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Synthesis of Nitrogen- and Oxygen-Containing Macrocycles by Palladium-Catalyzed Amination of 3,24-Bis(6-chloropyridin-2-yloxy)cholane

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Abstract—3,24-Bis(6-chloropyrdin-2-yloxy)cholane prepared from cholane-3,24-diol by the Mitsunobu reaction was successfully used to synthesize various polyaza macrocycles via palladium-catalyzed amination with linear polyamines. The contribution of side formation of cyclic oligomers was found to depend on the polyamine nature.

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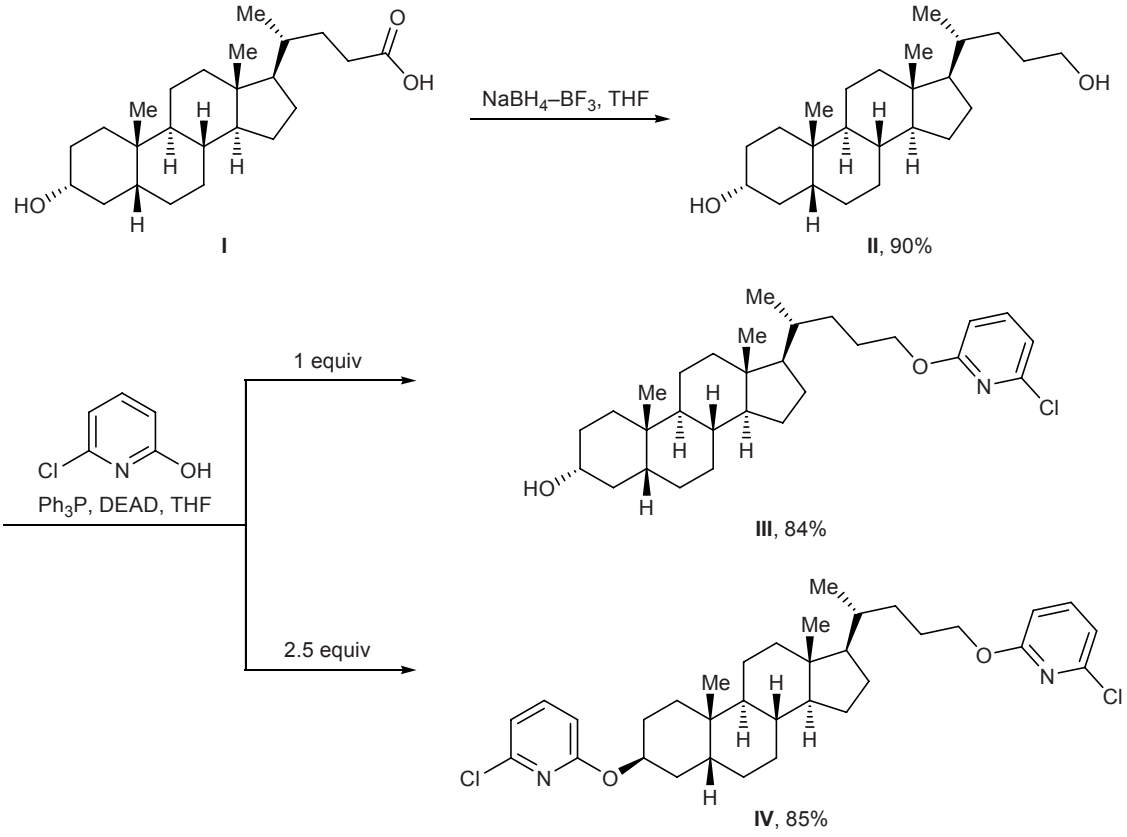
Macrocyclic compounds containing 2–4 cholic acid fragments that are linked through various spacers are referred to as cholaphanes, and they attract considerable interest from the viewpoint of design of molecular sensors. Steroid fragments can be linked to each other through amide [1–3], ether [4–8], and polyether (ethylene glycol) bridges [9]. Another group of macrocycles based on steroid scaffold includes those resembling crown ethers; such structures are obtained by attachment of a polyoxaalkyl chain at two positions of the steroid molecule [10–13]. We recently developed another synthetic approach to macrocycles containing steroid fragments. It is based on palladium-catalyzed amination of haloaryl derivatives of cholanediol with linear polyamines [14, 15]. In the present article we describe a catalytic synthesis of cholanediol-based macrocycles with pyridine fragments as aromatic spacers. Our choice was dictated by the presence of a nitrogen atom in the pyridine ring, which was expected to enhance complexing power of the resulting macrocycles and probably their biological activity.

Cholane-3,24-diol (**II**) was synthesized in 90% yield by reduction of lithocholic acid (**I**, 3α-hydroxy-5β-cholan-24-oic acid) with diborane in anhydrous tetrahydrofuran. The Mitsunobu reaction [16] of **II** with 1 equiv of 6-chloropyridin-2-ol gave 24-(6-chloropyridin-2-yloxy)cholane (**III**) in 84% yield (Scheme 1). In this case we observed selective and complete substitution at the C^{24} atom, in contrast to analogous reaction with 3-bromophenol [14]. Treatment of diol **II** with 2.5 equiv of 6-chloropyridin-2-ol under similar conditions gave 85% of 3,24-bis(6-chloropyridin-2-yloxy)-cholane (**IV**).

Compound **IV** was subjected to palladium-catalyzed amination [17, 18] with various polyamines **Va**–**Vi** (Scheme 2). The reactions were carried out in boiling dioxane at a reactant concentration of 0.02 M using $Pd(dba)_2$/BINAP (8–9 mol %) as catalyst and sodium *tert*-butoxide as base. The reactions were complete in 15 h, and the reaction mixtures were analyzed by ^1H and ^{13}C NMR spectroscopy before chromatographic separation. Macrocyclic compounds **VI** were isolated by column chromatography on silica gel, and their yields strongly depended on the polyamine nature, primarily on the length of the aminoalkyl chain.

In the reaction with short-chain propane-1,3-diamine (**Va**) we obtained only cyclic dimer **VIIa** in 38% yield (see table, run no. 1). An additional amount of compound **VIIa** (21%) was also isolated as a separate fraction which also contained BINAP dioxide and dioxane at a molar ratio of 4 : 1 : 2. The reaction with triamine **Vb** gave 25% of cyclic dimer **VIIb** and 46% of an inseparable mixture of cyclic dimer **VIIb**, trimer **VIIIb**, and tetramer **IXb** (run no. 2). The target macro-

Scheme 1.

