Palladium-Catalyzed Amination in the Synthesis of Polyazamacrocycles Containing a 1,3-Disubstituted Benzene Moiety

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Abstract: The synthesis of a new family of polyaza- and polyoxa-polyazamacrocycles by a simple and efficient one-pot palladium-catalyzed diamination of 1,3-dibromobenzene is described. The dependence of the nature of the starting polyamines on the yield of the products is demonstrated. The synthesis of N^{α},N^{ω}-bis(3-bromophenyl)-substituted polyamines is elaborated to obtain intermediates for the synthesis of polyazamacrocycles consisting of two polyamine and two benzene fragments (cyclodimers). The formation of tri- and tetraarylated polyamines is studied and regularities of the process are established. The synthesis of 1,3-bis(polyamino)-substituted benzenes is also described.

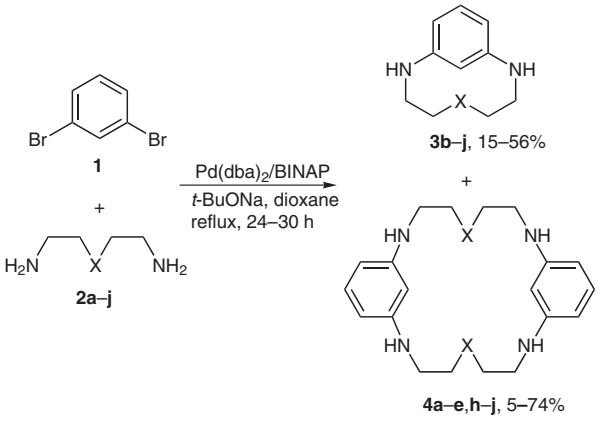
Key words: amines, aminations, haloarenes, homogenous catalysis, macrocycles

Polyazamacrocycles (or azacrown ethers) attract a keen and constant interest of researchers due to their unique ability of selective complexation with various metals, organic and inorganic anions, and some polar compounds. During the last decades hundreds of such compounds, which contain nitrogen, oxygen, and sulfur atoms, have been synthesized.[1] The main problem in these syntheses is the use of laborious multistep methods which result in rather low yields of the target products.[2–5] Many polyazamacrocycles can serve as molecular sensors due to their photochemical or redox properties; they contain aromatic moieties which can be present as substituents at nitrogen atoms or can be incorporated in the cycle. In the majority of cases, aromatic groups are separated from the nitrogen atom by at least one methylene or methine group.[6–11] According to literature data, a better response to the complexation is achieved when the nitrogen atom is directly linked to an aromatic substituent, but such compounds are still rare.[12–14]

Recently, using the method of palladium-catalyzed amination of haloarenes proposed by Buchwald and Hartwig,[15] we have elaborated an efficient approach to the synthesis of polyazamacrocycles using palladium-catalyzed diamination of dihaloarenes with linear polyamines. Thus, macrocycles containing 1,8- and 1,5-disubstituted anthracene and anthraquinone,[16] 2,6- and 3,5-disubstituted pyridine,[17–20] and 1,2-disubstituted benzene[21] have been synthesized. As only one example of a tetraazamacrocycle based on 1,3-diaminated benzene is as yet known,[21] we focused on the synthesis of macrocycles starting from 1,3-dibromobenzene. It was thought interesting to develop the synthesis of such macrocycles with different polyamine chains and also to synthesize compounds containing two polyamine and two benzene moieties, thus increasing both the cavity of the macrocycle and the number of donor nitrogen and oxygen atoms. We have chosen the $Pd(dba)_2$/BINAP catalytic system for our synthesis due to its versatility and convenience.[22]

The reactions between equimolar amounts of 1,3-dibromobenzene (**1**) and a polyamine **2a–j** were conducted in the presence of the $Pd(dba)_2$/BINAP catalytic system (4–8/4.5–9 mol%), in boiling 1,4-dioxane (concn = 0.02 M), using sodium *tert*-butoxide as base (Scheme 1). The reactions ran to completion in 24–30 hours, and the composition of the reaction mixtures was monitored using ^1H and ^{13}C NMR spectroscopy. The compounds were isolated using column chromatography on silica gel. The data concerning yields and reaction conditions are given in Table 1; byproducts formed in these reactions are indicated in Figure 1.

The yield of target macrocycles **3** was found to be strongly dependent on the nature of the starting polyamines **2**. Triamine **2a** did not provide the corresponding cycle **3a**, not



2a: X = NH; **2b**: X = CH_2NHCH_2; **2c**: X = $NH(CH_2)_2NH$;
2d: X = $NH(CH_2)_3NH$; **2e**: X = $CH_2NH(CH_2)_2NHCH_2$;
2f: X = $CH_2NH(CH_2)_3NHCH_2$; **2g**: X = $NH(CH_2)_2NH(CH_2)_2NH$;
2h: X = $O(CH_2)_2O$; **2i**: X = $CH_2O(CH_2)_4OCH_2$;
2j: X = $CH_2O(CH_2)_2O(CH_2)_2OCH_2$

Scheme 1 Synthesis of macrocycles **3b–j**

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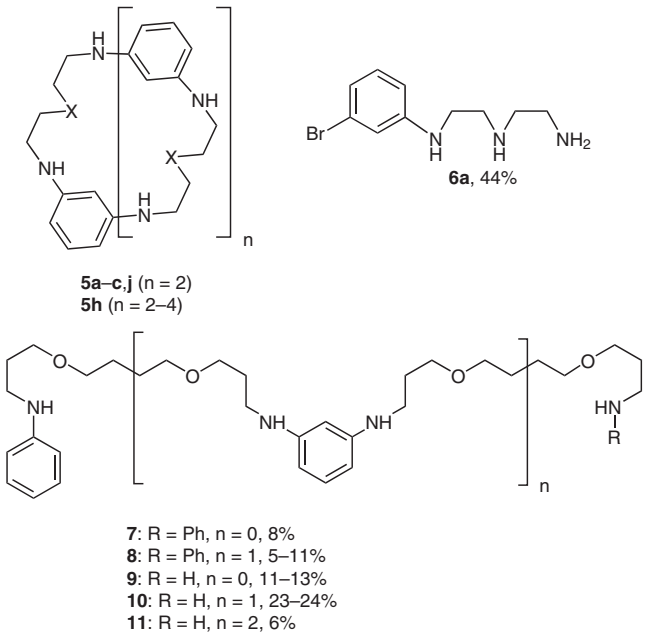


Figure 1 Byproducts in the synthesis of macrocycles **3**

Table 1 Synthesis of Macrocycles **3b–j**

Entry	Amine	$Pd(dba)_2$/BINAP (mol%/mol%)	Yield (%) of **3a–j**	Yield (%) of other products
1	**2a**	4/4.5	**3a**, 0	**6a**, 44
2	**2a**	8/9	**3a**, 0	**4a** + **5a** (n = 2), 74
3	**2b**	4/4.5	**3b**, 0	**4b**, 56
4	**2b**	8/9	**3b**, 15	**4b**, 60
5	**2c**	8/9	**3c**, 39	**4c**, 14
6	**2d**	4/4.5	**3d**, 31	**4d**, 26
7	**2d**	8/9		
8	**2e**	4/4.5	**3e**, 29	**4e**, 36
9	**2f**	4/4.5	**3f**, 56	
10	**2g**	8/9	**3g**, 33	
11	**2h**	4/4.5	**3h**, 27	**4h**, 28
12	**2i**	4/4.5	**3i**, 19	**4i**, 8; **8**, 14; **9**, 11; **10**, 23
13	**2i**	8/9	**3i**, 26	**4i**, 5; **7**, 8; **8**, 3; **9**, 13; **10**, 24; **11**, 6
14	**2j**	4/4.5	**3j**, 26	**4j**, 23

even in trace amounts, giving either linear derivative **6a** or cyclic dimer **4a** (Table 1, entries 1 and 2), whereas triamine **2b** with a longer chain afforded target **3b** in low yield (entry 4). Probably macrocycle **3a** does not form due to an unfavorable conformation of the triamine chain in this compound. Tetraamines **2c–f**, as well as pentaamine **2g**, gave the desired macrocycles in moderate to good yield (entries 5–10).

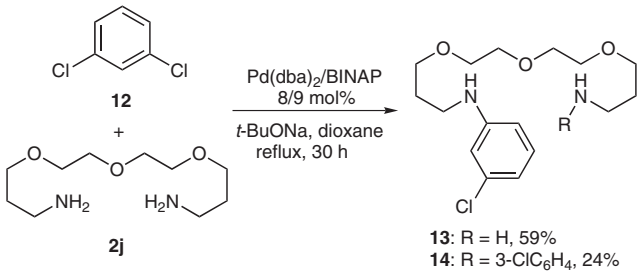
The formation of the macrocycles **3h–j** in the reactions with oxadiamines proceeded successfully though yields were somewhat lower (Table 1, entries 11–14). The main byproducts in most cases were cyclodimers **4** which consist of two benzene and two polyamine moieties; in the case of triamines **2a**,**b**, dimers **4a,b** were the main products of the reaction (entries 2–4). In some cases cyclotrimers **5a–c**,**h**,**j** (n = 2) and even cyclooligomers with higher masses (**5h**; n = 3, 4) were also detected in the MALDI–TOF spectra as admixtures to the corresponding cyclodimers, but they could not be separated chromatographically. Moreover, their NMR spectra are almost the same as those of cyclodimers **4**, and thus they cannot be distinguished spectroscopically. The use of 4 mol% of the catalyst was quite sufficient in many cases: in the reaction with tetraamine **2d**, NMR investigations demonstrated that there was no difference in the reaction mixture compositions when either 4 mol% or 8 mol% of the catalyst was used. However, in the case of triamines **2a**,**b**, the increase in the catalyst loading favored amination (entries 2 and 4).

The reaction of dioxadiamine **2i** with 1,3-dibromobenzene (**1**) gave a number of noncyclic byproducts **7–11** (entries 12 and 13); the corresponding byproducts were not registered in the reactions with other polyamines. These compounds resulted from reduction of the bromine atom, and no linear byproducts with a remaining bromine atom, such as **6a**, were isolated. An increase in the catalyst loading from 4 mol% to 8 mol% provided a better yield of the target macrocycle **3i**, as well as of other products of benzene diamination (**10**,**11**).

^{1}H NMR spectra of the macrocycles **3** are characterized by a strong dependence of the chemical shift of the 2-H atom

in the benzene ring on the macrocycle ring size. In the compounds with smaller cycles the signal of this hydrogen atom is shifted relatively downfield ($\delta_{2\text{-H}}$ 7.31 in **3b** and 6.96 in **3h**), while an increase in the cycle size leads to a substantial upfield shift ($\delta_{2\text{-H}}$ 6.48 in **3c**, 6.30 in **3d**, and 6.09 in **3f**). It means that this hydrogen atom is sensitive to the close proximity of the nitrogen or oxygen atoms of the aliphatic part of the molecule in smaller cycles. In cyclodimers **4** where these nitrogen atoms are most distant from the 2-H atom, the chemical shift $\delta_{2\text{-H}}$ lies between 5.8 and 5.9 ppm.

Previously, we have synthesized two series of polyazamacrocycles based on 2,6- and 3,5-disubstituted pyridines.[17,19,20] The yields of the present macrocycles derived from 1,3-dibromobenzene were found to be notably higher than the yields of pyridine-based macrocycles. The latter were formed in lower yields in the reaction mixtures, and the losses during column chromatography were also greater. While the reaction of 1,3-dibromobenzene (**1**) with triethylenetetraamine (**2c**) and tetraethylenepentaamine (**2g**) led to a 33–39% yield of the corresponding macrocycles (Table 1, entries 5 and 10), polyamines of such type provided very humble yields (3–5%) of macrocycles with dibromopyridines. Also, the formation of cyclic oligomers like **4** was not observed in almost all reactions of dihalopyridines with polyamines. These facts mean that the reactions of 1,3-dibromobenzene (**1**) with polyamines are more selective than similar reactions of dibromopyridines.

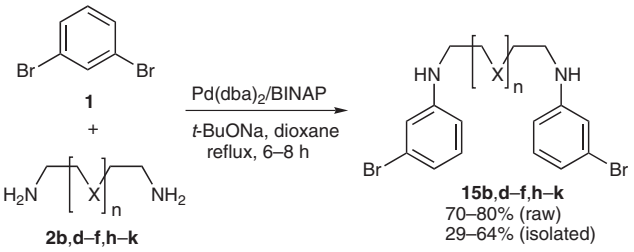


Scheme 2 Arylation of trioxadiamine **2j** with 1,3-dichlorobenzene (**12**)

We also used 1,3-dichlorobenzene (**12**) in the reaction with trioxadiamine **2j** using 8 mol% of the catalyst, but in this case the corresponding macrocycle **3j** was only registered in trace amounts according to the ^{1}H NMR spectrum of the reaction mixture. Instead of **3j**, the mono- and diaryl derivatives **13** and **14** were isolated in 59% and 24% yield, respectively (Scheme 2).

In contrast to 1,3-dichlorobenzene (**12**), 1-bromo-2,6-dichlorobenzene has been shown to provide macrocycles containing the 1,2-disubstituted benzene moiety in sufficient yields.[21]

While macrocycles **3** were isolated in pure state using column chromatography, cyclodimers **4** contained admixtures which could not be sufficiently separated by chromatography, and the purity of **4** generally did not exceed 90%. To synthesize these interesting macrocycles with larger cavities in a pure state, in the first stage we obtained N^{α},N^{ω}-bis(3-bromophenyl)-substituted polyamines **15b**,**d**–**f**,**h**–**k** starting from 1,3-dibromobenzene (**1**) and linear polyamines **2** taken in ca. 2:1 ratio. The reactions were conducted in the presence of the Pd(dba)$_2$/BINAP catalytic system, in boiling 1,4-dioxane, using sodium *tert*-butoxide as base (Scheme 3). The reactions ran to completion in 6–8 hours and the composition was monitored using ^{1}H and ^{13}C NMR spectroscopy. In all cases the yield of the target product **15** was found to be no less than 70–80% in the reaction mixture. The compounds were isolated using column chromatography on silica gel; the data concerning yields and reaction conditions are given in Table 2.



2b: n = 1, X = CH_2NHCH_2; **2d**: n = 1, X = $NH(CH_2)_3NH$;
2e: n = 1, X = $CH_2NH(CH_2)_2NHCH_2$; **2f**: n = 1, X = $CH_2NH(CH_2)_3NHCH_2$;
2h: n = 1, X = $O(CH_2)_2O$; **2i**: n = 1, X = $CH_2O(CH_2)_4OCH_2$;
2j: n = 1, X = $CH_2O(CH_2)_2O(CH_2)_2OCH_2$; **2k**: n = 0

Scheme 3 Synthesis of N^{α},N^{ω}-bis(3-bromophenyl)-substituted polyamines **15b**,**d**–**f**,**h**–**k**

In the majority of cases the diarylated polyamines **15** were isolated in yields from moderate to good (29–64%), but in all reactions the formation of byproducts was noted (Figure 2). Yields of compounds **15** and that of byproducts were shown to be strongly dependent on the reaction conditions and on the nature of the starting polyamines **2**. Application of 2–4 mol% of the catalyst, 2.2 equivalents of 1,3-dibromobenzene (**1**), and a polyamine concentration of 0.1 M provided the highest yields of desired products **15**; these conditions can be proposed as optimal, though in all cases the formation of linear byproducts **16** was observed. They were formed due to partial diamination of the benzene fragment. In some cases moderate yields of the target compounds after chromatography were due to very close R_f values of compounds **15** and **16**.

