Pergamon

SCIENCE DIRECT®

Tetrahedron: *Asymmetry* 14 (2003) 1025–1035

TETRAHEDRON: *ASYMMETRY*

Synthesis of chiral 1,3-calix[4](crown-6) ethers as potential mediators for asymmetric recognition processes

István Bitter,[a,*] Éva Kőszegi,[a] Alajos Grün,[a] Péter Bakó,[a] Krisztina Pál,[b] András Grofcsik,[b,d] Miklós Kubinyi,[b,d] Barbara Balázs[c] and Gábor Tóth[c]

[a]*Department of Organic Chemical Technology, Budapest University of Technology and Economics, H-1521 Budapest, Hungary*
[b]*Department of Physical Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary*
[c]*Technical Analytical Research Group of the Hungarian Academy of Sciences, Institute for General and Analytical Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary*
[d]*Chemical Research Center, Hungarian Academy of Sciences, H-1525 Budapest, Hungary*

Received 2 December 2002; revised 13 February 2003; accepted 17 February 2003

Abstract—Novel chromogenic 1,3-calix[4](crown-6) derivatives comprised of 1,1′-binaphthyl-, methyl-α-D-glucoside-and D-mannitol moieties in the crown ether ring have been synthesized. UV–vis spectroscopic measurements of the 2,4-dinitrophenylazo chromogenic molecules indicated noticeable chiral discrimination associated with coloration towards primary amine enantiomers.

1. Introduction

Since the discovery of crown ethers[1] the field of host–guest chemistry[2] has developed into the continuously widening and progressing research area of supramolecular chemistry[3,4] involving by now all of researches dealing with studies and applications of molecular recognitions in various branches of natural sciences. These phenomena play essential roles in biological systems where the life functions are primarily regulated by selective recognition processes.[5] Among them, chiral recognition, in which a chiral host molecule selectively binds one of the enantiomers, is of high interest for supramolecular chemists who have devoted much effort to the design, synthesis and investigation of synthetic chiral receptors.[6,7] Such host molecules not only provide a controlled means for studying the fundamentals of non-covalent interactions in nature, but also open new routes for developing novel enantioselective sensors, catalysts, selectors and other molecular devices.[3]

Among chiral guests, organic ammonium salts, aminoalcohol and aminoacid derivatives belong to the most attractive targets and a number of chiral macrocycles, especially crown ether hosts were described for the enantioselective complexation of these molecules.[8] Crown-6 ethers seem to be the hosts of choice for binding primary ammonium salts as the cations can reside in the cavity of crown stabilized by hydrogen bonds between the ammonium protons and the ether oxygens. Di-1,1′-binaphtho(22-crown-6) reported first by Cram et al.[9] was disclosed to exhibit remarkable chiral discrimination between the enantiomers of organic ammonium salts since the receptor possessing a C_{2v} axis of symmetry provides a chiral cavity due to the steric effect between the naphthalene rings. Subsequently a great number of crowns have been synthesized where the asymmetric rings were created with the help of natural sources, advantageously with carbohydrates. These molecules have been utilized, among others, as chiral mediators in alkali base catalyzed asymmetric reactions.[10] Recently, a number of supramolecules combining crown ethers and calixarenes have been described[11] and applied in analytical and separation chemistry.[12] It is surprising, however, that chiral calixcrowns are rarely found in the literature and monosaccharide-appended calixcrowns, to the best of our knowledge, have not been synthesized until now. Notably, the excellent chiral selector properties of 1,1′-binaphthocrowns have been utilized in the calixarene chemistry for the first time by Kubo et al. who pre-

* Corresponding author. Tel.: 36-1-463-1379; fax: 36-1-463-3648; e-mail: ibitter.@mail.bme.hu

0957-4166/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0957-4166(03)00174-5

pared chromogenic receptors (*S*)-**1c**,**d**[13] containing indophenol indicator units as part of the calixarene core (Fig. 1). Ligand (*S*)-**1c** (and to some extent (*S*)-**1d**) was disclosed to selectively recognize (*R*)-phenylglycinol in EtOH solution associated with a remarkable change of color, thus representing the first chiral sensor for the colorimetric determination of amine enantiomers.

As part of our ongoing program to synthesize chromoionophores for developing optical sensors, we have studied the optical properties of different chromophore groups (2,4-dinitrophenylazo, pyridinium, indophenol) introduced to various calix[4]arenes including bridged derivatives.[14–17] Recently, our interest has been focused to calixcrown ionophores comprising achiral crown ether ring(s) attached to the thiacalix[4]arene core.[18,19] Herein we report on the synthesis of novel chiral receptors based on protected α-D-glucoside, D-mannitol -and 1,1′-bi-2-naphthyl-appended calixcrowns and alkylated derivatives thereof (Fig. 1). These supramolecules may be utilized as chiral mediators in asymmetric processes. To obtain evidence for the recognition properties, some chromogenic molecules were also prepared and investigated their optical responses toward primary amine enantiomers by UV–vis spectroscopy.

2. Results and discussion

2.1. 1,1′-Binaphthyl-appended calix[4]crown-6 derivatives

Although binaphthocrown (*S*)-**1a** has been used and partly characterized by Kubo et al. for the synthesis of (*S*)-**1d**, experimental details on the cyclization of calix[4]arene **4a** with ditosylate (*S*)-**5**[20] were not given except for mentioning the base ($KOBu^t$) used in the ring closure.[13] We have found the cyclization smoothly takes place in boiling benzene in the presence of K_2CO_3 with a molar ratio of **4**/(*S*)-**5** or (*R*)-**5** /K_2CO_3 = 1:1.2:1 and both enantiomers of **1a**,**b** were obtained in 24–40% yields after chromatography (Scheme 1). The conformation of compounds **1a**,**b** was assigned as a *cone* from the ^1H and ^{13}C NMR spectra (δ $\underline{C}H_2 \approx 31$ ppm). The chiral discriminating power of the binaphtho(crown) moiety in (*R*)-**1b** toward α-methylbenzyl-ammonium perchlorate (MBA salt) enantiomers was assessed by the ^1H NMR titration method in $CDCl_3$. The CH_3 doublet of the MBA salt was shifted downfield (0.2 ppm) due to complexation indicating the guest is included by the crown ether and not by the calixarene cavity. We have found the formation of 1:1 complexes with some chiral discrimination of the (*S*)-enantiomer salt ($K_c \approx 80 \pm 8$ M^{-1}) over the (*R*)-salt ($K_c \approx 40 \pm 4$ M^{-1}).

