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Amination of *meso*-Bromophenyl(polyalkyl)porphyrins: Synthesis of Porphyrins Containing a Hydroxypiperidine Fragment

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Abstract—5,15-Bis(4-bromophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin and 5-(4-bromophenyl)-13,17-dibutyl-2,3,7,8,12,18-hexamethylporphyrin were synthesized, and their palladium-catalyzed amination with a number of cyclic secondary amines, including hydroxypiperidines, was studied [$Pd(OAc)_2$, ligand, THF or dioxane, *t*-BuONa, 80–100°C]. The reactions of the *meso*-bromophenylporphyrins with piperidine and morpholine gave the corresponding amination products in quantitative yield. The amination with hydroxypiperidines required excess amine (3 equiv per bromine atom) and excess base (6–8 equiv) and was accompanied by formation of hydrodebromination products; in the reactions with the bis(bromophenyl) derivative, mixed products resulting from amination at one phenyl group and reductive debromination at the other were also formed. The yields of the amination products varied from good {75–50% in the reactions with 4-hydroxypiperidine and *trans*-3-hydroxy-4-[4-(2-fluorophenyl)piperazin-1-yl]piperidine} to moderate (20–50%, 3-hydroxypiperidine) and poor [11–25%, *trans*-3,4-dihydroxypiperidine and *trans*-3-hydroxy-4-(4-hydroxypiperidin-1-yl)piperidine].

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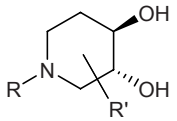
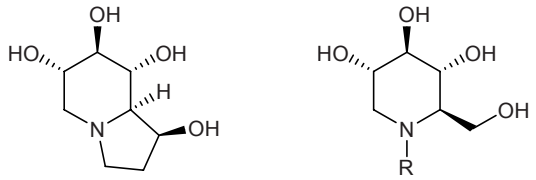
It is known that porphyrins possess versatile and sometimes unique properties which underlie their diverse applications, in particular as agents for therapy and diagnostics [1–3]. The goal of the present work was to create new pharmacological models, i.e., compounds whose molecules contain two pharmacophoric fragments (porphyrin macroring and piperidine ring) and their functionalized derivatives. Development of studies in the field of synthesis of such compounds has been stimulated by our recent data on the anti-HIV activity of *trans*-3,4-dihydroxypiperidines [4].



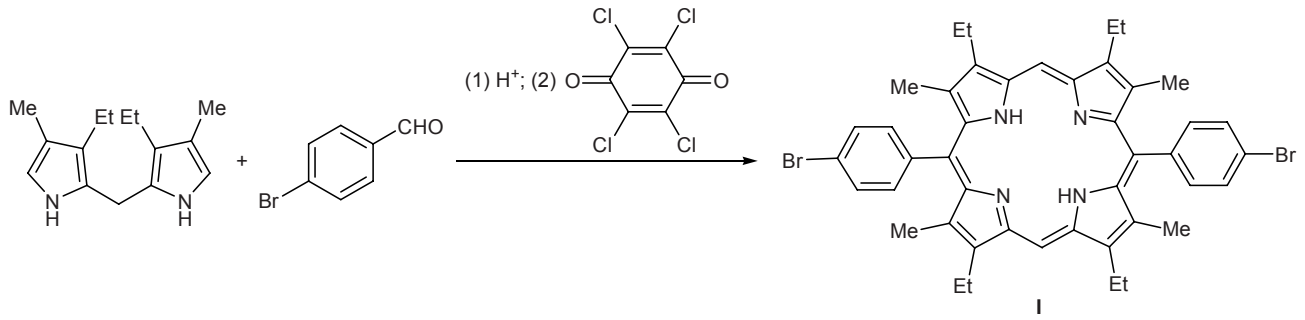
These piperidine derivatives are structurally and stereochemically simpler analogs of a new class of inhibitors of replication of HIV and other viruses, polyhydroxypiperidine alkaloids [4, 5]. Taking the above stated into account, we anticipated that a combination of two pharmacophoric fragments in a single molecule may be useful from the viewpoint of medical applications, e.g., for photodynamic therapy of cancer, fluorescent diagnostics, and design of new antiviral agents.



R = H, Me.

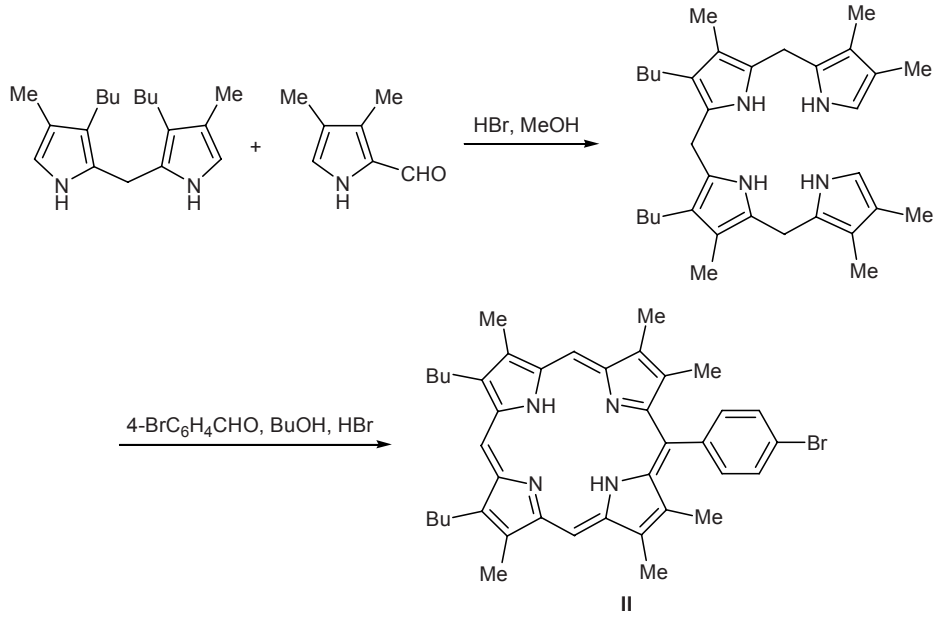
For this purpose, we synthesized previously unknown bis(bromophenyl)- and mono(bromophenyl)-porphyrins **I** and **II**. Compound **I** was obtained according to the procedure described in [6] by condensation of bis(4-ethyl-3-methyl-1*H*-pyrrol-2-yl)methane [7] with *p*-bromobenzaldehyde in methylene chloride in the presence of chloroacetic acid, followed by oxidation of intermediate porphyrinogen with tetrachloro-1,4-benzoquinone (Scheme 1).

Scheme 1.



I

Scheme 2.