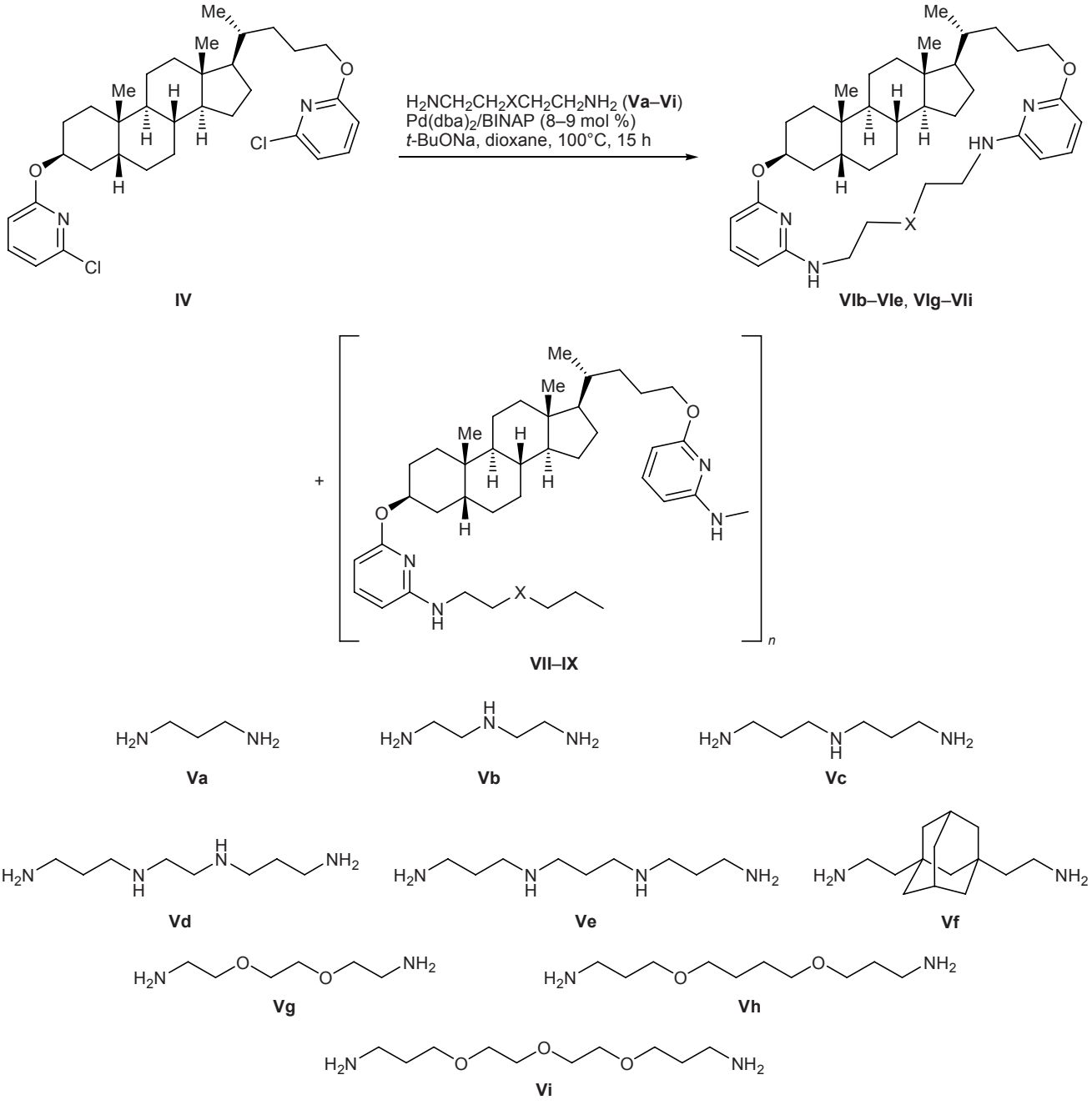


cycle **VIb** was detected only in trace amount by MALDI-TOF mass spectrometry (*m/z* 616.3 $[M + H]^+$). Triamine **Vc** having a longer aminoalkyl chain reacted with compound **IV** to afford 9% of macrocycle **VIc**; however, the latter was isolated in a mixture with cyclic dimer **VIIc** (12%). In addition, a fraction containing dimer **VIIc**, trimer **VIIIc**, and tetramer **IXc** (overall yield 33%, run no. 3) was isolated. Analogous result was obtained in the reaction with *N*,*N*′-bis(3-aminopropyl)ethane-1,2-diamine (**Vd**): the yield of **VId** was 7% (in a mixture with dimer **VIId**, run no. 4). Appreciably higher yield of the desired macrocyclic compound was obtained with *N*,*N*′-bis(3-aminopropyl)propane-1,3-diamine (**Ve**); compound **VIe** was isolated in 29% yield, and the product was separated from dimer **VIIe** (66%, run no. 5). The reaction with diamine **Vf** containing an adamantane fragment gave no corresponding macrocycle **VIf**, presumably because of insufficient length of the spacer; the yield of cyclic dimer **VIIf** was 15%, and the overall yield of higher cyclic oligomers was

Reaction of 3,24-bis(6-chloropyrdin-2-yloxy)cholane (**IV**) with polyamines **Va**–**Vi**

Run no.	Amine	Macrocycle, yield, %	Cyclic dimers and oligomers, yield, %
1	**Va**	**VIa**, 0	**VIIa**, 38; **VIIa**/BINAP dioxide/dioxane (4:1:2), 21
2	**Vb**	**VIb**, traces	**VIIb**, 25; **VIIb**/**VIIIb**/**IXb**, 46
3	**Vc**	**VIc**, 9	**VIIc**, 12; **VIIc**/**VIIIc**/**IXc**, 33
4	**Vd**	**VId**, 7	**VIId**, 19
5	**Ve**	**VIe**, 29	**VIIe**, 66
6	**Vf**	–	**VIIf**, 15; higher oligomers, 22
7	**Vg**	**VIg**, 6	**VIIg**/**VIIIg**, 14; higher oligomers, 60
8	**Vh**	**VIh**, 22	**VIIh**, 12; higher oligomers, 23
9	**Vi**	**VIi**, 21	**VIIi**, 10; higher oligomers, 33

Scheme 2.



VII, $n = 2$; **VIII**, $n = 3$; **IX**, $n = 4$; dba is dibenzylideneacetone.

22% (run no. 6). The reactions of **IV** with di- and trioxaalkane-α,ω-diamines **Vg**–**Vi** gave similar results. The shortest diamine **Vg** gave rise to only 6% of macrocycle **VIg** (run no. 7), while the yields of **VIh** and **VIi** from diamines **Vh** and **Vi** having a longer chain were 22 and 21%, respectively (run nos. 8, 9).

The results of catalytic amination of 3,24-bis(6-chloropyridin-2-yloxy)cholane (**IV**) somewhat differ from those obtained by us previously with 3,24-bis(3-bromophenoxy)cholane [14]. Poor yields of the target macrocyclic compounds **VI** and formation of large amounts of oligomeric products may be rationalized in terms of reduced reactivity of chlorine atom in catalytic amination. This may led to low rate of the intramolecular amination after replacement of the first chlorine atom in **IV**. The open-chain intermediate thus

formed is capable of reacting with the second molecule of **IV**, giving rise to oligomeric products despite low reactant concentration. It should also be noted that cyclic dimers **VII** may be formed as "head-to-head" and "head-to-tail" regioisomers. The number of possible regioisomers for higher oligomers **VIII** and **IX** is even greater.