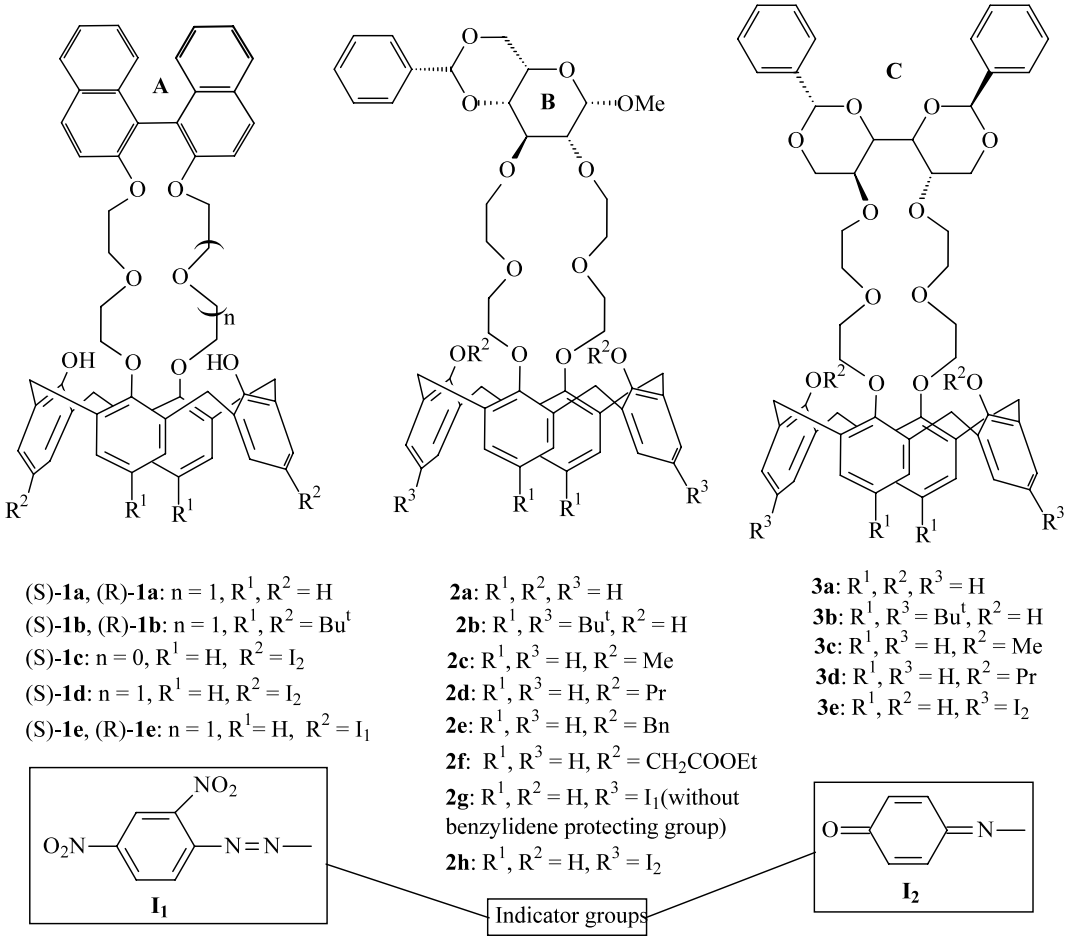
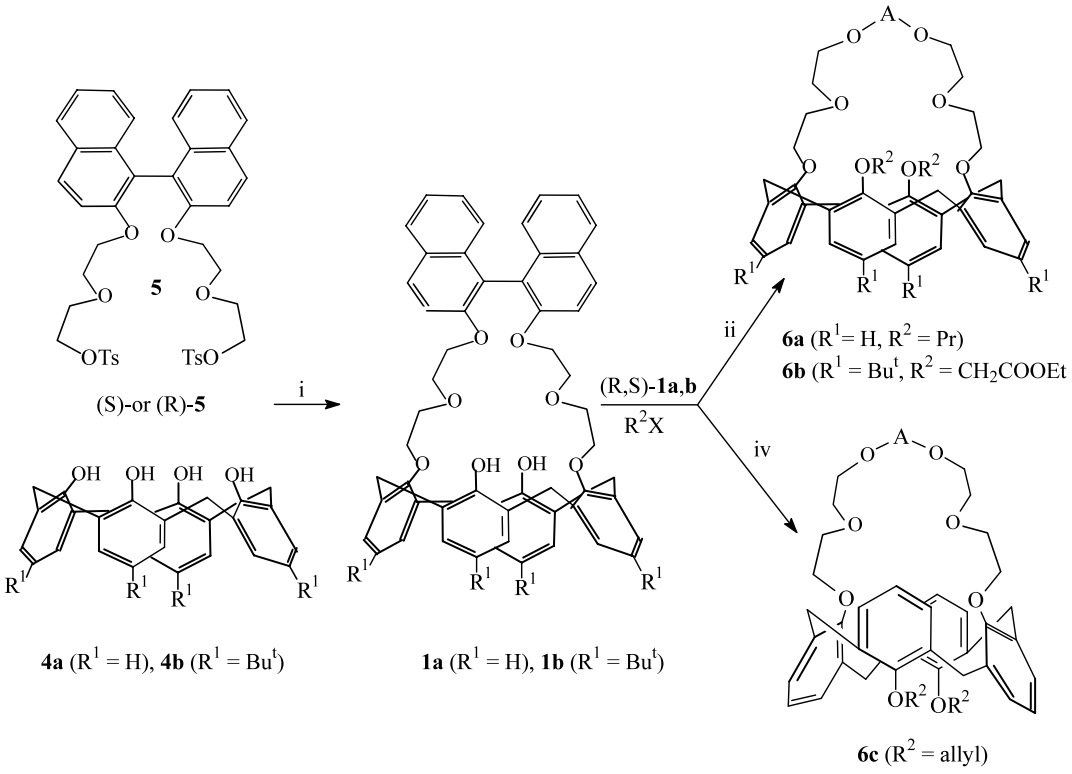


Figure 1. 1,1′-Binaphthyl-and protected carbohydrate-appended calix[4]crown-6 ether derivatives.



Scheme 1. Synthesis and alkylations of 1,1′-binaphtho-calix[4]crown-6 derivatives. *Reagents and conditions*: (i) K_2CO_3, benzene, 80°C, 2–3 days; (ii) a. R^2 = Pr, X = Br, aq. NaOH/toluene, $Bu_4N^+Br^-$ cat., 6 h, (b) $R^2 = CH_2COOEt$, X = Br, K_2CO_3, MeCN, 80°C, 2 days; (iv) X = Br, Cs_2CO_3, MeCN, 80°C, 2 days, A = 1,1′-bi-2-naphthyl.

Ligands (*R*)-and (*S*)-**1a**,**b** in hand provide the possibilities of obtaining novel chiral selectors in two ways: (a) by conformation selective alkylation of the free phenolic OH groups, chiral mediators (e.g. **1c**[13]) for asymmetric reactions and for development of chemical sensors to detect ammonium salt enantiomers will be available, (b) by introducing different chromogenic functions new proton ionizable chromoionophores can be prepared for optical recognition of chiral amines.

The stereochemical outcome of alkylation was checked with racemic **1a**,**b** using various alkylating agents under conditions we have described earlier.[21,22] As can be seen in Scheme 1. **6a**, **b** (*cone*) and **6c** (1,3-*alt*) were cleanly formed in conformationally pure forms. These results open the way to synthesize a series of chiral ligands in different conformations to test their asymmetric induction in alkaline base-catalyzed reactions, such as Michael additions and Darzens condensations.[10] Since in these reactions alkali cations (mostly Na^+, K^+) are required to be complexed by the chiral catalyst, (*S*)- and (*R*)-**6b** were prepared first and proved to be better complexants for both cations than **6a** and **6c** according to competitive FAB-MS measurements. Asymmetric induction of (*S*)-**6b** in the Michael addition of 2-nitropropane to chalcones is currently studied in our laboratory.