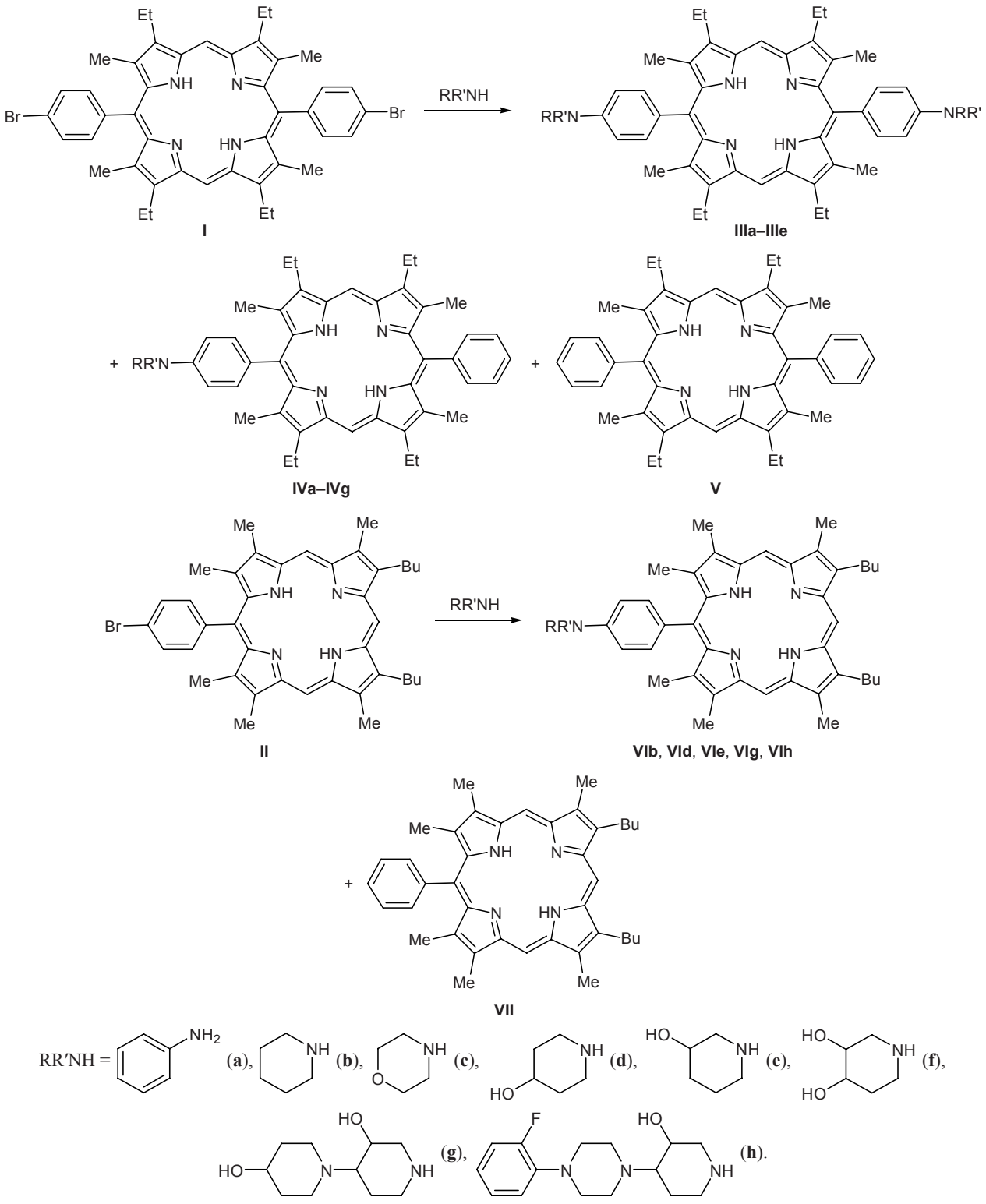


II

The reaction of bis(3-butyl-4-methyl-1*H*-pyrrol-2-yl)methane dihydrobromide with 3,4-dimethyl-1*H*-pyrrole-2-carbaldehyde according to the procedure reported in [8] gave biladiene-*ac* dihydrobromide having no substituents in the α- and α′-positions, and its subsequent condensation with *p*-bromobenzaldehyde led to the formation of *meso*-(4-bromophenyl)porphyrin **II** (Scheme 2). Polyalkyl-substituted porphyrins, such as **I** and **II**, attract interest as closest analogs of natural porphyrins. As far as we know, their amination was not reported.

Physical, chemical, and biological properties of porphyrins are known to strongly depend on the nature of peripheral substituents [1]. Therefore, much attention is given to the development of methods for introduction of various groups into the porphyrin macroring. Modern approaches to modification of porphyrins utilize catalytic reactions (such as Sonoganashira, Suzuki, and Stille) to build up new C–C bonds (see, e.g., [9–12] and references therein). Only in the recent years, some publications on the amination and amidation of *meso*-bromoporphyrins and (bromophenyl)porphyirins have appeared [13–16]. The amination reaction is fairly complex even with simple aryl halides, and its success depends on the number of factors, including the nature of amine and ligand in the palladium complex used as catalyst. Palladium-catalyzed amination of hydroxypiperidines was not studied previously. However, this problem seems to be fairly complex, taking into account that hydroxypiperidines having a secondary hydroxy group can act as strong reducing agents. Therefore, it was reasonable to begin study on the amination of bromophenylporphyrins **I** and **II** with simpler amines, such as piperidine and morpholine or even aniline. Gao et al. [15] reported on the amination of bis(bromophenyl)- and tetrakis(bromophenyl)porphyrins, but no data on reactions with cyclic secondary amines were given. As noted in [13], attempts to effect amination of *meso*-bromopor-

Scheme 3.



phyrins with piperidine and morpholine were unsuccessful. Takahami et al. [14] succeeded in aminating the nickel complex of *meso*-bromoporphyrin with piperidine, but in this case additional problems related to the synthesis of porphyrin complexes and subsequent demetalation of the amination products are involved. Aniline successfully reacted with both *meso*-bromoporphyrin [13] and poly(bromophenyl)porphyrins [15].

Table 1. Amination of 5,15-bis(4-bromophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**I**)

Run no.	Amine	Temperature, °C	Ligand	Solvent	Base	Yield, %		
						IIIa–IIIf	**IVa–IVf**	**V**
1	Aniline, 4 equiv	100	BINAP	THF	Cs_2CO_3, 4 equiv	80		
2	Piperidine, 20 equiv	100	L_1	THF	*t*-BuONa, 4 equiv	10.5	63.5	8
3	Piperidine, 20 equiv	100	L_2	THF	Cs_2CO_3, 4 equiv	81.5[b]	–	–
4	Piperidine, 20 equiv	100	L_4	Dioxane	*t*-BuONa, 4.5 equiv	82		
5	Piperidine, 20 equiv	100	L_4	Dioxane	*t*-BuONa, 4 equiv	76.5		
6	Morpholine, 5 equiv	100	L_2	Dioxane	*t*-BuONa, 4 equiv.	82.5		
7	4-Hydroxypiperidine, 6 equiv	100	L_3	Dioxane	*t*-BuONa, 16 equiv	44	30	
8	4-Hydroxypiperidine, 6 equiv	80	$(t\text{-Bu})_3P \cdot HBF_4$	Dioxane	*t*-BuONa, 14 equiv	7	21	26
9	4-Hydroxypiperidine, 6 equiv	100	$(t\text{-Bu})_3P \cdot HBF_4$	THF	*t*-BuONa, 16 equiv	8	25	43
10	4-Hydroxypiperidine, 6 equiv	100	L_3	THF	*t*-BuONa, 16 equiv	43	27	5
11	4-Hydroxypiperidine, 20 equiv	100	L_3	Dioxane	*t*-BuONa, 8 equiv	45	27	Traces
12	3-Hydroxypiperidine, 6 equiv	100	L_3	Dioxane	*t*-BuONa, 20 equiv	19	23	19.5
13	3-Hydroxypiperidine, 6 equiv	80	L_3	Dioxane	*t*-BuONa, 20 equiv	20	33	18
14	3-Hydroxypiperidine, 6 equiv	80	L_6	Dioxane	*t*-BuONa, 20 equiv	Traces	9	13.5
15	3-Hydroxypiperidine, 6 equiv	80	L_5	Dioxane	*t*-BuONa, 20 equiv	Traces	9	19
16	3-Hydroxypiperidine, 6 equiv	80	$(t\text{-Bu})_3P \cdot HBF_4$	Dioxane	*t*-BuONa, 16 equiv	11	28	28
17	*trans*-3,4-Dihydroxypiperidine, 6 equiv	80	L_3	Dioxane	*t*-BuONa, 18 equiv	[c]	[c]	35
18	*trans*-3,4-Dihydroxypiperidine, 6 equiv	80	$(t\text{-Bu})_3P \cdot HBF_4$	Dioxane	*t*-BuONa, 18 equiv	Traces	11	47
19	*trans*-3-Hydroxy-4-(4-hydroxypiperidin-1-yl)piperidine·2HCl, 3 equiv	80	$(t\text{-Bu})_3P \cdot HBF_4$	Dioxane	*t*-BuONa, 28 equiv	–	25	34