The ^{1}H NMR spectra of compounds **VI** characteristically contained a signal at δ 5.30–5.35 ppm from proton on C^3; in addition, a large difference in the chemical shifts of diastereotopic protons on C^{24} was observed (δ 4.0–4.3 ppm). Oxa diamine derivatives **VIg**–**VIi** displayed a large difference in the chemical shifts of the two NH protons (Δδ = 0.3–0.5 ppm). In the ^{1}H NMR spectra of cyclic dimers **VII**, protons on C^3 resonated in a stronger field (δ 5.0–5.2 ppm); in some cases the 3-H signal appeared as two nearby broadened singlets with different intensities due to the presence of two regioisomers. The spectra of cyclic dimers showed no difference in the chemical shifts of diastereotopic protons on C^{24} and NH protons; the corresponding signals were broadened singlets. In the ^{13}C NMR spectra of compounds **VI**, the C^{14} and C^{17} signals were located at δ_C 57–58 and 53–54 ppm, i.e. the difference in the chemical shifts is 3–4 ppm. Analogous signals in the spectra of cyclic dimers **VII** appeared close to each other (δ_C 55–56 ppm). Some carbon atoms in dimers **VII** gave rise to a set of closely located singlets with different intensities instead of one singlet. This pattern was observed for carbon atoms in the polyazaalkyl chain, C^{14} and C^{17} in the steroid fragment, and carbon atoms in positions *3* and *5* of the pyridine rings. Probable reasons are both the presence of two regioisomers and restricted rotation in the polyazaalkyl chains due to intramolecular hydrogen bonding. An indirect support for the latter factor is provided by appreciable reduction in the multiplicity of signals in going from $CDCl_3$ to DMSO-d_6. The ^{1}H NMR spectra recorded from solutions in DMSO-d_6 also revealed a considerable downfield shift of the NH signals (δ 6.5–6.7 ppm). Unfortunately, signals from several carbon atoms in the steroid skeleton were overlapped by the CD_3 multiplet of the solvent (DMSO-d_6). Finally, no appreciable differences in the spectral patterns of cyclic dimers and higher cyclic oligomers were observed, except for broadening of all signals in the ^{1}H and ^{13}C NMR spectra. Macrocycles **VI** give much more intense signals in the MALDI mass spectra, as compared to cyclic dimers **VII**; therefore, this method cannot be used to estimate their ratio in the reaction mixtures on a quantitative level.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker Avance-400 spectrometer at 400 and 100.6 MHz, respectively, using the solvent signals as reference ($CHCl_3$, δ 7.25 ppm; $CDCl_3$, δ_C 77.00 ppm). The MALDI-TOF mass spectra (positive ion registration) were obtained on a Bruker Daltonics Ultrafex instrument using 1,8,9-trihydroxyanthracene as matrix. Preparative column chromatography was performed on Merck silica gel (40–60 μm). Lithocholic acid (**I**), sodium tetrahydridoborate, boron trifluoride–ether complex, polyamines **Va**–**Ve** and **Vg**–**Vi**, sodium *tert*-butoxide, and cesium carbonate were commercial products which were used without additional purification. Bis(dibenzylideneacetone)palladium(0) [$Pd(dba)_2$] was synthesized according to the procedure described in [19] without additional recrystallization. 2,2′-(Adamantane-1,3-diyl)di(ethanamine) (**Vf**) was prepared as reported in [20]. Dioxane and tetrahydrofuran were distilled first over alkali and then over metallic sodium, diethyl ether was distilled over alkali, and methylene chloride and methanol were distilled prior to use.

3α,5β-Cholane-3,24-diol (II). A 500-ml two-necked flask equipped with a dropping funnel, reflux condenser, and magnetic stirrer was filled with argon and charged with 4.92 g (113 mmol) of sodium tetrahydridoborate, 5.61 g (15 mmol) of lithocholic acid (**I**), and 150 ml of anhydrous tetrahydrofuran, and 18.5 ml (150 mmol) of boron trifluoride–ether complex was added dropwise under stirring. During the addition, an abundant white curdy material separated. When the entire amount of $BF_3 \cdot Et_2O$ was added, the mixture was stirred for 24 h and carefully treated with 100 ml of a saturated aqueous solution of sodium chloride, 200 ml of water was added until complete dissolution of boric acid, and the mixture was extracted with methylene chloride (300 ml). The aqueous phase was washed with methylene chloride (2× 100 ml), the washings were combined with the extract and dried over sodium sulfate, and the solvent was distilled off under reduced pressure. The residue was cholanediol **II** as a colorless powder which was recrystallized from 400 ml of acetone. Yield 4.88 g (90%), mp 172–173°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.63 s (3H), 0.91 s (3H), 0.92 d (3H, ^3J = 5.6 Hz), 0.95–1.89 m (27H), 1.93–1.97 m (1H), 3.55–3.65 m (3H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.0, 18.6, 20.8, 23.4, 24.2, 26.4, 27.2, 28.3, 29.4, 30.6,

31.8, 34.6, 35.3, 35.6, 35.9, 36.5, 40.2, 40.5, 42.1, 42.7, 56.2, 56.5, 63.6, 71.9.

24-(6-Chloropyridin-2-yloxy)-3α,5β-cholane (III). A mixture of 3 mmol (1.086 g) of cholane-3,24-diol (**II**), 75 ml of anhydrous THF, 3 mmol (389 mg) of 6-chloropyridin-2-ol, 3 mmol (786 mg) of triphenylphosphine, and 3 mmol (534 mg or 1.38 ml of a 40% solution in toluene) of diethyl azodicarboxylate was stirred for 24 h under argon at room temperature. Most part of the solvent was distilled off under reduced pressure, diethyl ether was added to precipitate triphenylphosphine oxide, and the latter was filtered off. The transparent filtrate was evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel using methylene chloride as eluent. Yield 1.186 g (84%), colorless oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.60 s (3H), 0.87 s (3H), 0.90 d (3H, ^3J = 6.5 Hz), 0.95–1.96 m (28H), 2.14 br.s (1H), 3.52–3.61 m (1H), 4.15–4.24 m (2H), 6.58 d (1H, ^3J = 8.0 Hz), 6.82 d (1H, ^3J = 7.6 Hz), 7.45 t (1H, J = 7.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.1, 18.6, 20.8, 23.4, 24.2, 25.5, 26.4, 27.2, 28.2, 30.6, 32.0, 34.6, 35.3, 35.5, 35.8, 36.5, 40.2, 40.4, 42.1, 42.7, 56.2, 56.5, 67.2, 71.9, 109.1, 116.0, 140.4, 148.3, 163.8. MALDI-TOF mass spectrum: m/z 473.4 $[M]^+$.