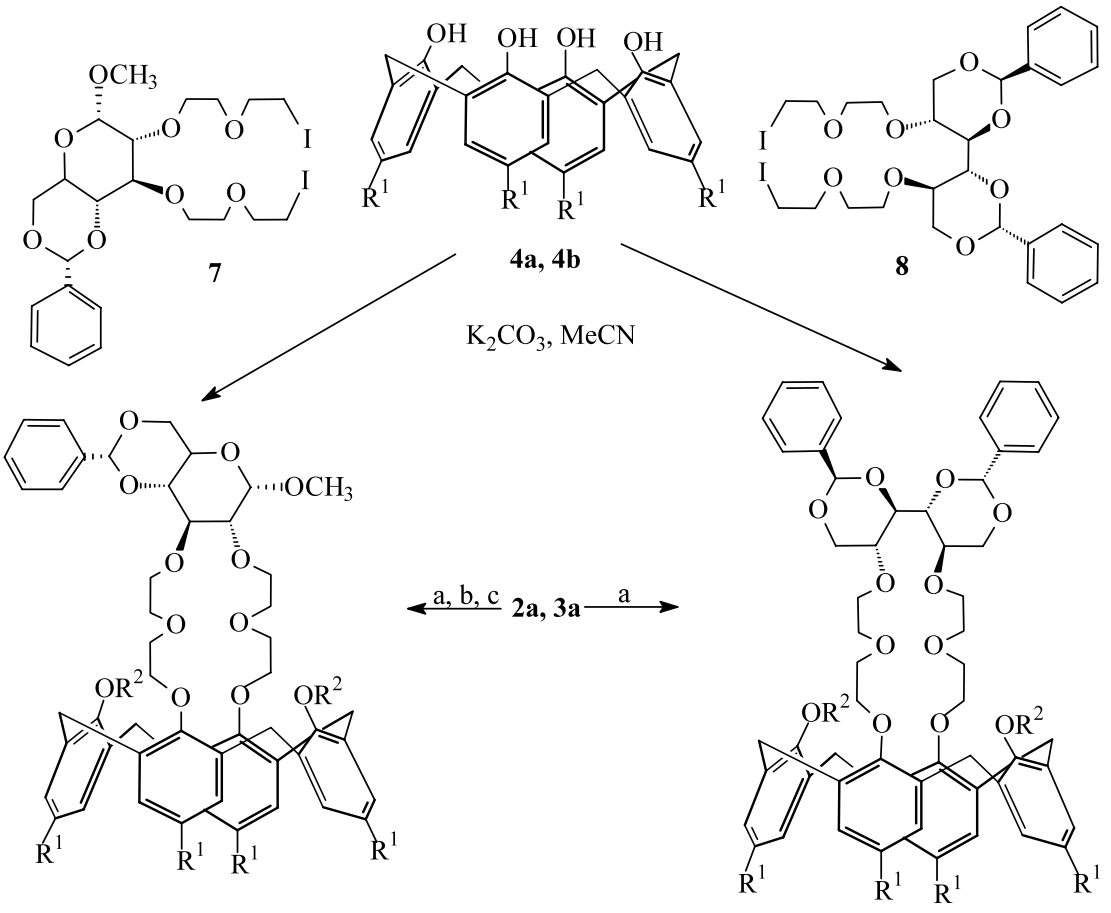
2.2. Protected α-D-glucoside-and D-mannitol-based calix[4](crown-6) ether derivatives 2 and 3

The synthesis of ligands **2a**,**b** and **3a**,**b** was based on the ring closure of calixarenes **4a**,**b** with equimolar amounts of diiodides **7**[23] or **8**[24] and in the presence of K_2CO_3 in MeCN under 4 days reflux (Scheme 2).

Alkylations of the free phenolic OH groups in compounds **2a** and **3a** with various alkylating reagents were performed in different ways as described above (a) under PTC conditions with MeI and *n*-PrBr affording dialkylated compounds **2c**,**d** and **3c**,**d**, (b) with BnBr/Cs_2CO_3 resulting in the formation of **2e**, (c) with ethyl bromoacetate/K_2CO_3 furnishing diester **2f** (Scheme 2). All compounds were fully characterized and their conformations were analyzed by NMR measurements.

2.3. Conformational analysis

In a series of 1,3-bridged calix[4]arenes we have recently found that the distortion of the conic conformation is reflected by the $\Delta\delta$ differences between the chemical shifts of the Ar 10,12-H and Ar 4,6-H protons[21] (Fig. 2). If $\Delta\delta = 0.1$-0.3 ppm then the conformation is symmetrically cone while $\Delta\delta \approx 1$ ppm is indicative of a strongly distorted (flattened) cone conformations (Fig.



2a (R^1, R^2= H, *cone*) 57%
2b (R^1= Bu^t, R^2= H, *cone*) 39%

3a (R^1, R^2= H, *cone*) 44%
3b (R^1= Bu^t, R^2= H, *cone*) 28%

2c (R^1= H, R^2= Me, *cone*/*paco* = 2:1) 32%
2d (R^1= H, R^2= Pr, *cone*) 29%
2e (R^1= H, R^2= Bn, *paco*/1,3-*alt* = 4:1) 23%
2f (R^1= H, R^2= CH_2COOEt, *cone*) 40%

3c (R^1= H, R^2= Me, *paco*/*cone* = 2:1) 43%

3d (R^1= H, R^2= Pr, *cone*) 41%

Scheme 2. Synthesis of carbohydrate-based calixcrowns **2**, **3** and alkylations of **2a** and **3a** under various conditions: (a) MeI or PrBr, 50% aq. NaOH/toluene, $Bu_4N^+Br^-$; (b) BnBr, Cs_2CO_3, MeCN; (c) $BrCH_2COOEt$, K_2CO_3, MeCN.

2). Utilizing this observations we have assigned the conformation of products in $CDCl_3$ and found that **2a**, **b** are ideal cones ($\Delta\delta \leq 0.3$), **3a**, **b** are slightly distorted cones ($\Delta\delta \approx 0.5$); dipropyl **2d**, **3d** and diester **2f** ($\Delta\delta \approx 1$) are flattened cone, where the assignment of signals was proved by HMBC measurements for **3d**. As was expected the methylated compounds **2c**, **3c** exist as mixtures of conformers but of reverse ratio: **2c** is *cone*/*paco* = 2:1, **3c** is *cone*/*paco* = 1:2. Unlike the binaphthocrown analogue **6d**, the conformation of the dibenzyl **2e** is *paco*/1,3-*alt* = 4:1 mixture. The reason of the reversed ratio of conformers of **2c** versus **3c** and the unexpected conformation of **2e** is unclear at this point.

Temperature dependent ^1H NMR spectra were recorded with dimethyl **2c** and **3c** in DMSO-d_6 to study the interconversion of *paco*/*cone* conformers. Although **2c** was decomposed but the Ar 4,6-H/16,18-H; 10,12-H/22,24-H; OCH_3, furthermore the OCHO signals of **3c**

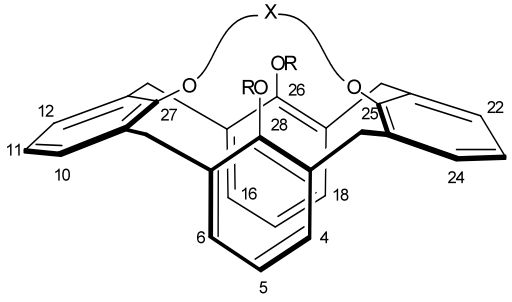


Figure 2. Flattened cone conformation of bridged calixarenes.

conformers were coalesced raising the temperature to 373 K ($\Delta G^* = 70$ kJ/mol). At 400 K only one set of signals attributed to the *cone* conformer of **3c** was observable.

