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Palladium-Catalyzed Amination in the Synthesis of Macrocyclic Compounds Containing 1,3-Disubstituted Adamantane Fragments

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Abstract—Palladium-catalyzed amination of 1,3-dibromobenzene, 2,6-dibromopyridine, 3,3′-dibromobiphenyl, 2,7-dibromonaphthalene, and 1,8-dichloroanthracene with an equimolar amount of 2,2′-(adamantane-1,3-diyl)diethanamine resulted in the formation of macrocyclic compounds containing one or several adamantane and one or several aromatic fragments. The reactions of 2,2′-(adamantane-1,3-diyl)diethanamine with excess 1,3-dibromobenzene, 2,6-dibromopyridine, 1,8-dichloroanthracene, and 1,8-dichloroanthraquinone gave the corresponding *N*,*N*′-diaryl derivatives. Polyaza macrocycles incorporating adamantane, aromatic, and 4,7,10-trioxatridecane-1,13-diamine fragments, were obtained by palladium-catalyzed amination of the *N*,*N*′-diaryl derivatives with 4,7,10-trioxatridecane-1,13-diamine.

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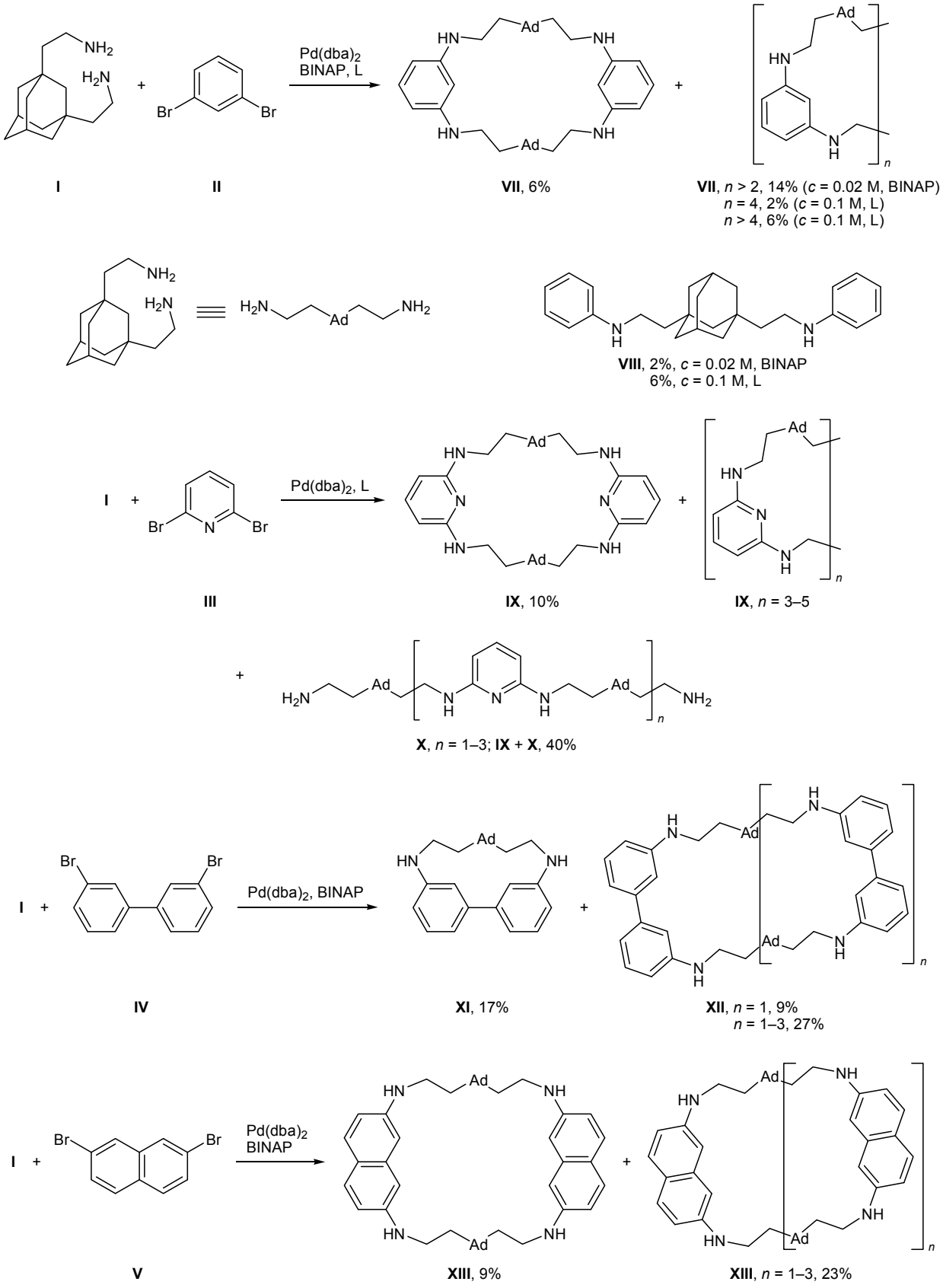
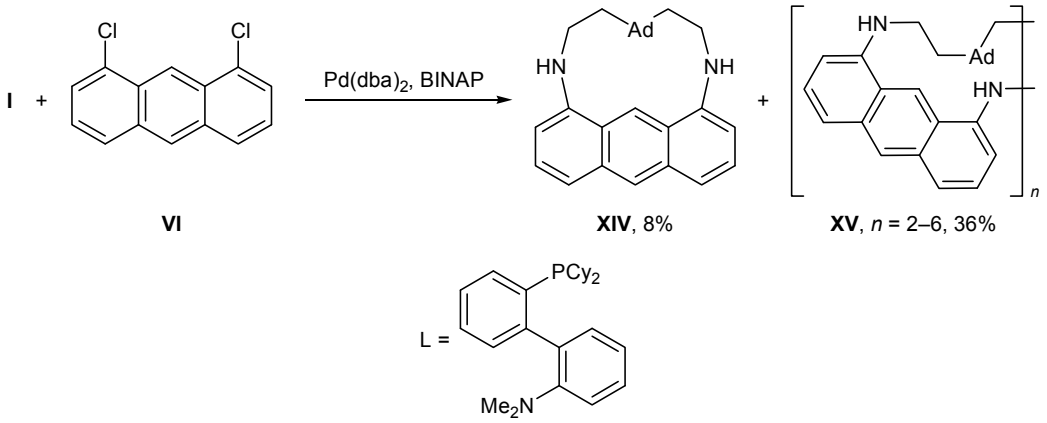
Thirty years ago Novikov et al. [1] proposed a convenient and reliable procedure for the preparation of 1,3-bis(2-aminoethyl)adamantane (**I**), and this compound was widely used in practice since that time. Diamine **I**, 1,3-bis(aminomethyl)adamantane, and the corresponding hydrochlorides were tested for antiviral activity [2], and the first of these turned out to be active against avian influenza [3], while the second was patented as antiviral drug for the treatment of domestic animals [4, 5]. Diamine **I** is used as a component in the preparation of epoxide polymers [6] with a view to improve their optical parameters and endurance [7], as well as for modification of aromatic polyimides [8–10]. Polyamides with enhanced hydrolytic and thermal stability were synthesized on the basis of compound **I** [11]. Chemical derivatives of diamine **I** have also found versatile applications; for example, the corresponding diisocyanates were introduced into polymeric chains of polyurethanes to improve their chemical stability and light resistance; addition of 1,3-bis(2-*m*-fluorobenzylideneaminoethyl)adamantane and 1,3-bis(2-*m*-methoxybenzylideneaminoethyl)adamantane improves mechanical properties of rubber [12]. Diamine **I** was also used to modify rubber [13, 14]. Cyclic Schiff base were synthesized from diamine **I**, and their biological activity was studied [15].

Our interest in diamine **I**, as well as in other adamantane-containing diamines, is related to the possibility of their catalytic *N*-arylation to obtain new potential pharmacologically active compounds. We recently synthesized *N*,*N*′-dipyridyl derivative of 1,3-bis(aminomethyl)adamantane, which showed nootropic effect in mice [16]. We believed that introduction of an adamantane fragment into polyaza macrocycles should enhance their lipophilicity and hence permeability through cell membranes. Therefore, we made an attempt to synthesize such macrocycles whose cavity be capable of transporting small organic molecules. Combination of adamantane and diaminoaryl fragments in a single molecule seems to be promising from the viewpoint of further biological studies. For example, diaminonaphthalenes exhibit versatile biological activity [17–21], diaminoanthraquinone derivatives were studied as anticarcinogenic agents [22], and di-

Scheme 1.


