Palladium-Catalysed Amination of 1,8- and 1,5-Dichloroanthracenes and 1,8- and 1,5-Dichloroanthraquinones

Irina P. Beletskaya,*[a] Alla G. Bessmertnykh,[a,b] Alexei D. Averin,[a,b] Franck Denat,[b] and Roger Guilard*[b]

Keywords: Amines / Aromatic substitution / Homogeneous catalysis / Macrocycles / Palladium

Diamino derivatives of anthracene and anthraquinone have been synthesised by palladium-catalysed coupling of 1,8-dichloroanthracene and 1,8-dichloroanthraquinone with a wide range of aliphatic and aromatic primary and secondary amines. The use of polyamines gave rise to a large number of new nitrogen- and oxygen-containing macrocycles incorporating anthracene or anthraquinone moieties. The method has also been employed for the preparation of bismacrocycles in which two cyclam or azacrown units are linked together by an anthracene bridge through C(sp^2)–N bonds.

Introduction

Amino derivatives of anthracene and anthraquinone have several applications in academic research and industry. Aminoanthraquinones have for a long time been used as dyes,[1] while in recent decades aminoanthracenes and aminoanthraquinones have been widely used in coordination chemistry, since their complexes possess interesting physical properties and have found applications as sensors,[2] photo- and redox-switchable molecules and multielectron catalysts.[3] The properties of such complexes are mainly the result of the interactions that can occur between transition metal ions and redox-active ligands, which induce different phenomena including facile redox behaviour[4] and valence tautomerism.[5] Ligands of different architectures have been synthesised, and among them a significant role is played by derivatives of anthracene and anthraquinone bearing nitrogen- and oxygen-containing macrocycles. In all these macrocycles, oxygen and nitrogen incorporated in the cycle are linked to arene moieties through at least one methylene group. Special attention has been devoted to saturated and tetrapyrrolic macrocyclic ligands containing anthracene or anthraquinone fragments either attached to the macrocycle or acting as a component of a macrocycle. The famous face-to-face porphyrins containing two tetrapyrrolic cycles bound through an anthracene spacer[6] have proved to be important models in studies of photosynthesis.[7] Their binuclear metal complexes are also important model catalysts in oxygen reduction.[8] Saturated polyazamacrocycles assembled in a face-to-face manner have been extensively studied in recent years,[9] and the synthesis of a variety of such bismacrocyclic molecules linked to the same aryl spacers has recently been described by our group.[10] Crown and azacrown ethers combined with anthracene or anthraquinone also demonstrate very promising properties. Proton sensors, for example, were produced by the attachment either of one or two crown ether cycles to the anthracene or of a macrocycle to positions 9 and 10 in the anthracene moiety.[2b] Crown ethers containing two anthracene moieties generated crown-cryptand photoswitches.[3c,3d] Anthracene linked to a crown ether has also been used for detecting Cu^{2+} ions and D-glucoseamine.[11]

Our goal was to synthesise ligands possessing C(sp^2)−N bonds and to study their binding properties. The presence of such a fragment in the ligand can significantly change its metal coordination and enhance the measurable response of the aromatic moiety in a complexation reaction. Literature data clearly show that the synthesis of such macrocyclic molecules has been strictly limited, due to the lack of convenient and general methods for C(sp^2)−N bond formation. Copper-catalysed Ullmann-type reactions have been extensively used to prepare aminoanthraquinones for decades,[12] but this synthetic method demands harsh conditions limiting the choice of appropriate substrates and the reaction yields are often poor. To the best of our knowledge, there is no convenient synthetic approach to aminoanthracenes. Finally, bis(dimethylamino)anthracene was only recently synthesised for the first time by direct nucleophilic substitution starting from 1,8-difluoroanthracene.[13]

Significant progress in the amination of aryl halides was achieved through the use of palladium catalysis, after

[a] Department of Chemistry, Lomonosov Moscow State University, Moscow, 119899, Russia
Fax: (internat.) + 7-095-9393618
E-mail: beletska@org.chem.msu.su
[b] Laboratoire d'Ingénierie Moléculaire pour la Séparation et les Applications des Gaz (LIMSAG UMR 5633), Université de Bourgogne, Faculté des Sciences "Gabriel",
6, Bd Gabriel, 21100, Dijon, France
Fax: (internat.) + 33-3-80396117
E-mail: Roger.Guilard@u-bourgogne.fr

pioneering work by Kosugi and Migita and extensive development by Buchwald's and Hartwig's groups.[14] An important survey on the amination of aryl halides (mainly aryl chlorides) through the use of electron-rich ligands such as 2-(di-*tert*-butylphosphanyl)-1,1′-biphenyl and 2-(dicyclohexylphosphanyl)-1,1′-biphenyl was published by Buchwald.[15] These ligands proved to be more efficient than the P*t*Bu$_3$ and PCy$_3$ ligands previously used in amination of aryl chlorides.[16] "Phosphane mimic" ligands were successfully used by Nolan for Pd-catalysed amination,[17] and nickel-mediated coupling of amines with aryl chlorides was described by Fort.[18] The synthesis of macrocycles containing anthracene and anthraquinone fragments being our main goal, we chose commercially available chloro derivatives (part of this work has been already published in preliminary reports[19]). Attempts to achieve the diamination of dichloroanthracene and dichloroanthraquinone face several serious problems: a) reduction of the second chlorine atom, affording monoamination products, b) the complexation of palladium by formed polyazamacrocycles, which may hinder amination, c) the formation of the cyclic and linear oligomers through amination reactions, due to the existence of two reaction sites in both starting compounds (i.e., polyamines and aryl dichlorides), and d) the polyarylation of polyamines. Here we show how some of these problems have been solved in the course of our investigations.

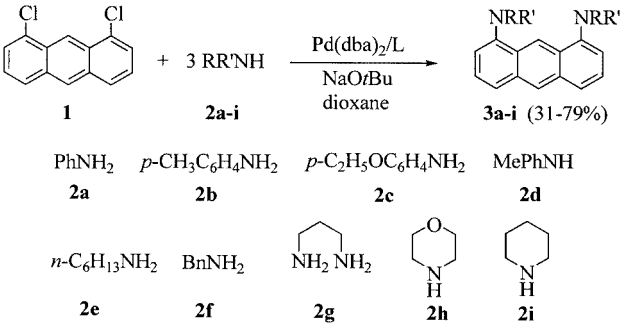
We first studied the feasibility of the diamination of 1,8-dichloroanthracene and 1,8-dichloroanthraquinone, and this method was then used for the construction of macrocycles based on anthracene and anthraquinone skeletons. Finally, the synthesis of bismacrocyclic molecules starting from nitrogen and oxygen-containing macrocycles was carried out.

Results and Discussion

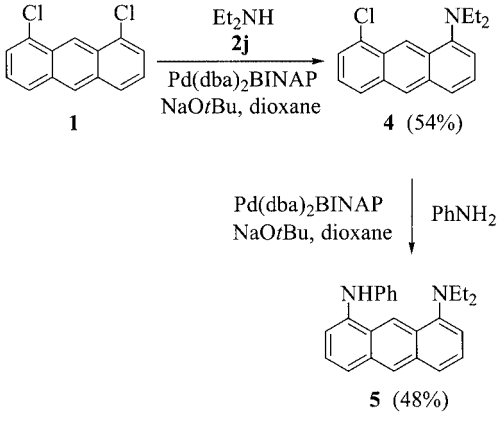
Synthesis of 1,8-Diaminoanthracenes and 1,8-Diaminoanthraquinones

In the course of our preliminary investigations into the palladium-catalysed amination reactions of aryl halides, dramatic differences between the reactivities of primary and secondary linear and cyclic polyamines were observed. A suitable choice of catalytic system was crucial for success of the reactions, and Pd(dba)$_2$ was chosen as a source of palladium in the catalytic coupling since it is known as a useful catalyst in a great number of aryl bromide and aryl chloride amination reactions. In preliminary experiments, electron-rich monophosphanes such as P*t*Bu$_3$ and PCy$_3$ surprisingly appeared to be inefficient in the reactions of 1,8-dichloroanthracene and -anthraquinone with amines. However, BINAP, previously used mainly in the amination of aryl bromides[14c] and of some chloro-substituted N-containing heteroarenes,[20] was found to be readily applicable to our purpose. Dppf was also used, but was less efficient than BINAP in most cases.

1,8-Dichloroanthracene **1** was successfully diaminated when treated with the different amines **2a**−**i**, giving the corresponding 1,8-diamino derivatives **3a**−**i** (Scheme 1). In a standard procedure, one equivalent of 1,8-dichloroanthracene **1** was treated with three equivalents of the corresponding amines **2a**−**i** in the presence of 4−8 mol % Pd(dba)$_2$ and 8−16 mol % BINAP or dppf in boiling dioxane, with NaO*t*Bu used as a base. The amount of the Pd catalyst was increased from the usual 1−2 mol % to 2−4 mol % per chlorine atom to promote good diamination, and the use of 1.5−2 equivalents of BINAP with respect to Pd was found to be best suited. The aromatic primary amines **2a**−**c** gave the corresponding diaminated products **3a**−**c** in good yields (Table 1, entries 1−4). In the case of aniline (**2a**), similar yields were obtained with both the Pd(dba)$_2$/dppf and the Pd(dba)$_2$/BINAP systems. The reaction with the secondary aromatic amine *N*-methylaniline (**2d**) showed a much higher efficiency of BINAP over dppf. Indeed, the diamino anthracene **3d** was prepared in good yield with use of BINAP (Table 1, entries 5, 6) while no reaction was observed with dppf. The primary aliphatic amines **2e** and **2f** gave the diamination products **3e** and **3f** in good yields (Table 1, entries 7, 8), while coupling with propane-1,3-diamine (**2g**) gave **3g** in moderate yield (Table 1, entry 9). It is worth noting that only monoarylation of this diamine was observed, as previously discussed.[21]

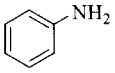
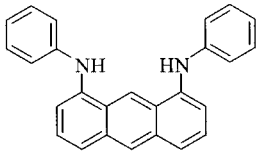
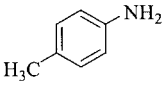
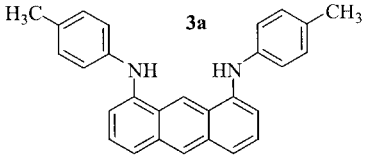
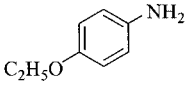
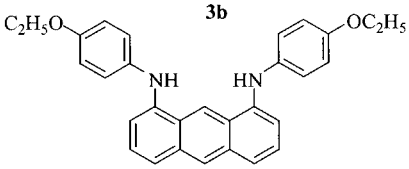
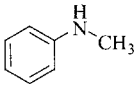
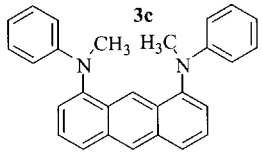
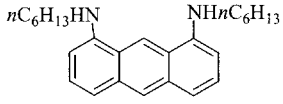
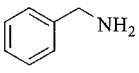
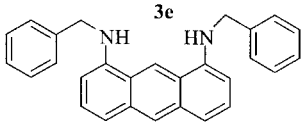
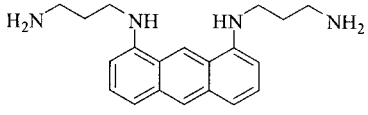
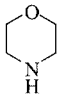
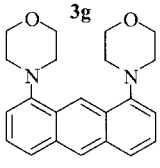
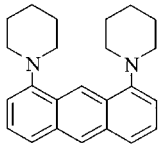


Scheme 1



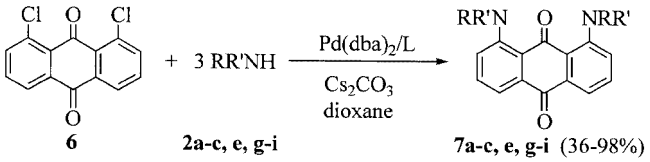
Scheme 2

Table 1. Palladium-catalysed amination of 1,8-dichloroanthracene[a]

Entry	Amine	$Pd(dba)_2$ / ligand, mol%	Ligand	Product	Isolated yield, %
1	 **2a**	8 / 12	dppf	 **3a**	56
2		4 / 8	BINAP		67
3	 **2b**	6 / 12	BINAP	 **3b**	43
4	 **2c**	4 / 8	BINAP	 **3c**	54
5	 **2d**	8 / 16	dppf	 **3d**	0
6		4 / 8	BINAP		56
7	$nC_6H_{13}NH_2$ **2e**	4 / 8	BINAP	 **3e**	79
8	 **2f**	8 / 16	BINAP	 **3f**	62
9	 **2g**	4 / 6	BINAP	 **3g**	48
10	 **2h**	8 / 12	BINAP	 **3h**	78
11		8 / 16	dppf		13
12	**2i**	8 / 16	BINAP	**3i**	31

[a] NaO*t*Bu was used as a base, dioxane as solvent.

The secondary cyclic amines morpholine (**2h**) and piperidine (**2i**) showed different reactivity towards 1,8-dichloroanthracene. The first gave the corresponding diamino product **3h** in high yield (Table 1, entry 10), but only a moderate yield was observed for **3i** (Table 1, entry 11). The higher efficiency of morpholine may be explained by the different basicities of morpholine (pK_a = 8.33) and piperidine (pK_a = 11.12). It is important to note that no diamination reaction was achieved with the acyclic aliphatic secondary amine diethylamine (**2j**), only the monoamino derivative **4**

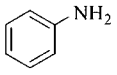
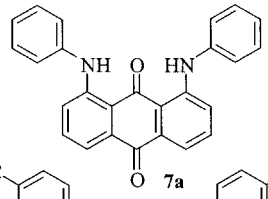
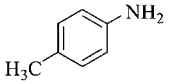
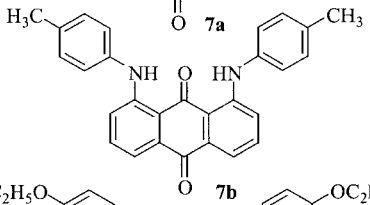
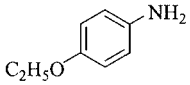
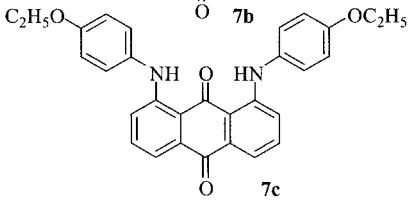
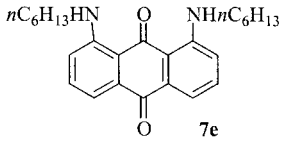
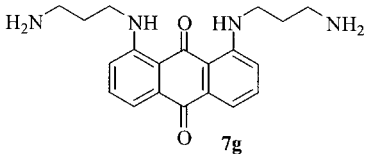
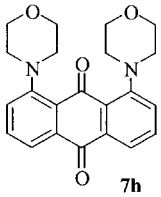
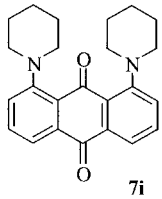


Scheme 3

being isolated, in 54% yield (Scheme 2). This compound may serve as a precursor for the synthesis of an unsymmetrically substituted anthracene, since the remaining chlorine atom can be substituted by aniline to form **5** in 48% yield.

The Pd-catalysed coupling of 1,8-dichloroanthraquinone (**6**) with amines was performed by the same method as de-

Table 2. Palladium-catalysed amination of 1,8-dichloroanthraquinone[a]

Entry	Amine	$Pd(dba)_2$ / ligand, mol%	Ligand	Product	Isolated yield, %
1	 **2a**	8 / 12	dppf	 **7a**	98
2	 **2b**	4 / 8	BINAP	 **7b**	95
3	 **2c**	4 / 8	BINAP	 **7c**	56[b]
4		8 / 12	BINAP		98
5	$nC_6H_{13}NH_2$ **2e**	4 / 8	BINAP	 **7e**	98
6	 **2g**	4 / 6	BINAP	 **7g**	48
7	 **2h**	8 / 12	BINAP	 **7h**	79
8	 **2i**	8 / 12	dppf	 **7i**	36
9		4 / 8	BINAP		31

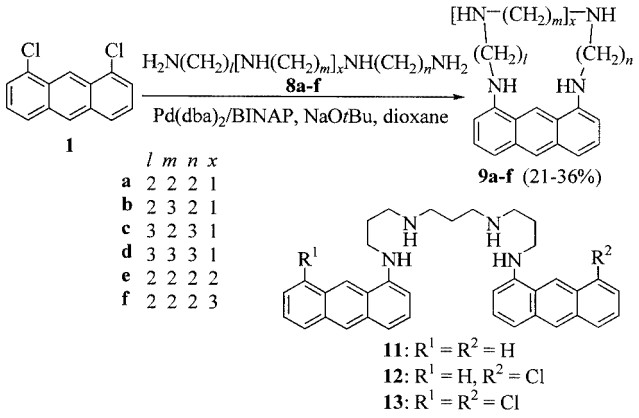
[a] Cs_2CO_3 was used as a base, dioxane as solvent. [b] +15% 1-chloro-8-(4-ethoxyphenylamino)anthraquinone.

scribed above, except for NaO*t*Bu being replaced by Cs_2CO_3, which does not affect anthraquinone (Scheme 3).

Treatment with the primary aromatic amines **2a**−**c** afforded the corresponding products **7a**−**c** in excellent yields (95−98%) (Table 2, entries 1, 2, 4). Dppf was shown to be quite efficient in the coupling reaction with aniline (Table 2, entry 1), and the primary aliphatic amine **2e** also gave the diamino derivative **7e** in remarkably high yield (Table 2, entry 5). Treatment with propane-1,3-diamine produced compound **7g** in good yield (Table 2, entry 6), again with only monoarylation of the diamine being observed. All these reactions proceeded more smoothly with dichloroanthraquinone than with dichloroanthracene. The reaction pattern with the cyclic aliphatic amines **2h** and **2i** was similar to that seen with 1,8-dichloroanthracene (Table 2, entries 7−9). In contrast, both the aromatic and the aliphatic acyclic secondary amines *N*-methylaniline (**2d**) and diethylamine (**2j**) proved to be inefficient reactants, since the corresponding diamino derivatives of anthraquinone were not obtained. Diamino derivatives of anthracene and anthraquinone were successfully prepared through Pd-catalysed treatment of 1,8-dichloroanthracene and 1,8-dichloroanthraquinone with aromatic and aliphatic primary amines and cyclic secondary amines. The substitution of one chlorine atom by an amino group does not substantially affect the reactivity of the remaining halogen atom, unlike in monoamination of dihalobenzenes, in which the second amination reaction is hindered.[22]

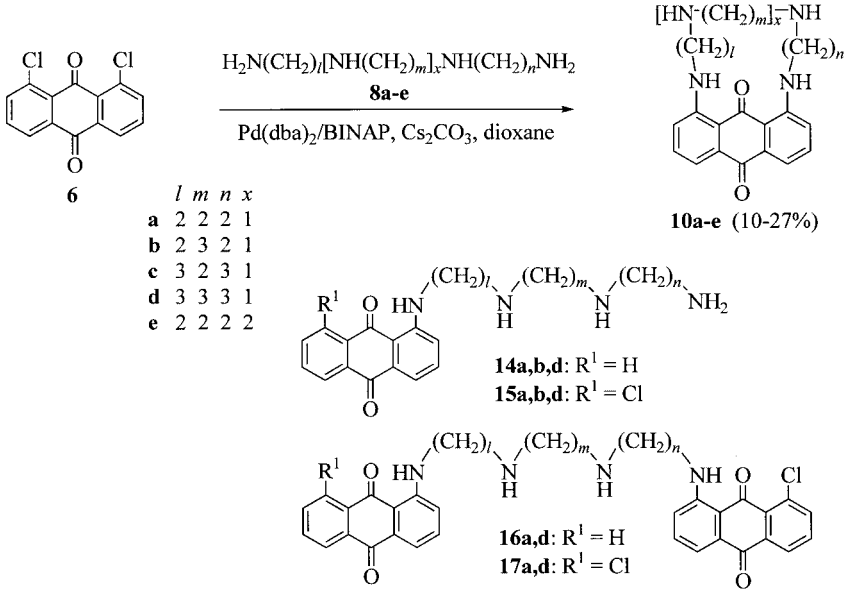
Polyazamacrocycles Derived from 1,8-Dichloroanthracene and 1,8-Dichloroanthraquinone

Macrocyclic compounds containing anthracene and anthraquinone moieties were synthesised by treatment of equimolar amounts of the linear polyamines **8a**−**f** with anthracene (**1**) (Scheme 4) and anthraquinone (**6**) (Scheme 5). The $Pd(dba)_2$/BINAP catalytic system (4−8 mol %) was used, in the presence of NaO*t*Bu or Cs_2CO_3 when the starting materials were dichloroanthracene and dichloroanthraquinone, respectively. Diluted solutions of the reagents in dioxane were used (0.017−0.025 M) to avoid undesirable formation of oligomers. Longer heating times (48−103 h) were required to complete the cyclisation reaction (Table 3).



