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Synthesis of *meso*-Mono-phenylporphyrins with Active Groups in the Benzene Rings

N. L. Pechnikova, A. V. Lyubimtsev, S. A. Syrbu, T. A. Ageeva, and A. S. Semeikin

Research Institute of Macroheterocyclic Compounds, Ivanovo State University of Chemistry and Technology, pr. Engel'sa 7, Ivanovo, 153000 Russia
e-mail: peclin@mail.ru

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Abstract—The mono-*meso*-allyloxy- and acrylamidophenylporphyrins were synthesized from the corresponding hydroxy- and aminophenylporphyrins. All the compounds were characterized by IR, UV-Vis, ^{1}H NMR and mass spectra.

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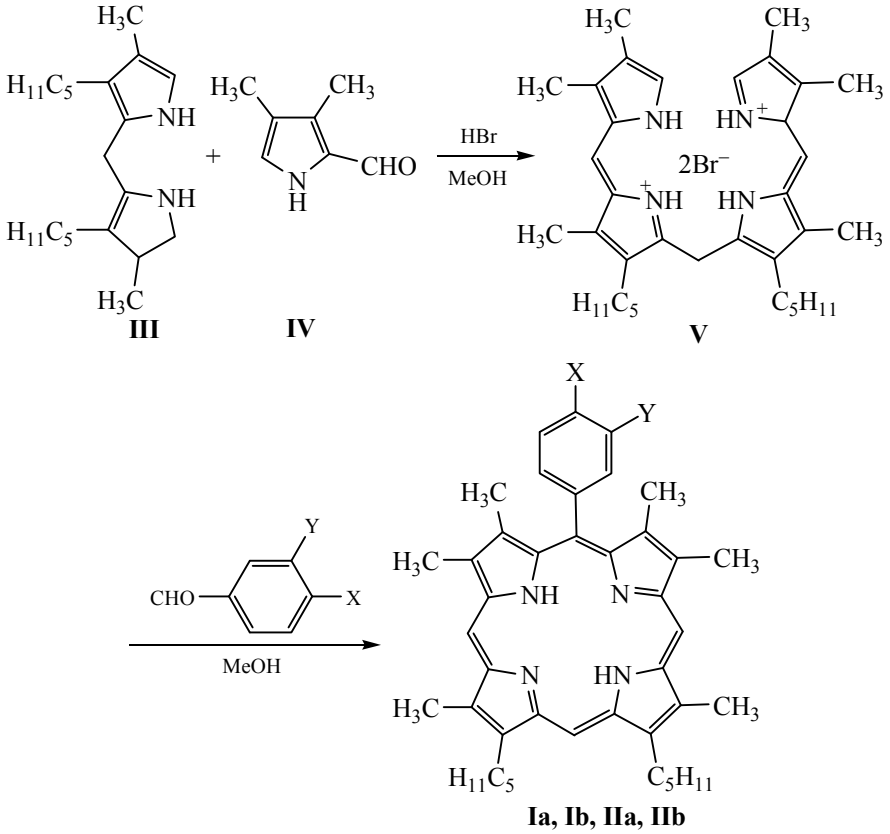
In recent years the interest increased to the study of models of natural supramolecular porphyrin-containing systems [1, 2]. In order to fix the porphyrin in a certain way on a polymer carrier, the macroheterocycles on their periphery should be active groups such as hydroxy and amino groups, which can be involved in further chemical reactions [3]. Of particular interest is the introduction of vinyl group into the porphyrin

Scheme 1.



I, X = OH, Y = H (**a**), X = H, Y = OH (**b**); **II**, X = NO_2, Y = H (**a**), X = H, Y = NO_2 (**b**).

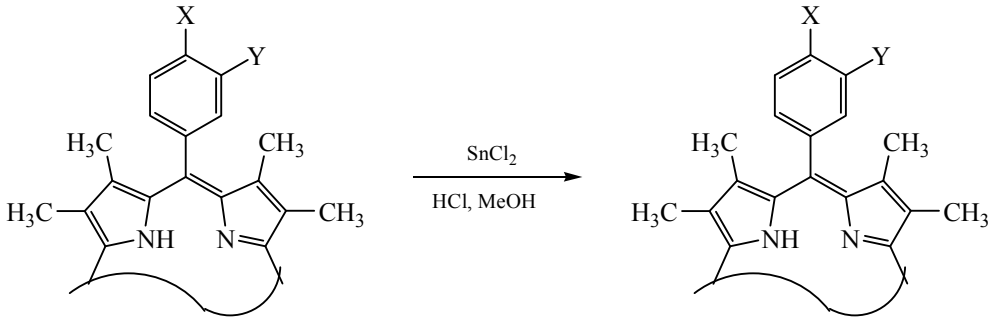
macroheterocycles allowing copolymerization with other comonomers of non-porphyrin nature [4, 5].

In this regard, the aim of this study is to obtain mono-*meso*-phenylporphyrins containing vinyl groups on the periphery of the tetrapyrrole macroheterocycle.

meso-Hydroxyphenyl- (**Ia, Ib**) and *meso*-aminophenylporphyrins (**IIc, IId**) were used as precursors of vinyl porphyrins. The *meso*-hydroxyphenylporphyrins **Ia**, **Ib** were synthesized with the yields 43.6 and 47.9%, respectively, by a one-pot procedure [6] from dipentyl-substituted dipyrrolylmethane **III** and 2-formyl-3,4-dimethylpyrrole **IV** with subsequent reaction of the resulting biladiene-*a,c* **V** with hydroxylbenzaldehyde (Scheme 1).

