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# 3,5-Di-*tert*-butyl-1,2-benzoquinone in the Synthesis of Quinolino[4,5-*bc*][1,5]benzoxazepines, Aminophenols, and Phenoxazines

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**Abstract**—Reaction of 3,5-di-*tert*-butyl-1,2-benzoquinone with 5-amino-4-chloroquinolines gave derivatives of a new fused heterocyclic system, substituted quinolino[4,5-*bc*][1,5]benzoxazepines. The molecular structure of 9,11-di-*tert*-butyl-2,4,6-trimethyl-7*H*-quinolino[4,5-*bc*][1,5]benzoxazepine was determined by X-ray analysis. 3,5-Di-*tert*-butyl-1,2-benzoquinone reacted with *o*-nitro-, *o*-acyl-, and *o*-methoxycarbonylanilines and some amino-substituted nitrogen-containing heterocycles to form the corresponding sterically hindered *N*-aryl-(hetaryl)-*o*-aminophenols. Di-*tert*-butyl-substituted phenoxazines were obtained as a result of thermal cyclization of intermediately formed quinone imines.

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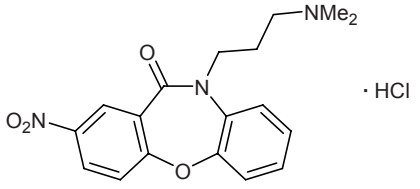
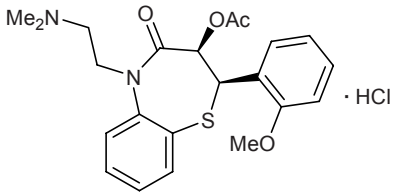
1,4(1,5)-Oxa(thia)zepine derivatives exhibit strong biological activity and are extensively studied. In particular, 10-[3-(dimethylamino)propyl]-2-nitrodibenzo[*b*,*f*][1,4]oxazepin-11(10*H*)-one (**I**) (Sintamil) is known as efficient antidepressant [1]. Dilthiazem (**II**, D-*cis*-3-acetoxy-2,3-dihydro-5-[2-(dimethylamino)-ethyl]-2-(2-methoxyphenyl)-1,5-benzothiazepin-4(5*H*)-one hydrochloride) is a benzothiazepine-type calcium antagonist possessing antianginal, antiarrhythmic, and hypotensive properties.

Substituted 5,11-dihydrobenzo[*b*,*e*][1,4]oxazepines exhibiting a lower anticholinergic activity [2–4] were also tested as calcium antagonists of new generation. Piperazinyldibenzo[*b*,*f*][1,4]oxa(thia)zepine derivatives belong to novel so-called atypical antipsychotic drugs that are effective in the treatment of psychoneurological disorders such as psychosis, depression, and schizophrenia [5]. Unlike traditionally used drugs, the above compounds more rarely cause extrapyramidal side effects and are more effective in the treatment of negative symptoms and treatment-resistant schizophrenia. 2,3,4,5-Tetrahydrobenzo[*f*][1,4]oxazepine-5-carboxamide showed a high inhibitory activity toward γ-secretase in the treatment of Alzheimer disease [6].

In the present article we describe a new procedure for the synthesis of 1,5-benzoxazepine derivatives fused to a heteroring. We have found that 3,5-di-*tert*-butyl-1,2-benzoquinone (**III**) reacts with 5-amino-4-

