One-Pot Synthesis of Tetraazabis(tropocoronand)s and Podands from Benzo[*b*]cyclohept[*e*][1,4]oxazine and α,ω-Polymethylenediamines[1)]

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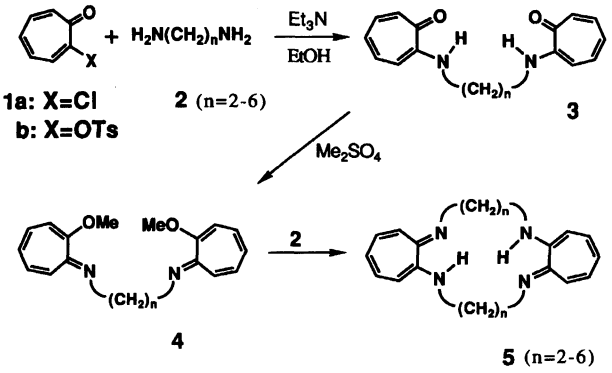
The reactions of benzo[*b*]cyclohept[*e*][1,4]oxazine (**9**) with a 1.2 equivalent of α,ω-alkanediamines (**2**, n= 4—12) in ethanol at 80 °C afforded tropocoronands (**5**, n,n'=4,4—12,12) in a one-pot procedure and in high yields, while the reaction of **9** with an excess of **2** mainly gave tropopodands **12** (n,n'=4,4—6,6). The reactions of **9** with short-chain diamines **2** (n=2,3) yielded bicyclic pyrazino or diazepino compounds as the main products. The reaction of **9** with ω-amino alcohol afforded the corresponding dihydroxy podands **23**. The predicted pathways of the reaction of **9** with **2** were experimentally confirmed.

Almost ten years ago, one of us (T.N.) and his co-workers synthesized a new class of metal-complexing macrocycles containing two 2-aminotroponimine units bridged by polymethylenes (**5**), which were called tropocoronands.[2a)] To be more exact, the name of these compounds should have been tetraazabis(tropocoronand)s.[3)] These crown-type compounds were synthesized from reactive troponoids **1** and α,ω-alkanediamines (**2**) via ditropones **3** and bis(enol ether)s **4** followed by treatment with another molecule of diamine **2** under high dilution conditions[2a)] (Scheme 1). They also synthesized tropocoronand **7** having an *O*- or *S*-atom in the linkage by similar method,[2)] using α,ω-diamines **6** (X=O or S) (Chart 1). Several interesting physicochemical properties were revealed for their transition metal complexes **8**. Nickel complex **8** (n,n'=3,3, M=Ni) has a square planer diamagnetic structure, whereas **8** (n,n'=6,6, M=Ni) has a pseudotetrahedral paramagnetic form.[2b)] If the size of cavity is sufficiently large two copper metals can be complexed in the cavity, and both Cu metals in **8** (n,n'=6,6, M=Cu_2) are coordinated with acetato and methoxo ligands.[4a)] Lippard and his co-workers also studied the catalytic effect of metal complexes of tropocoronands and chiral tropopodands.[4)] Since the overall yields of **5** from **1** were only 12—23% (for n,n'=3,3—6,6) and <1% (for n,n'=2,2), a more convenient synthetic method has been desired.

We then found that benzo[*b*]cyclohept[*e*][1,4]oxazine (**9**)[5)] reacts with various 1,2-difunctional nucleophiles, ethylenediamine, *o*-phenylenediamine or their *S*-, and *O*-analogs, to give various interesting heterocycles by novel intermolecular heterocycle-exchange reactions.[2d,6b)] We therefore expected that coronands **5** should be easily produced from **9** and diamines **2** in preference to the other competing pathways (i—vi) illustrated in Scheme 2, if suitable reaction conditions were employed. Namely, we thought that in the reactions of **9** with **2** the initially formed key intermediate **11** should react either with another molecule of **11** to yield tropocoronands **5** via a dimer **b**, extending two molar of *o*-aminophenol (**10**) (path i), or with another molecule of **9**, and then with **2**, to furnish **5** (via **c** and **d**, path ii). On the other hand, if an excess of diamine **2** exists, tropopodands **12** might be produced by a nucleophilic displacement reaction (path iii). Tropocoronands **5** may also be produced from **12** and **9** via **f** (path iv). If the methylene chain of diamine **2** is too short (n=2 or 3) or too long (n=12 or more), the corresponding bicyclic compounds **13** would be produced preferentially (path v). This synthesis must be carried out under anaerobic conditions, because the key intermediate **11** was oxidized into a stable, dehydrocyclized by-product **14** via a cyclo tautomer **11′** (path vi). Our experimental results have turned out to coincide exactly



Scheme 1.

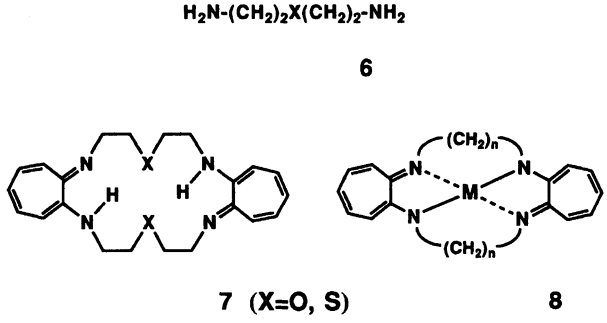
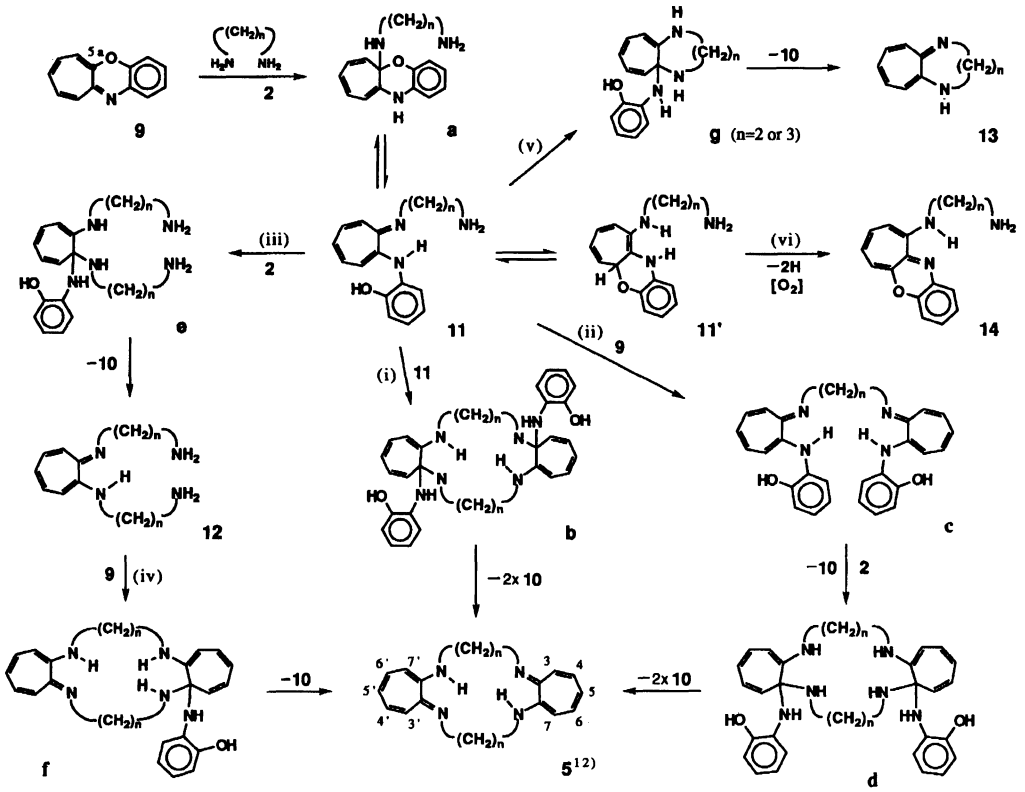


Chart 1.