It is known [7] that in the condensation reaction of aminobenzaldehydes with pyrrole and its derivatives the aminophenylporphyrins are formed in a very low yield. Therefore, amino-phenylporphyrins **IIb**, **IId** were synthesized by the reduction of the nitro group in the corresponding nitrophenylporphyrins **IIa**, **IIb** with tin dichloride [8]. The parent nitrophenylporphyrins were synthesized similarly to the hydroxyphenylporphyrins. The total yield of compounds **IIc** and **IId** was 43 and 40.2% respectively, with respect to the original dipyrrolylmethane **III** (Scheme 2).

Scheme 2.



IIa, IIb **IIc, IId**

X = NO_2, Y = H (**a**), X = H, Y = NO_2 (**b**), X = NH_2, Y = H (**c**), X = H, Y = NH_2 (**d**).

Allyloxyphenylporphyrins **VIa, VIb** were synthesized by alkylation of 5-(4'-hydroxyphenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphyrin **Ia** and 5-(3'-hydroxyphenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphyrin **Ib** with allyl bromide in dimethylformamide (DMF) in presence of potassium carbonate [9] (Scheme 3) in 62 and 70% yield respectively. The completeness of the reaction was monitored by TLC.

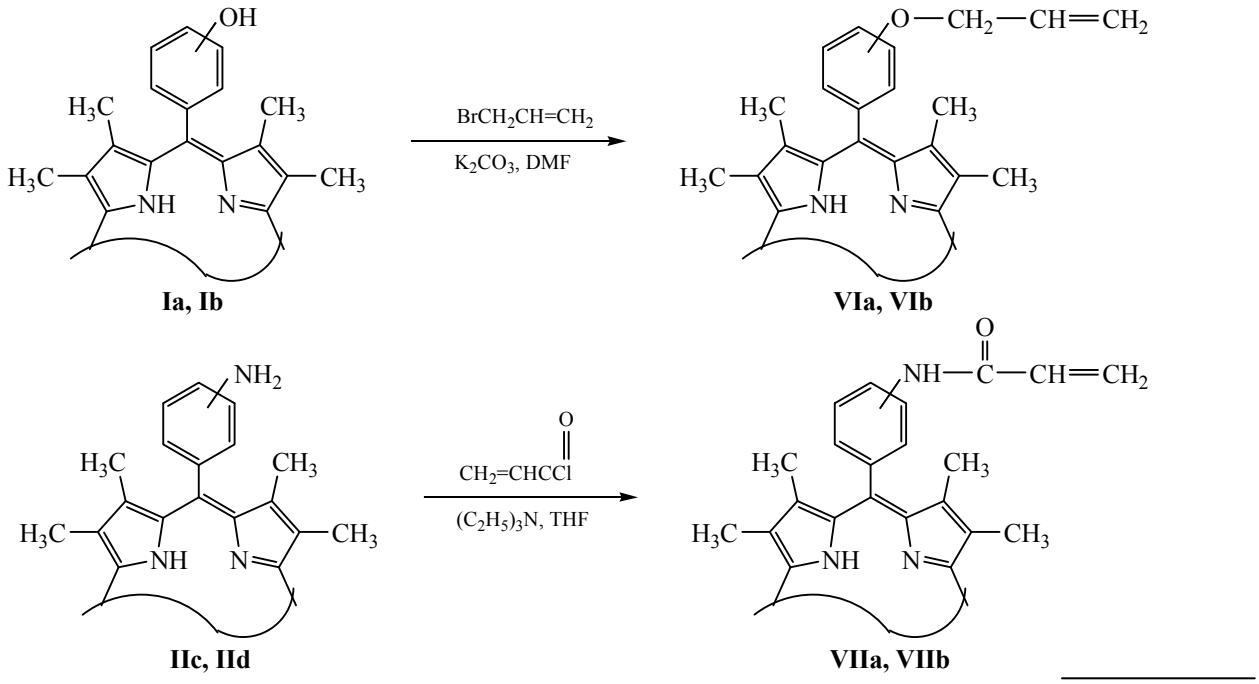
5-(4'-Acrylamidophenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphin **VIIa** and 5-(3'-acrylamidophenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphin **VIIb** were prepared by acylation of the *meso*-aminophenylporphyrins **IIb**, **IId** with acryloyl chloride in tetrahydrofuran (THF) in the presence of triethylamine as a base [10, 11] (Scheme 3). The yields of porphyrins **VIIa** and **VIIb** were 68% and 65% respectively.

The purification of the allyloxyphenylporphyrins **VIa**, **VIb** was performed by column chromatography on silica gel using chloroform as eluent, and acrylamidophenylporphyrins **VIIa**, **VIIb** were chromatographed on aluminium oxide eluting with chloroform. The structure of the compounds was confirmed by elemental analysis, electronic, ^{1}H NMR, IR spectroscopy and mass spectrometry.