[a] Reaction time 24 h.
[b] Reaction time 72 h.
[c] An inseparable mixture of unidentified products was obtained.

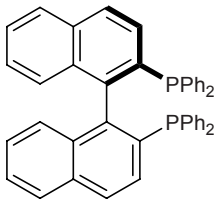
Table 2. Amination of 5-(4-bromophenyl)-13,17-dibutyl-2,3,7,8,12,18-hexamethylporphyrin (**II**)[a]

Run no.	Amine	Ligand	Solvent	Base	Yield, %	
					VIb, **VId–VIf**	**VII**
1	Piperidine, 20 equiv	L_4	THF	*t*-BuONa, 4 equiv	77.5	–
2	Piperidine, 20 equiv	L_4	Dioxane	*t*-BuONa, 4 equiv	83.5	–
3	4-Hydroxypiperidine, 3 equiv	L_3	Dioxane	*t*-BuONa, 4.5 equiv	53	45
4	4-Hydroxypiperidine, 3 equiv	L_3	Dioxane	*t*-BuONa, 8 equiv	70	17
5	4-Hydroxypiperidine, 20 equiv	L_3	Dioxane	*t*-BuONa, 4 equiv	44	45
6	4-Hydroxypiperidine, 20 equiv	L_4	Dioxane	*t*-BuONa, 24 equiv	–	90
7	3-Hydroxypiperidine, 20 equiv	L_3	Dioxane	*t*-BuONa, 7 equiv	41	48
8[b]	3-Hydroxypiperidine, 20 equiv	L_3	Dioxane	*t*-BuONa, 8 equiv	50	45
9[b]	3-Hydroxypiperidine, 20 equiv	L_4	Dioxane	*t*-BuONa, 8 equiv	12.5	41
10[b]	*trans*-3-Hydroxy-4-(4-hydroxypiperidin-1-yl)piperidine·2HCl, 3 equiv	*t*-$Bu_3P\cdot HBF_4$	Dioxane	*t*-BuONa, 16 equiv	18	48
11	1-(2-Fluorophenyl)-4-(*trans*-3-hydroxypiperidine-4-yl)piperazine·3HCl, 3 equiv	L_3	Dioxane	*t*-BuONa, 16 equiv	56	34

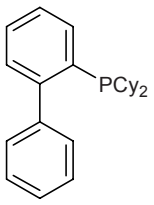
[a] At 100°C, reaction time 24 h.
[b] At 80°C.

In our experiments, the amination of bis(bromophenyl)porphyrin **I** with aniline in tetrahydrofuran using BINAP as ligand and Cs_2CO_3 as base (Table 1, run no. 1) gave the corresponding anilino-substituted derivative in high yield. In the general case, the amination of bromophenylporphyrins **I** and **II** is illustrated by Scheme 3. Using the reaction of porphyrin **I** with piperidine as an example, we examined the effects of solvent (THF, dioxane), base (*t*-BuONa, Cs_2CO_3), and ligand {2-(dicyclohexylphosphino)biphenyl (L_1), 2-(di-*tret*-butylphosphino)biphenyl (L_2), 2-(dicyclohexylphosphino)-2′-(dimethylamino)biphenyl (L_3), and *rac*-1-[2-(diphenylphosphino)ferrocenyl]ethyl methyl ether (L_4)} on the product yield.

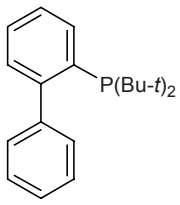
Except for ligand L_1 which ensured a very poor yield of the target product (**IIIb**; Table 1, run. no. 2), all other ligands (L_2–L_4) were approximately equally effective: the yields of **IIIb** ranged from 76.5 to 82% (Table 1, run nos. 3–5). Both THF and dioxane are appropriate solvents (Table 1, run nos. 3, 5). As shown in [13, 14], dioxane, as well as toluene, was ineffective in the amination of *meso*-bromoporphyrins, and the best results were obtained using THF as solvent. Tetrahydrofuran was also used as solvent in the amination of poly(bromophenyl)porphyrins [15]. We selected dioxane for the sake of convenience. Replacement of dioxane by THF did not affect the results of the reaction of 4-hydroxypiperidine with bis(bromophenyl)-



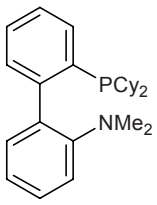
BINAP



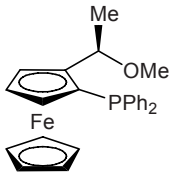
L_1



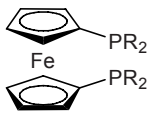
L_2



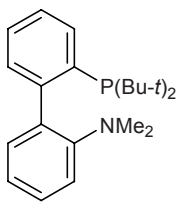
L_3



L_4



R = 2-(*i*-Pr)C_6H_4
L_5



L_6

porphyrine **I** (Table 1, run nos. 7, 10). The reaction in the presence of sodium *tert*-butoxide occurred at a much higher rate (reaction time ~20 h) than in the presence of cesium carbonate (~72 h; Table 1, cf. run nos. 3 and 4, 5). The amination of bromophenylporphyrin **II** with piperidine afforded compound **VIb** in high yield, 77.5% in THF and 83.5% in dioxane (L_4; Table 2, run nos. 1, 2). Likewise, the reaction of bis(bromophenyl)porphyrin **I** with morpholine in the presence of ligand L_2 involved no difficulties, and amination product **IIIc** was formed in 82.5% yield (Table 1, run no. 6). Thus the amination of porphyrins **I** and **II** with piperidine and morpholine in the system dioxane–$Pd(OAc)_2$ (2–3 mol %) using ligands L_2–L_4 (3–4.5 mol %) and *t*-BuONa (4 equiv per bromine atom) at 100°C fairly smoothly produces the target products in high yields (77–82%).

