Glycoluril-derived crown clips as new ditopic receptors

Mohammad Rahimizadeh, E. Rezaei Seresht, Mehdi Bakavoli, and Mehdi Pordel

Abstract: Several new ditopic receptors have been synthesized from 4,4′-bis(methoxyphenyl)glycoluril (**1**). The first receptor site is a cleft composed of two fused 2-imidazolone rings, which are flanked by two aromatic side walls, and the second site is a crown ether moiety.

Key words: receptors, crown compounds, glycoluril, molecular clips.

Résumé : On a effectué la synthèse de plusieurs nouveaux récepteurs ditopiques au départ de la 4,4′-bis(méthoxyphényl)glycoluril (**1**). Le premier site récepteur est une fente formée par deux noyaux 2-imidazole condensés flanqués de deux murs latéraux aromatiques alors que le second site récepteur est un éther couronne.

Mots-clés : récepteurs, composés couronnes, glycoluril, pinces moléculaires.

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Introduction

Receptors in living organisms play fundamental roles in the growth, nutrition, and differentiation of animal cells (1). Artificial receptors are capable of mimicking this function, which can lead to a better understanding of the natural processes and additionally to the development of new artificial systems for use in drug delivery, catalysis, and so forth (2).

Diphenylglycoluril-based clip molecules have been prepared and extensively studied in the Nolte group over the past decade (3). These molecules possess a well-defined cavity that allows the binding of different phenolic guests via a combination of several non-covalent interactions (H-bonding, π–π stacking, and the cavity effect) (3). The introduction of crown ether chains and alkyl tails to these receptors can lead to a new generation of the so-called amphiphilic basket receptors, which are also able to bind alkaline metal ions and aggregate in water into well-defined nanostructures (4, 5). Here, we describe the synthesis of new diphenylglycoluril-based ditopic receptors, bearing crown ether units, with potential ability to bind both neutral aromatic guests and alkaline metal ions, simultaneously.

Results and discussion

We have utilized the commercially available 4,4-dimethoxybenzil (**7**) as a potentially interesting candidate for the synthesis of more engineered clips, since the ring-activating *p*-methoxy group on the phenyl nucleus could allow the possibility of electrophilic aromatic substitution ortho- to it. Alternatively, the methoxy group could be demethylated to give the more-reactive hydroxy group that can start up a variety of methods for further structural elaboration and derivatization. Therefore, 4,4-bis(methoxyphenyl)glycoluril (**1**) was prepared quantitatively from compound **7** and urea in trifluoroacetic acid and toluene by azeotropic distillation according to a published method (Scheme 1) (6). The molecular clips **3a**–**3c** were subsequently synthesized from **1** by means of an amido alkylation reaction in the presence of potassium hydroxide in DMSO (Scheme 1). Notably, the clip-like structures of these molecules can be easily deduced from the X-ray structure of **3a** (6). Therein, the *o*-xylene rings define a tapered cavity, and the two fused five-membered rings of the glycoluril form a shallow floor, which is electron-rich with two hydrogen-bond-acceptor sites. ^{1}H NMR studies were the first to reveal that the molecular clips, with their pre-organized clefts, are excellent receptors for neutral aromatic guests, particularly dihydroxybenzenes (7–11). For example, upon binding of resorcinol, the guest simultaneously forms two hydrogen bonds to the π orbitals of the carbonyl groups of the clip. The binding strength of this type of guests within the molecular clips can span a wide range of values ($K_{association}$ = 0–10^5 (mol/L)$^{-1}$), which vary with simple modification in either host or guest molecule. Compounds **2b** and **2c** are more susceptible to nucleophilic attack by **1** than **2a**. So, the reaction time was changed from 2 h for **2a** to 4 h for **2b** and **2c**. The side wall **2a** is commercially available, and the other side walls (**2b** and **2c**) were prepared via chloromethylation of *o*-xylene and 1,2,3,4-tetramethylbenzene, recpectively. For the demethylation of the methoxy groups of the clips **3a**–**3c**, pyridine hydrochloride was used as a demethylating agent and as a result, compounds **4a**–**4c** were produced in yields higher than 65%. Then, the hydroxy-functionalized clips **4a**–**4c** were reacted with ditosylates **6a**–**6c** in acetonitrile with K_2CO_3 as a base to yield **5a**–**5i** (Scheme 2). The structures of compounds **5a**–**5i** were confirmed from their spectral and analytical data. For example, in the ^{1}H NMR spectrum of

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M. Rahimizadeh, E.R. Seresht, M. Bakavoli,[1] and Mehdi Pordel. Department of Chemistry, School of Sciences, Ferdowsi University, Mashhad 91375-1436, Iran.