Electron absorption spectra of solutions of mono-*meso*-allyloxyphenylporphyrins **VIa**, **VIb** in chloroform practically do not differ from the UV-Vis spectra of original porphyrins **Ia**, **Ib** (Fig. 1). The acylation of amino groups in porphyrins **IIc**, **IId** also virtually does not affect the position of the absorption bands in the UV-Vis spectra of porphyrins **VIIa**, **VIIb** compared with the initial aminophenylporphyrins **IIc**, **IId**.

The IR spectra of compounds **VIa**, **VIb** and **VIIa**, **VIIb** include the bands characteristic of the porphyrin macrocycle, like the bands of stretching and bending vibrations of intracyclic NH-groups (a weak band at about 3320 cm^{-1} and a strong band at 747 cm^{-1}). In the IR spectra of the allyloxyporphyrins **VIa**, **VIb** appear

Scheme 3.



high-intensity bands of asymmetric (near 1240 cm^{-1}) and of medium strong symmetric (near 1022 cm^{-1}) stretching vibrations of the ether C–O–C groups. The broad bands of stretching vibrations of hydroxy groups near 3300 cm^{-1} disappear.

In the IR spectra of acrylamidophenylporphyrins **VIIa**, **VIIb** appear characteristic strong bands of stretching vibrations of acylamido groups at 1669 cm^{-1}, which are absent in the spectra of the initial aminophenylporphyrins. In addition, the two bands of

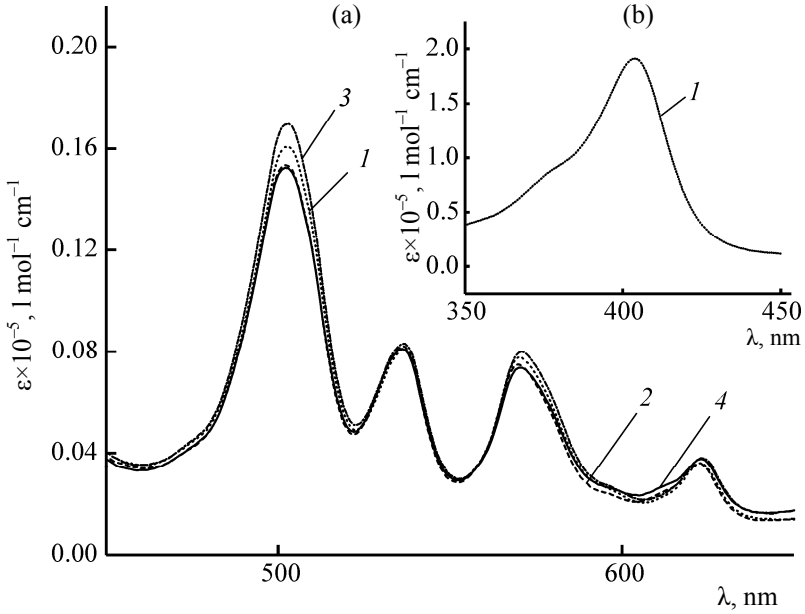


Fig. 1. UV-Vis spectra of porphyrins **Ia, Ib,** and **VIa, VIb** in chloroform. (a) λ= 450–650 nm (*l* 1 cm), (b) λ = 350–450 nm, Soret band; (*1*) **Ia**, (*2*) **Ib**, (*3*) **VIa**, and (*4*) **VIb**.

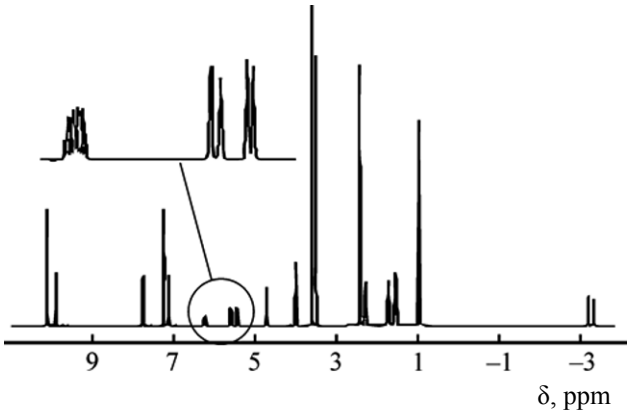


Fig. 2. ^{1}H NMR spectrum of compound **VIa** in $CDCl_3$.

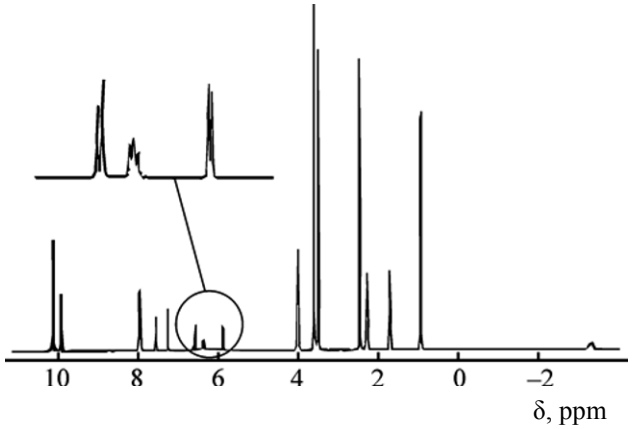


Fig. 3. ^{1}H NMR spectrum of compound **VIIa** in $CDCl_3$.

symmetric and asymmetric stretching vibrations of the amino groups merged into a single band of NH bond vibration of medium intensity near 3275 cm^{-1}.