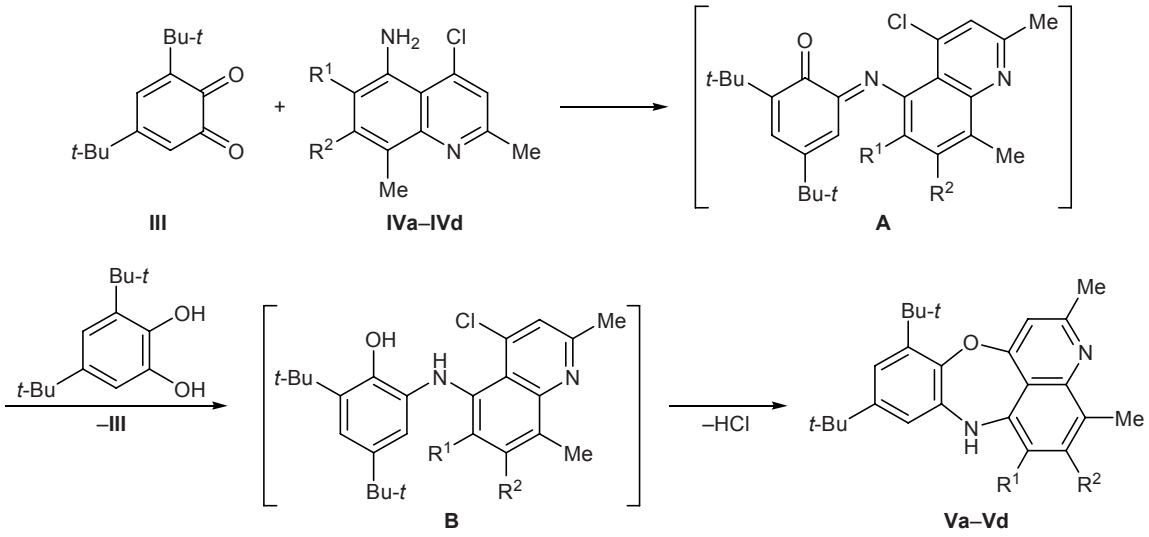



**I**




**II**

**Scheme 1.**

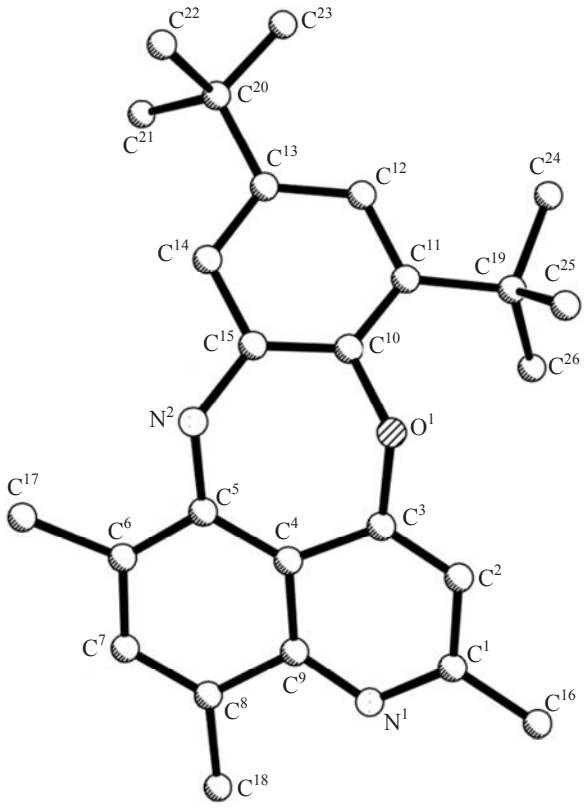



$R^1 = R^2 = H$ (**a**); $R^1 = H$, $R^2 = Me$ (**b**); $R^1 = Me$, $R^2 = H$ (**c**); $R^1 = Br$, $R^2 = H$ (**d**).

chloroquinolines **IVa**–**IVd** in the presence of 3,5-di-*tert*-butylbenzene-1,2-diol according to Scheme 1 to form derivatives of a new fused heterocyclic system, quinolino[4,5-*bc*][1,5]benzoxazepines **Va**–**Vd**. In keeping with the assumed mechanism, initially formed *o*-quinone imine **A** possesses pronounced oxidative power, and, like other *o*-quinones, it acts as dehydrogenating agent toward 3,5-di-*tert*-butylbenzene-1,2-diol. As a result, quinolylaminophenol **B** is formed, and it undergoes intramolecular cyclization to quinolinobenzoxazepine **V** (yield 50–60%). Initial 3,5-di-*tert*-butyl-1,2-benzoquinone (**III**) is regenerated by oxidation of 3,5-di-*tert*-butylbenzene-1,2-diol with quinone imine **A**. The reaction in the absence of reducing agent is characterized by poor yields. Compounds **V** were also isolated in poor yields (7–22%) when equimolar amounts of quinone **III** and quinoline **IV** were heated in *o*-xylene at 135–140°C or fused without a solvent.

