

# Design of Schiff Base-Like Postmetallocene Catalytic Systems for Polymerization of Olefins: V.\* Synthesis of Salicylaldehyde Imine Ligands Containing Cycloalkyl Substituents

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**Abstract**—Reactions of substituted cycloalkylanilines with salicylaldehyde, 3-*tert*-butylsalicylaldehyde, and 3,5-di-*tert*-butylsalicylaldehyde in methanol in the presence of formic acid gave a series of the corresponding Schiff bases as ligands for titanium(IV) complexes.

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Matsui et al. [2] showed that titanium and zirconium chelates derived from phenoxy imine ligands are highly efficient as catalysts for olefin polymerization. The catalytic properties of such complexes may be controlled by variation of substituents in the ligand; as a result, a broad spectrum of polyolefins with various parameters can be obtained [3–5].

From the practical viewpoint, an important parameter of a catalytic system used in polymerization processes is retention of its high activity at elevated temperature. We showed in [6] that the temperature range ensuring effective function of catalysts based on 2,6-bis(aryliminoalkyl)pyridine iron complexes and 1,2-bis(arylimino)acenaphthene nickel bromide complexes can be extended considerably via introduction of a cycloalkyl substituent into the *ortho* position of the aryl ring [6]. In order to verify the general character of the cycloalkyl substitution effect it was necessary to elucidate whether phenoxy imino chelates modified by such substituents are active at elevated temperature. For this purpose, in the present work we synthesized the corresponding ligands having cyclopentyl, cyclohexyl, and cyclooctyl groups.

The ligands were obtained by reaction of substituted salicylaldehydes with primary amines, such as aniline and its alkyl and fluoro derivatives [4, 5]. By

heating salicylaldehyde (**I**), 3-*tert*-butylsalicylaldehyde (**II**), and 3,5-di-*tert*-butylsalicylaldehyde (**III**) with *o*-cycloalkylanilines **IVa–IVd**, **Va–Vd**, and **VIa–VIc** in boiling methanol containing a catalytic amount of formic acid we obtained the corresponding Schiff bases **VII–XV** in high yields (91–99%) (Scheme 1).

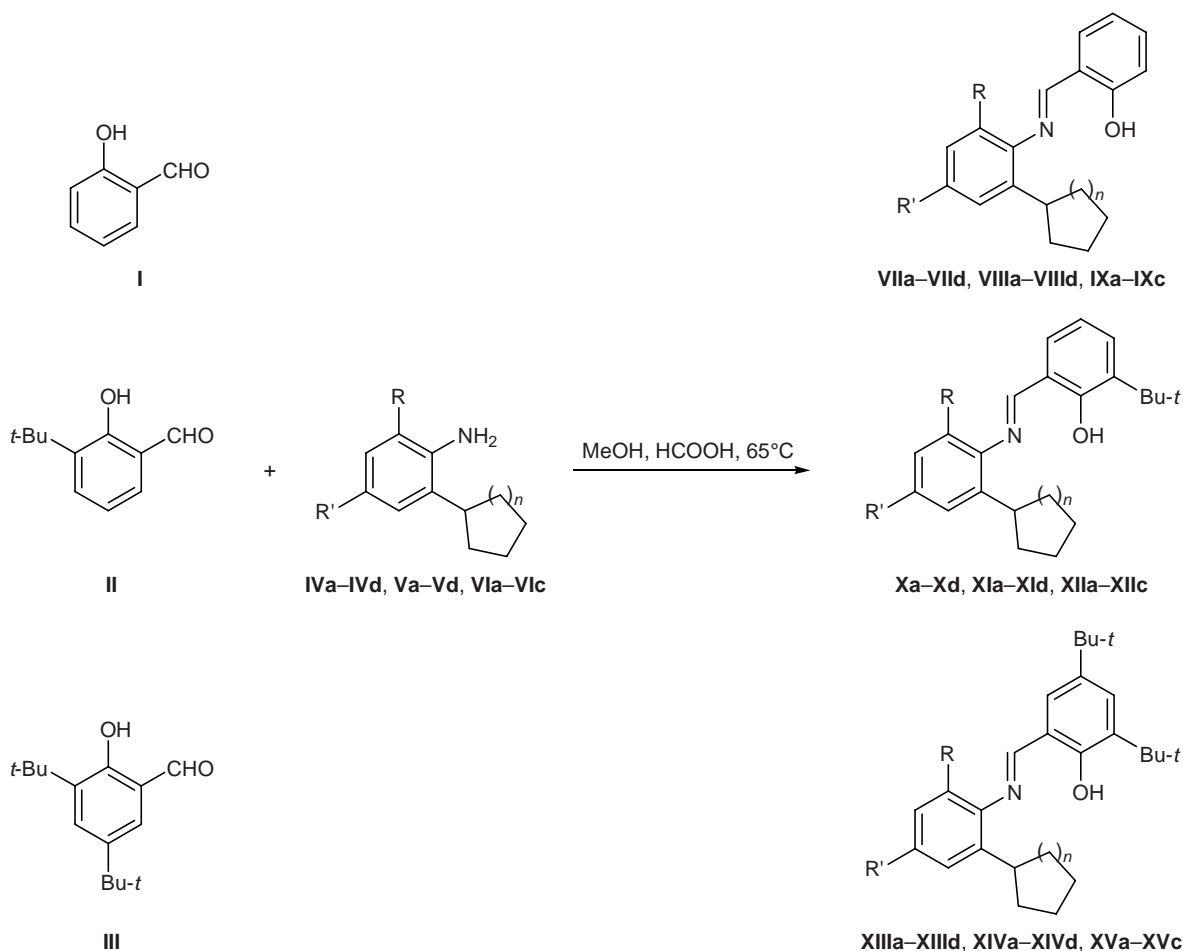
The structure of Schiff bases **VII–XV** was determined on the basis of their analytical and spectral data. According to the <sup>1</sup>H NMR spectra, the isolated compounds are individual *E* isomers. They showed multiplet signals from the cycloalkyl methylene protons at δ 1.15–2.15, a signal at δ 2.53–3.44 ppm from the CH proton in the cycloalkyl ring, a singlet at δ 8.18–8.56 ppm from the azomethine CH=N proton, and a singlet at δ 12.57–13.93 ppm from the hydroxy proton. The observed strongly downfield position of the OH signals is typical of compounds with intramolecular hydrogen bond. The IR spectra of **VII–XV** contained a strong absorption band in the region 1613–1624 cm<sup>-1</sup> due to stretching vibrations of the C=N bond. Compounds **VII–XV** gave intense molecular ion peaks in the mass spectra.