In ^{1}H NMR spectra of compounds **VIa** and **VIb** there are four groups of signals of the protons of allyl fragment: a multiplet of one H_β proton at 6.05–6.30 ppm, two doublets in the region 5.6–5.2 ppm, corresponding to two H_α protons, and a doublet of two protons of CH_2 group at 4.71–4.68 ppm (Fig. 2). All the signals of protons of the allyl fragment of the porphyrin **VIb** are shifted upfield compared with the corresponding signals of the porphyrin **VIa** because of the effect of the porphyrin ring current on the substituent. The position of the signals of other protons remains almost unchanged.

Due to the conjugation of vinyl and carbonyl groups, in the ^{1}H NMR spectra of acrylamidoporphyrins **VIIa** and **VIIb** the relative positions of the signals of H_β and H_α protons changed (Fig. 3). As a result, the multiplet corresponding to the proton H_β occurs between the two doublets of H_α protons. The signals of protons of acrylamido group are recorded as singlets at 7.55 and 8.02 ppm for compounds **VIIa** and **VIIb**, respectively. The signals of the substituent in the *para*-position are somewhat shifted upfield compared with those of the substituent in *meta*-position of the phenyl ring due to the influence of the ring current of the macrocycle.

EXPERIMENTAL

Thin layer chromatography was performed on the POLYGRAM SIL G/UV254 plates. The electron absorption spectra were recorded on a SHUMADZU UV-2550 spectrophotometer from $CHCl_3$ solutions, ^{1}H NMR spectra (internal TMS) were taken from $CDCl_3$ solutions on a Bruker ARX Avance 400 spectrometer (400 MHz). The IR spectra were taken from KBr tablets on an Avatar 360 FT-IR ESP instrument. The mass spectra (MALDI-TOF) were obtained on a Bruker Autoflex mass spectrometer. Elemental analysis was performed on the CHNS-O FlashEA 1112 series analyzer.

5-(4'-Hydroxyphenyl) -2,3,7,8,12,18-hexamethyl-13,17-dipentylporphin (Ia). To a solution of 0.69 g (2.19 mmol) of 4,4'-dimethyl-3,3'-dipentyldipyrromethane and 0.55 g (4.46 mmol) of 2-formyl-3,4-dimethylpyrrole in 50 ml of methanol at room temperature was added while stirring 1.0 ml (8.3 mmol) of concentrated hydrobromic acid (biladiene precipitated), and after 1 h 2.0 g (16.4 mmol, 8-fold excess) of 4-hydroxybenzaldehyde was added. The mixture was heated to boiling and refluxed for 4 h, then gradually 2 ml of concentrated ammonia solution was added, and the reaction mixture was cooled. The precipitate was filtered off, washed with water, and dried in air at 70ºC. Porphyrin was dissolved in methylene chloride and chromatographed on aluminum oxide (activity II) eluting with methylene chloride–methanol (100:1 by volume). The purple eluate was evaporated, the porphyrin was precipitated by adding methanol, the precipitate was filtered off, washed with methanol, and dried in air at 70ºC. Yield 0.59 g (43.6%), R_f 0.54 (benzene–methanol, 10:1). UV-Vis, λ_{max}, nm (log ε): 404 (5.29), 503 (4.21), 537 (3.90), 571 (3.88) 624 (3.51). ^{1}H NMR spectrum, δ, ppm: 10.13 s (2H, 10,20-H), 9.93 s (1H, 15-H), 7.85 d (J = 7.5 Hz, 2H, $Ph_{2',6'H}$), 7.15 d (J = 8.2 Hz, 2H, $Ph_{3',5'H}$), 4.02 t (J = 7.5 Hz, 4H, 13,17-$C\underline{H}_2CH_2CH_2CH_2CH_3$), 3.62 s (6H, 12,18-$CH_3$), 3.52 s

(6H, 2,8-CH_3), 2.50 s (6H, 3,7-CH_3), 2.30 m (4H, 13,17-$CH_2CH_2CH_2C\underline{H}_2CH_3$), 1.73 m (4H, 13,17-$CH_2CH_2C\underline{H}_2CH_2CH_3$), 1.54 m (4H, 13,17-$CH_2CH_2CH_2C\underline{H}_2CH_3$), 0.96 t ($J$ = 6.8 Hz, 6H, 13,17-$CH_2CH_2CH_2CH_2C\underline{H}_3$), –3.23 br.s (2H, –NH) Mass spectrum: m/z 626.490 $[M]^+$. IR spectrum, ν, cm^{-1}: 3417 [ν(OH)], 1384 [δ(OH)]. Found, %: C 79.83, H 7.93, N 9.03, O 2.60. $C_{42}H_{50}N_4O$. Calculated, %: C 80.47, H 7.88, N 8.94, O 2.55. M 626.889.