Pd(dba)2
BINAP, L
I
II
VII, 6%
VII, n > 2, 14% (c = 0.02 M, BINAP)
n = 4, 2% (c = 0.1 M, L)
n > 4, 6% (c = 0.1 M, L)
VIII, 2%, c = 0.02 M, BINAP
6%, c = 0.1 M, L
Pd(dba)2, L
III
IX, 10%
IX, n = 3–5
X, n = 1–3; IX + X, 40%
Pd(dba)2, BINAP
IV
XI, 17%
XII, n = 1, 9%
n = 1–3, 27%
V
XIII, 9%
XIII, n = 1–3, 23%

Scheme 1. (Contd.)



VI **XIV**, 8% **XV**, n = 2–6, 36%

aminobiphenyls were tested for carcinogenic activity [23, 24].

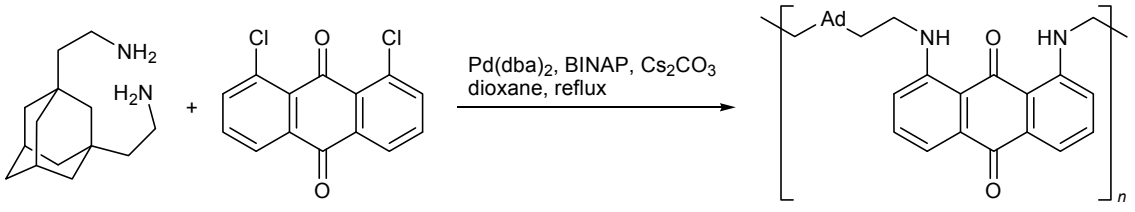
We previously synthesized various macrocyclic compounds via palladium-catalyzed amination [25–28]. In the present work we tried to apply the potential of palladium-catalyzed amination to the synthesis of new macrocycles having an adamantane fragment. For this purpose, 1,3-bis(2-aminoethyl)adamantane (**I**) was brought into reactions with equimolar amounts of various dihaloarenes in the presence of the catalytic system $Pd(dba)_2$/BINAP (8/9 mol %) and sodium *tert*-butoxide in dioxane. The results are shown in Scheme 1.

The reactions of diamine **I** with 1,3-dibromobenzene, 2,6-dibromopyridine, and 2,7-dibromonaphthalene gave macrocyclic compounds having two adamantane and two aromatic fragments, cyclic dimers **VII**, **IX**, and **XIII**, respectively, in 6–10% yield. Higher cyclic oligomers **VII** (n > 2), **IX** (n = 3–5), and **XIII** (n = 2, 3) were isolated as mixtures in 14–40% yield, and compound **IX** was isolated as a mixture with acyclic 2,6-diaminopyridine derivatives **X** (n = 1–3). Their formation was confirmed by the MALDI mass spectra. The structure of the initial compounds in these reactions cannot ensure formation of 1:1 adducts containing one adamantane and one aromatic fragment. In the reaction with 1,3-dibromobenzene both BINAP and *N*,*N*-dimethyl-2′-(dicyclohexyl-λ^3-phosphanyl)biphenyl-2-amine (DavePHOS) showed approximately similar catalytic activity, whereas only the latter ligand was effective in the reaction with 2,6-dibromopyridine. Furthermore, the reaction with 1,3-dibromobenzene was accompanied by its partial reduction with formation of a small amount of *N*,*N*′-diphenyl-2,2′-(adamantane-1,3-diyl)diethanamine (**VIII**). By contrast, 3,3′-dibromobiphenyl (**IV**) and 1,8-dichloroanthracene (**VI**) reacted with 2,2′-(adamantane-1,3-diyl)diethanamine (**I**) to give the corresponding 1:1 macrocyclic adducts **XI** and **XIV** which were isolated in 17 and 8% yield, respectively. Cyclic dimers and higher cyclic oligomers **XII** (n = 1–3) and **XV** (n = 2–6) were isolated as mixtures (yield 27 and 36%, respectively).

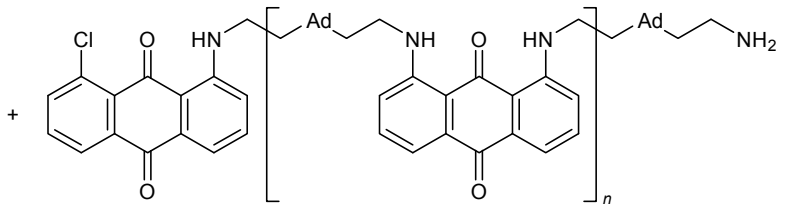
In the reactions of diamine **I** with 1,8- and 1,5-dichloroanthraquinones **XVI** and **XVII** and 1,5-dichloroanthracene (**XVIII**) cyclic dimers and oligomers were formed in very small amounts, and we failed to separate them from the major products, the corresponding linear oligomers. In the reaction mixture obtained from diamine **I** and 1,8-dichloroanthraquinone (**XVI**) we detected by MALDI–TOF mass spectrometry cyclic dimer **XIX** (n = 2) together with linear oligomers **XX** (n = 0–2) and **XXI** (n = 0, 1) (overall yield ~30%), while the reaction of **I** with isomeric 1,5-dichloroanthraquinone produced cyclic dimer **XXII** (n = 2), trimer **XXII** (n = 3), and oligomers **XXIII** (n = 1–3) and **XXIV** (n = 0–3) in an overall yield of ~30% (Scheme 2). Cesium carbonate was used instead of sodium *tert*-butoxide in the reactions of diamine **I** with dichloroanthraquinones. The reaction of **I** with 1,5-dichloroanthracene was accompanied by hydrodehalogenation to a considerable extent, and 18% of *N*,*N*′-bis(anthracen-1-yl)-2,2′-(adamantane-1,3-diyl)diethanamine (**XXV**) was obtained in a mixture with anthracene (**XXVI**), the latter being in fact the major product (Scheme 3).

Different results of the reactions of diamine **I** with different dihaloarenes are largely determined by their structure, specifically by the position of halogen atoms, as well as by the structure of acyclic amino-substituted intermediate, rather than by the reactant concentration. In fact, the reaction of diamine **I** with 1,3-dibromobenzene in a 0.1 M solution gave cyclic dimer **VII** (n = 2) with the same yield (6%) as in

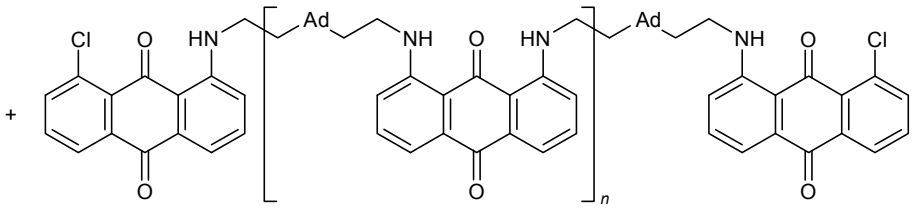
Scheme 2.



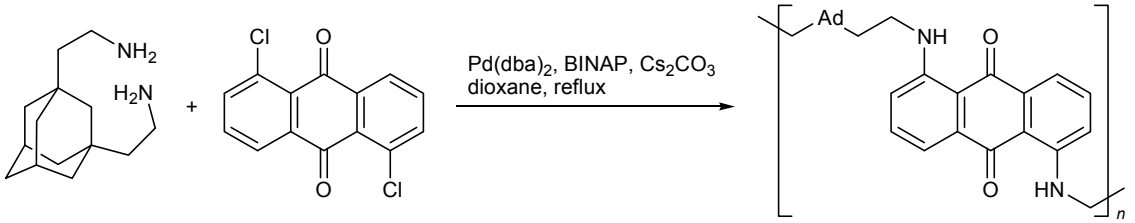
I **XVI** **XIX**, n = 2, m/z 852.39



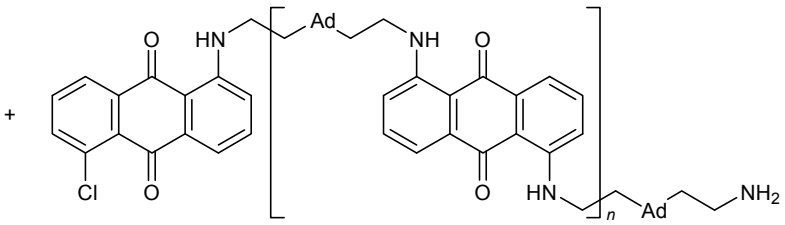
XX, n = 0–2, m/z 462.21, 888.59, 1314.68



