HETEROCYCLES, Vol. 90, No. 2, 2015, pp. 989 - 1017. © 2015 The Japan Institute of Heterocyclic Chemistry
Received, 30th June, 2014, Accepted, 14th August, 2014, Published online, 21st August, 2014
DOI: 10.3987/COM-14-S(K)71

MACROBICYCLIC AND MACROTRICYCLIC DERIVATIVES OF *N,N',N'', N'''*-TETRASUBSTITUTED CYCLEN AND CYCLAM

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Abstract – *N,N'N'',N'''*-Tetrabenzyl derivatives of cyclen and cyclam possessing two bromine atoms in *trans*-positioned phenyl rings were introduced in the Pd-catalyzed amination reactions with oxadiamines and polyamines to provide a wide series of macrobicyclic compounds with tetrabenzyl substituted cyclen and cyclam central moieties in yields up to 31%. Macrocycles based on 1,7-dibenzylcyclen were modified with two 3-bromobenzyl substituents and introduced in the Pd-catalyzed macrocyclization with di- and trioxadiamines to afford spherically shaped macrotricyclic cryptands in yields up to 33%. An alternative approach to isomeric macrotricyclic cryptands employed Pd-catalyzed amination of di(Boc)-di(3-bromobenzyl)cyclen followed by the dialkylation of the resulting bicycle with two bromobenzyl groups and final catalytic macrocyclization step (yields up to 24%).

INTRODUCTION

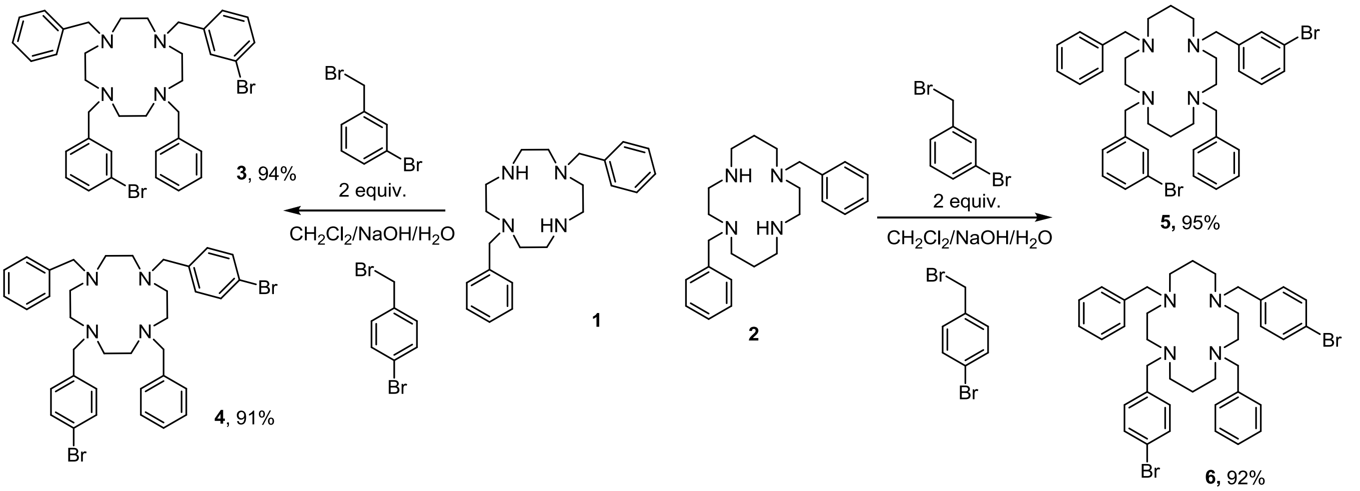
Polyazamacrocycles possess an important place among various macrocyclic compounds due to their unique properties of metal cations coordination, owing to which they find numerous applications as selective complexing agents, chemical sensors, catalysts of chemical and biological processes, contrast agents in MRI and PET, they have been studied in the transport of radioisotopes in radiotherapy and as saturated analogs of porphyrin systems in biological processes modeling. Most studied and widely spread are 1,4,7,10-tetraazacyclododecane (cyclen) and 1,4,8,11-tetraazacyclotetradecane (cyclam), and DOTA, the cyclen derivative, became the most demanded tetraazamacrocycle. These facts boost new research in the field of the chemistry of macropolycycles (cryptands) comprising structural fragments of mentioned tetraazamacrocycles.

Macropolycyclic compounds are suitable frameworks for the construction of many receptor sites.[1] Diazacrown ethers were the first to be employed in the creation of macrobicyclic and macrotricyclic compounds.[2] More simple molecules comprise several isolated diazacrown ethers,[3,4] spirocondensed macrocycles,[5] condensed macrocycles with saturated and unsaturated cyclic fragments.[6] Polymacrocyclic compounds may be of different geometry resulting from various modes of attaching several macrocycles. Spherical macrobicyclic polyether cryptates were designed by Lehn,[7] cage-type macrobicycles were thoroughly studied by Italian chemists.[8-12] More sophisticated spherical and cylindrical macrotricycles were developed,[13-15] cross-bridged tetramacrocyclic systems were created on the basis of diazacrown ethers.[16] Macrobicycles may combine classical crown ether moiety and more complex fragments including aromatics and heteroaromatics,[17] chiral biscrown ethers have been also reported.[18] Various methods were worked out for the introduction of arene moieties in the framework of macropolycyclic compounds which serve as sensing units. In the majority of these compounds the arene unit is linked to the nitrogen atoms of the macrocycle *via* methylene goups,[19-22] but in some compounds the arene moiety is attached through a direct C(sp^2)-N bond.[23,24] A number of macropolycycles derived from cyclam and cyclen were also reported,[25,26] their mutual feature being the attachment of two tetraazamacrocycles *via* xylyl linkers.

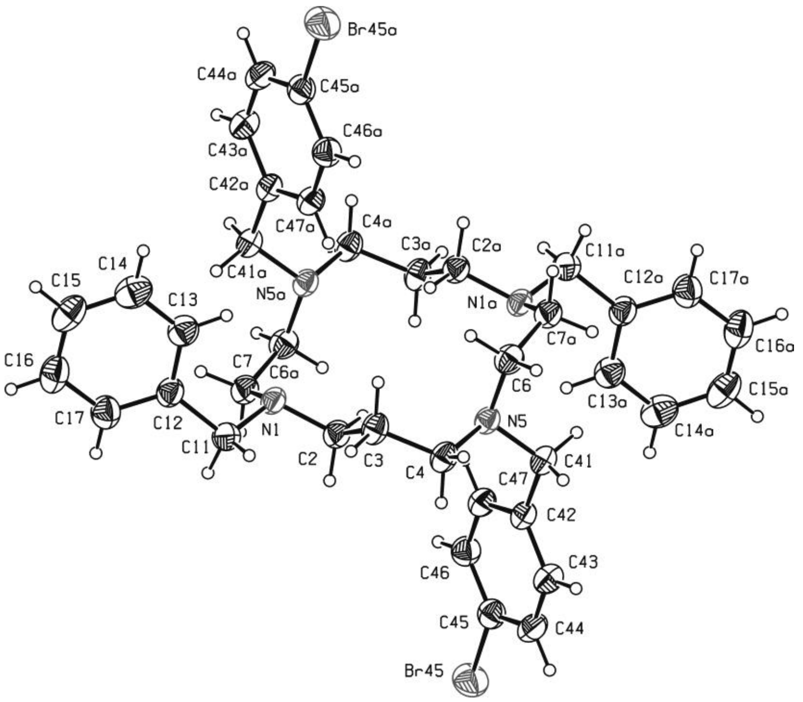
RESULTS AND DISCUSSION

In last years we elaborated a general route to macrobicycles based on tetraazamacrocycles and diazacrown ethers *via* Pd-catalyzed amination reaction of di(bromobenzyl)substituted macrocycles.[27,28] We investigated the possibility to synthesize the cryptands with pyridinyl spacers[28,29] and also introduced additional pyrimidinyl substituents.[30] The formation of the macrobicycles using adamantane-containing diamines was investigated,[31] and in this recent work the possibility to introduce tetrabenzyl substituted cyclen and cyclam in the macrocyclization reaction was demonstrated using an exemplary diamine. Taking this fact into consideration, we decided to synthesize a series of macrobicyclic cryptands with various di- and polyamine linkers comprising tetrabenzyl substituted tetraazamacrocycles, because such compounds are of interest for creating chemosensors on their basis, and for further transformations into macrotricycles.

To synthesize starting tetrabenzyl derivatives of cyclen and cyclam, the reaction of 1,7-dibenzylcyclen **1** or 1,8-dibenzylcyclam **2** with 2 equiv. of bromobenzyl bromides in H_2O/CH_2Cl_2 two-phase system was carried out in the presence of NaOH, and the target compounds **3-6** were obtained in 91-95% yields (Scheme 1). Crystal structure was obtained for compound **6** (Figure 1).



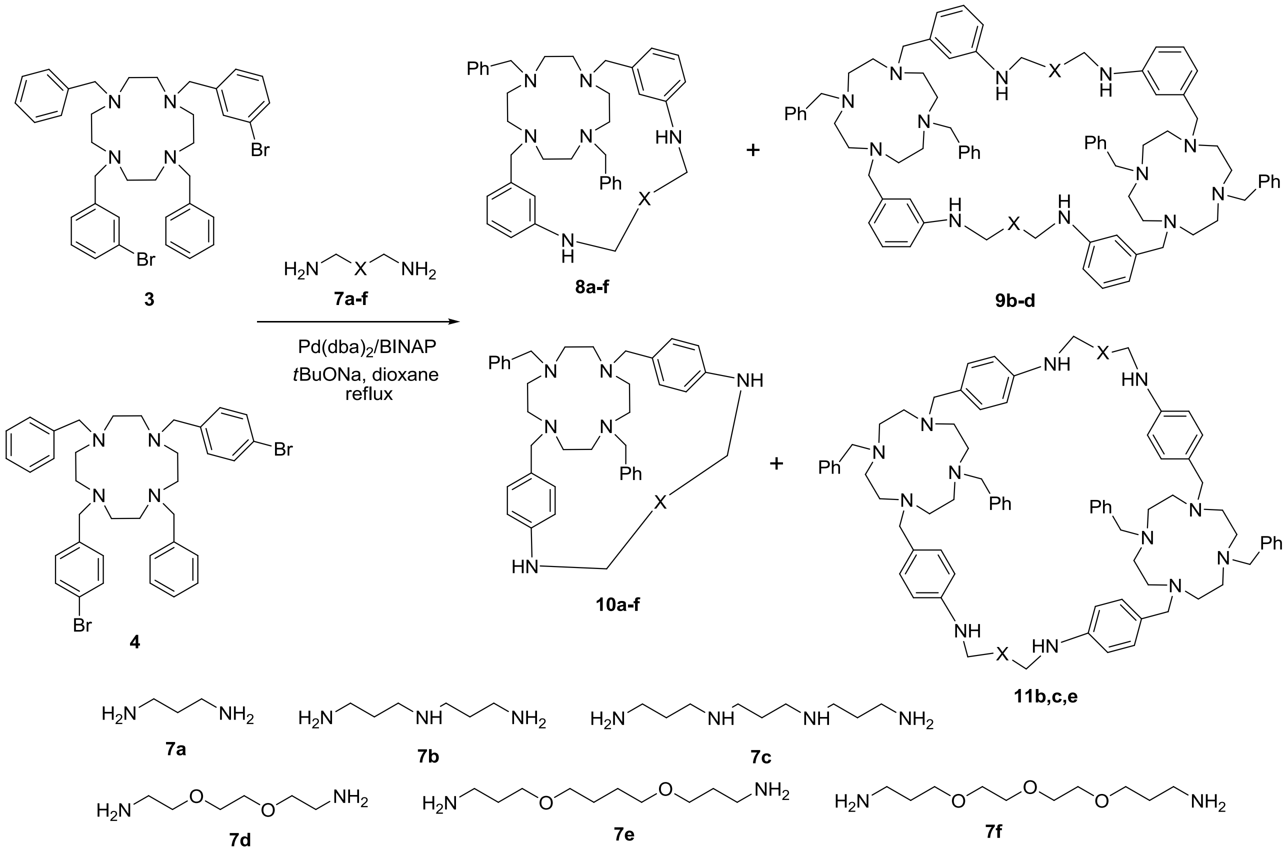
Scheme 1



Crystal system: triclinic
Space group: P1
a = 9.8236(18) Å
b = 10.263(2) Å
c = 11.666(3) Å
α = 102.44(2)°
β = 113.97(2)°
γ = 111.32°
Z = 4

Figure 1. ORTEP view for compound **6**

Compounds **3** and **4** were introduced in the Pd-catalyzed amination reaction with various di- and polyamines **7a-f** using a standard $Pd(dba)_2$/BINAP (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene) catalytic system with *t*BuONa as a base, reactions were conducted in boiling dioxane (c = 0.02 M) (Scheme 2). Target macrobicycles **8** and **10** were obtained almost in all reactions in yields ranging from 11 to 31% (Table 1). Cyclic and linear oligomers were also obtained as side products in all reactions, in some cases we managed to isolate interesting macrotricyclic cyclodimers **9** and **11** (entries 2-4, 8, 9), in other cases they were detected only in multicomponent mixtures. Higher yields of macrobicyclic cryptands were obtained for cyclen derivatives, especially in the reactions with di(3-bromobenzyl) derivative **3**.

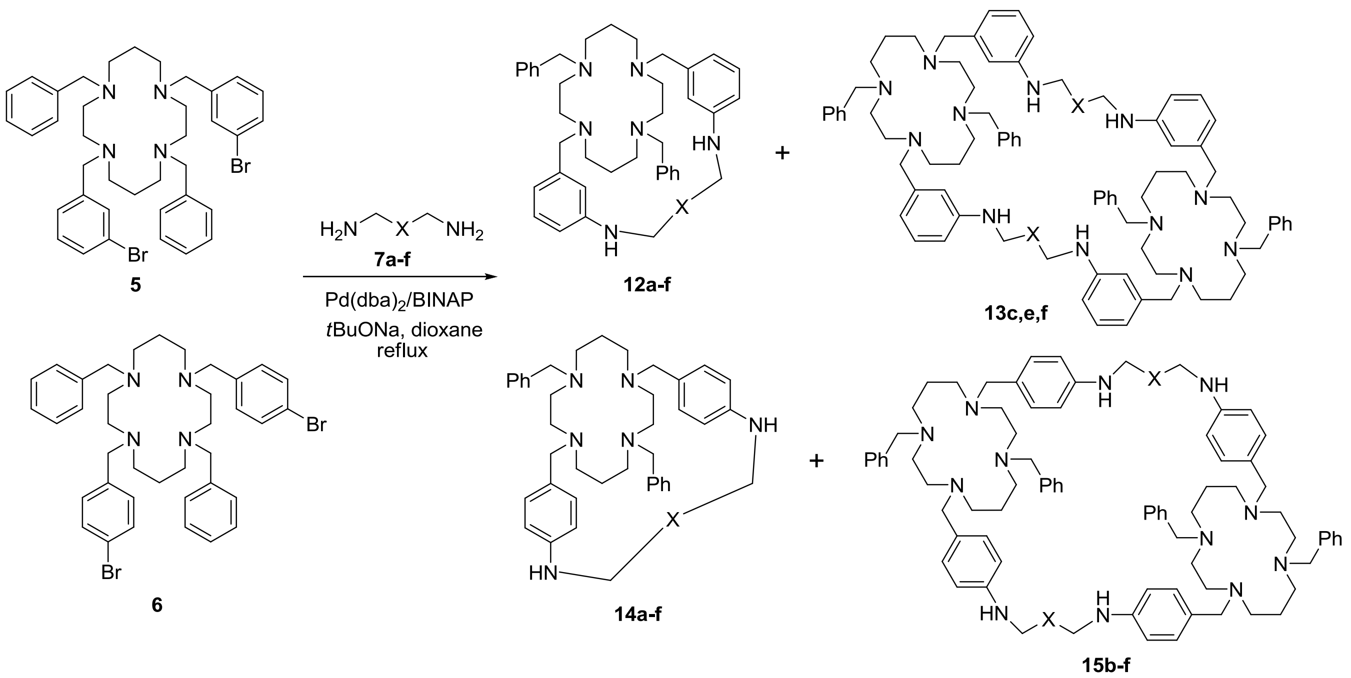


Scheme 2

Table 1. Synthesis of macrobicycles **8** and **10**

Entry	Starting compounds	Macrobicycles, yield, %	Macrotricycles, yield, %
1	**3** + **7a**	**8a**, 31	
2	**3** + **7b**	**8b**, 16	**9b**, 14
3	**3** + **7c**	**8c**, 18	**9c**, 7
4	**3** + **7d**	**8d**, 24	**9d**, 15
5	**3** + **7e**	**8e**, 22	
6	**3** + **7f**	**8f**, 19	
7	**4** + **7a**	**10a**, traces	
8	**4** + **7b**	**10b**, 14	**11b**, 18
9	**4** + **7c**	**10c**, 11	**11c,** 7
10	**4** + **7d**	**10d**, 16	
11	**4** + **7e**	**10e**, 15	**11e**, traces
12	**4** + **7f**	**10f**, 20	

The macrocyclization reactions with tetrasubstituted cyclams **5** and **6** were carried out under similar conditions and proved to be also enough efficient (Scheme 3, Table 2), and in some cases the yields of corresponding macrobicycles **12** and **14** were higher than the yields of the macrobicycles **8** and **10** based on cyclen (compare entries 3, 6, 7 in Tables 1 and 2).