Scheme 2.

with these predictions.

Results and Discussion

We first studied the reactions of **9** with **2** (n=2—12) in a 1:1.2 ratio in absolute ethanol at 80 °C under an inert atmosphere.[7] These reactions gave orange crystalline precipitates of tropocoronands **5** as the main products, except for the reaction with short-chain diamines **2** (n=2,3). Products **5b**—**e** (n,n'=3,3—6,6) were identified on the basis on UV, NMR, and mass spectra, as previously reported.[2] By this one-pot synthesis, we were able to obtain tropocoronands **5** in 70—86% yield (for n,n'=4,4—12,12) and 3% yield (for n,n'=3,3) (Table 1).

The by-products formed by the reaction of **9** with 1, 5-pentanediamine (**2**, n=5) were closely examined. The contents of the mother liquor were separated by silica-gel column chromatography into **A** to **E** (see Experimental section). A red compound **A** and pale-yellow compounds **B** and **C** were obtained from a benzene–methanol eluant, and high adsorptive compounds of red brown **D** and orange **E** were obtained from the eluant of methanol containing saturated aqueous solution of NaCl. Compound **A** (red needles, mp 146—150 °C) had no fragment peak between m/z 488 (M^+) and m/z 278 (M^+-210, due to β-cleavage) in the mass spectrum. It showed ^{1}H NMR signals at δ=1.56, 1.78, and 3.24 (2:4:4 proton ratio) due to ten protons of a symmetrical methylene chain and at δ=5.84—6.94 due to two sets of four adjacent protons on the seven-membered ring and benzene ring, indicating its symmetric structure **15d** (Chart 2). The position of the side chain of the seven-membered ring was determined based on the similarity of an analogous compound.[8] Compounds **B** and **C** were identified spectroscopically to be 2-phenylbenzoxazole **16** (1%)[9] and a known oxidative dimer (**17**)[10] of **10** produced by a heteroring-exchange reaction. The ring contraction of **11** to **16** is considered to proceed via intermediate **h** followed by norcaradiene **i**, as shown in Scheme 3.

Compound **D** showed a UV spectrum similar to that

Table 1. Synthesis of Tropocoronands **5** by the Reaction of **9** with **2**

Reagents	Products	Yield/%	Mp/°C	Color-shape
2a (n=2)	**5a**[2c]	0		
2b (n=3)	**5b**[2c]	3	214—229	Orange needles
2c (n=4)	**5c**[2c]	70	197—202	Orange crystals
2d (n=5)	**5d**[2c]	73	199—207	Orange needles
2e (n=6)	**5e**[2c]	76	120—122	Orange needles
2f (n=7)	**5f**	86	168—178	Orange needles
2g (n=8)	**5g**	81	75—77	Orange prisms
2h (n=9)	**5h**	72	162—164	Orange needles
2i (n=10)	**5i**	85	65—67	Orange prisms
2j (n=11)	**5j**	79	157—163	Orange needles
2k (n=12)	**5k**	84	71—73	Orange prisms

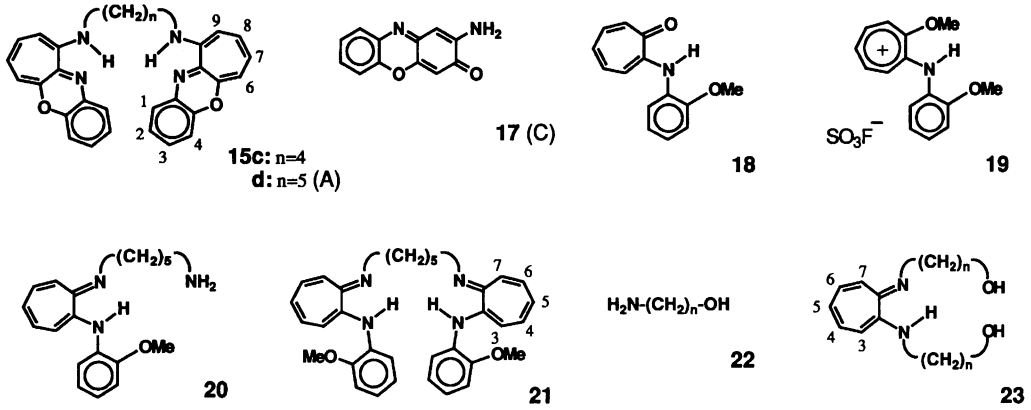
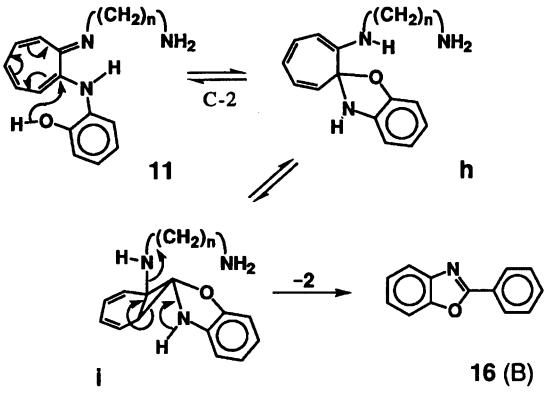


Chart 2.



Scheme 3.

of **15d** and a molecular ion peak at m/z 295 in the mass spectrum. The ^{1}H NMR spectrum closely resembled that of **15d** with the exception of the ratio of the ring protons to the methylene protons. From these spectra, the structure of **D** was identified as 10-(5-aminopentylamino)benzo[*b*]cyclohept[*e*][1,4]oxazine (**14d**, n=5). Compounds **14d** and **15d** were oxidative products formed from the key intermediates, **11d** (n=5) and **c** (n=5) (Scheme 2), by the action of a small amount of oxygen contaminated in the reaction media. Both the UV and ^{1}H NMR spectra of **E** resembled those of tropocoronand **5d** (n,n'=5,5), except for a 5 : 20 proton ratio (instead of 10 : 20) of ring protons to methylene protons of the side chains (linker chains), indicating a structure of tropopodand **12d** (n,n'=5,5) having two side chains for **E**. The treatment of **9** with **2d** (n=5) in ethanol at 80 °C in the atmosphere gave **14d** (n=5) and **15d** (n=5) as the main products.

The reaction of **9** with **2** (n=4) in methanol in a 1 : 1.2 ratio at 20 °C gave a readily crystallized key intermediate compound **11c** (n=4) in 84% yield. Upon heating under anaerobic conditions in ethanol **11c** was converted into coronand **5c** (n,n'=4,4) in 40% yield, while **11c** gave an oxidation product **14c** under atmospheric conditions. Another key intermediate **11** could not be obtained as precipitates under the same conditions.