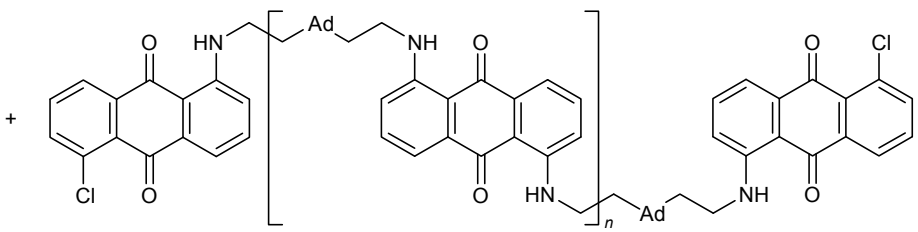
XXI, n = 0, 1; m/z 702.36, 1128.43



I **XVII** **XXII**, n = 2, 3; m/z 852.34, 1279.06

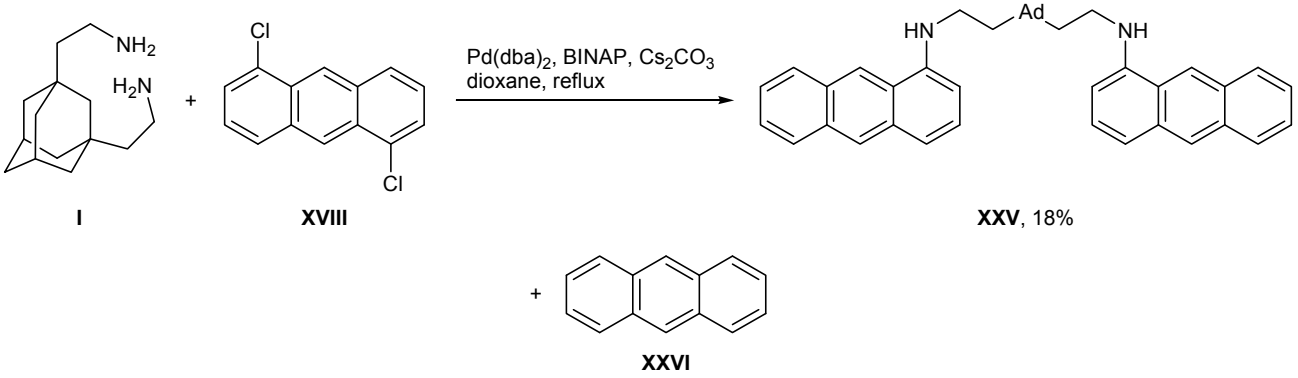


XXIII, n = 1–3; m/z 888.29, 1314.70, 1741.10



XXIV, n = 0–3; m/z 702.10, 1128.07, 1554.64, 1980.80

Scheme 3.



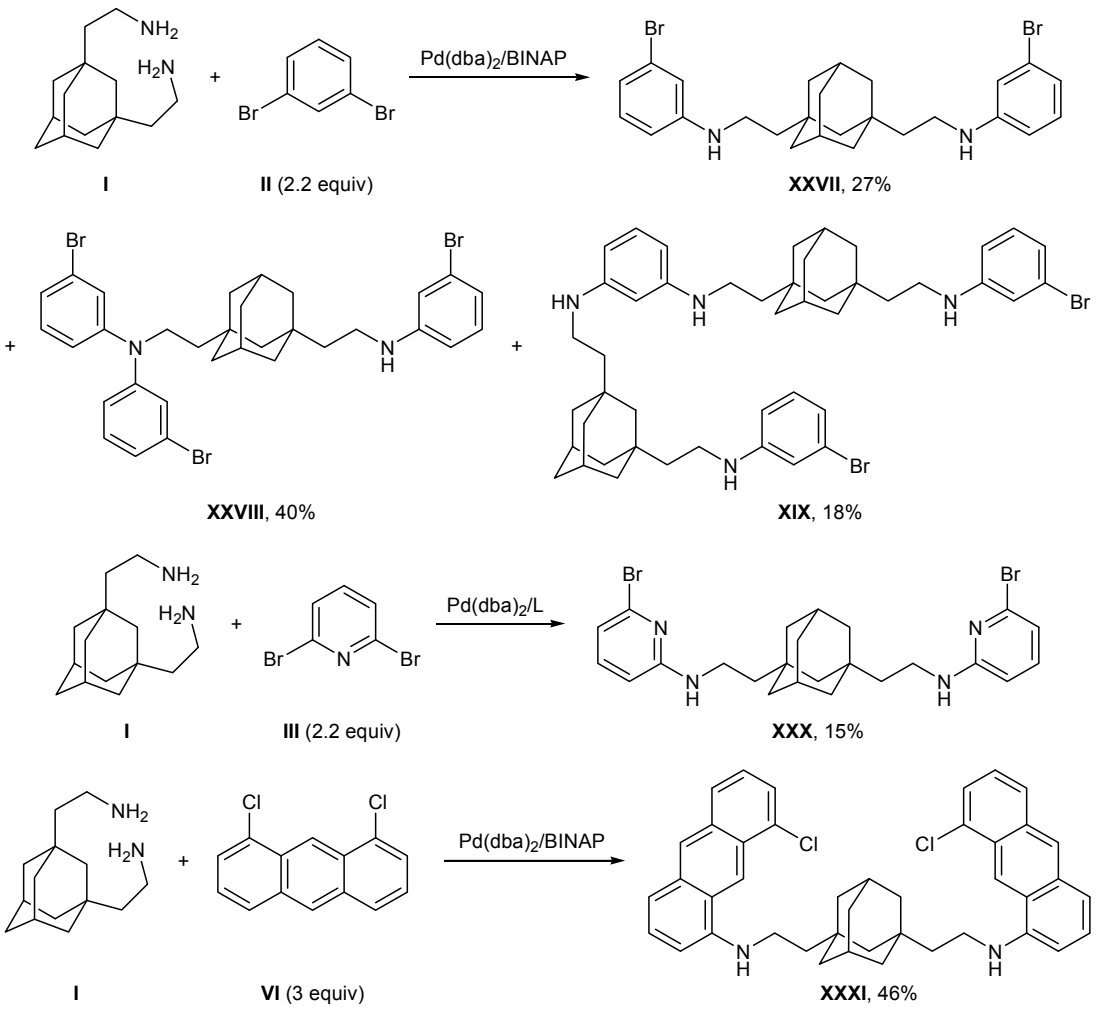
I **XVIII** **XXV**, 18%

+ **XXVI**

a 0.02 M solution; only the ratio of by-products, cyclic oligomers **VII** ($n > 2$) and hydrodebromination product **VIII**, changed in this case.

Surprisingly, cyclic dimer **XIII** ($n = 1$) turned out to be very poorly soluble in chloroform, so that it can be readily separated from higher cyclic oligomers. The NMR spectra of macrocycles **XI** and **XIV** with one adamantane and one aromatic fragment differ considerably from the spectra typical of cyclic dimers **XII** ($n = 1$) and **XV** ($n = 2$) due to close mutual location of the aromatic and aliphatic fragments in molecules **XI** and **XIV**.

Scheme 4.