Scheme 3

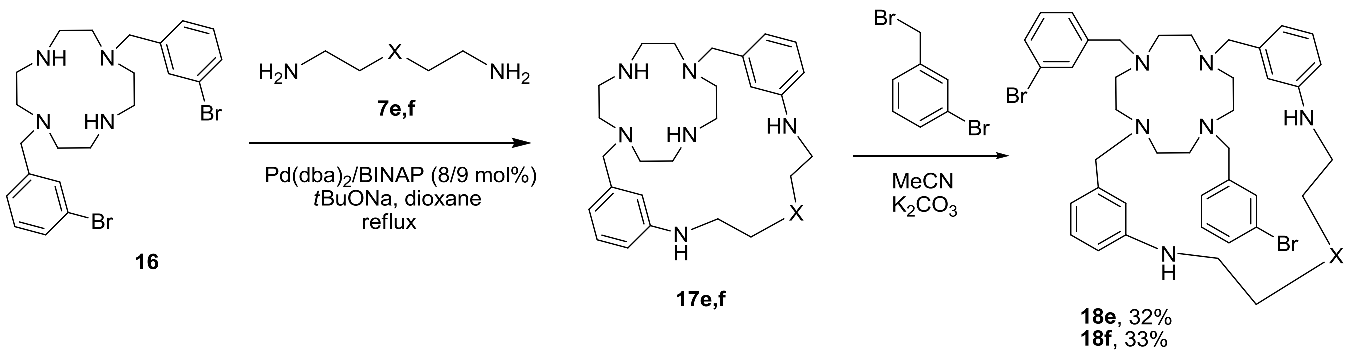
Table 2. Synthesis of macrobicycles **12** and **14**

Entry	Starting compounds	Macrobicycles, yield, %	Macrotricycles, yield, %
1	**5** + **7a**	**12a**, 12	
2	**5** + **7b**	**12b**, 16	
3	**5** + **7c**	**12c**, 20	**13c**, 9
4	**5** + **7d**	**12d**, 14	
5	**5** + **7e**	**12e**, 15	**13e**, 9
6	**5** + **7f**	**12f**, 24	**13f**, 10
7	**6** + **7a**	**14a**, 18	
8	**6** + **7b**	**14b**, 15	**15b**, 19
9	**6** + **7c**	**14c**, 14	**15c**, 11
10	**6** + **7d**	**14d**, 16	**15d**, 8
11	**6** + **7e**	**14e**, 18	**15e**, 14
12	**6** + **7f**	**14f**, 15	**15f**, 19

This may be explained by the fact that the introduction of two additional benzyl substituents changes the geometrical demands for the polyamine chain length for successful macrocyclization. Also, tetrabenzylcyclam may form less stable complexes with Pd(0) compared to 1,8-dibenzylcyclam, this equalizes the reactivity of tetrabenzylcyclam and tetrabenzylcyclen. It should be noted that our earlier experiments on the catalytic amination of cyclen and cyclam dibenzyl derivatives clearly demonstrated better reactivity of cyclen-based compounds.[32] Macrotricycles **13** and **15** were obtained as second products in all reactions, in the majority of cases they were isolated, and sometimes their yields were even higher than those of macrobicyclic cryptands (Table 2, entries 8, 12).

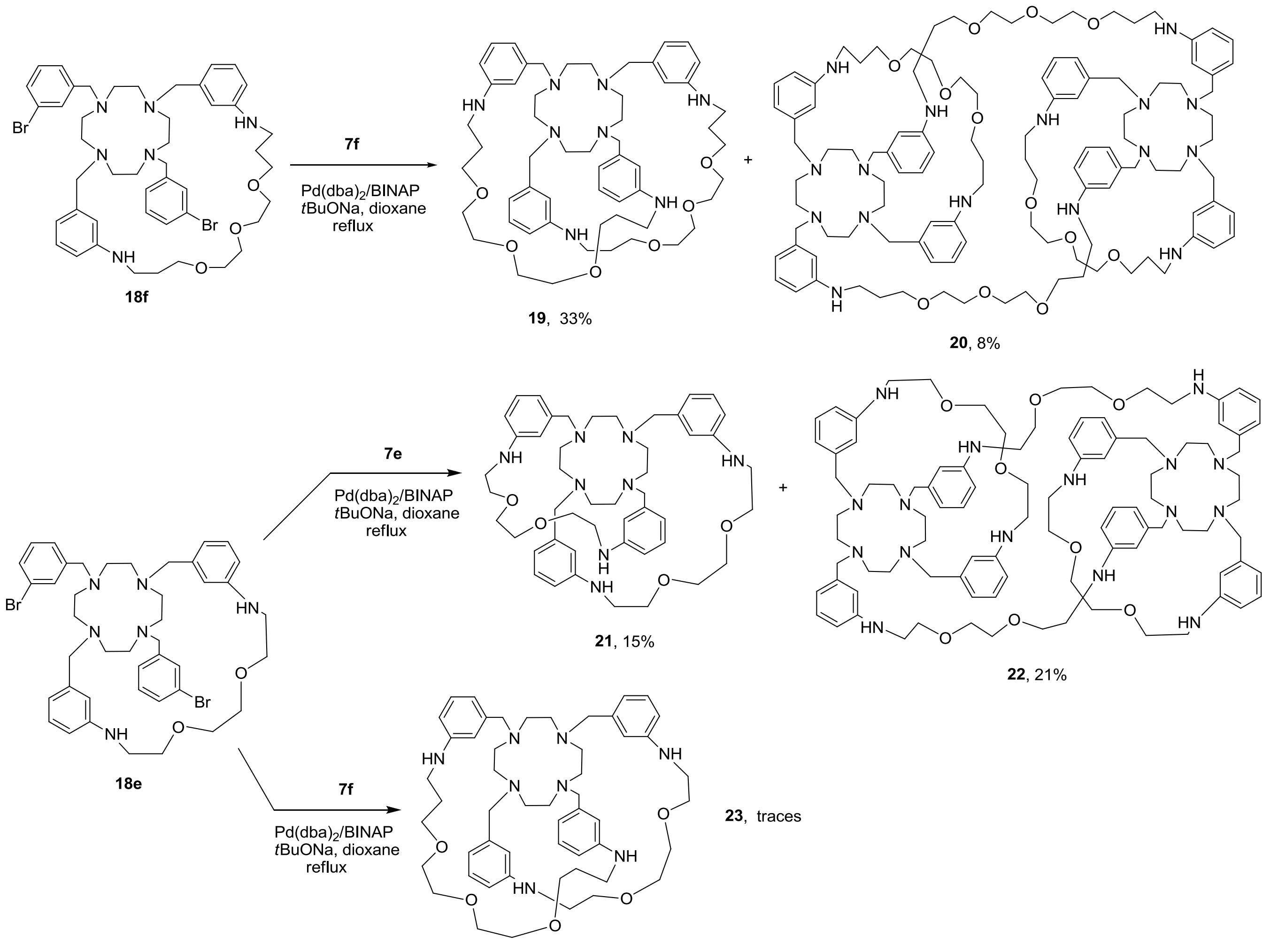
For many macrobicycles we noted substantial line broadening in ^{13}C NMR spectra, line broadening of the protons in *para*-disubstituted benzene rings was also observed. This effect may be due to hindered conformational changes in tetraazamacrocycle bearing four benzyl substituents. The problem could be partially solved by registering spectra in DMSO-d_6 at 363K.

The ability of tetrabenzyl substituted tetraazamacrocycles to normally form macrobicycles was employed for the synthesis of the spherically shaped cryptands using a three-step method. At the first step macrobicycles **17e,f** comprising cyclam and oxadiamine units were synthesized from 1,7-di(3-bromobenzyl)cyclen **16** according to an erlier described procedure.[28] Then these compounds were reacted with 1.7-1.8 equiv. of 3-bromobenzyl bromide to furnish tetrabenzyl macrobicycles **18e,f** in moderate yields (Scheme 4). The main difficulty of this step was the competing alkylation of the nitrogen atoms of the oxadiamine chain.

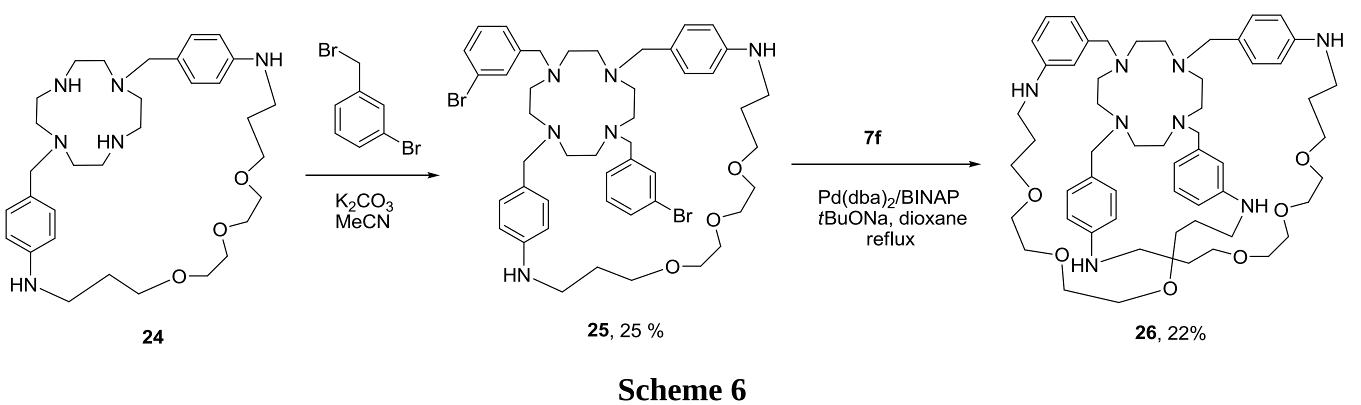


Scheme 4

Pd-Catalyzed macrocyclization of the compounds **18e,f** with oxadiamines **7e,f** using the same catalytic system afforded target spherically shaped macrotricycles **19** and **21**, their yields being strongly dependent on the nature of oxadiamine chains (Scheme 5). Interesting macropentacyclic dimers **20** and **22** were also isolated as the second products in these reactions. In the case of the reaction of **18e** with trioxadiamine **7f** cryptand **23** was obtained only in trace amounts among other unidentified reaction products. Macrotricyclic cryptand **26** possessing two trioxadimaine chains and two *p*-aminobenzyl spacers was synthesized in an analogous manner by the alkylation of the macrobicycle **24** with 3-bromobenzyl bromide followed by the catalytic macrocyclization involving derivative **25** (Scheme 6). It should be noted that the yields of macrotricycles **19**, **21** and **26** ranging from 15 to 33% are quite comparable to those of the parent macrobicylic compounds.

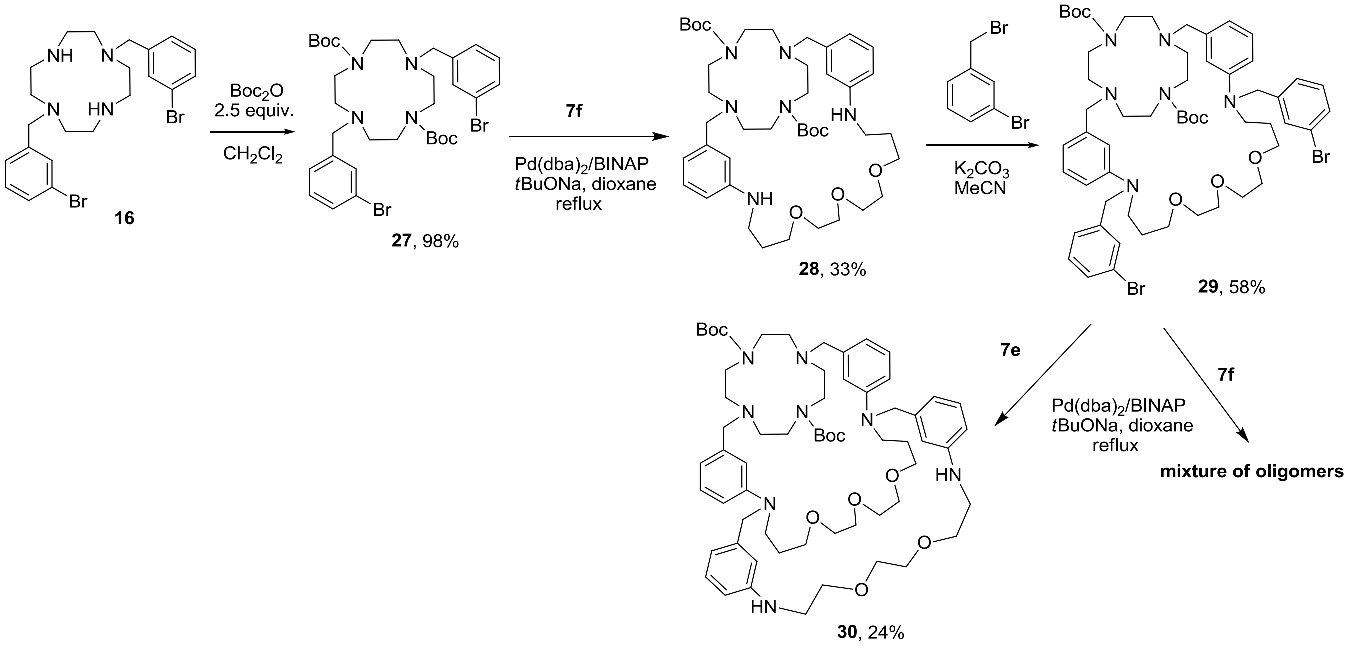


Scheme 5



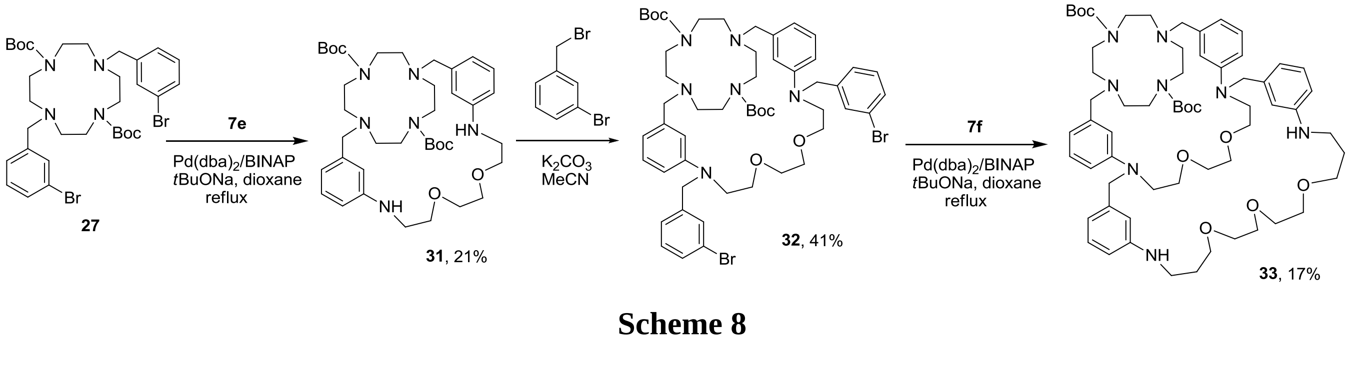
Scheme 6

This method for the construction of the third macroring was found to be enough laborious due to the difficulties with the dibenzylation of intermediate macrobicycles which substantially diminished overall yields of the target cryptands. Thus we worked out an alternative approach based on the protection of two secondary amino groups in starting 1,7-bis(3-bromobenzyl) cyclen **16** with *tert*-butoxycarbonyl (Boc) groups. The reaction was carried out in CH_2Cl_2 using 2.5 equiv. Boc_2O, and the tetrasubstituted cyclen derivative **27** was obtained in almost quantitative yield (Scheme 7). This compound was introduced in the Pd-catalyzed macrocyclization with trioxadiamine **7f** which produced macrobicycle **28** in 33% yield, which was modified with two 3-bromobenzyl substituents to give compound **29** in 58% yield. Side products were formed due to a partial quaternization of the tertiary amino groups with an active 3-bromobenzyl bromide. At the last step we attempted the catalytic macrocyclization using trioxadimaine **7f** but this reaction produced only a mixture of oligomers. The use of dioxadimaine **7e** was successful resulting in 24% yield of the target macrotricyclic cryptand **30** (Scheme 7).