Scheme 4

The reactions resulted in the formation of polyazamacrocycles **9a**−**f** and **10a**−**e** as results of intramolecular cyclisation. The macrocycles **9a**−**f** were prepared in 21 to 36% yields (Table 3, entries 1−6), whereas lower yields (10−27%, Table 3, entries 7−14) were generally observed for compounds **10a-e**. The macrocycles **9a**−**f** were obtained as brown solids after chromatography on silica, and compounds **10a/10b** and **10c**−**e** appeared as red and lilac solids,



Scheme 5

Table 3. Palladium-catalysed amination of 1,8-dichloroanthracene and 1,8-dichloroanthraquinone by polyamines

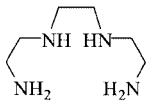
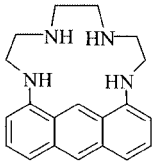
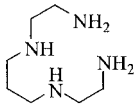
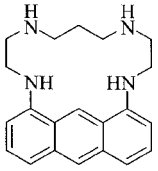
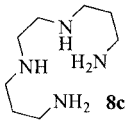
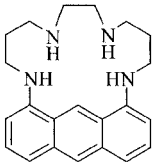
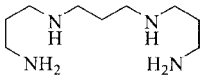
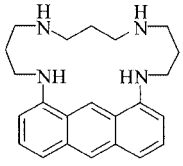
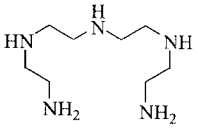
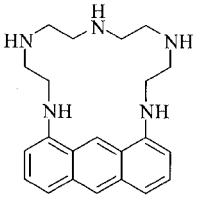
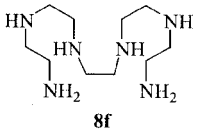
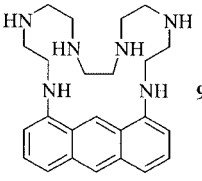
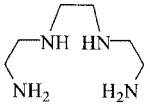
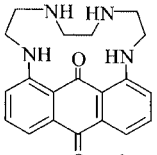
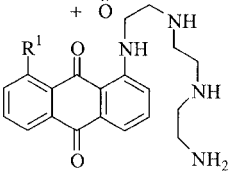
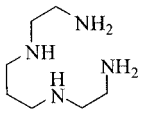
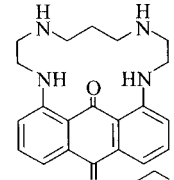
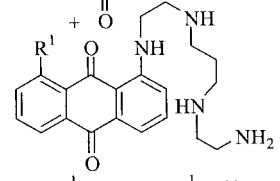
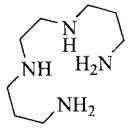
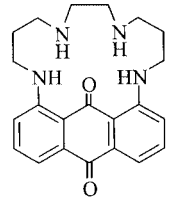
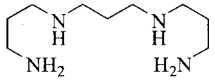
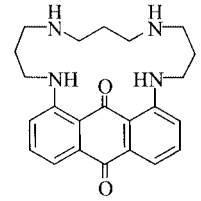
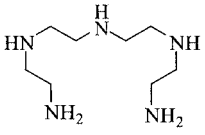
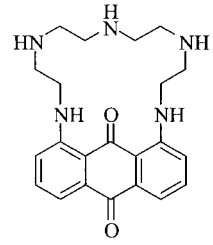
Entry	Amine	Aryl halide	$Pd(dba)_2$ / BINAP, mol%	Concentration of reagents, M	Reaction time (reflux), h	Product	Isolated yield, %
1	 **8a**	**1**	8/9	0.017	74	 **9a**	33
2	 **8b**	**1**	8/9	0.025	48	 **9b**	36
3	 **8c**	**1**	8/9	0.025	48	 **9c**	24
4	 **8d**	**1**	8/9	0.02	75	 **9d**	21[a]
5	 **8e**	**1**	4/4.5	0.017	72	 **9e**	26
6	 **8f**	**1**	4/4.5	0.017	72	 **9f**	22
7	 **8a**	**6**	8/9	0.017	73	 **10a**	14
8			16/18	0.01	103	 **14a**: R^1 = H; **15a**: R^1 = Cl	9 24 (entry 7) 30[b] (entry 8)

Table 3. *(continued)*

Entry	Amine	Aryl halide	$Pd(dba)_2$ / BINAP, mol%	Concentration of reagents, M	Reaction time (reflux), h	Product	Isolated yield, %
9	 **8b**	**6**	8/9	0.025	96	 **10b**	8
10			16/18	0.017	76		19
						 **14b**: R^1 = H; **15b:** R^1 = Cl	0 (entry 9) 18 (entry 10)
11	 **8c**	**6**	8/9	0.025	96	 **10c**	25
12	 **8d**	**6**	8/9	0.017	73	 **10d**	3[c]
13			16/18	0.01	102		10[d]
14	 **8e**	**6**	8/9	0.017	72	 **10e**	27

[a] 7% of a mixture of **11** + **12** + **13**. [b] 8% of a mixture of **16a** + **17a**. [c] 9% of a mixture of **14d** + **15d**. [d] 12% of a mixture of **16d** + **17d**.

respectively. Dichloroanthracene was totally converted in these reactions, whereas the consumption of dichloroanthraquinone was not complete (90−95%). Noticeable reduction of the chlorine atoms of dichloroanthraquinone was observed, generally resulting in mixtures of anthraquinone, 1-chloroanthraquinone and unchanged 1,8-dichloroanthraquinone in 1:2:1 mol ratio. Increasing the amount of catalyst may either enhance (Table 3, entries 10, 13) or lower the reaction yield (Table 3, entry 8). No oligomeric or monoaminated anthracenes were detected among the products obtained from treatment of dichloroanthracene with polyamines **8**. Only the reaction with **8d** produced − together with **9d** − a small amount of a mixture of bis(anthracenyl)substituted tetraamines **11**−**13**, as attested to by MALDI-TOF and NMR spectroscopy: a set of eight singlets in the 8.2−8.8 ppm region of the ^{1}H NMR spectrum attributable to H-9 and H-10 protons of the anthracene moiety was observed, together with a set of four signals in the 143−144 ppm area of the ^{13}C NMR spectrum corresponding to the C1 carbon atom of anthracene.

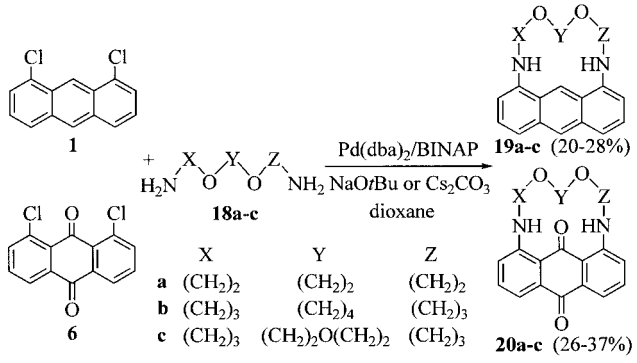
In contrast, treatment of dichloroanthraquinone (**6**) with polyamines resulted in substantial formation of linear compounds: mixtures of 1-amino- and 1-amino-8-chloroanthraquinones **14a**, **14b** and **14d** and **15a**, **15b** and **15d** (yields up to 30%), as well as some compounds with higher molecular weight and anthraquinone/amine ratios of 2:1 (**16a**, **16d**, **17a**, **17d**). Only primary nitrogen atoms were arylated in all

these reactions, as also reported for treatment of aryl halides with triamines.[21a]

It has been demonstrated above that 1,8-dichloroanthraquinone reacts more easily than 1,8-dichloroanthracene with monoamines, due to its more pronounced electron-deficient character. The opposite behaviour towards polyamines is surprising, but is probably due to the formation of intramolecular hydrogen bonds between NH protons and the oxygen in the anthraquinone. The formation of linear species and the partial reduction of the chlorine atom may have the same origin. This is not the case for anthracene or for the reactions with di- and trioxadiamines (vide infra).

Diazacrown Ethers Based on Anthracene and Anthraquinone Moieties

A new family of diazacrown ethers incorporating anthracene or anthraquinone moieties was synthesised by the same method of Pd-catalysed amination of 1,8-dichloroanthracene and 1,8-dichloroanthraquinone, through the employment of 3,6-dioxa-1,8-diaminooctane (**18a**), 4,9-dioxa-1,12-diaminododecane (**18b**) and 4,7,10-trioxa-1,13-diaminotridecane (**18c**). The experimental procedure defined for the synthesis of tetraazamacrocycles **9** and **10** was successfully used for the synthesis of diazacrown ethers **19a−c** and **20a−c** (Scheme 6, Table 4).



Scheme 6

The yields of the anthracene-based macrocycles **19a−c** ranged from 20 to 29% (Table 4, entries 1−3), while the anthraquinone-based crown ethers **20a−c** were obtained in higher yields 29−37% (Table 4, entries 4−7). Complete conversion of starting aryl halides was observed in all cases. The target macrocycles were isolated by column chromatography as either brown (**19a−c**) or red (**20a−c**) solids.

The by-products formed in these reactions were identified as cyclic and linear oligomers. Treatment of **1** with diamines provided rather small amounts (not exceeding 10%) of cyclic dimers **21a−c** ($x = 2$) (Figure 1). The cyclic trimer and tetramer **21c** ($x = 3$ and 4) were formed in 9% yield when the starting diamine was **18c**, while the linear compounds **22a−24a** were obtained in 3% yield when **1** was treated with **18a**. In the course of the amination by **18b**, 1-amino-8-chloroanthracene **25** was isolated in 18% yield and fully characterised.

Treatment of **6** with dioxa- and trioxadiamines **18a−c** resulted in higher ratios of cyclic oligomers **26a−c** (Figure 2). It is interesting to note that dioxadiamine **18a** generated only a tiny quantity (about 2%) of a mixture of cyclic tetra- and pentamers, while arylation of diamines **18b** and **18c** yielded significant amounts of cyclic and linear oligomers of type **26**, **27** and **28**. The cyclic dimers **26b** and **26c** ($x = 2$), as well as the cyclic trimer **26c** ($x = 3$), were isolated, while mixtures of higher mass oligomers were also obtained. The formation of cyclic oligomers with $n = 9-10$ and molecular weights over 4000 was observed in the MALDI-TOF spectra.

As expected, the compositions of the reaction mixtures strongly depended on the concentrations of the reagents. With dilution from 0.025 M to 0.017 M, the yield of the desired adduct **20c** was increased from 29% to 37%, while the amount of higher-mass oligomers was decreased.

Tetraaza and Diazapolyoxamacrocycles Derived from 1,5-Disubstituted Anthracene

The conditions described above for the catalytic amination of aryl halides were used for the synthesis of macrocycles based on 1,5-disubstituted anthracene. All four tetraamines **8a−d** were treated with 1,5-dichloroanthracene (**29**) (Scheme 7).

The geometry of the starting compound **29** suggests that the aliphatic chain should be long enough to be involved in a cyclisation reaction. Indeed, tetraamine **8a** was unable to form the desired macrocycle **30a** in a reasonable yield. Only traces of **30a** were detected, together with the cyclic dimer **31a** ($x = 2$), which was isolated in 18% yield, and trimer **31a** ($x = 3$). Higher selectivity was observed with the tetraamine **8b**, the chain of which is only one carbon atom longer than that of **8a**. In this case the monomeric cycle **30b** was obtained in 20% yield (Table 5, entry 2), together with a very small amount of a mixture of cyclic dimer and trimer (**31b**, $x = 2,3$). The cyclic dimer **31b** ($x = 2$) was also isolated in 10% yield as a separate fraction containing small amounts of the cyclic trimer and tetramer ($x = 3,4$). In addition, a mixture of the target macrocycle **30b** together with cyclic oligomers and linear compounds **32b** ($x = 1-3$) was isolated by column chromatography in 15% yield. The same reaction was successfully carried out with tetraamine **8c** to provide **30c** in 34% yield, together with traces of cyclic dimer and trimer **31c** ($x = 2, 3$) (Table 5, entry 3). Tetraazacyclophane **30d** was obtained in 22% yield (Table 5, entry 4).

Treatment of 1,5-dichloroanthracene (**29**) with dioxadiamine **18a**, with a chain length identical to that in **8a**, did not result in the formation of the macrocycle of type **33** but rather afforded a cyclic dimer **34a** in a low 8% yield and a mixture of linear oligomers **35a−37a** in 18% yield (Scheme 8, Table 5, entry 5). Both reactions starting from the diamines **18b** and **18c** resulted in the formation of the corresponding oxaazacyclophanes **33b** and **33c** in reasonable 20−24% yields (Table 5, entries 6, 7).

Linear by-products of the type **35−37b/37c** were formed in significant quantities (7−10%) while the cyclic dimer **34c**

Table 4. Palladium-catalysed amination of 1,8-dichloroanthracene and 1,8-dichloroanthraquinone by dioxa- and trioxadiamines[a]

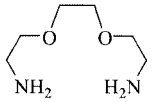
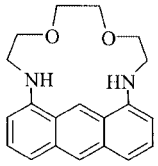
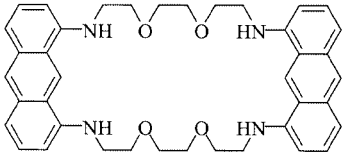
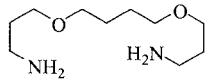
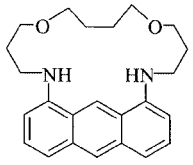
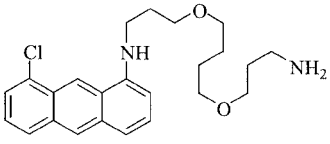
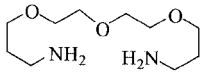
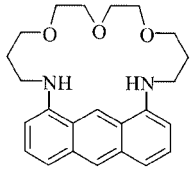
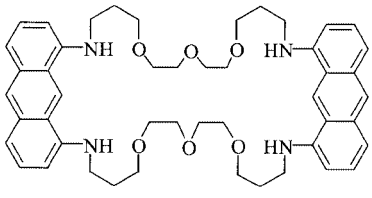
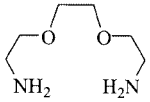
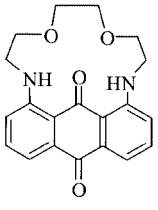
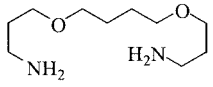
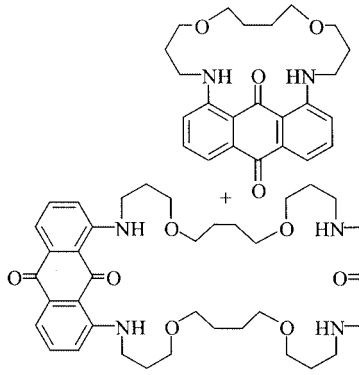
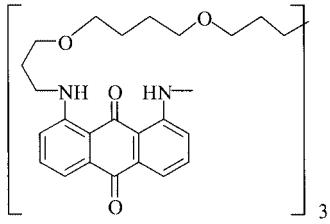
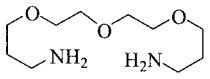
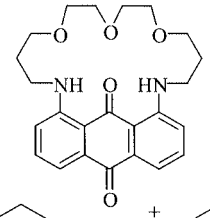
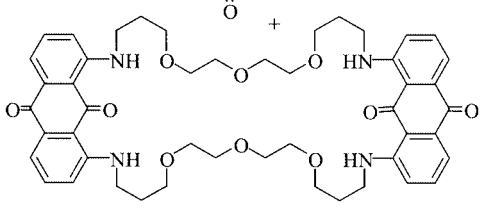
Entry	Amine	Aryl halide	Concentration of reagents, M	Reaction time (reflux), h	Product	Isolated yield, %
1	 **18a**	**1**	0.02	103	 **19a**	28[b]
					+	
					 **21a** ($x = 2$)	8
2	 **18b**	**1**	0.017	77	 **19b**	20[c]
					+	
					 **25**	18
3	 **18c**	**1**	0.025	78	 **19c**	25[d]
					+	
					 **21c** ($x = 2$)	10
4	 **18a**	**6**	0.017	96	 **20a**	36[e]

Table 4. *(continued)*

Entry	Amine	Aryl halide	Concentration of reagents, M	Reaction time (reflux), h	Product	Isolated yield, %
5	 **18b**	**6**	0.017	77	 **20b** + **26b** (x = 2) +  **26b** (x = 3)	33[f] 12 8
6	 **18c**	**6**	0.025	72	 **20c**	29[g] (entry 6) 37[h] (entry 7)
7		**6**	0.017	80	 **26c** (x = 2)	18[h] (entry 7)

[a] Pd(dba)$_2$/BINAP 8/9 mol %. [b] A mixture of **22a**+**23a**+**24a** (x = 1) isolated in 3% yield. [c] A mixture of **23b**, **24b** (x = 1) and **21b** (x = 2, 3) isolated in 4% yield. [d] A mixture of trimer and tetramer **21c** (x = 3, 4) isolated in 9% yield. [e] Tetramer and pentamer **26a** (x = 4, 5) obtained in 2% yield. [f] Higher mass cyclic (**26b**) and linear (**27b, 28b**) oligomers isolated in 20% yield. [g] Higher mass cyclic (**26c**, $x > 1$) and linear (**27c, 28c**) oligomers isolated in 48% yield. [h] Higher mass cyclic (**26c,** $x > 2$) and linear (**27c, 28c**) oligomers isolated in 25% yield.

(x = 2) was isolated only in a tiny 4% yield, with dimer **34b** (x = 2) and trimer **34b** (x = 3) being detected only by mass spectrometry (m/z = 755.96, 1134.63, respectively).

The ^{1}H NMR spectra of the macrocycles **30b**−**d** and **33b**/**33c** each present a similar feature: all the methylene protons of the aliphatic chain are diastereotopic. The closer the methylene group is to the centre of the chain (i.e., the closer it is located to the centre of the aromatic system), the lower the chemical shift of the corresponding protons. Typically, the protons of the central methylene group(s) are shifted upfield by 1.7−1.8 ppm from the shifts observed in cyclic dimers or in linear oligomers. A similar upfield shift was observed for methylene protons in polyazamacrocycles constructed from 9,10-anthracene.[23]

Amination of 1,5-Dichloroanthraquinone

The amination of 1,5-dichloroanthraquinone (**38**) with tetraamines **8a**−**d** and di- and trioxadiamines **18a**−**c** produced results substantially different from those observed with 1,5-dichloroanthracene (Scheme 9). The diazacrown

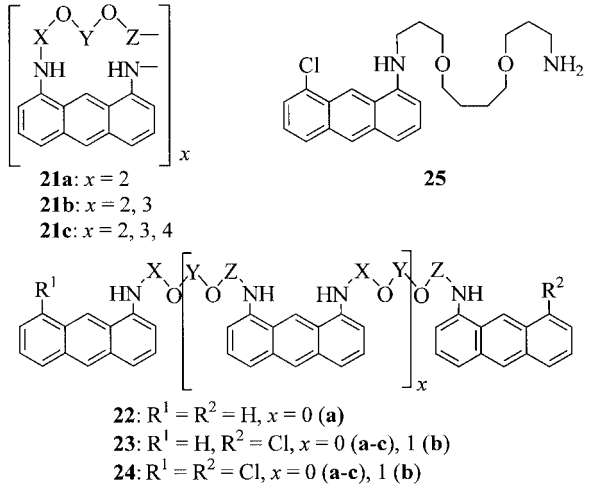


Figure 1. By-products formed upon treatment of **1** with dioxa- and trioxadiamines **18a**−**c**

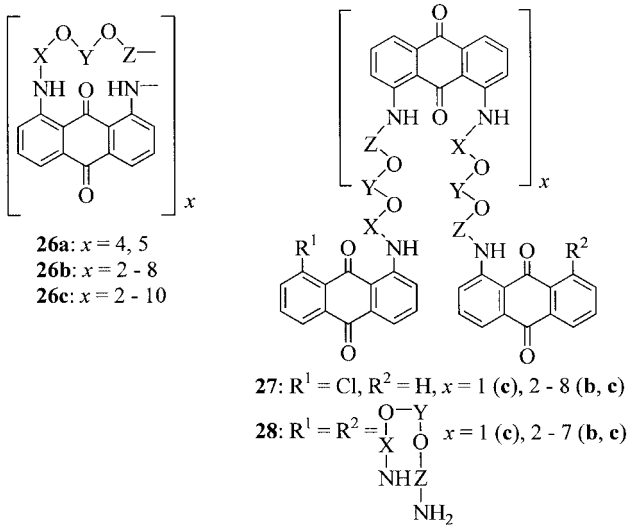
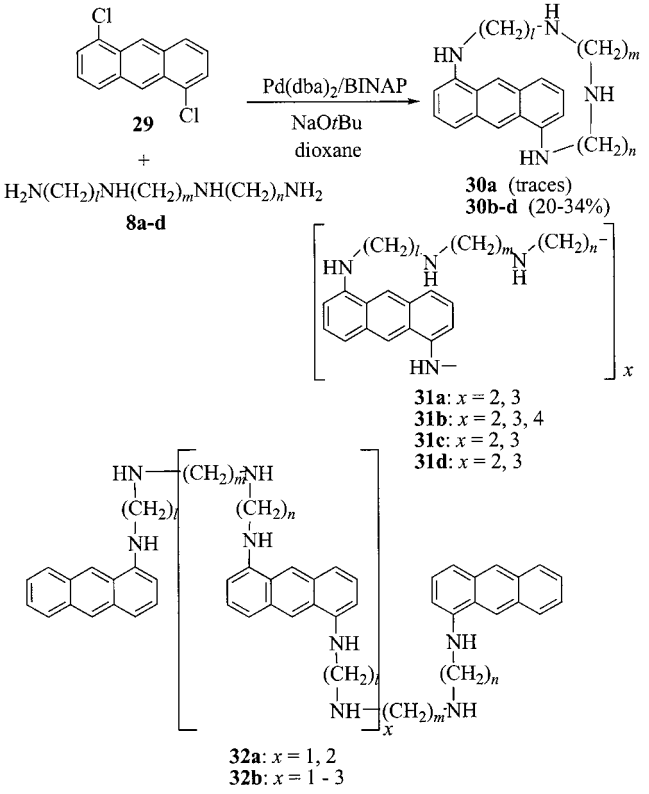


Figure 2. By-products formed upon treatment of **6** with dioxa- and trioxadiamines **18a**−**c**

ethers **39b** and **39c** (Table 6, entries 2,3) were obtained in good yields, provided that Cs_2CO_3 was employed as a base instead of NaO*t*Bu. The amination of the dioxadiamine **18a**, with the shorter chain, afforded not the target macrocycle **39a**, but the cyclic dimer **40a** in 18% yield (Table 6, entry 1). The higher linear oligomers **41a** and **42a** were also identified by MALDI-TOF spectrometry. In the case of **18b**, the target macrocycle **39b** was obtained in 30% yield and the cyclic dimer **40b** ($x = 2$) and trimer ($x = 3$) were isolated in 10% and 6% yields, respectively. In contrast, when **38** was treated with **18c**, besides the monomeric cycle **39c** (isolated in 28% yield), mixtures of other higher mass cyclic **40c** ($x = 2-9$) and linear oligomers **41c** and **43c** were collected.

The ^{1}H NMR spectra of the oxoazacyclophanes **39b** and **39c** show the same feature as described previously for **30b**−**d** and **33b**/**33c**: methylene protons located above the anthraquinone moiety are again shifted upfield, although



Scheme 7

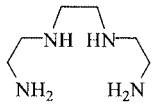
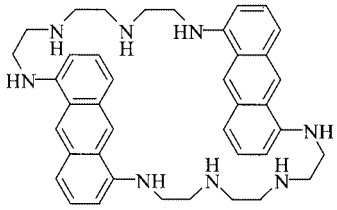
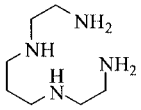
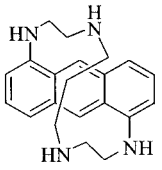
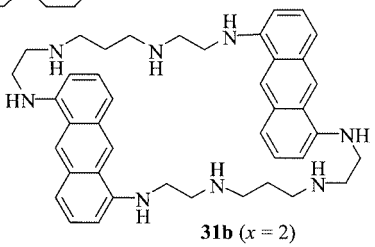
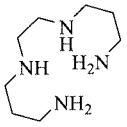
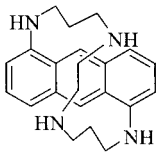
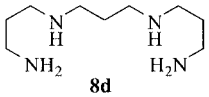
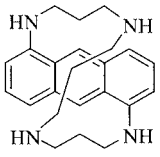
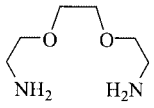
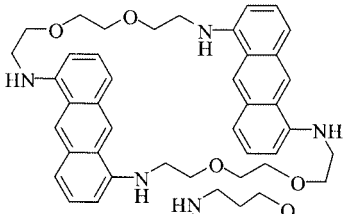
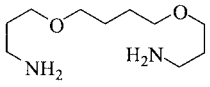
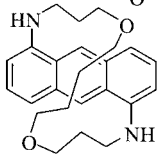
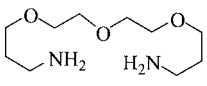
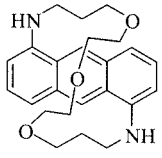
the shift is weaker than those observed for the anthracene-based cyclophanes and no higher than 1.2 ppm.

Surprisingly, the amination of 1,5-dichloroanthraquinone (**38**) by tetraamines **8a**−**d** did not result in the formation of the corresponding tetraazamacrocycles (Scheme 10). Only the 1-amino-5-chloro-substituted anthraquinones **44a**−**d** were obtained, in 16−28% yields, together with the bis-(aryl)substituted tetraamines **45a**−**d** and **46a**−**d**, which were formed in 5−26% yields (Table 6, entries 4−9). The consumption of 1,5-dichloroanthraquinone was not quantitative, as had already been found when 1,8-dichloroanthraquinone was treated with tetraamines (Scheme 5). Two attempts to promote cyclisation were undertaken. The first involved the use of double the amount of the $Pd(dba)_2$/BINAP catalytic system, the second the use of the new ligand 2-di-*tert*-butylphosphanylbiphenyl.[15] These attempts were unsuccessful, however, the formation of the desired cycle **47d** being observed only spectrally, together with **45d**; moreover, the latter ligand, which has proved efficient in other amination reactions of aryl halides, was found to be less active in our case.