In several cases the products of N,N-diarylation **17** were formed in small amounts (Table 2, entries 2 and 6–9); application of a greater excess of 1,3-dibromobenzene (**1**) led to an increase in the formation of **17** and a diminished yield of the target product (entry 2). Increasing the concentration of the polyamine **2** up to 0.2 M led to a substantial decrease in the yield of **15** caused by the formation of oligomers such as **18** (entries 6 and 12). Application of a greater amount of the catalyst (entry 10) did not improve the yield of the target product, but caused the formation of oligomeric products of homocoupling, according to the

Table 2 Synthesis of N^{α},N^{ω}-Bis(3-bromophenyl)-Substituted Polyamines **15b**,**d**–**f**,**h**–**k**

Entry	Amine	$Pd(dba)_2$/BINAP (mol%/mol%)	Ratio **1**:**2**	Concn (M) of **2**	Isolated yield (%)
1	**2b**	4/4.5	2.2:1	0.1	**15b**, 46 **16b**, 13
2	**2b**	12/13.5	3:1	0.1	**15b**, 38 **17b**, 3
3	**2d**	2/2.5	2.2:1	0.1	**15d**, 64 **16d**, 21
4	**2e**	2/2.5	2.2:1	0.1	**15e**, 52 **16e**, 10 **6e**, 7
5	**2f**	4/4.5	2.2:1	0.1	**15f**, 39 **16f**, 12
6	**2h**	4/4.5	2.5:1	0.2	**15h**, 11[a] **16h**, 14 **17h**, 4
7	**2h**	4/4.5	2.2:1	0.1	**15h**, 42 **16h**, 14 **17h**, 12
8	**2h**	2/2.5	2.2:1	0.1	**15h**, 46 **16h**, 16
9	**2h**	8/9	2.2:1	0.1	**17h**, 8
10	**2h**	4/4.5	1:1	0.1	**15h**, 0[b] **4h**, 7
11	**2i**	4/4.5	2.2:1	0.1	**15i**, 59[c] **16i**, 11
12	**2i**	4/4.5	2.2:1	0.2	**15i**, 38[d] **19i**, 9
13	**2j**	4/4.5	2.5:1	0.1	**15j**, 29 **16j**, 10 **19j**, 5
14	**2k**	4/4.5	2.2:1	0.1	**15k**, 32 **16k**, 14

[a] **18h** (2%) was also isolated in a mixture with higher linear oligomers.
[b] A complex mixture of linear oligomers was isolated (53%).
[c] **17i** and **19i** were isolated as admixtures to **15i**.
[d] **18i** (2%) was also isolated in a mixture with higher linear oligomers.

NMR spectroscopic data of the reaction mixture. Amounts of the catalyst lower than 2 mol% were not tested as monoarylated products such as **6e** may be obtained (entry 4). The formation of small amounts of the products **19** of partial reduction of the bromine atom was observed in only two cases (entries 12 and 13), which is in good accordance with the fact that primary amines normally do not cause the reduction of haloarenes provided BINAP is used. A change in the reagent ratio of **1**:**2** from 2.2:1 to 1:1 dramatically decreased the yield of **15** giving rise to oligomers of complex composition (entry 10).

Starting from diarylated polyamines **15b**,**d**–**f**,**h**–**j** we attempted the synthesis of the cyclodimers **4b**,**d**–**f**,**h**–**j** containing two benzene and two polyamine fragments (Scheme 4). Enough diluted solutions of equimolar amounts of the reagents were used to suppress the formation of linear byproducts. The amount of catalyst was increased to 8 mol%, and the reactions ran to completion in 24–30 hours. In all cases (except the reaction between **2d** and **15d**) formation of the desired macrocycles was observed and, after chromatography on silica gel, they were isolated in 16–44% yield (Table 3). In the reaction with polyamine **2d**, standard conditions led to a low 6% yield of the corresponding cyclodimer **4d**, while the formation of a linear derivative **20** was observed (entry 2). Application of the donor phosphane 2-dicyclohexylphosphano-2′-(dimethylamino)biphenyl, which was shown by Buchwald to be more efficient than BINAP,[23] did not improve

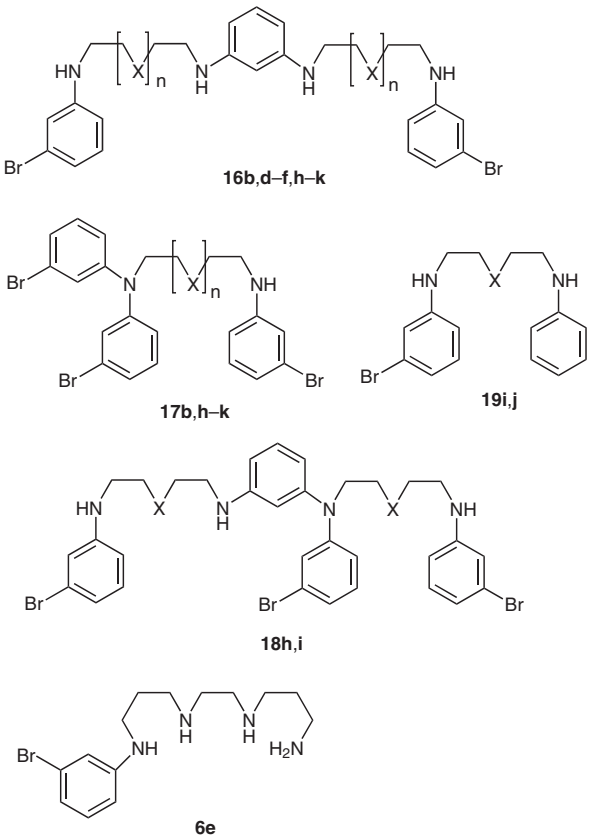
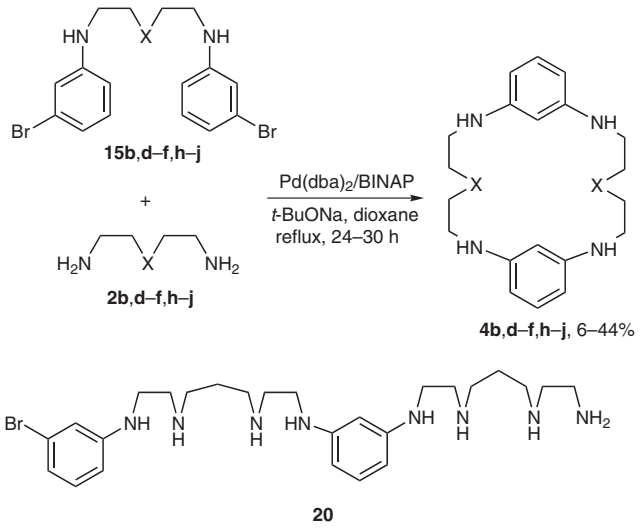


Figure 2 Isolated byproducts in the synthesis of N^{α},N^{ω}-bis(3-bromophenyl)-substituted polyamines **15**



Scheme 4 Synthesis of cyclodimers **4**

the result and the desired product was not isolated at all in this case (entry 3).

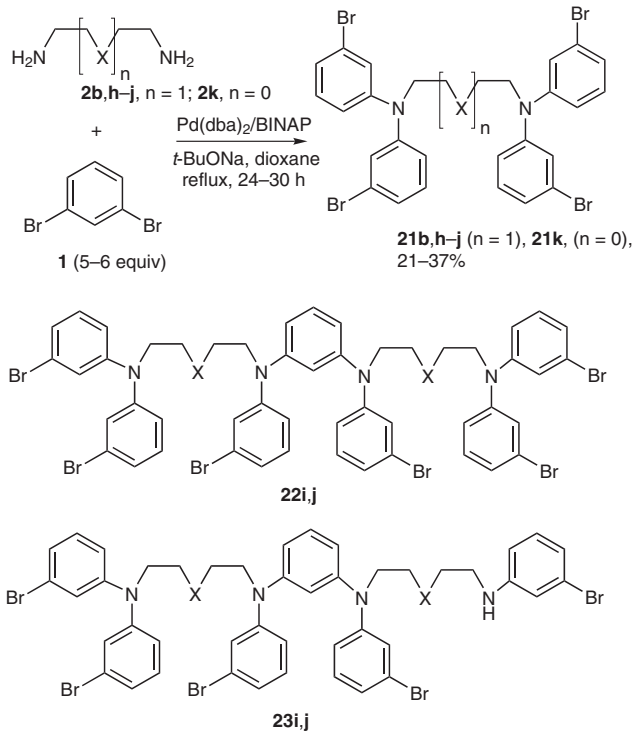
This reluctance of tetraamine **2d** to form a cyclodimer in the reaction with **15d** might be explained by the fact that it contains two ethylenediamine fragments which can form stable five-membered chelate complexes with palladium, which is thus eliminated from the catalytic cycle. In the case of triamine **2b** or tetraamine **2f**, only less stable six-membered chelates can be formed. It was also shown that lower catalyst loadings may be used for the synthesis of cyclodimers with normal yields (Table 3, entry 5).

Table 3 Synthesis of Cyclodimers **4b**,**d–f**,**h–j**

Entry	Reagents	$Pd(dba)_2$/BINAP (mol%/mol%)	Isolated yield (%)
1	**2b** + **15b**	8/9	**4b**, 44
2	**2d** + **15d**	8/9	**4d**, 6; **20**, 30
3	**2d** + **15d**	4/4.5[a]	**4d**, 0; **20**, 10
4	**2e** + **15e**	8/9	**4e**, 36[b]
5	**2e** + **15e**	4/4.5	
6	**2f** + **15f**	8/9	**4f**, 30
7	**2h** + **15h**	8/9	**4h**, 16
8	**2i** + **15i**	8/9	**4i**, 38
9	**2j** + **15j**	8/9	**4j**, 21

[a] 2-Dicyclohexylphosphano-2′-(dimethylamino)biphenyl was used instead of BINAP.
[b] Result of combined chromatography; composition of both reaction mixtures was identical.

All cyclodimers **4** were characterized by ^{1}H NMR, ^{13}C NMR, and MALDI–TOF spectroscopy. It is worth noting that the 1,3-diaminobenzene fragments possess hydrogen and carbon atoms with signals shifted strongly upfield (δ_H 5.8–6.0 and δ_C 96–102, respectively), which is useful for the identification of these compounds in the reaction mixtures. Signals for aliphatic hydrogen atoms are often broad, and singlets are sometimes observed instead of multiplets. In the NMR spectra of cyclodimers **4b**,**d–f** in $CDCl_3$ we observed the duplication of some or even all signals of the compounds; the chemical shifts of doubled signals are close, but they may differ in intensity and width. Sometimes duplication of the signals can also be noted in the reaction mixtures. The following is proposed as a possible explanation for these facts: four nitrogen atoms linked to benzene rings are formally chiral and, provided the inversion at these atoms is slow in $CDCl_3$, the cyclodimers can be viewed as *dl*- and *meso*-diastereomers which would possess different chemical shifts in their NMR spectra. This effect was not observed in the case of cyclodimers **4h–j** because, unlike compounds 4**b**,**d–f**, they do not possess secondary aliphatic amino groups which can form intramolecular hydrogen bonds, thus hindering the inversion at the nitrogen atoms. The dependence of the mentioned effect on the concentration of the macrocycle in the NMR sample, and on the solvent used, supports this suggestion.



Scheme 5 Synthesis of polyarylated polyamines **21b**,**h–k**

In the course of the synthesis of diarylated polyamines **15**, we observed the formation of triaryl derivatives **17** as byproducts in some cases. It was decided to specially investigate the exhaustive polyarylation of polyamines with 1,3-dibromobenzene as it may lead to the formation of valuable intermediates for the synthesis of polyamine-containing dendrimers. Previously we studied the palladium-mediated tetraarylation of ethane-1,2-diamine and propane-1,3-diamine and established that BINAP was suitable for this purpose.[24] Diamines **2h–k** and triamine **2b** were reacted with 5–6 equivalents of 1,3-dibromobenzene (**1**) in the presence of 16 mol% of the $Pd(dba)_2$/BINAP catalytic system (Scheme 5). Studies of the reaction mixture revealed that the target products of tetraarylation **21b**,**h–k** were formed in all cases in yields no less than 50%. They were isolated using column chromatography in 21–37% yield (Table 4). In the case of **21i**,**j**, byproducts of an oligomeric nature, **22i**,**j** and **23i**,**j**, were also obtained (entries 3–5). These compounds were probably formed via further amination of the tetraarylated compounds **21i**,**j**, like compounds **16** which were obtained by substitution of the remaining bromine atom in **15**.

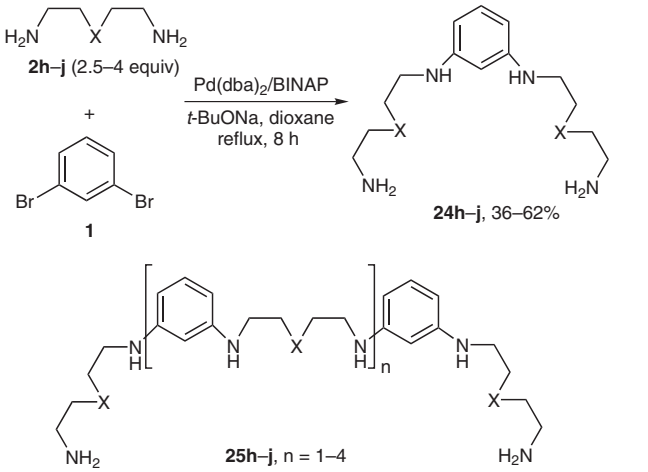
A decrease in the catalyst loading (Table 4, entry 3) did not lead to a lower yield of the product; also, the use of a greater excess of **1** does not result in a higher yield (entry 5). It is important to note that the reaction of triamine **2b** with six equivalents of **1** did not lead to the arylation of the central nitrogen atom due to very low reactivity of the secondary amino group in linear amines. Alkylarylamines proved to be more reactive possibly due to their lower basicity.[24] As in the synthesis of diarylated derivatives **15**, we did not observe the reduction of the bromine atom even though generous catalyst loadings were applied.

Table 4 Synthesis of Polyarylated Polyamines **21b**,**h–k**

Entry	Amine	Equiv of **1**	$Pd(dba)_2$/BINAP (mol%/mol%)	Isolated yield (%)
1	**2b**	6	16/18	**21b**, 37
2	**2h**	6	16/18	**21h**, 31
3	**2i**	5	8/9	**21i**, 33; **17i**, 11; **22i**, 9; **23i**, 5
4	**2j**	5	16/18	**21j**, 29; **17j**, 5; **22j**, 9
5	**2j**	6	16/18	**21j**, 21; **17j**, 25; **22j**, 5; **23j**, 5
6	**2k**	5	16/18	**21k**, 25

An alternative method for the synthesis of cyclodimers **4** could include the formation of 1,3-bis(polyamino)-substituted benzenes, followed by their reaction with a second molecule of 1,3-dibromobenzene. Therefore, we elaborated the synthesis of some 1,3-bis(polyamino)-substituted derivatives **24h–j** (Scheme 6). The reactions were conducted using 2.5–4 equivalents of polyamines **2h–j** in the presence of 8/9 mol% of the $Pd(dba)_2$/BINAP catalytic system. Only oxadiamines were chosen for this process because of the difficulties of separating bis(polyamino)-substituted arene derivatives from the starting polyamines when tetraamines are used. Experimental data are collected in Table 5.

In some cases an increase in the diamine/1,3-dibromobenzene ratio and the use of less concentrated solutions can lead to higher yields of the target product (Table 5, entries 1 and 2). In all cases the formation of oligomeric byproducts **25h–j** was observed; they were isolated as mixtures and their masses were established by MALDI–TOF spectroscopy. The NMR spectra of compounds **24h–j** show



Scheme 6 Synthesis of 1,3-bis(polyamino)-substituted benzenes **24h–j**

Table 5 Synthesis of 1,3-Bis(polyamino)-Substituted Benzenes **24h–j**

Entry	Amine	Equiv of **2**	$Pd(dba)_2$/BINAP (mol%/mol%)	Concn (M) of **1**	Isolated yield (%)
1	**2h**	3	8/9	0.2	**24h**, 36[a]
2	**2h**	4	8/9	0.1	**24h**, 59
3	**2i**	3	8/9	0.1	**24i**, 62[b]
4	**2i**	4	8/9	0.2	**24i**, 37
5	**2j**	2.5	8/9	0.2	**24j**, 56[c]

[a] Contains an admixture of **25h** (n = 1).
[b] Contains an admixture of **25i** (n = 1).
[c] A mixture of oligomers **25j** (n = 1–4) was isolated in 28% yield.

the similar peculiarities as those described for cyclodimers **4**: in $CDCl_3$ the signals of the hydrogen and carbon atoms are often doubled, and after a change of the solvent to DMSO or after simple addition of an excess of free oxadiamine this effect fully disappears. Despite reasonable yields of **24** they were not used in the synthesis of cyclodimers as they turned out to be inconvenient to handle, being very viscous oils, insufficiently soluble in 1,4-dioxane, and unstable upon storage. Also, their isolation by column chromatography is much more laborious than that of diarylated derivatives **15**.

To sum up, we have elaborated a convenient one-step method for the synthesis of polyazamacrocycles containing a 1,3-disubstituted benzene moiety and an easy procedure for obtaining cyclodimers consisting of two benzene and two polyamine moieties via intermediate formation of diarylated polyamines, and we have synthesized a number of such compounds with different numbers of nitrogen and oxygen atoms and different cavity sizes. We have found that the regularities of these processes and the product yields, as well as the formation of byproducts, depend on the nature of the starting polyamines and on the reaction conditions. Investigation of the complexing properties of the new macrocycles is underway. We have also studied the possibilities of polyarylation of the polyamines with 1,3-dibromobenzene and the synthesis of 1,3-bis(polyamino)-substituted benzenes. As these compounds possess several reaction centers, they may well find further applications in organic synthesis.