2.4. Chromogenic chiral calixcrowns 1e, 2g, 2h and 3e

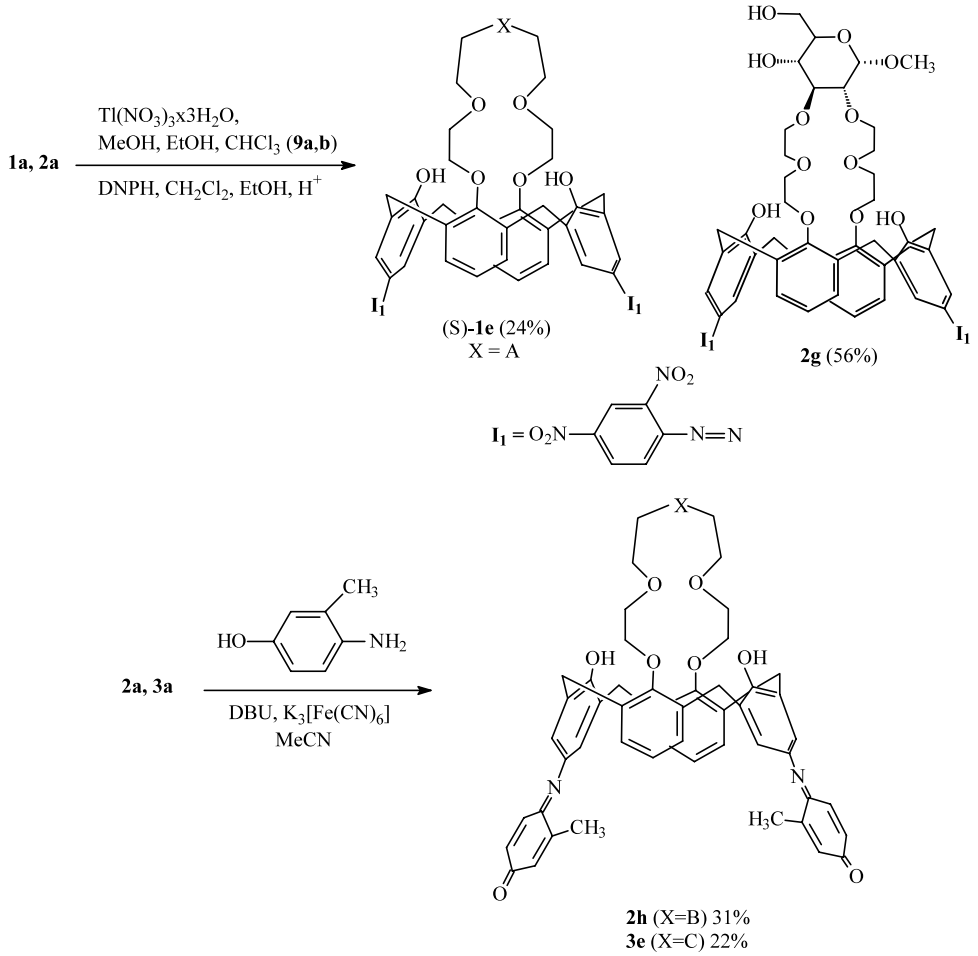
To obtain evidence for the chiral recognition properties of the novel binaphthol- and carbohydrate-based crown ethers towards primary amine enantiomers, chromogenic functions were introduced into ligand **1a**, **2a**, and **3a**. Thus the complexation process could be monitored by UV–vis spectrophotometry.

2,4-Dinitrophenylazo derivatives **1e** and **2g** were prepared in moderate yields by the oxidation of **1a**, and **2a** with $Tl(NO_3)_3$ to diquinone **9a**,**b** followed by condensation with 2,4-dinitrophenylhydrazine (DNPH) according to literature.[25] During the latter reaction of **9b** the benzylidene protecting group was cleaved by DNPH resulting in the formation of deprotected **2g** (Scheme 3). Calix(crown)-indophenols **2h** and **3e** were prepared by the oxidative treatment of **2a** and **3a** with $K_3Fe(CN)_6$ and 4-amino-*m*-cresol under basic conditions as proposed for related indophenols.[13,17]

Similarly to the starting compounds **2a** and **3a**, all chromogenic molecules **1e**, **2g** and **2h**, **3e** retained the *cone* conformation stabilized by internal H-bonds between the OH and the adjacent phenol ether groups (δ OH = 9.2–7.4 ppm). Identical conformations were assigned by Kubo for indophenols **1c**,**d**.[13] Earlier we have studied the tautomerization of the indophenol moiety with different capped calixarenes by NMR methods. A solvent dependent process affording an equilibrium of the *exo*-quinoide and the *endo*-quinoide tautomers (in the latter case the semiquinone moiety constitutes a part of the calixarene core) has been observed.[17] Since such an equilibrium has not been detected, the structure of indophenols **2h** and **3e** (including Kubo's **1c**,**d**) was assigned exclusively to the *exo*-quinoide tautomer as seen in Fig. 1.

The complexation model described by Kubo[13] for the interaction of ligands (*S*)-**1c**,**d** with chiral amines consists of a two-step process: first, the amine is protonated resulting in the formation of an ammonium-phenolate ion-pair followed by enantioselective complexation of the cation thus formed by the chiral crown ether ring. The coloration induced by the amine can be ascribed to ionization of the indophenol and analogously to that of the azophenol moiety in our ligand **1e**.

The UV–vis measurements were performed in MeCN with ligand (*S*)-**1e** ($\lambda_{max} = 412$ nm). Upon addition of



Scheme 3. Synthesis of chiral calixcrowns supplied with dinitrophenylazo **1e**, **2g** and indophenol **2h**, **3e** chromophores.

(*R*)- or (*S*)-α-methylbenzylamine (MBA) guests with molar proportions from 1:1 up to 500:1, a new band appeared at 604–610 nm (Fig. 3) and a linear Benesi–Hildebrand plot was obtained for the 1:1 complex stoichiometry. The apparent K_c values calculated from the slope were 410±40 M^{-1} for (*R*)-α-MBA) and 170± 20 M^{-1} for (*S*)-α-MBA), respectively. The selectivity $S_{R/S}=2.4$ is not high but the preference of the heterochiral complex formation is in accord with earlier results with binaphtho(crowns).[8,13]

Similar UV–vis spectroscopic experiments have been performed with the chromogenic carbohydrate-based crowns **2g**,**h** and **3e** in EtOH ($\lambda_{max}=406$, 520 and 510 nm, respectively). The (*R*)-and (*S*)-enantiomers of α-MBA and of phenylglycinols (PGL) have been chosen as guests. The reaction of each host with α-MBA enantiomers were found insensitive to the configuration of the guest. The quantitative analysis of the spectral data revealed that a simple proton transfer affording phenolate in an acid-base equilibrium ($K_1(S,R)=6.1\times 10^{-3}$) is the dominant reaction in this system. Upon the addition of (*R*)-and (*S*)-PGL, the spectra of indophenols **2h** and **3e** have displayed minor changes indicating

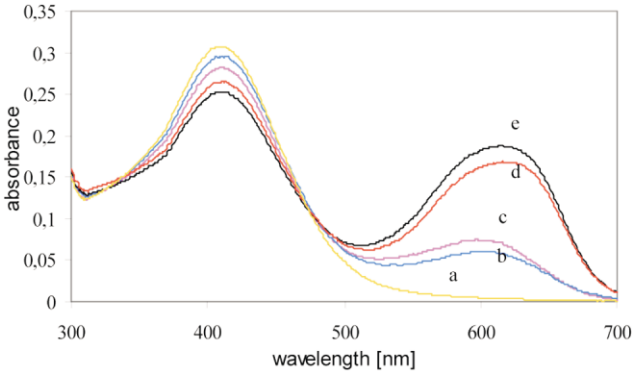


Figure 3. Absorption spectrum of (*S*)-**1e** (10^{-5} M/MeCN) (a) alone and in response to (b) 10^{-4} M (*S*)-MBA, (c) 10^{-4} M (*R*)-MBA, (d) 10^{-3} M (*S*)-MBA, (e) 10^{-3} M (*R*)-MBA.