Compound **11c** also reacted with **2c** to give podand **12c** quantitatively under anaerobic conditions. The reaction of **9** with **12c** gave coronand **5c** under anaerobic conditions. We were unable to obtain intermediate **c** of path (ii), due to the high reactivity of the OH groups. We therefore synthesized the bis(methoxyanilino) compound **21** in order to prove the existence of path (ii). The treatment of 2-(2-methoxyanilino)tropone[5] (**18**) with methyl fluorosulfate gave enol ether **19**, which reacted with **2d** to give **20**. Compound **21** was obtained by the reactions of **19** with **2d** (2 : 1) or with **20** (1.5 : 1) in high yields. Upon heating at 80 °C under atmospheric conditions **20** was converted into coronand **5d** (n,n'=5,5) in 89% yield. On the other hand, although the reaction of **21** with **2d** (n=5) (1 : 1.2) at 120 °C produced **5d** (n,n'=5,5) in 86%, the same reactions at 80—100 °C gave only a small amount of **5d**. A similar reaction of **9** with a shorter linker chain **2a** and **2b** (n=2,3) afforded, as expected, 2,3-dihydro-1*H*-cyclohepta[*b*]pyrazine (**13a**)[11] and 1,2,3,4-tetrahydrocyclohepta[*b*][1,4]diazepine (**13b**, n=3), respectively. No tropocoronand **5a** (n,n'=2,2) was produced under these reaction conditions.

We then tried to synthesize tropopodands **12** by the reaction of **9** with an excess of amines **2**. The reactions of **9** with **2a**—**e** (n=2—6) in a 1 : 4—8 ratio at 80 °C gave podands **12c**—**e** (n,n'=4,4—6,6) in 62—81% yield, while those of **9** with **2** (n=2,3), yielded **13a** and **13b** instead of the corresponding podands (see Table 2). The reactions of **9** with ω-amino alcohol **22a**—**e** (n=2—6) under the above conditions afforded **23a**—**e** (n,n'=2—6) in 58—90% yield (Table 2).

These experimental results definitely confirmed our prediction shown in Scheme 2 and proved the competitive formation of coronand **5** by three different paths (i, ii, and iii in Scheme 2), the ratio of which varies according to the kinds of reagent (**2**) and the reaction conditions employed.

The reasons for the high yields of coronand **5** by the present methode are considered to be as follows. On

Table 2. Synthesis of Tropopodands **12** and **23** by the Reaction of **9** with **2** and **22**

Reagents	Products	Yield/%	Mp/°C	Color-shape
2a (n=2)	**12a**	0		
2b (n=3)	**12b**	0		
2c (n=4)	**12c**[2c]	62	85—90	Orange crystals
2d (n=5)	**12d**	68		Orange oil
2e (n=6)	**12e**	81	72—75	Orange crystals
22a (n=2)	**23a**	58	77—79	Orange crystals
22b (n=3)	**23b**	72	59—65	Orange crystals
22c (n=4)	**23c**	68		Orange oil
22d (n=5)	**23d**	90	64—69	Orange crystals
22e (n=6)	**23e**	79	40—43	Orange crystals

macroheterocyclizations in paths i—iii, intermediates **h**, **i**, and **j** are the precusors of tricyclic intermediates **b**, **d**, and **f** (Scheme 2 and Chart 3). An intramolecular addition of the terminal amino group of the diaminopolymethylene branch of the intermediates **h**, **i** and **j**, would take place very easily to the C=N bonds on the seven-membered ring. An attack of the amino group to the overcrowded C=N site in another molecule is not likely to occur. Intermediates **b**, **d**, and **f**, thus formed, become aromatized by releasing *o*-aminophenol (**10**) to give coronands **5**. On the other hand, the products from intermediate **4** (Scheme 1) tend to become very complicated, giving **5** in smaller yields, mainly because of the competitive attack of α,ω-alkanediamine at both C–OMe and C=N on the seven-membered ring of **4**.

We were thus able to readily prepare the tetraazabis(tropocoronand)s and related tropopodands by a one-pot synthesis from benzo[*b*]cyclohept[*e*][1,4]oxazine and α,ω-alkanediamines and amines in good yields without using a high dilution technique.

Experimental

The melting points were determined with a Yanagimoto MP-3S melting-point apparatus and were uncorrected. The IR and electronic spectra were measured by using Shimadzu IR-450 and Shimadzu UV-265FS spectrophotometers, respectively; the UV spectra in acid and alkaline solutions were taken after adding a few drops of 6M HCl or 6M NaOH (1 M=1 mol dm^{-3}) to the sample solution. The NMR spectra were measured in $CDCl_3$ (unless otherwise specified) with a JEOL JNM-GX270 (270 MHz for ^{1}H and 67.8 MHz for ^{13}C) spectrometer using TMS as an internal standard. The assignments of all signals were made by employing a first-order analysis with the aid of a decoupling technique.[12] The mass spectra were taken on a JEOL JMS-DX300 mass spectrometer and a Shimadzu QP 2000 GC-mass spectrometer at 70 eV. The TLC analyses were carried out with Merck Kieselgel 60F-254 plates using benzene–methanol and methanol–NaCl aq (1 : 1) as an eluent.

General Procedures for the Equimolar Reactions 6,7,8,9,10,11,18,19,20,21,22,23-Dodecahydrodicyclohepta[*b*,*k*][1,4,10,13]tetraazacyclooctadecine (5d[2]), *n*,*n*′=5,5). A solution of **9** (200 mg, 1.03 mmol) and **2d** (125 mg, 1.23 mmol) in absolute ethanol (2 ml) was heated at 80 °C for 30 h under an argon atmosphere. After having been set aside overnight at room temperature, the orange precipitate which formed was collected and washed with cold methanol to give, upon recrystallization (chloroform–methanol), **5d**[2] as yellow needles (141 mg, 73% yield). The filtrate was concentrated in vacuo. The residue was dissolved in chloroform and passed through a silica-gel column. A red compound **15d** (5 mg, 2%)(**A**) and pale-yellow compounds **16**[9] (<1%)(**B**) and **17**[10](**C**) were obtained from the benzene–methanol (50 : 1) eluant and high absorptive compounds of reddish brown **14d** (9 mg, 3%)(**D**) and orange **12d** (12 mg, 4%)(**E**) were obtained from the methanol–NaCl aq (1 : 1) eluant.

***N*,*N*′- Bis(benzo[*b*]cyclohept[*e*][1, 4]oxazin- 10- yl)-1,5-pentanediamine (15d, *n*=5):** Red needles; mp 146—150 °C (from benzene); UV λ_{max} (MeOH) 234, 264, 297, 474, 525^{sh} nm; IR (KBr) 3270 cm^{-1} (NH); ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.56 (2H, m, CH_2), 1.78 (4H, m, CH_2), 3.24 (4H, m, NCH_2), 5.84 (2H, d, J=10.0 Hz, H-6,6′), 5.90 (2H, t, J=10.0 Hz, H-8,8′), 5.95 (2H, dd, J=10.0 and 1.8 Hz, H-9,9′), 6.24 (2H, td, J=10.0 and 1.8 Hz, H-7,7′), 6.37 (2H, m, J=8 and 2 Hz, H-4,4′), 6.66 (2H, m, J=8 and 2 Hz, H-2,2′), 6.69 (2H, m, J=8 and 2 Hz, H-3, 3′), 6.75 (2H, m, J=8 and 2 Hz, H-1,1′), 6.94 (2H, br, NH); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=24.96 (CH_2), 28.42 (CH_2), 42.89 (NCH_2), 108.20 (C-6,6′), 113.68 (C-4,4′), 116.29 (C-9, 9′), 120.82 (C-8,8′), 123.93 (C-2,2′), 124.85 (C-1,1′), 126.35 (C-3,3′), 128.42 (C-7,7′), 135.92 (C-4a,4a′), 146.39 (C-11a, 11a′), 148.04 (C-5a,5a′), 150.59 (C-10a,10a′); MS m/z 488 (M^+, 10%), 278 (71), 221 (70), 195 (100). Found: m/z 488.2236. Calcd for $C_{31}H_{28}N_4O_2$: M, 488.2210.