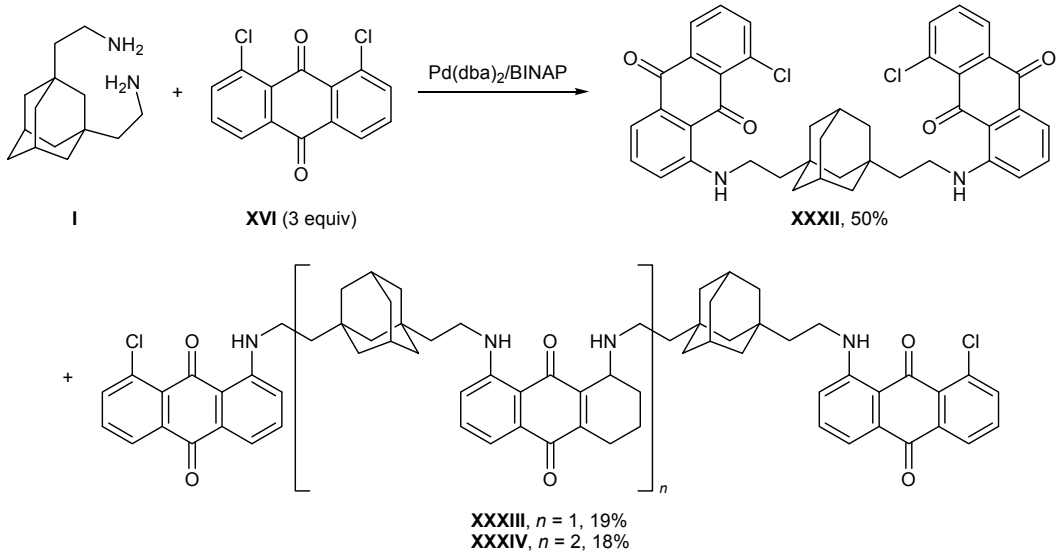
I **II** (2.2 equiv) **XXVII**, 27%

XXVIII, 40% **XIX**, 18%

I **III** (2.2 equiv) **XXX**, 15%

I **VI** (3 equiv) **XXXI**, 46%

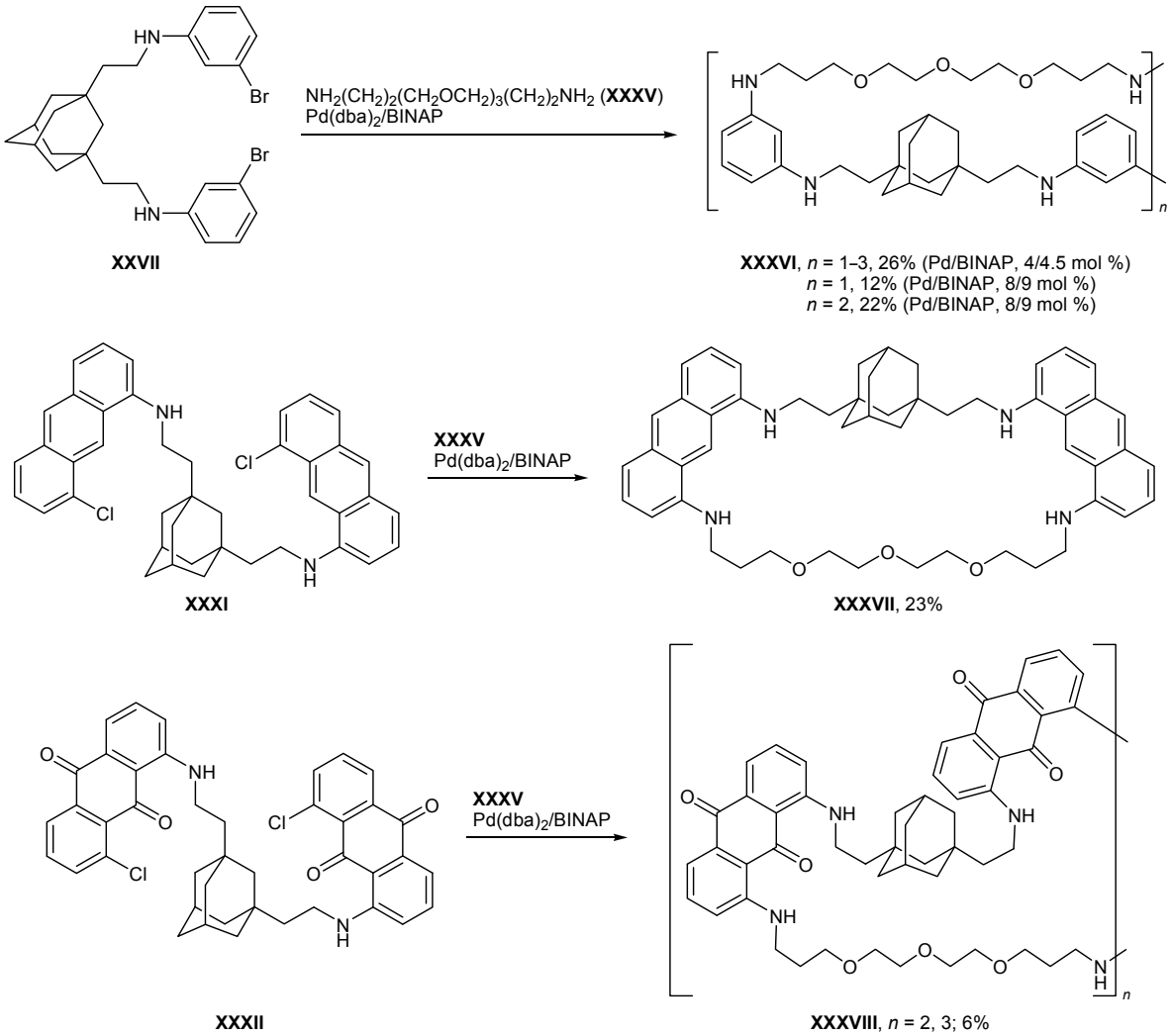
Scheme 4. (Contd.)



I **XVI** (3 equiv) **XXXII**, 50%

XXXIII, *n* = 1, 19%
XXXIV, *n* = 2, 18%

Scheme 5.



XXVII **XXXVI**, *n* = 1–3, 26% (Pd/BINAP, 4/4.5 mol %)
n = 1, 12% (Pd/BINAP, 8/9 mol %)
n = 2, 22% (Pd/BINAP, 8/9 mol %)

XXXI **XXXVII**, 23%

XXXII **XXXVIII**, *n* = 2, 3; 6%

In the next step, we tried to find optimal conditions for the synthesis of *N*,*N*′-bis(haloaryl) derivatives of diamine **I** with a view to effect their further cyclization with linear diamines (Scheme 4). The reaction of diamine **I** with 2.2 equiv of 1,3-dibromobenzene in the presence of 2 mol % (per halogen atom) of the catalytic system $Pd(dba)_2$/BINAP afforded compound **XXVII** in 27% yield. Triaryl derivative **XXVIII** and oligomer **XXIX** were isolated in 40 and 18% yield, respectively. Variation of the reactant ratio or raising the amount of the catalyst to 4 mol % almost did not change the yield of **XXVII**, but either other by-products were formed or their ratio changed. When the reaction was carried out in the presence of DavePHOS as ligand instead of BINAP, the yield of compound **XXVII** decreased due to formation of benzene-1,3-diamine derivatives. However, the former ligand turned out to be more effective in the synthesis of *N*,*N*′-bis(6-bromopyridin-2-yl)-2,2′-(adamantane-1,3-diyl)diethanamine (**XXX**), whereas BINAP gave rise to a complex mixture of products which we failed to identify. In the reaction of diamine **I** with 3 equiv of 1,8-dichloroanthracene, compound **XXXI** was isolated in 46% yield. 1,8-Dichloroanthraquinone (**VI**) reacted with 1,3-bis-(2-aminoethyl)adamantane (**I**) at a ratio of 3:1 to produce 50% of *N*,*N*′-diaryl derivative **XXXII** together with acyclic oligomers **XXXIII** and **XXXIV** (19 and 18%, respectively).

N,*N*′-Bis(haloaryl) derivatives **XXVII**–**XXXII** were brought into reaction with 4,7,10-trioxatridecane-1,13-diamine (**XXXV**) (Scheme 5). The reactions were carried out with equimolar amounts of the reactants in dioxane solution with a concentration of 0.02 M, and the reaction mixtures were heated for 24–30 h under reflux. Macrocyclic compound **XXXVII** with two anthracene fragments was isolated in 23% yield. However, the reaction of **XXVII** with diamine **XXXV** followed a more complex pattern. In the presence of 4 mol % of the catalyst we obtained a difficultly separable mixture of monomer, cyclic dimer, and cyclic trimer **XXXVI** (n = 1–3) with an overall yield of 26%, whereas the use of 8 mol % of the catalyst ensured formation of 12% of monomer **XXXVI** (n = 1) and unexpectedly large amount of cyclic dimer **XXXVI** (n = 2, 22%). In the reaction of diamine **XXV** with compound **XXXII** no analogous macrocycle with two anthraquinone fragments was detected in the reaction mixture, and only cyclic dimer and trimer **XXXVIII** (n = 2, 3) were isolated in poor yields (6%). We believe that in this case the structure of the corresponding acyclic intermediate is not favorable for its cyclization, probably due to formation of intramolecular hydrogen bonds N–H···O which make the molecule conformationally rigid. Cesium carbonate was used as a base in this reaction instead of sodium *tert*-butoxide.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400 and 100.6 MHz, respectively, from solutions in $CDCl_3$ (unless otherwise stated) using the solvent signals as reference ($CHCl_3$, δ 7.25; $CDCl_3$, δ_C 77.00 ppm). The mass spectra (MALDI–TOF, positive ion detection) were obtained on a Bruker Daltonics Ultrafex instrument using 1,8,9-trihydroxyanthracene as matrix. The UV spectra were measured on a Perkin–Elmer Lambda 40 spectrophotometer. Preparative column chromatography was performed on silica gel (40–60 μm, Merck). Commercially available 1,3-bromobenzene (**II**), 2,6-dibromopyridine (**III**), 1,8-dichloroanthraquinone (**XVI**), 1,5-dichloroanthraquinone (**XVII**), sodium *tert*-butoxide, BINAP, and DavePHOS were used without additional purification. 2,2′-(Adamantane-1,3-diyl)diethanamine (**I**) [1], 3,3′-dibromobiphenyl (**IV**) [29], and 2,7-dibromonaphthalene (**V**) [30] were synthesized according to known methods; 1,8-dichloroanthracene (**VI**) and 1,5-dichloroanthracene (**XVIII**) were synthesized by reduction of 1,8-dichloroanthraquinone and 1,5-dichloroantraquinone, respectively [31]; $Pd(dba)_2$ was prepared as described in [32] and was not recrystallized. Dioxane was distilled first over alkali and then over metallic sodium; methylene chloride and methanol were distilled.

