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The Synthesis of Macrocyclic Diamides and Tetramides Containing Phenol Units

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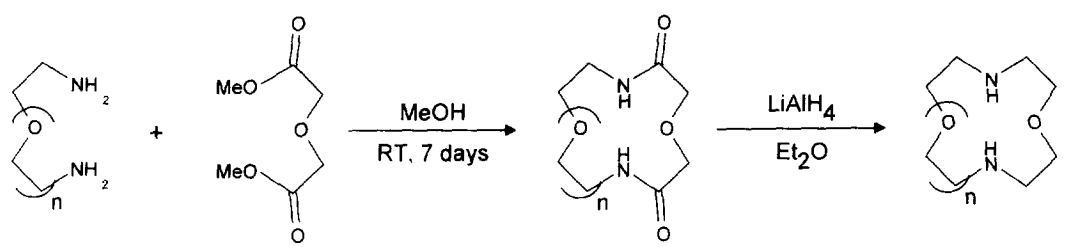
Abstract: Thirteen new macrocyclic diamides and tetramides have been synthesized by reaction of methyl phenoxyacetates (readily obtained from various phenols) with α,ω-diamines in methanol as a solvent. Relationship between structure of esters and ratio of diamides to tetraamides has been investigated.

There is a continuous interest in the preparation of diazacoronands which have important uses as macrocyclic molecular receptors[1] as well as valuable intermediates for the synthesis of cryptands and related compounds.[2] The methods for the formation of diazacoronands have been extensively revieved.[3-5] Among these methods, the high-dilution technique,[6] the route based on the template effect,[7] and the high-pressure approach[8] are frequently used as the most versatile procedures. Recently, we found that α,ω-diamino aliphatic ethers (e.g. **1** or **2**) react under ambient conditions with dimethyl α,ω-dicarboxylates (e.g. **3**), in methanol to afford the macrocyclic diamides **4** or **5**, respectively in good yields,[9-11] which *via* reduction were transformed into the respective diazacoronands **6** or **7** (Scheme 1).



1 n=1
2 n=2

3

4 n=1
5 n=2

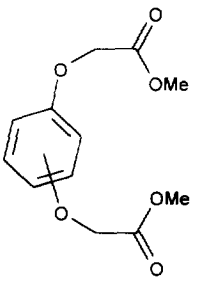
6 n=1
7 n=2

Scheme 1

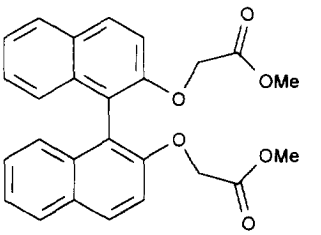
Deciding to continue this research we turned our attention on the influence of structure of the partially rigid esters on the results of macrocyclization reactions. Considering our preliminary results related to diester **8**,[11] we decided to modify its structure on two ways: 1° by changing the distance between the hydroxy groups in

starting phenols (diesters **9, 10, 11**); 2° by introducing the rigid and sterically large substituents to the basic structure (tetraester **12** and diester **13**) (Scheme 2). All esters were obtained in very good yields by simple elongation of respective phenols using methyl bromoacetate under basic conditions.

The reactions of the above-mentioned amines **1** and **2** with esters **8-13** were carried out under standard conditions (MeOH as a solvent, RT, several days) to give in all cases the expected macrocyclic diamides, as shown in Schemes 3-6 and in the Table.



o-**8**
m-**9**
p-**10**



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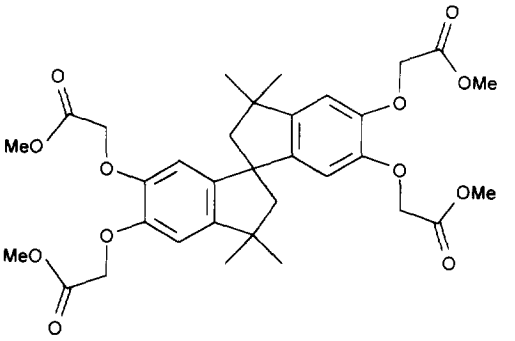