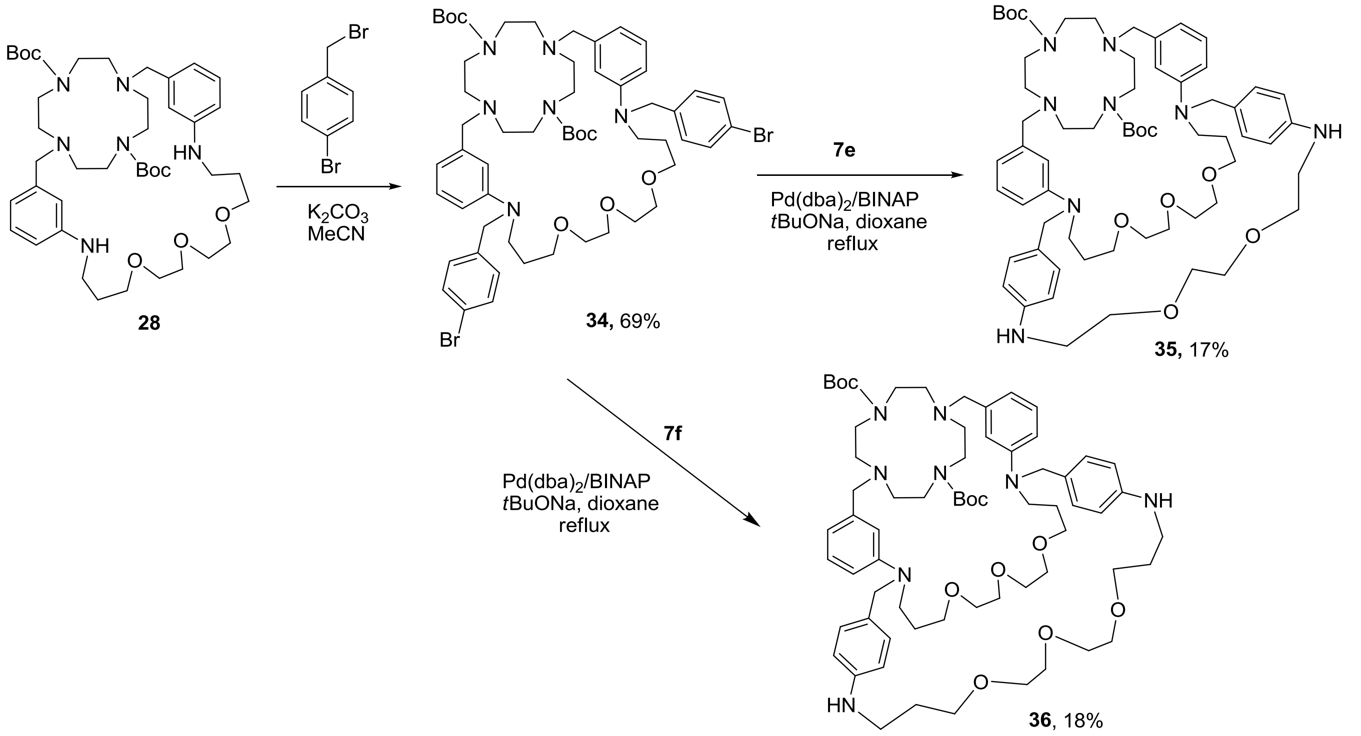
Scheme 7

An isomeric macrotricycle **33** was synthesized in an analogous manner *via* compounds **31** and **32**, though the yields at each step were lower (Scheme 8).



Scheme 8

In order to realize the scope of the proposed method, macrobicycle **28** was modified with two 4-bromobenzyl substituents to give compound **34** in 69% yield (Scheme 9). This compound was introduced in the Pd-catalyzed macrocyclization reactions with oxadiamines **7e,f**, and in both cases target macrotricycles **35** and **36** were synthesized in comparable yields (17 and 18%, resp.). Boc-substituted macrobicycles and macrotricycles often showed substantial line broadening of the signals in their NMR spactra due to hindered conformational changes, thus many of them were registered at elevated temperature in order to enhance resolution.



Scheme 9

In conclusion, we demonstrated the possibility of the synthesis of macrobicycles based on *N,N',N'',N'''*-tetrabenzyl substituted cyclen and cyclam *via* Pd-catalyzed amination, and employed it in the construction of spherically shaped macrotricyclic cryptands using two successive catalytic macrocyclization steps. Di-Boc-protected cyclen-containing macrobicycles were shown to be useful in the synthesis of macrotricycles of another topology. The dependence of the macrotricycles yields on the nature of oxadiamine linkers was demonstrated.

EXPERIMENTAL

All chemicals were purchased from Aldrich and Acros companies and used without further purification. 3- And 4-bromobenzyl bromides, polyamines **7a-f**, BINAP, sodium *tert*-butoxide were purchased from Aldrich Co and used without purification. 1,7-Dibenzylcyclen (**1**) and 1,8-dibenzylcyclam (**2**) were provided by CheMatech Co. Tetrabenzyl substituted cyclen and cyclam were synthesized according to a method described earlier.[31] 1,7-Di(3-bromobenzyl) cyclen (**16**) and macrobicycles **17e,f**, **24** were obtained using the method described in ref.[27] Pd(dba)$_2$ was synthesized in accordance with the method described by Ukai *et al*.[33] Commercial dioxane was distilled over NaOH and sodium under argon, acetonitrile was distilled over P_2O_5, dichloromethane and methanol were distilled prior to use. Column chromatography was carried out using silica gel (40-60 mkm) purchased from Fluka. ^{1}H and ^{13}C NMR spectra were registered in $CDCl_3$ or DMSO-d_6 using Bruker Avance 400 spectrometer at 400 and 100.6 MHz respectively. Chemical shift values δ are given in ppm and coupling constants *J* in Hz. MALDI-TOF spectra of positive ions were recorded with Bruker Ultraflex spectrometer using 1,8,9-trihydroxyanthracene as matrix and PEGs as internal standards. ESI-TOF spectra of positive ions were recorded with Bruker microQ-TOF spectrometer. Deposition number CCDC 1010639 for compound **6**. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Typical procedure for the synthesis of macrobicycles 8, 10, 12, 14.

A two-neck flask (25 mL) flushed with dry argon, equipped with a magnetic stirrer and condenser was charged with tetrabenzyl derivative of cyclen or cyclam **3-6** (0.2 mmol), Pd(dba)$_2$ (16 mol%, 18 mg), BINAP (18 mol%, 22 mg), and absolute dioxane (10 mL). The mixture was stirred for 2 min, then appropriate polyamine **7a-f** (0.2 mmol) was added followed by sodium *tert*-butoxide (0.6 mmol, 58 mg). The reaction mixture was refluxed for 24-30 h, after cooling to room temperature the residue was filtered off, washed with CH_2Cl_2 (5 mL), combined organic solvents were evaporated *in vacuo*, and the residue was analyzed by NMR spectroscopy. Column chromatography was carried out using a sequence of eluents CH_2Cl_2, CH_2Cl_2-MeOH 25:1 – 3:1, CH_2Cl_2-MeOH-NH_3(aq) 100:20:1 – 10:4:1.

22,27-Dibenzyl-1,8,12,19,22,27-hexaazatetracyclo[17.5.5.1^{3,7}.1^{13,17}]hentriaconta-3(31),4,6,13(30),14,16-hexaene (8a) was synthesized from compound **3** (138 mg, 0.20 mmol), diamine **7a** (15 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 147-149 ºC. Yield 38 mg (31%). ^{1}H NMR ($CDCl_3$): δ 1.81 (quintet, ^3J = 5.5 Hz, 2H), 2.73 (bs, 4H), 2.76-3.02 (m, 12H), 3.26 (bs, 8H), 3.63 (s, 4H), 6.34 (bs, 2H), 6.45 (d, ^3J = 8.1 Hz, 2H), 6.84 (bs, 2H), 6.95-7.05 (m, 6H), 7.19-7.24 (m, 6H), two NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 27.8 (1C), 41.8 (2C), 49.7 (4C, $\Delta\nu_{1/2}$ = 50 Hz), 51.5 (4C, $\Delta\nu_{1/2}$ = 100 Hz), 57.5 (2C, $\Delta\nu_{1/2}$ = 60 Hz), 60.1 (2C, $\Delta\nu_{1/2}$ = 50 Hz), 112.4 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 115.4 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 118.2 (2C, $\Delta\nu_{1/2}$ = 15 Hz), 128.1 (2C), 128.4 (4C), 129.2 (2C), 130.1 (4C), 135.4 (2C, $\Delta\nu_{1/2}$ = 80 Hz), 136.3 (2C, $\Delta\nu_{1/2}$ = 100 Hz), 149.1 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{39}H_{51}N_6$ $[M+H]^+$ 603.4175, found 603.4223.

26,31-Dibenzyl-1,8,12,16,23,26,31-heptaazatetracyclo[21.5.5.1^{3,7}.1^{17,21}]pentatriaconta-3(35),4,6,17(34),18,20-hexaene (8b) was synthesized from compound **3** (138 mg, 0.20 mmol), triamine **7b** (26 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:20:2. Pale-beige crystalline powder, mp 111-113 ºC. Yield 22 mg (16%). ^{1}H NMR ($CDCl_3$): δ 1.79 (quintet, ^3J = 5.5 Hz, 4H), 2.50-2.60 (m, 4H), 2.71 (bs, 12H), 2.81 (bs, 4H), 3.16 (t, ^3J = 5.5 Hz, 4H), 3.36 (s, 4H), 3.47 (s, 4H), 4.41 (bs, 2H), 6.38 (bd, $^3J_{obs}$ = 6.6 Hz, 2H), 6.46 (dd, ^3J = 8.2 Hz, ^4J 1.5 Hz, 2H), 6.95 (bs, 2H), 7.04 (t, ^3J = 7.7 Hz, 2H), 7.15-7.26 (m, 10H), one NH proton was not assigned; ^{13}C NMR ($CDCl_3$): δ 28.1 (2C, $\Delta\nu_{1/2}$ = 15 Hz), 42.4 (2C), 47.3 (2C), 51.6 (4C, $\Delta\nu_{1/2}$ = 10 Hz), 52.8 (4C, $\Delta\nu_{1/2}$ = 20 Hz), 59.8 (2C), 60.6 (2C), 111.6 (2C), 114.3 (2C), 118.2 (2C), 127.0 (2C), 128.2 (4C), 128.9 (2C), 129.3 (4C), 138.0 (2C), 139.3 (2C), 149.0 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{42}H_{58}N_7$ $[M+H]^+$ 660.4754, found 660.4711.

26,54,59,66-Tetrabenzyl-1,8,12,16,23,26,29,36,40,44,51,54,59,66-tetradecaazaheptacyclo-[49.5.5.5^{23,29}.1^{3,7}.1^{17,21}.1^{31,35}.1^{45,49}]heptaconta-3(70),4,6,17(69),18,20,31(63),32,34,45(62),46,48-dodecaene (9b) was obtained as the second product in the synthesis of macrobicycle **8b**. Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:20:3. Pale-yellow glassy compound. Yield 19 mg (14%). ^{1}H NMR ($CDCl_3$): δ 1.73 (bs, 8H), 2.52-2.72 (m, 40H), 3.10 (t, ^3J = 5.5 Hz, 8H), 3.36 (s, 8H), 3.44 (s, 8H), 6.43 (d, ^3J = 7.7 Hz, 4H), 6.59 (bs, 4H), 6.66 (bs, 4H), 7.02 (t, ^3J = 7.8 Hz, 4H), 7.12-7.28 (m, 12H), 7.30-7.35 (m, 8H), six NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 29.3 (4C, $\Delta\nu_{1/2}$ = 70 Hz), 42.6 (4C, $\Delta\nu_{1/2}$ = 15 Hz), 48.2 (4C, $\Delta\nu_{1/2}$ = 10 Hz), 52.7 (16C, $\Delta\nu_{1/2}$ = 30 Hz), 60.0 (8C), 110.9 (4C), 113.4 (4C), 118.0 (4C), 126.6 (4C), 128.0 (8C), 128.9 (12C, $\Delta\nu_{1/2}$ = 20 Hz), 140.1 (4C), 141.0 (4C), 148.4 (4C); HRMS (MALDI-TOF) *m/z* calcd for $C_{84}H_{115}N_{14}$ $[M+H]^+$ 1319.9429, found 1319.9563.

30,35-Dibenzyl-1,8,12,16,20,27,30,35-octaazatetracyclo[25.5.5.1^{3,7}.1^{21,25}]nonatriaconta-3(39),4,6,21(38),22,24-hexaene (8c) was synthesized from compound **3** (138 mg, 0.20 mmol), tetraamine **7c** (38 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:20:3. Pale-beige crystalline powder, mp 98-100 ºC. Yield 27 mg (18%). ^{1}H NMR ($CDCl_3$): δ 1.72 (quintet, ^3J = 5.8 Hz, 2H), 1.76 (quintet, ^3J = 6.4 Hz, 4H), 2.71 (t, ^3J = 6.4 Hz, 4H), 2.72 (bs, 16H), 2.74 (t, ^3J = 5.9 Hz, 4H), 3.13 (t, ^3J = 6.5 Hz, 4H), 3.38 (s, 4H), 3.47 (s, 4H), 6.48 (dd, ^3J = 8.1 Hz, ^4J 1.6 = Hz, 2H), 6.62 (bs, 2H), 6.83 (bs, 2H), 7.05 (t, ^3J = 7.7 Hz, 2H), 7.18-7.24 (m, 6H), 7.34 (bd, $^3J_{obs}$ = 6.8 Hz, 4H), four NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 28.4 (1C), 28.9 (2C), 42.8 (2C), 48.1 (2C), 49.0 (2C), 52.3 (4C, $\Delta\nu_{1/2}$ = 12 Hz), 52.9 (4C, $\Delta\nu_{1/2}$ = 10 Hz), 60.1 (4C), 111.0 (2C), 113.3 (2C, $\Delta\nu_{1/2}$ = 15 Hz), 117.8 (2C), 126.6 (2C), 128.0 (4C), 128.8 (2C), 129.0 (4C), 139.8 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 141.0 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 148.7 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{45}H_{65}N_8$ $[M+H]^+$ 717.5332, found 717.5370.

30,62,67,74-Tetrabenzyl-1,8,12,16,20,27,30,33,40,44,48,52,59,62,67,74-hexadecaazaheptacyclo-[57.5.5.5^{27,33}.1^{3,7}.1^{21,25}.1^{35,39}.1^{53,57}]octaheptaconta-3(78),4,6,21(77),22,24,35(71),36,38,53(70),54,56-

dodecaene (9c) was obtained as the second product in the synthesis of macrobicycle **8c**. Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:35:6. Pale-yellow glassy compound. Yield 10 mg (7%). ^{1}H NMR ($CDCl_3$): δ 1.62-1.73 (m, 12H), 2.45-2.78 (m, 48H), 3.09 (t, ^3J = 6.1 Hz, 8H), 3.35 (s, 8H), 3.45 (s, 8H), 6.43 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 4H), 6.56-6.67 (m, 8H), 7.02 (t, ^3J = 7.7 Hz, 4H), 7.15-7.26 (m, 12H), 7.32-7.38 (m, 8H), eight NH protons were not assigned ^{13}C NMR ($CDCl_3$): δ 29.1 (4C), 29.3 (2C), 42.6 (4C), 48.2 (4C), 48.4 (4C), 52.4 (8C), 52.8 (8C), 60.0 (4C), 60.4 (4C), 110.9 (4C), 113.2 (4C), 117.7 (4C), 126.5 (4C), 128.0 (8C), 128.8 (4C), 129.0 (8C), 140.0 (4C), 141.0 (4C), 148.4 (4C); MS (MALDI-TOF) *m/z* calcd for $C_{90}H_{129}N_{16}$ $[M+H]^+$ 1434.06, found 1434.04.

27,32-Dibenzyl-11,14-dioxa-1,8,17,24,27,32-hexaazatetracyclo[22.5.5.1^{3,7}.1^{18,22}]hexatriaconta-3(36),4,6,18(35),19,21-hexaene (8d) was synthesized from compound **3** (138 mg, 0.20 mmol), dioxadiamine **7d** (30 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 119-121 ºC. Yield 33 mg (24%). ^{1}H NMR ($CDCl_3$): δ 2.76 (t, ^3J = 4.9 Hz, 4H), 2.95 (t, ^3J = 4.7 Hz, 4H), 2.99 (t, ^3J = 4.8 Hz, 4H), 3.15 (t, ^3J = 4.7 Hz, 4H), 3.18 (bs, 4H), 3.26 (s, 4H), 3.54 (s, 4H), 3.68 (t, ^3J = 4.7 Hz, 4H), 3.71 (s, 4H), 4.43 (bs, 2H), 5.92 (bs, 2H), 6.40 (dd, ^3J = 8.2 Hz, ^4J = 2.0 Hz, 2H), 6.44 (d, ^3J = 7.3 Hz, 2H), 7.02-7.08 (m, 6H), 7.34 (t, ^3J = 7.4 Hz, 2H), 7.44 (t, ^3J = 7.5 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 43.3 (2C), 48.7 (4C), 51.1 (4C), 57.1 (2C), 60.1 (2C), 70.0 (2C), 70.6 (2C), 110.6 (2C), 115.7 (2C), 119.5 (2C), 128.4 (2C), 128.7 (4C), 129.3 (2C), 131.0 (4C), 134.1 (2C), 136.9 (2C), 148.6 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{42}H_{57}N_6O_2$ $[M+H]^+$ 677.4543, found 677.4520.