[1]Corresponding author (e-mail: mbakavoli@yahoo.com).

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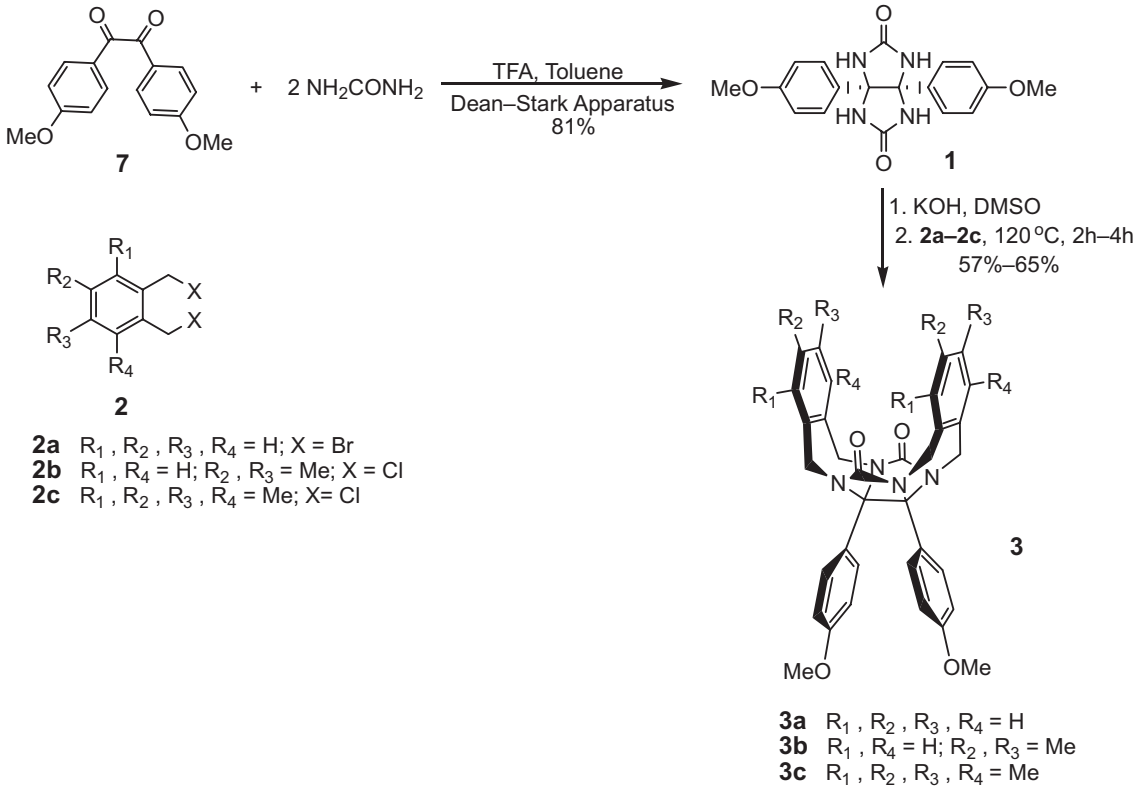
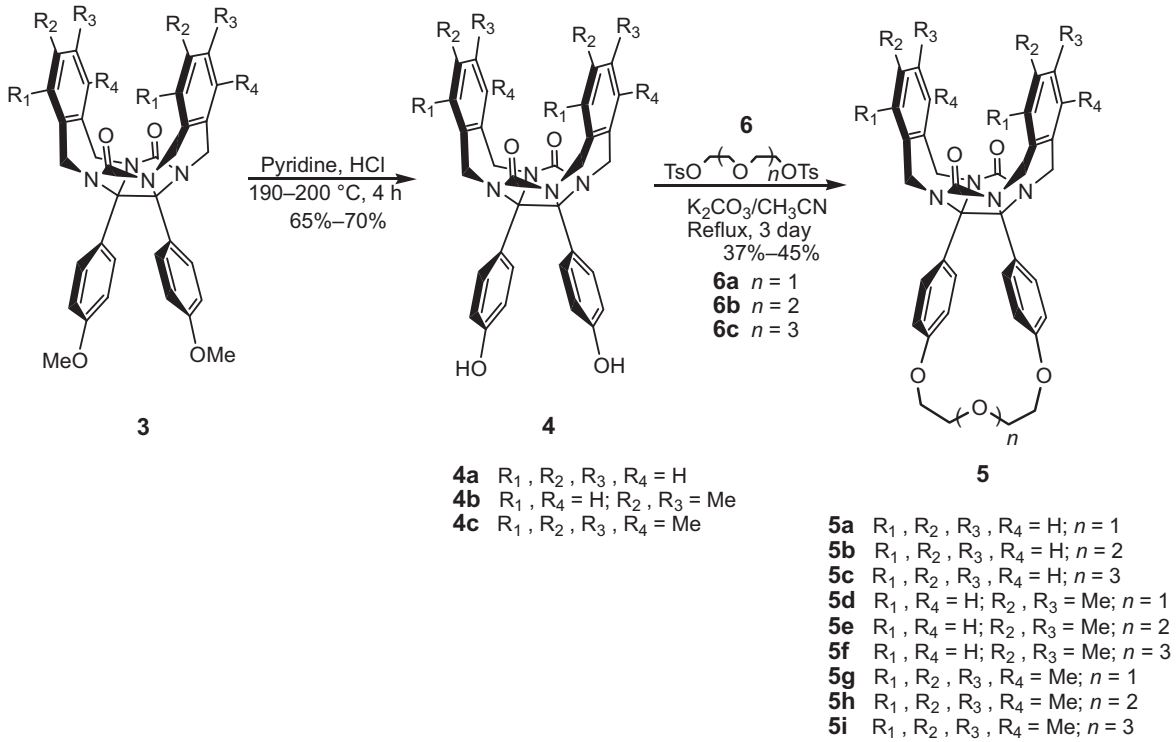
Scheme 1.