Macrocyclic compounds VII, IX, and XI–XIV (*general procedure*). Anhydrous dioxane, 5–25 ml, 2,2′-(adamantane-1,3-diyl)diethanamine (**I**), 0.5–2 mmol, and potassium *tert*-butoxide, 1.5–6 mmol, were added under argon to a mixture of 0.5–2 mmol of the corresponding dihaloarene, 2–8 mol % of $Pd(dba)_2$, and 2.5–9 mol % of BINAP or 2′-(dicyclohexyl-λ^3-phosphanyl)-*N*,*N*-dimethylbiphenyl-2-amine. The mixture was heated for 7–30 h under reflux and cooled, the precipitate was filtered off, the filtrate was evaporated under reduced pressure, and the solid residue was subjected to chromatographic separation on silica gel using (in succession) methylene chloride and methylene chloride–methanol (500:1 to 3:1) as eluent.

4,10,22,28-Tetraazanonacyclo[29.5.1.$1^{1,33}$.$1^{5,9}$.$1^{13,17}$.$1^{13,19}$.$1^{15,19}$.$1^{23,27}$.$1^{31,35}$]tetratetraconta-5(44),6,8,23(40),24,26-hexaene (VII) was synthesized from

0.5 mmol (118 mg) of 1,3-dibromobenzene and 0.5 mmol (111 mg) of diamine **I** in the presence of 8 mol % (23 mg) of $Pd(dba)_2$, 9 mol % (28 mg) of BINAP, and 1.5 mmol (150 mg) of sodium *tert*-butoxide in dioxane (reactant concentration 0.02 M); eluent CH_2Cl_2–MeOH (500:1). Yield 9 mg (6%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.30–1.64 m (24H), 1.45 t (8H, ^3J = 7.8 Hz), 2.06 s (4H), 3.11 t (8H, ^3J = 7.8 Hz), 3.41 br.s (4H), 5.86 s (2H), 5.93 d (4H, ^3J = 7.8 Hz), 6.87 t (2H, ^3J = 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.9 (4C), 32.7 (4C), 36.5 (2C), 38.5 (4C), 42.3 (8C), 43.9 (4C), 46.7 (2C), 94.1 (2C), 103.8 (4C), 129.5 (2C), 149.9 (4C). Mass spectrum: *m*/*z* 592.58 $[M]^+$.

Compounds **VII** (*n* = 4) and **VIII** were isolated as by-products in the reaction of 2 mmol (472 mg) of 1,3-dibromobenzene with 2 mmol (444 mg) of diamine **I** in the presence of 2 mol % (23 mg) of $Pd(dba)_2$, 2.5 mol % (20 mg) of DavePHOS, and 6 mmol (580 mg) of sodium *tert*-butoxide in dioxane (reactant concentration 0.1 M). Eluent CH_2Cl_2–MeOH (500:1).

Cyclic tetramer VII (*n* = 4). Yield 12 mg (2%), yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.33 s (8H), 1.38–1.58 m (48H), 1.62 s (8H), 2.06 s (8H), 3.05–3.15 m (16H), 3.47 br.s (8H), 5.85 s (4H), 5.99 d (8H, ^3J = 7.9 Hz), 6.98 t (4H, ^3J = 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.9 (8C), 32.7 (8C), 36.4 (4C), 38.6 (8C), 41.9 (16C), 43.7 (8C), 46.7 (4C), 97.2 (4C), 102.7 (8C), 129.9 (4C), 149.5 (8C). Mass spectrum: *m*/*z* 1184.70 $[M]^+$.

***N*,*N*′-[Adamantane-1,3-diylbis(ethane-2,1-diyl)]-dianiline (VIII).** Yield 46 mg (6%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.32 s (2H), 1.38–1.58 m (12H), 1.61 s (2H), 2.11 s (2H), 3.02–3.12 m (4H), 6.59 d (4H, ^3J = 7.9 Hz), 6.68 t (2H, ^3J = 7.2 Hz), 7.17 t (4H, ^3J = 7.5 Hz); signals from NH protons were not assigned unambiguously. ^{13}C NMR spectrum, δ_C, ppm: 28.6 (2C), 31.9 (2C), 35.7 (1C), 38.6 (2C), 41.2 (4C), 43.7 (2C), 47.8 (1C), 112.7 (4C), 117.1 (2C), 129.2 (4C), 149.6 (2C).

4,10,22,28,40,44-Hexaazanonacyclo[29.5.1.1^{1,33}.1^{5,9}.1^{13,17}.1^{13,19}.1^{15,19}.1^{23,27}.1^{31,35}]tetratetraconta-5(44),6,8,23(40),24,26-hexaene (IX) was synthesized from 0.5 mmol (118.5 mg) of 2,6-dibromopyridine and 0.5 mmol (111 mg) of diamine **I** in the presence of 8 mol % (23 mg) of $Pd(dba)_2$, 9 mol % (18 mg) of DavePHOS, and 1.5 mmol (150 mg) of sodium *tert*-butoxide in dioxane at a reactant concentration of 0.02 M. Eluent CH_2Cl_2–MeOH, 25:1. Yield 16 mg (10%), yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.36–1.60 m (24H), 1.39 t (8H, ^3J = 7.7 Hz), 2.01 br.s (4H), 3.28 t (8H, ^3J = 7.7 Hz), 4.14 br.s (4H), 5.62 d (4H, ^3J = 7.8 Hz), 7.12 t (2H, ^3J = 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.1 (4C), 32.8 (4C), 36.6 (2C), 36.7 (4C), 42.2 (8C), 44.0 (4C), 47.2 (2C), 94.9 (4C), 138.4 (2C), 158.8 (4C). Mass spectrum: *m*/*z* 594.25 $[M]^+$.

***N*,*N*′-Bis{2-[3-(2-aminoethyl)adamantan-1-yl]-ethyl}pyridine-2,6-diamine (X, *n* = 1)** was isolated as by-product in the synthesis of cyclic dimer **IX**. Eluent CH_2Cl_2–MeOH–aq. NH_3, 100:20:3. Yield 26 mg (10%), yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.24 s (4H), 1.32–1.54 m (24H), 1.57 s (4H), 1.99 s (4H), 2.05 br.s (4H), 2.68 t (4H, *J* = 8.1 Hz), 3.15 br.s (4H), 4.16 br.s (2H), 5.66 d (2H, *J* = 7.9 Hz), 7.22 t (1H, *J* = 7.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.0 (4C), 32.7 (4C), 36.5 (4C), 37.1 (2C), 42.0 (4C), 42.1 (4C), 43.7 (2C), 47.8 (2C), 48.2 (2C), 94.1 (2C), 139.1 (1C), 158.2 (2C). Mass spectrum: *m*/*z* 519.16 $[M]^+$.

4,15-Diazahexacyclo[16.5.1.1^{1,20}.1^{5,9}.1^{10,14}.1^{18,22}]-octacosa-5(28),6,8,10(27),11,13-hexaene (XI) was synthesized from 0.5 mmol (156 mg) of 3,3′-dibromobiphenyl and 0.5 mmol (111 mg) of diamine **I** in the presence of 8 mol % (23 mg) of $Pd(dba)_2$, 9 mol % (28 mg) of BINAP, and 1.5 mmol (150 mg) of sodium *tert*-butoxide in dioxane at a reactant concentration of 0.02 M. Eluent CH_2Cl_2–MeOH, 500:1. Yield 32 mg (17%), light brown crystalline substance. ^{1}H NMR spectrum, δ, ppm: 1.35–1.70 m (16H), 2.03 s (2H), 3.15 br.s (2H), 3.41 br.s (2H), 3.93 br.s (2H), 6.54 d (2H, ^3J = 7.9 Hz), 6.99 br.s (2H), 7.18 t (2H, ^3J = 7.8 Hz), 7.22 br.s (2H). ^{13}C NMR spectrum, δ_C, ppm: 29.0 (2C), 33.2 (2C), 36.8 (1C), 37.3 (2C), 38.7 (2C), 43.4 (2C), 44.4 (2C), 48.4 (1C), 109.2 (2C), 114.3 (2C), 115.1 (2C), 129.4 (2C), 147.8 (2C); signals from two quaternary aromatic carbon atoms were not assigned unambiguously. Mass spectrum: *m*/*z* 372.38 $[M]^+$.