27,56,61,68-Tetrabenzyl-11,14,40,43-tetraoxa-1,8,17,24,27,30,37,46,53,56,61,68-dodecaazaheptacyclo-[51.5.5.5^{24,30}.1^{3,7}.1^{18,22}.1^{32,36}.1^{47,51}]doheptaconta-3(72),4,6,18(71),19,21,32(65),33,35,47(64),48,50-dodecaene (9d) was obtained as the second product in the synthesis of macrobicycle **8d**. Eluent CH_2Cl_2 – MeOH 3:1. Pale-yellow glassy compound. Yield 20 mg (15%). ^{1}H NMR ($CDCl_3$): δ 2.77 (bs, 16H), 2.96 (bs, 16H), 3.22 (t, ^3J = 4.9 Hz, 8H), 3.55 (s, 8H), 3.59 (s, 8H), 3.61 (s, 8H), 3.64 (t, ^3J = 4.9 Hz, 8H), 5.10 (bs, 4H), 6.29 (d, ^3J = 7.6 Hz, 4H), 6.49 (d, $^3J_{obs}$ = 7.1 Hz, 4H), 6.50 (s, 4H), 7.02 (t, ^3J = 8.0 Hz, 4H), 7.09 (d, ^3J = 7.5 Hz, 8H), 7.22-7.30 (m, 12H); ^{13}C NMR ($CDCl_3$): δ 43.3 (4C), 49.1 (8C), 51.1 (8C), 57.6 (4C), 59.6 (4C), 69.5 (4C), 70.1 (4C), 111.7 (4C), 116.1 (4C), 118.9 (4C), 128.0 (4C), 128.6 (8C), 129.4 (4C), 130.3 (8C), 148.8 (4C), eight quaternary carbon atoms were not assigned due to line broadening; HRMS (MALDI-TOF) *m/z* calcd for $C_{84}H_{113}N_{12}O_4$ $[M+H]^+$ 1353.9008, found 1353.9095.

30,35-Dibenzyl-11,16-dioxa-1,8,20,27,30,35-hexaazatetracyclo[25.5.5.1^{3,7}.1^{21,25}]nonatriaconta-3(39),4,6,21(38),22,24-hexaene (8e) was synthesized from compound **3** (138 mg, 0.20 mmol), dioxadiamine **7e** (41 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 112-114 ºC. Yield 32 mg (22%). ^{1}H NMR ($CDCl_3$): δ 1.59-1.64 (m, 4H), 1.83 (quintet, ^3J = 5.7 Hz, 4H), 2.79 (bs, 8H), 3.02 (bs, 8H), 3.18 (t, ^3J = 6.3 Hz, 4H), 3.34-3.39 (m, 4H), 3.45 (t, ^3J = 5.6 Hz, 4H), 3.58

(bs, 8H), 4.68 (bs, 2H), 6.32 (d, ^3J = 7.5 Hz, 2H), 6.53 (d, ^3J = 8.1 Hz, 2H), 6.56 (bs, 2H), 7.02-7.07 (m, 6H), 7.22-7.28 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 26.4 (2C), 29.1 (2C), 40.8 (2C), 48.9 (4C), 51.3 (4C), 58.1 (2C), 59.5 (2C), 69.1 (2C), 70.6 (2C), 111.7 (2C), 115.2 (2C), 118.9 (2C), 128.0 (2C), 128.5 (4C), 129.5 (2C), 130.3 (4C), 134.5 (2C), 135.6 (2C), 149.1 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{46}H_{65}N_6O_2$ $[M+H]^+$ 733.5169, found 733.5204.

32,37-Dibenzyl-12,15,18-trioxa-1,8,22,29,32,37-hexaazatetracyclo[27.5.5.1^{3,7}.1^{23,27}]hentetraconta-3(41),4,6,23(40),24,26-hexaene (8f) was synthesized from compound **3** (138 mg, 0.20 mmol), trioxadiamine **7f** (44 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 109-111 ºC. Yield 28 mg (19%). ^{1}H NMR ($CDCl_3$): δ 1.82 (quintet, ^3J = 5.9 Hz, 4H), 2.77 (bs, 8H), 2.99 (bs, 8H), 3.16 (t, ^3J = 6.2 Hz, 4H), 3.43-3.46 (m, 4H), 3.47 (t, ^3J = 6.0 Hz, 4H), 3.55-3.60 (m, 12H), 4.29 (bs, 2H), 6.33 (d, ^3J = 7.5 Hz, 2H), 6.53 (dd, ^3J = 8.1 Hz, ^4J = 1.7 Hz, 2H), 6.59 (bs, 2H), 7.00-7.04 (m, 4H), 7.05 (t, ^3J = 7.8 Hz, 2H), 7.21-7.25 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 28.8 (2C), 41.3 (2C), 49.0 (4C), 51.4 (4C), 58.4 (2C), 59.4 (2C), 69.3 (2C), 70.1 (2C), 70.4 (2C), 111.6 (2C), 115.5 (2C), 118.8 (2C), 128.0 (2C), 128.5 (4C), 129.4 (2C), 130.3 (4C), 134.6 (2C), 135.5 (2C), 149.2 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{46}H_{65}N_6O_3$ $[M+H]^+$ 749.5118, found 749.5054.

24,29-Dibenzyl-1,7,11,15,21,24,29-heptaazatetracyclo[19.5.5.2^{3,6}.2^{16,19}]heptatriaconta-3,5,16,18,32,34-hexaene (10b) was synthesized from compound **4** (138 mg, 0.20 mmol), triamine **7b** (26 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:20:3. Pale-beige crystalline powder, mp 141-143 ºC. Yield 29 mg (14%). ^{1}H NMR ($CDCl_3$): δ 1.83 (quintet, ^3J = 6.0 Hz, 4H), 2.41-2.51 (m, 8H), 2.63-2.72 (m, 8H), 2.81 (t, ^3J = 5.4 Hz, 4H), 3.29 (t, ^3J = 6.8 Hz, 4H), 3.34 (s, 4H), 3.45 (s, 4H), 6.64 (d, $^3J_{obs}$ = 8.5 Hz, 4H), 7.20-7.28 (m, 6H), 7.22 (d, ^3J = 8.5 Hz, 4H), 7.31-7.36 (m, 4H), three NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 29.2 (2C), 44.3 (2C), 49.2 (2C), 52.7 (4C, $\Delta\nu_{1/2}$ = 50 Hz), 53.9 (4C), 59.2 (2C), 60.0 (2C), 112.8 (4C), 126.5 (2C), 128.0 (4C), 128.4 (2C), 128.9 (4C), 129.5 (4C), 140.4 (2C), 147.4 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{42}H_{58}N_7$ $[M+H]^+$ 660.4754, found 660.4724.

24,50,55,64-Tetrabenzyl-1,7,11,15,21,24,27,33,37,41,47,50,55,64-tetradecaazaheptacyclo-[45.5.5.5^{21,27}.2^{3,6}2^{16,19}.2^{29,32}.2^{42,45}]heptaconta-3,5,16,18,29,31,42,44,58,60,67,69-dodecaene (11b) was obtained as the second product in the synthesis of compound **9b**. Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:35:6. Yellowish glassy compound. Yield 24 mg (18%). ^{1}H NMR ($CDCl_3$): δ 1.86 (bs, 8H), 2.60-2.75 (m, 40H), 3.19 (bs, 8H), 3.35 (s, 8H), 3.43 (s, 8H), 6.49 (bd, $^3J_{obs}$ = 6.8 Hz, 8H), 7.08 (bd, $^3J_{obs}$ = 6.9 Hz, 8H), 7.15-7.28 (m, 12H), 7.33 (bs, 8H), six NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 29.4 (4C), 42.7 (4C), 48.2 (4C), 52.5 (16C, $\Delta\nu_{1/2}$ = 70 Hz), 59.4 (4C), 60.0 (4C), 112.4 (8C), 126.5 (4C), 128.0 (8C), 128.3 (4C), 129.0 (8C), 130.1 (8C), 140.0 (4C), 148.6 (4C); MS (MALDI-TOF) *m/z* calcd for $C_{84}H_{115}N_{14}$ $[M+H]^+$ 1319.94, found 1319.96.

28,33-Dibenzyl-1,7,11,15,19,25,28,33-octaazatetracyclo[23.5.5.2^{3,6}.2^{20,23}]nonatriaconta-3,5,20,22,36,38-hexaene (10c) was synthesized from compound **4** (138 mg, 0.20 mmol), tetraamine **7c** (38 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:35:6. Pale-beige crystalline powder, mp 98-100 ºC. Yield 16 mg (11%). ^{1}H NMR ($CDCl_3$): δ 1.73 (quintet, ^3J = 6.5 Hz, 2H), 1.80 (quintet, ^3J = 5.9 Hz, 4H), 2.66 (bs, 16H), 2.74 (t, ^3J = 6.6 Hz, 4H), 2.80 (t, ^3J = 5.9 Hz, 4H), 3.21 (t, ^3J = 6.2 Hz, 4H), 3.34 (s, 4H), 3.44 (s, 4H), 6.58 (d, $^3J_{obs}$ 8.3 Hz, 4H), 7.17-7.36 (m, 14H), four NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 28.6 (2C), 29.9 (1C), 43.9 (2C), 48.4 (2C), 48.8 (2C), 52.5 (4C), 53.5 (4C), 59.4 (2C), 60.0 (2C), 112.5 (4C), 126.4 (2C), 128.0 (4C), 128.9 (4C), 129.7 (4C), 140.0 (2C), 147.4 (2C), two quaternary carbon atoms were not assigned due to line broadening; HRMS (MALDI-TOF) *m/z* calcd for $C_{45}H_{65}N_8$ $[M+H]^+$ 717.5332, found 717.5305.

28,58,63,72-Tetrabenzyl-1,7,11,15,19,25,28,31,37,41,45,49,55,58,63,72-hexadecaazaheptacyclo-[53.5.5.5^{25,31}.2^{3,6}.2^{20,23}.2^{33,36}.2^{50,53}]octaheptaconta-3,5,20,22,33,35,50,52,66,68,75,77-dodecaene (11c) was obtained as the second product in the synthesis of compound **9c**. Eluent CH_2Cl_2 – MeOH – NH_3(aq) 10:4:1. Yellowish glassy compound. Yield 10 mg (7%). ^{1}H NMR ($CDCl_3$): δ 1.67-1.80 (m, 12H), 2.60-2.81 (m, 48H), 3.12 (bs, 8H), 3.32 (s, 8H), 6.48 (bd, $^3J_{obs}$ = 5.3 Hz, 8H), 7.08 (bs, 8H), 7.15-7.36 (m, 28H), eight NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 28.6 (4C), 29.9 (2C), 42.8 (4C), 48.2 (8C), 52.5 (8C), 53.1 (8C), 59.4 (4C), 60.2 (4C), 112.4 (8C), 126.4 (4C), 128.0 (8C), 129.0 (8C), 130.1 (8C), 140.0 (4C), 147.3 (4C), four quaternary carbon atoms were not assigned due to line broadening; HRMS (MALDI-TOF) *m/z* calcd for $C_{90}H_{129}N_{16}$ $[M+H]^+$ 1434.0586, found 1434.0512.

25,30-Dibenzyl-10,13-dioxa-1,7,16,22,25,30-hexaazatetracyclo[20.5.5.2^{3,6}.2^{17,20}]hexatriaconta-3,5,17,19,33,35-hexaene (10d) was synthesized from compound **4** (138 mg, 0.20 mmol), dioxadiamine **7d** (30 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 103-104 ºC. Yield 21 mg (16%). ^{1}H NMR ($CDCl_3$): δ 2.77 (bs, 4H), 2.98 (bs, 12H), 3.26 (t, ^3J = 5.1 Hz, 4H), 3.41 (s, 4H), 3.55 (s, 8H), 3.64 (t, ^3J = 5.1 Hz, 4H), 6.57 (d, ^3J = 7.8 Hz, 4H), 7.00 (bs, 4H), 7.03 (d, ^3J = 7.8 Hz, 4H), 7.22-7.26 (m, 6H), two NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 43.6 (2C), 50.5 (4C, $\Delta\nu_{1/2}$ = 20 Hz), 51.7 (4C, $\Delta\nu_{1/2}$ = 15 Hz), 56.1 (2C, $\Delta\nu_{1/2}$ = 30 Hz), 60.6 (2C, $\Delta\nu_{1/2}$ = 15 Hz), 69.0 (2C), 70.1 (2C), 113.1 (4C), 128.1 (2C), 128.5 (4C), 130.2 (4C), 131.1 (4C), 148.2 (2C), four quaternary carbon atoms were not assigned due to line broadening; HRMS (MALDI-TOF) *m/z* calcd for $C_{42}H_{57}N_6O_2$ $[M+H]^+$ 677.4543, found 677.4582.

29,34-Dibenzyl-11,16-dioxa-1,7,20,26,29,34-hexaazatetracyclo[24.5.5.2^{3,6}.2^{21,24}]tetraconta-3,5,21,23,37,39-hexaene (10e) was synthesized from compound **4** (138 mg, 0.20 mmol), dioxadiamine **7e** (41 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 112-114 ºC. Yield 21 mg (16%). ^{1}H NMR ($CDCl_3$): δ 1.70-1.75 (m, 4H), 1.85 (quintet, ^3J = 5.5 Hz, 4H), 2.70-2.75 (m, 8H), 3.05-3.10 (m, 8H), 3.24 (t, ^3J = 6.1 Hz, 4H), 3.33 (s, 4H), 3.40 (s, 4H), 3.41-3.45 (m, 4H), 3.56 (t, ^3J = 5.2 Hz, 4H), 4.32 (bs, 2H), 6.60 (d, ^3J = 8.3 Hz, 4H), 6.81 (bd, $^3J_{obs}$ = 6.6 Hz, 4H), 6.97 (d, ^3J = 8.3 Hz, 4H), 7.18-7.22 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 27.2 (2C), 29.1 (2C), 42.9 (2C), 48.7 (4C), 50.9 (4C), 57.7 (2C), 58.8 (2C), 70.5 (2C), 71.3 (2C), 112.2 (4C), 127.8 (2C), 128.4 (4C), 128.5 (2C), 130.2 (4C), 132.0 (4C), 135.6 (2C), 149.0 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{46}H_{65}N_6O_2$ $[M+H]^+$ 733.5169, found 733.5129.

30,35-Dibenzyl-11,14,17-trioxa-1,7,21,27,30,35-hexaazatetracyclo[25.5.5.2^{3,6}.2^{22,25}]hentetraconta-3,5,22,24,38,40-hexaene (10f) was synthesized from compound **4** (138 mg, 0.20 mmol), trioxadiamine **7e** (44 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 120-122 ºC. Yield 30 mg (20%). ^{1}H NMR ($CDCl_3$): δ 1.84 (quintet, ^3J = 5.8 Hz, 4H), 2.74 (bs, 8H), 3.03 (bs, 8H), 3.23 (t, ^3J = 6.3 Hz, 4H), 3.38 (s, 4H), 3.44 (s, 4H), 3.55-3.60 (m, 8H), 3.67-3.70 (m, 4H), 4.20 (bs, 2H), 6.60 (d, ^3J = 8.3 Hz, 4H), 6.89 (d, ^3J = 7.3 Hz, 4H), 6.97 (d, ^3J = 8.3 Hz, 4H), 7.18-7.22 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 28.8 (2C), 42.3 (2C), 48.9 (4C), 50.9 (4C), 58.1 (2C), 58.5 (2C), 70.1 (4C), 70.5 (2C), 112.4 (4C), 127.8 (2C), 128.4 (4C), 128.5 (2C), 130.1 (4C), 131.7 (4C), 135.3 (2C), 148.9 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{46}H_{65}N_6O_3$ $[M+H]^+$ 749.5118, found 749.5043.

22,28-Dibenzyl-1,8,12,19,22,28-hexaazatetracyclo[17.6.6.1^{3,7}.1^{13,17}]tritriaconta-3(33),4,6,13(32),14,16-hexaene (12a) was synthesized from compound **5** (144 mg, 0.20 mmol), diamine **7a** (15 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 147-149 ºC. Yield 15 mg (12%). ^{1}H NMR (DMSO-d_6, 363K): δ 1.69-1.76 (m, 6H), 2.52-2.80 (m, 16H), 3.21 (quintet, ^3J = 5.5 Hz, 4H), 3.45 (s, 4H), 3.60 (s, 4H), 6.39 (d, ^3J = 7.2 Hz, 2H), 6.53 (d, ^3J = 8.0 Hz, 2H), 6.83 (bs, 2H), 6.96 (t, ^3J = 7.6 Hz, 2H), 7.19-7.30 (m, 10H), two NH protons were not assigned; ^{13}C NMR (DMSO-d_6, 363K): δ 23.6 (2C), 29.0 (1C), 40.7 (2C), 50.1 (2C), 50.9 (4C), 51.4 (2C), 57.9 (2C), 58.1 (2C), 111.8 (2C), 112.1 (2C), 116.5 (2C), 121.4 (2C), 126.4 (2C), 127.4 (6C), 128.5 (2C), six quaternary carbon atoms were not assigned due to line broadening; HRMS (MALDI-TOF) *m/z* calcd for $C_{41}H_{55}N_6$ $[M+H]^+$ 631.4488, found 631.4465.