10- (5- Aminopentylamino)benzo[*b*]cyclohept[*e*][1,4]oxazine (14d, *n*=5): Reddish-brown oil; UV λ_{max} (MeOH) 234, 264, 296, 476, 530^{sh} nm; IR (KBr) 3350 and 3270 cm^{-1} (NH); ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.49 (2H, m, CH_2), 1.73 (2H, m, CH_2), 2.15 (2H, br, NH_2), 2.72 (2H, m, CH_2), 3.21 (2H, m, CH_2), 5.84 (1H, d, J=10.0 Hz, H-6), 5.90 (1H, t, J=10.0 Hz, H-8), 5.96 (1H, dd, J=10.0 and 2.0 Hz, H-9), 6.24 (1H, td, J=10.0 and 2.0 Hz, H-7), 6.37 (1H, m, J=8 and 2 Hz, H-4), 6.68 (1H, m, J=8 and 2 Hz, H-2), 6.76 (1H, m, J=8 and 2 Hz, H-3), 7.12 (1H, m, J=8 and 2 Hz, H-1); MS m/z 295 (M^+, 40%), 223 (73%), 195 (100%). Found: m/z 295.1673. Calcd for $C_{18}H_{21}N_3O$: M, 295.1686.

Synthesis of Other Tropocoronands. The reactions of **9** with α,ω-alkanediamines (n=3,4,6—12) (mole ratio, 1 : 1.2) as described above gave previously known **5b—e**[2] and unknown **5f—k**. The yields and melting points are shown in Table 1.

6, 7, 8, 9, 10, 11, 12, 13, 20, 21, 22, 23, 24, 25, 26, 27-Hexadecahydrodicyclohepta[*b*,*m*][1,4,12,15]tetraazacyclodocosine (5f, *n*,*n*′=7,7): Orange needles; mp 168—178 °C (from $CHCl_3$–MeOH); UV λ_{max} ($CHCl_3$) 260 (log ε 4.42), 328 (3.89, sh), 347 (4.10), 359 (4.11), 382 (3.92), 414 (4.07), 446 (3.83, sh), 465 (3.62), 513 nm (2.84, sh); IR (KBr) 3230cm^{-1} (NH); ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.43 (12H, m, CH_2), 1.72 (8H, m, CH_2), 3.27 (8H, t, J=7 Hz, CH_2), 6.11 (2H, t, J=10 Hz, H-5), 6.25 (4H, d, J=10 Hz, H-3,7), 6.72 (4H, t, J=10 Hz, H-4,6); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=27.55 (t, CH_2), 29.31 (t, CH_2), 29.99 (t, CH_2), 46.30 (t, CH_2), 109.99 (d, C-3,7), 117.45 (d, C-5), 132.86 (d, C-4,6), 152.88 (s, C-1,2); MS m/z 432 (M^+, 95%), 361 (69),

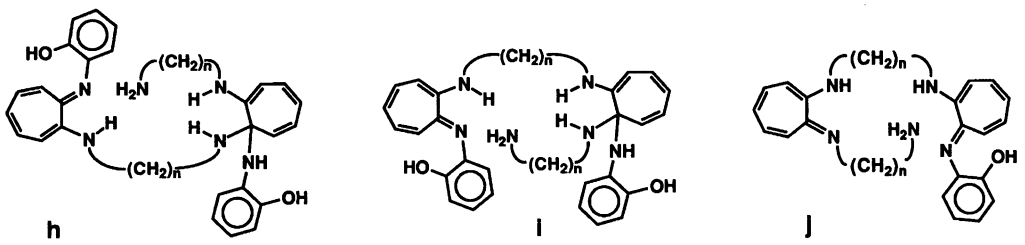


Chart 3.

131 (100). Found: C, 77.85; H, 9.12; N, 12.80%. Calcd for $C_{28}H_{40}N_4$: C, 77.73%; H, 9.32; N, 12.95%.

6,7,8,9,10,11,12,13,14,21,22,23,24,25,26,27,28,29-Octadecahydrodicyclohepta[*b*,*n*][1,4,13,16]tetraazacyclotetraicosine (5g, *n*,*n*′=8,8): Orange prisms; mp 75—77 °C (from $CHCl_3$–MeOH); UV λ_{max} (MeOH) 260 ($\log\varepsilon$ 4.50), 328 (3.95, sh), 346 (4.17), 359 (4.19), 382 (3.98, sh), 396 (4.04, sh), 415 (4.13), 442 (3.95, sh), 464 (3.69), 510 nm (2.89, sh); IR (KBr) 3200 cm^{-1} (NH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.39 (16H, m, CH_2), 1.73 (8H, m, CH_2), 3.18 (2H, br, NH), 3.30 (8H, m, CH_2), 6.12 (2H, t, J=10 Hz, H-5), 6.27 (4H, d, J=10 Hz, H-3,7), 6.73 (4H, t, J=10 Hz, H-4,6); MS m/z 460 (M^+, 72%), 375 (39), 195 (100), 131 (80). Found: C, 77.95; H, 9.28; N, 11.83%. Calcd for $C_{30}H_{44}N_4$: C, 78.21; H, 9.63; N, 12.16%.

6,7,8,9,10,11,12,13,14,15,22,23,24,25,26,27,28,29,30,31-Icosahydrodicyclohepta[*b*,*o*][1,4,14,17]tetraazacyclohexacosine (5h, *n*,*n*′=9,9): Orange needles; mp 162—164 °C (from $CHCl_3$–MeOH); UV λ_{max} (MeOH) 261 ($\log\varepsilon$ 4.53), 290 (4.15, sh), 330 (3.98, sh), 347 (4.19), 358 (4.19), 382 (3.99, sh), 414 (4.15), 444 (3.91, sh), 464 (3.67), 511 nm (2.71, sh); IR (KBr) 3220 cm^{-1} (NH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.34 (12H, m, CH_2), 1.43 (8H, m, CH_2), 1.72 (8H, m, J=7 Hz, CH_2), 3.29 (8H, m, J=7 Hz, CH_2), 6.10 (2H, t, J=10 Hz, H-5), 6.25 (4H, d, J=10 Hz, H-3,7), 6.72 (4H, t, J=10 Hz, H-4,6); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=27.59 (t, CH_2), 29.48 (t, CH_2), 29.66 (t, CH_2), 30.05 (t, CH_2), 46.32 (t, CH_2), 109.97 (d, C-3,7), 117.42 (d, C-5), 132.84 (d, C-4,6), 152.90 (s, C-1,2); MS m/z 488 (M^+, 48%), 389 (34), 131 (100). Found: C, 78.40; H, 9.72; N, 11.25%. Calcd for $C_{32}H_{48}N_4$: C, 78.64; H, 9.90; N, 11.46%.