The reactions of bromophenylporphyrins with hydroxypiperidines were not so smooth and were accompanied by formation of considerable amounts of the reduction products (Scheme 3). Nevertheless, using ligand L_3 in the reaction of porphyrin **II** with 4-hydroxypiperidine we succeeded in obtaining compound **VId** in a fairly high yield (~70%), while the yield of reduction product **VII** was 17% (Table 2, run no. 4). The amount of base in reactions with hydroxypiperidines should be increased in accordance with the hydroxypiperidine concentration. Reduction of the amount of base from 8 to 4–4.5 equiv (Table 2, run nos. 3–5) resulted in lower yield of the amination product (**VId**, 44–53%), and the yield of hydrodebromination product **VII** increased to 45%. Ligand L_4 turned out to be ineffective in this reaction (Table 2, run no. 6). Under analogous conditions, the reaction of porphyrin **II** with 3-hydroxypiperidine gave 41–50% of amination product **VIe**, and the yield of reduction product **VII** simultaneously increased (Table 2, run nos. 7, 8). Here, ligand L_4 was also weakly effective (Table 2, run no. 9).

Hydroxypiperidines are difunctional nucleophiles, and their arylation may involve both nitrogen and oxygen atoms. However, comparison of the ^{13}C NMR spectra of amination product **VId** and 4-hydroxypiperidine [17] showed that the reaction occurred only at the nitrogen atom. The position of the CHOH signal (δ_C 67.65 ppm) in the spectrum of **VId** was almost the same as in the spectrum of 4-hydroxypiperidine (δ_C 67.8 ppm), whereas the signal from the carbon atoms linked to nitrogen (δ_C 47.28 ppm) was displaced by almost 3 ppm (δ_C 44.4 ppm for 4-hydroxypiperidine [17]). An additional evidence in favor of regioselective reaction at the nitrogen atom was obtained from the ^1H NMR spectrum of **VId**. The signal prom protons in the α-position with respect to the nitrogen atom is located in a weaker field (δ 3.66 ppm against 3.1 ppm in the spectrum of initial 4-hydroxypiperidine), whereas the position of the C**H**OH signal changes insignificantly (δ 3.77 and 3.65 ppm for compound **VId** and 4-hydroxypiperidine, respectively).

As is typical of catalytic amination of polyhaloarenes, in the reactions of hydroxypiperidines with bis(bromophenyl)porphyrin **I** the contribution of side reduction processes increases (Scheme 3; Table 1, run nos. 7–16). 4-Hydroxypiperidine reacted with compound **I** to give amination product **IIId** still in a fairly good yield (44–45%), the yield of partially reduced product **IVd** was 27–30%, while only traces of the complete reduction product (compound **V**) were detected (Table 1, run nos. 7, 10, 11). The use of a large excess of the amine, as in the reaction with monobromo derivative **II**, had no appreciable effect on the product yield (Table 1, run nos. 7, 10, 11). In the reaction of bis(bromophenyl)porphyrin **I** with 3-hydroxypiperidine, all possible products (**IIIe**, **IVe**, and **V**) were formed (Table 1, run nos. 12–16). As with 4-hydroxypiperidine, the most effective ligand was L_3, but even in this case the yield of amination product **IIIe** did not exceed 19–20% (Table 1, run nos. 12, 13). On the other hand, monoamination product **IVe** was formed in a considerably larger yield (33%), so that the overall yield of amination products (53%) becomes even greater than in the reaction of 3-hydroxypiperidine with bromophenylporphyrin **II**.

Taking into account the above difficulties, we tried to use in the reaction under study some other ligands, 1,1-bis[(2-isopropylphenyl)phosphino]ferrocene (L_5), 2-dimethylamino-2′-[di(*tert*-butyl)phosphino]biphenyl (L_6), and $(t\text{-Bu})_3P\cdot HBF_4$. Ligands L_5 and L_6 turned out to be ineffective: compound **IIIe** was formed only in trace amount, while the yield of **IVe** was as poor as 9%, and the reaction was accompanied by tarring (Table 1, run nos. 14, 15). In the presence of $(t\text{-Bu})_3P\cdot HBF_4$ the yield of bis-amination product **IIIe** was lower than in the presence of L_3, though the yield of monoamino derivative **IVe** changed insignificantly (Table 1, cf. run nos. 12, 13 and 16). The difference in the effects of $(t\text{-Bu})_3P\cdot HBF_4$ and L_3 was much stronger in the reaction with 4-hydroxypiperidine: the yield of **IIId** decreased from 44–45 to 7–8% (Table 1, cf. run nos 7, 10, 11 and 8, 9). Lowering the temperature to

80°C almost did not affect the reaction course with porphyrins **I** and **II** (Table 1, run nos. 13–16; Table 2, run nos. 7, 8).

It was reasonable to presume that reactions of bromophenylporphyrins with dihydroxypiperidines should involve even more difficulties. In fact, bis(bromophenyl)porphyrin **I** reacted with *trans*-3,4-dihydroxypiperidine and *trans*-3-hydroxy-4-(4-hydroxypiperidin-1-yl)piperidine to give mainly hydrodebromination product **V** (Table 1, run nos. 17–19). Monoamination product **IVf** derived from *trans*-3,4-dihydroxypiperidine was isolated in 11% yield only in the presence of $(t\text{-Bu})_3\text{P}\cdot\text{HBF}_4$ as ligand (Table 1, run no. 18). Ligand L_3 gave rise to an inseparable mixture of products containing almost no compound **IVf**. Somewhat larger yield of monoamination product **IVg** (25%) was obtained in the reaction of *trans*-3-hydroxy-4-(4-hydroxypiperidin-1-yl)piperidine with bis(bromophenyl)porphyrin **I** (Table 1, run no. 19). Likewise, the reaction of the same amine with bromophenylporphyrin **II** gave 18% of **VIg** and 48% of reduction product **VII** (Table 2, run no. 10). On the other hand, porphyrin **II** reacted with *trans*-1-(3-hydroxypiperidin-4-yl)-4-(2-fluorophenyl)piperazine containing only one hydroxy group (Table 2, run no. 11) to produce amination product **VIh** in a fairly good yield (56%).

Thus palladium-catalyzed amination of *meso*-(bromophenyl)- and *meso*-bis(bromophenyl)porphyrins with secondary cyclic amines leads to the corresponding amino derivatives in high (piperidine, morpholine) or moderate yields (hydroxypiperidines).

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz for ^{1}H and 100.57 MHz for ^{13}C using tetramethylsilane as internal reference. The mass spectra (MALDI) were obtained on a Bruker Daltonics Autoflex II instrument (N_2 laser, λ = 337 nm; accelerating voltage 19 kV, positive ion detection).