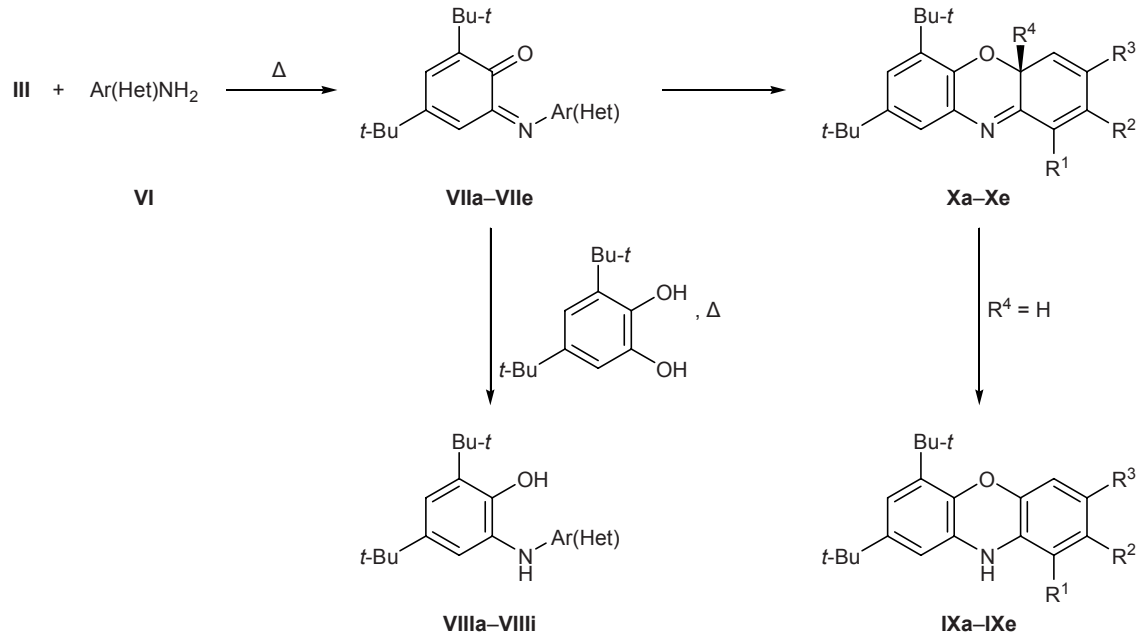
The structure of quinolinobenzoxazepines **Va**–**Vd** was confirmed by the $^1$H NMR, IR, and mass spectra. The molecular structure of compound **Vc** was determined by X-ray analysis (see figure). The central seven-membered ring is folded along the line passing through the $O^1$ and $N^2$ atoms. The dihedral angle between the corresponding planes is 38.8°, the $C^{18}$ atom deviates from the quinoline ring plane by 0.22 Å, and the $C^{19}$ and $C^{20}$ atoms in the *tert*-butyl groups deviate from the benzene ring plane in opposite directions by 0.25 and 0.23 Å, respectively.

With a view to confirm intermediate formation of quinone imines **A** and aminophenols **B** we examined reactions of quinone **III** with various aromatic and heteroaromatic amines containing electron-withdrawing groups ($NO_2$, COPh, COOMe). In fact, fusion of quinone **III** with amines **VI** gave aminophenol deriva-




Molecular structure of 9,11-di-*tert*-butyl-2,4,6-trimethyl-7*H*-quinolino[4,5-*bc*][1,5]benzoxazepine (**Vc**) according to the X-ray diffraction data (hydrogen atoms are not shown).

**Scheme 2.**




**VIII**, Ar = 2-$O_2NC_6H_4$ (**a**), 2-$O_2N$-4-$MeC_6H_3$ (**b**), 2-$O_2N$-4-$ClC_6H_3$ (**c**), 2-$PhCOC_6H_4$ (**d**), 2-$MeOCOC_6H_4$ (**e**), 2-MeOCO-3,4-$(MeO)_2C_6H_2$ (**f**); Het = pyridin-2-yl (**g**), pyrimidin-2-yl (**h**), 4-methylpyrimidin-2-yl (**i**); **IX**, **X**, $R^1 = O_2N$, $R^2 = R^3 = H$ (**a**); $R^2 = H$, $R^3 = Me$ (**b**); $R^2 = H$, $R^3 = Cl$ (**c**); $R^1 = PhCO$, $R^2 = R^3 = H$ (**d**); $R^1 = MeOCO$, $R^2 = R^3 = MeO$ (**e**).

tives **VIII** and (in some cases) phenoxazines **IX** (Scheme 2). When the reaction was performed in the presence of 3,5-di-*tert*-butylbenzene-1,2-diol, the yield of aminophenols **VIII** increased, while the formation of phenoxazines **IX** was suppressed. Presumably, phenoxazines **IX** are formed as a result of thermal cyclization of intermediate *o*-quinone imines **VII**. To verify this assumption, aminophenols **VIIIa**–**VIIIe** were oxidized with lead(IV) oxide in benzene to the corresponding *o*-quinone imines **VIIa**–**VIIe**. After removal of the solvent and heating for 1–1.5 h at 135–140°C we obtained phenoxazines **IXa**–**IXe** in 30–40% yield.

Analogous transformations were studied previously [7–9]. Sterically hindered *o*-quinone imines are stable compounds which can be isolated as individual substances under certain conditions [8, 9]. Abakumov et al. [8] described the reaction of quinone **III** with 2,6-dimethylaniline and 2,6-diisopropylaniline, which led to the formation of chiral 4a*H*-phenoxazines **Xf** and **Xg** ($R^1 = R^2 = R^3 = H$; $R^4$ = Me, *i*-Pr) as a result of intramolecular cyclization of the corresponding *o*-quinone imines **VII**. However, compounds **Xa**–**Xe** having no substituent on the $C^{4a}$ atom ($R^4 = H$) underwent aromatization via 1,3-sigmatropic (C–N) hydrogen shift to give 6,8-di-*tert*-butyl-10*H*-phenoxazines **IXa**–**IXe** (Scheme 2).