3,24-Bis(6-chloropyridin-2-yloxy)-3α,5β-cholane (IV) was synthesized in a similar way from 3.7 mmol (1.344 g) of diol **II** and 9.25 mmol (1.198 g) of 6-chloropyridin-2-ol in the presence of 9.25 mmol (2.424 g) of triphenylphosphine and 9.25 mmol (1.646 g or 4.25 ml of a 40% solution in toluene) of diethyl azodicarboxylate in 100 ml of anhydrous THF. Yield 1.841 g (85%), colorless oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.65 s (3H), 0.94 d (3H, ^3J = 6.4 Hz), 0.97 s (3H), 1.02–2.03 m (28H), 4.20–4.28 m (2H), 5.31 br.s (1H), 6.60 d.d (1H, ^3J = 8.2, ^4J = 0.6 Hz), 6.62 d.d (1H, ^3J = 8.2, ^4J = 0.6 Hz), 6.82 d.d (1H, ^3J = 7.4, ^4J = 0.6 Hz), 6.86 d.d (1H, ^3J = 7.4, ^4J = 0.6 Hz), 7.46 t (1H, ^3J = 7.8 Hz), 7.49 t (1H, ^3J = 7.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.1, 18.6, 21.1, 23.8, 24.2, 24.8, 25.4, 26.2, 26.6, 28.2, 30.4, 30.6, 32.0, 34.9, 35.4, 35.7, 37.2, 39.9, 40.2, 42.7, 56.1, 56.6, 67.2, 71.9, 109.1, 109.7, 115.6, 115.9, 140.4 (2C), 148.3 (2C), 163.2, 163.7. MALDI-TOF mass spectrum: m/z 584.5 $[M]^+$.

Macrocyclic compounds VI and cyclic dimers VII (*general procedure*). A mixture of 0.5 mmol of compound **IV**, 24 mg (8 mol%) of $Pd(dba)_2$, 28 mg (9 mol%) of BINAP, and 25 ml of anhydrous 1,4-dioxane was stirred for 2–3 min under argon, 0.5 mmol of polyamine **Va**–**Vi** and 144 mg (1.5 mmol) of sodium *tert*-butoxide were added, and the mixture was heated for 15 h under reflux. The mixture was cooled, the liquid phase was separated by decanting, the solid phase was washed with a small amount of methylene chloride, the washings were combined with the organic solution and evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel using the following solvent systems as eluents (in succession): CH_2Cl_2, CH_2Cl_2–MeOH (500:1 to 3:1), and CH_2Cl_2–MeOH–aq. NH_3 (100:20:1 to 10:4:1).

Cyclic dimer VIIa was obtained from 0.56 mmol (328 mg) of compound **IV** and 0.56 mmol (42 mg) of propane-1,3-diamine (**Va**). Eluent CH_2Cl_2–MeOH (25:1 to 5:1). Yield 126 mg (38%), light yellow crystals, mp 146–148°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.65 s (6H), 0.94 d (6H, ^3J = 6.4 Hz), 0.96 s (6H), 0.99–2.03 m (60H), 3.35 d.t (8H, ^3J = 7.3, 6.1 Hz), 4.08–4.18 m (4H), 4.49 br.s (4H), 5.15 s (2H), 5.88 d (2H, ^3J = 7.9 Hz), 5.91 d (2H, ^3J = 8.1 Hz), 5.98 d (4H, ^3J = 7.9 Hz), 7.29 t (2H, ^3J = 7.6 Hz), 7.30 t (2H, ^3J = 7.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.1 (2C), 18.7 (2C), 21.1 (2C), 23.8 (2C), 24.2 (2C), 25.0 (2C), 25.8 (2C), 26.3 (2C), 26.7 (2C), 28.3 (2C), 29.8 (2C), 30.7 (4C), 32.2 (2C), 34.9 (2C), 35.6 (2C), 35.7 (2C), 37.2 (2C), 39.8 (4C), 40.0 (2C), 40.3 (2C), 42.8 (2C), 56.3 (2C), 56.7 (2C), 66.3 (2C), 70.5 (2C), 97.3 (4C), 97.7 (2C), 98.2 (2C), 139.8 (2C), 139.9 (2C), 157.8 (4C), 163.0 (2C), 163.5 (2C). MALDI-TOF mass spectrum: m/z 1173.2 $[M]^+$. The subsequent elution with CH_2Cl_2–MeOH (50:1) gave a fraction containing 94 mg of a mixture of **VIIa** with BINAP dioxide and dioxane at a molar ratio 4:1:2 (weight fraction of **VIIa** 21%, 69 mg), mp 125–127°C.

Cyclic dimer VIIb was obtained from 0.4 mmol (234 mg) of compound **IV** and 0.4 mmol (41 mg) of triamine **Vb**. Eluent CH_2Cl_2–MeOH–aq. NH_3 (100:20:1 to 100:20:2). Yield 62 mg (25%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 0.65 (6H), 0.93 d (6H, ^3J = 7.2 Hz), 0.94 s (6H), 0.98–2.02 m (56H), 3.23 br.s (8H), 3.73 br.s (8H), 3.92–4.06 m (4H), 5.02 br.s (2H), 5.91 d (2H, ^3J = 7.8 Hz), 5.93 d (2H, ^3J = 7.9 Hz), 5.98 d (2H, ^3J = 8.4 Hz), 6.02 d (2H, ^3J = 8.4 Hz), 7.17–7.28 m (4H); signals from six NH protons were not assigned unambiguously; in DMSO-d_6: 0.58 s and 0.61 s (6H), 0.86 d (6H, ^3J = 5.4 Hz), 0.90 s and 0.91 s (6H), 0.95–1.95 m (56H), 3.10 t (8H, ^3J = 5.7 Hz), 3.50 br.s (8H), 4.01–4.18 m (4H), 5.12 s and 5.16 s (2H), 5.86 d (2H, ^3J = 7.3 Hz), 5.87 d (2H, ^3J = 7.2 Hz), 6.00 d (2H, ^3J = 8.0 Hz), 6.02 d (2H, ^3J = 7.7 Hz), 6.74 t (4H, ^3J =

5.5 Hz), 7.23–7.30 m (4H); signals from two NH protons were not assigned unambiguously. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.1 (2C), 18.7 (2C), 21.1 (2C), 23.8 (2C), 24.3 (2C), 24.9 (2C), 25.8 (2C), 26.3 (2C), 26.7 (2C), 28.3 and 28.4 (2C), 30.7 (2C), 32.2 and 32.3 (2C), 34.9 (2C), 35.7 (4C), 37.2 (2C), 38.3 and 38.5 (2C), 40.0 (4C), 40.3 (4C), 42.7 (2C), 48.3–48.7 m (4C), 56.1–56.7 m (4C), 66.5 and 66.6 (2C), 70.5 (2C), 96.6–100.9 m (8C), 139.9–140.6 m (4C), 156.5–156.7 m (4C), 162.6 (2C), 163.2 (2C). MALDI-TOF mass spectrum: *m*/*z* 1231.9 $[M + H]^+$.

Cyclic oligomer mixture VIIb/VIIIb/IXb was isolated as a separate fraction in the synthesis of dimer **VIIb** using CH_2Cl_2–MeOH–aq. NH_3 (100:20:3) as eluent. Yield 114 mg (46%), light yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.63 s (3*n*H), 0.93 br.s (6*n*H), 0.95–2.01 m (28*n*H), 3.02 br.s (4*n*H), 3.51 br.s (4*n*H), 4.02 br.s (2*n*H), 4.41 br.s (2*n*H), 5.05 br.s (*n*H), 5.92 br.s (4*n*H), 7.22 br.s (2*n*H); signals from 2*n* NH protons were not assigned unambiguously. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.1 (*n*C), 18.6 (*n*C), 21.1 (*n*C), 23.8 (*n*C), 24.2 (*n*C), 24.9 (*n*C), 25.8 (*n*C), 26.2 (*n*C), 26.6 (*n*C), 28.3 (*n*C), 30.7 (*n*C), 32.1 (*n*C), 34.8 (*n*C), 35.6 (2*n*C), 37.1 (*n*C), 39.9 (2*n*C), 40.2 (3*n*C), 42.7 (*n*C), 48.5 (2*n*C), 56.2 (*n*C), 56.6 (*n*C), 66.4 (*n*C), 70.5 (*n*C), 96.6–99.4 m (4*n*C), 139.9 (2*n*C), 157.2 (*n*C), 157.3 (*n*C), 162.7 (*n*C), 163.3 (*n*C); *n* = 2 (**VIIb**), 3 (**VIIIb**), 4 (**IXb**). MALDI-TOF mass spectrum: *m*/*z* 1847.4 $[M + H]^+$ (**VIIIb**), 2462.9 $[M + H]^+$ (**IXb**).