Dioxane and tetrahydrofuran were purified and dehydrated by standard methods and were stored over potassium diphenylketyl. Cesium carbonate was dried at 200°C under reduced pressure. Sodium *tert*-butoxide (Lancaster), palladium(II) acetate, 2-(di-*tert*-butylphosphino)biphenyl, 2-(dicyclohexylphosphino)biphenyl, 2-(dicyclohexylphosphino)-2′-(dimethylamino)-biphenyl, 2-dimethylamino-2′-[di(*tert*-butyl)phosphino]biphenyl (Stream), $(t\text{-Bu})_3\text{P}\cdot\text{HBF}_4$ (*Dal'khim* Ltd.), and 3-hydroxy- and 4-hydroxypiperidines (Ferak Berlin) were used without additional purification. *rac*-1-[2-(Diphenylphosphino)ferrocenyl]ethyl methyl ether [18], dichloro{1,1-bis[(2-isopropylphenyl)phosphino]ferrocene}palladium(II) [19], bis(4-ethyl-3-methyl-1*H*-pyrrol-2-yl)methane, bis(3-butyl-4-methyl-1*H*-pyrrol-2-yl)methane [7], *trans*-3′,4-dihydroxy-1,4′-bipiperidine dihydrochloride [20], and *trans*-1-(3-hydroxypiperidin-4-yl)-4-(2-fluorophenyl)piperazine trihydrochloride [20] were synthesized by known methods.

***trans*-Piperidine-3,4-diol.** A solution of 0.4 g (1.93 mmol) of *trans*-1-benzylpiperidine-3,4-diol in 15 ml of ethanol was hydrogenated over 0.1 g of 10% Pd/C at room temperature over a period of three days. The catalyst was filtered off, and the solvent and liberated toluene were removed under reduced pressure. Yield 0.2 g (90%), colorless crystalline substance, R_f 0.3 (Alufol, CH_2Cl_2–EtOH, 1 : 2), mp 99–100°C (from EtOH–Et_2O). Found: $[M]^+$ 117. $C_5H_{11}NO_2$. Calculated: M 117.4.

5,15-Bis(4-bromophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (I). A solution of 1.0 g (~10 mmol) of chloroacetic acid in 20 ml of methylene chloride was added to a solution of 1.2 g (5.2 mmol) of bis(4-ethyl-3-methyl-1*H*-pyrrol-2-yl)-methane and 0.96 g (5.2 mmol) of 4-bromobenzaldehyde in 400 ml of methylene chloride under stirring at 20°C in a carbon dioxide atmosphere. The mixture was stirred for 4 h, a solution of 1.9 g (7.8 mmol) of tetrachloro-1,4-benzoquinone in 50 ml of THF was added, and the mixture was stirred for 16 h at 20°C and evaporated to dryness under reduced pressure. The residue was treated with a 5% solution of sodium hydroxide, and the precipitate was filtered off, washed with water, and dried at 75°C. Yield 2.1 g. The crude product was dissolved in 150 ml of methylene chloride containing 2 ml of trifluoroacetic acid, the solution was filtered, and the filtrate was neutralized with 5 ml of diethylamine. After 2 h, the precipitate was filtered off, washed with methylene chloride, and dried at 75°C. Yield 1.5 g (73%). ^{1}H NMR spectrum ($CDCl_3$–CF_3COOH, 99:1), δ, ppm: 10.20 s (2H, 10-H, 20-H), 8.17 d (4H), 8.08 d (4H), 3.73 q (8H, CH_2), 2.27 s (12H), 1.36 t (12H, CH_3), –1.94 s (4H, NH). Found: m/z 788.87 $[M + H]^+$. $C_{44}H_{44}Br_2N_4$. Calculated: $[M + H]$ 789.19.

8,12-Dibutyl-2,3,7,13,17,18-hexamethylbiladiene-*ac* dihydrobromide. Concentrated hydrobromic

acid, 2 ml, was added to a solution of 0.65 g (2.27 mmol) of bis(3-butyl-4-methyl-1*H*-pyrrol-2-yl)-methane and 0.6 g (4.54 mmol) of 3,4-dimethyl-1*H*-pyrrole-2-carbaldehyde in 30 ml of methanol, and the mixture was stirred for 2 h at 20°C. The precipitate was filtered off, washed with methanol and diethyl ether, and dried. Yield 1.4 g (93%). Electronic absorption spectrum (chloroform), λ_{max}, nm ($\varepsilon\times10^{-3}$): 523 (113.8), 457 (25.5).

5-(4-Bromophenyl)-13,17-dibutyl-2,3,7,8,12,18-hexamethylporphyrin (II). A solution of 1.4 g (2.12 mmol) of 8,12-dibutyl-2,3,7,13,17,18-hexamethylbiladiene-*ac* dihydrobromide, 0.8 g (4.32 mmol) of 4-bromobenzaldehyde, and 0.5 ml of concentrated hydrobromic acid in 50 ml of butanol was heated to the boiling point and maintained boiling for 4 h, 0.3 g (1.2 mmol) of iodine was added, and the mixture was heated for 15 min under reflux. The solvent was removed by steam distillation, the precipitate was filtered off, washed with water, dried at 70°C, and dissolved in chloroform, and the solution was applied to a column charged with aluminum oxide. The first colored fraction was collected and evaporated to a minimal volume. The product was precipitated with methanol, filtered off, washed with methanol, and dried at 70°C. Yield 0.52 g (37%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.15 s (2H, 10-H, 20-H), 9.94 s (1H, 15-H), 7.86 q (4H, *AB* system), 4.02 t (4H, CH_2), 3.62 s (6H, CH_3), 3.53 s (6H, CH_3), 2.46 s (6H, CH_3), 2.30 m (4H, CH_2), 1.82 m (4H, CH_2), 1.14 t (6H, CH_3), –3.3 br.s (2H, NH). Found: *m*/*z* 660.95 $[M + H]^+$. $C_{40}H_{45}BrN_4$. Calculated: [*M* + H] 661.28.

General procedure for the amination of porphyrins I and II. A reactor was filled with argon and charged with 0.025–0.06 mmol of bromophenylporphyrin **I** or **II**, 0.15–1 mmol of the corresponding amine, 0.3–0.8 mmol of base, 1–2 mol % of $Pd(OAc)_2$, 1.5–4 mol % of ligand, and 5 ml of THF or dioxane. The mixture was degassed, the reactor was filled with argon, and the mixture was stirred at 80–100°C until the initial porphyrin disappeared (according to the TLC data or MALDI spectra). When the reaction was performed in the presence of *t*-BuONa, the mixture was evaporated under reduced pressure, 3–5 ml of methanol was added, the precipitate was separated by centrifugation, washed with methanol or acetone, subjected again to centrifugation, and dried under reduced pressure. When the reaction was performed using Cs_2CO_3 as base, the solution was separated from the solid residue by decanting, and the residue was washed with the corresponding solvent. The solution and the washings were combined and filtered or subjected to centrifugation. We thus isolated almost pure compounds **IIIa**–**IIIc** and **VIb**. If necessary, the products were purified by column chromatography on aluminum oxide (**VIb**, **IIIa**) or silica gel (**IIIb**, **IIIc**).

a. *Isolation and purification of amination products **VId**–**VIf** and **IVf***. The residue obtained after centrifugation was dissolved in chloroform, neutral aluminum oxide (5–40 μm) was added, the solution was evaporated, and the residue was applied to a column charged with aluminum oxide. Compounds **VId** and **VIe** were isolated using chloroform–petroleum ether (40 : 60); reduction product **VII** was eluted first, and then compound **VId** or **VIe** left the column. Compounds **IVf** and **VIf** were isolated by elution with chloroform–methanol (95 : 5) after isolation of reduction product **V** or **VII**.

b. *Isolation of amination products **IIId**, **IIIe**, **IVd**, and **IVe***. The residue obtained after centrifugation was dissolved in chloroform containing 1–2% of methanol and 0.1% of trifluoroacetic acid, and the solution was subjected to chromatography on silica gel (Merck, 40–60 μm). After elution of compound **V**, the concentration of methanol in the eluent was gradually raised to 4–6% (**IVd**, **IVe**) or 10–15% (**IIId**, **IIIe**). The eluate was evaporated to a volume of 1–2 ml, triethylamine was added to the residue until the color changed from black–green to bright red, the mixture was diluted with methanol to a volume of 5–8 ml, and the precipitate was separated by centrifugation, washed with methanol, subjected to centrifugation again, and dried under reduced pressure. Alternatively, porphyrin bases were isolated by filtration of acidic fractions obtained after chromatography through a layer of neutral aluminum oxide (5–40 μm) and subsequent evaporation.