NMR spectra were recorded on a Bruker Avance-400 spectrometer at room temperature; the chemical shifts (δ) were measured in ppm with respect to TMS. MALDI–TOF mass spectra were registered using a Bruker Daltonics Ultraflex spectrometer with dithranol (1,8,9-anthracenetriol) as matrix. Column chromatography was performed on silica gel (40–60 mesh) purchased from Fluka. 1,3-Dibromobenzene, 1,3-dichlorobenzene, amines, and phosphane ligands were purchased from Acros and Aldrich and used without special purification, except for pentaamine **2g**, whose adduct with water was recrystallized several times from toluene to increase its purity from ca. 60 to 90%. 1,4-Dioxane was distilled successively over NaOH and Na; CH_2Cl_2, MeOH, and petroleum ether were used freshly distilled. $Pd(dba)_2$ was obtained by a described method.[25]

Macrocycles 3b–j; General Procedure

A flask flushed with dry argon and equipped with a magnetic stirrer and condenser was charged with 1,3-dibromobenzene (**1**) (0.5 mmol), $Pd(dba)_2$ (4–8 mol%), BINAP (4.5–9 mol%), the appropriate amine **2b–j** (0.5 mmol), and abs 1,4-dioxane (25 mL). *t*-BuONa (1.5 mmol) was added and the mixture was stirred under reflux for 24–30 h; then, the mixture was cooled to r.t., the 1,4-dioxane was evaporated under reduced pressure, and the residue was chromatographed on silica gel using various eluents: CH_2Cl_2–MeOH, 200:1–3:1; CH_2Cl_2–MeOH–aq NH_3, 100:20:1–10:4:1.

2,6,10-Triazabicyclo[9.3.1]pentadeca-1(15),11,13-triene (3b)

Obtained from **1** (118 mg, 0.5 mmol) and triamine **2b** (66 mg, 0.5 mmol), in the presence of $Pd(dba)_2$ (24 mg, 8 mol%), BINAP (28 mg, 9 mol%), and *t*-BuONa (144 mg, 1.5 mmol), in abs 1,4-dioxane (25 mL).

Yield: 15 mg (15%); pale-yellow oil; eluent: CH_2Cl_2–MeOH, 100:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.60 (br s, 4 H), 2.65 (t, *J* = 5.6 Hz, 4 H), 3.38 (br s, 4 H), 5.91 (dd, *J* = 7.9, 2.2 Hz, 2 H), 6.84 (t, *J* = 7.9 Hz, 1 H), 7.31 (br s, 1 H) (the signals of the three NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 30.46 (2 C), 39.83 (2 C), 45.88 (2 C), 96.19 (1 C), 102.45 (2 C), 129.04 (1 C), 149.72 (2 C).

MALDI–TOF: *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{19}N_3$: 206.17; found: 206.29.

Cyclodimer **4b** (*vide infra*) was obtained as a second product in this reaction.

Yield: 62 mg (60%); yellow oil; eluent: CH_2Cl_2–MeOH–aq NH_3, 100:20:3, 10:4:1.

Contains an admixture of cyclotrimer **5b** (n = 2): MALDI–TOF: *m*/*z* $[M + H]^+$ calcd for $C_{36}H_{57}N_9$: 616.48; found: 616.49.

The use of $Pd(dba)_2$ (12 mg, 4 mol%) and BINAP (14 mg, 4.5 mol%) in this reaction gave no macrocycle **3b** and led only to the formation of cyclodimer **4b**.

Yield: 57 mg (56%); eluent: CH_2Cl_2–MeOH–aq NH_3, 100:20:3, 10:4:1.

2,5,8,11-Tetraazabicyclo[10.3.1]hexadeca-1(16),12,14-triene (3c)

Obtained from **1** (118 mg, 0.5 mmol) and tetraamine **2c** (72 mg, 0.5 mmol), in the presence of $Pd(dba)_2$ (24 mg, 8 mol%), BINAP (28 mg, 9 mol%), and *t*-BuONa (144 mg, 1.5 mmol), in abs 1,4-dioxane (25 mL).

Yield: 43 mg (39%); pale-yellow oil; eluent: CH_2Cl_2–MeOH–aq NH_3, 100:20:2, 100:20:3.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.77 (s, 4 H), 2.80 (t, *J* = 5.7 Hz, 4 H), 3.32 (t, *J* = 5.7 Hz, 4 H), 5.99 (dd, *J* = 7.9, 2.1 Hz, 2 H), 6.48 (s, 1 H), 6.88 (t, *J* = 7.9 Hz, 1 H) (the signals of the four NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 44.96 (2 C), 48.06 (2 C), 49.86 (2 C), 97.76 (1 C), 104.89 (2 C), 129.63 (1 C), 149.24 (2 C).

MALDI–TOF: *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{20}N_4$: 221.18; found: 221.18.

2,5,8,11,17,20,23,26-Octaazatricyclo[25.3.1.1^{12,16}]dotriaconta-1(31),12,14,16(32),27,29-hexaene (4c)

Obtained as a byproduct in the synthesis of **3c**.

Yield: 15 mg (14%); yellow oil; eluent: CH_2Cl_2–MeOH–aq NH_3, 10:4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.70 (br s, 8 H), 2.80 (br s, 8 H), 3.15 (br s, 8 H), 5.89 (s, 2 H), 6.00 (d, *J* = 7.1 Hz, 4 H), 6.94 (t,

J = 8.0 Hz, 2 H) (the signals of the eight NH protons were not unambiguously assigned).

MALDI–TOF: m/z [M + H]$^+$ calcd for $C_{24}H_{40}N_8$: 441.35; found: 441.33.

Contains an admixture of cyclotrimer **5c** (n = 2): MALDI–TOF: m/z [M + H]$^+$ calcd for $C_{36}H_{60}N_{12}$: 661.51; found: 661.48.

2,5,9,12-Tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (3d)

Obtained from **1** (118 mg, 0.5 mmol) and tetraamine **2d** (80 mg, 0.5 mmol), in the presence of $Pd(dba)_2$ (24 mg, 8 mol%), BINAP (28 mg, 9 mol%), and *t*-BuONa (144 mg, 1.5 mmol), in abs 1,4-dioxane (25 mL). Combined with the portion obtained from the same amounts of starting compounds in the presence of $Pd(dba)_2$ (12 mg, 4 mol%) and BINAP (14 mg, 4.5 mol%).

Yield: 72 mg (31%); pale-yellow oil; eluent: CH_2Cl_2–MeOH–aq NH_3, 100:20:3.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.54 (quin, J = 5.6 Hz, 2 H), 2.69 (t, J = 6.0 Hz, 4 H), 2.74 (t, J = 5.6 Hz, 4 H), 3.33 (t, J = 6.0 Hz, 4 H), 5.93 (dd, J = 8.0, 2.1 Hz, 2 H), 6.30 (s, 1 H), 6.85 (t, J = 8.0 Hz, 1 H) (the signals of the four NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.36 (1 C), 43.50 (2 C), 49.00 (2 C), 49.30 (2 C), 95.64 (1 C), 104.06 (2 C), 129.58 (1 C), 149.09 (2 C).

MALDI–TOF: m/z [M + H]$^+$ calcd for $C_{13}H_{22}N_4$: 235.19; found: 235.26.

Cyclodimer **4d** (*vide infra*) was obtained as a byproduct in this reaction.

Yield: 60 mg (26%); yellow oil; eluent: CH_2Cl_2–MeOH–aq NH_3, 10:4:1.

2,6,9,13-Tetraazabicyclo[12.3.1]octadeca-1(18),14,16-triene (3e)

Obtained from **1** (944 mg, 4 mmol) and tetraamine **2e** (696 mg, 4 mmol), in the presence of $Pd(dba)_2$ (92 mg, 4 mol%), BINAP (110 mg, 4.5 mol%), and *t*-BuONa (1152 mg, 12 mmol), in abs 1,4-dioxane (150 mL).

Yield: 288 mg (29%); pale-yellow oil; eluent: CH_2Cl_2–MeOH–aq NH_3, 100:20:2.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66 (quin, J = 5.8 Hz, 4 H), 2.65 (t, J = 5.4 Hz, 4 H), 2.66 (s, 4 H), 2.94 (br s, 2 H), 3.31 (t, J = 6.3 Hz, 4 H), 5.88 (dd, J = 7.9, 2.1 Hz, 2 H), 6.26 (s, 1 H), 6.83 (t, J = 7.9 Hz, 1 H) (the signals of two of the NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 31.35 (2 C), 41.34 (2 C), 46.01 (2 C), 49.21 (2 C), 94.34 (1 C), 103.63 (2 C), 129.62 (1 C), 150.32 (2 C).

Cyclodimer **4e** (*vide infra*) was obtained as a byproduct in this reaction.

Yield: 358 mg (36%); yellow oil; eluent: CH_2Cl_2–MeOH–aq NH_3, 100:20:3, 10:4:1.

2,6,10,14-Tetraazabicyclo[13.3.1]nonadeca-1(19),15,17-triene (3f)

Obtained from **1** (118 mg, 0.5 mmol) and tetraamine **2f** (94 mg, 0.5 mmol), in the presence of $Pd(dba)_2$ (12 mg, 4 mol%), BINAP (14 mg, 4.5 mol%), and *t*-BuONa (144 mg, 1.5 mmol), in abs 1,4-dioxane (25 mL).

Yield: 73 mg (56%); pale-yellow oil; eluent: CH_2Cl_2–MeOH–aq NH_3, 100:20:3, 10:4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.73 (quin, J = 6.0 Hz, 2 H), 1.75 (quin, J = 6.4 Hz, 4 H), 2.71 (t, J = 5.6 Hz, 4 H), 2.76 (t, J = 5.9 Hz, 4 H), 3.29 (t, J = 7.3 Hz, 4 H), 3.81 (br s, 2 H), 5.91 (dd, J = 7.8, 1.6 Hz, 2 H), 6.09 (s, 1 H), 6.89 (t, J = 7.8 Hz, 1 H) (the signals of two of the NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.65 (1 C), 29.16 (2 C), 42.29 (2 C), 47.50 (2 C), 49.32 (2 C), 95.43 (1 C), 103.28 (2 C), 129.82 (1 C), 149.51 (2 C).

MALDI–TOF: m/z [M + H]$^+$ calcd for $C_{15}H_{26}N_4$: 263.22; found: 263.16.

2,5,8,11,14-Pentaazabicyclo[13.3.1]nonadeca-1(19),15,17-triene (3g)

Obtained from **1** (118 mg, 0.5 mmol) and pentaamine **2g** (95 mg, 0.5 mmol), in the presence of $Pd(dba)_2$ (24 mg, 8 mol%), BINAP (28 mg, 9 mol%), and *t*-BuONa (144 mg, 1.5 mmol), in abs 1,4-dioxane (25 mL).

Yield: 44 mg (33%); pale-yellow oil; eluent: CH_2Cl_2–MeOH–aq NH_3, 100:20:3, 10:4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.64 (s, 4 H), 2.71 (s, 8 H), 3.32 (br s, 4 H), 5.96 (d, J = 7.7 Hz, 2 H), 6.24 (s, 1 H), 6.88 (t, J = 7.9 Hz, 1 H) (the signals of the five NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 43.74 (2 C), 48.29 (2 C), 48.48 (2 C), 49.59 (2 C), 96.55 (1 C), 103.84 (2 C), 129.70 (1 C), 149.65 (2 C).

MALDI–TOF: m/z [M + H]$^+$ calcd for $C_{14}H_{25}N_5$: 264.22; found: 264.30.

5,8-Dioxa-2,11-diazabicyclo[10.3.1]hexadeca-1(16),12,14-triene (3h)

Obtained from **1** (118 mg, 0.5 mmol) and dioxadiamine **2h** (74 mg, 0.5 mmol), in the presence of $Pd(dba)_2$ (12 mg, 4 mol%), BINAP (14 mg, 4.5 mol%), and *t*-BuONa (144 mg, 1.5 mmol), in abs 1,4-dioxane (25 mL).

Yield: 30 mg (27%); pale-yellow oil; eluent: CH_2Cl_2–MeOH, 50:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.40 (t, J = 5.1 Hz, 4 H), 3.62 (s, 4 H), 3.62 (t, J = 5.1 Hz, 4 H), 3.91 (br s, 2 H), 6.03 (dd, J = 7.8, 1.8 Hz, 2 H), 6.88 (t, J = 7.8 Hz, 1 H), 6.96 (t, J = 1.8 Hz, 1 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 45.28 (2 C), 70.11 (2 C), 71.61 (2 C), 99.71 (1 C), 105.24 (2 C), 129.12 (1 C), 149.08 (2 C).

MALDI–TOF: m/z [M$^+$] calcd for $C_{12}H_{18}N_2O_2$: 222.14; found: 222.17.

Cyclodimer **4h** (*vide infra*) was obtained as a byproduct in this reaction.

Yield: 31 mg (28%); yellow oil; eluent: CH_2Cl_2–MeOH, 20:1.

Contains an admixture of cyclotrimer **5h** (n = 2): MALDI–TOF: m/z [M$^+$] calcd for $C_{36}H_{54}N_6O_6$: 666.41; found: 666.16; cyclotetramer **5h** (n = 3): MALDI–TOF: m/z [M$^+$] calcd for $C_{48}H_{72}N_8O_8$: 888.55; found: 888.40; and cyclopentamer **5h** (n = 4): MALDI–TOF: m/z [M$^+$] calcd for $C_{60}H_{90}N_{10}O_{10}$: 1110.68; found: 1110.70.

6,11-Dioxa-2,15-diazabicyclo[14.3.1]eicosa-1(20),16,18-triene (3i)

Obtained from **1** (118 mg, 0.5 mmol) and dioxadiamine **2i** (102 mg, 0.5 mmol), in the presence of $Pd(dba)_2$ (12 mg, 4 mol%), BINAP (14 mg, 4.5 mol%), and *t*-BuONa (144 mg, 1.5 mmol), in abs 1,4-dioxane (25 mL).

Yield: 26 mg (19%); pale-yellow oil; eluent: CH_2Cl_2–MeOH, 20:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.74–1.80 (m, 4 H), 1.85 (quin, J = 6.0 Hz, 4 H), 3.28 (t, J = 6.1 Hz, 4 H), 3.42–3.48 (m, 4 H), 3.56

(t, *J* = 5.0 Hz, 4 H), 4.26 (br s, 2 H), 5.94 (dd, *J* = 7.9, 1.5 Hz, 2 H), 6.19 (s, 1 H), 6.95 (t, *J* = 7.9 Hz, 1 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.41 (2 C), 29.98 (2 C), 42.41 (2 C), 69.82 (4 C), 96.09 (1 C), 101.83 (2 C), 129.59 (1 C), 150.16 (2 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{16}H_{26}N_2O_2$: 278.20; found: 278.08.

Cyclodimer **4i** (*vide infra*) was obtained as a byproduct in this reaction.

Yield: 11 mg (8%); yellow oil; eluent: CH_2Cl_2–MeOH, 50:1.

N^1,N^3-Bis(3-{4-[3-(phenylamino)propoxy]butoxy}propyl)benzene-1,3-diamine (8)

Obtained as a byproduct in the synthesis of **3i**.

Yield: 12 mg (11%); pale-yellow oil; eluent: CH_2Cl_2–MeOH, 50:1, 20:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65–1.70 (m, 8 H), 1.82–1.90 (m, 8 H), 3.15–3.22 (m, 8 H), 3.40–3.45 (m, 8 H), 3.51–3.56 (m, 8 H), 5.85 (s, 1 H), 5.98 (dd, *J* = 7.9, 1.7 Hz, 2 H), 6.59 (d, *J* = 8.2 Hz, 4 H), 6.67 (t, *J* = 7.0 Hz, 2 H), 6.95 (t, *J* = 7.9 Hz, 1 H), 7.15 (t, *J* = 7.7 Hz, 4 H) (the signals of the four NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.54 (2 C), 26.65 (2 C), 29.38 (2 C), 29.47 (2 C), 41.88 (2 C), 41.97 (2 C), 69.32 (2 C), 69.37 (2 C), 70.77 (4 C), 96.97 (1 C), 102.58 (2 C), 112.65 (4 C), 116.99 (2 C), 129.15 (4 C), 129.84 (1 C), 148.56 (2 C), 149.69 (2 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{38}H_{58}N_4O_4$: 634.45; found: 634.53.