## EXPERIMENTAL

The <sup>1</sup>H NMR spectra were measured on a Bruker WP-200 SY spectrometer at 200 MHz from solutions in carbon tetrachloride using HMDS as internal refer-

\* For communication IV, see [1].

Scheme 1.



R = R' = H (a), Me (c); R = Me, R' = H (b); R = *cyclo*-C<sub>4</sub>H<sub>7</sub>(CH<sub>2</sub>)<sub>n</sub>, R' = H (d); **IV, VII, X, XIII**, *n* = 1; **V, VIII, XI, XIV**, *n* = 2; **VI, IX, XII, XV**, *n* = 4.

ence. The IR spectra were recorded on a Vector 22 spectrometer from samples prepared as KBr pellets or neat substances. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using chloroform as eluent. Flash chromatography [7] was performed on silica gel (5–40 μm; chloroform–hexane, 2:1). The elemental compositions were determined from the high-resolution mass spectra recorded on a Finnigan MAT-8200 spectrometer. The melting points were determined by heating samples placed between glass plates at a rate of 1 deg/min.

3,5-Di-*tert*-butylsalicylaldehyde and cycloalkylanilines **IV–VI** were synthesized according to the procedures reported in [8, 9]. 3-*tert*-Butylsalicylaldehyde was obtained by an improved procedure [10]; its spectral parameters were consistent with those reported in [4, 11].

**Schiff Bases VII–XV (general procedure).** A mixture of 1 mmol of salicylaldehyde **I–III**, 1 mmol of

cycloalkylaniline **IVa–IVd, Va–Vd, or VIa–VIc**, 10 ml of methanol, and 5 mg of anhydrous formic acid was heated under reflux for 6–12 h until the initial compounds disappeared according to the TLC data. The solvent was distilled off on a rotary evaporator under reduced pressure (water-jet pump) at a bath temperature of 45°C, and the residue was subjected to flash chromatography to isolate the first bright yellow fraction. The solvent was distilled off, and the solid residue was recrystallized from ethanol.