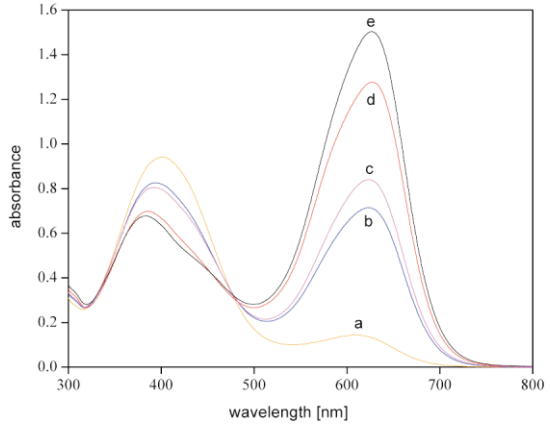


Figure 4. Absorption spectrum of **2g** (2.5×10^{-5} M/EtOH) (a) alone and in response to (b) 2.5×10^{-3} M (*R*)-PGL, (c) 2.5×10^{-3} M (*S*)-PGL, (d) 1.25×10^{-2} M (*R*)-PGL, (e) 1.25×10^{-2} M (*S*)-PGL.

a negligible chiral discrimination (e.g. for **2h** $K_2(R)=350\pm40$ M^{-1} and $K_2(S)=270\pm30$ M^{-1}). In contrast, azo compound **2g** gave different optical responses toward the (*R*)- and (*S*)-enantiomers (the yellow color turned to bluish–purple). In both cases there appeared a new band at 622 nm, the intensity of which grew more rapidly with the concentration of (*S*)-than with that of the (*R*)-PGL (Fig. 4).

The evaluation of the spectral data led to the conclusion that the host–guest interaction in these systems can be described in terms of a two-step reaction: a non-stereoselective proton transfer (1) followed by an enantioselective complexation. (2) The values of the equilibrium constants of the first process agree within the experimental error ($K_1(S)=1.9\pm0.3\times10^{-3}$ and $K_1(R)=2.1\pm0.3\times10^{-3}$). The consecutive complex formations are characterized by the equilibrium constants $K_2(S)=3500\pm400$ M^{-1} and $K_2(R)=240\pm30$ M^{-1}, indicating a remarkable chiral recognition.

3. Conclusions

We have synthesized a series of 1,3-calix[4]crown-6 ether derivatives comprising 1,1′-binaphthyl, α-D-glucoside and D-mannitol moieties in the crown ring. With the alkylation of the free phenolic OH groups in addition to the introduction of chromogenic functions, a number of novel chiral receptors have been obtained. Some chromogenic molecules **1e** and **2g** exhibited noticeable optical recognitions toward primary amine enantiomers. The conformationally pure alkylated derivatives are currently investigated as chiral mediators in Michael addition and Darzens condensation.

4. Experimental

Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ at 500/125 MHz on a Bruker Avance DRX-500 spectrometer. FAB-MS spectra were taken on a Varian MAT 312, UV–vis spectra were recorded on UNICAM SP8-500 and HP 8452A instruments. Optical rotations were measured on a Perkin–Elmer 241 polarimeter at 22°C. Precoated silica gel plates (Merck 60 F_{254}) were used for analytical TLC and Kieselgel 60 for column chromatography. All chemicals were reagent grade and used without further purification. Compounds **5**[20], **7**[23] and **8**[24] were prepared as described in the literature.

4.1. General procedure for the preparation of binaphtocalix(crown-6) 1a,b

The mixture of calixarenes **4a** or **4b** (1 mmol), ditosylate (*S*)-**5** or (*R*)-**5** (1.2 mmol) and K_2CO_3 (0.14 g, 1 mmol) in benzene (30 ml) was agitated under reflux for 4 days. After removal of the solvent the residue was dissolved in $CHCl_3$ (30 ml), washed with dilute aqueous HCl, dried (Na_2SO_4) to obtain (*S*)-**1a** (25%), (*R*)-**1a** (24%), and (*S*)-**1b** (41%), (*R*)-**1b** (38%) as white solids purified by column chromatography on silica (eluents:

hexane–EtOAc = 7:3 for **1a** and hexane–EtOAc = 8:2 for **1b**).

Compound (*S*)-**1a**: $[\alpha]_D = -61.3$ (*c* 1, THF); (*R*)-**1a**: $[\alpha]_D = +60.1$ (*c* 1, THF); mp 133–135°C. ^{1}H NMR: δ 8.05 (s, 2H, OH), 7.54 (d, 2H, $J = 9.1$ Hz, binaphthyl), 7.54 (d, 2H, $J = 9.1$ Hz, binaphthyl), 7.94 (d, 2H, $J = 8.1$ Hz, binaphthyl), 7.40 (t, 2H, $J = 8.1$ Hz, binaphthyl), 7.31 (m, 4H, binaphthyl), 7.24 (d, 2H, Ar*H*), 7.14 (d, 2H, Ar*H*), 7.00 (d, 2H, Ar*H*), 6.93 (d, 2H, Ar*H*), 6.82 (t, 2H, Ar*H*), 6.78 (t, 1H, Ar*H*), 6.76 (t, 1H, Ar*H*), 4.52 and 4.33 (m, 2+2H, OCH_2), 3.93 and 3.89 (m, 2+2H, OCH_2), 3.86 (m, 4H, OCH_2), 3.70 and 3.29 (m, 2+2H, OCH_2), 4.49 and 3.45 (d, 2+2H, $J = 12.4$ Hz, ArCH_2Ar), 4.47 and 3.46 (d, 2+2H, $J = 13.5$ Hz, ArCH_2Ar) (*cone*); ^{13}C NMR δ 154.4, 134.4, 129.6, 129.3, 128.4, 126.6, 125.7, 123.9, 120.8, 115.5 (binaphthyl), 153.6, 151.8, 148.9, 133.9, 133.1, 129.1, 128.8, 128.7, 128.0, 127.6, 125.5, 122.4, 119.0 (Ar), 76.3, 70.6, 70.4, 70.2 (OCH_2), 31.9, 31.6, 30.9 (ArCH$_2$Ar)(*cone*). Anal. calcd for $C_{56}H_{50}O_8$ (851.01): C, 79.04; H, 5.92; found: C, 78.46; H, 5.86%.

Compound (*S*)-**1b**: $[\alpha]_D = -110.8$ (*c* 1, THF), (*R*)-**1b**: $[\alpha]_D = +107.8$ (*c* 1, THF); mp 155–158°C. ^{1}H NMR: δ 7.52 (s, 2H, OH), 7.99 (d, 2H, $J = 9.0$ Hz, binaphthyl), 7.54 (d, 2H, $J = 9.0$ Hz, binaphthyl), 7.91 (d, 2H, $J = 8.1$ Hz, binaphthyl), 7.36 (t, 2H, $J = 8.1$ Hz, binaphthyl), 7.28 (t, 2H, $J = 8.1$ Hz, binaphthyl), 7.26 (d, 2H, binaphthyl), 7.20 (s, 2H, Ar*H*), 7.11 (s, 2H, Ar*H*), 6.91 (s, 2H, Ar*H*), 6.85 (s, 2H, Ar*H*), 4.49 and 4.30 (m, 2+2H, OCH_2), 3.91 and 3.84 (m, 4+4H, OCH_2), 3.64 and 3.32 (m, 2+2H, OCH_2), 4.41 and 3.36 (d, 4+4H, $J = 13.3$ Hz, ArCH_2Ar) (*cone*), 1.39 (s, 18H, C(CH_3)$_3$), 1.04 (s, 18H, C(CH_3)$_3$); ^{13}C NMR: δ 154.6, 134.5, 129.5, 128.0, 126.5, 125.8, 123.8, 120.7, 115.6 (binaphthyl), 151.1, 149.8, 147.0, 141.3, 133.3, 132.6, 128.4, 127.5, 125.9, 125.3, 125.1 (Ar), 76.2, 70.8, 70.5, 70.1 (OCH_2), 34.1, 34.0 (C(CH$_3$)$_3$)), 32.0, 31.2 (C(CH$_3$)$_3$), 31.9, 31.3 (ArCH$_2$Ar) (*cone*). Anal. calcd for $C_{72}H_{82}O_8$ (1075.44): C, 80.41; H, 7.69; found: C, 79.65; H, 7.62%.