Scheme 2.



5g, an AB system (3.97 and 5.17 ppm) with geminal coupling (J = 16 Hz) indicates the non-equivalent methylene protons of the clip moiety. The methyl groups on aromatic side walls appeared as two sharp singlets at δ 2.16 and 2.46 ppm, the protons of para-disubstituted aromatic rings as two doublets at δ 6.61 and 6.93 ppm (J = 9 Hz), and the methylene protons in polyether moiety as two triplets at δ 3.67 and 4.28 ppm (J = 4 Hz).

Conclusion

In summary, several new glycoluril-based receptors with crown ether moieties have been synthesized and characterized. These ditopic receptors are good candidates to bind with dihydroxybenzene derivatives as well as alkaline metal ions, simultaneously. We expect that the binding strength of dihydroxybenzenes with the cleft will be influenced by steric hindrance on side-wall rings. So, the repulsive van der Waals interactions between methyl groups in **3b** and **3c** can alter the cleft shape and hence causes an appreciable change in the binding strengths. On the other hand, it seems viable that compounds **5a**–**5i** are able to show allosteric behavior, as the binding of alkaline metal ions with the crown ether moiety may have influence on the binding of dihydroxybenzenes in the cleft. These studies are currently in progress in our laboratory.

Experimental

Toluene was distilled from sodium benzophenone ketyl. MeCN was distilled from $CaCl_2$. CH_2Cl_2 and MeOH were distilled from CaH_2. Silica gel 60 (0.040–0.063 mm, Merck) was used for column chromatography. 4,4′-Dimethoxybenzil (**7**) and 1,2-bis(bromomethyl)benzene (**2a**) were purchased from Merck company. 1,2,3,4-Tetramethylbenzene was purchased from Aldrich company. 1,2-Bis(chloromethyl)-4,5-dimethylbenzene (**2b**) (12), pyridine hydrochloride (13), and oligoethylene glycol ditosylates (**6a**–**6c**) (14) were prepared according to the literature. Melting points were recorded on an Electrothermal type 9100 melting-point apparatus and are uncorrected. The IR spectra were obtained on a 4300 Shimadzu spectrometer and only noteworthy absorptions are listed. The ^{1}H NMR (100 MHz) spectra were recorded on a Bruker AC 100 spectrometer. Chemical shifts are reported in ppm downfield from TMS as internal standard; coupling constants *J* are given in Hertz. The mass spectra were scanned on a Varian Mat. CH-7 at 70 eV. Elemental analysis was performed on a Thermo Finnigan Flash EA microanalyzer.