**2-[(2-Cyclopentylphenylimino)methyl]phenol (VIIa).** Yield 96%, oily substance. IR spectrum:  $\nu$  1618 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.41–2.10 m (8H, CH<sub>2</sub>), 3.41 m (1H, CH), 6.80–7.35 m (8H, H<sub>arom</sub>), 8.48 s (1H, CH=N), 13.04 s (1H, OH). Found: [M]<sup>+</sup> 265.1468. C<sub>18</sub>H<sub>19</sub>NO. Calculated: *M* 265.1467.

**2-[(2-Cyclopentyl-2-methylphenylimino)methyl]phenol (VIIb).** Yield 91%, oily substance. IR spectrum:  $\nu$  1624 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ ,

ppm: 1.45–2.05 m (8H, CH<sub>2</sub>), 2.15 s (3H, CH<sub>3</sub>), 3.00 m (1H, CH), 6.81–7.39 m (7H, H<sub>arom</sub>), 8.25 s (1H, CH=N), 12.80 s (1H, OH). Found:  $[M]^+$  279.1623. C<sub>19</sub>H<sub>21</sub>NO. Calculated: *M* 279.1623.

**2-[(2,4-Dimethyl-6-cyclopentylphenylimino)methyl]phenol (VIIC).** Yield 92%, mp 105–106°C. IR spectrum:  $\nu$  1623 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.45–1.98 m (8H, CH<sub>2</sub>), 2.12 s (3H, CH<sub>3</sub>), 2.28 s (3H, CH<sub>3</sub>), 2.98 m (1H, CH), 6.79–7.38 m (6H, H<sub>arom</sub>), 8.24 s (1H, CH=N), 12.90 s (1H, OH). Found:  $[M]^+$  293.1773. C<sub>20</sub>H<sub>23</sub>NO. Calculated: *M* 293.1779.

**2-[(2,6-Dicyclopentylphenylimino)methyl]phenol (VIId).** Yield 91%, mp 78–79°C. IR spectrum:  $\nu$  1624 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.54–1.96 m (16H, CH<sub>2</sub>), 2.97 m (2H, CH), 6.78–7.37 m (7H, H<sub>arom</sub>), 8.22 s (1H, CH=N), 12.60 s (1H, OH). Found:  $[M]^+$  333.2084. C<sub>23</sub>H<sub>27</sub>NO. Calculated: *M* 333.2093.

**2-[(2-Cyclohexylphenylimino)methyl]phenol (VIIIA).** Yield 91%, oily substance. IR spectrum:  $\nu$  1617 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.20–1.95 m (10H, CH<sub>2</sub>), 2.99 m (1H, CH), 6.80–7.35 m (8H, H<sub>arom</sub>), 8.50 s (1H, CH=N), 13.01 s (1H, OH). Found:  $[M]^+$  279.1620. C<sub>19</sub>H<sub>21</sub>NO. Calculated: *M* 279.1623.

**2-[(2-Cyclohexyl-6-methylphenylimino)methyl]phenol (VIIIB).** Yield 92%, oily substance. IR spectrum:  $\nu$  1624 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.20–1.85 m (10H, CH<sub>2</sub>), 2.16 s (3H, CH<sub>3</sub>), 2.58 m (1H, CH), 6.82–7.39 m (7H, H<sub>arom</sub>), 8.26 s (1H, CH=N), 12.75 s (1H, OH). Found:  $[M]^+$  293.1778. C<sub>20</sub>H<sub>23</sub>NO. Calculated: *M* 293.1779.

**2-[(2-Cyclohexyl-4,6-dimethylphenylimino)methyl]phenol (VIIIC).** Yield 91%, mp 71–72°C. IR spectrum:  $\nu$  1621 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.20–1.85 m (10H, CH<sub>2</sub>), 2.13 s (3H, CH<sub>3</sub>), 2.27 s (3H, CH<sub>3</sub>), 2.55 m (1H, CH), 6.75–7.37 m (6H, H<sub>arom</sub>), 8.22 s (1H, CH=N), 12.68 s (1H, OH). Found:  $[M]^+$  307.1911. C<sub>21</sub>H<sub>25</sub>NO. Calculated: *M* 307.1936.

**2-[(2,6-Dicyclohexylphenylimino)methyl]phenol (VIID).** Yield 90%, mp 119–120°C. IR spectrum:  $\nu$  1621 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.15–1.85 m (20H, CH<sub>2</sub>), 2.53 m (2H, CH), 6.83–7.42 m (7H, H<sub>arom</sub>), 8.21 s (1H, CH=N), 12.57 s (1H, OH). Found:  $[M]^+$  361.2402. C<sub>25</sub>H<sub>31</sub>NO. Calculated: *M* 361.2406.