5-(3'-Hydroxyphenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphin (Ib) was prepared similarly to compound **Ia**, solvent butanol. Purification of the porphyrin was carried out by column chromatography on aluminum oxide (activity II) with the eluent methylene chloride. Yield 0.67 g (47.9%). R_f = 0.64 (benzene–methanol, 10:1). UV-Vis, λ_{max}, nm (log ε): 404 (5.32), 503 (4.23), 537 (3.94), 570 (3.91), 623 (3.56). ^{1}H NMR spectrum, δ, ppm: 10.12 s (2H, 10,20-H), 9.88 s (1H, 15-H), 7.45 m (2H, $Ph_{4',5'H}$), 7.08 d (J = 7.0 Hz, 1H, $Ph_{6'H}$), 6.96 s (1H, $Ph_{2'H}$), 3.96 t (J = 7.0 Hz, 4H, 13,17-$C\underline{H}_2CH_2CH_2CH_2CH_3$), 3.58 s (6H, 12,18-$CH_3$), 3.49 s (6H, 2,8-$CH_3$), 2.37 s (6H, 3,7-$CH_3$), 2.26 m (4H, 13,17-$CH_2C\underline{H}_2CH_2CH_2CH_3$), 1.67 m (4H, 13,17-$CH_2CH_2C\underline{H}_2CH_2CH_3$), 1.52 m (4H, 13,17-$CH_2CH_2CH_2C\underline{H}_2CH_3$), 0.95 t ($J$ = 7.2 Hz, 6H, 13,17-$CH_2CH_2CH_2CH_2C\underline{H}_3$), –3.25 br.s (2H, –NH). Mass spectrum: m/z 626.507 $[M]^+$. IR spectrum, ν, cm^{-1}: 3417 [ν(OH)], 1300 [δ(OH)]. Found, %: C 79.97, H 7.95, N 9.02, O 2.51. $C_{42}H_{50}N_4O$. Calculated, %: C 80.47, H 7.88, N 8.94, O 2.55. M 626.889.

5-(4'-Nitrophenyl)-2,3,7,8,12,8-hexamethyl-13,17-dipentylporphin (IIa). To a solution of 0.69 g (2.19 mmol) of 4,4'-dimethyl-3,3'-dipentyldipyrromethane and 0.55 g (4.6 mmol) of 2-formyl-3,4-dimethylpyrrole in 50 ml of butanol at room temperature while stirring was added 1.0 ml (8.3 mmol) of concentrated hydrobromic acid (biladiene precipitated), after 1 h 4.0 g (26.47 mmol, a 12-fold excess) of 4-nitrobenzaldehyde was added, the mixture was heated to boiling and refluxed for 4 h. Then to the reaction mixture was slowly added 2 ml of concentrated ammonia solution and the mixture was cooled. The precipitate was filtered off, washed with methanol, and dried at 70ºC in air. Purification of the porphyrin was carried out by column chromatography on aluminum oxide (activity II) using as eluent methylene chloride. Yield 0.70 g (48.7%). R_f = 0.58 (benzene). UV-Vis, λ_{max}, nm (log ε): 402 (5.25), 504 (4.22), 538 (3.95), 572 (3.91), 624 (3.62). ^{1}H NMR spectrum, δ, ppm: 10.16 s (2H, 10,20-H), 9.96 s (1H, 15-H), 8.56 d (J = 8.2 Hz, 2H, $Ph_{2',6'H}$), 8.19 d (J = 7.9 Hz, 2H, $Ph_{3',5'H}$), 3.01 t (J = 7.0 Hz, 4H, 13,17-$C\underline{H}_2CH_2CH_2CH_2CH_3$), 3.62 s (6H, 12,18-$CH_3$), 3.52 s (6H, 2,8-$CH_3$), 2.37 s (6H, 3,7-$CH_3$), 2.29 m (4H, 13,17-$CH_2C\underline{H}_2CH_2CH_2CH_3$), 1.72 m (4H, 13,17-$CH_2CH_2C\underline{H}_2CH_2CH_3$), 1.57 m (4H, 13,17-$CH_2CH_2$·$CH_2C\underline{H}_2CH_3$), 0.95 t ($J$ = 7.0 Hz, 6H, CH_3), –3.22 s (1H, NH), –3.36 s (1H, NH). Mass spectrum: m/z 655.513 $[M]^+$. IR spectrum, ν, cm^{-1}: 1516 [$\nu_{as}(NO_2)$], 1343 [$\nu_s(NO_2)$]. Found, %: C 76.55, H 6.87, N 10.79, O 4.86. $C_{42}H_{49}N_5O_2$. Calculated, %: C 76.91, H 6.92, N 10.68, O 4.88. M 655.887.