6,18,28,40-Tetraazaundecacyclo[39.2.2.2^{2,5}.2^{19,22}.1^{9,13}.1^{9,15}.1^{11,15}.1^{23,27}.1^{31,35}.1^{31,37}.1^{33,37}]hexapentaconta-1(43),2,4,19,21,23(49),24,26,41,44,50,55-dodecaene (XII, *n* = 1) was isolated as by-product in the synthesis of compound **XI**. Eluent CH_2Cl_2–MeOH, 200:1. Yield 16 mg (9%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.25 s (4H), 1.40 s (4H), 1.48 t (8H, ^3J = 7.8 Hz), 1.51 br.s (12H), 1.63 s (4H), 2.05 s (4H), 3.15 t (8H, ^3J = 7.8 Hz), 3.56 br.s (4H), 6.55 d (4H, ^3J = 8.2 Hz), 6.78 s (4H), 6.89 d (4H, ^3J = 7.7 Hz), 7.18 t (4H, ^3J = 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.0 (4C), 32.8 (4C), 36.6 (2C), 38.7 (4C), 42.2 (8C),

43.7 (4C), 47.0 (2C), 111.5 (4C), 111.9 (4C), 116.5 (4C), 129.4 (4C), 143.2 (4C), 148.6 (4C). Mass spectrum: *m*/*z* 744.44 $[M]^+$.

Cyclic dimer XIII was synthesized from 0.5 mmol (143 mg) of 2,7-dibromonaphthalene and 0.5 mmol (111 mg) of diamine **I** in the presence of 8 mol % (23 mg) of $Pd(dba)_2$, 9 mol % (28 mg) of BINAP, and 1.5 mmol (150 mg) of sodium *tert*-butoxide in dioxane at a reactant concentration of 0.02 M. Eluent CH_2Cl_2–MeOH, 200:1. Yield 17 mg (9%), light brown crystalline substance. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.42–1.68 m (24H), 1.49 t (8H, ^3J = 8.0 Hz), 2.04 s (4H), 3.01 t (8H, ^3J = 8.0 Hz), 6.48 d (4H, ^4J = 1.8 Hz), 6.53 d.d (4H, ^3J = 8.6, ^4J = 1.8 Hz), 7.23 d (4H, ^3J = 8.6 Hz); signals from NH protons were not assigned unambiguously. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 28.7 (4C), 32.3 (4C), 36.5 (2C), 37.7 (4C), 42.4 (8C), 43.2 (4C), 44.7 (2C), 100.9 (4C), 113.9 (4C), 119.9 (2C), 127.8 (4C), 137.4 (2C), 147.2 (4C). Mass spectrum: *m*/*z* 692.49 $[M]^+$.

Macrocycle XIV was synthesized from 0.5 mmol (123.5 mg) of 1,8-dichloroanthracene and 0.5 mmol (111 mg) of diamine **I** in the presence of 8 mol % (23 mg) of $Pd(dba)_2$, 9 mol % (28 mg) of BINAP, and 1.5 mmol (150 mg) of sodium *tert*-butoxide in dioxane at a reactant concentration of 0.02 M. Eluent CH_2Cl_2–MeOH, 500:1. Yield 16 mg (8%), yellow–brown oily substance. ^{1}H NMR spectrum, δ, ppm: 1.26 s (2H), 1.34 d (4H, ^3J = 11.8 Hz), 1.49 d (4H, ^3J = 12.3 Hz), 1.61 s (2H), 1.64 t (4H, ^3J = 5.4 Hz), 2.01 br.s (2H), 3.30 t (4H, ^3J = 5.4 Hz), 4.20 br.s (2H), 6.77 d (2H, ^3J = 7.1 Hz), 7.32 d.d (2H, ^3J = 8.4, 7.1 Hz), 7.53 d (2H, ^3J = 8.4 Hz), 8.32 s (1H), 8.97 s (1H). ^{13}C NMR spectrum, δ_C, ppm: 29.0 (2C), 33.7 (2C), 36.8 (1C), 42.1 (4C), 43.4 (2C), 43.6 (2C), 46.7 (1C), 110.1 (2C), 116.8 (1C), 120.2 (2C), 125.0 (2C), 126.1 (2C), 126.3 (1C), 132.9 (2C), 145.5 (2C). Mass spectrum: *m*/*z* 396.33 $[M]^+$.

***N*,*N*′-[Adamantane-1,3-diylbis(ethane-2,1-diyl)]-dianthracen-1-amine (XXV)** was obtained in the reaction of 0.5 mmol (123.5 mg) of 1,5-dichloroanthracene with 0.5 mmol (111 mg) of diamine **I** in the presence of 8 mol % (23 mg) of $Pd(dba)_2$, 9 mol % (28 mg) of BINAP, and 1.5 mmol (150 mg) of sodium *tert*-butoxide in dioxane at a reactant concentration of 0.02 M. Compound **XXV** was isolated as a mixture with anthracene (eluent CH_2Cl_2). Yield 26 mg (18%). ^{1}H NMR spectrum, δ, ppm: 1.51–1.72 m (16H), 2.14 br.s (2H), 3.37 t (4H, ^3J = 7.9 Hz), 4.40 br.s (2H), 6.52 d (2H, ^3J = 6.8 Hz), 7.31–7.45 m (8H), 7.93–7.97 m (4H), 8.32 s (2H), 8.33 s (2H). ^{13}C NMR spectrum, δ_C, ppm: 29.0 (2C), 33.0 (2C), 36.5 (1C), 39.0 (2C), 42.1 (4C), 43.7 (2C), 48.0 (1C), 101.9 (2C), 117.3 (2C), 118.4 (2C), 125.0 (2C), 125.4 (2C), 126.3 (2C), 126.6 (2C), 127.8 (2C), 128.4 (2C), 143.4 (2C); signals from 8 aromatic quaternary carbon atoms were not assigned unambiguously. Mass spectrum: *m*/*z* 574.43 $[M]^+$.

***N*,*N*′-Diaryl-2,2′-(adamantan-1,3-diyl)diethanamines XXVII and XXX–XXXII (*general procedure*).** To a mixture of 2.2–3 equiv of the corresponding dihaloarene, 2–8 mol % of $Pd(dba)_2$, and 2.5–9 mol % of BINAP (or 4.5 mol % of DavePHOS in the reaction with 2,6-dibromopyridine) we added under argon anhydrous dioxane (to a reactant concentration of 0.1 M), 1 equiv of 1,3-bis(2-aminoethyl)adamantane (**I**), and 3 equiv of sodium *tert*-butoxide (or cesium carbonate in the reaction with 1,8-dichloroanthraquinone). The mixture was heated for 4–12 h under reflux and cooled, the precipitate was filtered off, the filtrate was evaporated under reduced pressure, and the solid residue was subjected to chromatographic separation on silica gel using the following solvent systems as eluents (in succession): petroleum ether–methylene chloride (4:1 to 1:4), methylene chloride, methylene chloride–methanol (500:1 to 3:1).

***N*,*N*′-[Adamantane-1,3-diylbis(ethane-2,1-diyl)]-bis(3-bromoaniline) (XXVII)** was synthesized from 0.5 mmol (111 mg) of diamine **I** and 1.1 mmol (260 mg) of 1,3-dibromobenzene. Eluent petroleum ether–CH_2Cl_2, 1:1. Yield 73 mg (27%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.32 s (2H), 1.41 t (4H, ^3J = 8.0 Hz), 1.44–1.56 m (8H), 1.62 br.s (2H), 2.06 br.s (2H), 3.07 t (4H, ^3J = 8.0 Hz), 3.55 br.s (2H), 6.48 d.d.d (2H, ^3J = 8.2, ^4J = 2.2, 0.9 Hz), 6.71 t (2H, ^4J = 2.0 Hz), 6.78 d.d.d (2H, ^3J = 7.8, ^4J = 1.8, 0.9 Hz), 6.99 t (2H, ^3J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.9 (2C), 32.7 (2C), 36.4 (1C), 38.5 (2C), 41.9 (4C), 43.5 (2C), 47.7 (1C), 111.5 (2C), 115.0 (2C), 119.8 (2C), 123.3 (2C), 130.4 (2C), 149.7 (2C). Mass spectrum: *m*/*z* 530.08 $[M]^+$.