**2-[(2-Cyclooctylphenylimino)methyl]phenol (IXA).** Yield 94%, oily substance. IR spectrum:  $\nu$  1617 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.45–

1.90 m (14H, CH<sub>2</sub>), 3.30 m (1H, CH), 6.82–7.36 m (8H, H<sub>arom</sub>), 8.50 s (1H, CH=N), 12.97 s (1H, OH). Found:  $[M]^+$  307.1935. C<sub>21</sub>H<sub>25</sub>NO. Calculated: *M* 307.1936.

**2-[(2-Cyclooctyl-6-methylphenylimino)methyl]phenol (IXB).** Yield 95%, oily substance. IR spectrum:  $\nu$  1624 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.42–1.80 m (14H, CH<sub>2</sub>), 2.14 s (3H, CH<sub>3</sub>), 2.95 m (1H, CH), 6.82–7.39 m (7H, H<sub>arom</sub>), 8.27 s (1H, CH=N), 12.76 s (1H, OH). Found:  $[M]^+$  321.2093. C<sub>22</sub>H<sub>27</sub>NO. Calculated: *M* 321.2093.

**2-[(2-Cyclooctyl-4,6-dimethylphenylimino)methyl]phenol (IXC).** Yield 93%, oily substance. IR spectrum:  $\nu$  1622 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.35–1.85 m (14H, CH<sub>2</sub>), 2.16 s (3H, CH<sub>3</sub>), 2.30 s (3H, CH<sub>3</sub>), 2.94 m (1H, CH), 6.82–7.41 m (6H, H<sub>arom</sub>), 8.28 s (1H, CH=N), 12.86 s (1H, OH). Found:  $[M]^+$  335.2257. C<sub>23</sub>H<sub>29</sub>NO. Calculated: *M* 335.2249.

**2-tert-Butyl-6-[(2-cyclopentylphenylimino)methyl]phenol (XA).** Yield 92%, oily substance. IR spectrum:  $\nu$  1613 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.44 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.53–1.88 m (6H, CH<sub>2</sub>), 1.96–2.15 m (2H, CH<sub>2</sub>), 3.44 m (1H, CH), 6.75 t (1H, H<sub>arom</sub>, *J* = 7.6 Hz), 6.89–6.99 m (1H, H<sub>arom</sub>), 7.01–7.18 m (3H, H<sub>arom</sub>), 7.19–7.32 m (2H, H<sub>arom</sub>), 8.46 s (1H, CH=N), 13.70 s (1H, OH). Found:  $[M]^+$  321.2101. C<sub>22</sub>H<sub>27</sub>NO. Calculated: *M* 321.2093.

**2-tert-Butyl-6-[(2-cyclopentyl-2-methylphenylimino)methyl]phenol (XB).** Yield 96%, oily substance. IR spectrum:  $\nu$  1619 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.46 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.55–1.84 m (6H, CH<sub>2</sub>), 1.85–2.05 m (2H, CH<sub>2</sub>), 2.41 s (3H, CH<sub>3</sub>), 3.04 m (1H, CH), 6.77 t (1H, H<sub>arom</sub>, *J* = 7.6 Hz), 6.92–7.05 m (2H, H<sub>arom</sub>), 7.07 d.d (2H, H<sub>arom</sub>, *J* = 7.4, 1.4 Hz), 7.31 d.d (1H, H<sub>arom</sub>, *J* = 7.7, 1.6 Hz), 8.27 s (1H, CH=N), 13.44 s (1H, OH). Found:  $[M]^+$  335.2244. C<sub>23</sub>H<sub>29</sub>NO. Calculated: *M* 335.2249.

**2-tert-Butyl-6-[(2-cyclopentyl-4,6-dimethylphenylimino)methyl]phenol (XC).** Yield 98%, mp 111.5–113.5°C. IR spectrum:  $\nu$  1620 cm<sup>-1</sup> (N=CH). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.45 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.51–1.68 m (4H, CH<sub>2</sub>), 1.71–1.79 m (2H, CH<sub>2</sub>), 1.85–1.98 m (2H, CH<sub>2</sub>), 2.15 s (3H, CH<sub>3</sub>), 2.28 s (3H, CH<sub>3</sub>), 3.00 m (1H, CH), 6.76 t (1H, H<sub>arom</sub>, *J* = 7.6 Hz), 6.77 s (1H, H<sub>arom</sub>), 6.86 s (1H, H<sub>arom</sub>), 7.05 d.d (1H, H<sub>arom</sub>, *J* = 7.6, 1.6 Hz), 7.30 d.d (1H, H<sub>arom</sub>, *J* = 7.6, 1.6 Hz), 8.24 s (1H, CH=N), 13.53 s (1H, OH). Found:  $[M]^+$  349.2407. C<sub>24</sub>H<sub>31</sub>NO. Calculated: *M* 349.2406.