2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-bis[4-(phenylamino)phenyl]porphyrin (IIIa) (Table 1, run no. 1) was obtained from 39 mg (0.05 mmol) of compound **I** and 42 mg (0.45 mmol) of aniline using 130 mg (0.4 mmol) of Cs_2CO_3, 1.12 mg (0.005 mmol) of $Pd(OAc)_2$, and 6.2 mg (0.01 mmol) of BINAP in 5 ml of THF. Yield 33.7 mg (80%). ^{1}H NMR spectrum ($CDCl_3$–CF_3COOH, 99 : 1), δ, ppm: 10.10 s (2H, 10-H, 20-H), 8.08 d (4H), 7.54 d (4H), 7.50–7.41 m (10H), 7.16 t (2H), 3.70 q (8H, CH_2), 2.33 s (12H, CH_3), 1.36 t (12H, CH_3), –1.86 s (4H, NH). Found: *m*/*z* 813.1 $[M + H]^+$. $C_{56}H_{56}N_6$. Calculated: [*M* + H] 813.5.

13,17-Dibutyl-2,3,7,8,12,18-hexamethyl-5-(4-piperidinophenyl)porphyrin (VIb) (Table 2, run no. 2)

was obtained from 33 mg (0.05 mmol) of porphyrin **II** and 0.1 ml (1 mmol) of piperidine using 19 mg (0.02 mmol) of *t*-BuONa, 1.14 mg (0.0053 mmol) of $Pd(OAc)_2$, and 4.3 mg (0.01 mmol) of ligand L_4 in 5 ml of dioxane. Yield 27.5 mg (82%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.13 s (2H, 10-H, 20-H), 9.92 s (1H, 15-H), 7.81 d (2H), 7.26 d (2H), 4.03 t (4H, CH_2), 3.62 s (6H, CH_3), 3.52 s (6H, CH_3), 3.45 m (4H, CH_2), 2.52 s (6H, CH_3), 2.27 m (4H, CH_2), 1.91 m (4H, CH_2), 1.75 m (6H, CH_2), 1.12 t (6H, CH_3), –3.19 s (1H, NH), –3.31 s (1H, NH). Found: *m*/*z* 666.34 $[M + H]^+$. $C_{45}H_{55}N_5$. Calculated: [*M* + H] 666.45.

2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-bis(4-piperidinophenyl)porphyrin (IIIb) (Table 1, run no. 4) was obtained from 39.4 mg (0.05 mmol) of porphyrin **I** and 0.1 ml (1 mmol) of piperidine using 38 mg (0.4 mmol) of *t*-BuONa, 2.2 mg (0.01 mmol) of $Pd(OAc)_2$, and 5.5 mg (0.0185 mmol) of ligand L_2 in 5 ml of THF. Yield 32.5 mg (82%). ^{1}H NMR spectrum ($CDCl_3$–CF_3COOH, 99:1), δ, ppm: 10.23 s (2H, 10-H, 20-H), 8.51 d (4H), 8.14 d (4H), 3.92 m (8H, CH_2), 3.72 q (8H, CH_2), 2.30 m (8H, CH_2), 2.17 s (12H, CH_3), 1.93 m (4H, CH_2), 1.35 t (12H, CH_3), –1.91 s (4H, NH). Found: *m*/*z* 797.5 $[M + H]^+$. $C_{54}H_{64}N_6$. Calculated: [*M* + H] 797.2.

2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-bis(4-morpholinophenyl)porphyrin (IIIc) (Table 1, run no. 6) was obtained from 47 mg (0.060 mmol) of porphyrin **I** and 0.08 ml (1 mmol) of morpholine using 50 mg (0.52 mmol) of *t*-BuONa, 2.24 mg (0.01 mmol) of $Pd(OAc)_2$, and 6 mg (0.02 mmol) of ligand L_2 in 5 ml of dioxane. After centrifugation, the precipitate was dissolved in chloroform containing 2% of methanol and 0.1% of trifluoroacetic acid, and the product was precipitated with triethylamine, washed with methanol, and dried. Yield 40 mg (82%). ^{1}H NMR spectrum ($CDCl_3$–CF_3COOH, 99:1), δ, ppm: 10.06 s (2H, 10-H, 20-H), 8.12 d (4H), 7.39 d (4H), 4.06 m (8H, CH_2), 3.67 q (8H, CH_2), 3.56 m (8H, CH_2), 2.24 s (12H), 1.36 t (12H, CH_3), –1.48 s (4H, NH). Found: *m*/*z* 801.3 $[M + H]^+$. $C_{52}H_{60}N_6O_2$. Calculated: [*M* + H] 801.5.

Reaction of porphyrin II with 4-hydroxypiperidine (Table 2, run no. 4)**.** The reaction was performed using 33 mg (0.05 mmol) of porphyrin **II**, 15 mg (0.15 mmol) of 4-hydroxypiperidine, 40 mg (0.42 mmol) of *t*-BuONa, 1.35 mg (0.006 mmol) of $Pd(OAc)_2$, and 4.8 mg (0.0122 mmol) ligand L_3 in 5 ml of dioxane. According to method *a* we isolated 5 mg (17%) of **VII** and 24 mg (70%) of **VId**.

13,17-Dibutyl-2,3,7,8,12,18-hexamethyl-5-phenylporphyrin (VII). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.16 s (2H, 10-H, 20-H), 9.95 s (1H, 15-H), 8.04 d (2H), 7.81 t (1H), 7.73 t (2H), 4.04 t (4H, CH_2), 3.63 s (6H, CH_3), 3.54 s (6H, CH_3), 2.45 s (6H, CH_3), 2.31 m (4H, CH_2), 1.80 m (4H, CH_2), 1.17 t (6H, CH_3), –3.2 br.s (2H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 145.66, 144.13, 143.68, 142.73, 140.14, 137.76, 136.74, 135.95 (pyrrole); 132.99, 128.12, 127.44 (C_{arom}); 118.72 (C^5); 96.47 (C^{10}, C^{20}); 95.63 (C^{15}); 35.18, 26.11, 23.00 (CH_2); 14.75, 14.14, 12.06, 11.66 (CH_3). Found: *m*/*z* 583.44 $[M + H]^+$. $C_{40}H_{46}N_4$. Calculated: [*M* + H] 583.38.