***N*-[2-(3-{2-[Bis(3-bromophenyl)amino]ethyl}-adamantan-1-yl)ethyl]-3-bromoaniline (XXVIII)** was isolated as the major product in the synthesis of compound **XXVII**. Eluent petroleum ether–CH_2Cl_2, 2:1. Yield 92 mg (40%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.31 s (2H), 1.38–1.52 m (12H), 1.62 s (2H), 2.06 br.s (2H), 3.07 t (2H, ^3J = 7.9 Hz), 3.54 br.s (1H), 3.68 t (2H, ^3J = 8.2 Hz), 6.48 d (1H, ^3J = 7.6 Hz), 6.71 s (1H), 6.78 d (1H, ^3J = 7.7 Hz), 6.88 d (2H, ^3J = 7.4 Hz), 6.99 t (1H, ^3J = 7.9 Hz), 7.06–7.14 m (6H). ^{13}C NMR spectrum, δ_C,

ppm: 28.8 (2C), 32.6 (2C), 36.4 (1C), 38.5 (1C), 40.2 (1C), 41.5 (2C), 41.9 (2C), 43.4 (1C), 47.2 (1C), 47.4 (1C), 111.5 (1C), 115.0 (1C), 119.5 (2C), 119.8 (1C), 123.1 (2C), 123.3 (1C), 123.7 (2C), 124.5 (2C), 130.4 (1C), 130.6 (2C), 148.6 (2C), 149.7 (1C). Mass spectrum: *m*/*z* 684.23 $[M]^+$.

***N*,*N*′-Bis[2-(3-{2-[(3-bromophenyl)amino]ethyl}-adamantan-1-yl)ethyl]benzene-1,3-diamine (XXIX)** was isolated as by-product in the synthesis of compound **XXVII**. Eluent CH_2Cl_2. Yield 38 mg (18%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.31 s (4H), 1.38–1.57 m (24H), 1.61 br.s (4H), 2.05 br.s (4H), 3.02–3.12 m (8H), 3.48 br.s (2H), 3.65 br.s (2H), 5.85 br.s (1H), 5.99 d.d (2H, ^3J = 8.1, ^4J = 2.1 Hz), 6.48 d.d (2H, ^3J = 8.2, ^4J = 2.1 Hz), 6.70 t (2H, ^4J = 1.8 Hz), 6.77 d (2H, ^3J = 7.9 Hz), 6.97 t (1H, ^3J = 8.2 Hz), 6.99 t (2H, ^3J = 8.1 Hz). Mass spectrum: *m*/*z* 826.45 $[M]^+$.

***N*,*N*′-[Adamantane-1,3-diylbis(ethane-2,1-diyl)]-bis(6-bromopyridin-2-amine) (XXX)** was synthesized from 0.5 mmol (111 mg) of diamine **I** and 1.1 mmol (261 mg) of 2,6-dibromopyridine. Eluent CH_2Cl_2–MeOH, 5:1. Yield 40 mg (15%), yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.32–1.60 m (16H), 2.00 br.s (2H), 4.12 t (4H, ^3J = 8.2 Hz), 4.82 br.s (2H), 7.00 d (2H, ^3J = 7.5 Hz), 7.08 d (2H, ^3J = 8.1 Hz), 7.35 t (2H, ^3J = 7.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.8 (2C), 32.6 (2C), 36.0 (1C), 36.3 (2C), 41.7 (4C), 43.8 (2C), 46.8 (1C), 112.5 (2C), 120.7 (2C), 139.3 (2C), 139.8 (2C), 150.1 (2C). Mass spectrum: *m*/*z* 532.19 $[M]^+$.

***N*,*N*′-[Adamantane-1,3-diylbis(ethane-2,1-diyl)]-bis(8-chloroanthracen-1-amine) (XXXI)** was synthesized from 1 mmol (222 mg) of diamine **I** and 3 mmol (741 mg) of 1,8-dichloroanthracene. Eluent CH_2Cl_2. Yield 300 mg (46%), yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.52–1.75 m (16H), 2.14 br.s (2H), 3.38 t (4H, ^3J = 7.9 Hz), 4.51 br.s (2H), 6.53–6.58 m (2H), 7.31 t (2H, ^3J = 7.8 Hz), 7.35–7.39 m (4H), 7.51 d (2H, ^3J = 7.2 Hz), 7.86 d (2H, ^3J = 8.4 Hz), 8.35 s (2H), 8.73 s (2H). ^{13}C NMR spectrum, δ_C, ppm: 29.1 (2C), 33.0 (2C), 36.6 (1C), 39.0 (2C), 42.2 (4C), 43.5 (2C), 48.0 (1C), 102.4 (2C), 115.6 (2C), 116.7 (2C), 124.1 (2C), 124.9 (2C), 125.0 (2C), 127.3 (6C), 127.9 (2C), 132.1 (2C), 132.2 (2C), 133.0 (2C), 143.7 (2C). Mass spectrum: *m*/*z* 642.37 $[M]^+$.

1,1′-[Adamantane-1,3-diylbis(ethane-2,1-diylimino)]bis(8-chloroanthra-9,10-quinone) (XXXII) was synthesized from 1 mmol (222 mg) of diamine **I** and 3 mmol (831 mg) of 1,8-dichloroanthra-9,10-quinone. Eluent CH_2Cl_2. Yield 355 mg (50%), dark red crystalline substance, mp 198–200°C (decomp.). UV spectrum (CH_2Cl_2), λ_{max}, nm (log ε): 248 (5.39), 280 (4.72), 322 (4.60), 520 (4.55). ^{1}H NMR spectrum, δ, ppm: 1.42 s (2H), 1.48–1.69 m (14H), 2.09 br.s (2H), 3.25–3.32 m (4H), 6.96–7.01 m (2H), 7.41–7.45 m (4H), 7.51 t (2H, ^3J = 7.8 Hz), 7.67 d.d (2H, ^3J = 8.0, ^4J = 1.2 Hz), 8.16 d.d (2H, ^3J = 7.7, 1.2 Hz), 9.47 t (2H, ^3J = 4.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.8 (2C), 32.7 (2C), 36.4 (1C), 37.8 (2C), 41.8 (4C), 42.9 (2C), 47.4 (1C), 113.5 (2C), 114.8 (2C), 118.1 (2C), 126.3 (2C), 128.9 (2C), 132.5 (2C), 133.5 (2C), 134.3 (2C), 134.8 (2C), 135.4 (2C), 137.8 (2C), 151.3 (2C), 182.8 (2C), 183.8 (2C). Mass spectrum: *m*/*z* 702.32 $[M]^+$.

Compounds **XXXIII** and **XXXIV** were isolated as by-products in the synthesis of **XXXII** (eluent methylene chloride).

8-Chloro-1-{[2-(3-{2-[(8-{[2-(3-{2-[(8-chloro-9,10-dioxo-9,10-dihydroanthracen-1-yl)amino]-ethyl}adamantan-1-yl)ethyl]amino}-9,10-dioxo-9,10-dihydroanthracen-1-yl)amino]ethyl}adamantan-1-yl)ethyl]amino}anthra-9,10-quinone (XXXIII). Yield 110 mg (19%), dark red crystalline substance, mp 158–160°C (decomp.). UV spectrum (CH_2Cl_2), λ_{max}, nm (log ε): 246 (5.47), 282 (4.95), 320 (4.70), 538 (4.72). ^{1}H NMR spectrum, δ, ppm: 1.40 s (4H), 1.46–1.58 m (24H), 1.62 s (4H), 2.05 s (4H), 3.15–3.27 m (8H), 6.85 d (2H, ^3J = 8.6 Hz), 6.89 d (2H, ^3J = 8.5 Hz), 7.32 t (2H, ^3J = 7.6 Hz), 7.34 t (2H, ^3J = 8.5 Hz), 7.37 t (2H, ^3J = 7.3 Hz), 7.44 d (2H, ^3J = 7.3 Hz), 7.48 d (2H, ^3J = 8.0 Hz), 7.64 d (2H, ^3J = 8.0 Hz), 8.13 d (2H, ^3J = 7.7 Hz), 9.39 t (2H, ^3J = 4.4 Hz), 9.43 t (2H, ^3J = 4.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.8 (4C), 32.7 (4C), 36.4 (2C), 37.7 (4C), 41.8 (8C), 42.9 (4C), 47.4 (2C), 113.4 (2C), 114.1 (2C), 114.6 (2C), 114.8 (2C), 117.5 (2C), 118.1 (2C), 126.2 (2C), 130.5 (2C), 132.4 (2C), 133.4 (2C), 133.9 (2C), 134.1 (2C), 134.3 (2C), 134.7 (2C), 135.4 (2C), 137.8 (2C), 150.9 (2C), 151.3 (2C), 182.7 (2C), 183.6 (2C), 184.4 (1C), 188.6 (1C). Mass spectrum: *m*/*z* 1128.59 $[M]^+$.