**2-tert-Butyl-6-[(2,6-dicyclopentylphenylimino)methyl]phenol (XD).** Yield 98%, oily substance. IR

spectrum:  $\nu$  1619  $\text{cm}^{-1}$  (N=CH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.47 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.51–1.84 m (12H, CH<sub>2</sub>), 1.85–2.05 m (4H, CH<sub>2</sub>), 3.00 m (2H, CH), 6.78 t (1H, H<sub>arom</sub>,  $J$  = 7.6 Hz), 6.99–7.11 m (4H, H<sub>arom</sub>), 7.32 d.d (1H, H<sub>arom</sub>,  $J$  = 7.8, 1.6 Hz), 8.23 s (1H, CH=N), 13.45 s (1H, OH). Found:  $[M]^+$  389.2717. C<sub>27</sub>H<sub>35</sub>NO. Calculated:  $M$  389.2719.

**2-tert-Butyl-6-[(2-cyclohexylphenylimino)methyl]phenol (XIa).** Yield 93%, oily substance. IR spectrum:  $\nu$  1613  $\text{cm}^{-1}$  (N=CH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.33–1.51 m (4H, CH<sub>2</sub>), 1.45 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.74–1.93 m (6H, CH<sub>2</sub>), 3.01 m (1H, CH), 6.77 t (1H, H<sub>arom</sub>,  $J$  = 7.6 Hz), 6.99–7.03 m (1H, H<sub>arom</sub>), 7.11–7.18 m (3H, H<sub>arom</sub>), 7.19–7.24 m (1H, H<sub>arom</sub>), 7.29 d (1H, H<sub>arom</sub>,  $J$  = 7.6 Hz), 8.53 s (1H, CH=N), 12.83 s (1H, OH). Found:  $[M]^+$  335.2241. C<sub>23</sub>H<sub>29</sub>NO. Calculated:  $M$  335.2249.

**2-tert-Butyl-6-[(2-cyclohexyl-6-methylphenylimino)methyl]phenol (XIb).** Yield 97%. IR spectrum:  $\nu$  1619  $\text{cm}^{-1}$  (N=CH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.21–1.41 m (4H, CH<sub>2</sub>), 1.46 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.63–1.90 m (6H, CH<sub>2</sub>), 2.20 s (3H, CH<sub>3</sub>), 2.58 m (1H, CH), 6.81 t (1H, H<sub>arom</sub>,  $J$  = 7.6 Hz), 6.89–7.09 m (4H, H<sub>arom</sub>), 7.32 d.d (1H, H<sub>arom</sub>,  $J$  = 7.6, 1.8 Hz), 8.26 s (1H, CH=N), 13.37 s (1H, OH). Found:  $[M]^+$  349.2410. C<sub>24</sub>H<sub>31</sub>NO. Calculated:  $M$  349.2406.

**2-tert-Butyl-6-[(2-cyclohexyl-4,6-dimethylphenylimino)methyl]phenol (XIc).** Yield 99%, oily substance. IR spectrum:  $\nu$  1619  $\text{cm}^{-1}$  (N=CH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.19–1.41 m (6H, CH<sub>2</sub>), 1.46 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.62–1.88 m (4H, CH<sub>2</sub>), 2.17 s (3H, CH<sub>3</sub>), 2.27 s (3H, CH<sub>3</sub>), 2.57 m (1H, CH), 6.76 t (1H, H<sub>arom</sub>,  $J$  = 7.6 Hz), 6.78 s (1H, H<sub>arom</sub>), 6.82 s (1H, H<sub>arom</sub>), 7.06 d.d (1H, H<sub>arom</sub>,  $J$  = 7.6, 1.6 Hz), 7.31 d.d (1H, H<sub>arom</sub>,  $J$  = 7.6, 1.6 Hz), 8.24 s (1H, CH=N), 13.55 s (1H, OH). Found:  $[M]^+$  363.2558. C<sub>25</sub>H<sub>33</sub>NO. Calculated:  $M$  363.2562.