6,7,8,9,10,11,12,13,14,15,16,23,24,25,26,27,28,29,30,31,32,33-Docosahydrodicyclohepta[*b*,*p*][1,4,15,18]-tetraazacyclooctacosine (5i, *n*,*n*′=10,10): Orange prisms; mp 65—67 °C (from $CHCl_3$–MeOH); UV λ_{max} (MeOH) 261 ($\log\varepsilon$ 4.50), 290 (4.15, sh), 328 (3.92, sh), 346 (4.14), 360 (4.15), 381 (3.97, sh), 416 (4.12), 443 (3.94, sh), 464 (3.73), 530 nm (2.89, sh); IR (KBr) 3220 cm^{-1} (NH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.32 (18H, m, CH_2), 1.42 (8H, m, CH_2), 1.72 (8H, m, J=7 Hz, CH_2), 3.28 (8H, m, J=7 Hz, CH_2), 6.10 (2H, t, J=10 Hz, H-5), 6.25 (4H, d, J=10 Hz, H-3.7), 6.72 (4H, t, J=10 Hz, H-4,6); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=27.60 (t, CH_2), 29.52 (t, CH_2), 29.65 (t, CH_2), 30.05 (t, CH_2), 46.32 (t, CH_2), 109.97 (d, C-3,7), 117.40 (d, C-5), 132.84 (d, C-4,6), 152.92 (s, C-1,2); MS m/z 516 (M^+, 17%), 403 (18), 288 (15), 195 (100). Found: C, 79.33; H, 9.80; N, 10.68%. Calcd for $C_{34}H_{52}N_4$: C, 79.02; H, 10.14; N, 10.84%.

6,7,8,9,10,11,12,13,14,15,16,17,24,25,26,27,28,29,30,31,32,33,34,35-Tetracosahydrodicyclohepta[*b*,*q*][1,4,16,19]tetraazacyclotriacontine (5j, *n*,*n*′=11,11): Orange needles; mp 157—163 °C (from $CHCl_3$–MeOH); UV λ_{max} (MeOH) 261 ($\log\varepsilon$ 4.49), 290 (4.23, sh), 346 (4.12), 359 (4.15), 380 (4.03), 415 (4.10), 436 (3.99, sh), 462 (3.83), 534 nm (2.90); IR (KBr) 3210 cm^{-1} (NH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.31 (20H, m, CH_2), 1.42 (8H, m, CH_2), 1.72 (8H, m J=7 Hz, CH_2), 3.28 (8H, m, H=7 Hz, CH_2), 6.11 (2H, t, J=10 Hz, H-5), 6.26 (4H, d, J=10 Hz, H-3,7), 6.73 (4H, t, J=10 Hz, H-4,6); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=27.60 (t, CH_2), 29.53 (t, CH_2), 29.65 (t, CH_2), 30.04 (t, CH_2), 46.32 (t, CH_2), 109.99 (d, C-3,7), 117.42 (d, C-5), 132.86 (d, C-4,6), 152.93 (s, C-1,2); MS m/z 544 (M^+, 73%), 417 (63), 302 (55), 195 (68). Found: C, 79.04; H, 10.23; N, 10.11%. Calcd for $C_{36}H_{56}N_4$: C, 79.36; H, 10.36; N, 10.28%.

6,7,8,9,10,11,12,13,14,15,16,17,18,25,26,27,28,29,30,31,32,33,34,35,36,37-Hexacosahydrodicyclohepta[*b*,*r*][1,4,17,20]tetraazacyclododriacontine (5k, *n*,*n*′=12,12): Orange prisms; mp 71—73 °C (from $CHCl_3$–MeOH); UV λ_{max} (MeOH) 263 ($\log\varepsilon$ 4.52), 289 (4.33, sh), 348 (4.17), 360 (4.21), 379 (4.15), 416 (4.13), 435 (4.06), 463 (3.96), 513 nm (3.10); IR (KBr) 3200 cm^{-1} (NH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.28 (24H, m, CH_2), 1.42 (8H, m, CH_2), 1.72 (8H, m, CH_2), 3.30 (8H, m, CH_2), 6.11 (2H, t, J=10 Hz, H-5), 6.27 (4H, d, J=10 Hz, H-3, 7), 6.74 (4H, t, J=10 Hz, H-4,6); MS m/z 572 (M^+, 90%), 431 (42), 195 (100), 131 (75). Found: C, 79.60; H, 10.49; N, 9.87%. Calcd for $C_{38}H_{60}N_4$: C, 79.67; H, 10.56; N, 9.77%.

6,7,8,9,10,17,18,19,20,21-Decahydrodicyclohepta-[*b*,*j*][1,4,9,12]tetraazacyclohexadecine (5c,[2] *n*,*n*′=4, 4). A mixture of **9** (200 mg, 1.03 mmol) and **2c** (108 mg, 1.23 mmol) in dry 1-butanol (2 ml) was heated at 100 °C for 30 h under an argon atmosphere. After one night at room temperature, the orange precipitate which formed was collected (as described above) to give **5c**[2] as yellow needles (125 mg, 70% yields). The filtrate was concentrated in vacuo, and the residue was passed through a silica-gel column to give **12c** (5 mg, 2% yield, see below) and **15c** (3 mg, 1% yield).

***N*,*N*′- Bis(benzo[*b*]cyclohept[*e*][1, 4]oxazin- 10- yl)-1,4-butanediamine (15c, *n*=4):** Reddish brown crystals; mp 146—151 °C (from benzene); UV λ_{max} (MeOH) 234, 266, 300, 475, 530 nm; IR (KBr) 3270 cm^{-1} (NH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.84 (4H, m, CH_2), 3.29 (4H, m, CH_2), 5.84 (2H, d, J=10 Hz, H-6,6′), 5.90 (2H, t, J=10 Hz, H-8,8′), 5.95 (2H, dd, J=10 and 1.8 Hz, H-9,9′), 6.23 (2H, td, J=10 and 1.8 Hz, H-7,7′), 6.38 (2H, m, J=8 and 2 Hz, H-4,4′), 6.67 (2H, m, J=8 and 2 Hz, H-2,2′), 6.70 (2H, m, J=8 and 2 Hz, H-3,3′), 6.75 (2H, m, J=8 and 2 Hz, H-1,1′), 6.95 (2H, br, NH); MS m/z 474 (M^+, 45%), 264

(100), 221 (81), 195 (85). Found: m/z 474.2076. Calcd for $C_{30}H_{26}N_4O_2$: M, 474.2054.

Reaction of 9 with 2a. A mixture of **9** (200 mg, 1.03 mmol) and **2a** (75 mg, 1.2 mmol) in absolute ethanol (2 ml) was treated as above to give, after chromatography, 2,3-dihydro-1*H*-cyclohepta[*b*]pyrazine (**13a**,[11]) (126 mg, 84%).

Reaction of 9 with 2b. A mixture of **9** (200 mg, 1.03 mmol) and **2b** (90 mg, 1.2 mmol) in absolute ethanol (2 ml) was treated as above to give **13b** (132 mg, 80%) and **5b**[2] (5 mg, 3%).

1, 2, 3, 4- Tetrahydrocyclohepta[*b*][1, 4]diazepine (13b): Yellow oil; UV λ_{max} ($CHCl_3$) 276 ($\log\varepsilon$ 3.14), 305 (2.86, sh), 337 (2.10), 384 (2.70, sh), 395 (2.73 sh), 405 (2.76), 474 (2.20), 506 nm (2.14, sh); IR (KBr) 3250 cm^{-1} (NH): ^1H NMR (270 MHz, $CDCl_3$) δ=1.83 (2H, m, J=6 Hz, CH_2), 3.64 (4H, t, J=6 Hz, CH_2), 4.48 (1H, br, NH), 7.35 (3H, m, H-3,5,7), 7.64 (2H, m, H-4,6); MS m/z 160 (M^+, 43%), 159 (100), 104 (55). Found: m/z 160.0973. Calcd for $C_{10}H_{12}N_2$: M, 160.0999.