***N*-{3-[4-(3-Aminopropoxy)butoxy]propyl}benzenamine (9)**

Obtained as a byproduct in the synthesis of **3i** as an inseparable mixture with **10**.

Yield: 16 mg (11%); yellow oil; eluent: CH_2Cl_2–MeOH–aq NH_3, 10:4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.59–1.64 (m, 4 H), 1.72 (quin, *J* = 6.4 Hz, 2 H), 1.86 (quin, *J* = 6.2 Hz, 2 H), 2.85 (t, *J* = 6.6 Hz, 2 H), 3.17 (t, *J* = 6.3 Hz, 2 H), 3.37–3.54 (m, 8 H), 4.35 (br s, 1 H), 6.58 (d, *J* = 7.7 Hz, 2 H), 6.65 (t, *J* = 7.3 Hz, 1 H), 7.14 (t, *J* = 7.9 Hz, 2 H) (the signals of two of the NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.45 (2 C), 29.35 (1 C), 29.44 (1 C), 39.25 (1 C), 41.85 (1 C), 68.80 (1 C), 69.30 (1 C), 70.62 (1 C), 70.72 (1 C), 112.61 (2 C), 116.95 (1 C), 129.14 (2 C), 148.53 (1 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{16}H_{28}N_2O_2$: 280.22; found: 280.14.

N^1-{3-[4-(3-Aminopropoxy)butoxy]propyl}-N^3-(3-{4-[3-(phenylamino)propoxy]butoxy}propyl)benzene-1,3-diamine (10)

Obtained as a byproduct in the synthesis of **3i** as an inseparable mixture with **9**.

Yield: 32 mg (23%); yellow oil; eluent: CH_2Cl_2–MeOH–aq NH_3, 10:4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58–1.66 (m, 8 H), 1.72 (quin, *J* = 6.4 Hz, 2 H), 1.82–1.90 (m, 6 H), 2.80 (t, *J* = 6.6 Hz, 2 H), 3.17 (t, *J* = 6.3 Hz, 2 H), 3.20 (t, *J* = 6.6 Hz, 4 H), 3.35–3.55 (m, 16 H), 4.35 (br s, 3 H), 5.84 (s, 1 H), 5.97 (d, *J* = 7.8 Hz, 2 H), 6.58 (d, *J* = 7.7 Hz, 2 H), 6.65 (t, *J* = 7.3 Hz, 1 H), 6.93 (t, *J* = 7.9 Hz, 1 H), 7.14 (t, *J* = 7.9 Hz, 2 H) (the signals of two of the NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.45 (4 C), 29.33 (2 C), 29.44 (2 C), 39.25 (1 C), 41.85 (1 C), 41.92 (2 C), 68.80 (1 C), 69.30 (1 C), 69.35 (1 C), 70.62 (1 C), 70.72 (4 C), 96.63 (1 C), 102.53 (2 C), 112.61 (2 C), 116.95 (1 C), 129.14 (2 C), 129.82 (1 C), 148.53 (1 C), 149.66 (2 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{54}N_4O_4$: 559.42; found: 559.20.

Synthesis of 3i Using a Double Amount of the Catalyst

Obtained from **1** (236 mg, 1 mmol) and dioxadiamine **2i** (204 mg, 1 mmol), in the presence of $Pd(dba)_2$ (48 mg, 8 mol%), BINAP (56 mg, 9 mol%), and *t*-BuONa (288 mg, 3 mmol), in abs 1,4-dioxane (50 mL).

Yield: 73 mg (26%); pale-yellow oil; eluent: CH_2Cl_2–MeOH, 100:1.

Cyclodimer **4i** (*vide infra*) was obtained as a byproduct in this reaction.

Yield: 14 mg (5%); yellow oil; eluent: CH_2Cl_2–MeOH, 50:1.

Compound **8** (*vide supra*) was also obtained as a byproduct in this reaction.

Yield: 11 mg (5%).

Compounds **9**, **10**, and **11** were obtained as fractionated mixtures in total yields of 35 mg (13%), 68 mg (24%), and 17 mg (6%), respectively; eluents: CH_2Cl_2–MeOH, 3:1; CH_2Cl_2–MeOH–aq NH_3, 10:4:1.

N^1-{3-[4-(3-Aminopropoxy)butoxy]propyl}-N^3-[3-(4-{3-[3-(3-{4-[3-(phenylamino)propoxy]butoxy}propylamino)phenylamino]propoxy}butoxy)propyl]benzene-1,3-diamine (11)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57–1.68 (m, 12 H), 1.81–1.90 (m, 10 H), 1.94 (br s, 2 H), 3.08 (br s, 2 H), 3.13–3.22 (m, 10 H), 3.37–3.54 (m, 24 H), 5.84 (s, 1 H), 5.88 (s, 1 H), 5.97 (br s, 4 H), 6.59 (d, *J* = 7.9 Hz, 2 H), 6.65 (t, *J* = 7.2 Hz, 1 H), 6.93 (t, *J* = 7.9 Hz, 2 H), 7.14 (t, *J* = 7.8 Hz, 2 H) (the signals of the seven NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.2–26.8 (m, 6 C), 29.3–29.4 (m, 6 C), 39.10 (1 C), 41.7–41.9 (m, 5 C), 69.0–71.1 (m, 12 C), 97.24 (1 C), 97.35 (1 C), 102.68 (2 C), 102.74 (2 C), 112.62 (2 C), 116.99 (1 C), 129.12 (2 C), 129.83 (2 C), 148.48 (1 C), 149.55 (2 C), 149.61 (2 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{48}H_{80}N_6O_6$: 837.62; found: 837.45.

***N*,*N*′-{3,3′-[Butane-1,4-diylbis(oxy)]bis(propane-3,1-diyl)}dibenzenamine (7)**

Obtained as a byproduct in the synthesis of **3i** using a double amount of the catalyst.

Yield: 14 mg (8%); yellowish oil; eluent: CH_2Cl_2–MeOH, 100:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67–1.72 (m, 4 H), 1.90 (quin, *J* = 6.3 Hz, 4 H), 3.24 (t, *J* = 6.5 Hz, 4 H), 3.28 (t, *J* = 5.7 Hz, 4 H), 3.56 (t, *J* = 5.0 Hz, 4 H), 6.61 (d, *J* = 7.8 Hz, 4 H), 6.69 (t, *J* = 7.3 Hz, 2 H), 7.18 (t, *J* = 7.7 Hz, 4 H) (the signals of the two NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.41 (2 C), 29.27 (2 C), 41.86 (2 C), 69.28 (2 C), 70.68 (2 C), 112.54 (4 C), 116.87 (2 C), 129.05 (4 C), 148.45 (2 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{22}H_{32}N_2O_2$: 356.25; found: 356.07.

6,9,12-Trioxa-2,16-diazabicyclo[15.3.1]heneicosa-1(21),17,19-triene (3j)

Obtained from **1** (118 mg, 0.5 mmol) and trioxadiamine **2j** (110 mg, 0.5 mmol), in the presence of $Pd(dba)_2$ (12 mg, 4 mol%), BINAP

(14 mg, 4.5 mol%), and *t*-BuONa (144 mg, 1.5 mmol), in abs 1,4-dioxane (25 mL).

Yield: 38 mg (26%); pale-yellow oil; eluent: CH_2Cl_2–MeOH, 50:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.81 (quin, *J* = 5.7 Hz, 4 H), 3.30 (t, *J* = 6.3 Hz, 4 H), 3.58 (t, *J* = 5.2 Hz, 4 H), 3.59–3.62 (m, 4 H), 3.67–3.70 (m, 4 H), 4.24 (br s, 2 H), 5.93 (dd, *J* = 7.9, 2.1 Hz, 2 H), 6.19 (s, 1 H), 6.91 (t, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.60 (2 C), 41.87 (2 C), 69.53 (2 C), 70.06 (2 C), 70.92 (2 C), 96.88 (1 C), 102.16 (2 C), 129.57 (1 C), 150.23 (2 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{16}H_{26}N_2O_3$: 294.19; found: 294.12.

Cyclodimer **4j** (*vide infra*) was obtained as a byproduct in this reaction.

Yield: 34 mg (23%); yellow oil; eluent: CH_2Cl_2–MeOH, 20:1.

Contains an admixture of cyclotrimer **5j** (n = 2): MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{48}H_{78}N_6O_9$: 882.58; found: 882.53.

N^1-(2-Aminoethyl)-*N*^{2}-(3-bromophenyl)ethane-1,2-diamine (6a)

Obtained from **1** (118 mg, 0.5 mmol) and triamine **2a** (52 mg, 0.5 mmol), in the presence of $Pd(dba)_2$ (12 mg, 4 mol%), BINAP (14 mg, 4.5 mol%), and *t*-BuONa (144 mg, 1.5 mmol), in abs 1,4-dioxane (25 mL).

Yield: 57 mg (44%); pale-yellow oil; eluent: CH_2Cl_2–MeOH–aq NH_3, 10:4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.66 (t, *J* = 5.2 Hz, 2 H), 2.79 (t, *J* = 5.5 Hz, 2 H), 2.81 (t, *J* = 5.4 Hz, 2 H), 3.12 (t, *J* = 5.3 Hz, 2 H), 6.50 (d, *J* = 7.9 Hz, 1 H), 6.73 (s, 1 H), 6.76 (d, *J* = 7.9 Hz, 1 H), 6.96 (t, *J* = 7.9 Hz, 1 H) (the signals of the four NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 41.04 (1 C), 43.04 (1 C), 47.98 (1 C), 50.96 (1 C), 111.52 (1 C), 115.16 (1 C), 119.77 (1 C), 123.14 (1 C), 130.37 (1 C), 149.74 (1 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{16}BrN_3$: 258.06; found: 257.99.

2,5,8,14,17,20-Hexaazatricyclo[19.3.1.1^{9,13}]hexacosa-1(25),9(26),10,12,21,23-hexaene (4a)

Obtained from **1** (118 mg, 0.5 mmol) and triamine **2a** (52 mg, 0.5 mmol), in the presence of $Pd(dba)_2$ (24 mg, 8 mol%), BINAP (28 mg, 9 mol%), and *t*-BuONa (144 mg, 1.5 mmol), in abs 1,4-dioxane (25 mL).

Yield: 66 mg [as a mixture with cyclotrimer **5a** (n = 2)] (74%); pale-yellow oil; eluent: CH_2Cl_2–MeOH–aq NH_3, 10:4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (br s, 2 H), 2.81 (t, *J* = 5.5 Hz, 8 H), 3.15 (t, *J* = 5.5 Hz, 8 H), 4.79 (br s, 4 H), 5.83 (s, 2 H), 6.01 (dd, *J* = 8.0, 2.0 Hz, 4 H), 6.96 (t, *J* = 7.9 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 43.44 (br s, 4 C), 48.43 (br s, 4 C), 98.17 (1 C), 99.30 (1 C), 102.79 (2 C), 102.99 (2 C), 130.05 (1 C), 130.14 (1 C), 149.43 (2 C), 149.53 (2 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{30}N_6$: 355.26; found: 355.25.

Contains cyclotrimer **5a** (n = 2): MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{45}N_9$: 532.39; found: 532.50.

N-(3-{2-[2-(3-Aminopropoxy)ethoxy]ethoxy}propyl)-3-chlorobenzenamine (13)

Obtained according to the procedure stated above using 1,3-dichlorobenzene (**12**) (74 mg, 0.5 mmol) and trioxadiamine **2j** (110 mg, 0.5 mmol), in the presence of $Pd(dba)_2$ (24 mg, 8 mol%), BINAP (28 mg, 9 mol%), and *t*-BuONa (144 mg, 1.5 mmol), in abs 1,4-dioxane (25 mL).

Yield: 98 mg (59%); pale-yellow oil; eluents: CH_2Cl_2–MeOH, 3:1; CH_2Cl_2–MeOH–aq NH_3, 100:20:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.70 (quin, *J* = 6.4 Hz, 2 H), 1.84 (quin, *J* = 6.1 Hz, 2 H), 2.77 (t, *J* = 6.6 Hz, 2 H), 2.87 (br s, 2 H), 3.17 (t, *J* = 6.4 Hz, 2 H), 3.50 (t, *J* = 6.1 Hz, 2 H), 3.56 (t, *J* = 6.1 Hz, 2 H), 3.55–3.58 (m, 4 H), 3.59–3.62 (m, 4 H), 4.91 (br s, 1 H), 6.43 (dd, *J* = 8.2, 1.3 Hz, 1 H), 6.53 (s, 1 H), 6.57 (d, *J* = 8.0 Hz, 1 H), 7.00 (t, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.86 (1 C), 28.74 (1 C), 39.18 (1 C), 41.30 (1 C), 69.50 (1 C), 69.68 (1 C), 69.82 (1 C), 69.95 (2 C), 70.38 (1 C), 111.07 (1 C), 112.14 (1 C), 116.50 (1 C), 130.04 (1 C), 134.80 (1 C), 149.84 (1 C).

HRMALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{16}H_{27}ClN_2O_3$: 330.1710; found: 330.1702.

N,*N*′-{3,3′-[2,2′-Oxybis(ethane-2,1-diyl)bis(oxy)]bis(propane-3,1-diyl)}bis(3-chlorobenzenamine) (14)

Obtained as a byproduct in the reaction of 1,3-dichlorobenzene (**12**) with trioxadiamine **2j**.

Yield: 26 mg (24%); pale-yellow oil; eluent: CH_2Cl_2–MeOH, 200:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (quin, *J* = 6.1 Hz, 4 H), 3.19 (t, *J* = 6.5 Hz, 4 H), 3.59 (t, *J* = 5.7 Hz, 4 H), 3.59–3.62 (m, 4 H), 3.65–3.69 (m, 4 H), 4.25 (br s, 2 H), 6.43 (dd, *J* = 8.2, 2.0 Hz, 2 H), 6.55 (t, *J* = 2.0 Hz, 2 H), 6.61 (dd, *J* = 7.8, 1.8 Hz, 2 H), 7.03 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.85 (2 C), 41.77 (2 C), 69.79 (2 C), 70.25 (2 C), 70.62 (2 C), 110.95 (2 C), 112.18 (2 C), 116.64 (2 C), 130.06 (2 C), 134.91 (2 C), 149.72 (2 C).

HRMALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{22}H_{30}Cl_2N_2O_3$: 440.1633; found: 440.1613.

N$^\alpha$,*N*$^\omega$-Bis(3-bromophenyl)-Substituted Polyamines 15b,d–f,h–k; General Procedure

A two-necked flask flushed with argon and equipped with a condenser and magnetic stirrer was charged with 1,3-dibromobenzene (**1**) (519 mg, 2.2 mmol), $Pd(dba)_2$ (23 mg, 0.04 mmol), BINAP (28 mg, 0.045 mmol), and abs 1,4-dioxane (10 mL). The mixture was stirred at r.t. for 1–2 min, then the appropriate polyamine **2** (1 mmol) and *t*-BuONa (150 mg, ca. 1.5 mmol) were added, and the reaction mixture was stirred under reflux for 6–8 h. After the reaction mixture was cooled to r.t., 1 drop of H_2O was added, the 1,4-dioxane was evaporated under reduced pressure, and the residue was chromatographed on silica gel using various eluents: CH_2Cl_2–petroleum ether, 1:1–4:1; CH_2Cl_2; CH_2Cl_2–MeOH, 500:1–10:1; CH_2Cl_2–MeOH–aq NH_3, 100:20:1–10:4:1.

N^1-(3-Bromophenyl)-*N*^{3}-[3-(3-bromophenylamino)propyl]propane-1,3-diamine (15b)

From triamine **2b** (131 mg, 1 mmol) and other reagents according to the procedure stated above, **15b** was obtained as a yellowish viscous oil.

Yield: 202 mg (46%); eluent: CH_2Cl_2–MeOH, 20:1, 10:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93 (quin, *J* = 6.5 Hz, 4 H), 2.86 (t, *J* = 6.7 Hz, 4 H), 3.14 (t, *J* = 6.4 Hz, 4 H), 3.68 (br s, 2 H), 6.46 (dd, *J* = 8.2, 2.0 Hz, 2 H), 6.68 (t, *J* = 2.0 Hz, 2 H), 6.76 (d, *J* = 8.2 Hz, 2 H), 6.95 (t, *J* = 8.2 Hz, 2 H) (the signal of the central NH proton was not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.64 (2 C), 41.15 (2 C), 46.63 (2 C), 111.53 (2 C), 115.12 (2 C), 119.98 (2 C), 123.20 (2 C), 130.52 (2 C), 149.41 (2 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{18}H_{23}Br_2N_3$: 439.03; found: 438.98.