1,2-Bis(chloromethyl)-3,4,5,6-tetramethylbenzene (2c)

The title compound was prepared similar to **2b** with slight modification as follows: a mixture of 1,2,3,4-tetramethylbenzene (26.8 g, 0.2 mol), paraformaldehyde (18 g, 0.6 mol) and concd. HCl (125 mL) was refluxed with stirring for 10 h. The reaction mixture was cooled, and the precipitated solid was filtered, washed with water (2 × 50 mL) and cold hexane (30 mL), and dried in vacuo.

Yield: 27.7 g (60%); white needles; mp 140–142 °C. IR (KBr): 2913, 1439, 1270, 685 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.25 (s, 6 H, 2 × CH_3), 2.36 (s, 6 H, 2 × CH_3), 4.80 (s, 4 H, 2×CH_2). EI-MS *m*/*z* (%): 231 (M^+). Anal. calcd. for $C_{12}H_{16}Cl_2$: C, 89.94; H, 10.06. Found: C, 89.76; H, 10.26.

*13b,13c-Di(4-methoxyphenyl)-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraaza-benzo[5,6]azuleno[2,1,8-*ija*]benzo[*f*]azulene-6,13-dione (3a)*

This compound was synthesized according to a literature procedure (6). Mp > 300 °C. ^{1}H NMR ($CDCl_3$) δ: 3.70 (s, 6 H, 2 × OCH_3), 4.15 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 4.76 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.67 (d, *J* = 8 Hz, 4 H, Ar–H), 6.97–7.30 (m, 12 H, Ar–H).

13b,13c-Di(4-methoxyphenyl)-2,3,9,10-tetramethyl-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetra-aza-benzo[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione (3b)

4,4-Bis(methoxyphenyl)glycoluril (**1**) (2.48 g, 7 mmol) and freshly ground potassium hydroxide (4.0 g, 70 mmol) in DMSO (50 mL) were heated to 120 °C with vigorous stirring for 30 min. Then, 1,2-bis(chloromethyl)-4,5-dimethylbenzene (**2b**) (3.04 g, 15.0 mmol) was added in one portion, and stirring was continued at this temperature for 4 h. On cooling, the reaction mixture was added to water (500 mL) and stirred for 30 min. The resulting light-brown precipitate was collected by filtration, washed with water (3 × 400 mL) and acetone (3 × 100 mL), and dried in vacuo.

Yield: 2.66 g (62%); mp > 300 °C. IR (KBr): 2963, 1709, 1611, 1512, 1458, 1253 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.12 (s, 12 H, 4 × CH_3), 3.70 (s, 6 H, 2 × OCH_3), 4.10 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 4.71 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.65 (d, *J* = 8 Hz, 4 H, Ar–H), 6.98 (d, *J* = 8 Hz, 4 H, Ar–H), 7.04 (s, 4 H, Ar–H). EI-MS *m*/*z* (%): 614 (M^+). Anal. calcd. for $C_{38}H_{38}N_4O_4$: C, 74.25; H, 6.23; N, 9.11. Found: C, 74.34; H, 6.48; N, 9.02.

*13b,13c-Di(4-methoxyphenyl)-1,2,3,4,8,9,10,11-octa-methyl-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraazabenzo[5,6]azuleno[2,1,8-*ija*]benzo[*f*]azulene-6,13-dion (3c)*

The title compound was prepared as described for **3b** using 3.46 g (15 mmol) of compound **2c** and 2.48 g (7 mmol) of compound **1**. Yield: 2.67 g (57%); mp > 300 °C. IR (KBr): 2912, 1703, 1610, 1512, 1460, 1253 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.15 (s, 12 H, 4 × CH_3), 2.43 (s, 12 H, 4 × CH_3), 3.67 (s, 6 H, 2 × OCH_3), 3.85 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 5.12 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.62 (d, *J* = 8 Hz, 4 H, Ar–H), 7.02 (d, *J* = 8 Hz, 4 H, Ar–H). EI-MS *m*/*z* (%): 670 (M^+). Anal. calcd. for $C_{42}H_{46}N_4O_4$: C, 75.20; H, 6.91; N, 8.35. Found: C, 74.98; H, 6.86; N, 8.12.