Macrocyclic compound VIc was synthesized from 0.37 mmol (216 mg) of compound **IV** and 0.37 mmol (48 mg) of triamine **Vc**. Eluent CH_2Cl_2–MeOH (3:1). Yield 22 mg (9%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 0.63 s (3H), 0.92 d (3H, ^3J = 6.2 Hz), 0.93 s (3H), 0.98–2.00 m (28H), 2.10 br.s (4H), 2.98 br.s (4H), 3.40–3.50 m (4H), 4.05–4.28 m (2H), 5.30 s (1H), 5.83 d (1H, ^3J = 7.8 Hz), 5.90 d (1H, ^3J = 8.1 Hz), 6.01 d (1H, ^3J = 7.4 Hz), 6.02 d (1H, ^3J = 7.3 Hz), 7.16–7.26 m (2H); signals from three NH protons were not assigned unambiguously; in DMSO-d_6: 0.58 s (3H), 0.87 br.s (6H), 0.92–2.00 m (32H), 2.93 br.s (4H), 3.29 br.s (4H), 4.12–4.30 m (2H), 5.31 s (1H), 5.76 d (1H, ^3J = 7.9 Hz), 5.79 d (1H, ^3J = 8.0 Hz), 5.92 d (1H, ^3J = 7.9 Hz), 6.03 d (1H, ^3J = 7.8 Hz), 6.49 t (1H, ^3J = 4.6 Hz), 6.77 t (1H, ^3J = 5.6 Hz), 7.18 t (1H, ^3J = 7.8 Hz), 7.24 t (1H, ^3J = 7.9 Hz; one NH proton signal was not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: in $CDCl_3$: 12.1, 18.6, 21.1, 23.5, 24.2, 25.0, 26.1, 26.2, 26.6, 28.4, 28.5, 28.9, 30.2, 30.5, 30.7, 34.4, 34.8, 35.1, 37.2, 39.7, 39.9, 40.6, 40.8, 42.7, 45.3, 45.4, 53.5, 58.0, 66.1, 70.0, 97.9, 98.0, 99.2, 99.3, 139.4, 139.8, 157.3, 157.6, 162.9, 163.2; in DMSO-d_6: 11.9, 18.5, 20.7, 23.0, 23.6, 23.8, 24.6, 25.7, 26.0, 26.3 (2C), 27.9 (2C), 29.0, 29.9, 34.1, 34.2, 34.7, 37.1, 37.7, 38.5, 42.1, 45.0, 45.8, 53.0, 57.1, 65.0, 69.4, 95.9, 96.0, 98.9, 99.2, 139.2, 139.3, 157.6, 157.8, 162.3, 162.6; two carbon signals were overlapped by the CD_3 multiplet of the solvent. MALDI-TOF mass spectrum: *m*/*z* 644.4 $[M + H]^+$.

Cyclic dimer VIIc was isolated in addition to compound **VIc** from the same reaction mixture using CH_2Cl_2–MeOH (3:1) as eluent. Yield 29 mg (12%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 0.63 s (6H), 0.94 br.s (12H), 0.96–2.01 m (56H), 2.10 br.s (8H), 2.98 br.s (8H), 3.31–3.45 m (8H), 4.02 br.s (4H), 5.01 s and 5.05 s (2H), 5.90 (4H, ^3J = 8.1 Hz), 5.94 d (4H, ^3J = 8.6 Hz), 7.20–7.27 m (4H); signals from six NH protons were not assigned unambiguously; in DMSO-d_6: 0.58 s and 0.60 s (6H), 0.98 br.s (12H), 0.95–2.01 m (64H), 2.80 br.s (8H), 3.24 br.s (8H), 4.08 br.s (4H), 5.15 br.s (2H), 5.77 d (4H, ^3J = 7.7 Hz), 5.94 d (2H, ^3J = 8.0 Hz), 5.96 d (2H, ^3J = 7.8 Hz), 6.60–6.67 m (4H), 7.19 t (2H, ^3J = 7.5 Hz), 7.21 t (2H, ^3J = 7.5 Hz); signals from two NH protons were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: in $CDCl_3$: 12.1 (2C), 18.6 (2C), 21.1 (2C), 23.8 (2C), 24.2 (2C), 24.9 (2C), 25.8 (2C), 26.2 (2C), 26.6 (2C), 28.2 (2C), 28.3 (2C), 30.7 (4C), 32.1 (2C), 34.8 (2C), 35.6 (4C), 37.2 (2C), 38.0 + 38.4 (2C), 39.7 (2C), 40.0 (2C), 40.3 (4C), 42.7 (2C), 45.3 (2C), 45.4 (2C), 56.1–56.7 m (4C), 66.7–66.9 (2C), 70.7 (2C), 95.6–100.7 m (8C), 140.0 (4C), 157.6–158.1 m (4C), 162.8 (2C), 163.4 (2C); in DMSO-d_6: 11.9 (2C), 18.5 (2C), 20.7 (2C), 23.4 (2C), 23.7 (2C), 24.6 (2C), 25.2 (2C), 25.6 (2C), 25.8 (2C), 26.2 (2C), 27.9 (2C), 28.6 (2C), 30.3 (2C), 30.5 (2C), 31.8 (2C), 34.4 (2C), 34.9 (2C), 35.2 (2C), 36.9 (2C), 38.0 (4C), 42.2 (2C), 45.1 (4C), 55.6 and 55.7 (2C), 56.1 and 56.2 (2C), 65.1 (2C), 69.1 and 69.2 (2C), 96.0 and 96.1 (4C), 99.2 (4C), 139.3 (4C), 157.7 (4C), 162.1 (2C), 162.7 (2C); signals from four carbon atoms were overlapped by the CD_3 multiplet of the solvent. MALDI-TOF mass spectrum: *m*/*z* 1288.0 $[M + H]^+$.