13,17-Dibutyl-5-[4-(4-hydroxypiperidin-1-yl)-phenyl]-2,3,7,8,12,18-hexamethylporphyrin (VId). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.13 s (2H, 10-H, 20-H), 9.92 s (1H, 15-H), 7.60 d (2H), 7.01 d (2H), 4.02 t (4H, CH_2), 3.77 m (1H), 3.66 m (2H), 3.61 s (6H, CH_3), 3.52 s (6H, CH_3), 2.99 m (2H), 2.41 s (6H, CH_3), 2.31 m (4H, CH_2), 1.99 m (2H), 1.70–1.84 m (6H), 1.17 t (6H, CH_3), –3.2 br.s (2H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 145.54, 144.73, 143.55, 142.72, 139.99, 137.40, 137.00, 135.82 (pyrrole); 151.03, 133.41, 133.26, 115.03 (C_{arom}); 118.87 (C^5); 96.34 (C^{10}, C^{20}); 95.41 (C^{15}); 67.65 (CHOH); 47.22 (CH_2N); 35.16, 33.84, 26.08, 23.00 (CH_2); 14.85, 14.12, 11.99, 11.58 (CH_3). Found: *m*/*z* 682.51 $[M + H]^+$. $C_{45}H_{55}N_5O$. Calculated: [*M* + H] 682.44.

Reaction of porphyrin II with 3-hydroxypiperidine (Table 2, run no. 8)**.** The reaction was performed using 34.7 mg (0.0523 mmol) of porphyrin **I**, 15 mg (0.15 mmol) of 3-hydroxypiperidine, 38 mg (0.4 mmol) of *t*-BuONa, 1.1 mg (0.005 mmol) of $Pd(OAc)_2$, and 4.0 mg (0.01 mmol) of ligand L_3 in 5 ml of dioxane. Following method *a*, we isolated 12 mg (41%) of compound **VII** and 17 mg (50%) of porphyrin **VIe**.

13,17-Dibutyl-5-[4-(3-hydroxypiperidin-1-yl)-phenyl]-2,3,7,8,12,18-hexamethylporphyrin (VIe). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.13 s (2H, 10-H, 20-H), 9.93 s (1H, 15-H), 7.75 d (2H), 7.17 d (2H), 4.08 m (1H), 4.03 t (4H, CH_2), 3.62 s (6H, CH_3), 3.48–3.59 m (2H), 3.52 s (6H, CH_3), 3.23–3.39 m (3H), 2.47 s (6H, CH_3), 2.29 m (4H, CH_2), 1.95 m (1H), 1.72–1.99 m (2H), 1.79 m (4H, CH_2), 1.15 t (6H, CH_3), –3.2 br.s (2H, NH). Found: *m*/*z* 682.40 $[M + H]^+$. $C_{45}H_{55}N_5O$. Calculated: [*M* + H] 682.44.

Reaction of porphyrin II with *trans*-3-hydroxy-4-(4-hydroxypiperidin-1-yl)piperidine (Table 2, run no. 10)**.** The reaction was performed using 33 mg

(0.05 mmol) of compound **II**, 40 mg (0.15 mmol) of 3-hydroxy-4-(4-hydroxypiperidin-1-yl)piperidine dihydrochloride, 77 mg (0.8 mmol) of *t*-BuONa, 2.24 mg (0.01 mmol) of $Pd(OAc)_2$, and 4.35 mg (0.015 mmol) of $(t\text{-}Bu)_3P \cdot HBF_4$ in 5 ml of dioxane. Following method *a*, we isolated 14 mg (48%) of compound **VII** and 7 mg (18%) of porphyrin **VIg**.

13,17-Dibutyl-5-{4-[*trans*-3-hydroxy-4-(4-hydroxypiperidin-1-yl)piperidin-1-yl]phenyl}-2,3,7,8,-12,18-hexamethylporphyrin (VIg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.13 s (2H, 10-H, 20-H), 9.93 s (1H, 15-H), 7.84 d (2H), 7.26 d (2H), 4.34 m (1H), 4.04 t (4H, CH_2), 3.90 m (1H), 3.76 m (1H), 3.62 s (6H, CH_3), 3.52 s (6H, CH_3), 3.05–2.7 m (4H), 2.51 s (6H, CH_3), 2.55–2.4 m (2H), 2.28 m (4H, CH_2), 2.1–1.46 m (8H), 1.77 m (4H, CH_2), 1.13 t (6H, CH_3), –3.2 br.s (1H, NH), –3.3 br.s (1H, NH). Found: *m*/*z* 781.61 $[M + H]^+$. $C_{50}H_{64}N_6O_2$. Calculated: [*M* + H] 781.51.

Reaction of porphyrin II with *trans*-4-(2-fluorophenyl)-1-(3-hydroxypiperidin-4-yl)piperazine (Table 2, run no. 11)**.** The reaction was performed using 33 mg (0.05 mmol) of porphyrin **II**, 58.7 mg (0.15 mmol) of *trans*-4-(2-fluorophenyl)-1-(3-hydroxypiperidin-4-yl)piperazine trihydrochloride, 80 mg (0.83 mmol) of *t*-BuONa, 2.8 mg (0.0125 mmol) of $Pd(OAc)_2$, and 6.7 mg (0.015 mmol) of ligand L_3 in 5 ml of dioxane. Following method *a*, we isolated 10 mg (34%) of compound **VII** and 24 mg (56%) of porphyrin **VIh**.

13,17-Dibutyl-5-(4-{*trans*-4-[4-(2-fluorophenyl)-piperazin-1-yl]-3-hydroxypiperidin-1-yl}phenyl)-2,3,7,8,12,18-hexamethylporphyrin (VIh). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.14 s (2H, 10-H, 20-H), 9.93 s (1H, 15-H), 7.87 d (2H), 7.29 d (2H), 7.14–6.97 m (4H), 4.34 m (1H), 4.04 t (4H, CH_2), 4.12–3.96 m (2H), 3.63 s (6H, CH_3), 3.53 s (6H, CH_3), 3.35–3.2 m (4H), 3.08 m (2H), 2.98 m (1H), 2.81 m (2H), 2.52 s (6H, CH_3), 2.35–2.23 m (1H), 2.28 m (4H, CH_2), 2.05 m (1H), 1.95–1.85 m (2H), 1.77 m (4H, CH_2), 1.13 t (6H, CH_3), –3.3 br.s (2H, NH). Found: *m*/*z* 860.43 $[M + H]^+$. $C_{55}H_{66}FN_7O$. Calculated: [*M* + H] 860.53.

Reaction of porphyrin I with 4-hydroxypiperidine (Table 1, run no. 7)**.** The reaction was carried out using 48 mg (0.06 mmol) of porphyrin **I**, 36 mg (0.36 mmol) of 4-hydroxypiperidine, 92 mg (0.95 mmol) of *t*-BuONa, 2.24 mg (0.01 mmol) of $Pd(OAc)_2$, and 8 mg (0.02 mmol) of ligand L_3 in 5 ml of dioxane. Following method *b*, we isolated 13 mg (30%) of compound **IVd** and 22 mg (44%) of **IIId**.

2,8,12,18-Tetraethyl-5,15-bis[4-(4-hydroxypiperidin-1-yl)phenyl]-3,7,13,17-tetramethylporphyrin (IIId). ^{1}H NMR spectrum ($CDCl_3$–CF_3COOH–CD_3OD, 94:1:5), δ, ppm: 10.09 s (2H, 10-H, 20-H), 8.28 d (4H), 7.84 d (4H), 4.15–4.02 m (6H), 3.55–3.68 m (12H), 2.38 m (4H), 2.16 s (12H), 2.08–2.00 m (4H), 1.33 t (12H, CH_3). Found: *m*/*z* 829.56 $[M + H]^+$. $C_{54}H_{64}N_6O_2$. Calculated: [*M* + H] 829.51.