***N*-[2-[(6-Aminohexyl)amino]-2,4,6-cycloheptatrienylidene]-1,6-hexanediamine (12e, n,n'=6,6):** A mixture of **9** (200 mg, 1.03 mmol) and 1,6-hexanediamine (**2e**, 480 mg, 4.1 mmol) in absolute ethanol (2 ml) was heated at 80 °C for 30 h under an argon atmosphere. After concentration in vacuo, the residue dissolved in chloroform was washed with aqueous NaOH and water, dried over magnesium sulfate and then concentrated in vacuo to give **12e** (265 mg, 81% yield) as orange crystals; mp 72—75 °C (from $CHCl_3$); UV λ_{max} (MeOH) 241 ($\log\varepsilon$ 4.04, sh), 250 (4.15, sh), 260 (4.20), 286 (3.80, sh), 345 (3.85), 355 (3.83), 410 (3.83), 457 (3.32), 495 nm (2.46); IR (KBr) 3350—3200 cm^{-1} (NH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.46 (12H, m, CH_2), 1.75 (4H, m, CH_2), 2.01 (5H, br, NH, NH_2), 2.70 (4H, t, J=7 Hz, CH_2), 3.20 (4H, t, J=7 Hz, CH_2), 6.13 (1H, t, J=9 Hz, H-5), 6.28 (2H, d, J=11 Hz, H-3,7), 6.75 (2H, dd, J=11 and 9 Hz, H-4,6); MS m/z 318 (M^+, 3%), 232 (100). Found: m/z 318.2776. Calcd for $C_{19}H_{34}N_4$: M, 318.2782.

Synthesis of Other Tropopodands. The reactions of **9** with α,ω-alkanediamines **2a**—**e** (n=2—6) (mole ratio 1 : 5) and ω-aminoalcohol **22a**—**e** (n=2—6) (mole ratio 1 : 6), as described above, gave **12c**—**e** and **23a**—**e**, respectively. The yields and melting points are given in Table 2.

***N*-[2-[(5-Aminopentyl)amino]-2,4,6-cycloheptatrienylidene]-1,5-pentanediamine (12d, n,n'=5,5):** Orange oil; UV λ_{max} (MeOH) 260 ($\log\varepsilon$ 4.18), 339 (3.83, sh), 346 (3.80), 356 (3.84), 380 (3.86), 412 (3.69), 437 (3.79, sh), 460 (3.60), 499 nm (3.37); IR (KBr) 3330, 3200 cm^{-1} (NH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.50 (6H, m, CH_2), 1.76 (4H, m, CH_2), 2.40 (4H, br, NH_2), 2.72 (4H, t, J=6.5 Hz, CH_2), 3.31 (4H, t, J=6.5 Hz, CH_2), 6.13 (1H, t, J=9 Hz, H-5), 6.27 (2H, d, J=11 Hz, H-3,7), 6.74 (2H, dd, J=11 and 9 Hz, H-4,6); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=24.85 (t, CH_2), 29.87 (t, CH_2), 33.64 (t, CH_2), 42.18 (t, CH_2), 46.19 (t, CH_2), 110.05 (d, C-3,7), 117.56 (d, C-5), 132.90 (d, C-4,6), 152.93 (s, C-1,2). Found: m/z 290.2485. Calcd for $C_{17}H_{30}N_4$: M, 290.2473.

***N*-[2-[(4-Aminobutyl)amino]-2,4,6-cycloheptatrienylidene]-1,4-butanediamine (12c,[2c] n,n'=4,4):** Orange crystals; mp 85—90 °C (from $CHCl_3$); UV λ_{max} (MeOH) 242 sh, 262, 348, 360, 410, 425, 465 nm sh; IR (KBr) 3400—3200 cm^{-1} (NH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.60 (4H, m, CH_2), 1.77 (4H, m, CH_2), 2.30 (4H, br, NH_2), 2.75 (4H, t, J=7 Hz, CH_2), 3.32 (4H, t, J=7 Hz, CH_2), 6.14 (1H, t, J=10 Hz, H-5), 6.27 (2H, d, J=10 Hz, H-3,7), 6.75 (2H, t, J=10 Hz, H-4,6); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=27.5 (CH_2), 31.8 (CH_2), 42.1 (CH_2), 46.1 (CH_2), 110.4 (C-3,6), 117.7 (C-5), 133.0 (C-4,6), 153.0 (C-1,2); MS m/z 320 (M^+, 22%), 233 (100), 219 (56). Found: C, 68.45; H, 10.21; N, 21.16. Calcd for $C_{15}H_{26}N_4$: C, 68.66; H, 9.99; N, 21.35.

6-[[2-[(6-Hydroxyhexyl)amino]-2,4,6-cycloheptatrienylidene]amino]-1-hexanol (23e, n,n'=6,6): Orange crystals; mp 40—43 °C (from $CHCl_3$); UV λ_{max} (MeOH) 261 ($\log\varepsilon$ 4.55), 347 (4.15), 414 (4.18), 452 (3.54, sh), 494 nm (2.76); IR (KBr) 3330 (OH) and 3250 cm^{-1} (NH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.46 (8H, m, CH_2), 1.60 (4H, m, CH_2), 1.75 (4H, m, CH_2), 3.30 (4H, t, J=6.6 Hz, CH_2), 3.38 (3H, br, NH, OH), 3.64 (4H, t, J=6.6 Hz, CH_2), 6.13 (1H, t, J=9 Hz, H-5), 6.27 (2H, d, J=11 Hz, H-3,7), 6.74 (2H, dd, J=11 and 9 Hz, H-4,6); MS m/z 320 (M^+, 22%), 233 (100), 219 (56). Found: m/z 320.2461. Calcd for $C_{19}H_{32}N_2O_2$: M, 320.2462.

2-[[2-[(2-Hydroxyethyl)amino]-2,4,6-cycloheptatrienylidene]amino]ethanol (23a, n,n'=2,2): Orange crystals; mp 77—79 °C (from $CHCl_3$); UV λ_{max} (MeOH) 260 ($\log\varepsilon$ 4.24), 346 (3.84), 414 (3.90), 494 nm (2.71); IR (KBr) 3300 (OH) and 3200 cm^{-1} (NH); ^1H NMR (270 MHz, $CDCl_3$) δ=3.43 (4H, t, J=5.1 Hz, CH_2), 3.91 (4H, t, J=5.1 Hz, CH_2), 4.67 (3H, br, NH, OH), 6.25 (1H, t, J=9 Hz, H-5), 6.34 (2H, d, J=11 Hz, H-3,7), 6.83 (2H, dd, J=11 and 9 Hz, H-4,6); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=48.56 (t, CH_2), 61.60 (t, CH_2), 111.35 (d, C-3,6), 119.14 (d, C-5), 133.89 (d, C-4,6), 153.86 (s, C-1,2); MS m/z 208 (M^+, 10%), 173 (100). Found: m/z 208.2618. Calcd for $C_{11}H_{16}N_2O_2$: M, 208.2624.

3-[[2-[(3-Hydroxypropyl)amino]-2,4,6-cycloheptatrienylidene]amino]-1-propanol (23b, n,n'=3,3): Orange crystals; mp 59—65 °C (from $CHCl_3$); UV λ_{max} (MeOH) 260 ($\log\varepsilon$ 4.21), 346 (3.82), 413 (3.87), 461 nm (2.58, sh); IR (KBr) 3370 (OH) and 3250 cm^{-1} (NH) ^1H NMR (270 MHz, $CDCl_3$) δ=1.97 (4H, m, J=6 Hz, CH_2), 3.44 (4H, t, J=6 Hz, CH_2), 3.80 (4H, t, J=6 Hz, CH_2), 4.98 (3H, br, NH, OH), 6.22 (1H, t, J=10 Hz, H-5), 6.32 (2H, d, J=10 Hz, H-3,7), 6.82 (2H, t, J=10 Hz, H-4,6); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=31.8 (t, CH_2), 44.5 (t, CH_2), 61.8 (t, CH_2), 110.9 (d, C-3,7), 118.5 (d, C-5), 133.8 (d, C-4,6), 153.5 (s, C-1,2); MS m/z 236 (M^+, 45%), 191 (100). Found: m/z 236.1528. Calcd for $C_{13}H_{20}N_2O_2$: M, 236.1523.