Cyclic oligomer mixture VIIc/VIIIc/IXc was isolated as a separate fraction in the synthesis of compound **VIc**. Eluent CH_2Cl_2–MeOH–aq. NH_3 (100:20:1 to 100:20:3). Yield 81 mg (33%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 0.64 s, 0.66 s, and 0.67 s (3*n*H); 0.90–0.96 m (6*n*H);

0.97–2.01 m (28*n*H); 2.12 br.s (4*n*H); 2.98 br.s (4*n*H); 3.40–3.53 m (4*n*H); 4.03 br.s (2*n*H); 4.99 s and 5.05 s (*n*H); 5.92 d (*n*H, ^3J = 7.7 Hz); 5.94 d (*n*H, ^3J = 7.6 Hz); 5.95–6.04 m (2*n*H); 7.22–7.31 m (2*n*H); signals from 3*n* NH protons were not assigned unambiguously; in DMSO-d_6: 0.58 s and 0.60 s (3*n*H), 0.89 br.s (6*n*H), 0.92–2.00 m (32*n*H), 2.84 br.s (4*n*H), 3.25 br.s (4*n*H), 4.08 br.s (2*n*H), 5.15 br.s (*n*H), 5.77 d (2*n*H, ^3J = 5.2 Hz), 5.94 d (*n*H, ^3J = 8.0 Hz), 5.96 d (*n*H, ^3J = 8.1 Hz), 6.65 br.s (2*n*H), 7.15–7.24 m (2*n*H); *n* = 2 (**VIIc**), 3 (**VIIIc**), 4 (**IXc**). MALDI-TOF mass spectrum: *m*/*z* 1931.6 $[M + H]^+$ (**VIIIc**), 2575.1 $[M + H]^+$ (**IXc**).

Macrocyclic compound VId was synthesized from 0.51 mmol (298 mg) of compound **IV** and 0.51 mmol (89 mg) of tetraamine **Vd**. Eluent CH_2Cl_2–MeOH–aq. NH_3 (10 : 3 : 1). Yield 25 mg (7%), light yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.62 s (3H), 0.92 br.s (6H), 0.95–2.01 m (32H), 2.81 br.s (4H), 2.91 br.s (4H), 3.23 br.s (4H), 4.05–4.28 m (2H), 5.30 br.s (2H), 5.31 s (1H), 5.82 d (1H, ^3J = 8.1 Hz), 5.91 d (1H, ^3J = 8.7 Hz), 5.94 d (1H, ^3J = 8.7 Hz), 6.01 d (1H, ^3J = 7.6 Hz), 7.17–7.25 m (2H); signals from two NH protons were not assigned unambiguously. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.1, 18.7, 21.1, 23.7, 24.1, 24.5, 25.3, 26.3, 26.6, 28.0, 28.9, 29.2, 30.7 (2C), 32.0, 34.3, 34.7, 35.3, 37.0, 39.5, 40.0, 40.4, 40.8, 42.5, 46.7, 47.0, 47.2, 47.3, 53.5, 57.5, 66.3, 69.7, 97.5, 98.6, 98.8, 99.2, 139.5, 139.6, 157.8, 157.9, 163.0, 163.1. MALDI-TOF mass spectrum: *m*/*z* 686.6 $[M]^+$.

Cyclic dimer VIId was isolated as the second product in the synthesis of compound **VId**. Eluent CH_2Cl_2–MeOH–aq. NH_3 (10 : 3 : 1). Yield 69 mg (19%), light yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.62 s (6H), 0.92 br.s (12H), 0.95–2.00 m (64H), 2.81 br.s (8H), 2.91 br.s (8H), 3.32 br.s (8H), 4.05 br.s (4H), 5.09 br.s (2H), 5.30 br.s (4H), 5.91 d (4H, ^3J = 8.7 Hz), 5.94 d (4H, ^3J = 8.7 Hz), 7.17–7.27 m (4H); signals from four NH protons were not assigned unambiguously. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 12.1 (2C), 18.7 (2C), 21.1 (2C), 23.9 (2C), 24.2 (2C), 25.0 (2C), 25.8 (2C), 26.3 (2C), 26.7 (2C), 28.3 (2C), 30.2–30.5 m (4C), 30.7 (2C), 32.2 (2C), 34.9 (2C), 35.7 (4C), 37.2 (2C), 40.0 (4C), 40.3 (4C), 40.4 (2C), 42.7 (2C), 46.5–47.7 m (8C), 55.2 (2C), 56.6 (2C), 66.5 (2C), 70.5 (2C), 96.0–99.5 m (8C), 139.8 (2C), 140.0 (2C), 157.8 (2C), 157.9 (2C), 162.8 (2C), 163.5 (2C). MALDI-TOF mass spectrum: *m*/*z* 1373.1 $[M]^+$.

Macrocyclic compounds VIe was synthesized from 0.45 mmol (264 mg) of compound **IV** and 0.45 mmol (85 mg) of tetraamine **Ve**. Eluent CH_2Cl_2–MeOH–aq. NH_3 (100 : 20 : 1 to 100 : 20 : 3). Yield 91 mg (29%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 0.63 s (3H), 0.92 d (3H, ^3J = 6.8 Hz), 0.94 s (3H), 0.96–2.15 m (34H), 2.78–2.95 m (8H), 3.35–3.50 m (4H), 4.08 br.s (2H), 4.14–4.28 m (2H), 5.30 s (1H), 5.84 d (1H, ^3J = 7.6 Hz), 5.93 d (1H, ^3J = 7.8 Hz), 5.96 d (2H, ^3J = 7.6 Hz), 7.23 t (1H, ^3J = 7.8 Hz), 7.25 t (1H, ^3J = 7.6 Hz); signals from two NH protons were not assigned unambiguously; in DMSO-d_6: 0.58 s (3H), 0.88 br.s (6H), 0.98–2.01 m (28H), 1.80 br.s (6H), 2.65–2.90 m (8H), 3.16 br.s (4H), 4.16 br.s (2H), 5.26 s (1H), 5.76 d (2H, ^3J = 6.9 Hz), 5.92 d (1H, ^3J = 7.5 Hz), 5.98 d (1H, ^3J = 7.8 Hz), 6.60 br.s (1H), 6.69 br.s (1H), 7.17 t (1H, ^3J = 7.9 Hz), 7.21 t (1H, ^3J = 7.9 Hz; signals from two NH protons were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: in $CDCl_3$: 12.0, 18.8, 21.1, 23.0, 23.6, 24.1, 25.5, 26.3, 26.4, 27.7, 27.9, 28.2, 30.5, 31.0 (2C), 32.1, 34.2, 34.6, 35.3, 37.1, 39.0, 39.5, 40.3 (2C), 42.5, 46.6, 46.8, 46.9, 47.0, 53.9, 57.2, 66.3, 69.7, 97.2, 98.2, 98.6, 99.0, 139.5, 139.7, 157.5, 157.6, 162.8, 163.1; in DMSO-d_6: 11.8, 18.7, 20.7, 22.9, 23.6, 23.7, 24.7, 24.8, 25.7, 26.1, 27.4 (2C), 27.9, 30.1, 30.7, 30.9, 33.8, 34.3, 35.0, 37.0, 38.0, 38.5, 42.1, 45.1, 45.7, 45.8, 46.1, 53.7, 56.2, 65.2, 69.1, 95.5, 96.1, 99.2, 99.3, 139.3 (2C), 157.7, 157.8, 162.2, 162.5; signals from two carbon atoms were overlapped by the CD_3 multiplet of the solvent. MALDI-TOF mass spectrum: *m*/*z* 701.4 $[M + H]^+$.