## EXPERIMENTAL

The $^1H$ NMR spectra were recorded on a Varian Unity-300 spectrometer. The mass spectra were obtained on a Finnigan MAT Incos 50 instrument. The IR spectra were measured from samples dispersed in mineral oil on a Specord 75IR spectrometer. Column chromatography was performed on aluminum oxide of activity grade II or III according to Brockmann. The melting points were determined in glass capillaries and were not corrected.

**9,11-Di-*tert*-butyl-2,4-dimethyl-7*H*-quinolino-[4,5-*bc*][1,5]benzoxazepine (Va).** A solution of 1.1 g (5 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone (**III**), 1.1 g (5 mmol) of 3,5-di-*tert*-butylbenzene-1,2-diol, and 1.03 g (5 mmol) of 4-chloro-2,8-dimethylquinolin-5-amine (**IVa**) in 10 ml of acetic acid was heated for 2 h at 65–70°C. The mixture as cooled, diluted with water, and extracted with chloroform. The extract was evaporated, and the residue was subjected to column chromatography on aluminum oxide using petroleum ether–chloroform (1:1) as eluent. The second bright yellow fraction was evaporated, and the residue was recrystallized from propan-2-ol. Yield 1.05 g (56%), light yellow crystals, mp 196–199°C. IR spectrum, ν, $cm^{-1}$: 3286 (NH), 1647, 1593, 1473, 1433, 1393, 1366,

1353, 1326, 1233. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 s (9H, 9-*t*-Bu), 1.50 s (9H, 11-*t*-Bu), 2.66 s (3H, 4-$CH_3$), 2.71 s (3H, 2-$CH_3$), 5.78 br.s (1H, NH), 6.74 d (1H, 5-H, *J* = 7.6 Hz), 6.84 d (1H, 10-H, *J* = 2.38 Hz), 7.04 d (1H, 8-H, *J* = 2.38 Hz), 7.13 br.s (1H, 1-H), 7.33 d (1H, 6-H, *J* = 7.69 Hz). Mass spectrum, *m*/*z* ($I_{rel}$, %): 374 (100) $[M]^+$, 359 (9), 303 (9), 259 (16), 187 (14), 128 (10), 115 (18), 91 (12), 77 (21), 63 (12), 57 (90), 41 (87). Found, %: C 80.15; H 7.99; N 7.42. $C_{25}H_{30}N_2O$. Calculated, %: C 80.17; H 8.07; N 7.48.

**9,11-Di-*tert*-butyl-2,4,5-trimethyl-7*H*-quinolino-[4,5-*bc*][1,5]benzoxazepine (Vb)** was synthesized in a similar way from 1.102 g of compound **IVb**. Yield 0.98 g (51%), light yellow crystals, mp 166–168°C. IR spectrum, ν, cm$^{-1}$: 3350 (NH), 1633, 1606, 1667, 1473, 1447, 1380, 1353, 1313, 1233. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 s (9H, 9-*t*-Bu), 1.50 s (9H, 11-*t*-Bu), 2.40 s (3H, 5-$CH_3$), 2.63 s (3H, 4-$CH_3$), 2.70 s (3H, 2-$CH_3$), 5.73 br.s (1H, NH), 6.70 s (1H, 6-H), 6.83 d (1H, 10-H, *J* = 2.2 Hz), 7.02 d (1H, 8-H, *J* = 2.2 Hz), 7.07 s (1H, 1-H). Found, %: C 80.35; H 8.27; N 7.18. $C_{26}H_{32}N_2O$. Calculated, %: C 80.37; H 8.30; N 7.21.

**9,11-Di-*tert*-butyl-2,4,6-trimethyl-7*H*-quinolino-[4,5-*bc*][1,5]benzoxazepine (Vc)** was synthesized in a similar way from 1.102 g of compound **IVc**. Yield 1.15 g (59%), light yellow crystals, mp 206–208°C. IR spectrum, ν, cm$^{-1}$: 3406 (NH), 1593, 1567, 1460, 1393, 1433, 1367, 1313, 1233. $^1$H NMR spectrum, δ, ppm: 1.29 s (9H, 9-*t*-Bu), 1.50 s (9H, 11-*t*-Bu), 2.49 s (3H, 4-$CH_3$), 2.64 s (3H, 6-$CH_3$), 2.69 s (3H, 2-$CH_3$), 5.81 s (1H, NH), 6.83 d (1H, 10-H, *J* 2.28 Hz), 7.04 d (1H, 8-H, *J* = 2.28 Hz), 7.12 s (1H, 5-H), 7.29 s (1H, 1-H). Mass spectrum, *m*/*z* ($I_{rel}$, %): 398 (95) $[M]^+$, 373 (5), 315 (6), 301 (6), 287 (5), 273 (14), 194 (13), 128 (11), 115 (19), 91 (16), 77 (20), 57 (98), 41 (100). Found, %: C 80.36; H 8.25; N 7.18. $C_{26}H_{32}N_2O$. Calculated, %: C 80.37; H 8.30; N 7.21.