4-[[2-[(4-Hydroxybutyl)amino]-2,4,6-cycloheptatrienylidene]amino]-1-butanol (23c, n,n'=4,4): Orange oil; UV λ_{max} (MeOH) 260 ($\log\varepsilon$ 4.41), 346 (4.01), 358 (3.95), 414 (4.04), 507 nm (2.50); IR (KBr) 3300 cm^{-1} (OH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.74 (4H, m, CH_2), 1.84 (4H, m, CH_2), 3.33 (4H, t, J=6.2 Hz, CH_2), 3.68 (4H, t, J=6.2 Hz, CH_2), 3.82 (2H, br, OH), 6.20 (1H, t, J=9.5 Hz, H-5), 6.31 (2H, d, J=11.0 Hz, H-3,7), 6.80 (2H, dd, J=11.0, 9.5 Hz, H-4,6); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=26.60 (t, CH_2), 30.91 (t, CH_2), 46.12 (t, CH_2), 62.49 (t, CH_2), 110.75 (d, C-3,7), 118.29 (d, C-5), 133.55 (d, C-4,6), 153.47 (s, C-1,2); MS m/z 264 (M^+, 24%), 205 (100), 173 (58). Found: m/z 264.1844. Calcd for $C_{15}H_{24}N_2O_2$: M, 264.1838.

5-[[2-[(5-Hydroxypentyl)amino]-2,4,6-cycloheptatrienylidene]amino]-1-pentanol (23d, n,n'=5,5): Orange crystals; mp 64—69 °C (from $CHCl_3$); UV λ_{max} (MeOH) 259 ($\log\varepsilon$ 4.45), 347 (4.08), 356 (4.06), 413 (4.06),

499 nm (2.58); IR (KBr) 3400 cm^{-1} (OH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.53 (4H, m, J=6 Hz, CH_2), 1.58 (4H, m, J=6 Hz, CH_2), 1.75 (4H, m, J=6 Hz, CH_2), 3.30 (4H, t, J=6 Hz, CH_2), 3.61 (4H, t, J=6 Hz, CH_2), 4.34 (3H, br, NH, OH), 6.14 (1H, t, J=10 Hz, H-5), 6.27 (2H, d, J=10 Hz, H-3,7), 6.75 (2H, t, J=10 Hz, H-4,6); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=23.79 (t, CH_2), 29.58 (t, CH_2), 32.45 (t, CH_2), 46.06 (t, CH_2), 62.45 (t, CH_2), 110.22 (d, C-3,7), 117.76 (d, C-5), 133.10 (d, C-4,6), 153.03 (s, C-1,2); MS m/z 292 (M^+, 20%), 219 (100), 205 (38), 187 (28). Found: m/z 292.2159. Calcd for $C_{17}H_{28}N_2O_2$: M, 292.2150.

***N*-[2-(2-Hydroxyanilino)-2,4,6-cycloheptatrienylidene]-1,4-butanediamine (11c, *n*=4):** A solution of **9** (200 mg, 1.03 mmol) and **2c** (110 mg, 1.23 mmol) in absolute ethanol (2 ml) was stirred for 1 d at room temperature under an argon atmosphere. The precipitates were collected, washed with cold methanol and dried to give **11c** (244 mg, 84% yield): Orange crystals (from benzene); mp 200—201 °C; UV λ_{max} (MeOH) 254 ($\log\varepsilon$ 4.39), 268 (4.32, sh), 340 (3.94, sh), 364 (4.04), 411 (4.14), 446 nm (3.94, sh); IR (KBr) 3400 (OH), 3380 (NH), and 3250 cm^{-1} (NH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.82 (4H, br, CH_2), 3.34 (4H, br, CH_2), 3.44 (2H, br, CH_2), 6.22 (1H, t, J=9 Hz, H-5), 6.30 (1H, t, J=10 Hz, H-3), 6.43 (1H, d, J=12 Hz, H-7), 6.70 (1H, ddd, J=12, 9, 2 Hz, H-6), 6.76 (2H, m, H-3′, 5′), 6.85 (2H, m, H-4′,6′), 6.89 (1H, ddd, J=10, 9, 2 Hz, H-4), 8.15 (1H, br, NH); MS m/z 283 (M^+, 15%), 195 (100). Found: C, 72.31; H, 7.57; N, 14.75. Calcd for $C_{17}H_{21}N_{30}$: C, 72.06; H, 7.47; N, 14.83.

Synthesis of 5c from 11c: A solution of **11c** (100 mg, 0.35 mmol) suspended in ethanol (1.5 ml) was heated in a sealed tube for 60 h at 100 °C. After removing the solvent, the residue was taken in chloroform and chromatographed on a silica-gel column with MeOH–NaCl aq (1 : 1) as the eluent, giving **5c** (24 mg, 40%) along with unreacted **11c** (53 mg, 53%).

Synthesis of 14c[1] from 11c: A solution of **11c** (20 mg, 0.07 mmol) suspended in ethanol (5 ml) was refluxed for 15 h. After removing the solvent, the residue was chromatographed on a silica-gel column with benzene-MeOH as an eluent, giving **14c** (14 mg, 71%) along with small amounts of **9** and **15c**.

Synthesis of 14d and 15d from 9 with 2d: A solution of **9** (200 mg, 1.03 mmol) and **2d** (126 mg, 1.23 mmol) in absolute ethanol (5 ml) was refluxed for 15 h under aerobic conditions. After removing the solvent, the residue was chromatographed on a slica-gel column with benzene–methanol as an eluent, giving **14d** (188 mg, 62%) and **15d** (20 mg, 8%).

Synthesis of 14c[1] and 15c from 9 with 2c: A solution of **9** (200 mg, 1.03 mmol) and **2c** (108 mg, 1.23 mmol) in dry 1-butanol (5 ml) was heated at 100 °C for 20 h under aerobic conditions. After concentration in vacuo, the residue was treated as above to give **14c**[1] (182 mg, 63%) and **15c** (22 mg, 9%), along with a trace amount of **5c**.

***N*,*N*′-Bis(benzo[*b*]cyclohept[*e*][1, 4]oxazin-10-yl)-1,4-butanediamine (15c, *n*=4):** Reddish brown crystals; mp 156—159 °C (from $CHCl_3$); UV λ_{max} (MeOH) 234, 266, 300, 475, 530 nm; IR (KBr) 3270 cm^{-1} (NH); ^1H NMR (270 MHz, $CDCl_3$) δ=1.84 (4H, m, CH_2), 3.39 (4H, m, CH_2), 5.84 (2H, d, J=10 Hz, H-6,6′), 5.90 (2H, t, J=10 Hz, H-8,8′), 5.95 (2H, dd, J=10 and 1.8 Hz, H-9,9′), 6.23 (2H, td, J=10 and 1.8 Hz, H-7,7′), 6.38 (2H, m, J=8 and 2 Hz, H-4,4′), 6.67 (2H, m, J=8 and 2 Hz, H-2,2′), 6.70 (2H, m, J=8 and 2 Hz, H-3,3′), 6.75 (2H, m, J=8 and 2 Hz, H-1,1′), 6.95 (2H, br, NH); MS m/z 474 (M^+, 45%), 264 (100), 221 (81), 195 (85). Found: m/z 474.2076. Calcd for $C_{30}H_{26}N_4O_2$: M, 474.2054.