Synthesis of Anthracene Derivatives Containing Two Macrocycles

1,4,8,11-Tetraazacyclotetradecane (cyclam) plays an outstanding role among the numerous saturated tetraazamacrocycles, due to its versatility in the complexation of metal ions. The synthesis of molecules with two cyclam rings arranged in a face-to-face manner is of great interest

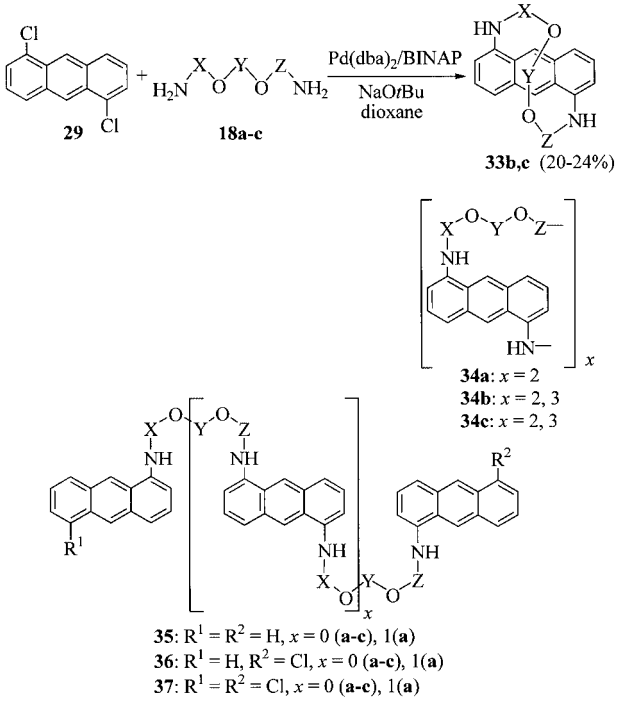
Table 5. Palladium-catalysed amination of 1,5-dichloroanthracene by tetraamines and di- and trioxadiamines[a]

Entry	Amine	Reaction time (reflux), h	Product	Isolated yield, %
1	 **8a**	72	 **31a** (x = 2)	18[b]
2	 **8b**	75	 **30b** +  **31b** (x = 2)	20 + 10[c]
3	 **8c**	78	 **30c**	34[d]
4	 **8d**	80	 **30d**	22[e]
5	 **18a**	58	 **34a** (x = 2)	8[f]
6	 **18b**	54	 **33b**	24[g]
7	 **18c**	56	 **33c**	20[h]

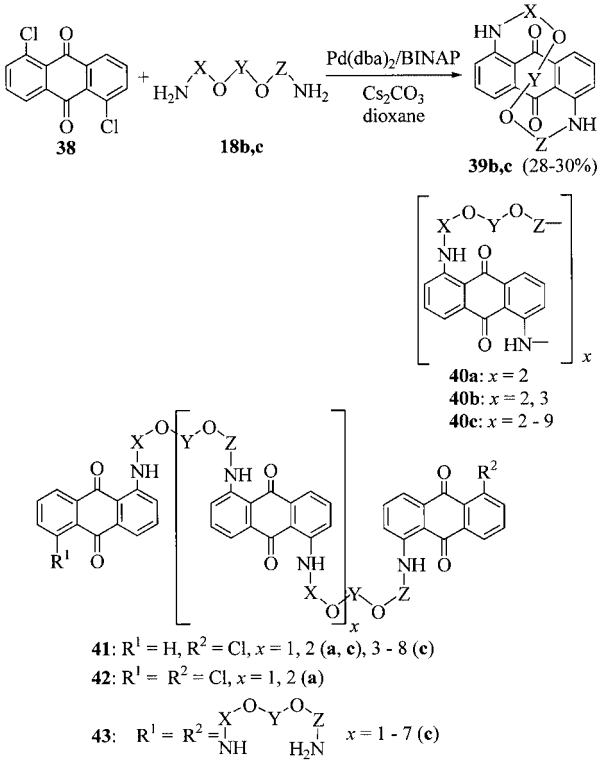
[a] $Pd(dba)_2$/BINAP 8/9 mol %, c = 0.01 M. [b] A mixture of **31a** (x = 3), **32a** (x = 1, 2), traces of **30a**. [c] 15% of **31b** (x = 2−4) **+32b** (x = 1−3). [d] Traces of **31c** (x = 2, 3). [e] 5% of **31d** (x = 2, 3). [f] 18% of **35a**−**37a** (x = 0, 1). [g] 10% of **35b**−**37b** (x = 0). [h] 7% of **35c**−**37c** (x = 0), 4% of dimer **34c** (x = 2).

to chemists, because of the intriguing properties of their bimetallic complexes. Recently we have observed the Pd-catalysed arylation of cyclam **48** by *p*-bromobiphenyl and *p*-bromobenzonitrile.[19c] We chose 1,8-disubstituted anthracene as a spacer to prepare a biscyclam. The $Pd(dba)_2$/BINAP catalytic system was initially preferred to the expensive PPF-OMe ligand[24] utilised for cyclam amination. Treatment of 1,8-dichloroanthracene with cyclam in the presence of 4−8 mol % of $Pd(dba)_2$/BINAP and NaO*t*Bu gave only unsubstituted anthracene **49**, the reduction product of the starting dichloride (Scheme 11).

The same reaction with the less basic cyclen **50** in the presence of 5 mol % $Pd(dba)_2$/BINAP successfully yielded a mixture of monocyclen-substituted anthracenes **51** (26%) and **52** (13%), together with anthracene **49** (Scheme 12). Heating of the reaction mixture for a longer time and ad-



Scheme 8



Scheme 9

dition of a larger amount of catalyst did not provide any biscyclen-substituted anthracene. The use of an electron-rich tri-*tert*-butylphosphane in this reaction was also unsuccessful.

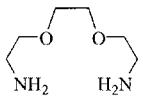
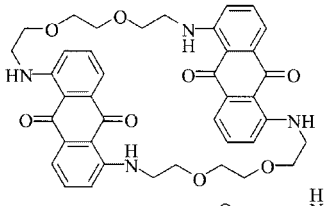
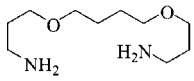
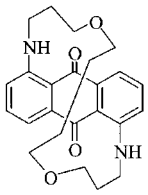
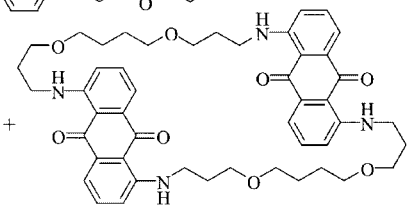
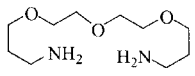
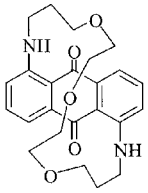
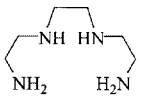
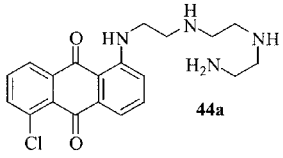
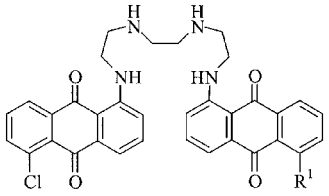
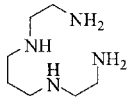
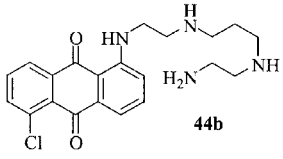
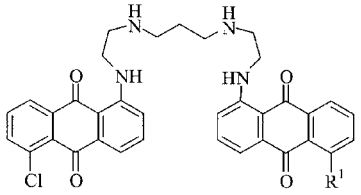
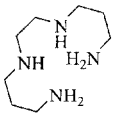
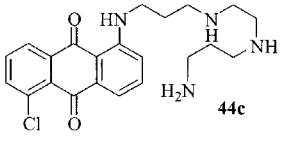
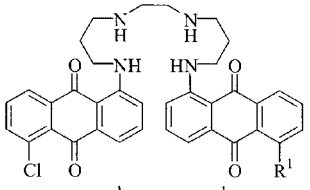
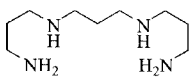
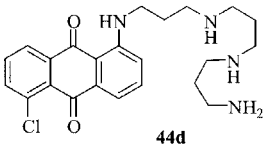
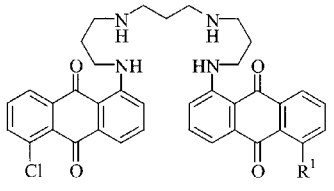
In order to avoid undesirable reduction, *N*,*N*′,*N*′′-trisubstituted cyclams − tritosyl and triBoc derivatives − were used instead of free cyclam, which contains four secondary amino groups capable of reducing dichloroanthracene. Nevertheless, no arylation occurred.[25] Another trimethyl derivative of cyclam − *N*,*N*′*N*′′-trimethylcyclam **53** − appeared to be appropriate for our purpose, with BINAP and P*t*Bu$_3$ as supporting ligands. Reactions promoted by Pd precursor [Pd(dba)$_2$, 16 mol %] with P*t*Bu$_3$ produced the monocyclam derivative of anthracene **54** in 45% yield, but only traces of the desired biscyclam **56** were detected in the mass spectrum (Scheme 13). The first attempt to synthesise **56** with the aid of the Pd(dba)$_2$/BINAP catalytic system (8 mol %) also yielded monocyclam-substituted anthracenes **54** and **55** (each in ca. 20% yield), the target compound **56** being detected only as a mixture with **54** and **55** (10% yield of the mixture). A twofold increase in the amount of the catalyst and ligand (16 mol %] resulted in the formation of the target biscyclam-substituted anthracene **56** in 10% yield, while the monosubstituted anthracene **54** was obtained in 35% yield. In all cases longer heating times in dioxane (ca. 100 h) were required to complete the reaction. Attempts to increase the yield of **56** by use of 2-(di-*tert*-butylphosphanyl)-1,1′-biphenyl were unsuccessful. The relatively good results obtained with *N*,*N*′,*N*′′-trimethylcyclam, in relation to those involving the free cyclam, may also be due to stronger complexation of palladium by cyclam than by its trimethyl derivative.

The same methodology was used for the synthesis of bisazacrown-substituted anthracene. We investigated the synthesis of face-to-face ring systems containing two azacrown moieties starting from 1-aza-15-crown-5 (**57**) and 1,8-dichloroanthracene in the presence of the Pd(dba)$_2$/BINAP catalytic system (Scheme 14). The target bisazacrown-substituted anthracene **58** was obtained in 11% yield. We also observed the formation of the monosubstituted anthracene **59** in 44% yield, as the product of monoarylation and chlorine reduction. It is clear that the formation of the monoamination product with the reduced second chlorine atom is the main hindrance on the pathway to the target bisazacrown molecule. However, monoamination by azacrown ethers can be performed under mild conditions. Arylation of azacrown ethers by aryl bromides was previously studied by Witulski and Buchwald.[2c,26] Very recently a non-catalytic method for the arylation of diazacrown ethers by difluoroanthraquinones has been put forward.[27]

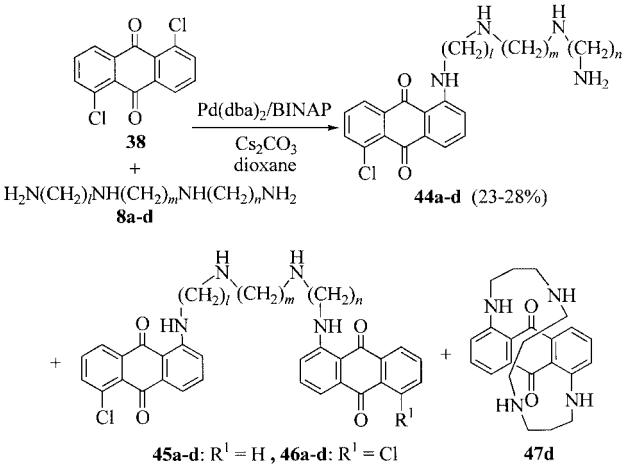
Conclusion

In conclusion, we have shown that Pd-catalysed amination of dichloroanthracene and dichloroanthraquinone is a convenient method to synthesise the otherwise not readily accessible corresponding diamino derivatives. Linear polyamines and polyoxapolyamines may be used for the one-pot synthesis of macrocycles of different sizes and possessing various numbers of nitrogen and oxygen atoms, and new types of nitrogen- and oxygen-containing macrocycles con-

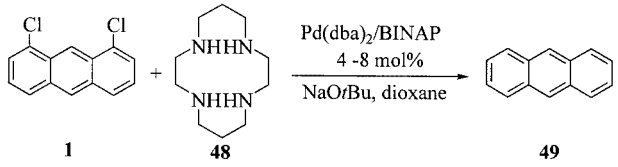
Table 6. Palladium-catalysed amination of 1,5-dichloroanthraquinone by tetraamines and di- and trioxadiamines[a]

Entry	Amine	Reaction time (reflux), h	Product	Isolated yield, %
1	 **18a**	70	 **40a** ($x = 2$)	18[b]
2	 **18b**	70	 **39b** +  **40b** ($x = 2$)	30 + 10[c]
3	 **18c**	94	 **39c**	28[d]
4	 **8a**	72	 **44a** +  **45a**: R^1 = H; **46a**: R^1 = Cl	28 + 10
5	 **8b**	72	 **44b** +  **45b**: R^1 = H; **46b**: R^1 = Cl	25 + 5
6	 **8c**	72	 **44c** +  **45c**: R^1 = H; **46c**: R^1 = Cl	23 + 10
7	 **8d**	72	 **44d** +  **45d**: R^1 = H; **46d**: R^1 = Cl	5 + 17[g]
8[e]		72		25 + 26[g,h]
9[f]		72		16 + 11

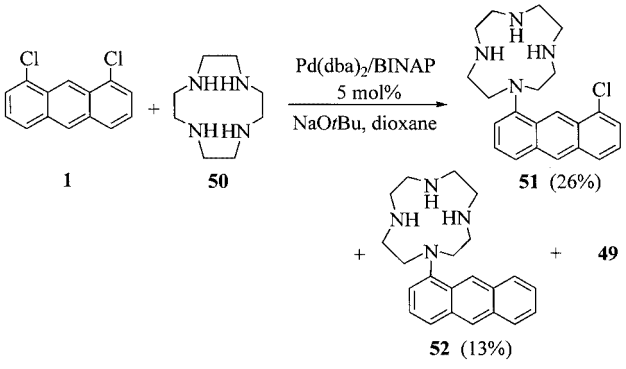
[a] $Pd(dba)_2$/BINAP 8/9 mol %, c = 0.01 M. [b] A mixture of **41a**, **42a** (x = 1, 2). [c] 6% of trimer **40b** (x = 3). [d] 43% of a mixture of **40c** (x = 2−9), **41c** (x = 1−8), **43c** (x = 1−7) (4 fractions). [e] $Pd(dba)_2$/BINAP 16/18 mol %. [f] $Pd(dba)_2$/L 10/10 mol %, L = 2-(di-*tert*-butylphosphanyl)biphenyl. [g] Contains **44d**. [h] Contains **47d**.



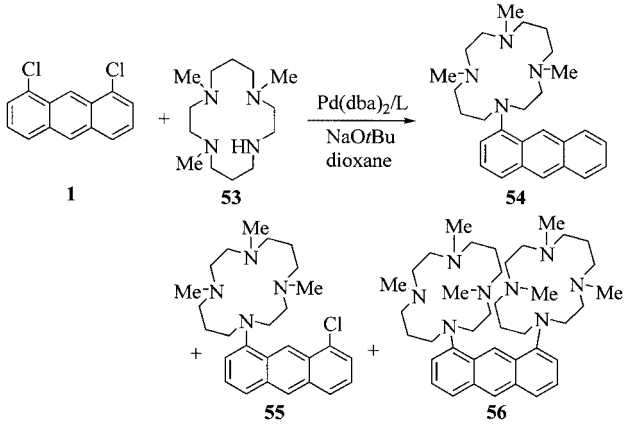
Scheme 10



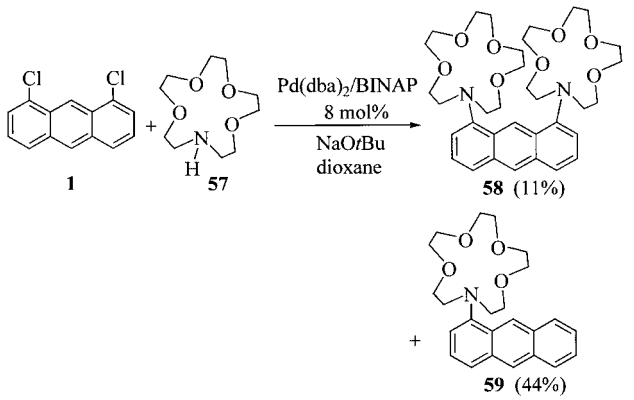
Scheme 11



Scheme 12



Scheme 13



Scheme 14

taining anthracene and anthraquinone moieties were thus obtained. Palladium-catalysed amination of 1,8-dichloroanthracene proved to be an useful tool for the synthesis of novel bistetraazamacrocycles and bisazacrown ethers in face-to-face arrangements. The capabilities of all these new macrocycles for complexation with transition metals are currently being studied.

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Bruker AM200 spectrometer, or at 500 and 125 MHz, respectively, on a Bruker DRX500 spectrometer, and referenced to the residual protons or carbon signals of the deuterated solvent. Infrared spectroscopy was carried out on a Perkin−Elmer 1600 Series FT-IR spectrometer. MALDI-TOF spectra were recorded on a Bruker Daltonics Proflex III device with dithranol as a matrix. Elemental analyses were carried out with a Fisons EA 1108 CHNS instrument. Gas chromatography analyses were carried out on a Hewlett−Packard HP-5890 Series II gas chromatograph fitted with a HP-1 capillary column (25 m, 0.20 mm, 0.11 mm). Thin-layer chromatography was carried out on E. Merck TLC plates (Silica Gel 60F-254).

Reactions under argon atmosphere were carried out by standard Schlenk techniques. All reagents were used directly as obtained commercially unless otherwise noted. Dioxane purchased from SDS Chemical Co. was distilled under argon from sodium benzophenone ketyl. Sodium *tert*-butoxide was purchased from Aldrich Chemical Co. and stored under nitrogen. Small amounts were taken as needed, stored in a Schlenk tube up to 2 weeks, and quickly weighed at the air. Cesium carbonate was purchased from Acros Chemical Co., dried in vacuo at 120−150 °C for several hours, stored in a Schlenk tube, and weighed in an argon-flushed vessel. Aniline (**2a**), 4-methylaniline (**2b**), 4-ethoxyaniline (**2c**), *N*-methylaniline (**2d**), *n*-hexylamine (**2e**), benzylamine (**2f**), propane-1,3-diamine (**2g**), morpholine (**2h**), piperidine (**2i**), diethylamine (**2j**), 1,8-dichloroanthraquinone (**6**), triethylenetetraamine (**8a**), *N*,*N*′-bis(2-aminoethyl)propane-1,3-diamine (**8b**), *N*,*N*′-bis(3-aminopropyl)ethane-1,2-diamine (**8c**), tetraethylenepentaamine (**8e**), pentaethylenehexaamine (**8f**), 2,2′-(ethylenedioxy)bis(ethylamine) (**9a**), 4,9-dioxadodecane-1,12-diamine (**9b**), 4,7,10-trioxatridecane-1,13-diamine (**9c**), 1,5-dichloroanthraquinone (**38**), 1-aza-15-crown-5 (**57**), BINAP, tri-*tert*-butylphosphane, tricyclohexylphosphane and PPF-OMe were purchased from Aldrich Chemical Co. *N*,*N*′-Bis(3-aminopropyl)propane-1,3-diamine was purchased

from Avocado Chemical Co. 2-(Di-*tert*-butylphosphanyl)-1,1′-biphenyl was purchased from Strem Chemical Co. $Pd(dba)_2$,[28] 1,8- and 1,5-dichloroanthracenes **1** and **29**,[29] cyclam **48**,[30] cyclen **50**,[31] and *N*,*N*′,*N*′′-trimethylcyclam **54**[32] were synthesised by the described procedures.

General Procedure for the Palladium-Catalysed Reactions of 1,8-Dichloroanthracene: A two-necked, argon-flushed flask fitted with a magnetic stirrer and condenser was charged with dioxane (10 mL), the indicated amount of $Pd(dba)_2$, the ligand (Table 1), 1,8-dichloroanthracene (1 mmol), the amine (3 mmol) and NaO*t*Bu (3 mmol). The reaction mixture was heated at reflux with stirring for 24 h. After cooling down to room temperature it was concentrated in vacuo, and the residue was taken up with a mixture of dichloromethane and water. The organic layer was separated and washed with water (10 mL) and then dried over anhydrous sodium sulfate, and the solvents were evaporated in vacuo. The crude material was purified by column chromatography on silica. The following compounds were prepared by this procedure; the results are summarised in Table 1.

***N*,*N*′-Diphenylanthracene-1,8-diamine (3a):** See Table 1, entries 1, 2. The reaction mixture was chromatographed with toluene to yield a brown solid: m.p. 110−112 °C. Yield 200 mg (56%, using dppf), 240 mg (67%, with BINAP). ^{1}H NMR ($CDCl_3$, ppm): δ = 5.94 (br. s, 2 H), 6.97 (br. t, J = 7.2 Hz, 2 H), 7.10 (br. d, J = 7.2 Hz, 4 H), 7.34 (m, 8 H), 7.68 (d, J = 7.2 Hz, 2 H), 8.41 (s, 1 H), 8.76 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 113.1 (2 C), 114.2 (4 C), 118.4 (1 C), 121.1 (2 C), 122.5 (2 C), 125.9 (2 C), 126.2 (1 C), 127.9 (2 C), 129.6 (4 C), 133.0 (2 C), 139.4 (2 C), 144.3 (2 C). IR (KBr): $\tilde{\nu}$ = 3376 cm^{-1}, 3050, 1618, 1599, 1560, 1497, 1453, 1320, 1297, 869, 782, 738. MS (EI): m/z = 360 [M$^+$]. $C_{26}H_{20}N_2$ (360.45): calcd. C 86.64, H 5.59, N 7.77; found C 86.31, H 5.24, N 7.48.

***N*,*N*′-Di-*p*-tolylanthracene-1,8-diamine (3b):** See Table 1, entry 3. The reaction mixture was chromatographed with toluene to yield a dark brown solid: m.p. 118−120 °C. Yield 167 mg (43%). ^{1}H NMR ($CDCl_3$, ppm): δ = 2.38 (s, 6 H), 5.98 (br. s, 2 H), 7.06 (d, J = 8.6 Hz, 4 H), 7.17 (d, J = 8.6 Hz, 4 H), 7.27 (d, J = 7.9 Hz, 2 H), 7.37 (br. t, J = 7.7 Hz, 2 H), 7.65 (d, J = 8.2 Hz, 2 H), 8.40 (s, 1 H), 8.77 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 20.9 (2 C), 111.5 (2 C), 113.7 (1 C), 119.4 (4 C), 121.7 (2 C), 125.7 (3 C), 125.9 (2 C), 127.4 (2 C), 130.1 (4 C), 132.9 (2 C), 140.2 (2 C), 141.4 (2 C). IR (KBr): $\tilde{\nu}$ = 3380 cm^{-1}, 3021, 1612, 1587, 1563, 1513, 1453, 1319, 1290, 812, 736. MS (EI): m/z = 388 [M$^+$].