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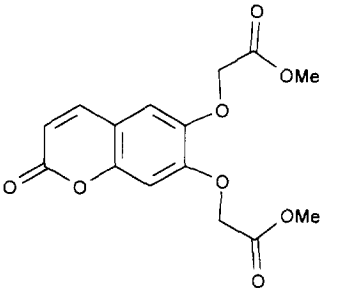
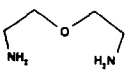
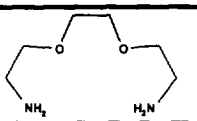
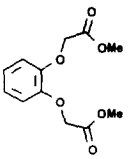
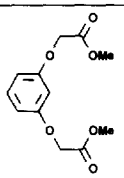
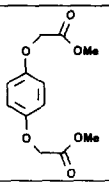
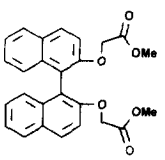
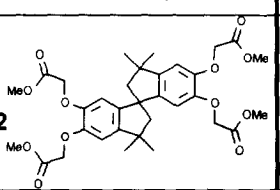
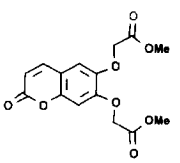


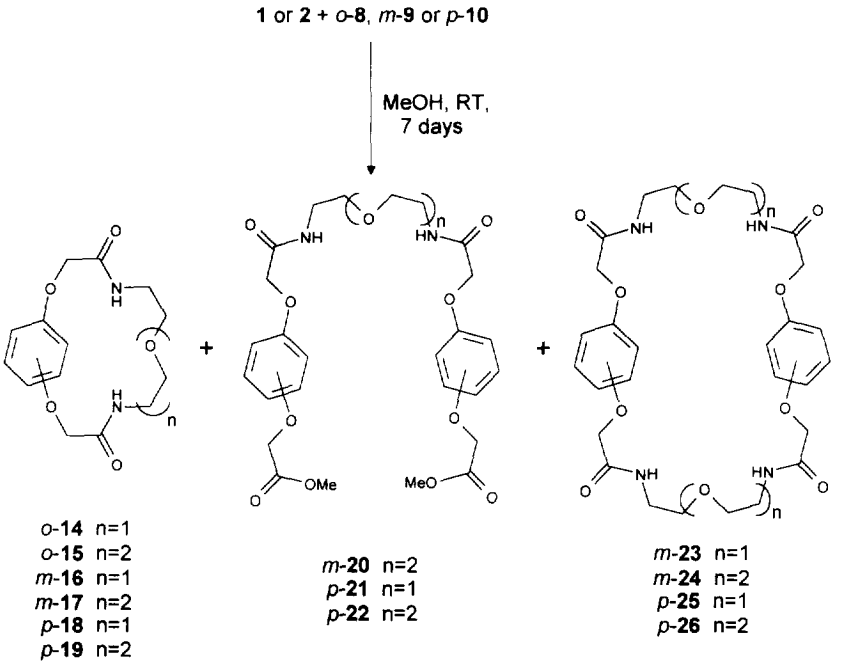
13

Scheme 2

It is obvious that yields of macrocyclic diamides decrease with increase the distance between ethereal oxygen atoms in esters. However, a difference in the yields between **16, 17** and **18, 19** is not as high as between **14**,[11] **15**[11] and **16, 17**. We obtained diamidodiesters **20, 21, 22** and tetramides **23, 24, 25, 26** using diesters **9** and **10**. Independently of the amine length, yields of tetramides are always higher for hydroquinone derivatives. Considering longer distances between ester groups in diesters **9, 10, 11** as compared with **8**, yields of macrocyclic products are higher in reactions with amine **2**, than **1**, in all cases. Especially drastic decrease of yields between **16** and **18** results from a steric strain in compound **18** (Scheme 3).

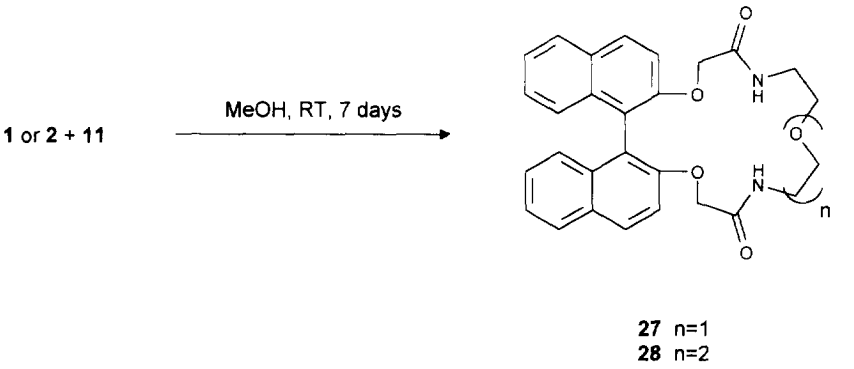
Table. Product Distribution in the Reactions of Amines **1** and **2** with Esters **8-13**