Cyclic dimer VIIe was isolated from the second fraction in the synthesis of compound **VIe**. Eluent CH_2Cl_2–MeOH–aq. NH_3 (10 : 3 : 1). Yield 209 mg (66%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 0.64 s (6H), 0.91 d (6H, ^3J = 6.3 Hz), 0.94 s (6H), 0.95–2.00 m (68H), 2.77–2.90 m (16H), 3.33 q (8H, ^3J = 5.9 Hz), 3.60 br.s (4H), 4.09 br.s (4H), 5.13 s (2H), 5.91–5.99 m (8H), 7.24–7.29 m (4H); signals from four NH protons were not assigned unambiguously; in DMSO-d_6: 0.58 s (6H), 0.87 br.s (12H), 0.90–2.02 m (68H), 2.75–3.00 m (16H), 3.24 br.s (8H), 4.07 br.s (4H), 5.13 s (2H), 5.76 br.s (4H), 5.96 br.s (4H), 6.59 br.s (4H), 7.19 br.s (4H); signals from four NH protons were not assigned unambiguously. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 11.9 (2C), 18.5 (2C), 23.0 (2C), 23.4 (2C), 23.7 (2C), 24.6 (2C), 25.3 (2C), 25.9 (2C), 26.1 (2C), 26.2 (2C), 27.8 (2C), 27.9 (2C), 28.6 (2C), 30.5 (2C), 30.6 (2C), 31.9 (2C), 34.5 (2C), 35.1 (2C), 35.2 (2C), 36.5

(2C), 38.0 (4C), 42.3 (2C), 44.5 (2C), 44.7 (2C), 44.8 (2C), 45.2 (2C), 55.7 (2C), 56.0 (2C), 65.2 (2C), 69.3 (2C), 95.4 (2C), 96.3 (2C), 99.0 (4C), 139.4 (4C), 157.7 (4C), 162.2 (2C), 162.8 (2C); signals from four carbon atoms were overlapped by the CD_3 multiplet of the solvent. MALDI-TOF mass spectrum: *m*/*z* 1402.2 $[M + H]^+$.

Cyclic dimer VIIf was obtained from 0.55 mmol (322 mg) of compound **IV** and 0.55 mmol (122 mg) of diamine **Vf**. Eluent CH_2Cl_2–MeOH (200:1 to 100:1). Yield 59 mg (15%), light yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.64 s (6H), 0.92 d (6H, ^3J = 6.2 Hz), 0.96 s (6H), 1.00–2.03 m (88H), 2.04 s (4H), 3.19 br.s (8H), 4.09–4.16 m (4H), 4.23 br.s (4H), 5.15 s (2H), 5.85 d (2H, ^3J = 8.0 Hz), 5.88 d (2H, ^3J = 7.9 Hz), 5.97 d (4H, ^3J = 7.8 Hz), 7.30 t (2H, ^3J = 7.9 Hz), 7.31 t (2H, ^3J = 7.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.1 (2C), 18.7 (2C), 21.1 (2C), 23.9 (2C), 24.3 (2C), 25.0 (2C), 25.8 (2C), 26.3 (2C), 26.7 (2C), 28.3 (2C), 29.0 (4C), 30.8 (4C), 32.2 (2C), 32.7 (4C), 34.9 (2C), 35.6 (2C), 35.7 (2C), 36.5 (2C), 37.2 (6C), 40.0 (2C), 40.3 (2C), 42.0 (8C), 42.8 (2C), 43.7 (4C), 47.7 (2C), 56.3 (2C), 56.7 (2C), 66.2 (2C), 70.4 (2C), 96.7 (2C), 97.2 (2C), 97.3 (2C), 98.2 (2C), 139.9 (4C), 157.8 (2C), 157.9 (2C), 162.9 (2C), 163.5 (2C). MALDI-TOF mass spectrum: *m*/*z* 1469.4 $[M]^+$.

Macrocyclic compound VIg was synthesized from 0.47 mmol (275 mg) of compound **IV** and 0.47 mmol (70 mg) of diamine **Vg**. Eluent CH_2Cl_2–MeOH (200:1). Yield 18 mg (6%), light yellow substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.64 s (3H), 0.94 d (3H, ^3J = 7.0 Hz), 0.95 s (3H), 0.99–2.05 m (28H), 3.40–3.48 m (2H), 3.58 q (2H, ^3J = 4.9 Hz), 3.61–3.72 m (8H), 4.07–4.17 m (1H), 4.28–4.34 m (1H), 4.36 br.s (1H), 4.67 t (1H, ^3J = 4.8 Hz), 5.35 s (1H), 5.87 d (1H, ^3J = 7.5 Hz), 5.94 d (1H, ^3J = 8.1 Hz), 5.96 d (1H, ^3J = 7.8 Hz), 5.98 d (1H, ^3J = 7.9 Hz), 7.24 t (1H, ^3J = 8.0 Hz), 7.28 t (1H, ^3J = 7.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.1, 18.6, 21.2, 22.6, 23.5, 24.0, 25.3, 26.0, 26.2, 28.3, 30.0, 30.3, 31.3, 34.5 (2C), 35.2, 37.2, 40.6, 40.7, 41.2, 41.4, 42.5, 53.4, 58.0, 66.3, 70.1, 70.2, 70.3, 70.5, 70.7, 98.2, 98.3, 98.6, 98.7, 139.5, 139.7, 157.1, 157.4, 163.0, 163.1. MALDI-TOF mass spectrum: *m*/*z* 660.7 $[M]^+$.

Cyclic oligomer mixture VIIg/VIIIg was isolated as a separate fraction in the synthesis of compound **VIg**. Eluent CH_2Cl_2–MeOH (200:1). Yield 42 mg (14%), light yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.64 s (3*n*H), 0.92 d (3*n*H, ^3J = 6.0 Hz), 0.95 s (3*n*H), 0.99–2.00 m (28*n*H), 3.45 br.s (4*n*H), 3.64 s (4*n*H), 3.67 br.s (4*n*H), 4.12 br.s (2*n*H), 4.79 br.s (2*n*H), 5.20 br.s (*n*H), 5.86 d (*n*H, ^3J = 7.7 Hz), 5.90 d (*n*H, ^3J = 7.8 Hz), 5.98 d (2*n*H, ^3J = 7.7 Hz), 7.29 t (2*n*H, ^3J = 7.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.0 (*n*C), 18.6 (*n*C), 21.1 (*n*C), 23.8 (*n*C), 24.2 (*n*C), 24.9 (*n*C), 25.7 (*n*C), 26.3 (*n*C), 26.6 (*n*C), 28.3 (*n*C), 30.6 (*n*C), 30.7 (*n*C), 21.1 (*n*C), 34.8 (*n*C), 35.5 (*n*C), 35.6 (*n*C), 37.1 (*n*C), 39.9 (*n*C), 40.3 (*n*C), 41.7 (2*n*C), 42.7 (*n*C), 56.1 (*n*C), 56.6 (*n*C), 66.2 (*n*C), 69.9 (2*n*C), 70.2 (3*n*C), 97.3 (2*n*C), 98.0 (*n*C), 98.5 (*n*C), 139.7 (*n*C), 139.8 (*n*C), 157.6 (2*n*C), 162.8 (*n*C), 163.4 (*n*C); *n* = 2 (**VIIg**), 3 (**VIIIg**). MALDI-TOF mass spectrum: *m*/*z* 1321.2 $[M]^+$ (**VIIg**), 1981.6 $[M]^+$ (**VIIIg**).