4.2. General procedure for the preparation of carbohydrate-appended calixcrowns 2 and 3

The mixture of **4a** or **4b** (1 mmol), diiodides **7** or **8** (1.2 mmol) and K_2CO_3 (0.14 g, 1 mmol; for the reaction of **4a** and **8** 1.38g, 10 mmol) in MeCN (30 ml) was agitated under reflux for 4 days. After removal of the solvent the residue was dissolved in $CHCl_3$ (30 ml), washed with dilute aqueous HCl, dried (Na_2SO_4). To obtain **2a** (39%), **2b** (57%), **3a** (28%), **3b** (44%) as white solids purified by column chromatography on silica (eluents: hexane–EtOAc = 7:3 for **2a**, **3a** and hexane–EtOAc = 4:6 for **2b**, **3b**).

Compound **2a** (*cone*). Mp 106–109°C; $[\alpha]_D = +36.7$ (*c* 1, THF). ^{1}H NMR: δ 7.96 (s, 1H, O*H*), 7.77 (s, 1H, O*H*), 7.50 (d, 2H, Ar*H*), 7.40 (t, 2H, Ar*H*), 7.38 (t, 1H, Ar*H*), 7.16 (d, 1H, *m*-Ar*H*), 7.11 (m, 3H, *m*-Ar*H*), 6.91 (m, 4H, *m*-Ar*H*), 6.74 (m, 4H, *p*-Ar*H*), 5.08 (s, 1H, OC*H*O), 4.96 (d, 1H, $J = 3.0$ Hz, OC*H*O), 4.44 (m, 3H, OCH_2), 4.23 (m, 2H, OCH_2), 4.17 (m, 2H, OCH_2), 4.04 (m, 3H, OCH_2), 3.95 (m, 2H, OCH_2), 3.77 (m, 3H, OCH_2), 3.47 (m, 3H, OCH_2), 3.95 (d, 1H, OC*H*), 3.77 (m, 1H, OC*H*), 3.71 (m, 1H, OC*H*), 2.86 (t, 1H, OC*H*), 3.47 (s, 3H, OCH_3), 4.73 (d, 1H, $J = 13.0$ Hz, ArCH_2Ar), 4.49 (d, 1H, $J = 13.0$ Hz, ArCH_2Ar), 4.39 (d, 1H, $J = 13.0$ Hz, ArCH_2Ar), 4.29 (d, 1H, $J = 13.0$ Hz, ArCH_2Ar), 3.45 (d, 1H, ArCH_2Ar), 3.42 (d, 2H, $J = 13.0$ Hz, ArCH_2Ar), 3.37 (d, 1H, $J = 13.0$ Hz, ArCH_2Ar); ^{13}C NMR δ 153.8, 153.4, 152.1, 151.7, 138.0, 133.7, 133.6, 133.3, 133.0, 129.3, 129.14, 129.06, 128.9, 128.7, 128.6, 128.4, 128.0, 125.6, 125.4, 119.2, 118.9, 118.8 (Ar), 100.9, 99.8 (OCHO), 81.2, 80.2, 79.0, 62.2 (OCH), 76.1, 72.9, 71.8, 71.2, 70.5, 69.3, 68.9 (OCH$_2$), 55.2 (OCH$_3$), 31.7, 31.3, 31.2, 31.1 (ArCH$_2$Ar); FAB-MS *m*/*z*: 869.4 [M+Na]$^+$ (calcd 869.4). Anal. calcd for $C_{50}H_{54}O_{12}$ (846.97): C, 70.91; H, 6.43; found: C, 70.43; H, 6.50%.

Compound **2b** (*cone*). Mp 113–116°C; $[\alpha]_D = +21.1$ (*c* 1, THF). ^{1}H NMR: δ 7.44 (d, 2H, Ar*H*), 7.37 (t, 2H, Ar*H*), 7.35 (t, 1H, Ar*H*), 7.22 (s, 1H, O*H*), 7.15 (d, 1H, $J = 2.4$ Hz, Ar*H*), 7.09 (d, 1H, $J = 2.4$ Hz, Ar*H*), 7.07 (d, 1H, $J = 2.4$ Hz, Ar*H*), 7.04 (s, 1H, O*H*), 7.03 (d, 1H, $J = 2.4$ Hz, Ar*H*), 6.80 (d, 1H, $J = 2.4$ Hz, Ar*H*), 6.76 (d, 2H, $J = 2.4$ Hz, Ar*H*), 6.75 (d, 1H, $J = 2.4$ Hz, Ar*H*), 4.93 (d, 1H, $J = 3.6$ Hz, OC*H*O), 4.81 (s, 1H, OC*H*O), 4.37 and 3.78 (m, 1+1H, OCH_2), 4.27 and 4.02 (m, 1+1H, OCH_2), 4.16 and 4.02 (m, 1+1H, OCH_2), 4.14 and 3.86 (m, 1+1H, OCH_2), 4.10 and 3.93 (m, 1+1H, OCH_2), 4.10 and 3.81 (m, 1+1H, OCH_2), 4.10 and 3.80 (m, 1+1H, OCH_2), 4.09 and 3.29 (m, 1+1H, OCH_2), 4.08 and 3.96 (m, 1+1H, OCH_2), 4.08 (m, 1H, OC*H*), 3.76 (m, 1H, OC*H*), 3.74 (t, 1H, OC*H*), 3.08 (t, 1H, $J = 9.5$, OC*H*), 3.44 (s, 3H, OCH_3), 4.59 and 3.30 (d, 1+1H, ArCH_2Ar), 4.46 and 3.30 (d, 1+1H, ArCH_2Ar), 4.34 and 3.27 (d, 1+1H, ArCH_2Ar), 4.20 and 3.35 (d, 1+1H, ArCH_2Ar), 1.33 (s, 9H, C(CH_3)$_3$), 1.29 (s, 9H, C(CH_3)$_3$), 0.93 (s, 18H, C(CH_3)$_3$); ^{13}C NMR: δ 151.2, 150.8, 150.1, 149.9, 146.9, 141.6, 141.3, 138.1, 133.1, 132.8, 132.6, 132.2, 128.8, 128.6, 128.4, 128.3, 128.0, 127.8, 126.2 (Ar), 100.6, 99.8 (OCHO), 81.7, 79.5, 79.0, 62.2 (OCH), 76.3, 75.9, 72.8, 72.0, 71.4, 70.7, 70.1, 68.8 (OCH$_2$), 55.2 (OCH$_3$), 34.1, 34.0 (C(CH$_3$)$_3$), 32.0, 31.4, 31.0 (ArCH$_2$Ar), 31.9, 31.2 (C(CH$_3$)$_3$); FAB-MS *m*/*z*: 1093.4 [M+Na]$^+$ (calcd 1093.4). Anal. calcd for $C_{66}H_{86}O_{12}$ (1071.40): C, 73.99; H, 8.09; found: C, 73.12; H, 8.01%.