Synthesis of hydroxy-funtionalized clips 4a–4c

General procedure

Compound **3** (2.5 mmol) was added to a flask containing pyridine hydrochloride (11.5 g, 0.1 mol), and the mixture was heated at 190–200 °C for 4 h. The hot brown syrup was poured into aq. HCl (5%, 50 mL), and the precipitated solid was filtered, washed with water (3 × 50 mL) and $CHCl_3$ (2 × 25 mL), and dried in vacuo at 80 °C to give compound **4**.

*13b,13c-Di(4-hydroxyphenyl)-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraaza-benzo[5,6]azuleno[2,1,8-*ija*]benzo[*f*]azulene-6,13-dione (4a)*

Yield: 0.93 g (70%); mp > 300 °C. IR (KBr): 3356 (br), 1682, 1614, 1516, 1464, 1277 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 4.08 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 4.60 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.58 (d, *J* = 8 Hz, 4 H, Ar–H), 6.83 (d, *J* = 8 Hz, 4 H, Ar–H), 6.97–7.30 (m, 8 H, Ar–H), 9.49 (s, 2 H, 2 × OH). EI-MS *m*/*z* (%): 530 (M^+). Anal. calcd. for $C_{32}H_{26}N_4O_4$: C, 72.44; H, 4.94; N, 10.56. Found: C, 72.60; H, 5.12; N, 10.38.

13b,13c-Di(4-hydroxyphenyl)-2,3,9,10-tetramethyl-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetra-aza-benzo[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione (4b)

Yield: 0.98 g (67%); mp > 300 °C. IR (KBr): 3374 (br), 1691, 1615, 1515, 1464, 1279 cm^{-1}. ^1H NMR (DMSO-d_6) δ: 2.09 (s, 12 H, 4 × CH_3), 3.99 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 4.52 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.56 (d, *J* = 8 Hz, 4 H, Ar–H), 6.81 (d, *J* = 8 Hz, 4 H, Ar–H), 6.94 (s, 4 H, Ar–H), 9.47 (s, 2 H, 2 × OH). EI-MS *m/z* (%): 586 (M^+). Anal. calcd. for $C_{36}H_{34}N_4O_4$: C, 73.70; H, 5.84; N, 9.55. Found: C, 73.95; H, 6.02; N, 9.73.

13b,13c-Di(4-hydroxyphenyl)-1,2,3,4,8,9,10,11-octamethyl-5,7,12,13b,13c,14-hexahydro-5a,6a, 12a,13a-tetraaza-benzo[5,6]azuleno[2,1,8-ija] benzo[f]azulene-6,13-dione (4c)

Yield: 1.04 g (65%); mp > 300 °C. IR (KBr): 3381 (br), 1685, 1614, 1515, 1470, 1278 cm^{-1}. ^1H NMR (DMSO-d_6) δ: 2.07 (s, 12 H, 4 × CH_3), 2.34 (s, 12 H, 4 × CH_3), 3.73 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 4.94 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.55 (d, *J* = 8 Hz, 4 H, Ar–H), 6.90 (d, *J* = 8 Hz, 4 H, Ar–H), 9.42 (s, 2 H, 2 × OH). EI-MS *m/z* (%): 642 (M^+). Anal. calcd. for $C_{40}H_{42}N_4O_4$: C, 74.74; H, 6.59; N, 8.72. Found: C, 74.48; H, 6.82; N, 8.55.

