–O), 471 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.44–1.56 m [12H, $\mathrm{C(CH_3)_2}$], 1.75–1.94 m (4H, $\mathbf{OCH_2}\mathrm{C\underline{H}_2CH_2CH{=}CH_2}$), 2.14–2.29 m (4H, $\mathbf{OCH_2}\mathrm{CH_2C\underline{H}_2CH{=}CH_2}$), 3.78–3.82 m (6H, $\mathrm{OCH_3}$), 3.86–4.01 m (4H, $\mathbf{OC\underline{H}_2}\mathrm{CH_2CH_2CH{=}CH_2}$), 5.00–5.14 m (4H, $\mathbf{OCH_2}\mathrm{CH_2CH_2CH{=}C\underline{H}_2}$), 5.80–5.95 m (2H, $\mathbf{OCH_2}\mathrm{CH_2CH_2C\underline{H}{=}CH_2}$), 6.47–7.64 m ($\mathrm{22H_{Ar}}$), 7.82–8.06 m (2H, HC=N). Found, %: C 68.96; H 6.32; Cl 7.18; N 2.79. $\mathrm{C_{56}H_{60}Cl_2N_2O_6Ti}$. Calculated, %: C 68.92; H 6.20; Cl 7.27; N 2.87.

Bis[2-{[4-(allyloxy)phenyl]iminomethyl}-4-methoxy-6-(2-phenylpropan-2-yl)phenoxy]titanium (IV) dichloride (IXd). Yield 96%. IR spectrum, ν, cm^{-1}: 1597 (C=N), 581 (Ti–O), 472 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.47–2.16 m [12H, $\mathrm{C(CH_3)_2}$], 3.63–3.87 m (6H, $\mathrm{OCH_3}$), 4.36–4.53 m (4H, $\mathbf{OC\underline{H}_2}\mathrm{CH{=}CH_2}$), 5.21–5.43 m (4H, $\mathrm{OCH_2CH{=}}\mathbf{C\underline{H}_2}$), 5.91–6.18 m (2H, $\mathrm{OCH_2}\mathbf{C\underline{H}}\mathrm{{=}CH_2}$), 6.42–6.89 m ($\mathrm{12H_{Ar}}$), 7.13–7.58 m ($\mathrm{10H_{Ar}}$), 7.71–7.89 m (2H, CH=N). Found, %: C 67.79; H 6.01; Cl 7.57; N 3.13. $\mathrm{C_{52}H_{52}Cl_2N_2O_6Ti}$. Calculated, %: C 67.90; H 5.70; Cl 7.71; N 3.05.

Bis[2-{[4-(but-3-enyloxy)phenyl]iminomethyl}-4-methoxy-6-(2-phenylpropan-2-yl)phenoxy]titanium(IV) dichloride (IXe). Yield 96%. IR spectrum, ν, cm^{-1}: 1610 (C=N), 581 (Ti–O), 470 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.44–2.12 m [12H, $\mathrm{C(CH_3)_2}$], 2.41–2.52 m (4H, $\mathbf{OCH_2}\mathrm{C\underline{H}_2CH{=}CH_2}$), 3.58–3.83 m (6H, $\mathrm{OCH_3}$), 3.86–3.97 m (4H, $\mathbf{OC\underline{H}_2}\mathrm{CH_2CH{=}CH_2}$), 5.01–5.16 m (4H, $\mathbf{OCH_2}\mathrm{CH_2CH{=}C\underline{H}_2}$), 5.75–5.91 m (2H, $\mathbf{OCH_2}\mathrm{CH_2C\underline{H}{=}CH_2}$), 6.37–6.84 m ($\mathrm{12H_{Ar}}$), 7.09–7.55 m ($\mathrm{10H_{Ar}}$), 7.73–7.85 m (2H, CH=N). Found, %: C 68.28; H 6.01; Cl 7.38; N 2.85. $\mathrm{C_{54}H_{56}Cl_2N_2O_6Ti}$. Calculated, %: C 68.43; H 5.96; Cl 7.48; N 2.96.