**2-tert-Butyl-6-[(2,6-dicyclohexylphenylimino)methyl]phenol (XIId).** Yield 96%, oily substance. IR spectrum:  $\nu$  1618  $\text{cm}^{-1}$  (N=CH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.23–1.48 m (8H, CH<sub>2</sub>), 1.48 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.55–1.90 m (12H, CH<sub>2</sub>), 2.55 m (2H, CH), 6.78 t (1H, H<sub>arom</sub>,  $J$  = 7.6 Hz), 6.88–7.11 m (4H, H<sub>arom</sub>), 7.33 d.d (1H, H<sub>arom</sub>,  $J$  = 7.6, 1.6 Hz), 8.20 s (1H, CH=N), 13.50 s (1H, OH). Found:  $[M]^+$  417.3017. C<sub>29</sub>H<sub>39</sub>NO. Calculated:  $M$  417.3031.

**2-tert-Butyl-6-[(2-cyclooctylphenylimino)methyl]phenol (XIIa).** Yield 98%, oily substance. IR spectrum:  $\nu$  1614  $\text{cm}^{-1}$  (N=CH).  $^1\text{H}$  NMR spectrum,  $\delta$ ,

ppm: 1.44 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.50–1.95 m (14H, CH<sub>2</sub>), 3.35 m (1H, CH), 6.75 t (1H, H<sub>arom</sub>,  $J$  = 7.8 Hz), 6.93–7.20 m (5H, H<sub>arom</sub>), 7.31 d.d (1H, H<sub>arom</sub>,  $J$  = 7.8, 1.6 Hz), 8.52 s (1H, CH=N), 13.93 s (1H, OH). Found:  $[M]^+$  363.2559. C<sub>25</sub>H<sub>33</sub>NO. Calculated:  $M$  363.2562.

**2-tert-Butyl-6-[(2-cyclooctyl-6-methylphenylimino)methyl]phenol (XIIb).** Yield 92%, oily substance. IR spectrum:  $\nu$  1620  $\text{cm}^{-1}$  (N=CH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.46 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.48–1.80 m (14H, CH<sub>2</sub>), 2.20 s (3H, CH<sub>3</sub>), 3.00 m (1H, CH), 6.79 t (1H, H<sub>arom</sub>,  $J$  = 7.6 Hz), 6.93–7.16 m (3H, H<sub>arom</sub>), 7.19 d.d (1H, H<sub>arom</sub>,  $J$  = 7.6, 1.6 Hz), 7.34 d.d (1H, H<sub>arom</sub>,  $J$  = 7.6, 1.6 Hz), 8.28 s (1H, CH=N), 13.60 s (1H, OH). Found:  $[M]^+$  377.2716. C<sub>26</sub>H<sub>35</sub>NO. Calculated:  $M$  377.2719.

**2-tert-Butyl-6-[(6-cyclooctyl-4,6-dimethylphenylimino)methyl]phenol (XIIc).** Yield 98%, oily substance. IR spectrum:  $\nu$  1617  $\text{cm}^{-1}$  (N=CH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.51 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.53–1.82 m (14H, CH<sub>2</sub>), 2.22 s (3H, CH<sub>3</sub>), 2.33 s (3H, CH<sub>3</sub>), 3.02 m (1H, CH), 6.82 t (1H, H<sub>arom</sub>,  $J$  = 7.6 Hz), 6.84 s (1H, H<sub>arom</sub>), 6.87 s (1H, H<sub>arom</sub>), 7.13 d.d (1H, H<sub>arom</sub>,  $J$  = 7.6, 1.6 Hz), 7.38 d.d (1H, H<sub>arom</sub>,  $J$  = 7.6, 1.6 Hz), 8.31 s (1H, CH=N), 13.70 s (1H, OH). Found:  $[M]^+$  391.2872. C<sub>27</sub>H<sub>37</sub>NO. Calculated:  $M$  391.2875.

**4,6-Di-tert-butyl-2-[(2-cyclopentylphenylimino)methyl]phenol (XIIIa).** Yield 92%, mp 95–96°C. IR spectrum:  $\nu$  1617  $\text{cm}^{-1}$  (N=CH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.30 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.44 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.55–2.12 m (8H, CH<sub>2</sub>), 3.43 m (1H, CH), 6.91–7.27 m (5H, H<sub>arom</sub>), 7.34 d (1H, 3-H,  $J$  = 2.5 Hz), 8.48 s (1H, CH=N), 13.42 s (1H, OH). Found:  $[M]^+$  377.2712. C<sub>26</sub>H<sub>35</sub>NO. Calculated:  $M$  377.2718.