Macrocyclic compound VIh was synthesized from 0.51 mmol (298 mg) of compound **IV** and 0.51 mmol (105 mg) of diamine **Vh**. Eluent CH_2Cl_2–MeOH (200:1). Yield 82 mg (22%), light yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.64 s (3H), 0.92 d (3H, ^3J = 6.8 Hz), 0.95 s (3H), 0.99–2.05 m (36H), 3.25–3.48 m (8H), 3.55 t (4H, ^3J = 6.2 Hz), 4.12–4.20 m (1H), 4.25–4.33 m (1H), 4.43 br.s (1H), 5.00 br.s (1H), 5.30 s (1H), 5.80 d (1H, ^3J = 7.7 Hz), 5.91 d (1H, ^3J = 7.8 Hz), 5.95 d (1H, ^3J = 7.9 Hz), 5.96 d (1H, ^3J = 7.7 Hz), 7.28 t (2H, ^3J = 7.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.0, 18.7, 21.1, 22.7, 23.8, 24.1, 25.2, 26.2, 26.4, 26.8, 26.9, 28.1, 29.3, 29.7, 30.3, 30.7, 30.9, 34.3, 34.7, 35.4, 37.2, 39.4, 40.3, 40.4, 41.6, 42.3, 53.8, 57.3, 66.4, 69.1, 69.6, 70.7, 71.0, 71.2, 96.4, 97.9, 98.2, 98.6, 139.6, 139.7, 157.6, 157.8, 162.8, 163.1. MALDI-TOF mass spectrum: *m*/*z* 716.7 $[M]^+$.

Cyclic dimer VIIh was isolated from the second fraction in the synthesis of compound **VIh**. Eluent CH_2Cl_2–MeOH (200:1). Yield 42 mg (12%), light yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.64 s (6H), 0.93 d (6H, ^3J = 5.9 Hz), 0.96 s (6H), 1.00–2.02 m (72H), 3.32 br.s (8H), 3.44 br.s (8H), 3.52 br.s (8H), 4.13 t (^3J = 6.4 Hz) and 4.15–4.25 m (4H), 4.67 br.s (4H), 5.16 s and 5.21 s (2H), 5.85 d (2H, ^3J = 7.4 Hz), 5.89 d (2H, ^3J = 8.4 Hz), 5.96 d (4H, ^3J = 7.8 Hz), 7.28 t (2H, ^3J = 7.6 Hz), 7.30 d (2H, ^3J = 7.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.0 (2C), 18.6 (2C), 21.1 (2C), 23.8 (2C), 24.2 (2C), 25.0 (2C), 25.7 (2C), 26.2 (2C), 26.5 (4C), 26.6 (2C), 28.3 (2C), 29.4 (4C), 30.7 (4C), 32.1 (2C), 34.9 (2C), 35.5 (2C), 35.6 (2C), 37.1 (2C), 40.0 (2C), 40.1 (2C), 40.2 (2C), 40.3 (2C), 42.7 (2C), 56.1 and 56.2 (2C), 56.7 (2C), 66.1 (2C), 69.1 (2C), 69.2 (2C), 70.1 and 70.3 (2C), 70.8 (4C), 96.8 and 96.9 (2C), 97.1

and 97.2 (4C), 98.0 and 98.3 (2C), 139.7 and 139.8 (4C), 157.9 (4C), 162.8 (2C), 163.4 (2C). MALDI-TOF mass spectrum: *m*/*z* 1433.3 $[M]^+$.

Macrocyclic compound VIi was synthesized from 0.38 mmol (222 mg) of compound **IV** and 0.38 mmol (84 mg) of diamine **Vi**. Eluent CH_2Cl_2–MeOH (100 : 1). Yield 58 mg (21%), light yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.64 s (3H), 0.91 d (3H, ^3J = 6.7 Hz), 0.95 s (3H), 1.00–2.01 m (28H), 1.87 quint (2H, ^3J = 6.1 Hz), 1.91 quint (2H, ^3J = 6.3 Hz), 3.33 br.s (2H), 3.38 q (2H, ^3J = 6.0 Hz), 3.56–3.65 m (12H), 4.17–4.23 m (1H), 4.24–4.31 m (1H), 4.47 br.s (1H), 4.75 br.s (1H), 5.31 s (1H), 5.81 d (1H, ^3J = 7.9 Hz), 5.89 d (1H, ^3J = 7.7 Hz), 5.94 d (1H, ^3J = 7.7 Hz), 5.96 d (1H, ^3J = 7.8 Hz), 7.26 t (1H, ^3J = 7.9 Hz), 7.28 t (1H, ^3J = 7.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.0, 18.7, 21.1, 23.0, 23.7, 24.1, 25.1, 26.1, 26.4, 28.0, 29.4, 29.5, 30.4, 30.9, 31.0, 34.4, 34.7, 35.4, 37.2, 39.3, 40.2, 40.3, 40.6, 42.5, 54.0, 57.2, 66.2, 69.4, 69.7, 70.1, 70.2, 70.5, 70.6, 70.7, 96.9, 97.8 (2C), 98.5, 139.6, 139.7, 157.5, 157.6, 162.8, 163.0. MALDI-TOF mass spectrum: *m*/*z* 732.7 $[M]^+$.

Cyclic dimer VIIi was isolated from the second fraction in the synthesis of compound **VIi**. Eluent CH_2Cl_2–MeOH (100 : 1). Yield 28 mg (10%), light yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.64 s (6H), 0.92 d (6H, ^3J = 6.2 Hz), 0.95 s (6H), 0.99–2.00 m (64H), 3.32 q (8H, ^3J = 6.9 Hz), 3.52–3.67 m (24H), 4.12 t (4H, ^3J = 5.6 Hz), 4.71 br.s (4H), 5.19 s (2H), 5.86 d (2H, ^3J = 7.9 Hz), 5.89 d (2H, ^3J = 8.0 Hz), 5.95 d (4H, ^3J = 7.8 Hz), 7.27 t (2H, ^3J = 7.7 Hz), 7.28 t (2H, ^3J = 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.1 (2C), 18.6 (2C), 21.1 (2C), 23.8 (2C), 24.2 (2C), 25.0 (2C), 25.7 (2C), 26.3 (2C), 26.6 (2C), 28.3 (2C), 29.3 (4C), 30.7 (4C), 32.1 (2C), 34.9 (2C), 35.6 (2C), 35.7 (2C), 37.1 (2C), 39.7 (2C), 39.8 (2C), 40.0 (2C), 40.3 (2C), 42.7 (2C), 56.2 (2C), 56.7 (2C), 66.2 (2C), 69.4 (6C), 70.2 (4C), 70.6 (4C), 97.0 (4C), 97.1 (2C), 97.5 (2C), 139.8 (4C), 157.9 (4C), 162.8 (2C), 163.4 (2C). MALDI-TOF mass spectrum: *m*/*z* 1465.3 $[M]^+$.

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