5-(3'-Nitrophenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphin (IIb) was prepared similarly to compound **IIa**. Yield 0.60 g (41.8%). R_f = 0.60 (benzene). UV-Vis, λ_{max}, nm (log ε): 403 (5.25), 505 (4.25), 539 (4.01), 572 (3.95), 625 (3.70). ^{1}H NMR spectrum, δ, ppm: 10.17 s (2H, 10,20-H), 9.98 s (1H, 15-H), 8.99 s (1H, $Ph_{2'H}$), 8.69 d (J = 8.0 Hz, 1H, $Ph_{6'H}$), 8.37 d (J = 6.4 Hz, 1H, $Ph_{4'H}$), 7.90 t (J = 7.0 Hz, 1H, $Ph_{5'H}$), 4.03 t (J = 7.2 Hz, 13,17-$C\underline{H}_2CH_2CH_2CH_2CH_3$), 3.63 s (6H, 12,18-$CH_3$), 3.53 s (6H, 2,8-$CH_3$), 2.40 s (6H, 3,7-$CH_3$), 2.30 m (4H, 13,17-$CH_2C\underline{H}_2CH_2CH_2CH_3$), 1.72 m (4H, 13,17-$CH_2CH_2C\underline{H}_2CH_2CH_3$), 1.53 m (4H, (4H, 13,17-$CH_2CH_2CH_2C\underline{H}_2CH_3$), 0.96 t ($J$ = 7.2 Hz, 6H, 13,17-$CH_2CH_2CH_2CH_2C\underline{H}_3$), –3.21 s (1H, NH), –3.35 s (1H, NH). Mass spectrum: m/z 655.436 $[M]^+$. IR spectrum, ν, cm^{-1}: 1531 [$\nu_{as}(NO_2)$], 1343 [$\nu_s(NO_2)$]. Found, %: C 76.63, H 6.88, N 10.72, O 4.86. $C_{42}H_{49}N_5O_2$. Calculated, %: C 76.91, H 6.92, N 10.68, O 4.88. M 655.887.

5-(4'-Aminophenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphin (IIc). To a solution of 0.5 g (0.76 mmol) of 5-(4'-nitrophenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphin **IIa** in 50 ml of MeOH was added 2.5 g (11.1 mmol) of $SnCl_2·2H_2O$, and 2 ml of concentrated HCl. The synthesis was carried out under continuous stirring for 20 h at room temperature. Then to the mixture was added 5.0 g (89.11 mmol) of potassium hydroxide and 50 ml of water. The precipitate was filtered off, washed with water, and dried at 70ºC. Purification of the porphyrin was carried out by column chromatography on aluminum oxide (activity II) using methylene chloride as eluent. Yield 0.42 g (88.3%). R_f = 0.66 (benzene–methanol, 10:1). UV-Vis, λ_{max}, nm (log ε): 405 (5.30), 504 (4.22), 537 (3.89), 571 (3.89), 624 (3.53). ^{1}H NMR spectrum, δ, ppm: 10.14 s (2H, 10,20-H), 9.93 s (1H, 15-H), 7.77 d (J = 8.1 Hz, 2H, $Ph_{2',6'H}$), 7.06 d (J = 8.1 Hz, 2H, $Ph_{3',5'H}$), 4.03 t (J = 8.1 Hz, 4H,

13,17-C$\underline{H}_2$CH$_2$CH$_2$CH$_2$CH$_3$), 3.62 s (6H, 12,18-CH$_3$), 3.53 s (6H, 2,8-CH$_3$), 2.57 s (6H, 3,7-CH$_3$), 2.30 m (4H, 13,17-CH$_2$C$\underline{H}_2$CH$_2$CH$_2$CH$_3$), 1.73 m (4H, 13,17-CH$_2$CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 1.54 m (4H, 13,17-CH$_2$CH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 0.96 t (J = 8.1 Hz, 6H, CH$_3$), –3.26 br.s. (2H, NH). Mass spectrum: m/z 625.720 $[M]^+$. IR spectrum, ν, cm^{-1}: 3440 [ν_{as}(NH)], 3382 [ν_s(NH)]. Found, %: C 79.84, H 8.30, N 11.25. $C_{42}H_{51}N_5$. Calculated, %: C 80.60, H 8.21, N 11.19. M 625.905.

5-(3'-Aminophenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphin (IId) was prepared similarly to compound **IIb**. Yield 0.46 g (96.1%). R_f = 0.72 (benzene–methanol, 10:1). UV-Vis, λ_{max}, nm (log ε): 404 (5.32), 503 (4.25), 537 (3.94), 571 (3.92), 623 (3.58). ^{1}H NMR spectrum, δ, ppm: 10.15 s (2H, 10,20-H), 9.93 s (1H, 15-H), 7.49 m (2H, Ph$_{5',6'H}$), 7.32 s (1H, Ph$_{2'H}$), 7.09 d (J = 7.4 Hz, 1H, Ph$_{4'H}$), 4.03 t (J = 7.5 Hz, 4H, 13,17-C$\underline{H}_2$CH$_2$CH$_2$CH$_2$CH$_3$), 3.63 s (6H, 12,18-CH$_3$), 3.54 s (6H, 2,8-CH$_3$), 2.61 s (6H, 3,7-CH$_3$), 2.30 m (4H, 13,17-CH$_2$C$\underline{H}_2$CH$_2$CH$_2$CH$_3$), 1.73 m (4H, 13,17-CH$_2$CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 1.54 m (4H, 13,17-CH$_2$CH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 0.96 t (J = 7.4 Hz, 6H), –3.29 br.s. (2H, NH). Mass spectrum: m/z 625.643 $[M]^+$. IR spectrum, ν, cm^{-1}: 3450 [ν_{as}(NH)], 3374 [ν_s(NH)]. Found, %: C 80.23, H 8.15, N 11.25. $C_{42}H_{51}N_5$. Calculated, %: C 80.60, H 8.21, N 11.19. M 625.905.