**4,6-Di-tert-butyl-2-[(6-cyclopentyl-6-methylphenylimino)methyl]phenol (XIIIb).** Yield 96%, mp 107–108°C. IR spectrum:  $\nu$  1622  $\text{cm}^{-1}$  (N=CH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.35 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.46 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.50–2.05 m (8H, CH<sub>2</sub>), 2.18 s (3H, CH<sub>3</sub>), 3.00 m (1H, CH), 6.92–7.15 m (4H, H<sub>arom</sub>), 7.36 d (1H, 3-H,  $J$  = 2.5 Hz), 8.26 s (1H, CH=N), 13.23 s (1H, OH). Found:  $[M]^+$  391.2880. C<sub>27</sub>H<sub>37</sub>NO. Calculated:  $M$  391.2875.

**4,6-Di-tert-butyl-2-[(2-cyclopentyl-4,6-dimethylphenylimino)methyl]phenol (XIIIc).** Yield 94%, mp 124–125°C. IR spectrum:  $\nu$  1620  $\text{cm}^{-1}$  (N=CH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.30 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.45 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.53–2.01 m (8H, CH<sub>2</sub>), 2.15 s (3H, CH<sub>3</sub>), 2.28 s (3H, CH<sub>3</sub>), 3.01 m (1H, CH), 6.77 s (1H, H<sub>arom</sub>), 6.85 s (1H, H<sub>arom</sub>), 7.00 d (1H, 5-H,  $J$  =



2.5 Hz), 7.34 d (1H, 3-H,  $J = 2.5$  Hz), 8.23 s (1H, CH=N), 13.32 s (1H, OH). Found:  $[M]^+$  405.3033.  $C_{28}H_{39}NO$ . Calculated:  $M$  405.3032.

**4,6-Di-*tert*-butyl-2-[(2,6-dicyclopentylphenylimino)methyl]phenol (XIII d)**. Yield 94%, mp 147–148°C. IR spectrum:  $\nu$  1622  $cm^{-1}$  (N=CH).  $^1H$  NMR spectrum,  $\delta$ , ppm: 1.31 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.47 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.50–2.05 m (16H, CH<sub>2</sub>), 3.00 m (2H, CH), 6.92–7.11 m (4H, H<sub>arom</sub>), 7.38 d (1H, 3-H,  $J = 2.5$  Hz), 8.21 s (1H, CH=N), 13.29 s (1H, OH). Found:  $[M]^+$  445.3348.  $C_{31}H_{43}NO$ . Calculated:  $M$  445.3345.

**4,6-Di-*tert*-butyl-2-[(2-cyclohexylphenylimino)methyl]phenol (XIV a)**. Yield 92%, mp 83–84°C. IR spectrum:  $\nu$  1616  $cm^{-1}$  (N=CH).  $^1H$  NMR spectrum,  $\delta$ , ppm: 1.30 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.46 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.58–1.95 m (10H, CH<sub>2</sub>), 3.01 m (1H, CH), 6.98–7.20 m (5H, H<sub>arom</sub>), 7.33 d (1H, 3-H,  $J = 2.5$  Hz), 8.53 s (1H, CH=N), 13.59 s (1H, OH). Found:  $[M]^+$  391.2880.  $C_{27}H_{37}NO$ . Calculated:  $M$  391.2875.

**4,6-Di-*tert*-butyl-2-[(2-cyclohexyl-6-methylphenylimino)methyl]phenol (XIV b)**. Yield 92%, mp 95–96°C. IR spectrum:  $\nu$  1624  $cm^{-1}$  (N=CH).  $^1H$  NMR spectrum,  $\delta$ , ppm: 1.31 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.45 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.55–1.95 m (10H, CH<sub>2</sub>), 2.20 s (3H, CH<sub>3</sub>), 2.61 m (1H, CH), 6.91–7.11 m (4H, H<sub>arom</sub>), 7.38 d (1H, 3-H,  $J = 2.5$  Hz), 8.26 s (1H, CH=N), 13.25 s (1H, OH). Found:  $[M]^+$  405.3036.  $C_{28}H_{39}NO$ . Calculated:  $M$  405.3032.