Ester \ Amine	**1** 			**2** 		
	Diamide	Diamide diester	Tetramide	Diamide	Diamide diester	Tetramide
8 	80% **14**[11]	—	—	73% **15**[11]	—	—
9 	16% **16**	—	3% **23**	24% **17**	5% **20**	3% **24**
10 	3% **18**	4% **21**	10% **25**	19% **19**	3% **22**	13% **26**
11 	36% **27**	—	—	45% **28**	—	—
12 	72% **29**	—	—	65% **30**	—	—
13 	—	—	—	61% **31**	—	—



Scheme 3

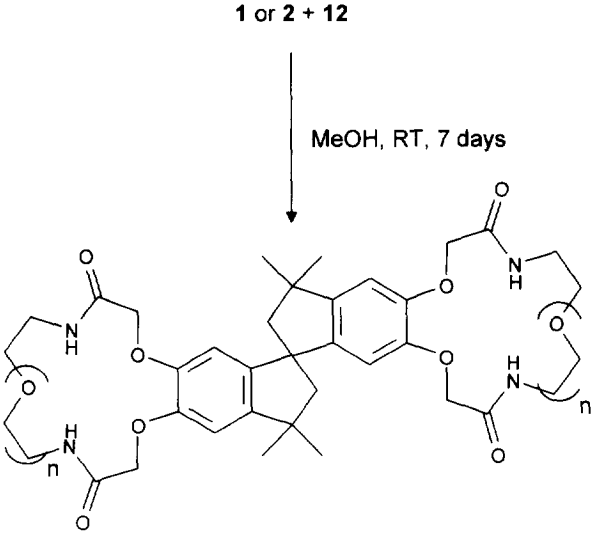
Reaction of chiral diester **11** with diamines **1** and **2** afforded diamides **27** and **28** in relatively high yields. We could use this reaction pathway in order to obtain chiral optically active diazacoronands.



Scheme 4

In the next part of our studies we selected two interesting esters, derivatives of spirobindane (ester **12**) and coumarine (ester **13**), respectively. Yields of bicyclic compounds **29** and **30** are only slightly lower than those of the corresponding diamides **14** and **15**. Thanks to presence of the spiro carbon atom, molecules **29** and **30** have

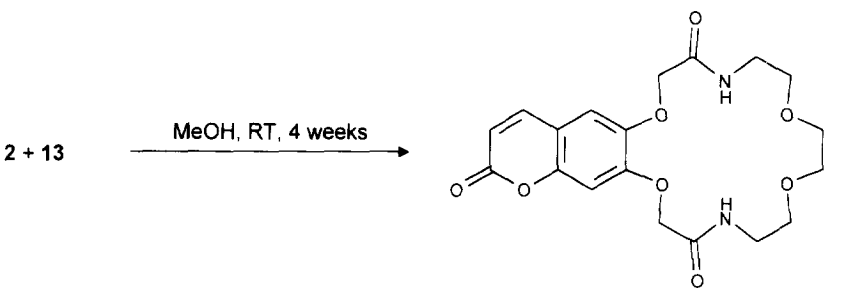
a specific molecular architecture. We expect that after reduction these compounds will be suitable for complexing of dications of type H_3N^+-$(CH_2)_n$-$^+NH_3$.[12]



29 n=1
30 n=2

Scheme 5

In the case of ester **13** we came across some unexpected difficulties. Reaction of this diester with one equivalent of diamine **2** did not result in the formation of diamide **31**. After many experiments we found that increase of amount of diamine to 6 equiv and elongation of reaction time to 4 weeks afforded the desired diamide **31** in 61% yield. No theoretical rationalization of this phenomenon was found. Macrocyclic diamide **31** has a strong fluorescence emission, and we expect that the absorption band and fluorescence intensity will change upon complexation of alkali metal cations with the diazacrown ring.[13]



31

Scheme 6

Even large substituents, if rigid and situated far from the reaction centres do not disturb preorganization of esters, which determine the formation of the presented macrocycles. In conclusion, we can state that it is possible to obtain various interesting macrocyclic compounds using our simple method. We are able to modify their structures in a number of ways according to our aims, all the more because substrates are commercially available or procurable with minimal expenditure of work.