**6-Bromo-9,11-di-*tert*-butyl-2,4-dimethyl-7*H*-quinolino[4,5-*bc*][1,5]benzoxazepine (Vd).** A mixture of 1.1 g (5 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone (**III**), 1.43 g (5 mmol) of 5-amino-6-bromo-4-chloro-2,8-dimethylquinoline (**IVd**), and 200 mg of *p*-toluenesulfonic acid was heated for 30 min at 160–170°C. The melt was cooled and dissolved in a 1:1 mixture of petroleum ether with chloroform, and the solution was passed through a column charged with $Al_2O_3$ (15×750 mm) using the same solvent mixture as eluent. The first colorless fraction was evaporated, and the residue was recrystallized from propan-2-ol. Yield 0.16 g (7%), colorless crystals, mp 139–141°C. IR spectrum, ν, cm$^{-1}$: 3353 (NH), 1593, 1567, 1460, 1433, 1393, 1367, 1313, 1233. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 s (9H, 9-*t*-Bu), 1.50 s (9H, 11-*t*-Bu), 2.63 s (3H, 4-$CH_3$), 2.68 s (3H, 2-$CH_3$), 6.62 s (1H, NH), 6.91 d (1H, 10-H, *J* = 2.08 Hz), 7.07 d (1H, 8-H, *J* = 2.08 Hz), 7.16 s (1H, 1-H), 7.59 s (1H, 5-H). Found, %: C 66.21; H 6.38; Br 17.59; N 6.12. $C_{25}H_{29}BrN_2O$. Calculated, %: C 66.22; H 6.45; Br 17.62; N 6.18.

**4,6-Di-*tert*-butyl-2-(2-nitrophenylamino)phenol (VIIIa) and 6,8-di-*tert*-butyl-1-nitrophenoxazine (IXa).** A mixture of 1.1 g (5 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone (**III**) and 0.69 g (5 mmol) of 2-nitroaniline (**VIa**) was heated for 1 h at 135–140°C. The melt was cooled and dissolved in a 2:1 mixture of petroleum ether with chloroform, and the solution was passed through a column charged with $Al_2O_3$ (15× 750 mm) using the same solvent mixture as eluent. Two fractions were collected. The first orange fraction contained compound **VIIIa**, and the second violet fraction, compound **IXa**. The solvent was distilled off from each fraction, and the residue was recrystallized from propan-2-ol.

Compound **VIIIa**. Yield 0.58 g (34%), yellow–orange crystals, mp 105–107°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.26 s (9H, 4-*t*-Bu), 1.42 s (9H, 6-*t*-Bu), 5.77 s (1H, OH), 6.65 d (1H, 6′-H, *J* = 7.69 Hz), 6.80 t (1H, 5′-H, *J* = 7.24 Hz), 7.00 d (1H, 5-H, *J* = 2.38 Hz), 7.33 d (1H, 3-H, *J* = 2.38 Hz), 7.36 t (1H, 4′-H, *J* = 7.04 Hz), 8.22 d (1H, 3′-H, *J* = 7.14 Hz), 8.88 s (1H, NH). Found, %: C 70.12; H 7.58; N 8.15. $C_{20}H_{26}N_2O_3$. Calculated, %: C 70.15; H 7.65; N 8.18.

Compound **IXa**. Yield 0.07 g (4%), bright violet crystals, mp 101–103°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.24 s (9H, 8-*t*-Bu), 1.36 s (9H, 6-*t*-Bu), 6.48 d (1H, 7-H, *J* = 2.2 Hz), 6.56 t (1H, 3-H, *J* = 8.78 Hz), 6.80 d (1H, 4-H, *J* = 2.2 Hz), 6.82 d (1H, 2-H, *J* = 6.66 Hz), 7.58 d (1H, 4-H, *J* = 7.62 Hz), 8.91 br.s (1H, NH). Found, %: C 70.55; H 7.04; N 8.20. $C_{20}H_{24}N_2O_3$. Calculated, %: C 70.57; H 7.11; N 8.23.