26,32-Dibenzyl-1,8,12,16,23,26,32-heptaazatetracyclo[21.6.6.1^{3,7}1^{17,21}]heptatriaconta-3(37),4,6,17(36),18,20-hexaene (12b) was synthesized from compound **5** (144 mg, 0.20 mmol), triamine **7b** (26 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 85-87 ºC. Yield 22 mg (16%). ^{1}H NMR ($CDCl_3$): δ 1.68-1.82 (m, 8H), 2.29-2.70 (m, 16H), 2.72 (t, ^3J = 6.3 Hz, 4H), 3.21 (quintet, ^3J = 7.0 Hz, 4H), 3.37 (s, 4H), 3.50 (s, 4H), 6.37 (bs, 2H), 6.45 (d, ^3J = 8.1 Hz, 2H), 6.87 (bs, 2H), 7.02 (t, ^3J = 7.7 Hz, 2H), 7.19-7.28 (m, 10H), three NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 25.1 (2C), 29.1 (2C, $\Delta\nu_{1/2}$ = 12 Hz), 42.6 (2C), 47.7 (2C, $\Delta\nu_{1/2}$ = 10 Hz), 51.2 (2C, $\Delta\nu_{1/2}$ = 25 Hz), 51.5 (2C), 51.9 (2C, $\Delta\nu_{1/2}$ = 10 Hz), 52.4 (2C, $\Delta\nu_{1/2}$ = 10 Hz), 59.3 (2C, $\Delta\nu_{1/2}$ = 12 Hz), 59.8 (2C), 111.6 (2C), 113.3 (2C), 117.9 (2C), 126.7 (2C), 128.0 (4C), 128.6 (2C), 129.1 (4C), 139.7 (2C), 140.8 (2C, $\Delta\nu_{1/2}$ = 25 Hz), 148.6 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{44}H_{62}N_7$ $[M+H]^+$ 688.5067, found 688.5103.

30,36-Dibenzyl-1,8,12,16,20,27,30,36-octaazatetracyclo[25.6.6.1^{3,7}.1^{21,25}]hentetraconta-3(41),4,6,21(40),22,24-hexaene (12c) was synthesized from compound **5** (144 mg, 0.20 mmol), tetraamine **7c** (38 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:20:2. Pale-beige crystalline powder, mp 96-98 ºC. Yield 30 mg (20%). ^{1}H NMR ($CDCl_3$): δ 1.68-1.81 (m, 10H), 2.45-2.63 (m, 16H), 2.70-2.77 (m, 8H), 3.16 (t, ^3J = 6.3 Hz, 4H), 3.36 (s, 4H), 3.49 (s, 4H), 4.21 (bs, 2H), 6.46 (d, ^3J = 8.1 Hz, 2H), 6.49 (bs, 2H), 6.75 (bs, 2H), 7.04 (t, ^3J = 7.6 Hz, 2H), 7.19-7.30 (m, 10H), two NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 24.9 (2C), 29.1 (3C), 42.9 (2C), 48.4 (2C), 48.9 (2C), 51.7 (6C), 52.3 (2C), 59.6 (4C), 111.2 (2C), 113.2 (2C), 117.9 (2C), 126.6 (2C), 128.0 (4C), 128.7 (2C), 129.0 (4C), 139.9 (2C), 141.1 (2C), 148.6 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{47}H_{69}N_8$ $[M+H]^+$ 745.5645, found 745.5690.

30,63,69,77-Tetrabenzyl-1,8,12,16,20,27,30,34,41,45,49,53,60,63,69,77-hexaazaheptacyclo-[58.6.6.6^{27,34}.1^{3,7}.1^{21,25}.1^{36,40}.1^{54,58}]dooctaconta-3(82),4,6,21(81),22,24,36(74),37,39,54(73),55,57-dodecaene (13c) was obtained as the second product in the synthesis of macrobicycle **12c**. Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:35:6. Pale-yellow glassy compound. Yield 14 mg (12%). ^{1}H NMR ($CDCl_3$): δ 1.66-1.82 (m, 20H), 2.46-2.64 (m, 32H), 2.68 (t, ^3J = 5.2 Hz, 16H), 3.06 (t, ^3J = 6.3 Hz, 8H), 3.37 (s, 8H), 3.43 c (8H), 3.99 (bs, 4H), 6.42 (d, ^3J = 7.6 Hz, 4H), 6.55-6.61 (m, 8H), 7.03 (t, ^3J = 7.1 Hz, 4H), 7.18-7.33 (m, 20H), four NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 23.7 (4C), 29.4 (4C), 30.1 (2C), 42.6 (4C), 48.2 (4C), 48.5 (4C), 50.0-52.3 м (16C), 59.0 (4C), 59.6 (4C), 110.9 (4C), 113.0 (4C), 117.7 (4C), 126.5 (4C), 128.0 (8C), 128.7 (4C), 128.9 (8C), 140.2 (4C), 141.1 (4C), 147.7 (4C); HRMS (MALDI-TOF) *m/z* calcd for $C_{94}H_{137}N_{16}$ $[M+H]^+$ 1490.1212, found 1490.1357.

27,33-Dibenzyl-11,14-dioxa-1,8,17,24,27,33-hexaazatetracyclo[22.6.6.1^{3,7}.1^{18,22}]octatriaconta-3(38),4,6,18(37),19,21-hexaene (12d) was synthesized from compound **5** (144 mg, 0.20 mmol), dioxadiamine **7d** (30 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 103-104 ºC. Yield 20 mg (14%). ^{1}H NMR (DMSO-d_6, 363K): δ 1.72 (bs, 4H), 2.50-2.70 (m, 16H), 3.24 (t, ^3J = 5.9 Hz, 4H), 3.44 (s, 4H), 3.57 (s, 8H), 3.60 (t, ^3J = 5.9 Hz, 4H), 5.00 (bs, 2H), 6.38 (bd, $^3J_{obs}$ = 6.6 Hz, 2H), 6.52 (d, ^3J = 7.5 Hz, 2H), 6.75 (bs, 2H), 6.95 (t, ^3J = 7.6 Hz, 2H), 7.15-7.27 (m, 10H); ^{13}C NMR (DMSO-d_6, 363K): δ 24.1 (2C), 42.8 (2C), 50.9 (6C), 51.6 (2C), 58.4 (2C), 58.7 (2C), 69.0 (2C), 69.5 (2C), 111.8 (4C), 116.6 (2C), 126.2 (2C), 127.4 (4C), 127.8 (2C), 128.4 (4C), 138.5 (2C), 139.7 (2C), 148.3 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{44}H_{61}N_6O_2$ $[M+H]^+$ 705.4856, found 705.4811.

31,37-Dibenzyl-12,17-dioxa-1,8,21,28,31,37-hexaazatetracyclo[26.6.6.1^{3,7}.1^{22,26}]dotetraconta-3(42),4,6,22(41),23,25-hexaene (12e) was synthesized from compound **5** (144 mg, 0.20 mmol), dioxadiamine **7e** (41 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige glassy compound. Yield

22 mg (15%). ^{1}H NMR (DMSO-d_6): δ 1.49-1.55 (m, 4H), 1.67 (bs, 4H), 1.72 (quintet, ^3J = 6.1 Hz, 4H), 2.40-2.56 (m, 16H), 3.03 (bs, 4H), 3.27-3.32 (m, 4H), 3.32 (s, 4H), 3.40 (t, ^3J = 5.8 Hz, 4H), 3.46 (s, 4H), 5.41 (bs, 2H), 6.28 (d, ^3J = 7.3 Hz, 2H), 6.43 (d, ^3J = 8.2 Hz, 2H), 6.53 (bs, 2H), 6.89 (t, ^3J = 7.6 Hz, 2H), 7.16-7.27 (m, 10H); ^{13}C NMR (DMSO-d_6): δ 23.8 (2C), 26.1 (2C), 29.1 (2C), 40.1 (2C), 49.9 (2C), 50.7 (4C), 51.4 (2C), 58.8 (2C), 58.9 (2C), 67.9 (2C), 69.9 (2C), 110.8 (2C), 112.2 (2C), 116.4 (2C), 126.7 (2C), 128.0 (4C), 128.2 (2C), 128.8 (4C), 139.3 (2C, $\Delta\nu_{1/2}$ = 40 Hz), 140.9 (2C), 148.9 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{48}H_{69}N_6O_2$ $[M+H]^+$ 761.5482, found 761.5550.

31,65,71,79-Tetrabenzyl-12,17,46,51-tetraoxa-1,8,21,28,31,35,42,55,62,65,71,79-dodecaazaheptacyclo-[60.6.6.6^{28,35}.1^{3,7}.1^{22,26}.1^{37,41}.1^{56,60}]tetraoctaconta-3(84),4,6,22(83),23,25,37(76),38,40,56(75),57,59-dodecaene (13e) was obtained as the second product in the synthesis of macrobicycle **12e**. Eluent CH_2Cl_2 – MeOH 3:1. Yellowish glassy compound. Yield 14 mg (9%). ^{1}H NMR ($CDCl_3$): δ 1.62-1.67 (m, 8H), 1.74 (bs, 8H), 1.79 (quintet, ^3J = 6.0 Hz, 8H), 2.48 (bs, 8H), 2.56 (bs, 8H), 2.56 (bs, 8H), 2.61 (bs, 8H), 3.11 (t, ^3J = 6.6 Hz, 8H), 3.37 (s, 8H), 3.39-3.48 (m, 24H), 4.50 (bs, 4H), 6.42 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 4H), 6.51-6.59 (m, 8H), 7.02 (t, ^3J = 7.7 Hz, 4H), 7.16-7.31 (m, 20H); ^{13}C NMR ($CDCl_3$): δ 23.9 (4C, $\Delta\nu_{1/2}$ = 15 Hz), 26.5 (4C), 29.4 (4C), 41.8 (4C), 50.2 (8C), 51.3 (4C), 51.5 (4C), 59.0 (4C), 59.4 (4C), 69.3 (4C), 70.8 (4C), 111.0 (4C), 113.3 (4C, $\Delta\nu_{1/2}$ = 15 Hz), 117.8 (4C), 126.7 (4C), 128.0 (8C), 128.8 (4C), 129.0 (8C), 139.8 (4C, $\Delta\nu_{1/2}$ = 30 Hz), 140.4 (4C, $\Delta\nu_{1/2}$ = 20 Hz), 148.5 (4C); HRMS (MALDI-TOF) *m/z* calcd for $C_{96}H_{137}N_{12}O_4$ $[M+H]^+$ 1522.0886, found 1522.0973.

32,38-Dibenzyl-12,15,18-trioxa-1,8,22,29,32,38-hexaazatetracyclo[27.6.6.1^{3,7}.1^{23,27}]tritetraconta-3(43),4,6,23(42),24,26-hexaene (12f) was synthesized from compound **5** (144 mg, 0.20 mmol), trioxadiamine **7f** (44 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 86-88 ºC. Yield 37 мг (24%). ^{1}H NMR ($CDCl_3$): δ 1.86 (quintet, ^3J = 5.8 Hz, 8H), 2.43-2.90 (m, 16H), 3.20 (t, ^3J = 6.1 Hz, 4H), 3.35 (s, 4H), 3.54-3.62 (m, 12H), 3.63-3.67 (m, 4H), 4.80 (bs, 4H), 6.21 (bs, 2H), 6.47 (d, ^3J = 7.3 Hz, 2H), 6.87 (bs, 2H), 7.00 (t, ^3J = 7.6 Hz, 2H), 7.20-7.35 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 24.6 (2C, $\Delta\nu_{1/2}$ = 15 Hz), 29.0 (2C), 41.4 (2C), 50.4 (2C, $\Delta\nu_{1/2}$ = 60 Hz), 51.0 (2C, $\Delta\nu_{1/2}$ = 30 Hz), 51.4 (2C, $\Delta\nu_{1/2}$ = 30 Hz), 52.7 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 57.6 (2C, $\Delta\nu_{1/2}$ = 150 Hz), 59.2 (2C), 69.6 (2C), 70.2 (2C), 70.6 (2C), 111.3 (2C), 114.2 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 117.9 (2C), 127.4 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 128.3 (4C), 128.9 (2C), 129.8 (4C, $\Delta\nu_{1/2}$ = 20 Hz), very broad signal in 136-138 ppm region (4C, $\Delta\nu_{1/2}$ > 200 Hz), 149.1 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{48}H_{69}N_6O_3$ $[M+H]^+$ 777.5431, found 777.5342.

32,67,73,81-Tetrabenzyl-12,15,18,47,50,53-hexaoxa-1,8,22,29,32,36,43,57,64,67,73,81-dodecaazahepta-cyclo[62.6.6.6^{29,36}.1^{3,7}.1^{23,27}.1^{38,42}.1^{58,62}]hexaoctaconta-3(86),4,6,23(85),24,26,38(78),39,41,58(77),59,61-dodecaene (13f) was obtained as the second product in the synthesis of macrobicycle **12f**. Eluent CH_2Cl_2 – MeOH 3:1. Yellowish glassy compound. Yield 16 mg (10%). ^{1}H NMR ($CDCl_3$): δ 1.80 (bs, 16H), 2.43-2.77 (m, 32H), 3.12 (t, ^3J = 6.2 Hz, 8H), 3.41 (s, 8H), 3.46 (s, 8H), 3.52 (t, ^3J = 5.7 Hz, 8H), 3.54-3.58 (m, 8H), 3.61-3.65 (m, 8H), 6.44 (d, ^3J = 8.0 Hz, 4H), 6.57-6.62 (m, 8H), 7.02 (t, ^3J = 7.7 Hz, 4H), 7.18-7.31 (m, 20H), four NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 23.7 (4C), 29.2 (4C), 41.5 (4C), 50.0 (8C), 51.4 (8C), 58.9 (4C), 59.0 (4C), 69.6 (4C), 70.2 (4C), 70.6 (4C), 111.3 (4C), 113.5 (4C), 117.8 (4C), 126.9 (4C), 128.1 (8C), 128.9 (8C), 129.2 (4C), 139.2 (8C), 148.6 (4C); MS (MALDI-TOF) *m/z* calcd for $C_{96}H_{137}N_{12}O_6$ $[M+H]^+$ 1554.08, found 1554.11.

20,26-Dibenzyl-1,7,11,17,20,26-hexaazatetracyclo[15.6.6.2^{3,6}.2^{12,15}]tritriaconta-3,5,12,14,30,32-hexaene (14a) was synthesized from compound **6** (144 mg, 0.20 mmol), diamine **7a** (15 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 151-153 ºC. Yield 23 mg (18%). ^{1}H NMR ($CDCl_3$): δ 1.93 (quintet, ^3J = 6.1 Hz, 2H), 1.94 (bs, 4H), 2.52 (bs, 16H), 3.35 (bs, 4H), 3.57 (bs, 8H), 4.39 (bs, 2H), 6.46 (bs, 4H), 6.88 (bs, 4H), 7.19-7.30 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 23.8 (2C), 27.2 (1C), 40.8 (2C), 50.9 (8C), 58.7 (4C), 112.7 (4C), 127.1 (2C), 128.2 (8C), 129.6 (4C), six quaternary carbon atoms were not assigned due to line broadening; HRMS (MALDI-TOF) *m/z* calcd for $C_{41}H_{55}N_6$ $[M+H]^+$ 631.4488, found 631.4472.

24,30-Dibenzyl-1,7,11,15,21,24,30-heptaazatetracyclo[19.6.6.2^{3,6}.2^{16,19}]heptatriaconta-3,5,16,18,34,36-hexaene (14b) was synthesized from compound **6** (144 mg, 0.20 mmol), triamine **7b** (26 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige glassy compound. Yield 20 mg (15%). ^{1}H NMR (DMSO-d_6, 363K): δ 1.79 (bs, 4H), 1.93 (quintet, ^3J = 6.5 Hz, 4H), 2.50-2.82 (m, 16H), 3.00 (t, ^3J = 6.6 Hz, 4H), 3.19 (t, ^3J = 6.6 Hz, 4H), 3.56 (bs, 8H), 6.59 (d, ^3J = 8.5 Hz, 4H), 7.08 (d, ^3J = 8.5 Hz, 4H), 7.23-7.34 (m, 10H), three NH protons were not assigned; ^{13}C NMR (DMSO-d_6, 363K): δ 23.6 (2C, $\Delta\nu_{1/2}$ = 40 Hz), 25.7 (2C, $\Delta\nu_{1/2}$ = 40 Hz), 42.1 (2C, $\Delta\nu_{1/2}$ = 35 Hz), 46.4 (2C, $\Delta\nu_{1/2}$ = 30 Hz), 50.9 (4C, $\Delta\nu_{1/2}$ = 150 Hz), 51.8 (4C, $\Delta\nu_{1/2}$ = 100 Hz), 58.3 (4C, $\Delta\nu_{1/2}$ = 50 Hz), 113.3 (4C), 127.6 (2C), 128.3 (8C, $\Delta\nu_{1/2}$ = 20 Hz), 129.8 (4C, $\Delta\nu_{1/2}$ = 20 Hz), 135.7 (2C, $\Delta\nu_{1/2}$ = 70 Hz), 148.1 (2C, $\Delta\nu_{1/2}$ = 100 Hz), two quaternary carbon atoms were not assigned due to line broadening; HRMS (MALDI-TOF) *m/z* calcd for $C_{44}H_{62}N_7$ $[M+H]^+$ 688.5067, found 688.5120.

24,51,57,67-Tetrabenzyl-1,7,11,15,21,24,28,34,38,42,48,51,57,67-tetradecaazaheptacyclo-[46.6.6.6^{21,28}.2^{3,6}.2^{16,19}.2^{30,33}.2^{43,46}]tetraheptaconta-3,5,16,18,30,32,43,45,61,63,71,73-dodecaene (15b) was obtained as the second product in the synthesis of macrobicycle **14b**. Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:20:2. Yellowish glassy compound. Yield 27 mg (19%). ^{1}H NMR ($CDCl_3$): δ 1.71 (bs, 8H), 1.79 (quintet, ^3J = 5.8 Hz, 8H), 2.49 (bs, 16H), 2.59 (bs, 16H), 2.74 (bs, 8H), 3.16 (t, ^3J = 6.2 Hz, 8H), 3.34 (s, 8H), 3.44 (s, 8H), 6.49 (d, ^3J = 7.8 Hz, 8H), 7.04 (d, ^3J = 7.8 Hz, 8H), 7.17-7.30 (m, 20H), six NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 23.4 (4C), 23.6 (4C), 42.8 (4C), 48.3 (4C), 50.1 (8C), 51.4 (8C), 58.9 (4C), 59.4 (4C), 112.4 (8C), 126.5 (4C), 128.0 (8C), 128.9 (8C), 129.9 (8C), 140.0 (4C), 147.2 (4C), four quaternary carbon atoms were not assigned due to line broadening; MS (MALDI-TOF) *m/z* calcd for $C_{88}H_{123}N_{14}$ $[M+H]^+$ 1376.00, found 1376.03.