Bis[4-methoxy-2-{[4-(pent-4-enyloxy)phenyl]iminomethyl}-6-(2-phenylpropan-2-yl)phenoxy]titanium(IV) dichloride (IXf). Yield 95%. IR spectrum, ν, cm^{-1}: 1611 (C=N), 580 (Ti–O), 472 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.46–1.74 m [12H, $\mathrm{C(CH_3)_2}$], 1.78–1.91 m (4H, $\mathbf{OCH_2}\mathrm{C\underline{H}_2CH_2CH{=}CH_2}$), 2.14–2.26 m (4H, $\mathbf{OCH_2}\mathrm{CH_2C\underline{H}_2CH{=}CH_2}$), 3.74–3.83 m (6H, $\mathrm{OCH_3}$), 3.85–3.96 m (4H, $\mathbf{OC\underline{H}_2}\mathrm{CH_2CH_2CH{=}CH_2}$), 4.95–5.08 m (4H, $\mathbf{OCH_2}\mathrm{CH_2CH_2CH{=}C\underline{H}_2}$), 5.76–5.89 m (2H, $\mathbf{OCH_2}\mathrm{CH_2CH_2C\underline{H}{=}CH_2}$); 6.47–6.70, 7.22–7.58 m ($\mathrm{22H_{Ar}}$), 7.79–7.85 m (2H, CH=N). Found, %: C 68.60; H 6.20; Cl 7.10; N 2.40. $\mathrm{C_{56}H_{60}Cl_2N_2O_6Ti}$. Calculated, %: C 68.92; H 6.20; Cl 7.27; N 2.87.

Bis[2-{[3-(allyloxy)phenyl]iminomethyl}-4-methoxy-6-(1-phenylethyl)phenoxy]titanium(IV) dichloride (Xa). Yield 92%. IR spectrum, ν, cm^{-1}: 1597 (C=N), 575 (Ti–O), 476 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.38–1.73 m (6H, $\mathrm{CH_3}$), 3.59–3.89 m (6H, $\mathrm{OCH_3}$), 4.07–4.42 m (4H, $\mathbf{OC\underline{H}_2}\mathrm{CH{=}CH_2}$), 4.47–4.69 m (2H, CH), 5.16–5.44 m (4H, $\mathrm{OCH_2CH{=}}\mathbf{C\underline{H}_2}$), 5.80–6.10 m (2H, $\mathrm{OCH_2}\mathbf{C\underline{H}}\mathrm{{=}CH_2}$), 6.44–7.55 m ($\mathrm{22H_{Ar}}$), 7.80–8.07 m (2H, CH=N). Found, %: C 67.18; H 5.61; Cl 7.94; N 3.08. $\mathrm{C_{50}H_{48}Cl_2N_2O_6Ti}$. Calculated, %: C 67.35; H 5.43; Cl 7.95; N 3.14.

Bis[2-{[3-(but-3-enyloxy)phenyl]iminomethyl}-4-methoxy-6-(1-phenylethyl)phenoxy]titanium(IV) dichloride (Xb). Yield 92%. IR spectrum, ν, cm^{-1}: 1597 (C=N), 575 (Ti–O), 476 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.37–1.74 m (6H, $\mathrm{CH_3}$), 2.30–2.58 m (4H, $\mathbf{OCH_2}\mathrm{C\underline{H}_2CH{=}CH_2}$), 3.60–3.76 m (6H, $\mathrm{OCH_3}$), 3.84–4.15 m (4H, $\mathbf{OC\underline{H}_2}\mathrm{CH_2CH{=}CH_2}$), 4.30–4.70 m (2H, CH), 5.02–5.20 m (4H, $\mathbf{OCH_2}\mathrm{CH_2CH{=}C\underline{H}_2}$), 5.66–5.96 m (2H, $\mathbf{OCH_2}\mathrm{CH_2C\underline{H}{=}CH_2}$), 6.40–7.66 m ($\mathrm{22H_{Ar}}$), 7.89–8.08 m (2H, CH=N). Found, %: C 67.96; H 5.70; Cl 7.68; N 2.92. $\mathrm{C_{52}H_{52}Cl_2N_2O_6Ti}$. Calculated, %: C 67.90; H 5.70; Cl 7.71; N 3.05.

Bis[4-methoxy-2-{[3-(pent-4-enyloxy)phenyl]iminomethyl}-6-(1-phenylethyl)phenoxy]titanium (IV) dichloride (Xc). Yield 92%. IR spectrum, ν, cm^{-1}: 1597 (C=N), 575 (Ti–O), 476 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.37–1.57 m (6H, $\mathrm{CH_3}$), 1.73–1.92 m (4H, $\mathbf{OCH_2}\mathrm{C\underline{H}_2CH_2CH{=}CH_2}$), 2.02–2.27 m (4H, $\mathbf{OCH_2}\mathrm{CH_2C\underline{H}_2CH{=}CH_2}$), 3.58–3.74 m (6H, $\mathrm{OCH_3}$), 3.80–3.98 m (4H, $\mathbf{OC\underline{H}_2}\mathrm{CH_2CH_2CH{=}CH_2}$), 4.35–4.69 m (2H, CH), 4.85–5.09 m (4H, $\mathbf{OCH_2}\mathrm{CH_2CH_2CH{=}C\underline{H}_2}$), 5.71–5.90 m (2H, $\mathbf{OCH_2}\mathrm{CH_2CH_2C\underline{H}{=}CH_2}$), 6.45–7.60 m ($\mathrm{22H_{Ar}}$), 7.81–8.08 m (2H, CH=N). Found, %: C 68.32; H 6.05; Cl 7.14; N 2.86. $\mathrm{C_{54}H_{56}Cl_2N_2O_6Ti}$. Calculated, %: C 68.43; H 5.96; Cl 7.48; N 2.96.