Synthesis of 12c from 11c with 2c: A suspension of **11c** (50 mg, 0.18 mmol), and **2c** (24 mg, 0.27 mmol) in ethanol (2 ml) was heated at 80 °C for 6 h under an argon atmosphere. After concentration in vacuo, the residue was purified through a silica-gel column with MeOH–NaCl aq (1 : 1) as an eluent, giving **12c** (41 mg, 87% yield).

Synthesis of 5c from 9 with 12c: A solution of **9** (50 mg, 0.26 mmol) and **12c** (80 mg, 0.31 mmol) in absolute ethanol (2 ml) was heated at 80 °C in a sealed tube for 30 h. After having been set aside overnight, the precipitates were collected and washed with cold methanol to give **5c** (67 mg, 74%).

1-Methoxy-2-(2-methoxyanilino)tropylium Fluorosulfate (19): A solution of **18**[6] (150 mg, 0.66 mmol) and methyl fluorosulfate (226 mg, 1.98 mmol) in CH_2Cl_2 (10 ml) was stirred for 24 h at room temperature. After removing the solvent, the residue was washed with cold CH_2Cl_2 and dried in vacuo to give **19** (204 mg, 91% yield) as yellow needles; mp 91—94 °C; ^1H NMR (270 MHz, $CDCl_3$) δ=3.80 (3H, s, OCH_3), 4.36 (3H, s, OCH_3), 7.03—7.10 (2H, m, benzene ring H), 7.33 (1H, d, J=12 Hz, H-3 or 7), 7.38—7.47 (2H, m, benzene ring H), 7.55 (1H, t, J=9.5 Hz, H-5), 7.82 (1H, d, J=10.5 Hz, H-7 or 3), 7.84 (1H, dd, J=12, and 9.5 Hz, H-4 or 6), 7.96 (1H, dd, J=10.5 and 9.5 Hz, H-6 or 4); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=55.9, 58.7, 112.4, 121.7, 122.2, 123.1, 125.5, 127.2, 130.7, 133.9, 140.3, 143.9, 153.5, 156.8, 159.9; Found: C, 52.35; H, 4.67; N, 4.23%. Calcd for $C_{15}H_{16}NSO_5F$: C, 52.78; H, 4.72; N, 4.10%.

***N*-[2-(2-Methoxyanilino)-2,4,6-cycloheptatrienylidene]-1,5-pentanediamine (20):** A solution of **19** (200 mg, 0.59 mmol), **2d** (n=5, 100 mg, 0.98 mmol), Et_3N (100 mg) and Na_2CO_3 (100 mg) suspended in methanol (10 ml) was stirred for 24 h at room temperature. After removing the solvent, the residue was dissolved in chloroform and passed through a silica-gel column using methanol–NaCl aq (1 : 1) as an eluent to give **20** (158 mg, 86% yield) as yellow oil; UV λ_{max} (MeOH) 255, 350 sh, 360, 418 nm; ^1H NMR (270 MHz, $CDCl_3$) δ=1.49 (4H, m, CH_2), 1.79 (2H, m, CH_2), 2.71 (2H, m, CH_2), 3.35 (2H, m, CH_2), 3.75 (3H, s, OCH_3), 6.17 (1H, d, J=10.5 Hz, H-3 or 7), 6.26 (1H, t, J=8.5 Hz, H-5), 6.49 (1H, d, J=12 Hz, H-7 or 3), 6.63 (1H, ddd, J=12, 8.5 and 1.5 Hz, H-6 or 4), 6.81 (1H, dd, J=8 and 1.5 Hz, H-3′), 6.86 (1H, td, J=10.5 and 1.5 Hz, H-4 or 6), 6.93 (1H, td, J=8 and 1.5 Hz, H-4′), 6.97 (1H, dd, J=8 and 1.5 Hz, H-6′), 7.04 (1H, td, J=8 and 1.5 Hz, H-5); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=24.7, 28.5, 33.5, 42.1, 43.2, 55.7, 105.0, 112.0, 119.2, 120.9, 121.3, 122.0, 123.4, 132.8, 133.8, 140.3, 150.6, 151.0, 155.4; FAB-MS m/z 312 (MH^+). Found: m/z 311.1975. Calcd for $C_{18}H_{25}N_3O$: M, 311.1998.

***N*,*N*′-Bis[2-(2-methoxyanilino)-2,4,6-cycloheptatrienylidene]-1,5-pentanediamine (21):** (a) A suspension of **20** (106 mg, 0.34 mmol), **19** (115 mg, 0.34 mmol), Et_3N (100 mg) and Na_2CO_3 (100 mg) in methanol (10 ml) was stirred for 24 h at room temperature. After removing the solvent, the residue dissolved in chloroform was

washed with water, concentrated and then passed through a silica-gel column (benzene–MeOH 50:1 eluent) to give **21** (145 mg, 82% yield). (b) A suspension of **19** (92 mg, 0.27 mmol), **2d** (14 mg, 0.14 mmol), Et_3N (100 mg) and Na_2CO_3 (100 mg) in methanol (10 ml) was stirred for 24 h at room temperature. Precipitates were collected and washed with cold MeOH and water, then dried in vacuo to give **21** (117 mg, 83% yield): Yellow crystals; mp 96—99 °C; UV λ_{max} (MeOH) 250, 345 sh, 360, 415 nm; ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.61 (2H, quin, J=8 Hz, CH_2), 1.85 (4H, quin, J=8 Hz, CH_2), 3.37 (4H, t, J=8 Hz, CH_2), 3.74 (6H, s, OCH_3), 6.18 (2H, d, J=10.5 Hz, H-3 or 7), 6.22 (2H, t, J=9.5 Hz, H-5), 6.49 (2H, d, J=12 Hz, H-7 or 3), 6.64 (2H, ddd, J=12, 9.5, and 1 Hz, H-6 or 4), 6.81 (2H, dd, J=7.5 and 1.5 Hz, H-3′), 6.85 (2H, td, J=10.5 and 1 Hz, H-4 or 6), 6.92 (2H, td, J=7.5 and 1.5 Hz, H-4′), 6.97 (2H, dd, J=7.5 and 1.5 Hz, H-6′), 7.04 (2H, td, J=7.5 and 1.5 Hz, H-5′); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=25.1, 28.4, 3.1, 55.7, 105.1, 111.9, 119.3, 121.0, 121.3, 122.0, 123.4, 132.8, 133.8, 140.2, 150.6, 150.9, 155.4; FAB-MS m/z 521 (MH^+). Found: C, 75.94; H, 7.08; N, 10.69%. Calcd for $C_{33}H_{36}N_4O_2$: C, 76.13; H, 6.97; N, 10.76%.

Synthesis of 5d from 21 with 2d: A solution of **21** (50 mg, 0.096 mmol), **2d** (12 mg, 0.12 mmol) and a drop of acetic acid in ethanol (1.5 ml) was heated at 120 °C in a sealed tube for 30 h. After having been set aside overnight at room temperature, the precipitates formed were collected, washed with cold methanol and dried to give **5d** (31 mg, 86% yield).

Synthesis of 5d from 20: A solution of **20** (50 mg, 0.16 mmol) and a drop of acetic acid in ethanol (1.5 ml) was heated at 80 °C for 30 h. After one night at room temperature, the precipitates were collected (as described above) to give **5d** (27 mg, 89% yield).

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