28,34-Dibenzyl-1,7,11,15,19,25,28,34-octaazatetracyclo[23.6.6.2^{3,6}.2^{20,23}]hentetraconta-3,5,20,22,38,40-hexaene (14c) was synthesized from compound **6** (144 mg, 0.20 mmol), tetraamine **7c** (38 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:20:2. Pale-beige crystalline powder, mp 82-84 ºC. Yield 21 mg (14%). ^{1}H NMR ($CDCl_3$): δ 1.68-1.76 (m, 6H), 1.81 (quintet, ^3J = 6.1 Hz, 4H), 2.36 (t, ^3J = 5.4 Hz, 4H), 2.45-2.56 (m, 8H), 2.58 (bs, 4H), 2.74 (t, ^3J = 6.4 Hz, 4H), 2.78 (t, ^3J = 6.1 Hz, 4H), 3.22 (t, ^3J = 6.2 Hz, 4H), 3.30 (bs, 4H), 3.44 (s, 4H), 6.58 (d, ^3J = 8.5 Hz, 4H), 7.19 (d, ^3J = 8.5 Hz, 4H), 7.21-7.29 (m, 10H), four NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 25.5 (2C), 28.6 (2C), 29.2 (1C), 43.5 (2C), 48.5 (2C), 48.7 (2C), 52.1 (2C), 52.5 (2C), 52.7 (2C), 53.4 (2C), 59.5 (4C), 112.4 (4C), 126.5 (2C), 128.0 (4C), 128.9 (4C), 130.1 (4C), 140.2 (2C), 147.5 (2C), two quaternary carbon atoms were not assigned due to line broadening; HRMS (MALDI-TOF) *m/z* calcd for $C_{47}H_{69}N_8$ $[M+H]^+$ 745.5645, found 745.5692.

28,59,65,75-Tetrabenzyl-1,7,11,15,19,25,28,32,38,42,46,50,56,59,65,75-hexadecaazaheptacyclo-[54.6.6.6^{25,32}.2^{3,6}.2^{20,23}.2^{34,37}.2^{51,54}]dooctaconta-3,5,20,22,34,36,51,53,69,71,79,81-dodecaene (15c) was obtained as the second product in the synthesis of macrobicycle **14c**. Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:20:3. Yellowish glassy compound. Yield 16 mg (11%). ^{1}H NMR ($CDCl_3$): δ 1.67-1.83 (m, 20H), 2.49 (bs, 16H), 2.58 (bs, 16H), 2.69 (t, ^3J = 5.9 Hz, 8H), 2.72 (t, ^3J = 5.9 Hz, 8H), 3.13 (t, ^3J = 5.3 Hz, 8H), 3.33 (s, 8H), 3.44 (s, 8H), 6.49 (d, ^3J = 8.0 Hz, 8H), 7.04 (d, ^3J = 8.0 Hz, 8H), 7.16-7.29 (m, 20H), eight NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 23.5 (4C), 29.3 (4C), 29.7 (2C), 43.0 (4C), 48.4 (4C), 48.6 (4C), 50.2 (8C), 51.0 (4C), 51.4 (4C), 58.9 (4C), 59.4 (4C), 112.4 (8C), 126.5 (4C), 128.0 (8C), 128.9 (8C), 129.9 (8C), 140.1 (4C), 147.3 (4C), four quaternary carbon atoms were not assigned due to line broadening; HRMS (MALDI-TOF) *m/z* calcd for $C_{94}H_{137}N_{16}$ $[M+H]^+$ 1490.1212, found 1490.1125.

25,31-Dibenzyl-10,13-dioxa-1,7,16,22,25,31-hexaazatetracyclo[20.6.6.2^{3,6}.2^{17,20}]octatriaconta-3,5,17,19,35,37-hexaene (14d) was synthesized from compound **6** (144 mg, 0.20 mmol), dioxadiamine **7d** (30 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 119-120 ºC. Yield 23 mg (16%). ^{1}H NMR (DMSO-d_6, 363K): δ 1.77 (bs, 4H), 2.49 (bs, 4H), 2.49 (bs, 4H), 2.56 (bs, 4H), 2.65 (bs, 8H), 3.23 (t, ^3J = 5.7 Hz, 4H), 3.44 (s, 4H), 3.56 (s, 4H), 3.59 (s, 4H), 3.64 (t, ^3J = 5.7 Hz, 4H), 5.09 (bs, 2H), 6.56 (d, ^3J = 8.1 Hz, 4H), 7.05 (d, ^3J = 8.1 Hz, 4H), 7.18-7.32 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 27.5 (2C, $\Delta\nu_{1/2}$ = 25 Hz), 43.5 (2C), 51.9 (8C, $\Delta\nu_{1/2}$ = 30 Hz), 58.5 (4C, $\Delta\nu_{1/2}$ = 40 Hz), 69.2 (2C), 70.0 (2C), 113.0 (4C), 127.6 (2C, $\Delta\nu_{1/2}$ = 25 Hz), 128.4 (4C), 129.8 (4C), 131.2 (4C, $\Delta\nu_{1/2}$ = 40 Hz), 148.0 (2C, $\Delta\nu_{1/2}$ = 50 Hz), four quaternary carbon atoms were not assigned due to line broadening;

HRMS (MALDI-TOF) *m/z* calcd for $C_{44}H_{61}N_6O_2$ $[M+H]^+$ 705.4856, found 705.4808.

25,53,59,69-Tetrabenzyl-10,13,38,41-tetraoxa-1,7,16,22,25,29,35,44,50,53,59,69-dodecaazahepta-cyclo[48.6.6.6^{22,29}.2^{3,6}.2^{17,20}.2^{31,34}.2^{45,48}]hexaheptaconta-3,5,17,19,31,33,45,47,63,65,73,75-dodecaene (15d) was obtained as the second product in the synthesis of macrobicycle **14d**. Eluent CH_2Cl_2 – MeOH 3:1. Yellowish glassy compound. Yield 11 mg (8%). ^{1}H NMR ($CDCl_3$): δ 1.73 (bs, 8H), 2.47 (bs, 16H), 2.60 (bs, 16H), 3.25 (t, ^3J = 4.6 Hz, 8H), 3.44 (s, 8H), 3.63 (s, 8H), 3.68 (bs, 8H), 3.69 (s, 8H), 3.77 (bs, 4H), 6.48 (d, ^3J = 7.6 Hz, 8H), 7.01 (d, ^3J = 7.6 Hz, 8H), 7.16-7.28 (m, 20H); ^{13}C NMR ($CDCl_3$): δ 27.0 (4C), 43.6 (4C), 49.5-52.1 (m, 16C), 58.3 (4C), 59.2 (4C), 69.0 (4C), 70.0 (4C), 112.8 (8C), 127.2 (4C), 128.2 (8C), 129.2 (8C), 130.6 (8C), 139.3 (4C), 147.6 (4C), four quaternary carbon atoms were not assigned due to line broadening; MS (MALDI-TOF) *m/z* calcd for $C_{88}H_{121}N_{12}O_4$ $[M+H]^+$ 1409.96, found 1409.92.

29,35-Dibenzyl-11,16-dioxa-1,7,20,26,29,35-hexaazatetracyclo[24.6.6.2^{3,6}.2^{21,24}]dotetraconta-3,5,21,23,39,41-hexaene (14e) was synthesized from compound **6** (144 mg, 0.20 mmol), dioxadiamine **7e** (41 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 102-104 ºC. Yield 27 mg (18%). ^{1}H NMR ($CDCl_3$): δ 1.67 (bs, 4H), 1.85 (quintet, ^3J = 5.6 Hz, 4H), 1.87 (bs, 4H), 2.30-2.80 (m, 16H), 3.20 (bs, 4H), 3.44 (bs, 8H), 3.53 (t, ^3J = 4.8 Hz, 4H), 3.54 (s, 4H), 6.51 (d, ^3J = 8.1 Hz, 4H), 7.07 (bs, 4H), 7.20-7.30 (m, 10H), two NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 24.0 (2C, $\Delta\nu_{1/2}$ = 40 Hz), 26.8 (2C), 29.2 (2C, $\Delta\nu_{1/2}$ = 15 Hz), 42.5 (2C, $\Delta\nu_{1/2}$ = 12 Hz), 51.2 (4C, $\Delta\nu_{1/2}$ = 35 Hz), 51.6 (4C, $\Delta\nu_{1/2}$ = 25 Hz), 58.5 (4C, $\Delta\nu_{1/2}$ = 15 Hz), 69.8 (2C, $\Delta\nu_{1/2}$ = 15 Hz), 71.0 (2C), 112.4 (4C), 127.6 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 128.4 (4C), 129.8 (4C), 131.3 (4C, $\Delta\nu_{1/2}$ = 25 Hz), 148.5 (2C, $\Delta\nu_{1/2}$ = 30 Hz), four quaternary carbon atoms were not assigned due to line broadening; HRMS (MALDI-TOF) *m/z* calcd for $C_{48}H_{69}N_6O_2$ $[M+H]^+$ 761.5482, found 761.5438.

29,61,67,77-Tetrabenzyl-11,16,43,48-tetraoxa-1,7,20,26,29,33,39,52,58,61,67,77-dodecaazahepta-cyclo[56.6.6.6^{26,33}.2^{3,6}.2^{21,24}.2^{35,38}.2^{53,56}]tetraoctaconta-3,5,21,23,35,37,53,55,71,73,81,83-dodecaene (15e) was obtained as the second product in the synthesis of macrobicycle **14e**. Eluent CH_2Cl_2 – MeOH 3:1. Yellowish glassy compound. Yield 21 mg (14%). ^{1}H NMR ($CDCl_3$): δ 1.65 (bs, 8H), 1.85 (bs, 8H), 1.93 (bs, 8H), 2.35-2.95 (m, 32H), 3.16 (t, ^3J = 4.7 Hz, 8H), 3.43 (bs, 16H), 3.52 (t, ^3J = 5.1 Hz, 8H), 3.53 (s, 8H), 6.49 (d, ^3J = 7.7 Hz, 8H), 7.11 (bs, 8H), 7.17-7.30 (m, 20H), four NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 23.0 (4C), 29.2 (4C), 29.6 (4C), 42.0 (4C), 49.5 (8C), 51.5 (8C), 57.6 (4C), 58.6 (4C), 69.5 (4C), 70.8 (4C), 112.5 (8C), 127.4 (4C), 128.4 (8C), 129.6 (8C), 131.6 (8C), 139.0 (4C), 148.7 (4C), four quaternary carbon atoms were not assigned due to line broadening; HRMS (MALDI-TOF) *m/z* calcd for $C_{96}H_{137}N_{12}O_4$ $[M+H]^+$ 1522.0886, found 1522.0957.

30,36-Dibenzyl-11,14,17-trioxa-1,7,21,27,30,36-hexaazatetracyclo[25.6.6.2^{3,6}.2^{22,25}]tritetraconta-

3,5,22,24,40,42-hexaene (14f) was synthesized from compound **6** (144 mg, 0.20 mmol), trioxadiamine **7f** (44 mg, 0.20 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Pale-beige crystalline powder, mp 86-88 ºC. Yield 23 mg (15%). ^{1}H NMR ($CDCl_3$): δ 1.85 (quintet, ^3J = 5.0 Hz, 4H), 1.86 (bs, 4H), 2.48 (bs, 4H), 2.67 (bs, 12H), 3.22 (bs, 4H), 3.45 (bs, 4H), 3.50-3.65 (m, 12H), 3.66 (bs, 4H), 6.49 (bd, $^3J_{obs}$ = 7.2 Hz, 4H), 7.03 (bs, 4H), 7.19-7.30 (m, 10H), two NH protons were not assigned; ^{13}C NMR (DMSO-d_6): δ 23.0 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 29.0 (2C), 40.1 (2C), 50.1 (6C, $\Delta\nu_{1/2}$ = 50 Hz), 50.7 (2C, $\Delta\nu_{1/2}$ = 25 Hz), 57.2 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 58.1 (2C, $\Delta\nu_{1/2}$ = 25 Hz), 68.3 (2C), 69.7 (2C), 70.0 (2C), 111.5 (4C), 127.2 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 128.2 (4C), 129.4 (4C, $\Delta\nu_{1/2}$ = 15 Hz), 131.2 (4C, $\Delta\nu_{1/2}$ = 40 Hz), 148.7 (2C, $\Delta\nu_{1/2}$ = 40 Hz), four quaternary carbon atoms were not assigned due to line broadening; HRMS (MALDI-TOF) *m/z* calcd for $C_{48}H_{69}N_6O_3$ $[M+H]^+$ 777.5431, found 777.5389.

30,63,69,79-Tetrabenzyl-11,14,17,44,47,50-hexaoxa-1,7,21,27,30,34,40,54,60,63,69,79-dodecaazahepta-cyclo[58.6.6.6^{27,34}.2^{3,6}.2^{22,25}.2^{36,39}.2^{55,58}]hexaoctaconta-3,5,22,24,36,38,55,57,73,75,83,85-dodecaene (15f) was obtained as the second product in the synthesis of macrobicycle **14f**. Eluent CH_2Cl_2 – MeOH 3:1. Yellowish glassy compound. Yield 29 mg (19%). ^{1}H NMR ($CDCl_3$): δ 1.71 (bs, 8H), 1.86 (quintet, ^3J = 6.1 Hz 8H), 2.44-2.54 (m, 16H), 2.59 (bs, 16H), 3.18 (t, ^3J = 5.8 Hz, 8H), 3.34 (s, 8H), 3.43 (s, 8H), 3.55-3.61 (m, 16H), 3.63-3.68 (m 8H), 3.94 (bs, 4H), 6.48 (d, ^3J = 8.3 Hz, 8H), 7.03 (d, ^3J = 8.3 Hz, 8H), 7.17-7.29 (m, 20H); ^{13}C NMR ($CDCl_3$): δ 23.3 (4C), 29.1 (4C), 41.8 (4C), 49.9 (4C), 50.2 (4C), 50.9 (4C), 51.4 (4C), 58.9 (4C), 59.4 (4C), 69.7 (4C), 70.2 (4C), 70.6 (4C), 112.3 (8C), 126.5 (4C), 128.0 (8C), 128.9 (16C), 140.0 (4C), 147.3 (4C), four quaternary carbon atoms were not assigned due to line broadening; MS (MALDI-TOF) *m/z* calcd for $C_{96}H_{137}N_{12}O_6$ $[M+H]^+$ 1554.08, found 1554.10.

Typical procedure for the synthesis of macrobicycles 18e,f, 25.

A one-neck flask (10 mL) equipped with a magnetic stirrer was charged with corresponding macrobicycle (**17e,f, 24**) (1 equiv.) which was solubilized in CH_2Cl_2 (0.3-0.5 mL) and then dissolved in 3 mL MeCN. Potassium carbonate (3 equiv.) was added followed by 3-bromobenzyl bromide (1.7 equiv.) in 2 mL MeCN. The reaction mixture was stirred for 24 h, the residue was filtered off and washed with CH_2Cl_2 (10 mL). Combined organic sovents were evaporated *in vacuo* and chromatographed on silica gel using a sequence of eluents CH_2Cl_2, CH_2Cl_2-MeOH 25:1 – 3:1, CH_2Cl_2-MeOH-NH_3(aq) 100:20:1 – 10:4:1.

27,32-Bis(3-bromobenzyl)-11,14-dioxa-1,8,17,24,27,32-hexaazatetracyclo[22.5.5.1^{3,7}.1^{18,22}]hexatriaconta-3(36),4,6,18(35),19,21-hexaene (18e) was synthesized from macrobicycle **17e** (149 mg, 0.3 mmol), 3-bromobenzyl bromide (128 mg, 0.51 mmol) in MeCN (5 mL) in the presence of K_2CO_3 (136 mg, 0.9 mmol). Eluent CH_2Cl_2 – MeOH 3:1. Yellowish glassy compound. Yield 80 mg (32%). ^{1}H NMR ($CDCl_3$): δ 2.54-2.68 (m, 12H), 2.77-2.84 (m, 4H), 3.27 (bs, 4H), 3.34 (s, 8H), 3.67 (s, 4H), 3.68 (t, ^3J = 4.8 Hz, 4H), 4.11 (bs, 2H), 6.47 (d, ^3J = 8.0 Hz, 4H), 6.82 (bs, 2H), 7.05 (t, ^3J = 7.7 Hz, 2H), 7.16 (t, ^3J = 7.7 Hz, 2H), 7.30-7.39 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 43.7 (2C), 52.0 (4C), 52.9 (4C), 59.0 (2C), 61.2 (2C), 69.7 (2C), 70.6 (2C), 110.6 (2C), 114.3 (2C), 118.3 (2C), 122.1 (2C), 127.6 (2C), 128.7 (2C), 129.7 (2C), 129.8 (2C), 131.7 (2C), 140.9 (2C), 142.5 (2C), 148.3 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{42}H_{55}Br_2N_6O_2$ $[M+H]^+$ 833.2753, found 833.2716.