**4,6-Di-*tert*-butyl-2-(4-methyl-2-nitrophenyl-amino)phenol (VIIIb).** A mixture of 1.1 g (5 mmol) of 3,5-di-*tert*-butyl)-1,2-benzoquinone (**III**), 0.69 g (5 mmol) of 2-nitroaniline (**VIa**), and 0.56 g of 3,5-di-*tert*-butylbenzene-1,2-diol was heated for 1 h at 135–140°C. The melt was cooled and dissolved in a 2:1 mixture of petroleum ether with chloroform, and the

solution was passed through a column charged with aluminum oxide (15×750 mm) using the same solvent mixture as eluent. A light–orange fraction was collected, the solvent was distilled off, and the residue was recrystallized from propan-2-ol. Yield 0.68 g (38%), orange crystals, mp 137–140°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 s (9H, 4-*t*-Bu), 1.44 s (9H, 6-*t*-Bu), 2.30 s (3H, 4′-$CH_3$), 5.84 s (1H, OH), 6.58 d (1H, 5′-H, *J* = 8.64 Hz), 7.01 d (1H, 5-H, *J* = 2.27 Hz), 7.20 d (1H, 6′-H, *J* = 8.64 Hz), 7.30 d (1H, 3-H, *J* = 2.35 Hz), 8.04 br.s (1H, NH). Mass spectrum, *m*/*z* ($I_{rel}$, %): 356 (100) $[M]^+$, 341 (4), 321 (13), 310 (20), 295 (12), 279 (10), 268 (11), 253 (12), 237 (18), 223 (11), 211 (10), 146 (20), 133 (10), 117 (10), 105 (12), 91 (25), 77 (22), 65 (15), 57 (87), 41 (72). Found, %: C 70.74; H 7.88; N 7.85. $C_{21}H_{28}N_2O_3$. Calculated, %: C 70.76; H 7.92; N 7.86.

Compounds **VIIIc**–**VIIIf** were synthesized in a similar way.

**4,6-Di-*tert*-butyl-2-(4-chloro-2-nitrophenylamino)phenol (VIIIc)** was synthesized from 0.86 g of 4-chloro-2-nitroaniline. Yield 0.68 g (36%), orange crystals, mp 123–125°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.26 s (9H, 4-*t*-Bu), 1.42 s (9H, 6-*t*-Bu), 5.67 s (1H, OH), 6.63 d (1H, 6-H, *J* = 9.06 Hz), 7.00 d (1H, 5-H, *J* = 2.2 Hz), 7.30 t (1H, 5′-H, *J* = 2.93 Hz), 7.32 d (1H, 6′-H, *J* = 2.48 Hz), 8.22 d (1H, 3-H, *J* = 2.47 Hz), 8.85 br.s (1H, NH). Found, %: C 63.72; H 6.63; Cl 9.38; N 7.41. $C_{20}H_{25}ClN_2O_3$. Calculated, %: C 63.74; H 6.69; Cl 9.41; N 7.43.

**[2-(3,5-Di-*tert*-butyl-2-hydroxyphenylamino)-phenyl](phenyl)methanone (VIIId)** was synthesized from 0.99 g of 2-aminobenzophenone. Yield 0.64 g (32%), yellow crystals, mp 107–109°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 s (9H, 5-*t*-Bu), 1.45 s (9H, 3-*t*-Bu), 6.02 s (1H, OH), 6.61 d (1H, 6′-H, *J* = 8.51 Hz), 6.70 t (1H, 5′-H, *J* = 7.14 Hz), 7.06 d (1H, 4-H, *J* = 2.38 Hz), 7.24–7.70 m (8H, $H_{arom}$), 9.46 br.s (1H, NH). Found, %: C 80.74; H 7.71; N 3.41. $C_{27}H_{31}NO_2$. Calculated, %: C 80.76; H 7.78; N 3.49.

**Methyl 2-(3,5-di-*tert*-butyl-2-hydroxyphenylamino)benzoate (VIIIe)** was synthesized from 0.76 g of methyl 2-aminobenzoate. Yield 0.69 g (39%), colorless crystals, mp 109–110°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.27 s (9H, 5-*t*-Bu), 1.44 s (9H, 3-*t*-Bu), 3.93 s (3H, $COOCH_3$), 6.09 s (1H, OH), 6.52 d (1H, 6′-H, *J* = 8.28 Hz), 6.75 t (1H, 5′-H, *J* = 7.18 Hz), 7.02 d (1H, 4-H, *J* = 2.34 Hz), 7.24 t (1H, 4′-H, *J* = 4.47 Hz), 7.28 d (1H, 6-H, *J* = 2.34 Hz), 7.98 d (1H, 3:-H, *J* = 6.52 Hz), 8.83 br.s (1H, NH). Found, %: C 74.31; H 8.15; N 3.91. $C_{22}H_{29}NO_3$. Calculated, %: C 74.33; H 8.22; N 3.94.

**Methyl 2-(3,5-di-*tert*-butyl-2-hydroxyphenylamino)-4,5-dimethoxybenzoate (VIIIf)** was synthesized from 1.06 g of methyl 2-amino-4,5-dimethoxybenzoate. Yield 0.85 g (41%), colorless crystals, mp 139–141°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.27 s (9H, 5-*t*-Bu), 1.44 s (9H, 3-*t*-Bu), 3.65 s (3H, 4′-$OCH_3$), 3.86 s (3H, 5′-$OCH_3$), 3.91 s (3H, $COOCH_3$), 6.06 d (1H, 3′-H, *J* = 7.55 Hz), 7.03 d (1H, 4-H, *J* = 2.35 Hz), 7.21 d (1H, 6-H, *J* = 2.35 Hz), 7.26 s (1H, 6′-H), 7.42 s (1H, OH), 8.85 br.s (1H, NH). Found, %: C 69.34; H 7.93; N 3.31. $C_{24}H_{33}NO_5$. Calculated, %: C 69.37; H 8.00; N 3.37.