Bis[2-{[4-(allyloxy)phenyl]iminomethyl}-4-methoxy-6-(1-phenylethyl)phenoxy]titanium(IV) dichloride (Xd). Yield 94%. IR spectrum, ν, cm^{-1}: 1595 (C=N), 575 (Ti–O), 476 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.43–1.72 m (6H, CH_3), 3.60–3.88 m (6H, OCH_3), 4.07–4.45 m (4H, $OC\underline{\mathbf{H}}_2CH=CH_2$), 4.50–4.67 m (2H, CH), 5.20–5.43 m (4H, $OCH_2CH=\mathbf{C}\underline{\mathbf{H}}_2$), 5.86–6.09 m (2H, $OCH_2C\underline{\mathbf{H}}=CH_2$), 6.34–7.60 m ($22H_{Ar}$), 7.88–7.98 m (2H, CH=N). Found, %: C 67.56; H 5.94; Cl 7.70; N 2.94. $C_{50}H_{48}Cl_2N_2O_6Ti$. Calculated, %: C 67.35; H 5.43; Cl 7.95; N 3.14.

Bis[2-{[4-(but-3-enyloxy)phenyl]iminomethyl}-4-methoxy-6-(1-phenylethyl)phenoxy]titanium(IV) dichloride (Xe). Yield 95%. IR spectrum, ν, cm^{-1}: 1609 (C=N), 578 (Ti–O), 459 (Ti–N). ^1H NMR spectrum, δ, ppm: 1.42–1.70 m (6H, CH_3), 2.40–2.56 m (4H, $O\mathbf{CH_2}C\underline{H}_2CH=CH_2$), 3.60–3.76 m (6H, OCH_3), 3.89–3.99 m (4H, $OC\underline{\mathbf{H}}_2CH_2CH=CH_2$), 4.42–4.81 m (2H, CH), 5.07–5.20 m (4H, $O\mathbf{CH_2}CH_2CH=C\underline{H}_2$), 5.76–5.94 m (2H, $O\mathbf{CH_2}CH_2C\underline{H}=CH_2$), 6.39–7.66 m ($22H_{Ar}$), 7.87–7.98 m (2H, CH=N). Found, %: C 67.73; H 5.63; Cl 7.85; N 2.94. $C_{52}H_{52}Cl_2N_2O_6Ti$. Calculated, %: C 67.90; H 5.70; Cl 7.71; N 3.05.

Bis[4-methoxy-2-{[4-(pent-4-enyloxy)phenyl]iminomethyl}-6-(1-phenylethyl)phenoxy]titanium(IV) dichloride (Xf). Yield 91%. IR spectrum, ν, cm^{-1}: 1595 (C=N), 577 (Ti–O), 476 (Ti–N). ^1H NMR spectrum, δ, ppm: 1.38–1.70 m (6H, $CHC\underline{H}_3$), 1.75–1.90 m (4H, $O\mathbf{CH_2}C\underline{H}_2CH_2CH=CH_2$), 2.12–2.25 m (4H, $O\mathbf{CH_2}\cdot CH_2C\underline{H}_2CH=CH_2$), 3.60–3.70 m (6H, OCH_3), 3.75–3.92 m (4H, $OC\underline{\mathbf{H}}_2CH_2CH_2CH=CH_2$), 4.41–4.68 m (2H, $C\underline{H}CH_3$), 4.86–5.10 m (4H, $O\mathbf{CH_2}CH_2CH_2\cdot CH=C\underline{H}_2$), 5.75–5.91 m (2H, $O\mathbf{CH_2}CH_2CH_2C\underline{H}=CH_2$), 6.39–7.61 m ($22H_{Ar}$), 7.88–7.98 m (2H, CH=N). Found, %: 68.55; H 5.91; Cl 7.04; N 2.84. $C_{54}H_{56}Cl_2N_2O_6Ti$. Calculated, %: C 68.43; H 5.96; Cl 7.48; N 2.96.

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