EXPERIMENTAL

General methods

^{1}H NMR spectra were recorded with Varian Gemini (200 MHz) and/or Bruker AM500 (500 MHz) spectrometers in $CDCl_3$ or DMSO-d_6 using TMS as an internal standard. ^{13}C NMR spectra were recorded using also Varian Gemini (50 MHz) and/or Bruker AM500 (125 MHz) spectrometers. High-resolution mass spectrometry (HRMS) experiments were performed on an AMD-604 Intectra instrument. Column chromatography was carried out on silica gel (Merck Kieselgel-60, 200-400 mesh). Melting points were taken on a Boetius hot stage apparatus and were not corrected. α,ω-Diamines **1** and **2** were prepared according to the literature procedures.[6,7]

Methyl esters, general procedure

The following procedure was used to transform phenols into the corresponding methyl esters. The phenol was dissolved in 2-butanone or acetonitrile containing a 100% molar excess of anhydrous potassium carbonate and a 25% molar excess of methyl bromoacetate, and the mixture was stirred vigorously for 48 h at 70°C. After cooling, the reaction mixture was filtered and the solvent evaporated under reduced pressure to give a yellow-brown oil. This was purified by crystallization from methanol or by distillation at high vacuum. The following methyl esters were thus prepared:

Methyl 2-{2-[(methoxycarbonyl)methoxy]phenoxy} acetate (**8**, 74%): m.p. 56-57°C (lit.[14] m.p. 56-57°C); b.p. 150°C (0.2 mm); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.00-6.85 (m, 4H), 4.73 (s, 4H), 3.79 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.5, 148.1, 122.7, 115.7, 66.7, 52.2; HRMS m/z calculated for $C_{12}H_{14}O_6$ $(M)^+$ 254.0790, found 254.0788.

Methyl 2-{3-[(methoxycarbonyl)methoxy]phenoxy} acetate (**9**, 94%): m.p. 56-57°C (lit.[15] m.p. 57-58°C); b.p. 149°C (0.2 mm); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.23-7.10 (m, 1H), 6.55-6.45 (m, 3H), 4.59 (s, 4H), 3.77 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.3, 159.0, 130.2, 107.8, 102.2, 65.3, 52.3; HRMS m/z calculated for $C_{12}H_{14}O_6$ $(M)^+$ 254.0790, found 254.0787.

Methyl 2-{4-[(methoxycarbonyl)methoxy]phenoxy} acetate (**10**, 79%): m.p. 99-100°C (lit.[16] m.p. 98-99°C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.83 (s, 4H), 4.56 (s, 4H), 3.76 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.6, 152.8, 115.9, 66.1, 52.3; HRMS m/z calculated for $C_{12}H_{14}O_6$ $(M)^+$ 254.0790, found 254.0789.

Methyl 2-{2'-[(methoxycarbonyl)methoxy]-(1,1')-binaphthalenyl-2-yloxy} acetate (**11**, 93%): m.p. 134-136°C (lit.[17] m.p. 133-134 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.03-7.81 (m, 4H), 7.44-7.12 (m, 8H), 4.56 (s, 4H), 3.62 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.7, 153.6, 133.8, 129.7, 129.6 , 127.8, 126.4, 125.5, 124.1, 120.3, 115.6, 67.0, 51.7; HRMS m/z calculated for $C_{26}H_{22}O_6$ $(M)^+$ 430.1416, found 430.1408.

Spirotetraester (**12**, 75%): m.p. 115-117°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.69 (s, 2H), 6.26 (s, 2H), 4.74 (s, 4H), 4.59 (s, 4H), 3.82 (s, 6H), 3.71 (s, 6H), 2.21 (ABq, 4H, J=13.0 Hz, J=34.2 Hz), 1.33 (s, 6H), 1.29 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.6, 169.3, 147.7, 146.1, 143.9, 111.2, 109.4, 67.1, 66.8, 59.2, 57.2, 52.0, 51.9, 43.2, 31.4, 30.2; HRMS m/z calculated for $C_{33}H_{40}O_{12}$ $(M)^+$ 628.2520, found 628.2519.