**2,4-Di-*tert*-butyl-6-(pyridin-2-ylamino)phenol (VIIIg).** A mixture of 1.1 g (5 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone (**III**), 0.47 g (5 mmol) of pyridin-2-amine (**VIg**), and 0.55 g of 3,5-di-*tert*-butylbenzene-1,2-diol was heated for 1 h at 135–140°C. The melt was cooled and dissolved in a 2:1 mixture of petroleum ether with chloroform, and the solution was passed through a column charged with aluminum oxide (15×750 mm) using the same solvent mixture as eluent. The first colorless fraction was collected, the solvent was distilled off, and the residue was recrystallized from methanol. Yield 0.43 g (29%), colorless crystals, mp 133–135°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.27 s (9H, 4-*t*-Bu), 1.43 s (9H, 2-*t*-Bu), 6.59 t (1H, 4′-H, *J* = 4.95 Hz), 6.88 d (1H, 3′-H, *J* = 5.92 Hz), 6.95 d (1H, 3-H, *J* = 2.37 Hz), 6.98 d (1H, 6′-H, *J* = 5.92 Hz), 7.47 t (1H, 5′-H, *J* = 4.86 Hz), 7.99 d (1H, 5-H, *J* = 2.37 Hz), 8.40 s (1H, OH), 10.38 br.s (1H, NH). Mass spectrum, *m*/*z* ($I_{rel}$, %): 298 (94) $[M]^+$, 283 (100), 255 (29), 227 (47), 143 (16), 123 (26), 105 (29), 91 (36), 78 (45), 57 (53), 41 (71). Found, %: C 76.44; H 8.73; N 9.33. $C_{19}H_{26}N_2O$. Calculated, %: C 72.47; H 8.78; N 9.39.

**2,4-Di-*tert*-butyl-6-(pyrimidin-2-ylamino)phenol (VIIIh)** was synthesized from 0.48 g of pyrimidin-2-amine as described above for compound **VIIIg**. Yield 0.46 g (31%), colorless crystals, mp 189–191°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 s (9H, 4-*t*-Bu), 1.48 s (9H, 2-*t*-Bu), 6.70 t (1H, 5′-H, *J* = 4.90 Hz), 6.92 d (1H, 5-H, *J* = 2.35 Hz), 7.26 s (1H, OH), 8.38 s (2H, 4′-H, 6′-H), 9.34 br.s (1H, NH). Mass spectrum, *m*/*z* ($I_{rel}$, %): 299 (97) $[M]^+$, 284 (100), 256 (14), 242 (10), 228 (30), 135 (12), 115 (8), 96 (13), 79 (19), 57 (28), 41 (45). Found, %: C 72.19; H 8.35;

N 14.01. $C_{18}H_{25}N_3O$. Calculated, %: C 72.21; H 8.42; N 14.03.

**2,4-Di-*tert*-butyl-6-(4-methylpyrimidin-2-ylamino)phenol (VIIIi)** was synthesized from 0.55 g of 4-methylpyrimidin-2-amine according to the procedure described above for the synthesis of compound **VIIIg**. Yield 0.28 g (18%), colorless crystals, mp 189–191°C (from propan-2-ol). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 s (9H, 4-*t*-Bu), 1.49 s (9H, 2-*t*-Bu), 2.41 s (3H, 4′-$CH_3$), 6.56 d (1H, $H_{arom}$, $J$ = 5.15 Hz), 6.89 d (1H, 3-H, $J$ = 2.35 Hz), 7.10 s (1H, OH), 7.21 d (1H, 5-H, $J$ = 2.35 Hz), 8.23 d (1H, $H_{arom}$, $J$ = 5.15 Hz), 9.85 br.s (1H, NH). Found, %: C 72.78; H 8.61; N 14.37. $C_{19}H_{27}N_3O$. Calculated, %: C 72.81; H 8.68; N 14.41.