***N*,*N*′-Bis(4-ethoxyphenyl)anthracene-1,8-diamine (3c):** See Table 1, entry 4. The reaction mixture was chromatographed with toluene to yield a red-brown solid: m.p. 185−186 °C. Yield 242 mg (54%). ^{1}H NMR ($CDCl_3$, ppm): δ = 1.41 (t, J = 7.3 Hz, 6 H), 4.02 (q, J = 7.3 Hz, 4 H), 5.90 (br. s, 2 H), 6.88 (d, J = 8.8 Hz, 4 H), 7.01 (d, J = 6.8 Hz, 2 H), 7.12 (d, J = 8.8 Hz, 4 H), 7.30 (br. t, J = 7.3 Hz, 2 H), 7.54 (d, J = 8.2 Hz, 2 H), 8.38 (s, 1 H), 8.75 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 15.1 (2 C), 64.0 (2 C), 109.4 (2 C), 113.0 (1 C), 115.6 (4 C), 120.8 (2 C), 122.5 (4 C), 125.0 (1 C), 127.4 (2 C), 128.5 (2 C), 132.9 (2 C), 136.5 (2 C), 141.5 (2 C), 154.8 (2 C). IR (KBr): $\tilde{\nu}$ = 3366 cm^{-1}, 1597, 1563, 1513, 1441, 1283, 820, 732. MS (EI): m/z = 448 [M$^+$]. $C_{30}H_{28}N_2O_2$ (448.56): calcd. C 80.33, H 6.29, N 6.25; found C 79.81, H 6.25, N 5.98.

***N*,*N*′-Dimethyl-*N*,*N*′-diphenylanthracene-1,8-diamine (3d):** See Table 1, entries 5,6. The reaction mixture was chromatographed with toluene to yield a yellow-green solid: m.p. 140−142 °C. Yield 217 mg (56%, using BINAP). ^{1}H NMR ($CDCl_3$, ppm): δ = 3.18 (s, 6 H), 6.69 (d, J = 7.2 Hz, 4 H), 6.80 (t, J = 7.2 Hz, 2 H), 7.21 (br. t, J = 7.6 Hz, 4 H), 7.40 (d, J = 6.2 Hz, 2 H), 7.52 (br. t, J = 8.2 Hz, 2 H), 7.96 (d, J = 8.6 Hz, 2 H), 8.42 (s, 1 H), 8.59 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 40.3 (2 C), 114.6 (4 C), 117.7 (2 C), 120.3 (1 C), 124.2 (2 C), 126.1 (2 C), 126.4 (4 C), 127.8 (1 C), 128.9 (2 C), 129.2 (2 C), 133.5 (2 C), 146.1 (2 C), 150.3 (2 C). $C_{28}H_{24}N_2$ (388.50): calcd. C 86.56, H 6.23, N 7.23; found C 86.11, H 6.27, N 7.17.

***N*,*N*′-Dihexylanthracene-1,8-diamine (3e):** See Table 1, entry 7. The reaction mixture was chromatographed with toluene/pentane 1:1 to yield a dark brown solid: m.p. 83−85 °C. Yield 297 mg (79%). ^{1}H NMR ($CDCl_3$, ppm): δ = 0.99 (t, J = 7.3 Hz, 6 H), 1.33 (m, 12 H), 1.80 (m, 4 H), 3.28 (t, J = 7.3 Hz, 4 H), 5.50 (br. s, 2 H), 6.53 (d, J = 5.6 Hz, 2 H), 7.36 (m, 4 H), 8.24 (s, 1 H), 8.30 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 14.2 (2 C), 22.7 (2 C), 27.2 (2 C), 29.5 (2 C), 31.8 (2 C), 44.6 (2 C), 102.4 (2 C), 110.6 (1 C), 117.3 (2 C), 122.8 (1 C), 126.3 (2 C), 128.4 (2 C), 132.5 (2 C), 143.6 (2 C). IR (KBr): $\tilde{\nu}$ = 3403 cm^{-1}, 3054, 1616, 1569, 1500, 1466, 1284, 886, 773, 727. MS (EI): m/z = 376 [M$^+$]. $C_{26}H_{36}N_2$ (376.58): calcd. C 82.93, H 9.64, N 7.44; found C 82.60, H 9.96, N 7.23.

***N*,*N*′-Dibenzylanthracene-1,8-diamine (3f):** See Table 1, entry 8. The reaction mixture was chromatographed with toluene/pentane 1:1 to yield a yellow solid: m.p. 170−172 °C. Yield 241 mg (62%). ^{1}H NMR ($CDCl_3$, ppm): δ = 4.57 (s, 4 H), 4.91 (br. s, 2 H), 6.55 (d, J = 6.2 Hz, 2 H), 7.35 (m, 14 H), 8.34 (s, 1 H), 8.36 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 48.7 (2 C), 103.2 (2 C), 110.9 (1 C), 117.9 (2 C), 122.7 (1 C), 126.3 (2 C), 127.4 (4 C), 128.8 (4 C), 132.5 (4 C), 132.6 (2 C), 139.2 (2 C), 143.1 (2 C). IR (KBr): $\tilde{\nu}$ = 3431 cm^{-1}, 3057, 1617, 1568, 1502, 1467, 1452, 1356, 1276, 891, 836, 738, 727.

***N*,*N*′-Bis(3-aminopropyl)anthracene-1,8-diamine (3g):** See Table 1, entry 9. The reaction mixture was chromatographed with 10:3:1 CH_2Cl_2/CH_3OH/NH_3 to yield a brown solid: m.p. 81−82 °C. Yield 155 mg (48%). ^{1}H NMR ($CDCl_3$ + CH_3OH(5%), ppm): δ = 1.88 (q, J = 6.7 Hz, 4 H), 2.80 (br. s, 4 H), 2.91 (t, J = 6.6 Hz, 4 H), 3.34 (t, J = 6.7 Hz, 4 H), 5.60 (br. s, 2 H), 6.41 (m, 2 H), 7.30 (m, 4 H), 8.24 (s, 1 H), 8.47 (s, 1 H). ^{13}C NMR ($CDCl_3$ + CH_3OH(5%), ppm): δ = 31.7 (2 C), 41.1 (2 C), 43.3 (2 C), 101.4 (2 C), 112.0 (1 C), 116.7 (2 C), 122.6 (1 C), 126.5 (2 C), 126.8 (2 C), 132.5 (2 C), 144.1 (2 C). IR (KBr): $\tilde{\nu}$ = 3449 cm^{-1}, 3048, 1614, 1566, 1521, 1466, 1285, 887, 778, 730. MS (EI): m/z = 322 [M$^+$].

1,8-Dimorpholinoanthracene (3h): See Table 1, entry 10. The reaction mixture was chromatographed successively with pentane/dichloromethane 1:1 and dichloromethane to yield a yellow-green solid: m.p. 220 °C (dec.). Yield 271 mg (78%). ^{1}H NMR ($CDCl_3$, ppm): δ = 3.20 (m, 8 H), 4.07 (m, 8 H), 7.02 (d, J = 6.8 Hz, 2 H), 7.35 (br. t, J = 8.1 Hz, 2 H), 7.70 (d, J = 8.8 Hz, 2 H), 8.38 (s, 1 H), 9.19 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 53.8 (4 C), 67.9 (4 C), 113.6 (2 C), 118.3 (1 C), 123.9 (2 C), 125.6 (2 C), 127.3 (1 C), 127.5 (2 C), 133.1 (2 C), 149.8 (2 C). IR (KBr): $\tilde{\nu}$ = 1617 cm^{-1}, 1561, 1448, 1240, 888, 741. MS (EI): m/z = 348 [M$^+$].

1,8-Dipiperidin-1-ylanthracene (3i): See Table 1, entries 11, 12. The reaction mixture was chromatographed with pentane/dichloromethane 1:1 to yield a yellow-green solid: m.p. 229−231 °C. Yield 107 mg (31%, BINAP). ^{1}H NMR ($CDCl_3$, ppm): δ = 1.73 (br. s, 4 H), 1.95 (m, 8 H), 3.14 (br. s, 8 H), 6.98 (d, J = 7.3 Hz, 2 H), 7.32 (t, J = 8.3 Hz, 2 H), 7.64 (d, J = 8.3 Hz, 2 H), 8.34 (s, 1 H), 9.17 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 25.0 (2 C), 27.1 (4 C), 55.0 (4 C), 113.1 (2 C), 119.1 (1 C), 123.0 (2 C), 125.6 (2 C), 126.9 (1 C), 127.5 (2 C), 133.0 (2 C), 151.6 (2 C). IR (KBr): $\tilde{\nu}$ = 1614 cm^{-1}, 1562, 1448, 1243, 896, 742. MS (EI): m/z = 344 [M$^+$]. $C_{24}H_{28}N_2$ (344.49): calcd. C 83.68, H 8.19, N 8.13; found C 83.51, H 8.29, N 7.96.

(8-Chloroanthracen-1-yl)diethylamine (4): 1,8-Dichloroanthraquinone (277 mg, 1 mmol), diethylamine (74 mg, 1.05 mmol), and NaO*t*Bu (144 mg, 1.5 mmol) were added to a solution of $Pd(dba)_2$ (11 mg, 0.02 mmol) and BINAP (18 mg, 0.03 mmol) in dioxane (10 mL) in an argon-flushed flask. The mixture was heated at reflux with stirring until **1** had been consumed (GC analysis of the reaction mixture). After the reaction mixture had been cooled to room temperature and concentrated in vacuo, the residue was taken up with a mixture of dichloromethane and water. The organic layer was washed with water and dried over anhydrous sodium sulfate, and the solvents were evaporated in vacuo. The crude material was purified by column chromatography on silica with toluene as an eluent to provide the pure product (153 mg, 54%) as a yellow-green oil. ^{1}H NMR ($CDCl_3$, ppm): δ = 1.20 (t, J = 7.4 Hz, 6 H), 3.32 (q, J = 7.4 Hz, 4 H), 7.11 (d, J = 7.4 Hz, 1 H), 7.33 (br. t, J = 7.2 Hz, 1 H), 7.46 (br. t, J = 7.6 Hz, 1 H), 7.54 (d, J = 7.4 Hz, 1 H), 7.71 (d, J = 8.4 Hz, 1 H), 7.89 (d, J = 8.6 Hz, 1 H), 8.40 (s, 1 H), 9.34 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 12.8 (2 C), 47.8 (2 C), 116.7 (1 C), 120.7 (1 C), 122.9 (1 C), 124.9 (1 C), 125.2 (1 C), 126.2 (1 C), 127.1 (1 C), 127.4 (1 C), 128.6 (1 C), 130.4 (1 C), 132.4 (1 C), 133.4 (1 C), 133.6 (1 C), 148.5 (1 C). MS (EI): m/z = 283, 285 [M^+].

***N*,*N*-Diethyl-*N*′-phenylanthracene-1,8-diamine (5):** (8-Chloroanthracen-1-yl)diethylamine (**4**; 283 mg, 1 mmol), aniline (102 mg, 1.1 mmol), and NaO*t*Bu (144 mg, 1.5 mmol) were added to a solution of $Pd(dba)_2$ (11 mg, 0.02 mmol) and BINAP (18 mg, 0.03 mmol) in dioxane (10 mL) in an argon-flushed flask. The mixture was heated at reflux with stirring until **4** had been consumed (GC analysis of the reaction mixture). After cooling down to room temperature the mixture was concentrated in vacuo, and the residue was taken up with a mixture of dichloromethane and water. The organic layer was washed with water and dried over anhydrous sodium sulfate, and the solvents were evaporated in vacuo. The crude material was purified by column chromatography on silica with toluene as an eluent to provide the pure product (163 mg, 48%) as a yellow-green oil. ^{13}C NMR ($CDCl_3$, ppm): δ = 12.5 (2C), 47.8 (2 C), 112.7 (1 C), 116.6 (1 C), 117.1 (1 C), 118.4 (2 C), 120.9 (1 C), 122.5 (1 C), 123.2 (1 C), 125.6 (3 C), 126.0 (1 C), 127.1 (1 C), 129.5 (2 C), 132.8 (1 C), 133.4 (1 C), 139.4 (1 C), 144.7 (1 C). MS (EI): m/z = 340 [M^+]. $C_{24}H_{24}N_2$ (340.46): calcd. C 84.67, H 7.11, N 8.23; found C 84.45, H 7.33, N 7.96.

General Procedure for the Palladium-Catalysed Reactions of 1,8-Dichloroanthra-9,10-quinone: Dioxane (10 mL), the indicated amounts of $Pd(dba)_2$ and ligand (Table 2), Cs_2CO_3 (3 mmol), 1,8-dichloroanthraquinone (277 mg, 1 mmol) and the amine (3 mmol) were placed in an argon-flushed two-neck flask fitted with a magnetic stirrer and condenser. The reaction mixture was heated at reflux for 24 h, cooled down to room temperature and concentrated in vacuo. The residue was taken up with a mixture of dichloromethane and water, the organic layer was washed with water and dried over anhydrous sodium sulfate, and the solvents were evaporated in vacuo. The crude material was purified by column chromatography on silica. The following compounds were prepared by the above procedure; the results are summarised in Table 2.

1,8-Bis(phenylamino)anthraquinone (7a): See Table 2, entry 1. The reaction mixture was chromatographed with toluene to yield a violet solid: m.p. 230−232 °C. Yield 382 mg (98%). ^{1}H NMR ($CDCl_3$, ppm): δ = 7.31 (m, 14 H), 7.69 (dd, J = 7.0, 1.8 Hz, 2 H), 11.20 (br. s, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 115.6 (2 C), 117.6 (2 C), 120.3 (2 C), 124.0 (4 C), 124.9 (2 C), 129.7 (4 C), 134.2 (2 C), 134.3 (2 C), 139.9 (2 C), 148.9 (2 C), 184.0 (1 C), 189.1 (1 C). IR (KBr): $\tilde{\nu}$ = 3236 cm^{-1}, 3073, 1659, 1620, 1593, 1568, 1511, 1445, 1300, 1237, 749. MS (EI): m/z = 390 [M^+].

1,8-Bis(*p*-tolylamino)anthraquinone (7b): See Table 2, entry 2. The reaction mixture was chromatographed with toluene to yield a violet solid: m.p. 203−205 °C. Yield 398 mg (95%). ^{1}H NMR ($CDCl_3$, ppm): δ = 2.35 (s, 6 H), 7.17 (br. s, 8 H), 7.39 (m, 4 H), 7.62 (dd, J = 6.3, 2.3 Hz, 2 H), 11.19 (br. s, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 21.1 (2 C), 115.3 (2 C), 117.2 (2 C), 120.1 (2 C), 124.4 (2 C), 130.2 (2 C), 134.0 (4 C), 134.4 (2 C), 134.7 (2 C), 137.2 (2 C), 149.3 (2 C), 183.9 (1 C), 188.8 (1 C). MS (EI): m/z = 418 [M^+].

1,8-Bis(4-ethoxyphenylamino)anthraquinone (7c): See Table 2, entries 3, 4. The reaction mixture was chromatographed with toluene to yield a violet solid: m.p. 190−192 °C. Yield 467 mg (98%, BINAP), 268 mg (56%, dppf). ^{1}H NMR ($CDCl_3$, ppm): δ = 1.44 (t, J = 7.3 Hz, 6 H), 4.03 (q, J = 7.3 Hz, 4 H), 6.92 (d, J = 8.8 Hz, 4 H), 7.19 (d, J = 8.8 Hz, 4 H), 7.26 (br. d, J = 7.2 Hz, 2 H), 7.37 (br. t, J = 7.4 Hz, 2 H), 7.62 (dd, J = 7.0, 1.4 Hz, 2 H), 11.11 (br. s, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 15.0 (2 C), 63.8 (2 C), 115.0 (2 C), 115.5 (4 C), 116.9 (2 C), 120.0 (2 C), 126.8 (4 C), 132.4 (2 C), 134.1 (2 C), 134.4 (2 C), 150.2 (2 C), 156.8 (2 C), 184.2 (1 C), 189.0 (1 C). IR (KBr): $\tilde{\nu}$ = 3222 cm^{-1}, 1657, 1612, 1566, 1511, 1479, 1289, 747. MS (EI): m/z = 478 [M^+]. $C_{30}H_{26}N_2O_4$ (478.54): calcd. C 75.30, H 5.48, N 5.85; found C 75.16, H 5.55, N 5.95.

1,8-Bis(hexylamino)anthraquinone (7e): See Table 2, entry 5. The reaction mixture was chromatographed with toluene to yield a violet solid: m.p. 182−184 °C. Yield 398 mg (98%). ^{1}H NMR ($CDCl_3$, ppm): δ = 0.92 (t, J = 7.3 Hz, 6 H), 1.38 (m, 12 H), 1.76 (m, 4 H), 3.28 (m, 4 H), 6.92 (d, J = 8.5 Hz, 2 H), 7.44 (br. t, J = 7.2 Hz, 2 H), 7.51 (d, J = 7.6 Hz, 2 H), 9.60 (br. s, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 14.3 (2 C), 22.8 (2 C), 27.1 (2 C), 29.3 (2 C), 31.8 (2 C), 43.5 (2 C), 114.9 (2 C), 115.1 (2 C), 118.0 (2 C), 134.3 (2 C), 134.5 (2 C), 151.2 (2 C), 184.8 (1 C), 189.1 (1 C). IR (KBr): $\tilde{\nu}$ = 3276 cm^{-1}, 1660, 1620, 1596, 1567, 1516, 1299, 835, 742. MS (EI): m/z = 406 [M^+]. $C_{26}H_{34}N_2 \cdot CH_3OH$ (406.56·CH_3OH): calcd. C 73.94, H 8.73, N 6.39; found C 74.14, H 8.63, N 6.45.

1,8-Bis[(3-aminopropyl)amino]anthraquinone (7g): See Table 2, entry 6. The reaction mixture was chromatographed with CH_2Cl_2/CH_3OH/NH_3 10:3:1 to yield a violet solid: m.p. 164−166 °C. Yield 169 mg (48%). ^{1}H NMR ($CDCl_3$, ppm): δ = 1.26 (br. s, 4 H), 1.88 (q, J = 6.8 Hz, 4 H), 2.86 (t, J = 6.8 Hz, 4 H), 3.28 (q, J = 6.8 Hz, 4 H), 6.89 (dd, J = 7.2, 1.8 Hz, 2 H), 7.36 (br. t, J = 7.6 Hz, 2 H), 7.44 (dd, J = 8.4, 1.8 Hz, 2 H), 9.49 (br. s, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 33.0 (2 C), 40.1 (2 C), 40.7 (2 C), 114.4 (2 C), 114.9 (2 C), 117.6 (2 C), 134.1 (2 C), 134.3 (2 C), 151.1 (2 C), 184.6 (1 C), 188.9 (1 C). IR (KBr): $\tilde{\nu}$ = 3287 cm^{-1}, 1658, 1620, 1568, 1514, 1472, 1285, 835, 743. MS (EI): m/z = 352 [M^+].

1,8-Dimorpholinoanthraquinone (7h): See Table 2, entry 7. The reaction mixture was chromatographed with pentane/ethyl acetate 1:2 to yield a dark crimson solid: m.p. 206−208 °C. Yield 299 mg (79%). ^{1}H NMR ($CDCl_3$, ppm): δ = 3.13 (m, 8 H), 3.94 (m, 8 H), 7.31 (d, J = 6.1 Hz, 2 H), 7.54 (br. t, J = 7.4 Hz, 2 H), 7.81 (d, J = 7.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 53.5 (4 C), 67.3 (4 C), 120.7 (2 C), 125.1 (2 C), 127.4 (2 C), 133.4 (2 C), 135.1 (2 C), 152.3 (2 C), 183.7 (1 C), 184.9 (1 C). IR (KBr): $\tilde{\nu}$ = 1661 cm^{-1}, 1638, 1583, 1425, 892, 747. MS (EI): m/z = 378 [M^+].

1,8-Dipiperidinoanthraquinone (7i): See Table 2, entries 8, 9. The reaction mixture was chromatographed with pentane/ethyl acetate 9:1 to yield a dark crimson solid: m.p. 182−184 °C. Yield 135 mg (36%, dppf), 116 mg (31%, BINAP). ^{1}H NMR ($CDCl_3$, ppm): δ =

1.62 (br. s, 4 H), 1.82 (m, 8 H), 3.01 (br. s, 8 H), 7.34 (d, J = 7.2 Hz, 2 H), 7.48 (br. t, J = 7.4 Hz, 2 H), 7.75 (d, J = 7.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 24.4 (2 C), 26.4 (4 C), 54.6 (4 C), 119.5 (2 C), 125.4 (2 C), 127.4 (2 C), 132.7 (2 C), 135.1 (2 C), 153.4 (2 C), 183.9 (1 C), 185.4 (1 C). IR (KBr): $\tilde{\nu}$ = 1666 cm^{-1}, 1649, 1584, 1558, 1468, 1448, 887, 841, 790, 752. MS (EI): m/z = 374 [M^+].

General Procedure for the Palladium-Catalysed Synthesis of the Macrocycles Derived from Anthracene and Anthraquinone: A two-necked flask fitted with a magnetic stirrer and condenser and flushed with argon was charged with 1,8-(or 1,5-)dichloroanthracene or 1,8- (or 1,5-)dichloroanthraquinone (1−2 mmol), the indicated amount of $Pd(dba)_2$, BINAP, absolute dioxane (40−120 mL), polyamine (1−2 mmol), and the appropriate base (NaOtBu or Cs_2CO_3, 2−4 mmol). The reaction mixture was heated at reflux with stirring (times are indicated in Tables 3−6), and after the mixture had cooled down to room temperature the reaction solvents were evaporated in vacuo, the residue was treated with dichloromethane (30−40 mL) and washed once with water (10−20 mL), the water layer was extracted with dichloromethane (3 × 20 mL), the combined organic fractions were dried over anhydrous sodium sulfate, and the solvents were evaporated in vacuo. The crude product was chromatographed on silica.

Compound 9a: See Table 3, entry 1. This compound was synthesised from 1,8-dichloroanthracene (**1**; 1 mmol) and triethylenetetraamine **8a** (1 mmol). The reaction mixture was chromatographed with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield a dark yellow-brown solid. Yield 105 mg (33%). ^{1}H NMR* ($CDCl_3$, ppm): δ = 2.74 (s, 4 H), 2.87 (dd, J = 5.7, 5.3 Hz, 4 H), 3.25 (dd, J = 5.7, 5.3 Hz, 4 H), 6.59 (d, J = 6.9 Hz, 2 H), 7.29 (dd, J = 8.3, 6.9 Hz, 2 H), 7.42 (d, J = 8.3 Hz, 2 H), 8.25 (s, 1 H), 9.16 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 46.5 (2 C), 48.1 (2 C), 48.9 (2 C), 106.9 (2 C), 114.8 (1 C), 118.5 (2 C), 124.1 (1 C), 126.1 (2 C), 126.3 (2 C), 132.7 (2 C), 145.2 (2 C). MALDI-TOF: m/z = 320.65 [M^+]. * NH signals are not indicated.