N^1,$N^{1'}$-(1,3-Phenylene)bis{N^3-[3-(3-bromophenylamino)propyl]propane-1,3-diamine} (16b)
Obtained as a byproduct in the synthesis of **15b**.

Yield: 41 mg (13%); eluent: CH_2Cl_2–MeOH–aq NH_3, 10:4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.81 (quin, *J* = 6.1 Hz, 4 H), 1.82 (quin, *J* = 6.1 Hz, 4 H), 2.76 (t, *J* = 6.4 Hz, 8 H), 3.11 (t, *J* = 6.6 Hz, 4 H), 3.13 (t, *J* = 6.6 Hz, 4 H), 4.43 (br s, 4 H), 5.87 (s, 1 H), 5.96 (d, *J* = 7.9 Hz, 2 H), 6.45 (d, *J* = 8.0 Hz, 2 H), 6.68 (s, 2 H), 6.74 (d, *J* = 7.6 Hz, 2 H), 6.92 (t, *J* = 7.5 Hz, 1 H), 6.94 (t, *J* = 7.8 Hz, 2 H) (the signals of the two central NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.10 (2 C), 28.60 (2 C), 42.01 (2 C), 42.19 (2 C), 47.55 (2 C), 47.63 (2 C), 97.29 (1 C), 102.76 (2 C), 111.46 (2 C), 115.03 (2 C), 119.65 (2 C), 123.23 (2 C), 130.04 (1 C), 130.44 (2 C), 149.51 (2 C), 149.75 (2 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{42}Br_2N_6$: 645.19; found: 644.97.

N^1,N^1-Bis(3-bromophenyl)-N^3-[3-(3-bromophenylamino)propyl]propane-1,3-diamine (17b)
Obtained as a byproduct in the synthesis of **15b**.

Yield: 14 mg (3%); eluent: CH_2Cl_2–MeOH, 20:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.77 (quin, *J* = 6.5 Hz, 2 H), 1.80 (quin, *J* = 7.1 Hz, 2 H), 2.64 (t, *J* = 6.8 Hz, 2 H), 2.70 (t, *J* = 6.6 Hz, 2 H), 3.13 (t, *J* = 6.6 Hz, 2 H), 3.73 (t, *J* = 7.2 Hz, 2 H), 6.45 (dd, *J* = 8.0, 2.0 Hz, 1 H), 6.69 (t, *J* = 2.0 Hz, 1 H), 6.78 (d, *J* = 8.0 Hz, 1 H), 6.89–6.91 (m, 2 H), 6.96 (t, *J* = 8.0 Hz, 1 H), 7.04–7.10 (m, 4 H), 7.14 (br s, 2 H) (the signals of the two NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.49 (1 C), 28.80 (1 C), 42.32 (1 C), 46.97 (1 C), 47.94 (1 C), 50.17 (1 C), 111.52 (1 C), 114.99 (1 C), 119.77 (3 C), 123.15 (2 C), 123.28 (1 C), 123.95 (2 C), 124.84 (2 C), 130.39 (1 C), 130.64 (2 C), 148.78 (2 C), 149.74 (1 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{26}Br_3N_3$: 593.98; found: 593.84.

N^1,$N^{1'}$-(Propane-1,3-diyl)bis[N^2-(3-bromophenyl)ethane-1,2-diamine] (15d)
From tetraamine **2d** (400 mg, 2.5 mmol) and other reagents according to the procedure stated above, **15d** was obtained as a yellowish viscous oil.

Yield: 753 mg (64%); eluent: CH_2Cl_2–MeOH–aq NH_3, 100:20:1, 100:20:3.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65 (quin, *J* = 6.5 Hz, 2 H), 2.07 (br s, 2 H), 2.71 (t, *J* = 6.5 Hz, 4 H), 2.84 (t, *J* = 5.6 Hz, 4 H), 3.16 (t, *J* = 5.4 Hz, 4 H), 4.47 (br s, 2 H), 6.50 (d, *J* = 8.0 Hz, 2 H), 6.73 (s, 2 H), 6.77 (d, *J* = 7.8 Hz, 2 H), 6.97 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.01 (1 C), 42.77 (2 C), 48.07 (4 C), 111.60 (2 C), 115.12 (2 C), 119.89 (2 C), 123.19 (2 C), 130.43 (2 C), 149.59 (2 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{26}Br_2N_4$: 469.06; found: 469.12, 389.21 [M – Br]$^+$.

N^1,$N^{1'}$-{2,2′-[1,3-Phenylenebis(azanediyl)]bis(ethane-2,1-diyl)}bis{N^3-[2-(3-bromophenylamino)ethyl]propane-1,3-diamine} (16d)
Obtained as a byproduct in the synthesis of **15d**.

Yield: 188 mg (21%); eluent: CH_2Cl_2–MeOH–aq NH_3, 10:4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65 (quin, *J* = 6.6 Hz, 4 H), 2.36 (br s, 4 H), 2.62–2.70 (m, 8 H), 2.81 (t, *J* = 5.1 Hz, 8 H), 3.08–3.19 (m, 8 H), 4.40 (br s, 4 H), 5.90 (s, 1 H), 6.00 (d, *J* = 8.0 Hz, 2 H), 6.49 (d, *J* = 7.9 Hz, 2 H), 6.71 (s, 2 H), 6.75 (d, *J* = 7.9 Hz, 2 H), 6.92–6.98 (m, 3 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.61 (2 C), 42.95 (2 C), 43.23 (2 C), 47.95 (4 C), 48.18 (2 C), 48.61 (2 C), 97.40 (1 C), 102.81 (2 C), 111.57 (2 C), 115.12 (2 C), 119.73 (2 C), 123.14 (2 C), 129.95 (1 C), 130.37 (2 C), 149.51 (2 C), 149.71 (2 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{48}Br_2N_8$: 703.25; found: 703.04, 623.12 [M – Br]$^+$.

N^1,$N^{1'}$-(Ethane-1,2-diyl)bis[N^3-(3-bromophenyl)propane-1,3-diamine] (15e)
From tetraamine **2e** (435 mg, 2.5 mmol) and other reagents according to the procedure stated above, **15e** was obtained as a yellowish viscous oil.

Yield: 632 mg (52%); eluent: CH_2Cl_2–MeOH–aq NH_3, 100:20:1, 100:20:2.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.77 (quin, *J* = 6.5 Hz, 4 H), 2.74 (s, 4 H), 2.75 (t, *J* = 6.5 Hz, 4 H), 3.13 (t, *J* = 6.5 Hz, 4 H), 6.48 (dd, *J* = 8.2, 1.4 Hz, 2 H), 6.70 (s, 2 H), 6.75 (dd, *J* = 7.8, 1.4 Hz, 2 H), 6.97 (t, *J* = 8.0 Hz, 2 H) (the signals of the four NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.87 (2 C), 42.34 (2 C), 48.20 (2 C), 49.07 (2 C), 112.39 (2 C), 115.94 (2 C), 120.02 (2 C), 124.04 (2 C), 131.46 (2 C), 151.75 (2 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{28}Br_2N_4$: 483.08; found: 483.06, 403.12 [M – Br]$^+$.

N^1,$N^{1'}$-(1,3-Phenylene)bis(N^3-{2-[3-(3-bromophenylamino)propylamino]ethyl}propane-1,3-diamine) (16e)
Obtained as a byproduct in the synthesis of **15e**.

Yield: 90 mg (10%); eluent: CH_2Cl_2–MeOH–aq NH_3, 100:20:3.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.73 (quin, *J* = 6.6 Hz, 4 H), 1.75 (quin, *J* = 6.4 Hz, 4 H), 2.71 (br s, 16 H), 3.11 (t, *J* = 6.6 Hz, 4 H), 3.13 (t, *J* = 6.8 Hz, 4 H), 5.85 (s, 1 H), 5.99 (dd, *J* = 8.0, 1.9 Hz, 2 H), 6.46 (dd, *J* = 8.1, 1.3 Hz, 2 H), 6.69 (d, *J* = 1.9 Hz, 2 H), 6.74 (d, *J* = 7.0 Hz, 2 H), 6.94 (t, *J* = 7.9 Hz, 1 H), 6.96 (t, *J* = 8.1 Hz, 2 H) (the signals of the NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.99 (2 C), 29.52 (2 C), 42.50 (4 C), 48.00 (4 C), 49.21 (4 C), 96.97 (1 C), 102.52 (2 C), 111.29 (2 C), 114.88 (2 C), 119.41 (2 C), 123.13 (2 C), 129.81 (1 C), 130.32 (2 C), 149.60 (2 C), 149.80 (2 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{52}Br_2N_8$: 731.28; found: 731.07, 651.12 [M – Br]$^+$.

N^1-[2-(3-Aminopropylamino)ethyl]-N^3-(3-bromophenyl)propane-1,3-diamine (6e)
Obtained as a byproduct in the synthesis of **15e**.

Yield: 56 mg (7%); eluent: CH_2Cl_2–MeOH–aq NH_3, 10:4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65 (quin, *J* = 6.4 Hz, 2 H), 1.75 (quin, *J* = 6.4 Hz, 2 H), 2.67 (t, *J* = 6.7 Hz, 2 H), 2.72 (br s, 6 H), 2.80 (t, *J* = 6.1 Hz, 2 H), 3.10 (t, *J* = 5.6 Hz, 2 H), 6.46 (d, *J* = 7.4 Hz, 1 H), 6.68 (s, 1 H), 6.72 (d, *J* = 7.8 Hz, 1 H), 6.95 (t, *J* = 7.4 Hz, 1 H) (the signals of the five NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.45 (1 C), 31.40 (1 C), 40.16 (1 C), 42.11 (1 C), 47.61 (1 C), 47.74 (1 C), 48.60 (1 C), 48.70 (1 C), 111.28 (1 C), 114.88 (1 C), 119.37 (1 C), 123.15 (1 C), 130.36 (1 C), 149.84 (1 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{25}BrN_4$: 329.14; found: 329.04, 249.10 [M – Br]$^+$.

N^1,$N^{1'}$-(Propane-1,3-diyl)bis[N^3-(3-bromophenyl)propane-1,3-diamine] (15f)

From tetraamine **2f** (187 mg, 1 mmol) and other reagents according to the procedure stated above, **15f** was obtained as a yellowish viscous oil.

Yield: 191 mg (39%); eluent: CH_2Cl_2–MeOH–aq NH_3, 100:20:1, 100:20:2.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68 (quin, *J* = 6.7 Hz, 2 H), 1.74 (quin, *J* = 6.5 Hz, 4 H), 2.68 (t, *J* = 6.7 Hz, 4 H), 2.71 (t, *J* = 6.6 Hz, 4 H), 3.11 (t, *J* = 6.5 Hz, 4 H), 4.51 (br s, 2 H), 6.46 (dd, *J* = 8.1, 1.4 Hz, 2 H), 6.69 (t, *J* = 2.0 Hz, 2 H), 6.75 (dd, *J* = 7.8, 1.8 Hz, 2 H), 6.96 (t, *J* = 8.0 Hz, 2 H) (the signals of the two central NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.77 (2 C), 29.70 (1 C), 42.60 (2 C), 48.20 (2 C), 48.40 (2 C), 111.29 (2 C), 114.86 (2 C), 119.40 (2 C), 123.12 (2 C), 130.30 (2 C), 149.79 (2 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{30}Br_2N_4$: 497.09; found: 497.23, 417.27 [M – Br]$^+$.

N^1,$N^{1'}$-(1,3-Phenylene)bis(N^3-{3-[3-(3-bromophenylamino)propylamino]propyl}propane-1,3-diamine) (16f)

Obtained as a byproduct in the synthesis of **15f**.

Yield: 48 mg (12%); eluent: CH_2Cl_2–MeOH–aq NH_3, 10:3:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.74 (br s, 12 H), 2.73 (br s, 16 H), 3.05–3.35 (m, 8 H), 4.17 (br s, 4 H), 5.90 (s, 1 H), 5.96 (d, *J* = 6.9 Hz, 2 H), 6.47 (d, *J* = 7.4 Hz, 2 H), 6.68 (s, 2 H), 6.72 (d, *J* = 6.8 Hz, 2 H), 6.92–6.97 (m, 3 H) (the signals of the four central NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.99 (2 C), 28.29 (2 C), 28.68 (2 C), 42.20 (2 C), 42.30 (2 C), 47.63 (2 C), 47.70 (2 C), 48.51 (2 C), 48.57 (2 C), 97.25 (1 C), 102.53 (2 C), 111.36 (2 C), 114.89 (2 C), 119.39 (2 C), 123.15 (2 C), 129.89 (1 C), 130.38 (2 C), 149.59 (2 C), 149.86 (2 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{36}H_{56}Br_2N_8$: 759.31; found: 759.22, 679.13 [M – Br]$^+$.

***N*,*N*′-{2,2′-[Ethane-1,2-diylbis(oxy)]bis(ethane-2,1-diyl)}bis(3-bromobenzenamine) (15h)**

From dioxadiamine **2h** (148 mg, 1 mmol) and other reagents according to the procedure stated above, **15h** was obtained as a yellowish viscous oil.

Yield: 210 mg (46%); eluent: CH_2Cl_2–petroleum ether, 1:1–2:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.26 (t, *J* = 5.2 Hz, 4 H), 3.64 (s, 4 H), 3.68 (t, *J* = 5.2 Hz, 4 H), 4.17 (br s, 2 H), 6.51 (ddd, *J* = 8.3, 2.0, 1.0 Hz, 2 H), 6.74 (t, *J* = 2.0 Hz, 2 H), 6.81 (ddd, *J* = 7.8, 2.0, 1.0 Hz, 2 H), 6.99 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 43.12 (2 C), 69.25 (2 C), 70.08 (2 C), 111.68 (2 C), 115.26 (2 C), 119.99 (2 C), 123.07 (2 C), 130.32 (2 C), 149.36 (2 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{22}Br_2N_2O_2$: 457.01; found: 456.92, 377.03 [M – Br]$^+$.

N^1,N^3-Bis(2-{2-[2-(3-bromophenylamino)ethoxy]ethoxy}ethyl)benzene-1,3-diamine (16h)

Obtained as a byproduct in the synthesis of **15h**.

Yield: 54 mg (16%); eluent: CH_2Cl_2–MeOH, 100:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.25 (t, *J* = 5.2 Hz, 4 H), 3.26 (t, *J* = 5.1 Hz, 4 H), 3.63 (s, 8 H), 3.67 (t, *J* = 5.2 Hz, 8 H), 5.89 (s, 1 H), 6.03 (dd, *J* = 7.9, 2.1 Hz, 2 H), 6.51 (dd, *J* = 8.1, 2.0 Hz, 2 H), 6.73 (t, *J* = 2.0 Hz, 2 H), 6.79 (dd, *J* = 7.9, 2.0 Hz, 2 H), 6.97 (t, *J* = 8.1 Hz, 1 H), 6.98 (t, *J* = 8.0 Hz, 2 H) (the signals of the four NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 43.28 (2 C), 43.50 (2 C), 69.36 (2 C), 69.74 (2 C), 70.14 (2 C), 70.25 (2 C), 97.96 (1 C), 103.33 (2 C), 111.86 (2 C), 115.41 (2 C), 120.13 (2 C), 123.20 (2 C), 129.96 (1 C), 130.41 (2 C), 149.29 (2 C), 149.51 (2 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{40}Br_2N_4O_4$: 679.15; found: 678.89, 599.01 [M – Br]$^+$.

3-Bromo-*N*-(3-bromophenyl)-*N*-(2-{2-[2-(3-bromophenylamino)ethoxy]ethoxy}ethyl)benzenamine (17h)

Obtained as a byproduct in the synthesis of **15h**.

Yield: 17 mg (4%); eluent: CH_2Cl_2–petroleum ether, 1:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.23 (t, *J* = 5.0 Hz, 2 H), 3.59 (br s, 4 H), 3.65 (t, *J* = 5.9 Hz, 2 H), 3.66 (t, *J* = 5.1 Hz, 2 H), 3.88 (t, *J* = 5.8 Hz, 2 H), 4.10 (br s, 1 H), 6.47 (dd, *J* = 7.9, 1.8 Hz, 1 H), 6.71 (br s, 1 H), 6.79 (d, *J* = 7.8 Hz, 1 H), 6.91–6.95 (m, 2 H), 7.10 (t, *J* = 8.0 Hz, 1 H), 7.06–7.10 (m, 4 H), 7.20 (br s, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 43.24 (1 C), 51.80 (1 C), 68.07 (1 C), 69.44 (1 C), 70.32 (1 C), 70.75 (1 C), 111.77 (1 C), 115.40 (1 C), 119.79 (2 C), 120.10 (1 C), 123.04 (1 C), 124.00 (2 C), 124.81 (2 C), 130.32 (2 C), 130.42 (1 C), 130.54 (2 C), 148.57 (2 C), 149.43 (1 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{24}H_{25}Br_3N_2O_2$: 609.95; found: 610.05, 531.10 [M – Br]$^+$, 452.18 [M – 2 Br]$^+$.