**6,8-Di-*tert*-butyl-1-nitro-10*H*-phenoxazine (IXa).** Lead(IV) oxide, 4 g, was added to a solution of 0.52 g (1.5 mmol) of 2,4-di-*tert*-butyl-6-(2-nitrophenylamino)phenol (**VIIIa**) in 8 ml of benzene, and the mixture was vigorously stirred for 2 h at room temperature. The mixture was filtered, the filtrate was evaporated, and the residue was heated for 1 h at 135–140°C. The resulting melt was cooled and dissolved in petroleum ether–chloroform (2:1), and the solution was passed through a column charged with aluminum oxide (15×550 mm) using the same solvent mixture as eluent. A violet fraction was collected, the solvent was distilled off, and the residue was recrystallized from propan-2-ol. Yield 0.19 g (36%), bright violet crystals, mp 101–103°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.24 s (9H, 8-*t*-Bu), 1.36 s (9H, 6-*t*-Bu), 6.48 d (1H, 7-H, $J$ = 2.2 Hz), 6.56 t (1H, 3-H, $J$ = 8.78 Hz), 6.80 d (1H, 9-H, $J$ = 2.2 Hz), 6.82 d (1H, 2-H, $J$ = 6.66 Hz), 7.58 d (1H, 4-H, $J$ = 7.62 Hz), 8.91 br.s (1H, NH). Found, %: C 70.55; H 7.04; N 8.20. $C_{20}H_{24}N_2O_3$. Calculated, %: C 70.57; H 7.11; N 8.23.

Compounds **IXb**–**IXe** were synthesized in a similar way.

**6,8-Di-*tert*-butyl-3-methyl-1-nitro-10*H*-phenoxazine (IXb)** was synthesized from 0.54 g (0.15 mmol) of compound **VIIIb**. Yield 0.21 g (39%), dark red crystals, mp 152–154°C. $^1$H NMR spectrum, δ, ppm: 1.24 s (9H, 8-*t*-Bu), 1.36 s (9H, 6-*t*-Bu), 2.18 s (3H, 3-$CH_3$), 6.47 d (1H, 7-H, $J$ = 2.27 Hz), 6.68 d (1H, 2-H, $J$ = 1.76 Hz), 6.80 d (1H, 9-H, $J$ = 2.27 Hz), 7.38 d (1H, 4-H, $J$ = 1.83 Hz), 8.83 br.s (1H, NH). Found, %: C 71.15; H 7.38; N 7.87. $C_{21}H_{26}N_2O_3$. Calculated, %: C 71.16; H 7.39; N 7.90.

**6,8-Di-*tert*-butyl-3-chloro-1-nitro-10*H*-phenoxazine (IXc)** was synthesized from 0.57 g (0.15 mmol) of compound **VIIIc**. Yield 0.09 g (14%), dark red crystals, mp 171–173°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.24 s (9H, 8-*t*-Bu), 1.34 s (9H, 6-*t*-Bu), 6.48 d (1H, 7-H, $J$ = 2.05 Hz), 6.79 d (1H, 2-H, $J$ = 1.98 Hz), 6.83 d (1H, 9-H, $J$ = 2.05 Hz), 7.57 d (1H, 4-H, $J$ = 2.2 Hz), 8.93 br.s (1H, NH) Found, %: C 64.05; H 6.12; Cl 9.42; N 7.42. $C_{20}H_{23}ClN_2O_3$. Calculated, %: C 64.08; H 6.18; Cl 9.46; N 7.47.

**(6,8-di-*tert*-Butyl-10*H*-phenoxazin-1-yl)(phenyl)methanone (IXd)** was synthesized from 0.6 g (0.15 mmol) of compound **VIIId**. Yield 0.23 g (38%), bright orange crystals, mp 129–132°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.23 s (9H, 8-*t*-Bu), 1.38 s (9H, 6-*t*-Bu), 6.42 d (1H, 7-H, $J$ = 2.02 Hz), 6.47 t (1H, 3-H, $J$ = 7.6 Hz), 6.73 d (1H, 9-H, $J$ = 2.02 Hz), 6.77 d (1H, 2-H, $J$ = 7.6 Hz), 6.98 d (1H, 4-H, $J$ = 8.2 Hz), 7.41–7.63 m (5H, $H_{arom}$), 9.41 br.s (1H, NH). Found, %: C 81.16; H 7.27; N 3.46. $C_{27}H_{29}NO_2$. Calculated, %: C 81.17; H 7.32; N 3.51.

**Methyl 6,8-di-*tert*-butyl-3,4-dimethoxy-10*H*-phenoxazine-1-carboxylate (IXe)** was synthesized from 0.62 g (0.15 mmol) of compound **VIIIf**. Yield 0.17 g (27%), bright yellow crystals, mp 125–127°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 s (9H, 8-*t*-Bu), 1.44 s (9H, 6-*t*-Bu), 3.78 s (3H, 3-$OCH_3$), 3.85 s (3H, 4-$OCH_3$), 3.90 s (3H, $COOCH_3$), 6.48 d (1H, 7-H, $J$ = 1.35 Hz), 6.63 s (1H, 2-H), 6.83 d (1H, 9-H, $J$ = 1.35 Hz), 8.55 br.s (1H, NH). Found, %: C 69.68; H 7.48; N 3.32. $C_{24}H_{31}NO_5$. Calculated, %: C 69.71; H 7.56; N 3.39.

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