Compound 9b: See Table 3, entry 2. This compound was synthesised from 1,8-dichloroanthracene (**1**; 1 mmol) and tetraamine **8b** (1 mmol). The reaction mixture was chromatographed with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield a brown solid. Yield 121 mg (36%). ^{1}H NMR ($CDCl_3$, ppm): δ = 1.59 (q, J = 6.4 Hz, 2 H), 2.58 (br. s, 2 H), 2.76 (t, J = 6.4 Hz, 4 H), 2.91 (t, J = 5.3 Hz, 4 H), 3.20 (t, J = 5.3 Hz, 4 H), 5.35 (br. s, 2 H), 6.50 (d, J = 7.4 Hz, 2 H), 7.34 (dd, J = 8.5, 7.4 Hz, 2 H), 7.40 (dd, J = 8.5 Hz, 2 H), 8.27 (s, 1 H), 8.49 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 31.1 (1 C), 44.9 (2 C), 48.6 (2 C), 49.4 (2 C), 103.2 (2 C), 112.2 (1 C), 117.2 (2 C), 123.2 (1 C), 126.5 (2 C), 126.6 (2 C), 132.6 (2 C), 144.4 (2 C). MALDI-TOF: m/z = 333.91 [M^+]. $C_{21}H_{26}N_4$ (334.22): calcd. C 75.41, H 7.84, N 16.75; found C 75.51, H 7.86, N 16.24.

Compound 9c: See Table 3, entry 3. This compound was synthesised from 1,8-dichloroanthracene (**1**; 1 mmol) and tetraamine **8c** (1 mmol). The reaction mixture was chromatographed with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield a brown solid. Yield 82 mg (24%). ^{1}H NMR* ($CDCl_3$, ppm): δ = 1.93 (br. q, J = 5.4 Hz, 4 H), 2.78 (s, 4 H), 2.87 (dd, J = 5.1, 4.9 Hz, 4 H), 3.41 (dd, J = 5.8, 5.2 Hz, 4 H), 6.41 (m, 2 H), 7.31 (m, 4 H), 8.26 (s, 1 H), 8.45 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 26.9 (2 C), 46.2 (2 C), 50.9 (2 C), 51.5 (2 C), 101.0 (2 C), 112.9 (1 C), 116.5 (2 C), 122.9 (1 C), 126.5 (2 C), 126.8 (2 C), 132.6 (2 C), 145.0 (2 C). * NH signals are not indicated.

Compound 9d: See Table 3, entry 4. This compound was synthesised from 1,8-dichloroanthracene (**1**; 1 mmol) and tetraamine **8d** (1 mmol). The reaction mixture was chromatographed with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield a brown solid. Yield 75 mg (21%). ^{1}H NMR* ($CDCl_3$, ppm): δ = 1.63 (q, J = 5.6 Hz, 2 H), 1.95 (br. q, J = 4.9 Hz, 4 H), 2.71 (t, J = 5.6 Hz, 4 H), 2.81 (t, J = 5.0 Hz, 4 H), 3.42 (t, J = 4.8 Hz, 4 H), 6.46 (dd, J = 5.9, 2.4 Hz, 2 H), 7.34 (m, 4 H), 8.28 (s, 1 H), 8.56 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 27.5 (2 C), 29.8 (1 C), 44.7 (2 C), 48.9 (2 C), 50.1 (2 C), 101.8 (2 C), 112.5 (1 C), 116.8 (2 C), 123.1 (1 C), 126.3 (2 C), 126.4 (2 C), 132.5 (2 C), 144.2 (2 C). MALDI-TOF: m/z = 362.78 [M^+]. * NH signals are not indicated.

Anthraceno-1,4,7,10,13-pentaazacyclooctadecane (9e): See Table 3, entry 5. This compound was synthesised from 1,8-dichloroanthracene (**1**; 2 mmol) and pentaamine **8e** (2 mmol). The reaction mixture was chromatographed with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield a brown-green solid. Yield 190 mg (26%). ^{1}H NMR*,** ($CDCl_3$, ppm): δ = 2.82 (m, 12 H), 3.30 (br. s, 4 H), 6.50 (br. s, 2 H), 7.30 (m, 4 H), 7.98 (br. s, 1 H), 8.40 (br. s, 1 H). ^{13}C NMR** ($CDCl_3$, ppm): δ = 41.3 (2 C), 47.1 (2 C), 51.5 (4 C), 101.2 (2 C), 113.0 (1 C), 116.0 (2 C), 121.8 (1 C), 125.6 (2 C), 127.7 (2 C), 131.7 (2 C), 143.1 (2 C). MALDI-TOF: m/z = 363.30 [M^+]. * NH signals are not indicated. ** Broad signals, multiplets were not resolved.

Anthraceno-1,4,7,10,13,16-hexaazacycloheneicosane (9f): See Table 3, entry 6. This compound was synthesised from 1,8-dichloroanthracene (**1**; 2 mmol) and hexaamine **8f** (2 mmol). The reaction mixture was chromatographed with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield a brown-green solid. Yield 180 mg (22%). ^{1}H NMR*,** ($CDCl_3$, ppm): δ = 2.72 (m, 16 H), 3.30 (br. s, 4 H), 6.40 (br. s, 2 H), 7.28 (m, 4 H), 7.95 (br. s, 1 H), 8.30 (br. s, 1 H). ^{13}C NMR** ($CDCl_3$, ppm): δ = 41.4 (2 C), 45.7 (4 C), 50.2 (4 C), 100.0 (2 C), 112.9 (1 C), 115.8 (2 C), 121.8 (1 C), 125.6 (2 C), 127.7 (2 C), 131.7 (2 C), 143.5 (2 C). MALDI-TOF: m/z = 406.91 [M^+]. * NH signals are not indicated. ** Broad signals, multiplets were not resolved.

Compound 10a: See Table 3, entries 7, 8. This compound was synthesised from 1,8-dichloroanthraquinone (**4**; 1 mmol) and triethylenetetraamine **8a** (1 mmol). The reaction mixture was chromatographed with CH_2Cl_2/CH_3OH 10:1 to yield **10a** as a red solid: yield 48 mg (14%, entry 7) or 33 mg (9%, entry 8), together with **compound 17a** (25 mg, 8%, red solid). Further chromatography with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 gave a red solid, which was identified as a mixture of **compound 14a** and **compound 15a** in 1:3 ratio: yield 91 mg (24%, entry 7) or 113 mg (30%, entry 8). **10a**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.90 (br. s, 2 H), 2.70 (s, 4 H), 2.74 (t, J = 5.3 Hz, 4 H), 3.45 (br. q, J = 5.2 Hz, 4 H), 7.05 (dd, J = 7.1, 2.4 Hz, 2 H), 7.42 (m, 4 H), 9.19 (t, J = 5.0, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 45.7 (2 C), 48.8 (2 C), 49.4 (2 C), 115.7 (2 C), 118.3 (2 C), 120.8 (2 C), 133.9 (2 C), 134.8 (2 C), 151.5 (2 C), 185.2 (1 C), 188.9 (1 C). MALDI-TOF: m/z = 350.81 [M^+]. **14a**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.95 (br. s, 4 H), 2.68 (m, 2 H), 2.77 (m, 6 H), 3.00 (t, J = 5.8 Hz, 2 H), 3.43 (br. q, J = 5.5 Hz, 2 H), 7.04 (d, J = 8.9 Hz, 1 H), 7.52 (m, 4 H), 7.74 (d, J = 8.0 Hz, 1 H), 8.24 (d, J = 7.7 Hz, 1 H), 9.86 (t, J = 4.6 Hz, 1 H). ^{13}C NMR*** ($CDCl_3$, ppm): δ = 42.1 (1 C), 43.1 (1 C), 48.7 (1 C), 49.3 (1 C), 49.6 (1 C), 52.8 (1 C), 114.4 (1 C), 116.1 (1 C), 118.3 (1 C), 126.8 (1 C), 127.1 (1 C), 132.9 (1 C), 134.1 (1 C), 137.3 (1 C), 152.0 (1 C), 184.1 (1 C), 185.0 (1 C). MALDI-TOF: m/z = 352.80 [M^+]. **15a**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.95 (br. s, 4 H), 2.68 (m, 2 H), 2.77 (m, 6 H), 2.99 (t, J = 6.0 Hz, 2 H), 3.44 (t, J = 5.8 Hz, 2 H), 7.07 (dd, J = 7.0, 2.5 Hz, 1 H), 7.49 (m, 2 H), 7.54 (br. t, J = 7.7 Hz, 1 H), 7.72 (dd, J = 8.0, 1.4 Hz, 1 H), 8.20 (dd, J = 7.4, 1.4 Hz, 1 H), 9.70 (t, J = 4.9 Hz, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 42.1 (1 C), 43.3 (1 C), 48.7 (1 C), 49.4 (1 C), 49.6 (1 C), 52.7

(1 C), 115.6 (1 C), 118.8 (1 C), 124.7 (1 C), 126.2 (1 C), 126.8 (1 C), 133.1 (1 C), 134.4 (1 C), 135.5 (1 C), 135.7 (1 C), 136.0 (1 C), 138.4 (1 C), 151.9 (1 C), 183.5 (1 C), 184.5 (1 C). MALDI-TOF: *m*/*z* = 386.89 [M$^+$]. **17a**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.90 (br. s, 2 H), 2.93 (s, 4 H), 3.07 (t, *J* = 5.7 Hz, 4 H), 3.40 (br. q, *J* = 5.2 Hz, 4 H), 6.81 (dd, *J* = 8.0, 1.6 Hz, 2 H), 7.49 (m, 6 H), 7.58 (dd, *J* = 8.0, 1.5 Hz, 2 H), 8.07 (dd, *J* = 7.3, 1.5 Hz, 2 H), 9.71 (t, *J* = 4.8 Hz, 2 H). MALDI-TOF: *m*/*z* = 626.59 [M$^+$]. **17a** contained a small amount of **compound 16a**: MALDI-TOF: *m*/*z* = 592.71 [M$^+$]. *** Some quaternary carbon signals of the anthraquinone system were not unambiguously determined.

Compound 10b: See Table 3, entries 9, 10. This compound was synthesised from 1,8-dichloroanthraquinone (**4**; 1 mmol) and tetraamine **8b** (1 mmol). The reaction mixture was chromatographed with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield **10b** as a violet solid: yield 70 mg (8%, entry 9; 19%, entry 10). Further chromatography with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 yielded a violet solid, which was identified as a mixture of **compound 14b** and **compound 15b** in 1:2 ratio: yield 69 mg (18%, entry 10). **10b**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.68 (q, *J* = 6.6 Hz, 2 H), 1.86 (br. s, 2 H), 2.93 (t, *J* = 6.6 Hz, 4 H), 3.00 (t, *J* = 5.0 Hz, 4 H), 3.28 (q, *J* = 5.0 Hz, 4 H), 6.90 (m, 2 H), 7.42 (m, 4 H), 10.10 (t, *J* = 5.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 31.3 (1 C), 44.0 (2 C), 48.3 (2 C), 49.2 (2 C), 114.4 (2 C), 115.3 (2 C), 118.0 (2 C), 133.9 (2 C), 134.4 (2 C), 150.9 (2 C), 185.2 (1 C), 188.2 (1 C). MALDI-TOF: *m*/*z* = 365.01 ([M + H]$^+$). **14b**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.72 (q, *J* = 6.4 Hz, 2 H), 2.38 (br. s, 4 H), 2.66 (m, 8 H), 2.87 (t, *J* = 6.2 Hz, 2 H), 3.43 (br. q, *J* = 5.7 Hz, 2 H), 7.09 (m, 1 H), 7.54 (m, 4 H), 7.69 (dd, *J* = 7.5, 1.6 Hz, 1 H), 8.24 (dd, *J* = 7.5, 1.6 Hz, 1 H), 9.83 (br. s, 1 H). ^{13}C NMR*** ($CDCl_3$, ppm): δ = 29.9 (1 C), 41.2 (1 C), 42.7 (1 C), 48.2 (1 C), 48.3 (1 C), 52.1 (1 C), 52.2 (1 C), 113.8 (1 C), 115.7 (1 C), 117.9 (1 C), 126.4 (1 C), 126.7 (1 C), 132.6 (1 C), 133.9 (1 C), 135.3 (1 C), 151.5 (1 C), 184.1 (1 C), 184.9 (1 C). MALDI-TOF: *m*/*z* = 366.93 [M$^+$]. **15b**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.72 (q, *J* = 6.4 Hz, 2 H), 2.38 (br. s, 4 H), 2.66 (m, 8 H), 2.87 (t, *J* = 6.2 Hz, 2 H), 3.44 (br. q, *J* = 5.6 Hz, 2 H), 7.04 (m, 1 H), 7.50 (m, 2 H), 7.55 (t, *J* = 8.0 Hz, 1 H), 7.73 (dd, *J* = 8.0, 1.3 Hz, 1 H), 8.21 (dd, *J* = 8.0, 1.3 Hz, 1 H), 9.67 (t, *J* = 4.5 Hz, 1 H). ^{13}C NMR*** ($CDCl_3$, ppm): δ = 29.8 (1 C), 41.2 (1 C), 42.9 (1 C), 48.2 (1 C), 48.4 (1 C), 52.1 (1 C), 52.2 (1 C), 115.2 (1 C), 118.3 (1 C), 126.7 (1 C), 132.9 (1 C), 134.4 (1 C), 135.0 (1 C), 138.0 (1 C), 151.5 (1 C), 183.0 (1 C), 184.1 (1 C). MALDI-TOF: *m*/*z* = 400.93 [M$^+$]. *** Some quaternary carbon signals of the anthraquinone system were not unambiguously determined.

Compound 10c: See Table 3, entry 11. This compound was synthesised from 1,8-dichloroanthraquinone (**4**; 1 mmol) and tetraamine **8c** (1 mmol). The reaction mixture was chromatographed with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield **10c** as a violet solid: yield 95 mg (25%). ^{1}H NMR ($CDCl_3$, ppm): δ = 1.90 (br. s, 2 H), 1.95 (br. q, *J* = 6.0, 4 H), 2.84 (s, 4 H), 2.89 (dd, *J* = 5.6, 5.2 Hz, 4 H), 3.32 (br. q, *J* = 6.2 Hz, 4 H), 6.89 (d, *J* = 7.8 Hz, 2 H), 7.40 (br. t, *J* = 7.7 Hz, 2 H), 7.48 (d, *J* = 7.5 Hz, 2 H), 9.94 (br. s, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 28.3 (2 C), 44.1 (2 C), 50.6 (2 C), 50.9 (2 C), 114.6 (2 C), 115.1 (2 C), 117.4 (2 C), 134.1 (2 C), 134.3 (2 C), 150.9 (2 C), 184.9 (1 C), 188.5 (1 C). $C_{22}H_{26}N_4O_2 \cdot 0.5H_2O$ (378.21·0.5H_2O): calcd. C 67.95, H 6.59; found C 68.19, H 7.02.

Compound 10d: See Table 3, entries 12, 13. This compound was synthesised from 1,8-dichloroanthraquinone (**4**; 1 mmol) and tetraamine **8d** (1 mmol). The reaction mixture was chromatographed with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield a mixture of **compound 16d** and **Compound 17d:** (1:2) as a violet solid: yield 35 mg (3%, entry 12; 10%, entry 13), and **10d** as a violet solid: yield 39 mg (12%, entry 13). **10d**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.59 (br. s, 2 H), 1.80 (q, *J* = 7.1 Hz, 2 H), 1.91 (br. q, *J* = 6.0 Hz, 4 H), 2.79 (t, *J* = 7.1 Hz, 4 H), 2.79 (t, *J* = 6.2 Hz, 4 H), 3.42 (br. q, *J* = 5.8 Hz, 4 H), 7.01 (dd, *J* = 7.8, 1.6 Hz, 2 H), 7.46 (br. t, *J* = 7.7 Hz, 2 H), 7.53 (dd, *J* = 7.6, 1.6 Hz, 2 H), 9.83 (br. s, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 28.6 (2 C), 30.8 (1 C), 42.0 (2 C), 47.9 (2 C), 48.1 (2 C), 115.1 (2 C), 115.3 (2 C), 118.1 (2 C), 134.5 (2 C), 134.8 (2 C), 151.5 (2 C), 185.3 (1 C), 189.2 (1 C). MALDI-TOF: *m*/*z* = 392.65 [M$^+$]. **16d**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.81 (q, *J* = 6.2 Hz, 2 H), 1.94 (br. q, *J* = 6.6 Hz, 4 H), 2.72 (br. s, 2 H), 2.82 (br. t, *J* = 6.4 Hz, 8 H), 3.37 (br. q, *J* = 6.0 Hz, 4 H), 6.95 (m, 1 H), 7.07 (m, 1 H), 7.46 (m, 6 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.67 (dd, *J* = 7.6, 1.3 Hz, 1 H), 7.70 (dd, *J* = 8.0, 1.3 Hz, 1 H), 8.12 (dd, *J* = 7.6, 1.3 Hz, 1 H), 8.17 (dd, *J* = 7.6, 1.6 Hz, 1 H), 9.58 (t, *J* = 5.1 Hz, 1 H), 9.59 (t, *J* = 5.0 Hz, 1 H). MALDI-TOF: *m*/*z* = 634.87 [M$^+$]. **17d**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.81 (q, *J* = 6.2 Hz, 2 H), 1.94 (br. q, *J* = 6.6 Hz, 4 H), 2.72 (br. s, 2 H), 2.82 (br. t, *J* = 6.4 Hz, 8 H), 3.37 (br. q, *J* = 6.0 Hz, 4 H), 6.95 (m, 2 H), 7.46 (m, 4 H), 7.50 (t, *J* = 7.6 Hz, 2 H), 7.67 (dd, *J* = 7.6, 1.3 Hz, 2 H), 8.12 (dd, *J* = 7.6, 1.3 Hz, 2 H), 9.58 (t, *J* = 5.1 Hz, 2 H). MALDI-TOF: *m*/*z* = 668.73 [M$^+$].

Anthraquinono-1,4,7,10,13-pentaazacyclooctadecane 10e: See Table 3, entry 14. This compound was synthesised from dichloroanthraquinone (**4**; 2 mmol) and pentaamine **8e** (2 mmol). The reaction mixture was chromatographed on silica with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield **10e** (212 mg, 27%) as a violet solid. ^{1}H NMR ($CDCl_3$, ppm): δ = 1.95 (br. s, 3 H), 2.79 (m, 4 H), 2.94 (m, 4 H), 3.02 (t, *J* = 5.3 Hz, 4 H), 3.34 (dd, *J* = 5.3, 4.0 Hz, 4 H), 6.93 (d, *J* = 8.5 Hz, 2 H), 7.41 (br. t, *J* = 7.8 Hz, 2 H), 7.49 (d, *J* = 7.4 Hz, 2 H), 9.98 (t, *J* = 4.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 41.5 (2 C), 47.4 (2 C), 48.9 (2 C), 49.3 (2 C), 113.8 (4 C), 116.7 (2 C), 133.1 (2 C), 133.5 (2 C), 149.9 (2 C), 184.1 (1 C), 187.7 (1 C). MALDI-TOF: *m*/*z* = 394.20 ([M + H]$^+$).

Compound 19a: See Table 4, entry 1. This compound was synthesised from dichloroanthracene (**1**; 1 mmol) and dioxadiamine **18a** (1 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2/CH_3OH 100:1 to give brown-greenish **19a** (90 mg, 28%) and the cyclic dimer **21a** (27 mg, 8%) as a brown solid. **19a**: ^{1}H NMR ($CDCl_3$, ppm): δ = 3.53 (t, *J* = 4.8 Hz, 4 H), 3.81 (t, *J* = 4.8 Hz, 4 H), 3.82 (s, 4 H), 4.92 (br. s, 2 H), 6.78 (d, *J* = 7.0 Hz, 2 H), 7.42 (dd, *J* = 8.5, 7.0 Hz, 2 H), 7.59 (d, *J* = 8.5 Hz, 2 H), 8.41 (s, 1 H), 9.15 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 47.4 (2 C), 70.3 (2 C), 71.1 (2 C), 108.2 (2 C), 114.7 (1 C), 119.5 (2 C), 124.4 (1 C), 126.1 (2 C), 126.5 (2 C), 132.8 (2 C), 144.9 (2 C). MALDI-TOF: *m*/*z* = 321.83 [M$^+$]. $C_{20}H_{22}N_2O_2$ (322.40): calcd. C 74.51, H 6.88; found C 75.30, H 7.06. **21a**: ^{1}H NMR ($CDCl_3$, ppm): δ = 3.47 (t, *J* = 4.8 Hz, 8 H), 3.72 (s, 8 H), 3.89 (t, *J* = 4.8 Hz, 8 H), 5.10 (br. s, 4 H), 6.38 (dd, *J* = 7.1, 1.0 Hz, 4 H), 7.27 (br. t, *J* = 7.2 Hz, 4 H), 7.34 (dd, *J* = 7.3, 1.0 Hz, 4 H), 8.26 (s, 2 H), 8.72 (s, 2 H). MALDI-TOF: *m*/*z* = 644.09 [M$^+$].

Compound 19b: See Table 4, entry 2. This compound was synthesised from dichloroanthracene (**1**; 1 mmol) and dioxadiamine **18b** (1 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2/CH_3OH 200:1 to yield **19b** (75 mg, 20%) as a brown-greenish solid), and further chromatography with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 gave 108 mg (27%) of a mixture of **19b** and **compound 25** (1:2). **19b**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.74 (q, *J* = 2.8 Hz, 4 H), 2.11 (q, *J* = 5.3 Hz, 4 H), 3.50 (m, 8 H), 3.65 (t, *J* = 5.3 Hz, 4 H), 5.47 (br. s, 2 H), 6.51 (m, 2 H), 7.38 (m, 4 H), 8.33 (s, 1 H), 8.35 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 26.6 (2 C), 27.8 (2 C), 43.4 (2 C), 70.5 (2 C), 70.9 (2 C), 101.4 (2 C), 111.3 (1 C), 116.7 (2

C), 122.8 (1 C), 126.3 (2 C), 127.2 (2 C), 132.6 (2 C), 144.0 (2 C). MALDI-TOF: *m/z* = 377.96 [M$^+$]. **25**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.64 (m, 8 H), 2.60 (br. s, 2 H), 2.77 (m, 2 H), 3.37 (m, 6 H), 3.46 (t, *J* = 6.5 Hz, 2 H), 3.61 (t, *J* = 4.7 Hz, 2 H), 5.46 (br. s, 1 H), 6.46 (dd, *J* = 5.9, 2.3 Hz, 1 H), 7.36 (m, 3 H), 7.50 (d, *J* = 7.2 Hz, 1 H), 7.85 (d, *J* = 8.5 Hz, 1 H), 8.32 (s, 1 H), 8.74 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 26.9 (2 C), 29.4 (1 C), 33.2 (1 C), 39.8 (1 C), 43.7 (1 C), 69.2 (1 C), 69.3 (1 C), 71.0 (1 C), 71.1 (1 C), 102.5 (1 C), 116.9 (1 C), 117.3 (1 C), 125.3 (2 C), 126.9 (1 C), 127.6 (1 C), 127.7 (1 C), 127.8 (1 C), 128.3 (1 C), 129.1 (1 C), 132.5 (1 C), 133.5 (1 C), 145.0 (1 C). MALDI-TOF: *m/z* = 413.90 [M$^+$].