Methyl 2-({6-[(methyloxycarbonyl)methoxy]-2-oxo-2H-7-chromenyl}-oxy) acetate (**13**, 78%) from esculetin: m.p. 124-126°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.60 (d, 1H, J=9.6 Hz), 7.00 (s, 1H), 6.76 (s, 1H), 6.30 (d, 1H, J=9.5 Hz), 4.80 (s, 2H), 4.76 (s, 2H), 3.83 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.0, 168.1, 160.7, 151.5, 150.4, 144.5, 142.9, 114.3, 113.6, 112.5, 102.0, 67.1, 65.7, 52.4, 52.2; HRMS (LSIMS) m/z calculated for $C_{15}H_{15}O_8$ $(M)^+$ 323.0767, found 323.0768.

Macrocyclization procedure

General procedure for the synthesis of macrocyclic diamides and tetramides. An equimolar 0.01 M methanolic solution (ca. 2 mmol) of α,ω-diamine and di-(tri-,tetra-)methyl esters was left at ambient temperature for 7 days. Then the solvent was evaporated and the residue was chromatographed on a silica gel column using 0-3% solutions of methanol in chloroform.

2,8,14-Trioxa-5,11-diazabicyclo[13.3.1]nonadeca-1(18),15(19),16-triene-4,12-dione (**16**, 16%): m.p. 230-232°C; R_f 0.52 ($CHCl_3$/MeOH 9:1); ^{1}H NMR (200 MHz, DMSO-d_6) δ 7.61 (br, 2H), 7.12 (t, 1H, J=8 Hz), 6.56 (dd, 2H, J=8.1 Hz, J=2.6 Hz), 6.39 (t, 1H, J=2.5 Hz), 4.48 (s, 4H), 3.34-3.14 (m, 8H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 168.6, 159.9, 130.7, 110.5, 101.3, 68.8, 68.2; HRMS m/z calculated for $C_{14}H_{18}N_2O_5$ $(M)^+$ 294.1216, found 294.1214.

2,8,11,17-Tetraoxa-5,14-diazabicyclo[16.3.1]docosa-1(21),13,18(22)-triene-4,15-dione (**17**, 24%): m.p. 144-147°C; R_f 0.56 ($CHCl_3$/MeOH 9:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30-7.17 (m, 1H), 6.57-6.53 (m, 3H), 6.77 (br, 2H), 4.55 (s, 4H), 3.49-3.48 (m, 8H), 3.43 (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 168.5, 158.7, 130.4, 107.5, 102.7, 70.6, 69.6, 67.6, 38.8; HRMS m/z calculated for $C_{16}H_{22}N_2O_6$ $(M)^+$ 338.1478, found 338.1479.

2,8,14-Trioxa-5,11-diazabicyclo[13.2.2]nonadeca-1(17),15,18-triene-4,12-dione (**18**, 3%): m.p. 178-180°C; R_f 0.52 ($CHCl_3$/MeOH 9:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (s, 4H), 5.97 (br, 2H), 4.66 (s, 4H), 3.36-3.30 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 151.1, 115.6, 70.4, 66.8, 39.6; HRMS m/z calculated for $C_{14}H_{18}N_2O_5$ $(M)^+$ 294.1216, found 294.1235.

2,8,11,17-Tetraoxa-5,14-diazabicyclo[16.2.2]docosa-1(20),18,21-triene-4,15-dione (**19**, 19%): m.p. 195-197°C; R_f 0.62 ($CHCl_3$/MeOH 9:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.96 (br, 2H), 6.79 (s,4H), 4.45 (s, 4H), 3.37-3.30 (m, 8H), 3.17 (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 168.3, 151.6, 114.6, 69.2, 67.2, 38.2; HRMS m/z calculated for $C_{16}H_{22}N_2O_6$ $(M)^+$ 338.1478, found 338.1482.

Methyl 2-[3-({2-(2-{2-[(3-methyloxycarbonyl) methoxy] phenoxy} methyl) carboxamido] ethoxy) ethyl] carbamoyl}methoxy)phenoxy] acetate (**20,** 5%): oil; R_f 0.62 ($CHCl_3$/MeOH 9:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24-7.16 (m, 2H), 6.99 (br, 2H), 6.57-6.55 (m, 2H), 6.53-6.49 (m, 4H), 4.62 (s, 4H), 4.45 (s, 4H), 3.81 (s, 6H), 3.60-3.53 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.1, 168.1, 159.0, 158.4, 130.4, 107.9, 107.7, 102.4, 70.2, 69.7, 67.4, 65.2, 52.3, 38.7; HRMS m/z calculated for $C_{28}H_{36}N_2O_{12}$ $(M)^+$ 592.2268, found 592.2258.