Compound **3a** (*cone*). Mp 131–134°C; $[\alpha]_D = -31.0$ (*c* 1, THF). ^{1}H NMR: δ 7.47 (d, 4H, Ar*H*), 7.39 (t+t, 2+4H, Ar*H*), 7.15 (d, 2H, *m*-Ar*H*), 7.13 (d, 2H, *m*-Ar*H*), 6.85 (d, 2H, *m*-Ar*H*), 6.84 (d, 2H, *m*-Ar*H*), 6.76 (t, 2H, *p*-Ar*H*), 6.70 (t, 2H, *p*-Ar*H*), 5.29 (s, 2H, OC*H*O), 4.34 and 3.55 (m+t, 2+2H, OCH_2), 4.32 and 4.16 (m, 2+2H, OCH_2), 3.96 and 3.93 (m, 2+2H, OCH_2), 3.83 and 3.78 (m, 2+2H, OCH_2), 3.77 and 3.73 (m, 2+2H, OCH_2), 4.15 (d, 1H, OC*H*), 3.95 (m, 1H, OC*H*), 4.59 and 3.37 (d, 2+2H, ArCH_2Ar), 4.50 and 3.45 (d, 2+2H, ArCH_2Ar), ^{13}C NMR $\delta = 153.5$, 152.0, 138.2, 133.7, 132.9, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.3, 128.2, 126.4, 125.3 (Ar), 100.8, (OCHO), 77.5, 67.3 (OCH), 75.8, 70.8, 70.2, 69.8, 69.2 (OCH$_2$), 31.3, 30.9 (ArCH$_2$Ar); FAB-MS *m*/*z*: 945.2 [M+Na]$^+$ (calcd

945.4). Anal. calcd for $C_{56}H_{58}O_{12}$ (923.07): C, 72.87; H, 6.33; found: C, 72.11; H, 6.28%.

Compound **3b** (*cone*). Mp: 87–89°C; $[\alpha]_D = -31.6$ (*c* 1, THF). ^{1}H NMR: δ 7.54 (t, 2H, Ar*H*), 7.45 (d, 4H, Ar*H*), 7.37 (m, 4H, Ar*H*), 7.11 (s, 4H, Ar*H*), 6.74 (s, 4H, Ar*H*), 5.31 (s, 2H, OC*H*O), 4.32 and 3.55 (dd+t, 2+2H, OCH_2), 4.25 and 4.15 (m, 2+2H, OCH_2), 3.96 and 3.87 (m, 2+2H, OCH_2), 3.82 and 3.79 (m, 2+2H, OCH_2), 3.76 and 3.63 (m, 2+2H, OCH_2), 4.16 (d, 1H, OC*H*), 3.91 (m, 1H, OC*H*), 4.51 and 3.28 (d, 2+2H, ArCH_2Ar), 4.44 and 3.34 (d, 2+2H, ArCH_2Ar), 1.34 (s, 18H, C(CH_3)$_3$), 0.92 (s, 18H, C(CH_3)$_3$); ^{13}C NMR: δ 150.8, 149.9, 146.8, 141.5, 138.4, 133.0, 132.3, 128.2, 126.4, 125.7, 125.5, 125.3, 125.2 (Ar), 100.7, (O*C*HO), 77.7, 67.6 (O*C*H), 75.7, 70.8, 70.3, 69.9, 69.2 (O*C*H$_2$), 34.0 (*C*(CH$_3$)$_3$), 31.7, 31.5 (Ar*C*H$_2$Ar), 32.0, 31.2 (C(*C*H$_3$)$_3$); FAB-MS *m*/*z*: 1169.4 $[M+Na]^+$ (calcd 1169.6). Anal. calcd for $C_{72}H_{90}O_{12}$ (1147.50): C, 75.36; H, 7.91; found: C, 74.63; H, 7.79%.

4.3. General procedures for the alkylations of 1a,b, 2a and 3a

4.3.1. Method (a). A mixture of the starting compound (1 mmol), alkylating reagent (MeI, PrBr, 10 mmol) and $Bu_4N^+Br^-$ catalyst (0.03 g) in toluene (20 ml)/50% aq. NaOH (1 ml) was vigorously stirred at 100°C for 6 h. After cooling water (10 ml) was added and the organic phase was separated, washed with dilute aq. HCl and water, subsequently. The toluene solution was dried (Na_2SO_4) then evaporated to dryness and the residue was purified by chromatography on silica (eluents: hexane–EtOAc = 6:4 for **2c** and 8:2 for **6a**) to obtain white solids.

Compound **2c** (*cone*/*paco* = 2:1). Yield: 32%, mp 117–120°C; $[\alpha]_D = +21.8$ (*c* 1, THF). ^{1}H NMR (*cone*): δ 7.50 (d, 2H, Ar*H*), 7.39 (t, 2H, Ar*H*), 7.38 (t, 1H, Ar*H*), 7.08 (d, 4H, *m*-Ar*H*), 6.90 (m, 2H, *p*-Ar*H*), 6.60 (m, 1H, *p*-Ar*H*), 6.48 (d, 4H, *m*-Ar*H*), 6.43 (m, 1H, *p*-Ar*H*), 5.45 (s, 1H, OC*H*O), 4.84 (d, 1H, OC*H*O), 4.37–3.69 (m, 18H, OCH_2), 3.81 (m, 1H, OC*H*), 3.80 (m, 1H, OC*H*), 3.58 (m, 1H, OC*H*), 3.50 (t, 1H, *J* = 9.5 Hz, OC*H*), 3.43 (s, 3H, OCH_3), 4.48 (d, 1H, *J* = 12.9 Hz, ArCH_2Ar), 4.46 (d, 1H, *J* = 12.9 Hz, ArCH_2Ar), 4.41 (d, 2H, *J* = 12.9 Hz, ArCH_2Ar), 3.23 (d, 1H, ArCH_2Ar), 3.21 (d, 3H, ArCH_2Ar), 4.12 (s, 3H, OCH_3), 4.04 (s, 3H, OCH_3), ^{13}C NMR δ = 31.1, 29.9 (Ar*C*H$_2$Ar). ^{1}H NMR (*paco*): δ 5.04 (s, 0.5H, OC*H*O), 4.80 (s, 0.5H, OC*H*O), 4.27 (d, 0.5H, ArCH_2Ar), 4.26 (d, 0.5H, ArCH_2Ar), 3.75 (2H, ArCH_2Ar), 3.04 (br, 1H, ArCH_2Ar); ^{13}C NMR: δ 37.0, 31.1 (Ar*C*H$_2$Ar); FAB-MS *m*/*z*: 897.5.4 $[M+Na]^+$ (calcd 897.4). Anal. calcd for $C_{52}H_{58}O_{12}$ (875.02): C, 71.38; H, 6.68; found: C, 71.02; H, 6.58%.