2,8,12,18-Tetraethyl-5-[4-(4-hydroxypiperidin-1-yl)phenyl]-3,7,13,17-tetramethyl-15-phenylporphyrin (IVd). ^{1}H NMR spectrum ($CDCl_3$–CF_3COOH, 99:1), δ, ppm: 10.22 s (2H, 10-H, 20-H), 8.53 d (2H), 8.26 m (2H), 8.14 d (2H), 7.93 m (3H), 4.42 m (1H), 4.18 t (2H), 3.95 m (2H), 3.73 q (8H, CH_2), 2.60 m (2H), 2.3–2.2 m (2H), 2.22 s (6H), 2.18 s (6H), 1.35 t (12H, CH_3), –1.97 br.s (4H, NH). Found: *m*/*z* 730.49 $[M + H]^+$. $C_{49}H_{55}N_5O$. Calculated: [*M* + H] 730.44.

Reaction of porphyrin I with 3-hydroxypiperidine (Table 1, run no. 13)**.** The reaction was performed using 39 mg (0.05 mmol) of porphyrin **I**, 32 mg (0.32 mmol) of 3-hydroxypiperidine, 77 mg (0.8 mmol) of *t*-BuONa, 2.2 mg (0.01 mmol) of $Pd(OAc)_2$, and 7.9 mg (0.02 mmol) of ligand L_3 in 5 ml of dioxane. Following method *b*, we isolated 5.7 mg (18%) of compound **V**, 12 mg (33%) of **IVe**, and 9 mg (20%) of porphyrin **IIIe**.

2,8,12,18-Tetraethyl-5,15-bis[4-(3-hydroxypiperidin-1-yl)phenyl]-3,7,13,17-tetramethylporphyrin (IIIe). ^{1}H NMR spectrum ($CDCl_3$–CF_3COOH–CD_3OD, 97:1:2), δ, ppm: 10.02 s (2H, 10-H, 20-H), 8.09 d (4H), 7.48 d (4H), 4.11 m (2H), 3.86 m (2H), 3.7–3.6 m (12H), 3.28–3.41 m (4H), 2.20 s (12H), 2.10 m (2H), 1.91 m (2H), 1.73 m (2H), 1.34 t (12H, CH_3). Found: *m*/*z* 829.45 $[M + H]^+$. $C_{54}H_{64}N_6O_2$. Calculated: [*M* + H] 829.51.

2,8,12,18-Tetraethyl-15-[4-(3-hydroxypiperidin-1-yl)phenyl]-3,7,13,17-tetramethyl-5-phenylporphyrin (IVe). ^{1}H NMR spectrum ($CDCl_3$–CF_3COOH, 99:1), δ, ppm: 10.21 s (2H, 10-H, 20-H), 8.53 d (2H), 8.26 m (2H), 8.14 d (2H), 7.93 m (3H), 4.60 m (1H), 3.97 m (1H), 3.87 m (3H), 3.73 q (8H, CH_2), 2.58 m (1H), 2.22 s (6H), 2.18 s (6H), 2.0–2.3 m (3H), 1.38 t, 1.36 t (12H, CH_3), –1.93 s, –1.95 s (4H, NH). Found: *m*/*z* 730.34 $[M + H]^+$. $C_{49}H_{55}N_5O$. Calculated; [*M* + H] 730.44.

2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin (V). ^{1}H NMR spectrum ($CDCl_3$),

δ, ppm: 10.24 s (2H, 10-H, 20-H), 8.08 d (4H), 7.83–7.72 m (6H), 4.03 q (8H, CH_2), 2.50 s (12H, CH_3), 1.78 t (12H, CH_3), –2.40 br.s (2H, NH). Found: *m*/*z* 631.25 $[M + H]^+$. $C_{44}H_{46}N_4$. Calculated: [*M* + H] 631.38.

Reaction of porphyrin I with *trans*-3,4-dihydroxypiperidine (Table 1, run no. 18)**.** The reaction was performed using 39.6 mg (0.050 mmol) of porphyrin **I**, 35 mg (0.3 mmol) of *trans*-3,4-dihydroxypiperidine, 86 mg (0.9 mmol) of *t*-BuONa, 2.2 mg (0.010 mmol) of $Pd(OAc)_2$, and 5.1 mg (0.018 mmol) of $(t\text{-Bu})_3P \cdot HBF_4$ in 5 ml of dioxane. Following method *a*, we isolated 15 mg (47%) of compound **V** and 4.0 mg (11%) of **IVf**.

15-[4-(*trans*-3,4-Dihydroxypiperidin-1-yl)-phenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5-phenylporphyrin (IVe). ^{1}H NMR spectrum ($CDCl_3$–CF_3COOH–CD_3OD, 97:1:2), δ, ppm: 10.08 s (2H, 10-H, 20-H), 8.23 m (2H), 8.11 d (2H), 7.87 m (3H), 7.43 d (2H), 4.19 m (1H), 4.06 m (1H), 3.80 m (1H), 3.66 m (9H), 3.18 t (1H), 3.01 t (1H), 2.22 s (6H), 2.17 s (6H), 1.8–2.25 m (2H), 1.36 t (12H, CH_3). Found: *m*/*z* 746.33 $[M + H]^+$. $C_{49}H_{55}N_5O_2$. Calculated: [*M* + H] 746.44.

Reaction of porphyrin I with *trans*-3-hydroxy-4-(4-hydroxypiperidin-1-yl)piperidine (Table 1, run no. 19)**.** The reaction was carried out using 39.6 mg (0.050 mmol) of porphyrin **I**, 82 mg (0.3 mmol) of 3-hydroxy-4-(4-hydroxypiperidin-1-yl)piperidine dihydrochloride, 154 mg (1.6 mmol) of *t*-BuONa, 2.24 mg (0.010 mmol) of $Pd(OAc)_2$, and 4.4 mg (0.015 mmol) of $(t\text{-Bu})_3P \cdot HBF_4$ in 5 ml of dioxane. Following method *a*, we isolated 10.3 mg (34%) of compound **V** and 10.5 mg (25%) of **IVg**.

2,8,12,18-Tetraethyl-15-{4-[*trans*-3-hydroxy-4-(4-hydroxypiperidin-1-yl)piperidin-1-yl]phenyl}-3,7,13,17-tetramethyl-5-phenylporphyrin (IVg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.22 s (2H, 10-H, 20-H), 8.06 d (2H), 7.86 m (2H), 7.70–7.80 m (3H), 7.25 d (2H), 4.32 m (1H), 4.02 q (8H, CH_2), 3.87 m (1H), 3.69 m (1H), 3.09 m (1H), 2.6–3.0 m (5H), 2.54 s (6H), 2.48 s (6H), 2.26 m (1H), 1.5–2.0 m (7H), 1.77 t (12H, CH_3), –2.44 s (2H, NH). Found: *m*/*z* 829.63 $[M + H]^+$. $C_{54}H_{64}N_6O_2$. Calculated: [*M* + H] 829.51.

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