5-(4'-Allyloxyphenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphyn (VIa). To a solution of 63 mg (0.1 mmol) of porphyrin **Ia** in 10 ml DMF was added 138 mg (1 mmol) of potassium carbonate and 0.08 ml (1 mmol) of allyl bromide. The mixture was heated at 100°C in an oil bath and kept at this temperature with stirring for 2 h. The reaction mixture was poured into water, the precipitate was filtered off, washed with water, methanol, and dried in a vacuum at 70ºC. Purification of the porphyrin was carried out by column chromatography on silica gel, eluting porphyrin with chloroform. Yield 41.4 mg (62%). R_f = 0.50 (benzene–methanol, 10:0.05). UV-Vis, λ_{max}, nm (log ε): 404 (5.29), 503 (4.23) and 536 (3.92), 571 (3.91), 623 (3.61). ^{1}H NMR spectrum, δ, ppm: 10.11 s (2H, 10,20-H), 9.90 s (1H, 15-H), 7.76 d (J = 8.0 Hz, 2H, Ph$_{2',6'H}$), 7.13 d (J = 8.0 Hz, 2H, Ph$_{3',5'H}$), 6.24 m (1H, OCH$_2$C$\underline{H}$=CH$_2$), 5.59 d.d (J = 17.0 Hz, J = 1.3 Hz, 1H, OCH$_2$CH=C$\underline{H}_2$), 5.44 d.d (J = 17.0 Hz, J = 1.3 Hz, 1H, OCH$_2$CH=C$\underline{H}_2$), 4.71 d (J = 5.3 Hz, 2H, OC$\underline{H}_2$CH=CH$_2$), 3.99 t (J = 7.6 Hz, 4H, 13,17-C$\underline{H}_2$CH$_2$CH$_2$CH$_2$CH$_3$), 3.59 s (6H, 12,18-CH$_3$), 3.50 s (6H, 2,8-CH$_3$), 2.42 s (6H, 3,7-CH$_3$), 2.28 m (4H, 13,17-CH$_2$C$\underline{H}_2$CH$_2$CH$_2$CH$_3$), 1.72 m (4H, 13,17-CH$_2$CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 1.52 m (4H, 13,17-CH$_2$CH$_2$·CH$_2$C$\underline{H}_2$CH$_3$), 0.96 t (J = 7.1 Hz, 6H, 13,17-CH$_2$CH$_2$·CH$_2$CH$_2$C$\underline{H}_3$), –3.20 s (1H, NH), –3.33 s (1H, NH). Mass spectrum: m/z 666.511 $[M]^+$. IR spectrum, ν, cm^{-1}: 1240 [ν_{as}(COC)], 1022 [ν_s(COC)]. Found, %: C 80.70, H 8.22, N 8.44, O 2.42. $C_{45}H_{54}N_4O$. Calculated, %: C 81.04, H 8.16, N 8.40, O 2.40. M 666.954.

5-(3'-Allyloxyphenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphyn (VIb) was prepared similarly to compound **VIa** from 5-(3'-hydroxyphenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphin **Ib**. Yield 46.7 mg (70%). R_f = 0.70 (benzene–methanol, 10:0.05). UV-Vis, λ_{max}, nm (log ε): 403 (5.22), 502 (4.16), 536 (3.90), 570 (3.86), 623 (3.57). ^{1}H NMR spectrum, δ, ppm: 10.15 s (2H, 10,20-H), 9.94 s (1H, 15-H), 7.62 m (3H, Ph$_{2',5',6'H}$), 7.35 d (J = 7.9 Hz, 1H, Ph$_{4'H}$), 6.11 m (1H, OCH$_2$C$\underline{H}$=CH$_2$), 5.45 d (J = 17.0 Hz, 1H, OCH$_2$CH=C$\underline{H}_2$), 5.29 d (J = 17.0 Hz, 1H, OCH$_2$CH=C$\underline{H}_2$), 4.68 d (J = 5.2 Hz, 2H, OC$\underline{H}_2$CH=CH$_2$), 4.02 t (J = 7.6 Hz, 4H, 13,17-C$\underline{H}_2$CH$_2$CH$_2$CH$_2$CH$_3$), 3.61 s (6H, 12,18-CH$_3$), 3.52 s (6H, 2,8-CH$_3$), 2.50 s (6H, 3,7-CH$_3$), 2.28 m (4H, 13,17-CH$_2$C$\underline{H}_2$CH$_2$CH$_2$CH$_3$), 1.71 m (4H, 13,17-CH$_2$·CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 1.53 m (4H, 13,17-CH$_2$CH$_2$CH$_2$·CH$_2$CH$_2$CH$_3$), 0.94 t (J = 7.3 Hz, 6H, 13,17-CH$_2$CH$_2$·CH$_2$CH$_2$C$\underline{H}_3$), –3.22 s (1H, NH), –3.36 s (1H, NH). Mass spectrum: m/z 666.489 $[M]^+$. IR spectrum, ν, cm^{-1}: 1240 [ν_{as}(COC)], 1022 [ν_s(COC)]. Found, %: C 80.78, H 8.28, N 8.24, O 2.38. $C_{45}H_{54}N_4O$. Calculated, %: C 81.04, H 8.16, N 8.40, O 2.40. M 666.954.