Compound 19c: See Table 4, entry 3. This compound was synthesised from dichloroanthracene (**1**; 1 mmol) and trioxadiamine **18c** (1 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2/CH_3OH 100:1 to yield **19c** (100 mg, 25%) as a dark yellow-greenish solid, and further chromatography with CH_2Cl_2/CH_3OH 50:1 gave the cyclic dimer **21c** (*x* = 2, 38 mg, 10%) as a brown-greenish solid and 35 mg (9%) of a mixture of cyclic trimer **21c** (*x* = 3) and tetramer **21c** (*x* = 4). **19c**: ^{1}H NMR ($CDCl_3$, ppm): δ = 2.05 (q, *J* = 5.5. Hz, 4 H), 3.57 (t, *J* = 5.5 Hz, 4 H), 3.72 (m, 12 H), 5.70 (br. s, 2 H), 6.47 (m, 2 H), 7.31 (m, 4 H), 8.26 (s, 1 H), 8.49 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 28.1 (2 C), 42.5 (2 C), 70.1 (2 C), 70.2 (2 C), 70.6 (2 C), 101.5 (2 C), 112.1 (1 C), 116.7 (2 C), 123.1 (1 C), 126.7 (2 C), 127.3 (2 C), 133.1 (2 C), 144.3 (2 C). MALDI-TOF: *m/z* = 394.51 [M$^+$]. $C_{24}H_{30}N_2O_3$ (394.51): calcd. C 73.07, H 7.66; found C 73.24, H 7.35. **21c** (*x* = 2): ^{1}H NMR ($CDCl_3$, ppm): δ = 1.98 (br. q, *J* = 6.0 Hz, 8 H), 3.37 (t, *J* = 6.3 Hz, 8 H), 3.51 (t, *J* = 5.5 Hz, 8 H), 3.54 (m, 8 H), 3.69 (m, 8 H), 5.50 (br. s, 4 H), 6.42 (m, 4 H), 7.29 (m, 8 H), 8.23 (s, 2 H), 8.45 (s, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 29.0 (4 C), 42.9 (4 C), 70.5 (4 C), 70.6 (8 C), 101.8 (4 C), 112.4 (2 C), 117.0 (4 C), 123.1 (2 C), 126.8 (4 C), 127.1 (4 C), 132.9 (4 C), 144.5 (4 C). MALDI-TOF: *m/z* = 788.06 [M$^+$]. **21c** (*x* = 3): MALDI-TOF: *m/z* = 1182.96 [M$^+$]. **21c** (*x* = 4): MALDI-TOF: *m/z* = 1576.37 [M$^+$].

Compound 20a: See Table 4, entry 4. This compound was synthesised from dichloroanthraquinone (**4**; 1 mmol) and dioxadiamine **18a** (1 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2/CH_3OH 100:1 to yield **20a** (127 mg, 36%) as a violet solid, and 7 mg (2%) of a mixture of cyclic tetramer and pentamer **26a** (*x* = 4, 5). **20a**: ^{1}H NMR ($CDCl_3$, ppm): δ = 3.46 (m, 4 H), 3.50 (m, 4 H), 3.54 (s, 4 H), 7.03 (m, 2 H), 7.41 (m, 4 H), 9.25 (t, *J* = 4.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 45.4 (2 C), 69.1 (2 C), 70.6 (2 C), 115.5 (2 C), 119.0 (2 C), 120.4 (2 C), 133.7 (2 C), 134.8 (2 C), 151.3 (2 C), 176.3 (1 C), 179.0 (1 C). MALDI-TOF: *m/z* = 353.18 ([M + H]$^+$).

Compound 20b: See Table 4, entry 5. This compound was synthesised from dichloroanthraquinone (**4**; 1 mmol) and dioxadiamine **18b** (1 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2/CH_3OH 200:1 to yield **20b** (134 mg, 33%) as a violet solid. Further chromatography with CH_2Cl_2/CH_3OH 100:1 gave cyclic dimer **26b** (*x* = 2, 48 mg, 12%) and cyclic trimer **26b** (*x* = 3, 35 mg, 8%). Chromatography with CH_2Cl_2/CH_3OH 50:1 produced 82 mg (ca. 20%) of a complex mixture of higher mass cyclic (**26b**, *x* = 4−8) and linear (**27b**, *x* = 2−8, **28b**, *x* = 2−7) oligomers. **20b**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.75 (br. s, 4 H), 1.90 (br. q, *J* = 5.0 Hz, 4 H), 3.34 (br. q, *J* = 4.8 Hz, 4 H), 3.48 (br. s, 4 H), 3.53 (t, *J* = 5.4 Hz, 4 H), 6.87 (d, *J* = 8.2 Hz, 2 H), 7.34 (br. t, *J* = 7.9 Hz, 2 H), 7.44 (d, *J* = 7.5 Hz, 2 H), 9.77 (t, *J* = 4.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 26.3 (2 C), 28.2 (2 C), 40.9 (2 C), 68.8 (2 C), 71.3 (2 C), 114.4 (4 C), 117.2 (2 C), 133.8 (2 C), 134.3 (2 C), 150.9 (2 C), 184.7 (1 C), 188.3 (1 C). MALDI-TOF: *m/z* = 408.13 [M$^+$]. $C_{24}H_{28}N_2O_4$ (408.49): calcd. C 70.57, H 6.91, N 6.86; found C 70.38, H 7.01, N 6.67. **26b** (*x* = 2): ^{1}H NMR ($CDCl_3$, ppm): δ = 1.72 (br. s, 8 H), 1.98 (q, *J* = 6.2 Hz, 8 H), 3.39 (q, *J* = 6.2 Hz, 8 H), 3.50 (br. s, 8 H), 3.58 (t, *J* = 6.2 Hz, 8 H), 6.98 (d, *J* = 7.9 Hz, 4 H), 7.46 (m, 8 H), 9.64 (t, *J* = 6.2 Hz, 4 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 26.4 (4 C), 29.0 (4 C), 40.3 (4 C), 68.2 (4 C), 70.8 (4 C), 114.5 (4 C), 115.1 (4 C), 117.8 (4 C), 134.1 (4 C),134.3 (4 C), 150.8 (4 C), 184.5 (2 C), 188.5 (2 C). MALDI-TOF: *m/z* = 816.75 [M$^+$]. **26b** (*x* = 3): ^{1}H NMR ($CDCl_3$, ppm): δ = 1.77 (q, *J* = 2.6 Hz, 12 H), 1.95 (q, *J* = 6.2 Hz, 12 H), 3.32 (q, *J* = 6.2 Hz, 12 H), 3.46 (t, *J* = 2.6 Hz, 12 H), 3.53 (t, *J* = 5.9 Hz, 12 H), 6.94 (dd, *J* = 8.2, 1.4 Hz, 6 H), 7.38 (dd, *J* = 8.2, 7.2 Hz, 6 H), 7.45 (dd, *J* = 7.2, 1.4 Hz, 6 H), 9.58 (t, *J* = 6.2 Hz, 6 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 26.5 (6 C), 29.3 (6 C), 40.1 (6 C), 68.2 (6 C), 70.8 (6 C), 114.3 (6 C), 114.8 (6 C), 117.5 (6 C), 134.0 (6 C), 134.2 (6 C), 151.0 (6 C), 184.4 (3 C), 188.7 (3 C). MALDI-TOF: *m/z* = 1224.83 [M$^+$].

Compound 20c: See Table 4, entries 6, 7. Method (a), entry 6. The compound was synthesised from dichloroanthraquinone (**4**; 0.5 mmol) and dioxadiamine **18c** (0.5 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2/CH_3OH 200:1 to yield **20c** (62 mg, 29%) as a violet solid. Further chromatography with CH_2Cl_2/CH_3OH 100:1 gave 67 mg (ca. 32%) of a mixture of higher mass cyclic (**26c**, *x* = 2−4) and linear (**27c**, *x* = 1−4) oligomers. Chromatography with CH_2Cl_2/CH_3OH 40:1 yielded 32 mg (ca. 16%) of a mixture of cyclic (**26c**, *x* = 5, 6) and linear (**27c**, *x* = 5−8) oligomers. **20c**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.95 (br. q, *J* = 5.5 Hz, 4 H), 3.44 (br. q, *J* = 5.4 Hz, 4 H), 3.66 (t, *J* = 5.6 Hz, 4 H), 3.69 (m, 4 H), 3.82 (m, 4 H), 6.95 (dd, *J* = 8.2, 1.4 Hz, 2 H), 7.41 (dd, *J* = 8.2, 7.3 Hz, 2 H), 7.48 (dd, *J* = 7.3, 1.4 Hz, 2 H), 9.74 (t, *J* = 4.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 28.2 (2 C), 40.5 (2 C), 69.1 (2 C), 70.5 (2 C), 71.1 (2 C), 114.6 (4 C), 117.3 (2 C), 133.9 (2 C), 134.4 (2 C), 150.9 (2 C), 184.5 (1 C), 188.3 (1 C). MALDI-TOF: *m/z* = 424.77 [M$^+$]. $C_{24}H_{28}N_2O_5$ (424.49): calcd. C 67.91, H 6.65, N 6.60; found C 67.40, H 6.84, N 6.04.

Method (b), entry 7. The compound was synthesised from dichloroanthraquinone (**4**; 1 mmol) and dioxadiamine **18c** (1 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2/CH_3OH 200:1 to yield **20c** (159 mg, 37%) as a violet solid. Further chromatography with CH_2Cl_2/CH_3OH 100:1 gave the cyclic dimer **26c** (*x* = 2, 79 mg, 18%) as a violet solid, then with CH_2Cl_2/CH_3OH 50:1 a mixture of **26c** (*x* = 3−6), **27c** (*x* = 2−7) and **28c** (*x* = 1−6) was collected (64 mg, ca. 14%), and finally with CH_2Cl_2/CH_3OH 20:1 a mixture of **26c** (*x* = 6−8), **27c** (*x* = 6−8) and **28c** (*x* = 5−7) was collected (48 mg, ca. 11%). **26c** (*x* = 2): ^{1}H NMR ($CDCl_3$, ppm): δ = 1.98 (br. q, *J* = 6.1 Hz, 8 H), 3.30 (br. q, *J* = 6.0 Hz, 8 H), 3.62 (t, *J* = 6.2 Hz, 8 H), 3.63 (m, 8 H), 3.70 (m, 8 H), 6.88 (dd, *J* = 8.5 Hz, 4 H), 7.34 (dd, *J* = 8.5, 7.0 Hz, 4 H), 7.39 (d, *J* = 7.0 Hz, 4 H), 9.54 (br. t, *J* = 4.8 Hz, 4 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 29.7 (4 C), 40.5 (4 C), 69.2 (4 C), 70.8 (4 C), 71.1 (4 C), 114.7 (4 C), 115.2 (4 C), 117.8 (4 C), 134.3 (4 C), 134.6 (4 C), 151.4 (4 C), 184.8 (2 C), 188.9 (2 C). MALDI-TOF: *m/z* = 848.11 [M$^+$].

Compound 31a (*x* = 2): See Table 5, entry 1. This compound was synthesised from 1,5-dichloroanthracene (**29**; 1 mmol) and tetraamine **8a** (1 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2/CH_3OH/NH_3 30:6:1 to yield cyclic dimer **31a** (*x* = 2, 58 mg, 18%) as a brown solid. ^{1}H NMR*,** ($CDCl_3$, ppm): δ = 2.88 (br. s, 8 H), 3.02 (br. s, 8 H), 3.34 (br. s, 8 H), 6.48 (br. s, 4 H), 7.39 (m, 8 H), 8.37 (br. s, 4 H). MALDI-TOF: *m/z* = 640.36 [M$^+$]. * NH signals are not indicated. ** Broad signals, multiplets were not resolved.

Anthraceno-1,4,8,11-tetraazacyclononadecane 30b: See Table 5, entry 2. This compound was synthesised from 1,5-dichloroanthracene (**29**; 1 mmol) and tetraamine **8b** (1 mmol). The reaction mixture was chromatographed on silica with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield first 49 mg (15%) of a complex mixture of **30b** with **31b** ($x = 2-4$) and **32b** ($x = 1-3$), and then free **30b** (67 mg, 20%) and the cyclic dimer **31b** ($x = 2$, 35 mg, 10%) as yellow-brown solids. **30b**: ^{1}H NMR ($CDCl_3$, ppm): $\delta = 0.29$ (q, $J = 7.5$ Hz, 2 H), 0.90 (m, 4 H), 1.32 (m, 4 H), 1.73 (br. s, 2 H), 3.70 (m, 4 H), 5.35 (br. s, 2 H), 6.82 (dd, $J = 7.0$, 0.6 Hz, 2 H), 7.28 (dd, $J = 8.6$, 7.0 Hz, 2 H), 7.59 (dd, $J = 8.6$, 0.6 Hz, 2 H), 8.65 (s, 2 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 29.7$ (1 C), 45.7 (2 C), 47.1 (2 C), 49.1 (2 C), 112.8 (2 C), 121.1 (2 C), 121.7 (2 C), 125.2 (2 C), 125.9 (2 C), 131.9 (2 C), 144.3 (2 C). MALDI-TOF: $m/z = 334.90$ [M$^+$]. **31b** ($x = 2$): ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.70$ (q, $J = 5.6$ Hz, 4 H), 2.00 (br. s, 4 H), 2.69 (t, $J = 5.6$ Hz, 8 H), 2.77 (t, $J = 5.5$ Hz, 8 H), 2.84 (t, $J = 5.5$ Hz, 8 H), 4.27 (br. s, 4 H), 5.97 (d, $J = 7.0$ Hz, 4 H), 7.17 (dd, $J = 8.3$, 7.0 Hz, 4 H), 7.32 (d, $J = 8.3$ Hz, 4 H), 8.02 (s, 4 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 29.5$ (2 C), 42.6 (4 C), 47.2 (4 C), 48.4 (4 C), 102.1 (4 C), 117.5 (4 C), 118.9 (4 C), 123.5 (4 C), 125.7 (4 C), 131.4 (4 C), 142.8 (4 C). MALDI-TOF: $m/z = 668.66$ [M$^+$].

Anthraceno-1,5,8,12-tetraazacycloeicosane 30c: See Table 5, entry 3. This compound was synthesised from 1,5-dichloroanthracene (**29**; 1 mmol) and tetraamine **8c** (1 mmol). The reaction mixture was chromatographed on silica with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield **30c** (120 mg, 34%) as a yellow-brown solid together with traces of cyclic dimer and trimer **31c** ($x = 2$, 3). **30c**: ^{1}H NMR* ($CDCl_3$, ppm): $\delta = 0.81$ (m, 2 H), 1.38 (m, 2 H), 1.72 (m, 4 H), 2.26 (ddd, $J = 12.1$, 7.3, 4.8 Hz, 2 H), 2.48 (m, 2 H), 3.44 (dt, $J = 14.9$, 4.7 Hz, 2 H), 3.66 (ddd, $J = 14.9$, 9.2, 3.5 Hz, 2 H), 6.79 (d, $J = 7.0$ Hz, 2 H), 7.26 (dd, $J = 8.3$, 7.0 Hz, 2 H), 7.51 (d, $J = 8.3$ Hz, 2 H), 8.53 (s, 2 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 28.7$ (2 C), 44.4 (2 C), 47.7 (2 C), 49.0 (2 C), 110.9 (2 C), 120.2 (2 C), 121.3 (2 C), 124.9 (2 C), 125.7 (2 C), 131.7 (2 C), 144.8 (2 C). MALDI-TOF: $m/z = 347.98$ [M$^+$]. **31c**: MALDI-TOF: $m/z = 696.65$ ($x = 2$, M$^+$), 1043.94 ($x = 3$, M$^+$). * NH signals are not indicated.

Anthraceno-1,5,9,13-tetraazacycloheneicosane 30d: See Table 5, entry 4. This compound was synthesised from 1,5-dichloroanthracene (**29**; 1 mmol) and tetraamine **8d** (1 mmol). The reaction mixture was chromatographed on silica with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield **30d** (78 mg, 22%) as a yellow-brown solid together with 5% of cyclic dimer and trimer **31d** ($x = 2$, 3). **30d**: ^{1}H NMR* ($CDCl_3$, ppm): $\delta = 0.19$ (q, $J = 7.8$ Hz, 2 H), 1.33 (m, 2 H), 1.54 (m, 2 H), 1.78 (m, 2 H), 1.93 (m, 2 H), 2.13 (ddd, $J = 11.8$, 7.0, 4.4 Hz, 2 H), 2.28 (ddd, $J = 11.8$, 7.0, 4.4 Hz, 2 H), 3.45 (ddd, $J = 15.0$, 9.2, 3.5 Hz, 2 H), 3.63 (dt, $J = 15.0$, 4.3 Hz, 2 H), 6.68 (d, $J = 7.3$ Hz, 2 H), 7.28 (dd, $J = 8.6$, 7.3 Hz, 2 H), 7.43 (d, $J = 8.6$ Hz, 2 H), 8.45 (s, 2 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 26.5$ (2 C), 28.9 (1 C), 44.7 (2 C), 46.6 (2 C), 47.2 (2 C), 107.9 (2 C), 119.0 (2 C), 120.2 (2 C), 124.6 (2 C), 125.9 (2 C), 131.9 (2 C), 143.4 (2 C). MALDI-TOF: $m/z = 362.01$ [M$^+$]. **31d** ($x = 2$, 3): MALDI-TOF: $m/z = 724.65$ ($x = 2$, M$^+$), 1086.34 ($x = 3$, M$^+$). * NH signals are not indicated.

Compound 34a ($x = 2$): See Table 5, entry 5. This compound was synthesised from 1,5-dichloroanthracene (**29**; 1 mmol) and dioxadiamine **18a** (1 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2 to yield 53 mg (ca. 18%) of a mixture of **35a**, **36a** and **37a** ($x = 0$, 1) (brown solid), and then with CH_2Cl_2/CH_3OH 100:1 to yield cyclic dimer **34a** ($x = 2$, 25 mg, 8%) as a brown-greenish solid. **34a**: ^{1}H NMR ($CDCl_3$, ppm): $\delta = 3.44$ (t, $J = 4.8$ Hz, 8 H), 3.86 (s, 8 H), 3.96 (t, $J = 4.8$ Hz, 8 H), 4.90 (br. s, 4 H), 6.23 (d, $J = 7.0$ Hz, 4 H), 6.71 (d, $J = 8.3$ Hz, 4 H), 6.88 (dd, $J = 8.3$, 7.0 Hz, 4 H), 7.50 (s, 4 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 43.8$ (4 C), 69.8 (4 C), 70.4 (4 C), 102.5 (4 C), 118.3 (4 C), 118.6 (4 C), 125.5 (4 C), 129.1 (4 C), 132.6 (4 C), 142.8 (4 C). MALDI-TOF: $m/z = 644.75$ [M$^+$].

Anthraceno-1,14-diaza-5,10-dioxacyclodocosane 33b: See Table 5, entry 6. This compound was synthesised from 1,5-dichloroanthracene (**29**; 1 mmol) and dioxadiamine **18b** (1 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2/CH_3OH 500:1 to yield 32 mg (ca. 10%) of a mixture of **35b**, **36b** and **37b** ($x = 0$) in 1:4:2 mol ratio (brown solid), and then with CH_2Cl_2/CH_3OH 250:1 to yield **33b** (92 mg, 24%) as a brown-green solid. **33b**: ^{1}H NMR ($CDCl_3$, ppm): $\delta = -0.22$ (m, 2 H), 0.55 (m, 2 H), 1.47 (m, 2 H), 1.82 (td, $J = 9.0$, 6.0 Hz, 2 H), 2.14 (m, 2 H), 2.59 (td, $J = 9.0$, 6.0 Hz, 2 H), 3.22 (ddd, $J = 8.5$, 6.0, 2.5 Hz, 2 H), 3.55 (ddd, $J = 8.5$, 6.0, 2.5 Hz, 2 H), 3.60 (ddd, $J = 14.5$, 6.0, 3.0 Hz, 2 H), 3.73 (ddd, $J = 14.5$, 6.0, 3.0 Hz, 2 H), 4.60 (br. s, 2 H), 6.67 (d, $J = 7.0$ Hz, 2 H), 7.24 (dd, $J = 8.5$, 7.0 Hz, 2 H), 7.38 (d, $J = 8.5$ Hz, 2 H), 8.38 (s, 2 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 25.9$ (2 C), 26.9 (2 C), 44.5 (2 C), 70.2 (2 C), 70.9 (2 C), 105.4 (2 C), 118.4 (2 C), 120.1 (2 C), 124.7 (2 C), 125.4 (2 C), 131.8 (2 C), 144.3 (2 C). MALDI-TOF: $m/z = 378.66$ [M$^+$].

Anthraceno-1,15-diaza-5,8,11-dioxacyclotricosane 33c: See Table 5, entry 7. This compound was synthesised from 1,5-dichloroanthracene (**29**; 1 mmol) and dioxadiamine **18c** (1 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2/CH_3OH 500:1 to yield 23 mg (ca. 7%) of a mixture of **35c**, **36c** and **37c** ($x = 0$) in 1:4:2 mol ratio (brown solid), and then with CH_2Cl_2/CH_3OH 200:1 to yield **33c** (78 mg, 20%) as a brown-green solid. Further chromatography with CH_2Cl_2/CH_3OH 100:1 gave the cyclic dimer **34c** ($x = 2$, 15 mg, 4%). **33c**: ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.68$ (dtt, $J = 14.0$, 7.5, 3.5 Hz, 2 H), 2.06 (dtt, $J = 14.0$, 7.5, 3.5 Hz, 2 H), 2.19 (ddd, $J = 10.0$, 7.5, 6.0 Hz, 2 H), 2.42 (ddd, $J = 10.0$, 7.5, 5.5 Hz, 2 H), 2.65 (ddd, $J = 9.5$, 7.5, 6.0 Hz, 2 H), 2.75 (ddd, $J = 9.5$, 7.5, 5.5 Hz, 2 H), 3.25 (ddd, $J = 10.0$, 7.0, 3.0 Hz, 2 H), 3.50 (ddd, $J = 10.0$, 7.0, 3.0 Hz, 2 H), 3.56 (ddd, $J = 11.0$, 7.5, 3.5 Hz, 2 H), 3.64 (ddd, $J = 11.0$, 7.5, 3.5 Hz, 2 H), 4.50 (br. s, 2 H), 6.65 (d, $J = 7.0$ Hz, 2 H), 7.32 (dd, $J = 8.3$, 7.0 Hz, 2 H), 7.42 (d, $J = 8.3$ Hz, 2 H), 8.36 (s, 2 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 27.2$ (2 C), 44.1 (2 C), 68.2 (2 C), 68.6 (2 C), 70.3 (2 C), 104.4 (2 C), 117.4 (2 C), 119.0 (2 C), 124.0 (2 C), 125.2 (2 C), 131.2 (2 C), 143.8 (2 C). MALDI-TOF: $m/z = 394.09$ [M$^+$]. $C_{24}H_{30}N_2O_3$ (394.51): calcd. C 73.07, H 7.66, N 7.10; found C 73.49, H 7.55, N 6.56. **34c** (x = 2): ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.88$ (br. q, $J = 5.9$ Hz, 8 H), 3.20 (t, $J = 6.2$ Hz, 8 H), 3.53 (t, $J = 5.1$ Hz, 8 H), 3.68 (m, 16 H), 5.10 (br. s, 4 H), 6.31 (d, $J = 6.7$ Hz, 4 H), 7.31 (m, 8 H), 8.13 (s, 4 H). MALDI-TOF: $m/z = 788.50$ [M$^+$].

Compound 40a ($x = 2$): See Table 6, entry 1. This compound was synthesised from 1,5-dichloroanthraquinone (**38**; 1 mmol) and dioxadiamine **18a** (1 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2/CH_3OH 100:1 to yield **40a** ($x = 2$, 64 mg, 18%) as a red solid (containing admixed **41**, **42a** ($x = 1$, 2)). **40a**: ^{1}H NMR ($CDCl_3$, ppm): $\delta = 3.43$ (br. q, $J = 4.7$ Hz, 8 H), 3.82 (s, 8 H), 3.91 (t, $J = 5.3$ Hz, 8 H), 6.85 (d, $J = 8.0$ Hz, 4 H), 7.35 (m, 8 H), 9.59 (t, $J = 3.4$ Hz, 4 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 43.1$ (4 C), 69.9 (4 C), 71.3 (4 C), 113.4 (4 C), 115.0 (4 C), 116.0 (4 C), 134.9 (4 C), 135.0 (4 C), 151.2 (4 C), 184.8 (4 C). MALDI-TOF: $m/z = 704.16$ [M$^+$]. **41a**: MALDI-TOF: $m/z = 946.37$ ($x = 1$, M$^+$), 1298.85 ($x = 2$, M$^+$). **42a**: MALDI-TOF: $m/z = 980.17$ ($x = 1$, M$^+$), 1332.65 ($x = 2$, M$^+$).