32,37-Bis(3-bromobenzyl)-12,15,18-trioxa-1,8,22,29,32,37-hexaazatetracyclo[27.5.5.1^{3,7}.1^{23,27}]hentetra-conta-3(41),4,6,23(40),24,26-hexaene (18f) was synthesized from macrobicycle **17f** (130 mg, 0.23 mmol), 3-bromobenzyl bromide (115 mg, 0.46 mmol) in MeCN (5 mL) in the presence of K_2CO_3 (95 mg, 0.69 mmol). Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:20:1. Yellowish glassy compound. Yield 69 mg (33%). ^{1}H NMR ($CDCl_3$): δ 1.85 (quintet, ^3J = 6.1 Hz, 4H), 2.64-2.74 (m, 16H), 3.19 (quintet, ^3J = 5.8 Hz, 4H), 3.38 (s, 4H), 3.41 (s, 4H), 3.57 (t, ^3J = 6.0 Hz, 4H), 3.59-3.62 (m, 4H), 3.65-3.70 (m, 4H), 3.96 (t, ^3J = 5.4 Hz, 2H), 6.48 (d, ^3J = 8.0 Hz, 2H), 6.60 (d, ^3J = 7.3 Hz, 2H), 6.74 (s, 2H), 7.06 (t, ^3J = 7.6 Hz, 2H), 7.11 (t, ^3J = 7.8 Hz, 2H), 7.31 (d, ^3J = 7.7 Hz, 2H), 7.36 (d, ^3J = 8.3 Hz, 2H), 7.52 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 29.1 (2C), 41.6 (2C), 52.5 (4C), 53.0 (4C), 59.2 (2C), 60.5 (2C), 69.6 (2C), 70.2 (2C), 70.6 (2C), 110.8 (2C), 113.2 (2C), 117.6 (2C), 122.1 (2C), 127.5 (2C), 128.7 (2C), 129.7 (4C), 131.7 (2C), 141.0 (2C), 142.6 (2C), 148.6 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{46}H_{63}Br_2N_6O_3$ $[M+H]^+$ 905.3328, found 905.3271.

30,35-Bis(3-bromobenzyl)-11,14,17-trioxa-1,7,21,27,30,35-hexaazatetracyclo[25.5.5.2^{3,6}.2^{22,25}]hentetra-conta-3,5,22,24,38,40-hexaene (25) was synthesized from macrobicycle **24** (385 mg, 0.68 mmol), 3-bromobenzyl bromide (298 mg, 1.19 mmol) in MeCN (15 mL) in the presence of K_2CO_3 (235mg, 1.70 mmol). Eluent CH_2Cl_2 – MeOH 10:1. Yellowish glassy compound. Yield 154 mg (25%). ^{1}H NMR ($CDCl_3$): δ 1.91 (quintet, ^3J = 5.8 Hz, 4H), 2.63 (bs, 8H), 2.71 (bs, 8H), 3.27 (bs, 4H), 3.32 (s, 4H), 3.38 (s, 4H), 3.63-3.68 (m, 8H), 3.74-3.78 (m, 4H), 4.22 (bs, 2H), 6.58 (d, ^3J = 8.2 Hz, 4H), 7.12 (t, ^3J = 7.7 Hz, 2H), 7.22 (d, ^3J = 8.2 Hz, 4H), 7.31 (d, ^3J = 7.8 Hz, 2H), 7.34 (d, ^3J = 7.7 Hz, 2H), 7.48 (bs, 2H); ^{13}C NMR ($CDCl_3$): δ 28.9 (2C), 42.4 (2C), 52.7 (4C), 53.1 (4C), 59.4 (2C), 59.7 (2C), 70.1 (4C), 70.6 (2C), 112.3 (4C), 122.0 (2C), 127.4 (2C), 128.2 (2C), 129.4 (2C), 129.5 (2C), 129.8 (4C), 131.6 (2C), 142.7 (2C), 147.2 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{46}H_{63}Br_2N_6O_3$ $[M+H]^+$ 905.3328, found 905.3296.

Typical procedure for the synthesis of macrotricycles 19, 21, 26 is essentially the same as for macrobicycles **8, 10, 12, 14**.

12,15,18,43,46,49-Hexaoxa-1,8,22,29,32,39,53,60-octaazaheptacyclo[30.30.2.2^{29,60}.1^{3,7}.1^{23,27}.1^{34,38}.1^{54,58}]-heptaconta-3(70),4,6,23(69),24,26,34(68),35,37,54(67),55,57-dodecaene (19) was synthesized from compound **18f** (130 mg, 0.14 mmol) and trioxadiamine **7f** (31 mg, 0.14 mmol) in the presence of $Pd(dba)_2$ (6.5 mg, 8 mol%), BINAP (8 mg, 9 mol%), *t*BuONa (40 mg, 0.42 mmol) in boiling dioxane (6 mL). Eluent CH_2Cl_2 – MeOH 3:1. Yellowish glassy compound. Yield 45 mg (33%). ^{1}H NMR (DMSO-d_6): δ 1.73 (quintet, ^3J = 6.2 Hz, 8H), 2.72-2.87 (m, 16H), 3.07 (t, ^3J = 6.8 Hz, 8H), 3.38-3.48 (m, 16H), 3.50-3.55 (m, 16H), 5.27 (bs, 4H), 6.39 (d, ^3J = 7.7 Hz, 4H), 6.51 (s, 4H), 6.53 (d, ^3J = 8.3 Hz, 4H), 7.01 (t, ^3J = 7.5 Hz, 4H); ^{13}C NMR (DMSO-d_6): δ 28.8 (4C), 40.1 (4C), 50.0 (8C), 58.9 (4C), 68.1 (4C), 69.2 (4C), 69.5 (4C), 112.0 (4C), 113.0 (4C), 117.2 (4C), 128.3 (4C), 135.7 (4C), 148.8 (4C); MS (MALDI-TOF) *m/z* calcd for $C_{56}H_{85}N_8O_6$ [M+H]$^+$ 965.66, found 965.64.

12,15,18,43,46,49,74,77,80,105,108,111-Dodecaoxa-1,8,22,29,32,39,53,60,63,70,84,91,94,101,115,122-hexadecaazatridecacyclo[92.30.2.2^{29,60}.2^{32,63}.2^{91,122}.1^{3,7}.1^{23,27}.1^{34,38}.1^{54,58}.1^{65,69}.1^{85,89}.1^{96,100}.1^{116,120}]-tetracontahecta-3(140),4,6,23(139),24,26,34(138),35,37,54(137),55,57,65(132),66,68,85(131),86,88,96(130),97,99,116(129),117,119-tetracosaene (20) was obtained as the second product in the synthesis of macrotricycle **19**. Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:20:2. Yellowish glassy compound. Yield 21 mg (8%). ^{1}H NMR ($CDCl_3$): δ 1.74-1.86 (m, 16H), 2.40-2.95 (m, 32H), 3.12 (t, ^3J = 7.0 Hz, 16H), 3.43-3.65 (m, 64H), 6.35-6.59 (m, 24H), 6.97-7.07 (m, 8H), eight NH protons were not assigned; MS (MALDI-TOF) *m/z* calcd for $C_{112}H_{169}N_{16}O_{12}$ [M+H]$^+$ 1930.31, found 1931.26.

11,14,37,40-Tetraoxa-1,8,17,24,27,34,43,50-octaazaheptacyclo-[25.25.2.2^{24,50}.1^{3,7}.1^{18,22}.1^{29,33}.1^{44,48}]-hexaconta-3(60),4,6,18(59),19,21,29(58),30,32,44(57),45,47-dodecaene (21) was synthesized from compound **18e** (65 mg, 0.08 mmol) and dioxadiamine **7e** (12 mg, 0.08 mmol) in the presence of Pd(dba)$_2$ (7 mg, 16 mol%), BINAP (9 mg, 18 mol%), *t*BuONa (23 mg, 0.24 mmol) in boiling dioxane (4 mL). Eluent CH_2Cl_2 – MeOH 3:1. Yellowish glassy compound. Yield 10 mg (15%). ^{1}H NMR ($CDCl_3$): δ 2.83 (bs, 16H), 3.25 (t, ^3J = 4.5 Hz, 8H), 3.46 (bs, 8H), 3.68 (s, 8H), 3.72 (t, ^3J = 4.5 Hz, 8H), 6.43 (d, ^3J = 7.1 Hz, 4H), 6.52 (d, ^3J = 7.6 Hz, 4H), 6.78 (bs, 4H), 7.08 (t, ^3J = 7.8 Hz, 4H), four NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 43.7 (4C), 50.1 (4C), 50.3 (4C), 57.9 (2C), 58.6 (2C), 69.4 (4C), 70.3 (4C), 111.9 (4C), 115.4 (4C), 118.8 (4C), 129.5 (4C), 149.0 (4C), four quaternary carbon atoms were not assigned; HRMS (MALDI-TOF) *m/z* calcd for $C_{48}H_{69}N_8O_4$ [M+H]$^+$ 821.5442, found 821.5402.

11,14,37,40,63,66,89,92-Octaoxa-1,8,17,24,27,34,43,50,53,60,69,76,79,86,95,102-hexadecaaza-tridecacyclo[77.25.2.2^{24,50}.2^{27,53}.2^{76,102}.1$^{3.7}$.1^{18,22}.1^{29,33}.1^{44,48}.1^{55,59}.1^{70,74}.1^{81,85}1^{96,100}]eicosahecta-3(120),4,6,18(119),19,21,29(118),30,32,44(117),45,47,55(112),56,58,70(111),71,73,81(110),82,84,96(109),97,99-tetracosaene (22) was obtained as the second product in the synthesis of macrotricycle **21**. Eluent CH_2Cl_2 – MeOH – NH_3(aq) 100:20:3. Yellowish glassy compound. Yield 14 mg (21%). ^{1}H NMR ($CDCl_3$): δ 2.50-2.73 (m, 32H), 3.26 (bs, 16H), 3.36 (s, 16H), 3.55-3.67 (m, 32H), 6.47 (bd, $^3J_{obs}$ = 6.8 Hz, 16H), 6.66 (bs, 8H), 7.05 (bt, $^3J_{obs}$ = 6.0 Hz, 8H), eight NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 43.7 (8C), 51.9 (16C), 60.9 (8C), 69.7 (8C), 70.2 (8C), 111.3 (8C), 114.0 (8C), 118.5 (8C), 129.0 (8C), 140.8 (8C), 148.4 (8C); MS (MALDI-TOF) *m/z* calcd for $C_{96}H_{137}N_{16}O_8$ [M+H]$^+$ 1642.08, found 1642.05.

12,15,18,42,45,48-Hexaoxa-1,8,22,29,32,38,52,58-octaazaheptacyclo[30.28.2.2^{29,58}.2^{34,37}.2^{53,56}.1^{3,7}.1^{23,27}]-heptaconta-3(70),4,6,23(69),24,26,34,36,53,55,65,67-dodecaene (26) was synthesized from compound **25** (93 mg, 0.11 mmol) and trioxadiamine **7f** (25 mg, 0.11 mmol) in the presence of Pd(dba)$_2$ (10 mg, 16 mol%), BINAP (13 mg, 18 mol%), *t*BuONa (33 mg, 0.34 mmol) in boiling dioxane (6 mL). Eluent CH_2Cl_2 – MeOH 10:1 – 3:1. Yellowish glassy compound. Yield 23 mg (22%). ^{1}H NMR ($CDCl_3$): δ 1.83 (quintet, ^3J = 5.9 Hz, 4H), 1.91 (quintet, ^3J = 5.4 Hz, 4H), 2.51 (bs, 8H), 3.01 (bs, 8H), 3.17 (bt, $^3J_{obs}$ = 5.2 Hz, 4H), 3.27 (t, ^3J = 6.0 Hz, 4H), 3.33 (s, 4H), 3.37 (s, 4H), 3.56 (t, ^3J = 5.7 Hz, 4H), 3.57-3.69 (m, 16H), 3.70-3.74 (m, 4H), 4.19 (bs, 4H), 6.46 (d, ^3J = 7.5 Hz, 2H), 6.52 (bd, $^3J_{obs}$ = 5.9 Hz, 2H), 6.59 (s, ^3J = 8.0 Hz, 4H), 6.71 (bs, 2H), 7.04 (t, ^3J = 7.7 Hz, 2H), 7.20 (bs, 4H); ^{13}C NMR ($CDCl_3$): δ 29.0 (2C), 29.1 (2C), 41.6 (2C), 42.5 (2C), 53.2 (8C, $\Delta\nu_{1/2}$ = 70 Hz), 59.7 (2C), 60.9 (2C), 69.6 (2C), 70.2 (4C), 70.3 (2C), 70.7 (4C), 110.9 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 112.4 (4C), 113.4 (2C, $\Delta\nu_{1/2}$ = 30 Hz), 117.6 (2C), 128.8 (2C), 130.2 (4C, $\Delta\nu_{1/2}$ = 20 Hz), 147.6 (2C, $\Delta\nu_{1/2}$ = 25 Hz), 148.7 (2C), four quaternary carbon atomns were not assigned due to line broadening; HRMS (MALDI-TOF) *m/z* calcd for $C_{56}H_{85}N_8O_6$ [M+H]$^+$ 965.6592, found 965.6638.

Synthesis of di-Boc substituted macrotricylces comprising cyclen moiety. Pd-catalyzed amination steps were carried out in the same way as described above for the synthesis of macrobicycles **8, 10, 12, 14** and macrotricycles **19, 21, 26**.

Di-*tert*-butyl-4,10-bis(3-bromobenzyl)-1,4,7,10-tetraazacyclododecaene-1,7-dicarboxylate (27) was synthesized from compound **16** (510 mg, 1 mmol) and Boc$_2$O (545 mg, 2.5 mmol) in CH_2Cl_2 (1.5 mL) at room temperature, the reaction mixture was stirred for 24 h. Then the reactione mixture was washed with water (5 mL), water layer was extracted with CH_2Cl_2 (5 mL), combined organic fractions were dried over anhydrous sodium sulfate, the solvent was evaporated *in vacuo*. Yellowish glassy compound. Yield 694 mg (98%). ^{1}H NMR ($CDCl_3$): δ 1.27 (s, 18H), 2.61 (bs, 8H), 3.29 (bs, 4H), 3.40 (bs, 4H), 3.52 (s, 4H), 7.12 (bt, $^3J_{obs}$ = 6.3 Hz, 2H), 7.17 (bs, 2H), 7.31 (bd, $^3J_{obs}$ = 6.5 Hz, 2H), 7.44 (bs, 2H); ^{13}C NMR ($CDCl_3$, 328K): δ 28.2 (6C), 45.9 (4C), 54.7 (4C), 59.1 (2C), 79.5 (2C), 122.2 (2C), 127.7 (2C), 129.6 (2C), 130.0 (2C), 132.2 (2C), 141.5 (2C), 155.6 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{32}H_{47}Br_2N_4O_4$ [M+H]$^+$ 709.1964, found 709.1920.

Di-*tert*-butyl-12,15,18-trioxa-1,8,22,29,32,37-hexaazatetracyclo[27.5.5.1^{3,7}.1^{23,27}]hentetraconta-3(41),4,6,23(40),24,26-hexaene-32,37-dicarboxylate (28) was synthesized from compound **27** (694 mg, 0.98 mmol) and trioxadiamine **7f** (220 mg, 1 mmol) in the presence of Pd(dba)$_2$ (92 mg, 16 mol%), BINAP (112 mg, 18 mol%), *t*BuONa (290 mg, 3.02 mmol) in boiling dioxane (50 mL). Eluent CH_2Cl_2 – MeOH 25:1. Yellowish glassy compound. Yield 294 mg (33%). ^{1}H NMR ($CDCl_3$, 328K): δ 1.35 (s, 18H), 1.84 (quintet, ^3J = 5.5 Hz, 4H), 2.78 (bs, 8H), 3.23 (t, ^3J = 6.0 Hz, 4H), 3.36 (bs, 8H), 3.54 (bs, 4H), 3.55-3.60 (m, 8H), 3.65-3.68 (m, 4H), 6.46 (d, ^3J = 7.5 Hz, 2H), 6.56 (bd, $^3J_{obs}$ = 6.6 Hz, 2H), 6.65 (bs, 2H), 7.04 (bt, $^3J_{obs}$ = 7.3 Hz, 2H), two NH protons were not assigned; ^{13}C NMR ($CDCl_3$, 328K): δ 28.5 (6C), 29.6 (2C), 41.9 (2C), 47.4 (4C), 54.4 (4C), 60.6 (2C), 69.8 (2C), 70.4 (2C), 70.8 (2C), 79.5 (2C), 111.8 (2C), 113.6 (2C), 118.3 (2C), 128.9 (2C), 140.0 (2C), 148.9 (2C), 156.1 (2C); HRMS (ESI-TOF) *m/z* calcd for $C_{42}H_{69}N_6O_7$ $[M+H]^+$ 769.5228, found 769.5212.