Methyl 2-(4-{[(2-{2-[({4-[(methyloxycarbonyl) methoxy] phenoxy} methyl) carboxamido] ethoxy} ethyl) carbamoyl]methoxy}phenoxy) acetate (**21,** 4%): oil; R_f 0.62 ($CHCl_3$/MeOH 9:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.02 (br, 2H), 6.87 (s, 8H), 4.70 (s, 4H), 4.39 (s, 4H), 3.68 (s, 6 H), 3.47-3.41 (m, 4H), 3.36-3.24 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.3, 167.8, 152.2, 152.1, 115.6, 115.3, 79.1, 68.5, 67.6, 65.1, 51.7, 38.2, 38.2; HRMS m/z calculated for $C_{26}H_{32}N_2O_{11}$ $(M)^+$ 548.2006, found 548.2028.

Methyl (2-[4-({[2-(2-{2-[(4-methyloxycarbonyl)methoxy]phenoxy}methyl)carboxamido]ethoxy}ethoxy) ethyl]carbamoyl}methoxy)phenoxy] acetate (**22,** 3%): oil; R_f 0.56 ($CHCl_3$/MeOH 9:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.99 (br, 2H), 6.89-6.84 (m, 8H), 4.69 (s, 4H), 4.38 (s, 4H), 3.68 (s, 6H), 3.49 (s, 4H), 3.45-3.42 (m, 4H), 3.30-3.26 (m, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.3, 167.8, 152.2, 152.1, 95.4, 69.5, 68.8, 67.6, 65.1, 51.7, 38.2; HRMS m/z calculated for $C_{28}H_{36}N_2O_{12}$ $(M)^+$ 592.2268, found 592.2264.

2,8,14,20,26,32-Hexaoxa-5,11,23,29-tetraazatricyclo[31.3.1.1^{15,19}] octatriaconta-1(36),15(38),16,18,33(37), 34 -hexaene-4,12,22,30-tetraone (**23**, 3%): m.p. 256-258°C; R_f 0.45 ($CHCl_3$/MeOH 9:1); the substance is not soluble enough to perform spectroscopic measurements in solution; Anal. Calcd. for $C_{28}H_{36}N_4O_{10}$: C, 57.14; H, 6.16; N, 9.52; Found C, 57.11; H, 6.09; N, 9.47; HRMS m/z calculated for $C_{28}H_{36}N_4O_{10}$ $(M)^-$ 588.2431, found 588.2433.

2,8,11,17,23,29,32,38-Octaoxa-5,14,26,35-tetraazatricyclo[37.3.1.1^{18,22}]tetratetraaconta-1(42),18,19,21,39(43),40-hexaene-4,15,25,36-tetraone (**24**, 3%): m.p. 214°C; R_f 0.44 ($CHCl_3$/MeOH 9:1); the substance is not soluble enough to perform spectroscopic measurements in solution; Anal. Calcd. for $C_{32}H_{44}N_4O_{12}$: C, 56.80; H, 6.55; N, 8.28; Found C, 56.76; H, 6.49; N, 8.26; HRMS m/z calculated for $C_{32}H_{44}N_4O_{12}$ $(M)^+$ 676.2956, found 676.2954.

2,8,14,19,25,31-Hexaoxa-5,11,22,28-tetraazatricyclo[30.2.2.2^{15,18}]octatriaconta-1(34),15,17,32,35,37-hexaene-4,12,21,29-tetraone (**25**, 10%): m.p. 252°C; R_f 0.38 ($CHCl_3$/MeOH 9:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.88 (br, 4H), 6.80 (s, 8H), 4.34 (s, 8H), 3.46 (t, 8H, J=5.1 Hz), 3.32-3.26 (m, 8H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.7, 152.1, 115.6, 68.4, 67.6, 38.2; HRMS m/z calculated for $C_{28}H_{36}N_4O_{10}$ $(M)^+$ 588.2431, found 588.2468.