Oligomer XXXIV. Yield 95 mg (18%), dark red crystalline substance, mp 188–190°C (decomp.). UV spectrum (CH_2Cl_2), λ_{max}, nm (log ε): 248 (5.38), 286 (4.87), 320 (4.68), 538 (4.74). ^{1}H NMR spectrum, δ, ppm: 1.39 s (6H), 1.44–1.58 m (36H), 1.61 s (6H), 2.04 s (6H), 3.12–3.25 m (12H), 6.80–6.90 m (6H), 7.26–7.49 m (14H), 7.62 d.d (2H, ^3J = 8.0, ^4J = 0.8 Hz), 8.11 d.d (2H, ^3J = 7.6, ^4J = 0.9 Hz), 9.38 t (4H, ^3J = 4.5 Hz), 9.42 t (2H, ^3J = 4.8 Hz). ^{13}C NMR

spectrum, δ_C, ppm: 28.8 (6C), 32.7 (6C), 36.3 (3C), 37.7 (6C), 41.8 (12C), 42.9 (6C), 47.4 (3C), 113.4 (2C), 114.1 (4C), 114.6 (4C), 114.8 (4C), 126.2 (2C), 130.5 (2C), 132.4 (2C), 133.4 (2C), 133.9 (4C), 134.1 (4C), 134.3 (2C), 134.7 (2C), 135.4 (2C), 150.9 (4C), 151.2 (2C), 182.7 (2C), 183.6 (2C), 184.3 (2C), 188.6 (2C). Mass spectrum: *m*/*z* 1554.46 $[M]^+$.

Macrocycles XXXVI–XXXVIII (*general procedure*). To a mixture of 1 equiv of *N*,*N*′-diaryl-2,2′-(adamantane-1,3-diyl)diethanamine **XXVII**, **XXXI**, or **XXXII**, 8 mol % of $Pd(dba)_2$, and 9 mol % of BINAP we added under argon anhydrous dioxane (to a reactant concentration of 0.02 M), 1 equiv of 4,7,10-trioxatridecane-1,13-diamine (**XXXV**), and 3 equiv of sodium *tert*-butoxide (or cesium carbonate in the reaction with **XXXII**). The mixture was heated for 24–30 h under reflux and cooled, the precipitate was filtered off, the filtrate was evaporated under reduced pressure, and the solid residue was subjected to chromatography on silica gel using (in succession) methylene chloride and methylene chloride–methanol (500:1 to 3:1) as eluents.

14,17,20-Trioxa-4,10,24,30-tetraazahexacyclo-[31.5.1.1^{1,35}.1^{5,9}.1^{25,29}.1^{33,37}]tritetraconta-5(43),6,8,-25(42),26,28-hexaene (XXXVI, *n* = 1) was synthesized from 0.26 mmol (140 mg) of compound **XXVII** and 0.26 mmol (58 mg) of diamine **XXXV**. Eluent CH_2Cl_2–MeOH, 5:1. Yield 28 mg (12%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.30 s (2H), 1.36–1.56 m (12H), 1.60 s (2H), 1.85 quint (4H, ^3J = 5.9 Hz), 2.03 s (2H), 3.06 t (4H, ^3J = 7.4 Hz), 3.18 t (4H, ^3J = 6.5 Hz), 3.52–3.60 m (8H), 3.60–3.66 m (4H), 4.05 br.s (4H), 5.84 s (2H), 5.97 br.s (4H), 6.94 t (2H, ^3J = 7.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.9 (2C), 29.3 (2C), 32.7 (2C), 36.5 (1C), 38.6 (2C), 41.6 (2C), 42.0 (4C), 43.8 (2C), 47.8 (1C), 69.6 (2C), 70.2 (2C), 70.6 (2C), 97.1 (2C), 102.4 (2C), 102.7 (2C), 129.9 (2C), 149.7 (4C). Mass spectrum: *m*/*z* 590.25 $[M]^+$.

14,17,20,52,55,58-Hexaoxa-4,10,24,30,42,48,62,68-octaazaundecacyclo[69.5.1.1^{1,73}.1^{5,9}.1^{25,29}.1^{33,37}.1^{33,39}.-1^{35,39}.1^{43,47}.1^{63,67}.1^{71,75}]hexaoctaconta-5(86),6,8,-25(85),26,28,43(81),44,46,63(80),64,66-dodecaene (XXXVI, *n* = 2) was isolated as the second product in the reaction of **XXVII** with **XXXV**. Eluent CH_2Cl_2–MeOH, 10:1. Yield 49 mg (22%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 1.30–1.61 m (32H), 1.85 quint (8H, ^3J = 5.9 Hz), 2.03 s (4H), 3.05 br.s (8H), 3.18 t (8H, ^3J = 6.0 Hz), 3.52–3.60 m (16H), 3.60–3.66 m (8H), 5.84 s (4H), 5.97 br.s (8H), 6.94 t (4H, ^3J = 7.9 Hz); signals from NH protons were not assigned unambiguously. Mass spectrum: *m*/*z* 1180.95 $[M]^+$.

Macrocycle XXXVII was synthesized from 0.21 mmol (135 mg) of compound **XXXI** and 0.21 mmol (46 mg) of diamine **XXXV**. Eluent CH_2Cl_2–MeOH, 100:1. Yield 38 mg (23%), yellow–brown oily substance. ^{1}H NMR spectrum, δ, ppm: 1.53–1.74 m (16H), 2.00–2.06 m (6H), 3.32–3.41 m (8H), 3.55–3.60 m (4H), 3.66–3.75 m (8H), 5.20 br.s (2H), 5.71 br.s (2H), 6.45–6.50 m (4H), 7.29–7.34 m (6H), 8.26 s (2H), 8.49 s (2H). Mass spectrum: *m*/*z* 790.67 $[M]^+$.

Macrocycle XXXVIII (*n* = 2) was synthesized from 0.23 mmol (163 mg) of compound **XXXII** and 0.23 mmol (51 mg) of diamine **XXXV**. Eluent CH_2Cl_2–MeOH, 50:1. Yield 12 mg (6%), dark red oily substance. ^{1}H NMR spectrum, δ, ppm: 1.42 s (4H), 1.48–1.65 m (28H), 1.95 quint (8H, ^3J = 6.3 Hz), 2.07 s (4H), 3.19–3.25 m (8H), 3.29 q (8H, ^3J = 6.0 Hz), 3.59 t (8H, ^3J = 6.0 Hz), 3.60–3.63 m (8H), 3.65–3.68 m (8H), 6.86 d (4H, ^3J = 8.4 Hz), 6.90 d (4H, ^3J = 8.5 Hz), 7.32–7.38 m (8H), 7.44 d (8H, ^3J = 7.3 Hz), 9.40 t (4H, ^3J = 4.7 Hz), 9.54 t (4H, ^3J = 5.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.9 (4C), 29.4 (4C), 32.8 (4C), 36.4 (2C), 37.8 (4C), 40.0 (4C), 41.9 (8C), 43.1 (4C), 48.1 (2C), 68.8 (4C), 70.4 (4C), 70.8 (4C), 114.3 (8C), 114.7 (4C), 114.8 (4C), 117.4 (4C), 117.5 (4C), 134.0 (8C), 134.3 (4C), 135.2 (4C), 151.0 (8C), 184.4 (4C), 188.8 (4C). Mass spectrum: *m*/*z* 1700.24 $[M]^+$.

Macrocycle XXXVIII (*n* = 3) was isolated as the second product. Yield 12 mg (6%), dark red oily substance. ^{1}H NMR spectrum, δ, ppm: 1.40 s (6H), 1.48–1.61 m (36H), 1.62 s (6H), 1.86–1.96 m (12H), 2.06 s (6H), 3.19 br.s (12H), 3.25–3.34 m (12H), 3.52–3.60 m (24H), 3.60–3.64 m (12H), 6.84 d (6H, ^3J = 8.9 Hz), 6.88 d (6H, ^3J = 9.0 Hz), 7.30–7.37 m (12H), 7.42 d (12H, ^3J = 8.4 Hz), 9.34 t (6H, ^3J = 4.2 Hz), 9.49 t (6H, ^3J = 5.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.9 (6C), 29.5 (6C), 32.8 (6C), 36.4 (3C), 37.8 (6C), 40.0 (6C), 41.9 (12C), 43.1 (6C), 47.6 (3C), 68.7 (6C), 70.4 (6C), 70.7 (6C), 114.2 (6C), 114.3 (6C), 114.7 (6C), 114.8 (6C), 117.4 (6C), 117.5 (6C), 133.9 (12C), 134.2 (12C), 151.0 (6C), 151.1 (6C), 184.4 (6C), 188.7 (6C). Mass spectrum: *m*/*z* 2550.83 $[M]^+$.

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