**4,6-Di-*tert*-butyl-2-[(2-cyclohexyl-4,6-dimethylphenylimino)methyl]phenol (XIV c)**. Yield 99%, mp 137–138°C. IR spectrum:  $\nu$  1620  $cm^{-1}$  (N=CH).  $^1H$  NMR spectrum,  $\delta$ , ppm: 1.31 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.40 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.48–1.87 m (10H, CH<sub>2</sub>), 2.17 s (3H, CH<sub>3</sub>), 2.27 s (3H, CH<sub>3</sub>), 2.58 m (1H, CH), 6.78 s (1H, H<sub>arom</sub>), 6.81 s (1H, H<sub>arom</sub>), 7.00 d (1H, 5-H,  $J = 2.5$  Hz), 7.35 d (1H, 3-H,  $J = 2.5$  Hz), 8.23 s (1H, CH=N), 13.38 s (1H, OH). Found:  $[M]^+$  419.3187.  $C_{29}H_{41}NO$ . Calculated:  $M$  419.3188.

**4,6-Di-*tert*-butyl-2-[(2,6-dicyclohexylphenylimino)methyl]phenol (XIV d)**. Yield 91%, mp 185–186°C. IR spectrum:  $\nu$  1617  $cm^{-1}$  (N=CH).  $^1H$  NMR spectrum,  $\delta$ , ppm: 1.33 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.48 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.55–1.95 m (20H, CH<sub>2</sub>), 2.55 m (2H, CH), 6.97–7.04 m (4H, H<sub>arom</sub>), 7.39 d (1H, 3-H,  $J = 2.5$  Hz), 8.18 s (1H, CH=N), 13.27 s (1H, OH). Found:  $[M]^+$  473.3649.  $C_{33}H_{47}NO$ . Calculated:  $M$  473.3657.

**4,6-Di-*tert*-butyl-2-[(2-cyclooctylphenylimino)methyl]phenol (XV a)**. Yield 98%, mp 74–75°C. IR spectrum:  $\nu$  1617  $cm^{-1}$  (N=CH).  $^1H$  NMR spectrum,  $\delta$ ,

ppm: 1.35 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.47 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.55–1.98 m (14H, CH<sub>2</sub>), 3.42 m (1H, CH), 6.99–7.22 m (5H, H<sub>arom</sub>), 7.39 d (1H, 3-H,  $J = 2.5$  Hz), 8.56 s (1H, CH=N), 13.73 s (1H, OH). Found:  $[M]^+$  419.3168.  $C_{29}H_{41}NO$ . Calculated:  $M$  419.3188.

**4,6-Di-*tert*-butyl-2-[(2-cyclooctyl-6-methylphenylimino)methyl]phenol (XV b)**. Yield 92%, mp 89–90°C. IR spectrum:  $\nu$  1621  $cm^{-1}$  (N=CH).  $^1H$  NMR spectrum,  $\delta$ , ppm: 1.31 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.46 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.49–1.82 m (14H, CH<sub>2</sub>), 2.21 s (3H, CH<sub>3</sub>), 3.01 m (1H, CH), 6.92–7.01 m (3H, H<sub>arom</sub>), 7.04 d (1H, 5-H,  $J = 2.5$  Hz), 7.39 d (1H, 3-H,  $J = 2.5$  Hz), 8.28 s (1H, CH=N), 13.35 s (1H, OH). Found:  $[M]^+$  433.3345.  $C_{30}H_{43}NO$ . Calculated:  $M$  433.3345.

**4,6-Di-*tert*-butyl-2-[(2-cyclooctyl-4,6-dimethylphenylimino)methyl]phenol (XV c)**. Yield 92%, mp 85–86°C. IR spectrum:  $\nu$  1621  $cm^{-1}$  (N=CH).  $^1H$  NMR spectrum,  $\delta$ , ppm: 1.31 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.48 s [9H, C(CH<sub>3</sub>)<sub>3</sub>], 1.40–1.80 m (14H, CH<sub>2</sub>), 2.17 s (3H, CH<sub>3</sub>), 2.27 s (3H, CH<sub>3</sub>), 2.99 m (1H, CH), 6.79 s (1H, H<sub>arom</sub>), 6.82 s (1H, H<sub>arom</sub>), 7.03 d (1H, 5-H,  $J = 2.5$  Hz), 7.37 d (1H, 3-H,  $J = 2.5$  Hz), 8.25 s (1H, CH=N), 13.40 s (1H, OH). Found:  $[M]^+$  447.3503.  $C_{31}H_{45}NO$ . Calculated:  $M$  447.3501.

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