N^1-(3-Bromophenyl)-N^1,N^3-bis(2-{2-[2-(3-bromophenylamino)ethoxy]ethoxy}ethyl)benzene-1,3-diamine (18h)

Obtained as a byproduct in the synthesis of **15h**. Isolated together with higher-mass oligomers.

Yield: 10 mg (2%); eluent: CH_2Cl_2–MeOH, 200:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.20–3.27 (m, 6 H), 3.58–3.70 (m, 16 H), 3.85 (t, *J* = 6.1 Hz, 2 H), 4.11 (br s, 3 H), 6.37 (s, 1 H), 6.46 (d, *J* = 8.2 Hz, 1 H), 6.48 (d, *J* = 8.7 Hz, 1 H), 6.68–6.83 (m, 6 H), 6.89–7.22 (m, 7 H).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{36}H_{43}Br_3N_4O_4$: 832.08; found: 832.22, 753.30 [M – Br]$^+$, 674.38 [M – 2 Br]$^+$.

***N*,*N*′-{3,3′-[Butane-1,4-diylbis(oxy)]bis(propane-3,1-diyl)}bis(3-bromobenzenamine) (15i)**

From dioxadiamine **2i** (204 mg, 1 mmol) and other reagents according to the procedure stated above, **15i** was obtained as a yellowish viscous oil.

Yield: 306 mg (59%); eluent: CH_2Cl_2–MeOH, 200:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68 (quin, *J* = 4.3 Hz, 4 H), 1.86 (quin, *J* = 6.1 Hz, 4 H), 3.18 (t, *J* = 6.4 Hz, 4 H), 3.45 (br s, 4 H), 3.53 (t, *J* = 5.8 Hz, 4 H), 4.17 (br s, 2 H), 6.48 (ddd, *J* = 8.1, 2.2, 0.8 Hz, 2 H), 6.71 (t, *J* = 2.0 Hz, 2 H), 6.77 (ddd, *J* = 7.8, 1.8, 0.8 Hz, 2 H), 6.98 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.52 (2 C), 29.09 (2 C), 41.90 (2 C), 69.36 (2 C), 70.79 (2 C), 111.35 (2 C), 114.91 (2 C), 119.55 (2 C), 123.20 (2 C), 130.35 (2 C), 149.78 (2 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{22}H_{30}Br_2N_2O_2$: 512.07; found: 512.23, 433.28 [M – Br]$^+$.

N^1,N^3-Bis(3-{4-[3-(3-bromophenylamino)propoxy]butoxy}propyl)benzene-1,3-diamine (16i)

Obtained as a byproduct in the synthesis of **15i**.

Yield: 44 mg (11%); eluent: CH_2Cl_2–MeOH, 50:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66 (br s, 8 H), 1.85 (quin, *J* = 5.8 Hz, 8 H), 3.18 (t, *J* = 5.9 Hz, 8 H), 3.44 (br s, 8 H), 3.52 (t, *J* = 5.6

Hz, 8 H), 4.15 (br s, 4 H), 5.85 (s, 1 H), 5.98 (d, *J* = 8.0 Hz, 2 H), 6.47 (d, *J* = 7.8 Hz, 2 H), 6.70 (s, 2 H), 6.76 (d, *J* = 7.6 Hz, 2 H), 6.96 (t, *J* = 8.0 Hz, 1 H), 6.98 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.53 (4 C), 29.10 (2 C), 29.45 (2 C), 41.90 (4 C), 69.35 (4 C), 70.72 (2 C), 70.84 (2 C), 96.92 (1 C), 102.57 (2 C), 111.38 (2 C), 114.93 (2 C), 119.56 (2 C), 123.23 (2 C), 129.85 (1 C), 130.36 (2 C), 149.67 (2 C), 149.82 (2 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{38}H_{56}Br_2N_4O_4$: 790.27; found: 790.18, 711.20 [M – Br]$^+$.

N^1-(3-Bromophenyl)-N^1,N^3-bis(3-{4-[3-(3-bromophenylamino)propoxy]butoxy}propyl)benzene-1,3-diamine (18i)
Obtained as a byproduct in the synthesis of **15i**. Isolated together with higher-mass oligomers.

Yield: 10 mg (2%); eluent: CH_2Cl_2–MeOH, 200:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67 (br s, 8 H), 1.77–1.90 (m, 8 H), 3.14–3.30 (m, 8 H), 3.38–3.48 (m, 8 H), 3.52 (t, *J* = 5.5 Hz, 4 H), 3.54 (t, *J* = 5.0 Hz, 4 H), 4.14 (br s, 3 H), 6.32 (s, 1 H), 6.35 (d, *J* = 8.1 Hz, 1 H), 6.43 (d, *J* = 9.0 Hz, 1 H), 6.48 (dd, *J* = 8.1, 1.6 Hz, 2 H), 6.59 (d, *J* = 7.6 Hz, 2 H), 6.71 (s, 2 H), 6.74–6.80 (m, 1 H), 6.90–7.18 (m, 6 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.56 (4 C), 27.85 (1 C), 29.14 (2 C), 29.37 (1 C), 41.97 (2 C), 42.53 (1 C), 48.97 (1 C), 69.39 (4 C), 69.92 (1 C), 70.72 (1 C), 70.80 (1 C), 70.92 (1 C), 108.63 (1 C), 108.84 (1 C), 111.40 (2 C), 113.44 (1 C), 114.96 (2 C), 117.01 (1 C), 119.60 (2 C), 119.86 (1 C), 121.36 (1 C), 122.94 (1 C), 123.26 (2 C), 130.08 (1 C), 130.37 (2 C), 132.21 (1 C), 147.75 (1 C), 149.83 (2 C), 150.08 (1 C), 150.26 (1 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{44}H_{59}Br_3N_4O_4$: 944.21; found: 944.41.

3-Bromo-*N*-(3-{4-[3-(phenylamino)propoxy]butoxy}propyl)benzenamine (19i)
Obtained as a byproduct in the synthesis of **15i**.

Yield: 38 mg (9%); eluent: CH_2Cl_2–MeOH, 500:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68 (quin, *J* = 4.3 Hz, 4 H), 1.86 (quin, *J* = 6.1 Hz, 4 H), 3.18 (t, *J* = 6.4 Hz, 2 H), 3.21 (t, *J* = 6.4 Hz, 2 H), 3.45 (br s, 4 H), 3.53 (t, *J* = 5.8 Hz, 4 H), 4.17 (br s, 2 H), 6.48 (dd, *J* = 8.0, 1.3 Hz, 1 H), 6.60 (d, *J* = 8.2 Hz, 2 H), 6.68 (t, *J* = 7.4 Hz, 1 H), 6.71 (s, 1 H), 6.77 (d, *J* = 7.7 Hz, 1 H), 6.98 (t, *J* = 7.9 Hz, 1 H), 7.16 (t, *J* = 7.7 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.30 (2 C), 29.08 (2 C), 41.87 (2 C), 69.33 (2 C), 70.77 (2 C), 111.34 (1 C), 112.59 (2 C), 114.90 (1 C), 116.95 (1 C), 119.52 (1 C), 123.19 (1 C), 129.12 (2 C), 130.33 (1 C), 148.47 (1 C), 149.78 (1 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{31}BrN_2O_2$: 435.17; found: 435.22.

N,N′-{3,3′-[2,2′-Oxybis(ethane-2,1-diyl)bis(oxy)]bis(propane-3,1-diyl)}bis(3-bromobenzenamine) (15j)
From trioxadiamine **2j** (220 mg, 1 mmol) and other reagents according to the procedure stated above, **15j** was obtained as a yellowish viscous oil.

Yield: 156 mg (29%); eluent: CH_2Cl_2–MeOH, 200:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85 (quin, *J* = 6.1 Hz, 4 H), 3.18 (t, *J* = 6.5 Hz, 4 H), 3.48 (t, *J* = 5.5 Hz, 4 H), 3.59–3.62 (m, 4 H), 3.66–3.69 (m, 4 H), 4.24 (br s, 2 H), 6.48 (dd, *J* = 8.1, 2.0 Hz, 2 H), 6.71 (t, *J* = 2.0 Hz, 2 H), 6.76 (dd, *J* = 7.8, 2.0 Hz, 2 H), 6.97 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.69 (2 C), 41.60 (2 C), 69.63 (2 C), 70.10 (2 C), 70.47 (2 C), 111.22 (2 C), 114.90 (2 C), 119.33 (2 C), 123.08 (2 C), 130.27 (2 C), 149.78 (2 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{22}H_{30}Br_2N_2O_3$: 528.06; found: 527.93, 449.04 [M – Br]$^+$.

N^1,N^3-Bis[3-(2-{2-[3-(3-bromophenylamino)propoxy]ethoxy}ethoxy)propyl]benzene-1,3-diamine (16j)
Obtained as a byproduct in the synthesis of **15j**.

Yield: 43 mg (10%); eluent: CH_2Cl_2–MeOH, 50:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85 (quin, *J* = 6.0 Hz, 8 H), 3.18 (t, *J* = 6.4 Hz, 8 H), 3.55–3.62 (m, 16 H), 3.64–3.69 (m, 8 H), 4.21 (br s, 4 H), 5.85 (s, 1 H), 5.97 (d, *J* = 7.8 Hz, 2 H), 6.47 (d, *J* = 7.8 Hz, 2 H), 6.71 (s, 2 H), 6.75 (d, *J* = 7.8 Hz, 2 H), 6.95 (t, *J* = 8.1 Hz, 1 H), 6.97 (t, *J* = 7.9 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.87 (2 C), 29.36 (2 C), 41.57 (2 C), 41.70 (2 C), 69.62 (2 C), 69.72 (2 C), 70.24 (4 C), 70.62 (4 C), 97.03 (1 C), 102.56 (2 C), 111.34 (2 C), 115.06 (2 C), 119.47 (2 C), 123.19 (2 C), 129.82 (1 C), 130.33 (2 C), 149.67 (2 C), 149.91 (2 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{38}H_{56}Br_2N_4O_6$: 822.26; found: 822.16.

3-Bromo-*N*-[3-(2-{2-[3-(phenylamino)propoxy]ethoxy}ethoxy)propyl]benzenamine (19j)
Obtained as a byproduct in the synthesis of **15j**.

Yield: 24 mg (5%); eluent: CH_2Cl_2–MeOH, 100:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (quin, *J* = 6.1 Hz, 2 H), 1.87 (quin, *J* = 6.3 Hz, 2 H), 3.17 (t, *J* = 6.5 Hz, 2 H), 3.22 (t, *J* = 6.4 Hz, 2 H), 3.55–3.63 (m, 8 H), 3.65–3.70 (m, 4 H), 4.20 (br s, 2 H), 6.47 (dd, *J* = 7.6, 1.5 Hz, 1 H), 6.59 (d, *J* = 7.8 Hz, 2 H), 6.67 (t, *J* = 7.5 Hz, 1 H), 6.71 (t, *J* = 2.0 Hz, 1 H), 6.75 (d, *J* = 7.6 Hz, 1 H), 6.97 (t, *J* = 8.0 Hz, 1 H), 7.15 (dd, *J* = 8.4, 7.6 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.89 (2 C), 41.76 (2 C), 69.77 (2 C), 70.26 (2 C), 70.64 (2 C), 111.36 (1 C), 112.69 (2 C), 115.11 (1 C), 116.99 (1 C), 119.54 (1 C), 123.23 (1 C), 129.15 (2 C), 130.35 (1 C), 149.91 (2 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{22}H_{31}BrN_2O_3$: 450.15; found: 450.06.

N^1,N^3-Bis(3-bromophenyl)propane-1,3-diamine (15k)
From diamine **2k** (74 mg, 1 mmol) and other reagents according to the procedure stated above, **15k** was obtained as a yellowish viscous oil.

Yield: 121 mg (32%); eluent: CH_2Cl_2–petroleum ether, 4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.88 (quin, *J* = 6.7 Hz, 2 H), 3.19 (br s, 4 H), 3.75 (br s, 2 H), 6.51 (ddd, *J* = 8.2, 2.0, 1.0 Hz, 2 H), 6.74 (t, *J* = 2.0 Hz, 2 H), 6.83 (ddd, *J* = 7.8, 2.0, 1.0 Hz, 2 H), 7.03 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.73 (1 C), 41.50 (2 C), 111.54 (2 C), 115.14 (2 C), 120.11 (2 C), 123.23 (2 C), 130.48 (2 C), 149.27 (2 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{15}H_{16}Br_2N_2$: 382.00; found: 382.03.

N^1,$N^{1'}$-(1,3-Phenylene)bis[N^3-(3-bromophenyl)propane-1,3-diamine] (16k)
Obtained as a byproduct in the synthesis of **15k**.

Yield: 37 mg (14%); eluent: CH_2Cl_2–MeOH, 200:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.89 (quin, *J* = 6.7 Hz, 4 H), 3.15 (t, *J* = 6.8 Hz, 8 H), 5.86 (s, 1 H), 6.02 (dd, *J* = 8.0, 2.0 Hz, 2 H), 6.49 (dd, *J* = 8.3, 2.0 Hz, 2 H), 6.72 (t, *J* = 2.0 Hz, 2 H), 6.79 (dd, *J* = 8.0, 2.0 Hz, 2 H), 6.98 (t, *J* = 8.0 Hz, 1 H), 6.99 (t, *J* = 8.0 Hz, 2 H) (the signals of the four NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.01 (2 C), 41.71 (2 C), 41.83 (2 C), 97.21 (1 C), 103.09 (2 C), 111.54 (2 C), 115.17 (2 C), 120.00 (2 C), 123.27 (2 C), 130.10 (1 C), 130.47 (2 C), 149.30 (2 C), 149.46 (2 C).

MALDI–TOF: *m*/*z* [M^+] calcd for $C_{24}H_{28}Br_2N_4$: 530.07; found: 529.97.

***N*^{1},*N*^{1},*N*^{3}-Tris(3-bromophenyl)propane-1,3-diamine (17k)**
Detected as an admixture to **15k**; eluent: CH_2Cl_2–petroleum ether, 2:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93 (quin, *J* = 6.7 Hz, 2 H), 3.15 (t, *J* = 6.8 Hz, 2 H), 3.77 (t, *J* = 7.0 Hz, 2 H), 3.78 (br s, 1 H), 6.47 (d, *J* = 8.0 Hz, 1 H), 6.70 (s, 1 H), 6.82 (d, *J* = 8.0 Hz, 1 H), 6.89–6.92 (m, 2 H), 7.01 (t, *J* = 8.0 Hz, 1 H), 7.07–7.14 (m, 6 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.19 (1 C), 41.15 (1 C), 49.84 (1 C), 111.58 (1 C), 115.30 (1 C), 119.73 (2 C), 120.31 (1 C), 122.97 (2 C), 123.89 (2 C), 124.99 (2 C), 130.49 (1 C), 130.69 (3 C), 148.58 (2 C), 149.27 (1 C).

Macrocycles 4b,d–f,h–j; General Procedure
A two-necked flask flushed with argon and equipped with a magnetic stirrer and condenser was charged with a N^{α},N^{ω}-bis(3-bromophenyl)-substituted polyamine **15** (1 mmol), $Pd(dba)_2$ (46 mg, 8 mol%), BINAP (56 mg, 9 mol%), and abs 1,4-dioxane (50 mL). The mixture was stirred for several minutes, then the appropriate polyamine **2** (1 mmol) was added followed by *t*-BuONa (150 mg, ca. 1.5 mmol), and the reaction mixture was stirred under reflux for 24–30 h. After the reaction mixture was cooled to r.t., 1 drop of H_2O was added, the 1,4-dioxane was evaporated under reduced pressure, and the residue was chromatographed on silica gel using various eluents: CH_2Cl_2; CH_2Cl_2–MeOH, 200:1–10:1; CH_2Cl_2–MeOH–aq NH_3, 100:20:3–10:4:1.

2,6,10,16,20,24-Hexaazatricyclo[23.3.1.1^{11,15}]triaconta-1(29),11(30),12,14,25,27-hexaene (4b)
From compound **15b** (146 mg, 0.33 mmol) and other reagents according to the procedure stated above, **4b** was obtained as a yellow viscous oil.