5-(4'-Acrylamidophenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphin (VIIa). To a solution of 100 mg (0.16 mmol) of porphyrin **IIb** in 10 ml of tetrahydrofuran (THF) was added 0.22 ml (1.6 mmol) of anhydrous triethylamine. Then, while stirring and cooling with ice water, to it was added dropwise in 5 min a solution of 0.13 ml (1.6 mmol) of acryloyl chloride in 5 ml of THF. The reaction mixture was stirred for 24 h at room temperature, and them the solvent was evaporated. The dry residue was dissolved in 20 ml of chloroform and washed successively with 5% HCl, saturated aqueous solution of NH_4OH, and then with water. The organic layer was dried over $MgSO_4$, the solvent was distilled off to dryness. Purification of the porphyrin was carried out by column chromatography on aluminum oxide (activity II) using chloroform as eluent. Yield 74 mg (68%). R_f = 0.72 (benzene–methanol, 10:1). UV-Vis, λ_{max}, nm (log ε): 404 (5.26), 503 (4.17), 537 (3.86), 570 (3.84), 623 (3.51). ^{1}H NMR spectrum, δ, ppm: 10.12 s (2H,

10,20-H), 9.92 s (1H, 15-H), 7.97 d (J = 8.2 Hz, 2H, $Ph_{2',6'H}$), 7.93 d (J = 7.9 Hz, 2H, $Ph_{3',5'H}$), 7.55 s (1H, N<u>H</u>COCH=CH_2), 6.58 d (J = 17.1 Hz, 1H, NHCO·CH=C<u>H</u>$_2$), 6.36 m (1H, NHCOC<u>H</u>=CH_2), 5.87 d (J = 10.4 Hz, 1H, NHCOCH=C<u>H</u>$_2$), 4.01 t (J = 7.6 Hz, 4H, 13,17-C<u>H</u>$_2$$CH_2CH_2CH_2CH_3$), 3.60 s (6H, 12,18-$CH_3$), 3.49 s (6H, 2,8-$CH_3$), 2.47 s (6H, 3,7-$CH_3$), 2.27 m (4H, 13,17-$CH_2$C<u>H</u>$_2$$CH_2CH_2CH_3$), 1.72 m (4H, 13,17-$CH_2$·$CH_2$C<u>H</u>$_2$$CH_2CH_3$), 1.55 m (4H, 13,17-$CH_2CH_2$·C<u>H</u>$_2$$CH_2CH_3$), 0.94 t ($J$ = 7.3 Hz, 6H, 13,17-CH_2CH_2·CH_2CH_2C<u>H</u>$_3$), –3.33 br.s. (2H, NH). Mass spectrum: m/z 680.495 $[M]^+$. IR spectrum, ν, cm^{-1}: 1669 [ν(CO)], 3275 [ν(NHCO)]. Found, %: C 79.27, H 7.80, N 10.38, O 2.38. $C_{45}H_{53}N_5O$. Calculated, %: C 79.49, H 7.86, N 10.30, O 2.35. M 679.953.

5-(3'-Acrylamidophenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphyn (VIIb) was prepared similarly to compound **VIIa** from 5-(3'-aminophenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphin **IId**. Yield 70.7 mg (65%). R_f = 0.62 (benzene–methanol, 10:1). UV-Vis, λ_{max}, nm (log ε): 403 (4.50), 503 (4.12), 536 (3.84), 570 (3.81), 623 (3.50). ^{1}H NMR spectrum, δ, ppm: 10.14 s (2H, 10,20-H), 9.93 s (1H, 15-H), 8.26 d (J = 6.1 Hz, 1H, $Ph_{6'H}$), 8.02 s (1H, N<u>H</u>COCH=CH_2), 7.83 d (J = 6.9 Hz, 1H, $Ph_{4'H}$), 7.70 t (J = 7.9 Hz, 1H, $Ph_{5'H}$), 7.41 s (1H, $Ph_{2'H}$), 6.46 d (J = 16.7 Hz, 1H, NHCOCH=C<u>H</u>$_2$), 6.24 m (1H, NHCOC<u>H</u>=CH_2), 5.77 d (J = 10.1 Hz, 1H, NHCOCH=C<u>H</u>$_2$), 4.01 t (J = 7.6 Hz, 4H, 13,17-C<u>H</u>$_2$$CH_2CH_2CH_2CH_3$), 3.61 s (6H, 12,18-$CH_3$), 3.50 s (6H, 2,8-$CH_3$), 2.50 s (6H, 3,7-$CH_3$), 2.28 m (4H, 13,17-$CH_2$C<u>H</u>$_2$$CH_2CH_2CH_3$), 1.71 m (4H, 13,17-$CH_2CH_2$C<u>H</u>$_2$$CH_2CH_3$), 1.53 m (4H, 13,17-$CH_2CH_2CH_2$C<u>H</u>$_2$$CH_3$), 0.94 t ($J$ = 7.3 Hz, 6H, 13,17-$CH_2CH_2CH_2CH_2$C<u>H</u>$_3$), –3.31 br.s. (1H, NH). Mass spectrum: m/z 680.380 $[M]^+$. IR spectrum, ν, cm^{-1}: 1669 [ν(CO)], 3275 [ν(NHCO)]. Found, %: C 79.17, H 7.93, N 10.40, O 2.38. $C_{45}H_{53}N_5O$. Calculated, %: C 79.49, H 7.86, N 10.30, O 2.35. M 679.953.

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