Synthesis of crown clips 5a–5i

General procedure

Ditosylate **6** (1.5 mmol) was added in small portions during a period of 12 h to the refluxing mixture of **4** (1.5 mmol) and K_2CO_3 (0.83 g, 6 mmol) in dry MeCN (60 mL). The reflux was continued for 3 days. Then, the solvent was evaporated in vacuo, and the light-brown solid was partitioned between aq. NaOH (5%, 75 mL) and CH_2Cl_2 (75 mL). The organic layer was washed with water (75 mL), dried (Na_2SO_4), and evaporated to dryness. After column chromatography (eluent: CH_2Cl_2 – MeOH, 100:3, *v/v*), compound **5** was obtained as white powder.

Crown clip 5a

The title compound was obtained according to the general procedure, starting with **4a** and **6a**.

Yield: 0.39 g (44%); mp > 300 °C. IR (KBr): 2917, 2849, 1703, 1509, 1455, 1233 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.68 (t, *J* = 6 Hz, 4 H, CH_2OCH_2), 4.19–4.34 (m, 8 H, 4 × *CH*H, 2 × $ArOCH_2$), 4.81 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.66 (d, *J* = 8 Hz, 4 H, Ar–H), 6.95–7.30 (m, 12 H, Ar–H). EI-MS *m/z* (%): 600 (M^+). Anal. calcd. for $C_{36}H_{32}N_4O_5$: C, 71.99; H, 5.37; N, 9.33. Found: C, 72.10; H, 5.42; N, 9.38.

Crown clip 5b

The title compound was obtained according to the general procedure, starting with **4a** and **6b**.

Yield: 0.40 g (42%); mp > 300 °C. IR (KBr): 2925, 2854, 1706, 1512, 1454, 1256 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.65–3.85 (m, 8 H, OCH_2CH_2O, 2 × OCH_2), 4.05–4.30 (m, 8 H, 4 × *CH*H, 2 × $ArOCH_2$), 4.78 6.91–7.30 (m, 12 H, Ar–H). EI-MS *m/z* (%): 644 (M^+). Anal. calcd. for $C_{38}H_{36}N_4O_6$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.51; H, 5.53; N, 8.83.

Crown clip 5c

The title compound was obtained according to the general procedure, starting with **4a** and **6c**.

Yield: 0.39 g (38%); mp > 300 °C. IR (KBr): 2917, 2852, 1709, 1610, 1457, 1254 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.68 (s, 8 H, 2 × OCH_2CH_2O), 3.80 (t, *J* = 5 Hz, 4 H, 2 × OCH_2), 4.02 (t, *J* = 5 Hz, 4 H, 2 × $ArOCH_2$), 4.18 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 4.77 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.66 (d, *J* = 8 Hz, 4 H, Ar–H), 6.93–7.30 (m, 12 H, Ar–H). EI-MS *m/z* (%): 688 (M^+). Anal. calcd. for $C_{40}H_{40}N_4O_7$: C, 69.75; H, 5.85; N, 8.13. Found: C, 69.98; H, 5.91; N, 8.18.

Crown clip 5d

The title compound was obtained according to the general procedure, starting with **4b** and **6a**.

Yield: 0.44 g (45%); mp > 300 °C. IR (KBr): 2922, 1706, 1608, 1508, 1455, 1236 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.10 (s, 12 H, 4 × CH_3), 3.63 (t, *J* = 4 Hz, 4 H, CH_2OCH_2), 4.08–4.25 (m, 8 H, 4 × *CH*H, 2 × $ArOCH_2$), 4.71 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.60 (d, *J* = 9 Hz, 4 H, Ar–H), 6.84 (d, *J* = 9 Hz, 4 H, Ar–H), 6.99 (s, 4 H, Ar–H). EI-MS *m/z* (%): 656 (M^+). Anal. calcd. for $C_{40}H_{40}N_4O_5$: C, 73.15; H, 6.14; N, 8.53. Found: C, 73.40; H, 6.22; N, 8.41.

Crown clip 5e

The title compound was obtained according to the general procedure, starting with **4b** and **6b**.

Yield: 0.44 g (42%); mp > 300 °C. IR (KBr): 2920, 1708, 1610, 1509, 1457, 1253 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.13 (s, 12 H, 4 × CH_3), 3.65–3.84 (m, 8 H, OCH_2CH_2O, 2 × OCH_2), 4.90–4.22 (m, 8 H, 4 × *CH*H, 2 × $ArOCH_2$), 4.72 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.63 (d, *J* = 8 Hz, 4 H, Ar–H), 6.92 (d, *J* = 8 Hz, 4 H, Ar–H), 7.02 (s, 4 H, Ar–H). EI-MS *m/z* (%): 700 (M^+). Anal. calcd. for $C_{42}H_{44}N_4O_6$: C, 71.98; H, 6.33; N, 7.99. Found: C, 71.82; H, 6.37; N, 8.06.