Anthraquinono-1,14-diaza-5,10-dioxacyclodocosane 39b: See Table 6, entry 2. This compound was synthesised from 1,5-di-

chloroanthraquinone (**38**; 1 mmol) and dioxadiamine **18b** (1 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2/CH_3OH 200:1 to yield **39b** (123 mg, 30%) as a violet solid. Further chromatography with CH_2Cl_2/CH_3OH 100:1 yielded the cyclic dimer **40b** ($x = 2$, 44 mg, 10%), and the cyclic trimer **40b** ($x = 3$, 27 mg, 6%) as violet solids. **39b**: ^{1}H NMR ($CDCl_3$, ppm): $\delta = 0.60$ (br. s, 4 H), 1.55 (m, 2 H), 1.96 (m, 2 H), 2.42 (m, 2 H), 2.62 (m, 2 H), 3.29 (m, 6 H), 3.76 (m, 2 H), 7.06 (dd, $J = 8.3$, 1.0 Hz, 2 H), 7.41 (dd, $J = 8.3$, 7.3 Hz, 2 H), 7.51 (dd, $J = 7.3$, 1.0 Hz, 2 H), 9.51 (dd, $J = 9.2$, 4.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 26.5$ (2 C), 28.2 (2 C), 42.2 (2 C), 69.7 (2 C), 70.8 (2 C), 115.0 (2 C), 115.3 (2 C), 118.6 (2 C), 134.3 (2 C), 136.2 (2 C), 152.8 (2 C), 185.2 (2 C). MALDI-TOF: $m/z = 408.54$ [M$^+$]. $C_{24}H_{28}N_2O_4$ (408.49): calcd. C 70.57, H 6.91, N 6.86; found C 70.23, H 6.85, N 6.48. **40b** ($x = 2$): ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.72$ (br. s, 8 H), 1.91 (br. q, $J = 5.6$ Hz, 8 H), 3.32 (br. q, $J = 5.7$ Hz, 8 H), 3.51 (br. s, 8 H), 3.54 (t, $J = 5.4$ Hz, 8 H), 6.81 (m, 4 H), 7.31 (m, 8 H), 9.58 (t, $J = 4.8$ Hz, 4 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 26.4$ (4 C), 29.3 (4 C), 39.9 (4 C), 67.9 (4 C), 70.9 (4 C), 112.7 (4 C), 114.5 (4 C), 116.0 (4 C), 134.8 (4 C), 135.9 (4 C), 151.2 (4 C), 185.2 (4 C). MALDI-TOF: $m/z = 816.09$ [M$^+$]. **40b** ($x = 3$): ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.67$ (m, 12 H), 1.92 (br. q, $J = 6.0$ Hz, 12 H), 3.35 (br. q, $J = 6.1$ Hz, 12 H), 3.44 (t, $J = 5.5$ Hz, 12 H), 3.52 (t, $J = 5.8$ Hz, 12 H), 6.88 (m, 6 H), 7.42 (m, 12 H), 9.67 (t, $J = 5.2$ Hz, 6 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 26.4$ (6 C), 29.4 (6 C), 39.9 (6 C), 68.0 (6 C), 70.9 (6 C), 112.8 (6 C), 114.6 (6 C), 116.2 (6 C), 135.0 (6 C), 136.1 (6 C), 151.4 (6 C), 185.1 (6 C). MALDI-TOF: $m/z = 1224.26$ [M$^+$].

Anthraquinono-1,15-diaza-5,8,11-dioxacyclotricosane 39c: See Table 6, entry 3. This compound was synthesised from 1,5-dichloroanthraquinone (**38**; 1 mmol) and trioxadiamine **18c** (1 mmol). The reaction mixture was chromatographed on silica with CH_2Cl_2/CH_3OH 100:1 to yield **39c** (119 mg, 28%) as a violet solid. Further chromatography with CH_2Cl_2/CH_3OH 50:1 and 20:1 yielded fractions containing mixtures of cyclic and linear oligomers: **40c** ($x = 2-9$), **41c** ($x = 1-8$), **43c** ($x = 1-7$) (194 mg, 44%). **39c**: ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.61$ (m, 2 H), 1.97 (m, 2 H), 2.68 (m, 4 H), 2.92 (m, 4 H), 3.34 (m, 6 H), 3.71 (m, 2 H), 7.04 (dd, $J = 8.5$, 1.0 Hz, 2 H), 7.43 (dd, $J = 8.5$, 7.2 Hz, 2 H), 7.52 (dd, $J = 7.2$, 1.0 Hz, 2 H), 9.50 (dd, $J = 9.2$, 3.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 28.3$ (2 C), 41.8 (2 C), 68.8 (2 C), 69.5 (2 C), 69.8 (2 C), 114.8 (2 C), 115.0 (2 C), 118.6 (2 C), 134.5 (2 C), 136.1 (2 C), 152.8 (2 C), 185.1 (2 C). MALDI-TOF: $m/z = 424.15$ [M$^+$]. $C_{24}H_{28}N_2O_5$ (424.49): calcd. C 67.91, H 6.65, N 6.60; found C 67.99, H 6.53, N 6.14. **40c** ($x = 2$): ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.92$ (q, $J = 5.3$ Hz, 8 H), 3.29 (q, $J = 6.2$ Hz, 8 H), 3.62 (m, 24 H), 6.82 (m, 4 H), 7.27 (m, 8 H), 9.40 (t, $J = 5.1$ Hz, 4 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 29.8$ (4 C), 39.7 (4 C), 68.3 (4 C), 70.4 (4 C), 70.8 (4 C), 112.3 (4 C), 114.6 (4 C), 115.8 (4 C), 134.6 (4 C), 135.7 (4 C), 151.1 (4 C), 184.6 (4 C). MALDI-TOF: $m/z = 848.68$ [M$^+$].

Compound 44a: See Table 6, entry 4. This compound was synthesised from 1,5-dichloroanthraquinone (**38**; 1 mmol) and tetraamine **8a** (1 mmol). The reaction mixture was chromatographed on silica with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield **44a** (110 mg, 28%) as a deep-red solid and **compound 46a** (32 mg, 10%), also as a deep-red solid, together with traces of **compound 45a**. **44a**: ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.86$ (br. s, 4 H), 2.74 (m, 8 H), 2.97 (t, $J = 6.0$ Hz, 2 H), 3.38 (br. q, $J = 5.5$ Hz, 2 H), 6.96 (m, 1 H), 7.47 (m, 2 H), 7.57 (dd, $J = 8.3$, 7.3 Hz, 1 H), 7.65 (dd, $J = 8.3$, 1.9 Hz, 1 H), 8.21 (dd, $J = 7.3$, 1.9 Hz, 1 H), 9.70 (t, $J = 4.4$ Hz, 1 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 41.2$ (1 C), 42.6 (1 C), 48.1 (1 C), 48.9 (1 C), 49.2 (1 C), 52.5 (1 C), 112.3 (1 C), 115.9 (1 C), 117.3 (1 C), 126.2 (1 C), 129.2 (1 C), 133.4 (1 C), 134.4 (1 C), 135.6 (2 C), 136.3 (1 C), 137.5 (1 C), 151.2 (1 C), 183.2 (2 C). MALDI-TOF: $m/z = 387.08$ ([M + H]$^+$). **46a**: ^{1}H NMR ($CDCl_3$, ppm): $\delta = 2.39$ (br. s, 2 H), 2.94 (s, 4 H), 2.92 (t, $J = 6.7$ Hz, 4 H), 3.32 (br. q, $J = 5.8$ Hz, 4 H), 6.74 (dd, $J = 7.3$, 2.2 Hz, 2 H), 7.42 (m, 4 H), 7.56 (m, 4 H), 8.14 (dd, $J = 7.3$, 1.3 Hz, 2 H), 9.61 (t, $J = 4.1$ Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 40.1$ (2 C), 42.6 (2 C), 45.7 (2 C), 112.3 (2 C), 115.8 (2 C), 117.2 (2 C), 126.2 (2 C), 129.0 (2 C), 133.1 (2 C), 133.3 (2 C), 135.6 (4 C), 136.3 (2 C), 137.4 (2 C), 151.0 (2 C), 182.4 (2 C), 182.5 (2 C). MALDI-TOF: $m/z = 626.81$ [M$^+$]. **45a**: MALDI-TOF: $m/z = 592.93$ [M$^+$].

Compound 44b: See Table 6, entry 5. This compound was synthesised from 1,5-dichloroanthraquinone (**38**; 1 mmol) and tetraamine **8b** (1 mmol). The reaction mixture was chromatographed on silica with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield **44b** (102 mg, 25%) as a deep-red solid and **compound 46b** (15 mg, 5%), also as a deep-red solid, together with traces of **compound 45b**. **44b**: ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.68$ (q, $J = 6.8$ Hz, 2 H), 1.98 (br. s, 4 H), 2.68 (m, 8 H), 2.93 (t, $J = 6.0$ Hz, 2 H), 3.38 (br. q, $J = 5.7$ Hz, 2 H), 6.95 (m, 1 H), 7.45 (m, 2 H), 7.55 (dd, $J = 8.9$, 7.9 Hz, 1 H), 7.62 (dd, $J = 7.9$, 1.6 Hz, 1 H), 8.18 (dd, $J = 8.9$, 1.6 Hz, 1 H), 9.62 (t, $J = 4.8$ Hz, 1 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 30.1$ (1 C), 41.5 (1 C), 42.7 (1 C), 48.1 (2 C), 48.3 (1 C), 52.4 (1 C), 112.3 (1 C), 115.9 (1 C), 117.3 (1 C), 126.2 (1 C), 129.2 (1 C), 133.4 (1 C), 134.3 (1 C), 135.6 (2 C), 136.3 (1 C), 137.5 (1 C), 151.3 (1 C), 183.1 (2 C). MALDI-TOF: $m/z = 400.77$ [M$^+$]. **46b**: ^{1}H NMR* ($CDCl_3$, ppm): $\delta = 1.73$ (q, $J = 6.2$ Hz, 2 H), 2.89 (t, $J = 6.2$ Hz, 4 H), 2.98 (t, $J = 6.0$ Hz, 4 H), 3.32 (q, $J = 6.0$ Hz, 4 H), 6.77 (dd, $J = 7.9$, 1.9 Hz, 2 H), 7.45 (m, 4 H), 7.56 (m, 4 H), 8.10 (dd, $J = 7.6$, 1.6 Hz, 2 H), 9.56 (t, $J = 4.9$ Hz, 2 H). MALDI-TOF: $m/z = 640.49$ [M$^+$]. **45b**: MALDI-TOF: $m/z = 606.70$ [M$^+$]. * NH signals are not indicated.

Compound 44c: See Table 6, entry 6. This compound was synthesised from 1,5-dichloroanthraquinone (**38**; 1 mmol) and tetraamine **8c** (1 mmol). The reaction mixture was chromatographed on silica with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield **44c** (96 mg, 23%) as a deep-red solid and **compound 46c** (32 mg, 10%), also as a deep-red solid, together with traces of **compound 45c**. **44c**: ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.58$ (br. q, $J = 6.9$ Hz, 2 H), 1.86 (br. q, $J = 6.7$ Hz, 2 H), 2.07 (br. s, 4 H), 2.62 (t, $J = 7.0$ Hz, 2 H), 2.70 (s, 4 H), 2.71 (t, $J = 7.0$ Hz, 2 H), 2.74 (t, $J = 7.3$ Hz, 2 H), 3.32 (br. q, $J = 6.3$ Hz, 2 H), 6.93 (m, 1 H), 7.41 (m, 2 H), 7.53 (dd, $J = 7.9$, 7.3 Hz, 1 H), 7.6 (dd, $J = 7.9$, 1.9 Hz, 1 H), 8.16 (dd, $J = 7.3$, 1.9 Hz, 1 H), 9.52 (t, $J = 4.9$ Hz, 1 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 29.4$ (1 C), 33.4 (1 C), 40.4 (1 C), 41.0 (1 C), 47.4 (1 C), 47.7 (1 C), 49.4 (2 C), 112.0 (1 C), 115.8 (1 C), 117.2 (1 C), 126.1 (1 C), 129.2 (1 C), 133.3 (1 C), 134.3 (1 C), 135.6 (2 C), 136.3 (1 C), 137.4 (1 C), 151.2 (1 C), 183.0 (2 C). MALDI-TOF: $m/z = 414.84$ [M$^+$]. **46c**: ^{1}H NMR* ($CDCl_3$, ppm): $\delta = 1.92$ (br. q, $J = 6.7$ Hz, 4 H), 2.68 (t, $J = 7.1$ Hz, 4 H), 2.85 (s, 4 H), 3.37 (br. q, $J = 5.9$ Hz, 4 H), 6.98 (m, 2 H), 7.45 (m, 4 H), 7.55 (t, $J = 7.9$, 7.3 Hz, 2 H), 7.63 (dd, $J = 7.9$, 1.6 Hz, 2 H), 8.19 (dd, $J = 7.3$, 1.6 Hz, 2 H), 9.59 (t, $J = 4.6$ Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 28.9$ (2 C), 40.9 (2 C), 52.4 (2 C), 52.7 (2 C), 112.1 (2 C), 115.8 (2 C), 117.3 (2 C), 126.1 (2 C), 129.1 (2 C), 133.3 (2 C), 134.3 (2 C), 135.6 (4 C), 136.3 (2 C), 137.5 (2 C), 151.3 (2 C), 182.3 (4 C). MALDI-TOF: $m/z = 654.08$ [M$^+$]. **45c**: MALDI-TOF: $m/z = 620.18$ [M$^+$]. * NH signals are not indicated.

Compound 44d (Table 6, entries 7–9): Method (a), entry 7. The compound was synthesised from 1,5-dichloroanthraquinone (**38**; 1 mmol) and tetraamine **8d** (1 mmol) by treatment with $Pd(dba)_2$/

BINAP (8/9 mol %). The reaction mixture was chromatographed on silica with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield **44d** (22 mg, 5%) as a deep-red solid and **compound 46d** (58 mg, 17%), also as a deep-red solid, together with traces of **compound 45d**. **44d**: ^{1}H NMR* ($CDCl_3$, ppm): δ = 1.68 (br. q, J = 6.7 Hz, 2 H), 1.89 (q, J = 7.3 Hz, 4 H), 2.45 (m, 6 H), 2.78 (br. t, J = 6.4 Hz, 4 H), 3.37 (br. q, J = 6.0 Hz, 2 H), 7.02 (m, 1 H), 7.49 (m, 2 H), 7.59 (dd, J = 8.0, 7.3 Hz, 1 H), 7.67 (dd, J = 8.0, 1.6 Hz, 1 H), 8.24 (dd, J = 7.3, 1.6 Hz, 1 H), 9.59 (t, J = 5.3 Hz, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 24.0 (1 C), 27.0 (1 C), 27.2 (1 C), 41.4 (2 C), 53.0 (3 C), 53.8 (1 C), 112.5 (1 C), 116.2 (1 C), 117.8 (1 C), 126.6 (1 C), 129.6 (1 C), 133.7 (1 C), 134.7 (1 C), 136.0 (2 C), 136.6 (1 C), 137.9 (1 C), 151.7 (1 C), 182.7 (1 C), 183.4 (1 C). MALDI-TOF: m/z = 428.70 [M$^+$]. **46d**: ^{1}H NMR* ($CDCl_3$, ppm): δ = 1.74 (br. q, J = 7.2 Hz, 2 H), 1.90 (br. q, J = 6.5 Hz, 4 H), 2.76 (t, J = 6.4 Hz, 4 H), 2.79 (t, J = 6.0 Hz, 4 H), 3.32 (br. q, J = 4.5 Hz, 4 H), 6.96 (m, 2 H), 7.45 (m, 4 H), 7.60 (m, 4 H), 8.16 (dd, J = 7.6, 1.6 Hz, 2 H), 9.55 (t, J = 4.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 29.1 (2 C), 32.0 (1 C), 43.4 (2 C), 47.4 (2 C), 48.2 (2 C), 112.5 (2 C), 116.2 (2 C), 117.7 (2 C), 126.6 (2 C), 129.7 (2 C), 133.7 (2 C), 134.8 (2 C), 136.0 (4 C), 136.7 (2 C), 137.9 (2 C), 151.8 (2 C), 182.8 (2 C), 183.5 (2 C). MALDI-TOF: m/z = 668.84 [M$^+$]. **45d**: MALDI-TOF: m/z = 634.81 [M$^+$]. * NH signals are not indicated.

Method (b), entry 8. The compound was synthesised from 1,5-dichloroanthraquinone (**38**; 1 mmol) and tetraamine **8d** (1 mmol) by treatment with $Pd(dba)_2$/BINAP (16/18 mol %). The reaction mixture was chromatographed on silica with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield **44d** (110 mg, 25%) and **46d** (89 mg, 26%), together with traces of **45d** and **47d**: ^{1}H NMR**** ($CDCl_3$, ppm): δ = 0.65 (q, J = 8.2 Hz, 2 H), 3.76 (ddd, J = 14.6, 10.2, 4.5 Hz, 2 H), 7.18 (dd, J = 8.3, 1.6 Hz, 2 H), 7.58 (m, 4 H), 9.11 (dd, J = 9.8, 4.5 Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 23.6 (1 C), 29.7 (2 C), 41.2 (2 C), 47.7 (2 C), 49.3 (2 C), 116.5 (2 C), 117.5 (2 C), 120.8 (2 C), 134.8 (2 C), 136.4 (2 C), 152.9 (2 C), 185.5 (2 C). MALDI-TOF: m/z = 393.14 ([M + H]$^+$). **** Signals of other aliphatic protons of **47d** were not determined due to their overlapping with the signals of corresponding aliphatic protons of the major compound **46d**.

Method (c), entry 9. The compound was synthesised from 1,5-dichloroanthraquinone (**38**; 1 mmol) and tetraamine **8d** (1 mmol) by treatment with $Pd(dba)_2$/2-(di-*tert*-butylphosphanyl)biphenyl (10/10 mol %). The reaction mixture was chromatographed on silica with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to yield **46d** (37 mg, 11%) and **44d** (68 mg, 16%).

1-(8-Chloro-1-anthracenyl)-1,4,7,10-tetraazacyclododecane (51) and 1-(1-Anthracenyl)-1,4,7,10-tetraazacyclododecane (52): Method (a). 1,8-Dichloroanthracene (**1**; 247 mg, 1 mmol), cyclen (**50**; 172 mg, 1 mmol), NaO*t*Bu (200 mg, 2.1 mmol), $Pd(dba)_2$ (23 mg, 0.05 mmol) and BINAP (62 mg, 0.1 mmol) were dissolved under argon in dioxane (40 mL) in a two-necked flask. The reaction mixture was heated at reflux for 24 h, and then cooled down to room temperature and concentrated in vacuo. The residue was taken up with dichloromethane (30 mL), washed with water (15 mL), and dried over anhydrous sodium sulfate, and the solvents were evaporated in vacuo. The crude product was chromatographed on silica successively with CH_2Cl_2 and with $CH_2Cl_2/CH_3OH/NH_3$ 10:3:1 to yield a mixture of **51** and **52** in 2:1 ratio (172 mg, yields 26 and 13% respectively). **51**: ^{1}H NMR ($CDCl_3$, ppm): δ = 2.63 (m, 11 H), 2.75 (m, 4 H), 3.21 (m, 4 H), 7.26 (d, J = 7.8 Hz, 1 H), 7.38 (m, 2 H), 7.51 (d, J = 7.7 Hz, 1 H), 7.74 (dd, J = 8.5, 7.7 Hz, 1 H), 7.83 (d, J = 8.5 Hz, 1 H), 8.35 (s, 1 H), 9.56 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 46.2 (2 C), 46.7 (2 C), 47.5 (2 C), 52.5 (2 C), 119.7 (1 C), 119.9 (1 C), 124.9 (2 C), 125.3 (1 C), 125.9 (1 C), 127.1 (1 C), 127.2 (1 C), 129.0 (1 C), 130.7 (1 C), 132.3 (1 C), 132.7 (1 C), 133.4 (1 C), 149.4 (1 C). **52**: ^{1}H NMR ($CDCl_3$, ppm): δ = 2.63 (m, 11 H), 2.75 (m, 4 H), 3.21 (m, 4 H), 7.24 (d, J = 8.4 Hz, 1 H), 7.30 (m, 3 H), 7.74 (d, J = 8.3 Hz, 1 H), 7.90 (m, 1 H), 8.01 (m, 1 H), 8.35 (s, 1 H), 9.22 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 46.5 (2 C), 47.6 (2 C), 48.0 (2 C), 52.1 (2 C), 119.0 (1 C), 122.6 (1 C), 125.1 (1 C), 125.3 (1 C), 125.5 (1 C), 126.5 (1 C), 127.7 (1 C), 129.1 (1 C), 129.3 (1 C), 130.0 (1 C), 131.4 (1 C), 131.6 (1 C), 133.2 (1 C), 148.4 (1 C). MALDI-TOF: m/z = 348.84 [M$^+$].

Method (b). 1,8-Dichloroanthracene (**1**; 738 mg, 3.0 mmol), cyclen (**50**; 550 mg, 3.2 mmol), NaO*t*Bu (600 mg, 6.25 mmol), $Pd(dba)_2$ (103 mg, 0.18 mmol) and BINAP (165 mg, 0.265 mmol) were dissolved under argon in dioxane (80 mL) in a two-necked flask. The reaction mixture was heated at reflux for 50 h, cooled down to room temperature, and concentrated in vacuo. The residue was taken up with dichloromethane (30 mL), washed with water (15 mL) and dried over anhydrous sodium sulfate, and the solvents were evaporated in vacuo. The crude product was chromatographed on silica successively with CH_2Cl_2 and $CH_2Cl_2/CH_3OH/NH_3$ 10:3:1 to yield **52** (565 mg, 54%).

1-(1-Anthracenyl)-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane (54): A two-necked flask filled with argon was charged with 1,8-dichloroanthracene (**1**; 247 mg, 1 mmol), *N*,*N*′,*N*′′-trimethylcyclam (**53**; 484 mg, 2 mmol), $Pd(dba)_2$ (92 mg, 0.16 mmol), P*t*Bu$_3$ (26 mg, 0.14 mmol), NaO*t*Bu (400 mg, 4.2 mmol) and dioxane (10 mL). The reaction mixture was heated at reflux for ca. 100 h and then cooled down to room temperature, dioxane was evaporated in vacuo, the reaction mixture was taken up with dichloromethane (30 mL) and washed with water (15 mL), the water layer was washed twice with dichloromethane (20 mL), the organic layers were combined and dried over anhydrous sodium sulfate, and the solvent was evaporated in vacuo. The residue was chromatographed on silica with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 to afford **54** (190 mg, 45%) as a brown solid. ^{1}H NMR ($CDCl_3$, ppm): δ = 1.67 (br. q, J = 6.5 Hz, 2 H), 1.78 (br. q, J = 6.2 Hz, 2 H), 2.14 (s, 3 H), 2.17 (s, 3 H), 2.30 (s, 3 H), 2.52 (m, 12 H), 3.21 (t, J = 6.4 Hz, 2 H), 3.36 (t, J = 6.7 Hz, 2 H), 7.12 (d, J = 7.3 Hz, 1 H), 7.28 (dd, J = 8.3, 7.3 Hz, 1 H), 7.39 (m, 2 H), 7.68 (d, J = 8.3 Hz, 1 H), 7.95 (dd, J = 6.2, 3.7 Hz, 1 H), 8.03 (dd, J = 6.5, 3.4 Hz, 1 H), 8.34 (s, 1 H), 9.21 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 24.3 (1 C), 24.7 (1 C), 43.1 (2 C), 43.4 (1 C), 49.5 (1 C), 51.0 (1 C), 53.0 (1 C), 53.7 (1 C), 53.9 (1 C), 54.8 (1 C), 55.0 (1 C), 55.3 (1 C), 117.6 (1 C), 123.5 (1 C), 123.7 (1 C), 124.8 (1 C), 125.3 (1 C), 126.9 (1 C), 127.2 (1 C), 127.8 (1 C), 129.7 (1 C), 130.4 (1 C), 131.3 (1 C), 131.5 (1 C), 133.2 (1 C), 149.1 (1 C). MALDI-TOF: m/z = 418.65 [M$^+$].