Di-*tert*-butyl-8,22-bis(3-bromobenzyl)-12,15,18-trioxa-1,8,22,29,32,37-hexaazatetracyclo[27.5.5.1^{3,7}.1^{23,27}]-hentetraconta-3(41),4,6,23(40),24,26-hexaene-32,37-dicarboxylate (29) was synthesized as described above for compounds **18e,f, 25** from compound **28** (315 mg, 0.4 mmol), 3-bromobenzyl bromide (200 mg, 0.8 mmol) in the presence of K_2CO_3 (138 mg, 1 mmol). Eluent CH_2Cl_2 – MeOH 25:1. Yellowish oil. Yield 255 mg (58%). ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 18H), 1.88 (quintet, ^3J = 6.1 Hz, 4H), 2.70 (bs, 8H), 3.31 (bs, 8H), 3.45-3.59 (m, 16H), 3.65-3.69 (m, 4H), 4.48 (s, 4H), 6.50 (bd, $^3J_{obs}$ = 6.2 Hz, 2H), 6.61 (d, ^3J = 7.2 Hz, 2H), 6.73 (bs, 2H), 7.06 (t, ^3J = 7.9 Hz, 2H), 7.11 (bs, 2H), 7.12 (t, ^3J = 7.6 Hz, 2H), 7.33 (bd, $^3J_{obs}$ = 7.1 Hz, 2H), 7.34 (bs, 2H); ^{13}C NMR ($CDCl_3$, 328K): δ 27.8 (2C), 28.5 (6C), 46.9 (4C), 48.2 (2C), 54.3 (2C), 54.5 (4C), 60.6 (2C), 68.8 (2C), 70.5 (2C), 70.9 (2C), 79.5 (2C), 111.9 (2C), 113.6 (2C), 118.3 (2C), 122.8 (2C), 125.4 (2C), 129.8 (2C), 129.9 (2C), 130.1 (4C), 139.9 (2C), 142.1 (2C), 148.7 (2C), 155.9 (2C); HRMS (ESI-TOF) *m/z* calcd for $C_{56}H_{79}Br_2N_6O_7$ $[M+H]^+$ 1105.4377, found 1105.4373.

Di-*tert*-butyl-12,15,18,52,55,58-hexaoxa-1,8,22,29,36,39,42,65-octaazaheptacyclo[27.19.13.5^{36,42}.1^{3,7}.1^{23,27}.1^{30,34}.1^{44,48}]heptaconta-3(70),4,6,23(69),24,26,30(68),31,33,44(62),45,47-dodecaene-39,65-dicarboxylate (30) was synthesized from compound **29** (126 mg, 0.114 mmol) and dioxadiamine **7e** (17 mg, 0.115 mmol) in the presence of Pd(dba)$_2$ (10.5 mg, 16 mol%), BINAP (13 mg, 18 mol%), *t*BuONa (33 mg, 0.34 mmol) in boiling dioxane (6 mL). Eluent CH_2Cl_2 – MeOH 10:1. Yellowish glassy compound. Yield 30 mg (24%). ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 18H), 1.86 (bs, 4H), 2.60-2.95 (m, 8H), 3.17 (bs, 4H), 3.30-3.70 (m, 36H), 4.41 (s, 2H), 4.43 (s, 2H), 6.44 (bs, 4H), 6.50-6.61 (m, 6H), 6.72 (bs, 2H), 7.05 (bs, 4H), two NH protons were not assigned; ^{13}C NMR ($CDCl_3$, 328K): δ 27.9 (2C), 28.5 (6C), 43.8 (2C), 47.0 (4C), 48.0 (2C), 54.5 (4C), 54.7 (2C), 60.9 (2C), 68.9 (2C), 69.9 (2C), 70.5 (4C), 70.9 (2C), 110.8 (2C), 112.2 (4C), 113.7 (2C), 116.1 (2C), 117.8 (2C), 128.9 (2C), 129.4 (2C), 139.0 (2C), 140.5 (2C), 148.8 (2C), 149.3 (2C), 156.1 (2C), two quaternary carbom atoms of Boc groups were not assigned; HRMS (MALDI-TOF) *m/z* calcd for $C_{62}H_{93}N_8O_9$ $[M+H]^+$ 1093.7066, found 1093.7032.

Di-*tert*-butyl-11,14-dioxa-1,8,17,24,27,32-hexaazatetracyclo[22.5.5.1^{3,7}.1^{18,22}]hexatriaconta-3(36),4,6,18(35),19,21-hexaene-27,32-dicarboxylate (31) was synthesized from compound **27** (584 mg, 0.83 mmol) and dioxadiamine **7e** (123 mg, 0.83 mmol) in the presence of Pd(dba)$_2$ (76 mg, 16 mol%), BINAP (93 mg, 18 mol%), *t*BuONa (245 mg, 2.50 mmol) in boiling dioxane (42 mL). Eluent CH_2Cl_2 –

MeOH 25:1. Yellowish glassy compound. Yield 122 mg (21%). ^{1}H NMR ($CDCl_3$): δ 1.35 (s, 18H), 2.74 (bs, 8H), 3.22 (bs, 4H), 3.30 (bs, 4H), 3.42 (bs, 4H), 3.55 (bs, 4H), 3.67 (s, 4H), 3.72 (bs, 4H), 4.17 (bs, 2H), 6.50 (d, ^3J = 7.7 Hz, 2H), 6.53 (d, ^3J = 7.2 Hz, 2H), 6.75 (bs, 2H), 7.05 (t, ^3J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 28.3 (6C), 43.6 (2C), 46.9 (4C), 54.5 (4C, $\Delta\nu_{1/2}$ = 150 Hz), 60.1 (2C, $\Delta\nu_{1/2}$ = 130 Hz), 69.5 (4C, $\Delta\nu_{1/2}$ = 20 Hz), 79.2 (2C), 111.8 (2C, $\Delta\nu_{1/2}$ = 90 Hz), 113.7 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 118.8 (2C, $\Delta\nu_{1/2}$ = 60 Hz), 128.8 (2C), 140.1 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 148.4 (2C), 155.9 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{38}H_{61}N_6O_6$ $[M+H]^+$ 697.4653, found 697.4624.

Di-*tert*-butyl-8,17-bis(3-bromobenzyl)-11,14-dioxa-1,8,17,24,27,32-hexaazatetracyclo[22.5.5.1^{3,7}.1^{18,22}]-hexatriaconta-3(36),4,6,18(35),19,21-hexaene-27,32-dicarboxylate (32) was synthesized from compound **31** (119 mg, 0.17 mmol), 3-bromobenzyl bromide (85 mg, 0.34 mmol) in the presence of K_2CO_3 (60 mg, 0.43 mmol). Eluent CH_2Cl_2 – MeOH 50:1 – 25:1. Yellowish oil. Yield 71 mg (41%). ^{1}H NMR ($CDCl_3$): δ 1.36 (s, 18H), 2.75 (bs, 8H), 3.18 (bs, 4H), 3.46 (bs, 8H), 3.56 (s, 4H), 3.61 (bs, 4H), 3.70 (bs, 4H), 4.58 (s, 4H), 6.53 (bd, $^3J_{obs}$ = 5.3 Hz, 2H), 6.57 (d, ^3J = 7.1 Hz, 2H), 6.84 (bs, 2H), 7.04-7.13 (m, 6H), 7.28-7.36 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 28.4 (6C), 48.8 (4C, $\Delta\nu_{1/2}$ = 30 Hz), 50.8 (2C), 53.7 (4C, $\Delta\nu_{1/2}$ = 120 Hz), 54.5 (2C), 60.4 (2C, $\Delta\nu_{1/2}$ = 40 Hz), 69.1 (2C), 70.8 (2C), 79.2 (2C), 111.6 (2C), 113.0 (2C, $\Delta\nu_{1/2}$ = 35 Hz), 118.4 (2C, $\Delta\nu_{1/2}$ = 50 Hz), 122.7 (2C), 125.1 (2C), 128.9 (2C), 129.5 (2C), 129.8 (2C), 130.1 (2C), 139.7 (2C, $\Delta\nu_{1/2}$ = 30 Hz), 141.8 (2C), 148.5 (2C), 155.8 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{52}H_{71}Br_2N_6O_6$ $[M+H]^+$ 1033.3802, found 1033.3765.

Di-*tert*-butyl-12,15,18,51,54-pentaoxa-1,8,22,29,36,39,42,60-octaazaheptacyclo[27.19.8.5^{36,42}.1^{3,7}.1^{23,27}.1^{30,34}.1^{44,48}]pentahexaconta-3(65),4,6,23(64),24,26,30(63),31,33,44(57),45,47-dodecaene-39,60-dicarboxylate (33) was synthesized from compound **32** (69 mg, 0.07 mmol) and trioxadiamine **7f** (15 mg, 0.07 mmol) in the presence of $Pd(dba)_2$ (6 mg, 16 mol%), BINAP (8 mg, 18 mol%), *t*BuONa (20 mg, 0.21 mmol) in boiling dioxane (4 mL). Eluent CH_2Cl_2 – MeOH 10:1. Yellowish glassy compound. Yield 13 mg (17%). ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 18H), 1.79 (quintet, ^3J = 5.6 Hz, 4H), 2.80 (bs, 8H), 3.11 (t, ^3J = 5.9 Hz, 8H), 3.33-3.70 (m, 32H), 4.49 (s, 4H), 6.38 (d, ^3J = 8.0 Hz, 2H), 6.42 (bd, $^3J_{obs}$ = 6.2 Hz, 2H), 6.45 (bd, J_{obs} = 6.8 Hz, 2H), 6.48-6.56 (m, 4H), 6.83 (bs, 2H), 7.02 (bt, J_{obs} = 6.5 Hz, 4H), two NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 28.4 (6C), 29.2 (2C), 41.5 (2C), 46.7 (4C, $\Delta\nu_{1/2}$ = 45 Hz), 50.5 (6C, $\Delta\nu_{1/2}$ = 20 Hz), 54.8 (2C), 60.2 (2C, $\Delta\nu_{1/2}$ = 50 Hz), 69.0 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 69.6 (2C), 70.2 (2C), 70.6 (2C), 70.9 (2C, $\Delta\nu_{1/2}$ = 15 Hz), 79.3 (2C), 110.3-113.1 (bm, 6C), 115.0 (2C), 117.6 (2C), 117.9 (2C), 128.7 (2C, $\Delta\nu_{1/2}$ = 15 Hz), 129.4 (2C), 135.2 (2C), 140.0 (2C), 148.8 (2C), 149.0 (2C), 155.9 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{62}H_{93}N_8O_9$ $[M+H]^+$ 1093.7066, found 1093.7134.

Di-*tert*-butyl-8,22-bis(4-bromobenzyl)-12,15,18-trioxa-1,8,22,29,32,37-hexaazatetracyclo-[27.5.5.1^{3,7}.1^{23,27}]hentetraconta-3(41),4,6,23(40),24,26-hexaene-32,37-dicarboxylate (34) was synthesized from compound **28** (223 mg, 0.29 mmol), 4-bromobenzyl bromide (145 mg, 0.58 mmol) in the presence of K_2CO_3 (100 mg, 0.73 mmol). Yellowish oil. Yield 220 mg (69%). ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 18H), 1.87 (quintet, ^3J = 5.4 Hz, 4H), 2.69 (bs, 8H), 3.31 (bs, 8H), 3.46 (bs, 4H), 3.48 (bs, 4H), 3.53 (bs, 4H), 3.54-3.58 (m, 4H), 3.64-3.68 (m, 4H), 4.45 (s, 4H), 6.48 (bd, $^3J_{obs}$ = 7.1 Hz, 2H), 6.60 (d, ^3J = 7.2 Hz, 2H), 6.71 (bs, 2H), 7.02-7.07 (m, 6H), 7.36 (d, ^3J = 8.2 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 27.6 (2C), 28.3 (6C), 46.4 (4C, $\Delta\nu_{1/2}$ = 40 Hz), 48.0 (2C), 53.7 (2C), 54.0 (4C, $\Delta\nu_{1/2}$ = 100 Hz), 60.4 (2C, $\Delta\nu_{1/2}$ = 30 Hz), 68.6 (2C), 70.3 (2C), 70.7 (2C), 79.1 (2C), 111.4 (2C), 113.0 (2C, $\Delta\nu_{1/2}$ = 50 Hz), 118.0 (2C, $\Delta\nu_{1/2}$ = 45 Hz), 120.3 (2C), 128.3 (4C), 129.0 (2C), 131.5 (4C), 138.2 (2C), 139.8 (2C), 148.3 (2C), 155.8 (2C); HRMS (MALDI-TOF) *m/z* calcd for $C_{56}H_{79}Br_2N_6O_7$ $[M+H]^+$ 1105.4377, found 1105.4317.

Di-*tert*-butyl-10,13,45,48,51-pentaoxa-1,7,16,22,29,32,35,58-octaazaheptacyclo [20.19.13.5^{29,35}.2^{3,6}.2^{17,20}.1^{23,27}.1^{37,41}]pentahexaconta-3,5,17,19,23(61),24,26,37(55),38,40,62,64-dodecaene-32,58-dicarboxylate (35) was synthesized from compound **34** (139 mg, 0.13 mmol) and dioxadiamine **7e** (19 mg, 0.13 mmol) in the presence of $Pd(dba)_2$ (12 mg, 16 mol%), BINAP (15 mg, 18 mol%), *t*BuONa (38 mg, 0.39 mmol) in boiling dioxane (7 mL). Eluent CH_2Cl_2 – MeOH 10:1. Yellowish glassy compound. Yield 24 mg (17%). ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 18H), 1.85 (bs, 4H), 2.70 (bs, 8H), 3.21 (bt, $^3J_{obs}$ = 4.4 Hz, 4H), 3.34-3.69 (m, 36H), 4.41 (s, 4H), 6.42 (d, ^3J = 7.6 Hz, 4H), 6.48-6.65 (m, 4H), 6.73 (bs, 2H), 6.86 (bs, 4H), 7.07 (bs, 2H), two NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 27.6 (2C), 29.4 (6C), 43.6 (2C), 46.6 (4C, $\Delta\nu_{1/2}$ = 80 Hz), 47.7 (2C), 53.6 (2C), 53.9 (4C, $\Delta\nu_{1/2}$ = 140 Hz), 60.6 (2C, $\Delta\nu_{1/2}$ = 80 Hz), 68.6-70.7 (m, 10C), 79.2 (2C), 111.4 (2C, $\Delta\nu_{1/2}$ = 20 Hz), 113.2 (2C), 113.3 (4C), 117.5 (2C, $\Delta\nu_{1/2}$ = 90 Hz), 127.6 (4C), 128.8 (2C), 139.8 (2C), 146.9 (2C), 148.8 (2C), two quaternary carbon atoms were not assigned; HRMS (MALDI-TOF) *m/z* calcd for $C_{62}H_{93}N_8O_9$ $[M+H]^+$ 1093.7066, found 1093.7162.

Di-*tert*-butyl-11,14,17,50,53,56-hexaoxa-1,7,21,27,34,37,40,63-octaazaheptacyclo-[25.19.13.5^{34,40}.2^{3,6}.2^{22,25}.1^{28,32}.1^{42,46}]heptaconta-3,5,22,24,28(66),29,31,42(60),43,45,67,69-dodecaene-37,63-dicarboxylate (36) was synthesized from compound **34** (134 mg, 0.12 mmol) and trioxadiamine **7f** (27 mg, 0.12 mmol) in the presence of $Pd(dba)_2$ (11 mg, 16 mol%), BINAP (13 mg, 18 mol%), *t*BuONa (35 mg, 0.38 mmol) in boiling dioxane (6 mL). Eluent CH_2Cl_2 – MeOH 10:1. Yellowish glassy compound. Yield 25 mg (18%). ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 18H), 1.84 (bs, 8H), 2.69 (bs, 8H), 3.16 (bs, 4H), 3.37-3.69 (m, 40H), 4.38 (s, 4H), 6.42-6.65 (m, 8H), 6.74 (bs, 2H), 6.93 (d, ^3J = 7.8 Hz, 4H), 7.04 (t, ^3J = 7.5 Hz, 2H), two NH protons were not assigned; ^{13}C NMR ($CDCl_3$): δ 27.4 (2C), 28.3 (6C), 29.1 (2C), 41.8 (2C), 46.7 (4C, $\Delta\nu_{1/2}$ = 80 Hz), 47.6 (2C), 54.0 (6C, $\Delta\nu_{1/2}$ = 120 Hz), 60.4 (2C, $\Delta\nu_{1/2}$ = 100 Hz), 68.7-70.6 (m, 12C), 79.1 (2C), 111.4 (2C, $\Delta\nu_{1/2}$ = 30 Hz), 127.8 (4C), 114.1 (2C), 117.7 (2C), 127.6 (4C), 128.9 (2C), 148.7 (4C, $\Delta\nu_{1/2}$ = 60 Hz), 155.9 (2C), four quaternary carbon atoms were not assigned; HRMS (MALDI-TOF) *m/z* calcd for $C_{66}H_{101}N_8O_{10}$ $[M+H]^+$ 1165.7641, found 1165.7693.

ACKNOWLEDGEMENTS

This work was carried out in the frame of the International Associated French–Russian Laboratory of Macrocycle Systems and Related Materials (LAMREM) of RAS and CNRS, the work was financially supported by the RFBR grant N 13-03-90453, CNRS, and the Russian Academy of Sciences program "Elaboration of the methods for the synthesis of chemical compounds and construction of new materials. CheMatech Co is acknowledged for a generous supply of cyclen and cyclam.

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