Yield: 60 mg (44%); eluent: CH_2Cl_2–MeOH–aq NH_3, 10:3:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.75 (quin, *J* = 6.0 Hz, 8 H), 2.68 (br s, 4 H), 2.72 (t, *J* = 6.0 Hz, 4 H), 3.14 (t, *J* = 6.3 Hz, 4 H), 3.19 (t, *J* = 6.2 Hz, 4 H), 5.85 (s, 2 H), 5.98 (dd, *J* = 7.8, 1.9 Hz, 4 H), 6.94 (t, *J* = 7.9 Hz, 2 H) (the signals of the six NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.01 (2 C), 29.36 (br s, 2 C), 42.68 (br s, 2 C), 42.75 (2 C), 48.22 (4 C), 97.10 (br s, 1 C), 97.37 (1 C), 102.43 (2 C), 102.49 (br s, 2 C), 129.87 (2 C), 149.68 (4 C).

MALDI–TOF: *m*/*z* [M^+] calcd for $C_{24}H_{38}N_6$: 410.32; found: 410.31.

2,5,9,12,18,21,25,28-Octaazatricyclo[27.3.1.1^{13,17}]tetratriaconta-1(33),13(34),14,16,29,31-hexaene (4d)
From compound **15d** (141 mg, 0.3 mmol) and other reagents according to the procedure stated above, **4d** was obtained as a yellow viscous oil.

Yield: 9 mg (6%); eluent: CH_2Cl_2–MeOH–aq NH_3, 10:4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.64 (br s, 4 H), 2.63 (br s, 8 H), 2.80 (br s, 8 H), 3.11 (br s, 8 H), 5.85 (s, 2 H), 5.98 (d, *J* = 7.0 Hz, 4 H), 6.92 (t, *J* = 7.0 Hz, 2 H) (the signals of the eight NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.16 (2 C), 41.26 (4 C), 48.03 (4 C), 48.36 (4 C), 97.93 (2 C), 102.39 (4 C), 129.86 (2 C), 149.70 (4 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{44}N_8$: 469.38; found: 469.51.

***N*^{1}-[2-({3-[(2-Aminoethyl)amino]propyl}amino)ethyl]-*N*^{3}-(2-{[3-({2-[(3-bromophenyl)amino]ethyl}amino)propyl]amino}ethyl)benzene-1,3-diamine (20)**
Obtained as a byproduct in the synthesis of **4d**.

Yield: 50 mg (30%); eluent: CH_2Cl_2–MeOH–aq NH_3, 10:4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.64 (br s, 2 H), 1.65 (br s, 2 H), 2.55–2.85 (m, 18 H), 3.05–3.20 (m, 6 H), 5.90 (s, 1 H), 5.98 (d, *J* = 7.0 Hz, 2 H), 6.48 (d, *J* = 7.6 Hz, 1 H), 6.70 (s, 1 H), 6.74 (d, *J* = 7.2 Hz, 1 H), 6.93 (t, *J* = 7.6 Hz, 1 H), 6.95 (t, *J* = 8.0 Hz, 1 H) (the signals of the nine NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.65 (1 C), 29.76 (1 C), 42.94 (1 C), 43.01 (1 C), 43.23 (2 C), 47.86 (2 C), 48.12 (1 C), 48.17 (1 C), 48.45 (1 C), 48.60 (2 C), 52.07 (1 C), 97.35 (1 C), 102.69 (1 C), 102.75 (1 C), 111.52 (1 C), 115.07 (1 C), 119.95 (1 C), 123.09 (1 C), 129.86 (1 C), 130.33 (1 C), 149.49 (3 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{45}BrN_8$: 549.31; found: 549.47.

2,6,9,13,19,23,26,30-Octaazatricyclo[29.3.1.1^{14,18}]hexatriaconta-1(35),14(36),15,17,31,33-hexaene (4e)
From compound **15e** (338 mg, 0.7 mmol) and other reagents according to the procedure stated above, **4e** was obtained as a yellow viscous oil.

Yield: 125 mg (36%); eluent: CH_2Cl_2–MeOH–aq NH_3, 10:3:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.70 (quin, *J* = 6.0 Hz, 8 H), 2.71 (br s, 16 H), 3.11 (t, *J* = 5.9 Hz, 8 H), 5.90 (s, 2 H), 5.95 (d, *J* = 7.9 Hz, 4 H), 6.92 (t, *J* = 7.9 Hz, 2 H) (the signals of the eight NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.00 (4 C), 42.72 (4 C), 47.79 (4 C), 48.49 (4 C), 97.55 (2 C), 102.30 (4 C), 129.80 (2 C), 149.65 (4 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{48}N_8$: 497.41; found: 497.50.

2,6,10,14,20,24,28,32-Octaazatricyclo[31.3.1.1^{15,19}]octatriaconta-1(37),15(38),16,18,33,35-hexaene (4f)
From compound **15f** (190 mg, 0.38 mmol) and other reagents according to the procedure stated above, **4f** was obtained as a yellow viscous oil.

Yield: 60 mg (30%); eluent: CH_2Cl_2–MeOH–aq NH_3, 100:20:3–10:3:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.73 (br s, 12 H), 2.47 (br s, 8 H), 2.60–2.90 (m, 8 H), 2.95–3.20 (m, 8 H), 5.81–6.02 (m, 6 H), 6.91 (br s, 2 H) (the signals of the eight NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.37 (4 C), 27.67 (2 C), 43.34 (4 C), 52.92 (4 C), 53.51 (4 C), 97.58 (2 C), 101.83 (4 C), 129.77 (2 C), 149.47 (4 C).

MALDI–TOF: *m*/*z* [M^+] calcd for $C_{30}H_{52}N_8$: 524.43; found: 524.37.

5,8,20,23-Tetraoxa-2,11,17,26-tetraazatricyclo[25.3.1.1^{12,16}]dotriaconta-1(31),12(32),13,15,27,29-hexaene (4h)
From compound **15h** (194 mg, 0.424 mmol) and other reagents according to the procedure stated above, **4h** was obtained as a yellow viscous oil.

Yield: 30 mg (16%); eluent: CH_2Cl_2–MeOH, 200:1, 100:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.24 (t, *J* = 4.9 Hz, 8 H), 3.64 (s, 8 H), 3.68 (t, *J* = 4.9 Hz, 8 H), 5.86 (s, 2 H), 6.03 (d, *J* = 7.9 Hz, 4

H), 6.98 (t, *J* = 8.0 Hz, 2 H) (the signals of the four NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 43.49 (4 C), 69.44 (4 C), 70.05 (4 C), 98.85 (2 C), 102.69 (4 C), 129.90 (2 C), 149.30 (4 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{24}H_{36}N_4O_4$: 444.27; found: 444.00.

6,11,25,30-Tetraoxa-2,15,21,34-tetraazatricyclo[33.3.1.1^{16,20}]tetraconta-1(39),16(40),17,19,35,37-hexaene (4i)
From compound **15i** (132 mg, 0.257 mmol) and other reagents according to the procedure stated above, **4i** was obtained as a yellow viscous oil.

Yield: 54 mg (38%); eluent: CH_2Cl_2–MeOH, 50:1, 20:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68 (br s, 8 H), 1.85 (quin, *J* = 6.1 Hz, 8 H), 3.19 (t, *J* = 6.5 Hz, 8 H), 3.45 (br s, 8 H), 3.53 (t, *J* = 5.7 Hz, 8 H), 3.99 (br s, 4 H), 5.88 (t, *J* = 1.8 Hz, 2 H), 5.98 (dd, *J* = 7.9, 2.1 Hz, 4 H), 6.95 (t, *J* = 7.9 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.62 (4 C), 29.36 (4 C), 42.11 (4 C), 69.49 (4 C), 70.77 (4 C), 97.32 (2 C), 102.39 (4 C), 129.84 (2 C), 149.79 (4 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{32}H_{52}N_4O_4$: 556.40; found: 556.26.

6,9,12,26,29,32-Hexaoxa-2,16,22,36-tetraazatricyclo[35.3.1.1^{17,21}]dotetraconta-1(41),17(42),18,20,37,39-hexaene (4j)
From compound **15j** (400 mg, 0.75 mmol) and other reagents according to the procedure stated above, **4j** was obtained as a yellow viscous oil.

Yield: 93 mg (21%); eluent: CH_2Cl_2–MeOH, 20:1, 10:1

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85 (br s, 8 H), 3.16 (br s, 8 H), 3.45–3.70 (m, 24 H), 3.99 (br s, 4 H), 5.85 (s, 2 H), 5.98 (d, *J* = 7.5 Hz, 4 H), 6.94 (t, *J* = 7.5 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.14 (4 C), 41.35 (4 C), 69.44 (4 C), 70.05 (4 C), 70.45 (4 C), 97.23 (2 C), 102.30 (4 C), 129.61 (2 C), 149.55 (4 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{32}H_{52}N_4O_6$: 588.39; found: 588.52.

Tetraarylated Polyamines 21b,h–k; General Procedure
A two-necked flask flushed with argon and equipped with a condenser and magnetic stirrer was charged with 1,3-dibromobenzene (**1**) (1.18–1.42 g, 5–6 mmol), $Pd(dba)_2$ (46–92 mg, 0.08–0.16 mmol), BINAP (56–112 mg, 0.09–0.18 mmol), and abs 1,4-dioxane (10 mL). The mixture was stirred at r.t. for 1–2 min, then the appropriate polyamine **2** (1 mmol) and *t*-BuONa (576 mg, 6 mmol) were added, and the reaction mixture was stirred under reflux for 24–30 h. After the reaction mixture was cooled to r.t., 1 drop of H_2O was added, the 1,4-dioxane was evaporated under reduced pressure, and the residue was chromatographed on silica gel using various eluents: CH_2Cl_2–petroleum ether, 1:2–4:1; CH_2Cl_2; CH_2Cl_2–MeOH, 500:1–100:1.

***N*^{1}-{3-[Bis(3-bromophenyl)amino]propyl}-*N*^{3},*N*^{3}-bis(3-bromophenyl)propane-1,3-diamine (21b)**
From triamine **2b** (33 mg, 0.25 mmol) and other reagents stated above, **21b** was obtained as a yellow oil.

Yield: 70 mg (37%); eluent: CH_2Cl_2–MeOH, 200:1, 100:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.80 (quin, *J* = 7.1 Hz, 4 H), 2.62 (t, *J* = 6.9 Hz, 4 H), 3.72 (t, *J* = 7.2 Hz, 4 H), 6.88–6.91 (m, 4 H), 7.07–7.12 (m, 8 H), 7.14 (br s, 4 H) (the signal of the NH proton was not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.83 (2 C), 46.82 (2 C), 50.11 (2 C), 119.76 (4 C), 123.15 (4 C), 123.93 (4 C), 124.81 (4 C), 130.61 (4 C), 148.74 (4 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{30}H_{29}Br_4N_3$: 746.91; found: 746.96.

***N*,*N*′-{2,2′-[Ethane-1,2-diylbis(oxy)]bis(ethane-2,1-diyl)}bis[3-bromo-*N*-(3-bromophenyl)benzenamine] (21h)**
From dioxadiamine **2h** (37 mg, 0.25 mmol) and other reagents stated above, **21h** was obtained as a yellow oil.

Yield: 60 mg (31%); eluent: CH_2Cl_2–petroleum ether, 2:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.54 (s, 4 H), 3.63 (t, *J* = 5.9 Hz, 4 H), 3.85 (t, *J* = 5.9 Hz, 4 H), 6.89–6.93 (m, 4 H), 7.05–7.10 (m, 8 H), 7.17–7.20 (m, 4 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 51.83 (2 C), 68.15 (2 C), 70.86 (2 C), 119.79 (4 C), 123.07 (4 C), 124.03 (4 C), 124.80 (4 C), 130.54 (4 C), 148.61 (4 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{30}H_{28}Br_4N_2O_2$: 763.89; found: 763.67, 684.78 [M – Br]$^+$, 605.90 [M – 2 Br]$^+$, 526.99 [M – 3 Br]$^+$.

***N*,*N*′-{3,3′-[Butane-1,4-diylbis(oxy)]bis(propane-3,1-diyl)}bis[3-bromo-*N*-(3-bromophenyl)benzenamine] (21i)**
From dioxadiamine **2i** (51 mg, 0.25 mmol) and other reagents stated above, **21i** was obtained as a yellow oil.

Yield: 68 mg (33%); eluent: CH_2Cl_2–petroleum ether, 2:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69 (br s, 4 H), 1.86 (quin, *J* = 6.2 Hz, 4 H), 3.44 (br s, 8 H), 3.80 (t, *J* = 7.0 Hz, 4 H), 6.90–6.94 (m, 4 H), 7.02–7.12 (m, 8 H), 7.17 (br s, 4 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.56 (2 C), 27.63 (2 C), 49.00 (2 C), 67.42 (2 C), 70.82 (2 C), 119.68 (4 C), 123.09 (4 C), 123.83 (4 C), 124.58 (4 C), 130.48 (4 C), 148.77 (4 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{34}H_{36}Br_4N_2O_2$: 819.95; found: 819.81, 740.87 [M – Br]$^+$.

3-Bromo-*N*-(3-bromophenyl)-*N*-(3-{4-[3-(3-bromophenylamino)propoxy]butoxy}propyl)benzenamine (17i)
Obtained as a byproduct in the synthesis of **21i**.

Yield: 19 mg (11%); eluents: CH_2Cl_2; CH_2Cl_2–MeOH, 500:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (br s, 2 H), 1.57 (br s, 2 H), 1.87 (quin, *J* = 6.1 Hz, 2 H), 1.93 (quin, *J* = 6.4 Hz, 2 H), 3.19 (t, *J* = 6.3 Hz, 2 H), 3.37 (t, *J* = 6.0 Hz, 2 H), 3.40–3.51 (m, 4 H), 3.53 (t, *J* = 5.8 Hz, 2 H), 3.79 (t, *J* = 6.9 Hz, 2 H), 4.17 (br s, 1 H), 6.47 (ddd, *J* = 8.2, 2.3, 0.9 Hz, 1 H), 6.71 (t, *J* = 2.0 Hz, 1 H), 6.77 (ddd, *J* = 6.8, 1.8, 0.9 Hz, 1 H), 6.90–6.94 (m, 2 H), 6.97 (t, *J* = 8.0 Hz, 1 H), 7.03–7.12 (m, 4 H), 7.15–7.17 (m, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.20 (1 C), 26.59 (1 C), 28.15 (1 C), 29.15 (1 C), 42.02 (1 C), 49.42 (1 C), 67.49 (1 C), 69.44 (1 C), 70.46 (1 C), 70.96 (1 C), 111.41 (1 C), 114.98 (1 C), 119.65 (1 C), 119.73 (2 C), 123.12 (2 C), 123.28 (1 C), 123.88 (2 C), 124.63 (2 C), 130.38 (1 C), 130.52 (2 C), 148.83 (2 C), 149.83 (1 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{28}H_{33}Br_3N_2O_2$: 666.01; found: 665.88.

***N*^{1},*N*^{3}-Bis[3-(4-{3-[bis(3-bromophenyl)amino]propoxy}butoxy)propyl]-*N*^{1},*N*^{3}-bis(3-bromophenyl)benzene-1,3-diamine (22i)**
Obtained as a byproduct in the synthesis of **21i**.

Yield: 33 mg (9%); eluent: CH_2Cl_2–MeOH, 500:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66 (br s, 8 H), 1.85 (quin, *J* = 6.1 Hz, 8 H), 3.37–3.45 (m, 16 H), 3.77 (t, *J* = 6.6 Hz, 4 H), 3.79 (t, *J* = 6.8 Hz, 4 H), 6.71 (t, *J* = 2.0 Hz, 1 H), 6.74–6.78 (m, 2 H), 6.83–

6.86 (m, 2 H), 6.90–6.95 (m, 4 H), 6.97 (t, *J* = 8.0 Hz, 1 H), 7.02–7.12 (m, 12 H), 7.15–7.17 (m, 6 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.58 (4 C), 27.67 (2 C), 27.74 (2 C), 48.96 (2 C), 49.05 (2 C), 67.47 (2 C), 67.72 (2 C), 70.82 (2 C), 70.86 (2 C), 117.29 (2 C), 117.59 (2 C), 118.08 (1 C), 119.73 (4 C), 121.47 (2 C), 122.70 (2 C), 123.00 (2 C), 123.12 (4 C), 123.88 (4 C), 124.63 (4 C), 130.28 (2 C), 130.52 (5 C), 148.04 (2 C), 148.83 (4 C), 149.53 (2 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{62}H_{68}Br_6N_4O_4$: 1406.03; found: 1405.94, 1327.03 [M – Br]$^+$.