1-(8-Chloro-1-anthracenyl)-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane (55): The procedure used was analogous to that described for the synthesis of **54**, except that $Pd(dba)_2$ (46 mg, 0.08 mmol) and BINAP (55 mg, 0.088 mmol) were employed instead of P*t*Bu$_3$. Chromatography of the crude material on silica with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 gave an equimolar mixture of **54** and **55** (172 mg, 39%). **55**: ^{1}H NMR ($CDCl_3$, ppm): δ = 1.68 (br. q, J = 6.5 Hz, 2 H), 1.73 (br. q, J = 6.2 Hz, 2 H), 2.15 (s, 3 H), 2.19 (s, 3 H), 2.27 (s, 3 H), 2.51 (m, 12 H), 3.23 (t, J = 6.7 Hz, 2 H), 3.33 (t, J = 6.6 Hz, 2 H), 7.17 (dd, J = 7.3, 1.0 Hz, 1 H), 7.38 (m, 2 H), 7.50 (dd, J = 7.3, 1.0 Hz, 1 H), 7.82 (d, J = 8.6 Hz, 1 H), 8.01 (d, J = 7.3 Hz, 1 H), 8.33 (s, 1 H), 9.41 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 22.7 (1 C), 23.7 (1 C), 41.3 (1 C), 41.5 (1 C), 42.0 (1 C), 51.8 (1 C), 53.5 (1 C), 53.7 (1 C), 54.0 (4 C), 54.5 (1 C), 119.0 (1 C), 119.2 (1 C), 125.1 (2 C), 125.6 (1 C), 126.1 (1 C), 127.6 (2 C), 128.7 (1 C), 130.5 (1 C), 132.0 (1 C), 132.3 (1 C), 133.4 (1 C), 148.0 (1 C). MALDI-TOF: m/z = 452.91 [M$^+$].

1,1′-(1,8-Anthracenediyl)bis(4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane) (56): The procedure used was analogous to that described for the synthesis of **55**, except that double quantities of $Pd(dba)_2$ (92 mg, 0.16 mmol) and BINAP (110 mg, 0.176 mmol) were employed. Chromatography of the reaction mixture on silica with $CH_2Cl_2/CH_3OH/NH_3$ 30:6:1 gave **54** (145 mg, 35%) and **56** (67 mg, 10%) as a brown solid. ^{1}H NMR ($CDCl_3$, ppm): δ = 1.71 (q, J = 6.4 Hz, 4 H), 1.75 (q, J = 6.4 Hz, 4 H), 2.17 (s, 6 H), 2.20 (s, 6 H), 2.30 (s, 6 H), 2.51 (m, 24 H), 3.38 (t, J = 6.4 Hz, 4 H), 3.48 (t, J = 6.4 Hz, 4 H), 7.11 (d, J = 7.0 Hz, 2 H), 7.35 (dd, J = 8.3, 7.0 Hz, 2 H), 7.65 (d, J = 8.3 Hz, 2 H), 8.33 (s, 1 H), 9.26 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 24.0 (4 C), 43.6 (4 C), 43.8 (2 C), 50.5 (2 C), 51.9 (2 C), 53.3 (2 C), 53.4 (2 C), 53.7 (2 C), 54.8 (2 C), 55.0 (2 C), 55.5 (2 C), 116.5 (2 C), 119.4 (1 C), 123.1 (2 C), 125.2 (2 C), 126.6 (1 C), 128.1 (2 C), 133.0 (2 C), 149.6 (2 C). MALDI-TOF: m/z = 658.71 [M^+].

13,13′-(1,8-Anthracenediyl)bis(1,4,7,10-tetraoxo-13-azacyclopentadecane) (58): 1,8-Dichloroanthracene (**1**; 123 mg, 0.5 mmol), 1-aza-15-crown-5 (**57**; 264 mg, 1.0 mmol), NaO*t*Bu (200 mg, 2.1 mmol), $Pd(dba)_2$ (23 mg, 0.04 mmol) and BINAP (62 mg, 0.1 mmol) were dissolved under argon in dioxane (40 mL) in a two-necked flask. The reaction mixture was heated at reflux for 48 h. After cooling down to room temperature it was concentrated in vacuo. The residue was taken up with CH_2Cl_2 (30 mL), washed with water (15 mL) and dried over anhydrous sodium sulfate, and the solvents were evaporated in vacuo. The residue was chromatographed on silica with CH_2Cl_2/MeOH 100:3 to give **58** (36 mg, 11%) as a brown solid and **13-(1-anthracenyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane** (**59**; 97 mg, 44%) as a brown solid. **58**: ^{1}H NMR ($CDCl_3$, ppm): δ = 3.68 (m, 40 H), 7.23 (d, J = 7.2 Hz, 2 H), 7.35 (dd, J = 8.6, 7.2 Hz, 2 H), 7.67 (d, J = 8.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 54.3 (4 C), 70.3 (4 C), 70.6 (4 C), 70.8 (4 C), 71.0 (4 C), 117.0 (2 C), 119.6 (1 C), 123.4 (2 C), 125.4 (2 C), 126.9 (1 C), 128.4 (2 C), 133.2 (2 C), 148.7 (2 C). **59**: ^{1}H NMR ($CDCl_3$, ppm): δ = 3.65 (m, 4 H), 3.70 (m, 16 H), 7.23 (d, J = 7.0 Hz, 1 H), 7.41 (m, 3 H), 7.73 (d, J = 8.3 Hz, 1 H), 7.95 (m, 1 H), 8.05 (m, 1 H), 8.36 (s, 1 H), 9.04 (s, 1 H). ^{13}C NMR ($CDCl_3$, ppm): δ = 54.6 (2 C), 69.0 (2 C), 70.6 (2 C), 70.8 (2 C), 71.1 (2 C), 117.0 (1 C), 123.5 (1 C), 124.0 (1 C), 125.2 (1 C), 125.6 (1 C), 126.4 (1 C), 127.9 (1 C), 129.0 (1 C), 129.3 (1 C), 131.1 (1 C), 131.5 (1 C), 131.7 (1 C), 133.3 (1 C), 148.6 (1 C).

Acknowledgments

The authors are grateful to INTAS (grant 97−0791) and PICS (n° 2105) for financial support.

[1] [1a] J. Houben, *Das Anthracen und die Anthrachinone*, W. Fischer, Ed., Georg Thieme Verlag: Leipzig, **1929**. [1b] K. Venkatamaran, *The Chemistry of Synthetic Dyes*, Academic Press Inc.: New York, **1952**, *2*. [1c] H.-S. Bien, J. Stawitz, K. Wunderlich, in *Ullmann's Encyclopedia of Industrial Chemistry*, Eds. W. Gerhartz, Y. S. Yamamoto, F. T. Campbell, R. Pfefferkorn, J. F. Rounsaville, VCH: Weinheim, **1985**, *A2*.

[2] [2a] M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435−461. [2b] R. A. Bissell, E. Calle, A. P. DeSilva, S. A. DeSilva, H. Q. N. Gunaratne, J.-L. Habib-Jiwan, S. L. A. Peiris, R. A. D. D. Rupasinghe, T. K. S. D. Samarasinghe, K. R. A. S. Sandanayake, J.-P. Soumillon, *J. Chem. Soc., Perkin Trans. 2* **1992**, 1559−1564. [2c] B. Witulski, M. Weber, U. Bergstraesser, J.-P. Desvergne, D. M. Bassani, H. Bouas-Laurent, *Org. Lett.* **2001**, *3*, 1467−1470.

[3] [3a] M. D. R. Benites, F. R. Fronczek, R. P. Hammer, A. W. Maverick, *Inorg. Chem.* **1997**, *36*, 5826−5831. [3b] R. W. Wagner, T. E. Johnson, J. S. Lindsey, *Tetrahedron* **1997**, *53*, 6755−6790. [3c] D. Marquis, J.-P. Desvergne, H. Bouas-Laurent, *J. Org. Chem.* **1995**, *60*, 7984−7996. [3d] J. H. R. Tucker, H. Bouas-Laurent, P. Marsau, S. W. Riley, J.-P. Desvergne, *Chem. Commun.* **1997**, 1165−1166. [3e] L. E. Echegoyen, H. K. Yoo, V. J. Gatto, G. W. Gokel, L. Echegoyen, *J. Am. Chem. Soc.* **1989**, *111*, 2440−2443. [3f] Z. H. Chen, O. F. Shall, M. Alcala, Y. Li, G. W. Gokel, L. Echegoyen, *J. Am. Chem. Soc.* **1992**, *114*, 444−451. [3g] A. M. Allgeier, C. A. Mirkin, *Angew. Chem.* **1998**, *110*, 936−952, *Angew. Chem. Int. Ed.* **1998**, *37*, 894−908. [3h] J. L. Sessler, T. D. Mody, D. A. Ford, V. Lynch, *Angew. Chem.* **1992**, *104*, 461−464, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 452−455. [3i] D. H. Vance, A. W. Czarnik, *J. Am. Chem. Soc.* **1993**, *115*, 12165−12166. [3j] S. Meyer, B. Andrioletti, J. L. Sessler, V. Lynch, *J. Org. Chem.* **1998**, *63*, 6752−6756.

[4] [4a] H. L. Kaufmann, L. Liable-Sands, A. L. Rheingold, S. J. N. Burgmayer, *Inorg. Chem.* **1999**, *38*, 2592−2599. [4b] B. L. Westcott, N. E. Gruhn, J. H. Enemark, *J. Am. Chem. Soc.* **1998**, *120*, 3382−3386. [4c] K. Wang, J. M. McConnachie, E. I. Stiefel, *Inorg. Chem.* **1999**, *38*, 4334−4341.

[5] [5a] D. M. Adams, L. Noodleman, D. N. Hendrickson, *Inorg. Chem.* **1997**, *36*, 3966−3984. [5b] A. Caneschi, A. Cornia, A. Dei, *Inorg. Chem.* **1998**, *37*, 3419−3421. [5c] A. S. Attia, C. G. Pierpont, *Inorg. Chem.* **1998**, *37*, 3051−3056. [5d] D. Ruiz-Molina, J. Veciana, K. Wurst, D. N. Hendickson, C. Rovira, *Inorg. Chem.* **2000**, *39*, 617−619. [5e] C. Roux, D. M. Adams, J. P. Ifie, A. Polian, D. N. Hendrickson, M. Verdaguer, *Inorg. Chem.* **1996**, *35*, 2846−2852. [5f] D. M. Adams, A. Dei, A. L. Rheingold, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 8221−8229. [5g] D. M. Adams, D. N. Hendrickson, *J. Am. Chem. Soc.* **1996**, *118*, 11515−11528. [5h] M. W. Lynch, D. N. Hendrickson, *J. Am. Chem. Soc.* **1981**, *103*, 3961−3963. [5i] R. M. Buchanan, C. G. Pierpont, *J. Am. Chem. Soc.* **1980**, *102*, 4951−4957.

[6] [6a] C. K. Chang, I. Abdalmuhdi, *J. Org. Chem.* **1983**, *48*, 5388−5390. [6b] R. Guilard, M. A. Lopez, A. Tabard, P. Richard, C. Lecomte, S. Brandès, J. E. Hutchison, J. P. Collman, *J. Am. Chem. Soc.* **1992**, *114*, 9877−9889. [6c] C. K. Chang, I. Abdalmuhdi, *Angew. Chem.* **1984**, *96*, 154−155, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 164−165. [6d] J. P. Collman, J. E. Hutchison, M. A. Lopez, A. Tabard, R. Guilard, W. K. Seok, J. A. Ibers, M. L′Her, *J. Am. Chem. Soc.* **1992**, *114*, 9869−9877.

[7] J. P. Collman, P. S. Wagenknecht, J. E. Hutchison, *Angew. Chem.* **1994**, *106*, 1620−1639, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1537−1554.

[8] [8a] R. Guilard, S. Brandès, C. Tardieux, A. Tabard, M. L'Her, C. Miry, P. Gouerec, Y. Knop, J. P. Collman, *J. Am. Chem. Soc.* **1995**, *117*, 11721−11729. [8b] M. Lachkar, A. Tabard, S. Brandès, R. Guilard, A. Atmani, A. De Cian, J. Fischer, R. Weiss, *Inorg. Chem.* **1997**, *36*, 4141−4146.

[9] [9a] J. S. Bradshaw, K. E. Krakowiak, R. M. Izatt, *Aza-Crown Macrocycles* Wiley: New York, **1993**. [9b] L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes* Cambridge Univ. Press: Cambridge, **1989**. [9c] R. Schneider, A. Riesen, T. A. Kaden, *Helv. Chim. Acta* **1986**, *68*, 53−61. [9d] M. Ciampolini, L. Fabbrizzi, A. Perotti, A. Poggi, B. Seghi, F. Zanobini, *Inorg. Chem.* **1987**, *26*, 3527−3533. [9e] A. Urfer, T. A. Kaden, *Helv. Chim. Acta* **1994**, *77*, 23−35. [9f] G. J. Bridger, R. T. Skerlj, D. Thornton, S. Padmanabhan, S. A. Martellucci, G. W. Henson, M. J. Abrams, N. Yamamoto, K. De Vreese, R. Pauwels, E. De Clercq, *J. Med. Chem.* **1995**, *38*, 366−378. [9g] A. Buttafava, L. Fabbrizzi, A. Perotti, B. Seghi, *J. Chem. Soc., Chem. Commun.* **1982**, 1166−1167. [9h] L. Fabbrizzi, L. Montagna, A. Poggi, T. A. Kaden, L. C. Siegfried, *Inorg. Chem.* **1986**, *25*, 2672−2674. [9i] A. Buttafava, L. Fabbrizzi, A. Perotti, A. Poggi, B. Seghi, *Inorg. Chem.* **1984**, *23*, 3917−3922. [9j] T. Kajiwara, T. Yamaguchi, H. Kido, S. Kawabata, R. Kuroda, T. Ito, *Inorg. Chem.* **1993**, *32*, 4990−4991.

[10] [10a] S. Brandès, C. Gros, F. Denat, P. Pullumbi, R. Guilard, *Bull. Soc. Chim. Fr.* **1996**, *133*, 65−73. [10b] F. Jérôme, C. P. Gros, C. Tardieux, J.-M. Barbe, R. Guilard, *Chem. Commun.* **1998**, 2007−2008. [10c] F. Jérôme, C. P. Gros, C. Tardieux, J.-M. Barbe, R. Guilard, *New. J. Chem.* **1998**, 1327−1329. [10d] B. Andrioletti, B. Boitrel, R. Guilard, *J. Org. Chem.* **1998**, *63*, 1312−1314. [10e] S. Brandès, S. Lacour, F. Denat, P. Pullumbi, R. Guilard, *J. Chem. Soc., Perkin Trans. 1* **1998**, 639−641. [10f] C. Comte, C. P. Gros, R. Guilard, R. G. Khoury, K. M. Smith, *J. Porphyrins Phthalocyanines* **1998**, *2*, 377−382. [10g] S. Brandès, F. Denat, S. Lacour, F. Rabiet, F. Barbette, P. Pullumbi, R. Guilard, *Eur. J. Org. Chem.* **1998**, 2349−2360. [10h] F. Denat, S. Lacour, S. Brandès, R. Guilard, *Tetrahedron Lett.* **1997**, *38*, 4417−4420. [10i] S. Brandès, P. Cocolios, R. Guilard, *C. R. Acad. Sc. Ser. II* **1996**, *328*, 827−833. [10j] F. Rabiet, F. Denat, R. Guilard, *Synthetic Commun*. **1997**, *27*, 979−987.

[11] [11a] G. DeSantis, L. Fabbrizzi, M. Licchelli, C. Mangano, D. Sacchi, N. Sardone, *Inorg. Chim. Acta* **1997**, *257*, 69−76. [11b] C. R. Cooper, T. D. James, *Chem. Commun.* **1997**, 1419−1420.

[12] [12a] M. S. Gibson, R. W. Bradshaw, *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 919−930. [12b] S. Arai, T. Yamagishi, S. Ototake, M. Hida, *Bull. Chem. Soc., Jpn.* **1977**, *50*, 547−548. [12c] S. Arai, A. Tanaka, M. Hida, T. Yamagishi, *Bull. Chem. Soc., Jpn.* **1979**, *52*, 1731−1734. [12d] S. Arai, M. Hida, T. Yamagishi, *Bull. Chem. Soc., Jpn.* **1978**, *51*, 277−282. [12e] K. Yoshida, M. Matsuoka, T. Ueyama, Y. Yamashita, T. Kitao, *Chem. Lett.* **1978**, 765−768. [12f] A. J. Belfield, G. R. Brown, A. J. Foubister, *Tetrahedron* **1999**, *55*, 11399−11428.

[13] M. W. Haenel, S. Oevers, J. Bruckmann, J. Kuhnig, C. Kruger, *Synlett* **1998**, 301−303.

[14] [14a] B. H. Yang, S. L. Buchwald, *J. Organomet. Chem.* **1999**, *576*, 125−146. [14b] J. F. Hartwig, *Angew. Chem.* **1998**, *110*, 2154−2177, *Angew. Chem. Int. Ed.* **1998**, *37*, 2046−2067. [14c] J. P. Wolfe, S. L. Buchwald, *J. Org. Chem.* **2000**, *65*, 1144−1157. [14d] M. Kosugi, M. Kameyama, T. Migita, *Chem. Lett.* **1983**, 927−928.

[15] J. P. Wolfe, H. Tomori, J. P. Sadighi, J. Yin, S. L. Buchwald, *J. Org. Chem.* **2000**, *65*, 1158−1174.

[16] [16a] N. P. Reddy, M. Tanaka, *Tetrahedron Lett.* **1997**, *38*, 4807−4810. [16b] M. Nishiyama, T. Yamamoto, Y. Koie, *Tetrahedron Lett.* **1998**, *39*, 617−620.

[17] [17a] J. Huang, G. Grasa, S. P. Nolan, *Org. Lett.* **1999**, *1*, 1307−1309. [17b] G. A. Grasa, M. S. Viciu, J. Huang, S. P. Nolan, *J. Org. Chem.* **2001**, *66*, 7729−7737.

[18] [18a] E. Brenner, R. Schneider, Y. Fort, *Tetrahedron* **1999**, *55*, 12829−12842. [18b] E. Brenner, Y. Fort, *Tetrahedron Lett.* **1998**, *39*, 5359−5362. [18c] C. Desmartes, R. Schneider, Y. Fort, *Tetrahedron Lett.* **2000**, *41*, 2875−2879. [18d] E. Brenner, R. Schneider, Y. Fort, *Tetrahedron Lett.* **2000**, *41*, 2881−2884. [18e] B. Gradel, E. Brenner, R. Schneider, Y. Fort, *Tetrahedron Lett.* **2001**, *42*, 5689−5692.

[19] [19a] I. P. Beletskaya, A. D. Averin, A. G. Bessmertnykh, R. Guilard, *Tetrahedron Lett.* **2001**, *42*, 4983−4986. [19b] I. P. Beletskaya, A. D. Averin, A. G. Bessmertnykh, R. Guilard, *Tetrahedron Lett.* **2001**, *42*, 4987−4989. [19c] I. P. Beletskaya, A. D. Averin, A. G. Bessmertnykh, F. Denat, R. Guilard, *Tetrahedron Lett.* **2002**, *43*, 1193−1196.

[20] [20a] S. Wagaw, S. L. Buchwald, *J. Org. Chem.* **1996**, *61*, 7240−7241. [20b] Y. Hong, C. H. Senanayake, T. Xiang, C. P. Vandenbossche, G. J. Tanoury, R. P. Bakale, S. A. Wald, *Tetrahedron Lett.* **1998**, *39*, 3121−3124. [20c] J. Kosmrlj, B. U. W. Maes, G. L. F. Lemiere, A. Haemers, *Synlett* **2000**, 1581−1584.

[21] [21a] R. Guilard, A. G. Bessmertnykh, I. P. Beletskaya, *Tetrahedron Lett.* **1997**, *38*, 2287−2290. [21b] R.Guilard, A. G. Bessmertnykh, I. P. Beletskaya, *Synlett* **1999**, 1459−1461. [21c] I. P. Beletskaya, A. G. Bessmertnykh, A. D. Averin, F. Denat, R. Guilard, *Eur. J. Org. Chem.* submitted.

[22] [22a] R. Guilard, A. G. Bessmertnykh, I. P. Beletskaya, *Tetrahedron Lett.* **1999**, *40*, 6393−6397. [22b] F. M. Rivas, U. Riaz, S. T. Diver, *Tetrahedron: Asymmetry* **2000**, *11*, 1703−1707.

[23] [23a] B. Altava, M. I. Burguete, B. Escuder, S. V. Luis, *Tetrahedron* **1997**, *53*, 2629−2640. [23b] M. I. Burguete, B. Escuder, S. V. Luis, J. F. Miravet, M. Querol, E. Garcia-Espana, *Tetrahedron Lett.* **1998**, *39*, 3799−3802.

[24] D. W. Old, J. P. Wolfe, S. L. Buchwald, *J. Am. Chem. Soc.* **1998**, *120*, 9722−9723.

[25] M. Subat, B. Koenig, *Synthesis* **2001**, *12*, 1818−1825.

[26] [26a] X. X. Zhang, S. L. Buchwald, *J. Org. Chem.* **2000**, *65*, 8027−8031. [26b] B. Witulski, *Synlett* **1999**, 1223−1226. [26c] B. Witulski, Y. Zimmerman, V. Dacros, J.-P. Desvergne, D. M. Bassani, H. Bouas-Laurent, *Tetrahedron Lett.* **1998**, *39*, 4807−4808.

[27] A Gouloumis, R. C. Lawson, P. Vazquez, L. Echegoyen, T. Torres, *Tetrahedron* **2002**, *58*, 961−966.

[28] T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, J. A. Ibers, *J. Organomet. Chem.* **1974**, *65*, 253−266.

[29] R. Golden, L. M. Stock, *J. Am. Chem. Soc.* **1972**, *94*, 3080−3088.

[30] E. K. Barefield, *Inorg. Chem*. **1972**, *11*, 2273−2274.

[31] G. Herve, H. Bernard, N. Le Bris, J.-J. Yaouanc, H. Handel, L. Toupet, *Tetrahedron Lett.* **1998**, *39*, 6861−6864.

[32] R. Guilard, F. Denat, O. Pernelet, R. Tripier, H. Ledon, C. Devos, *FR 2789380* **2000**, CAN 133:283719.

Received July 1, 2004