2,8,11,17,22,28,31,37-Octaoxa-5,14,25,34-tetraazatricyclo[36.2.2.2^{18,22}]tetratetraaconta-1(40),18,19,21(43),38,41-hexaene-4,15,24,35-tetraone (**26**, 13%): m.p. 198-200°C; R_f 0.42 ($CHCl_3$/MeOH 9:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.92 (br, 4H), 6.87 (s, 8H), 4.39 (s, 8H), 3.47-3.28 (m, 24H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.9, 152.3, 115.7, 96.5, 68.8, 67.7, 38.3; HRMS (LSIMS) m/z calculated for $C_{32}H_{45}N_4O_{12}$ $(M+H)^+$ 677.3034, found 677.3037.

Diamide (**27**, 36%): m.p. 245°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.03-7.87 (m, 4H), 7.38-7.21 (m, 6H), 7.09-7.05 (m, 2H), 6.43 (br, 2H), 4.48 (ABq, 4H), 3.70-3.56 (m, 2H), 3.49-3.27 (m, 4H), 2.98-2.84 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 168.3, 152.5, 133.5, 130.1, 129.6, 127.9, 127.1, 124.9, 124.5, 119.5, 113.9, 68.7, 68.5, 38.3; HRMS m/z calculated for $C_{28}H_{26}N_2O_5$ $(M)^+$ 470.1842, found 470.1819.

Diamide (**28**, 45%): m.p. 248°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 8.09-7.93 (m, 4H), 7.52-7.47 (m, 2H), 7.40-7.21 (m, 6H), 7.03 (br, 2H), 4.46 (ABq, 4H), 3.43-3.14 (m, 10 H), 2.90-2.78 (m, 2H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 167.6, 153.1, 133.1, 129.7, 129.2, 127.9, 126.6, 124.5, 123.9, 118.9, 115.2, 69.7, 68.6, 68.2, 38.2; HRMS m/z calculated for $C_{30}H_{30}N_2O_6$ $(M)^+$ 514.2104, found 514.2106.

Spirotetramide (**29**, 72%): m.p. 350°C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35 (br, 4H), 6.66 (s, 2H), 6.17 (s, 2H), 4.55 (s, 4H) 2.27 (ABq, 4H), 3.65-3.59 (m, 16H), 2.27 (ABq, 4H), 1.39 (s, 6H), 1.33 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.5, 167.4, 146.2, 145.5, 143.0, 107.9, 106.2, 69.3, 69.2, 67.4, 59.4, 57.6, 43.7, 38.5, 38.4, 31.8, 30.5; HRMS m/z calculated for $C_{37}H_{48}N_4O_{10}$ $(M)^+$ 708.3370, found 708.3364.

Spirotetramide (**30**, 65%): m.p. 254-255°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.41 (br, 4H), 6.66 (s, 2H), 6.21 (s, 2H), 4.58 (s, 4H) 4.34 (s, 4H), 3.54-3.48 (m, 24H), 2.18 (ABq, 4H), 1.31 (s, 6H), 1.25 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 168.2, 168.0, 146.8, 146.6, 145.9, 43.1, 108.7, 106.9, 70.2, 69.8, 69.7, 68.0, 59.3, 57.5, 43.5, 38.8, 31.5, 30.3; HRMS (LSIMS) m/z calculated for $C_{41}H_{57}N_4O_{12}$ $(M+H)^+$ 797.3972, found 797.3982.

2,3,4,5,6,8,9,12,13,14,15,19-Dodecahydro-11H-chromeno[6,7-b][1,4,7,10,13,16]tetraoxadiazacycloocta decine-3,14,19-trione (**31**, 61%): m.p. 242-244°C; ^{1}H NMR (200 MHz, DMSO) δ 7.94 (d, 1H, J=9.6 Hz), 7.95-7.81 (m, 2H), 7.43 (s, 1H), 7.21 (s, 1H), 6.34 (d, 1H, J=9.6Hz), 4.65 (s, 2H), 4.56 (s, 2H), 3.55-3.35 (m, 12H); ^{13}C NMR (50 MHz, DMSO) δ 166.9, 166.6, 160.3, 150.0, 149.5, 144.0, 143.5, 113.5, 112.0, 111.1, 101.8, 69.6, 68.9, 67.9, 40.2; HRMS m/z calculated for $C_{19}H_{22}N_2O_8$ $(M)^+$ 406.1376, found 406.1375.

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