N^1-[3-(4-{3-[Bis(3-bromophenyl)amino]propoxy}butoxy)propyl]-N^1,N^3-bis(3-bromophenyl)-N^3-(3-{4-[3-(3-bromophenylamino)propoxy]butoxy}propyl)benzene-1,3-diamine (23i)
Obtained as a byproduct in the synthesis of **21i**.

Yield: 15 mg (5%); eluent: CH_2Cl_2–MeOH, 200:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65 (br s, 4 H), 1.66 (br s, 4 H), 1.80–1.90 (m, 8 H), 3.18 (t, *J* = 6.4 Hz, 2 H), 3.35–3.48 (m, 14 H), 3.53 (t, *J* = 5.8 Hz, 2 H), 3.73–3.81 (m, 6 H), 4.32 (br s, 1 H), 6.47 (d, *J* = 8.4 Hz, 1 H), 6.70 (t, *J* = 2.0 Hz, 2 H), 6.73–6.78 (m, 3 H), 6.84 (d, *J* = 8.4 Hz, 2 H), 6.90–6.98 (m, 4 H), 7.00–7.12 (m, 8 H), 7.16 (br s, 4 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.58 (4 C), 27.67 (2 C), 27.74 (2 C), 42.00 (1 C), 48.95 (2 C), 49.04 (1 C), 67.46 (1 C), 67.72 (1 C), 69.43 (1 C), 70.81 (3 C), 70.87 (2 C), 111.41 (1 C), 114.98 (1 C), 117.28 (2 C), 117.58 (2 C), 118.08 (1 C), 119.65 (1 C), 119.73 (2 C), 121.39 (1 C), 121.46 (2 C), 122.70 (2 C), 123.00 (2 C), 123.12 (2 C), 123.88 (2 C), 124.63 (2 C), 130.22 (1 C), 130.28 (2 C), 130.39 (1 C), 130.52 (2 C), 148.03 (2 C), 148.83 (4 C), 149.83 (1 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{56}H_{65}Br_5N_4O_4$: 1252.09; found: 1252.21, 1173.15 [M – Br]$^+$, 1094.21 [M – 2 Br]$^+$, 1015.32 [M – 3 Br]$^+$.

***N*,*N*′-{3,3′-[2,2′-Oxybis(ethane-2,1-diyl)bis(oxy)]bis(propane-3,1-diyl)}bis[3-bromo-*N*-(3-bromophenyl)benzenamine] (21j)**
From trioxadiamine **2j** (55 mg, 0.25 mmol) and other reagents stated above, **21j** was obtained as a yellow oil.

Yield: 60 mg (29%); eluent: CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (quin, *J* = 5.8 Hz, 4 H), 3.49 (t, *J* = 5.3 Hz, 4 H), 3.58 (t, *J* = 4.3 Hz, 4 H), 3.71 (t, *J* = 4.3 Hz, 4 H), 3.79 (t, *J* = 6.5 Hz, 4 H), 6.90–6.94 (m, 4 H), 7.04–7.12 (m, 8 H), 7.16 (br s, 4 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.51 (2 C), 48.89 (2 C), 67.96 (2 C), 70.32 (2 C), 70.66 (2 C), 119.71 (4 C), 123.07 (4 C), 123.83 (4 C), 124.60 (4 C), 130.53 (4 C), 148.76 (4 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{34}H_{36}Br_4N_2O_3$: 835.95; found: 835.69, 756.80 [M – Br]$^+$, 677.99 [M – 2 Br]$^+$.

3-Bromo-*N*-(3-bromophenyl)-*N*-[3-(2-{2-[3-(3-bromophenylamino)propoxy]ethoxy}ethoxy)propyl]benzenamine (17j)
Obtained as a byproduct in the synthesis of **21j**.

Yield: 9 mg (5%); eluent: CH_2Cl_2–MeOH, 500:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (quin, *J* = 6.1 Hz, 4 H), 3.19 (t, *J* = 6.5 Hz, 2 H), 3.48 (t, *J* = 5.8 Hz, 2 H), 3.55–3.62 (m, 6 H), 3.66–3.72 (m, 4 H), 3.79 (t, *J* = 7.0 Hz, 2 H), 4.27 (s, 1 H), 6.48 (dd, *J* = 8.1, 2.3 Hz, 1 H), 6.71 (t, *J* = 2.0 Hz, 1 H), 6.75 (dd, *J* = 7.8, 1.8 Hz, 1 H), 6.89–6.94 (m, 2 H), 6.96 (t, *J* = 8.0 Hz, 1 H), 7.05–7.12 (m, 4 H), 7.16 (t, *J* = 1.9 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.51 (1 C), 28.82 (1 C), 41.79 (1 C), 48.91 (1 C), 68.00 (1 C), 69.80 (1 C), 70.24 (1 C), 70.31 (1 C), 70.63 (2 C), 111.33 (1 C), 115.04 (1 C), 119.50 (1 C), 119.73 (2 C), 123.07 (2 C), 123.20 (1 C), 123.84 (2 C), 124.60 (2 C), 130.54 (2 C), 130.55 (1 C), 148.77 (2 C), 149.86 (1 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{28}H_{33}Br_3N_2O_3$: 682.00; found: 681.82, 602.93 [M – Br]$^+$, 524.05 [M – 2 Br]$^+$.

N^1,N^3-Bis{3-[2-(2-{3-[bis(3-bromophenyl)amino]propoxy}ethoxy)ethoxy]propyl}-N^1,N^3-bis(3-bromophenyl)benzene-1,3-diamine (22j)
Obtained as a byproduct in the synthesis of **21j**.

Yield: 31 mg (9%); eluent: CH_2Cl_2–MeOH, 200:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85 (quin, *J* = 6.3 Hz, 8 H), 3.47 (t, *J* = 5.7 Hz, 8 H), 3.53–3.61 (m, 8 H), 3.64–3.70 (m, 8 H), 3.76 (t, *J* = 8.1 Hz, 4 H), 3.78 (t, *J* = 7.3 Hz, 4 H), 6.70 (s, 1 H), 6.73–6.76 (m, 2 H), 6.82–6.85 (m, 2 H), 6.89–6.93 (m, 4 H), 6.96 (t, *J* = 7.9 Hz, 1 H), 7.01–7.12 (m, 12 H), 7.14–7.16 (m, 6 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.65 (2 C), 27.69 (2 C), 48.89 (2 C), 49.00 (2 C), 68.05 (2 C), 68.28 (2 C), 70.34 (4 C), 70.69 (4 C), 117.40 (2 C), 117.62 (2 C), 118.08 (1 C), 119.79 (4 C), 121.55 (2 C), 122.78 (2 C), 123.00 (2 C), 123.12 (4 C), 123.93 (4 C), 124.68 (4 C), 130.32 (3 C), 130.55 (4 C), 148.07 (4 C), 148.86 (4 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{62}H_{68}Br_6N_4O_6$: 1438.02; found: 1437.72, 1358.82 [M – Br]$^+$.

N^1-{3-[2-(2-{3-[Bis(3-bromophenyl)amino]propoxy}ethoxy)ethoxy]propyl}-N^1,N^3-bis(3-bromophenyl)-N^3-[3-(3-bromophenylamino)propoxy]ethoxy}ethoxy)propyl]benzene-1,3-diamine (23j)
Obtained as a byproduct in the synthesis of **21j**.

Yield: 18 mg (5%); eluent: CH_2Cl_2–MeOH, 200:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (quin, *J* = 6.1 Hz, 8 H), 3.18 (t, *J* = 6.5 Hz, 2 H), 3.47 (t, *J* = 5.8 Hz, 8 H), 3.54–3.62 (m, 10 H), 3.63–3.70 (m, 8 H), 3.76 (t, *J* = 8.1 Hz, 2 H), 3.78 (t, *J* = 7.0 Hz, 2 H), 6.48 (dd, *J* = 8.3, 2.3 Hz, 1 H), 6.71 (t, *J* = 2.2 Hz, 2 H), 6.72–6.77 (m, 3 H), 6.84 (dd, *J* = 8.1, 2.3 Hz, 2 H), 6.89–6.94 (m, 2 H), 6.97 (t, *J* = 8.0 Hz, 2 H), 7.00–7.12 (m, 8 H), 7.14–7.16 (m, 4 H) (the signal of the NH proton was not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.54 (2 C), 27.59 (2 C), 41.77 (1 C), 48.82 (2 C), 48.92 (1 C), 69.80 (2 C), 70.25 (2 C), 70.30 (4 C), 70.63 (2 C), 70.66 (2 C), 111.36 (1 C), 115.08 (1 C), 117.31 (2 C), 117.60 (2 C), 118.07 (1 C), 119.54 (1 C), 119.75 (2 C), 121.43 (3 C), 122.70 (2 C), 122.97 (2 C), 123.10 (2 C), 123.86 (2 C), 124.63 (2 C), 130.37 (4 C), 130.55 (2 C), 147.98 (2 C), 148.79 (2 C), 149.51 (2 C), 149.88 (1 C).

MALDI–TOF: *m*/*z* [M$^+$] calcd for $C_{56}H_{65}Br_5N_4O_6$: 1284.02; found: 1283.79, 1204.78 [M – Br]$^+$.

N^1,N^1,N^3,N^3-Tetrakis(3-bromophenyl)propane-1,3-diamine (21k)
From diamine **2k** (37 mg, 0.5 mmol) and other reagents stated above, **21k** was obtained as a yellow oil.

Yield: 85 mg (25%); eluent: CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.98 (quin, *J* = 7.0 Hz, 2 H), 3.74 (t, *J* = 7.0 Hz, 4 H), 6.83–6.88 (m, 4 H), 7.07–7.13 (m, 12 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.40 (1 C), 49.84 (2 C), 119.76 (4 C), 123.01 (4 C), 124.00 (4 C), 125.14 (4 C), 130.71 (4 C), 148.55 (4 C).

MALDI–TOF: *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{22}Br_4N_2$: 690.86; found: 690.68, 610.85 [M – Br]$^+$.

1,3-Bis(polyamino)-Substituted Benzenes 24h–j; General Procedure

A two-necked flask flushed with argon and equipped with a condenser and magnetic stirrer was charged with 1,3-dibromobenzene (**1**) (236 mg, 1 mmol), $Pd(dba)_2$ (46 mg, 0.08 mmol), BINAP (56 mg, 0.09 mmol), and abs 1,4-dioxane (5–10 mL). The mixture was stirred at r.t. for 1–2 min, then the appropriate polyamine **2** (2.5–4 mmol) and *t*-BuONa (150 mg, ca. 1.5 mmol) were added, and the reaction mixture was stirred under reflux for 8 h. After the reaction mixture was cooled to r.t., 1 drop of H_2O was added, the 1,4-dioxane was evaporated under reduced pressure, and the residue was chromatographed on silica gel using various eluents: CH_2Cl_2; CH_2Cl_2–MeOH, 50:1–3:1; CH_2Cl_2–MeOH–aq NH_3, 100:20:1–10:4:1.

***N*^{1},*N*^{3}-Bis{2-[2-(2-aminoethoxy)ethoxy]ethyl}benzene-1,3-diamine (24h)**

From dioxadiamine **2h** (592 mg, 4 mmol), 1,3-dibromobenzene (**1**) (236 mg, 1 mmol), and other reagents stated above, **24h** was obtained as a yellow oil.

Yield: 220 mg (59%); eluent: CH_2Cl_2–MeOH, 5:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.83 (t, *J* = 4.9 Hz, 4 H), 3.20 (t, *J* = 4.9 Hz, 4 H), 3.48 (t, *J* = 4.9 Hz, 4 H), 3.55 (br s, 8 H), 3.62 (t, *J* = 4.9 Hz, 4 H), 3.70 (br s, 4 H), 5.89 and 5.94 (br s, 1 H), 5.98 (d, *J* = 7.9 Hz, 2 H), 6.89 (t, *J* = 7.9 Hz, 1 H) (the signals of some of the NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 40.86 and 40.94 (2 C), 43.32 (2 C), 69.52 (2 C), 69.93 (4 C), 71.18 and 72.10 (2 C), 97.88 and 98.04 (1 C), 102.82 and 102.98 (2 C), 129.71 (1 C), 149.18 (2 C).

In the presence of a twofold excess of dioxadiamine **2h**, the duplication of proton and carbon signals disappears:

^{1}H NMR (400 MHz, $CDCl_3$ + 2 equiv of **2h**): δ = 2.82 (t, *J* = 5.0 Hz, 4 H), 3.18 (t, *J* = 5.0 Hz, 4 H), 3.47 (t, *J* = 5.0 Hz, 4 H), 3.56 (br s, 8 H), 3.60 (t, *J* = 5.0 Hz, 4 H), 3.72 (br s, 4 H), 5.88 (br s, 1 H), 5.99 (d, *J* = 7.8 Hz, 2 H), 6.92 (t, *J* = 7.8 Hz, 1 H) (the signals of some of the NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$ + 2 equiv of **2h**): δ = 41.15 (2 C), 43.00 (2 C), 69.26 (2 C), 69.81 (4 C), 72.94 (2 C), 97.40 (1 C), 102.76 (2 C), 129.46 (1 C), 148.95 (2 C).

MALDI–TOF: *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{34}N_4O_4$: 371.27; found: 371.26.

***N*^{1},*N*^{3}-Bis{3-[4-(3-aminopropoxy)butoxy]propyl}benzene-1,3-diamine (24i)**

From dioxadiamine **2i** (816 mg, 4 mmol), 1,3-dibromobenzene (**1**) (236 mg, 1 mmol), and other reagents stated above, **24i** was obtained as a yellow oil.

Yield: 180 mg (37%); eluent: CH_2Cl_2–MeOH, 5:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.61 (br s, 8 H), 1.78 (quin, *J* = 6.4 Hz, 4 H), 1.84 (quin, *J* = 6.0 Hz, 4 H), 2.87 (t, *J* = 6.6 Hz, 4 H), 3.16 (t, *J* = 6.4 Hz, 4 H), 3.36–3.74 (m, 16 H), 4.00 (br s, 4 H), 5.83 and 5.87 (s, 1 H), 5.96 (d, *J* = 7.8 Hz, 2 H), 6.92 (t, *J* = 7.8 Hz, 1 H) (the signals of some of the NH protons were not unambiguously assigned).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.49 (br s, 8 H), 1.62 (quin, *J* = 6.5 Hz, 4 H), 1.70 (quin, *J* = 6.1 Hz, 4 H), 2.64 (t, *J* = 7.0 Hz, 4 H), 2.95 (br s, 4 H), 3.27–3.43 (m, 16 H), 5.11 (br s, 2 H), 5.74 (s, 1 H), 5.77 (d, *J* = 7.8 Hz, 2 H), 6.73 (t, *J* = 7.8 Hz, 1 H) (the signals of some of the NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.09 (4 C), 29.04 (2 C), 33.12 (2 C), 39.14 (2 C), 41.40 (2 C), 68.52 (2 C), 68.95 (2 C), 70.29 (2 C), 70.37 (2 C), 96.48 (1 C), 102.70 (2 C), 129.40 (1 C), 149.30 (2 C).

MALDI–TOF: *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{50}N_4O_4$: 483.39; found: 483.20.

***N*^{1},*N*^{3}-Bis(3-{2-[2-(3-aminopropoxy)ethoxy]ethoxy}propyl)benzene-1,3-diamine (24j)**

From trioxadiamine **2j** (550 mg, 2.5 mmol), 1,3-dibromobenzene (**1**) (236 mg, 1 mmol), and other reagents stated above, **24j** was obtained as a yellow oil.

Yield: 288 mg (56%); eluent: CH_2Cl_2–MeOH–aq NH_3, 10:4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.70 (quin, *J* = 6.4 Hz, 4 H), 1.85 (quin, *J* = 6.2 Hz, 4 H), 2.36 (br s, 4 H), 2.77 (t, *J* = 6.7 Hz, 4 H), 3.17 (t, *J* = 6.5 Hz, 4 H), 3.52 (t, *J* = 6.3 Hz, 4 H), 3.55–3.65 (m, 20 H), 5.84 and 5.86 (s, 1 H), 5.98 (d, *J* = 7.9 Hz, 2 H), 6.92 (t, *J* = 7.9 Hz, 1 H) (the signals of some of the NH protons were not unambiguously assigned).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.23 (2 C), 32.71 (2 C), 39.49 (2 C), 41.49 (2 C), 69.40 (2 C), 69.56 (2 C), 70.07 (2 C), 70.14 (2 C), 70.51 (4 C), 97.01 (1 C), 102.50 (2 C), 129.77 (1 C), 149.62 (2 C).

MALDI–TOF: *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{50}N_4O_6$: 515.38; found: 515.19.

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