Crown clip 5f

The title compound was obtained according to the general procedure, starting with **4b** and **6c**.

Yield: 0.43 g (39%); mp > 300 °C. IR (KBr): 2917, 1714, 1609, 1509, 1452, 1251 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.12 (s, 12H, 4 × CH_3), 3.68–3.82 (m, 12 H, $OCH_2CH_2OCH_2CH_2O$, 2 × OCH_2), 3.98–4.20 (m, 8 H, 4 × *CH*H, 2 × $ArOCH_2$), 4.72 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.65 (d, *J* = 8 Hz, 4 H, Ar–H), 6.94 (d, *J* = 8 Hz, 4 H, Ar–H), 7.01 (s, 4 H, Ar–H). EI-MS *m/z* (%): 744 (M^+). Anal. calcd. for $C_{44}H_{48}N_4O_7$: C, 70.95; H, 6.49; N, 7.52. Found: C, 71.12; H, 6.52; N, 7.36.

Crown clip 5g

The title compound was obtained according to the general procedure, starting with **4c** and **6a**.

Yield: 0.46 g (43%); mp > 300 °C. IR (KBr): 2925, 1705, 1508, 1458, 1427, 1227 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.16 (s, 12 H, 4 × CH_3), 2.46 (s, 12 H, 4 × CH_3), 3.67 (t, *J* = 4 Hz, 4 H, CH_2OCH_2), 3.97 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 4.28 (t, *J* = 4 Hz, 4 H, 2 × $ArOCH_2$), 5.17 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.61 (d, *J* = 9 Hz, 4 H, Ar–H), 6.93 (d, *J* = 8 Hz, 4 H, Ar–H). EI-MS *m/z* (%): 712 (M^+). Anal. calcd. for $C_{44}H_{48}N_4O_5$: C, 74.13; H, 6.79; N, 7.86. Found: C, 74.36; H, 6.87; N, 7.76.

Crown clip 5h

The title compound was obtained according to the general procedure, starting with **4c** and **6b**.

Yield: 0.44 g (39%); mp > 300 °C. IR (KBr): 2917, 1714, 1509, 1453, 1421, 1252 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.16 (s, 12 H, 4 × CH_3), 2.43 (s, 12 H, 4 × CH_3), 3.60–3.75 (m, 8 H, OCH_2CH_2O, 2 × OCH_2), 3.88–4.15 (m, 8 H, 4 × *CH*H, 2 × $ArOCH_2$), 5.14 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.60 (d, *J* = 8 Hz, 4 H, Ar–H), 6.95 (d, *J* = 8 Hz, 4 H, Ar–H). EI-MS *m*/*z* (%): 756 (M^+). Anal. calcd. for $C_{46}H_{52}N_4O_6$: C, 72.99; H, 6.92; N, 7.40. Found: C, 72.81; H, 6.97; N, 7.26.

Crown clip 5i

The title compound was obtained according to the general procedure, starting with **4c** and **6c**.

Yield: 0.44 g (37%); mp > 300 °C. IR (KBr): 2914, 1705, 1509, 1458, 1427, 1253 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.15 (s, 12 H, 4 × CH_3), 2.43 (s, 12 H, 4 × CH_3), 3.66–4.10 (m, 16 H, $OCH_2CH_2OCH_2CH_2O$, 2 × OCH_2, 4 × *CH*H), 5.16 (d, *J* = 16 Hz, 4 H, 4 × *CH*H), 6.61 (d, *J* = 8 Hz, 4 H, Ar–H), 6.95 (d, *J* = 8 Hz, 4 H, Ar–H). EI-MS *m*/*z* (%): 800 (M^+). Anal. calcd. for $C_{48}H_{56}N_4O_7$: C, 71.98; H, 7.05; N, 6.99. Found: C, 71.85; H, 7.08; N, 6.87.

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