Compound **3c** (*paco*/*cone* = 2:1). Yield: 43%, mp 137–140°C; $[\alpha]_D = -27.6$ (*c* 1, THF). ^{1}H NMR (*paco*): δ 7.49 (d, 4H, Ar*H*), 7.36 (m, 6H, Ar*H*), 7.42 (d, 2H, *m*-Ar*H*), 7.36 (d, 2H, *m*-Ar*H*), 7.30 (d, 1H, *m*-Ar*H*), 7.26 (d, 1H, *m*-Ar*H*), 7.15 (d, 1H, *m*-Ar*H*), 7.07 (d, 1H, *m*-Ar*H*), 6.99 (t, 1H, *p*-Ar*H*), 6.97 (t, 2H, *p*-Ar*H*), 6.35 (t, 1H, *p*-Ar*H*), 5.48 (s, 1H, OC*H*O), 4.46 (s, 1H, OC*H*O), 4.40–2.70 (24H, OCH_2+OC*H*), 4.11 (s, 3H, OCH_3), 3.27 (s, 3H, OCH_3), 4.60 (d, 1H, *J* = 13.3 Hz, ArCH_2Ar), 4.47 (d, 1H, ArCH_2Ar), 3.09 (d, 1H, *J* = 13.5 Hz, ArCH_2Ar), 3.07 (d, 1H, *J* = 13.3 Hz, ArCH_2Ar), 3.71 (4H, ArCH_2Ar), ^{13}C NMR δ = 36.7, 36.6, 30.7, 30.6 (Ar*C*H$_2$Ar). ^{1}H NMR (*cone*) δ = 5.16 (s, 1H, OC*H*O), 4.61 (d, 1H, ArCH_2Ar), 4.52 (d, 1H, ArCH_2Ar), 3.19 (d, 2H, ArCH_2Ar), 3.49 (s, 3H, OCH_3); ^{13}C NMR: δ 30.9 (Ar*C*H$_2$Ar); FAB MS *m*/*z*: 973.5 $[M+Na]^+$ (calcd 973.4). Anal. calcd for $C_{58}H_{62}O_{12}$ (951.12): C, 73.24; H, 6.57; found: C, 72.82; H, 6.49%.

Compound **2d** (*cone*). Yield: 29%, mp 98–101°C; $[\alpha]_D = +27.6$ (*c* 1, THF). ^{1}H NMR: δ 7.53 (d, 2H, Ar*H*), 7.41 (t+t, 2+1H, Ar*H*), 7.18 (d, 4H, *m*-Ar*H*), 7.00 (t, 2H, *p*-Ar*H*), 6.24 (t, 2H, *p*-Ar*H*), 6.13 (d, 2H, *m*-Ar*H*), 6.11 (d, 2H, Ar*H*), 5.59 (s, 1H, OC*H*O), 4.89 (d, 1H, *J* = 3.4 Hz, OC*H*O), 4.37 and 4.26 (m, 2+2H, OCH_2), 4.33 and 4.00 (dd+m, 1+1H, OCH_2), 4.13 and 4.07 (m, 1+1H, OCH_2), 4.10 and 3.94 (m, 1+1H, OCH_2), 4.07 and 3.79 (m, 1+1H, OCH_2), 3.93 and 3.75 (m, 1+1H, OCH_2), 3.87 and 3.80 (m, 1+1H, OCH_2), 3.87 and 3.75 (m, 1+1H, OCH_2), 3.74 (m, 4H, OCH_2), 3.86 (t, 1H, *J* = 13.2 Hz, OC*H*), 3.85 (t, 1H, *J* = 8.8 Hz, OC*H*), 3.62 (t, 1H, *J* = 9.3 Hz, OC*H*), 3.52 (dd, 1H, *J* = 9.2; 3.7 Hz, OC*H*), 3.50 (s, 3H, OCH_3), 4.46 (d, 1H, *J* = 12.9 Hz, ArCH_2Ar), 4.44 (d, 1H, *J* = 12.0 Hz, ArCH_2Ar), 4.43 (d, 1H, *J* = 12.3 Hz, ArCH_2Ar), 4.42 (d, 1H, *J* = 12.4 Hz, ArCH_2Ar), 3.23 (d, 1H, ArCH_2Ar), 3.22 (d, 1H, ArCH_2Ar), 3.21 (d, 2H, ArCH_2Ar), 1.96 (quin., 4H, CH_2CH$_3$), 1.14 (t, 6H, CH$_2$CH_3); ^{13}C NMR: δ 31.0, 30.9 (Ar*C*H$_2$Ar); FAB-MS *m*/*z*: 953.5 $[M+Na]^+$ (calcd 953.4). Anal. calcd for $C_{56}H_{66}O_{12}$ (931.13): C, 72.24; H, 7.14; found: C 71.74; H, 7.01%.

Compound **3d** (*cone*). Yield: 41%, mp 108–110°C; $[\alpha]_D = -36.0$ (*c* 1, THF). ^{1}H NMR: δ 7.57 (d, 4H, Ar*H*), 7.40 (t+t, 2+4H, Ar*H*), 7.08 (d, 4H, *m*-Ar*H*), 6.91 (t, 2H, *p*-Ar*H*), 6.34 (t, 2H, *p*-Ar*H*), 6.24 (d, 4H, *m*-Ar*H*), 5.54 (s, 2H, OC*H*O), 4.49 (m, 2H, OCH_2), 4.38 (m, 2H, OCH_2), 4.26 (m, 2H, OCH_2), 4.11 (m, 2H, OCH_2), 4.00 (m, 2H, OCH_2), 3.86–3.60 (m, 14H, OCH_2), 4.17 (d, 2H, OC*H*), 3.92 (m, 2H, OC*H*), 4.51 (d, 2H, ArCH_2Ar), 4.50 (d, 2H, ArCH_2Ar), 3.23 (d, 2H, ArCH_2Ar), 3.22 (d, 2H, ArCH_2Ar); ^{13}C NMR: δ 31.2 (Ar*C*H$_2$Ar); FAB-MS *m*/*z*: 1029.5 $[M+Na]^+$ (calcd 1029.5). Anal. calcd for $C_{62}H_{70}O_{12}$ (1007.23): C, 73.93; H, 7.00; found: C, 73.58; H, 6.89%.

Compound (*rac*)-**6a** (*cone*). Yield: 37%, mp 193–196°C. ^{1}H NMR: δ 7.86 (d, 2H, *J* = 9.0 Hz, Ar*H*), 7.77 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.44 (d, 2H, *J* = 9.0 Hz, Ar*H*), 7.23 (t, 2H, Ar*H*), 7.00–7.13 (m, 6H, Ar*H*), 6.85 (t, 2H, Ar*H*), 6.51 (m, 2H, Ar*H*), 6.10 (t, 2H, Ar*H*), 5.97 (d, 4H, *J* = 7.5 Hz Ar*H*), 3.48–4.35 (m, 24H, OCH_2, ArCH_2Ar), 3.10 (d, 2H, *J* = 14 Hz, ArCH_2Ar), 3.04 (d, 2H, *J* = 13.5 Hz, ArCH_2Ar), 1.73 (m, 4H, CH_2), 0.93 (m, 6H, CH_3). Anal. calcd for $C_{62}H_{62}O_8$ (935.17): C, 79.63; H, 6.68; found: C, 79.23; H, 6.72%.

4.3.2. Method (b). A mixture of the starting compound (1 mmol), alkylating reagent (BnBr, allylbromide, 4 mmol) and Cs_2CO_3 (0.98 g, 3 mmol) in MeCN (20 ml) was vigorously stirred at reflux temperature for 12 h. After CH_2Cl_2 (20 ml) extraction work-up the residue was purified by chromatography on silica (eluents: hexane–EtOAc = 1:1 for **2e** and 7:3 for **6c**) to obtain white solids.

Compound **2e** (*paco*/1,3-*alt* = 4:1). Yield: 23%, mp 102–104°C; $[\alpha]_D = +3.0$ (*c* 1, THF). ^{1}H NMR (*paco*): δ 7.53 (d, 2H, Ar*H*), 7.41 (t+t, 2+1H, Ar*H*), 7.38 (m, 2H, Ar*H*), 7.37 (d, 1H, Ar*H*), 7.34 (d, 1H, Ar*H*), 7.27 (m, 3H, ArH), 7.15 (m, 2H, ArH), 7.14 (m, 1H, ArH), 7.06 (t, 1H, Ar*H*), 6.86 (d, 1H, Ar*H*), 6.83 (d, 2H, Ar*H*), 6.82 (d, 1H, Ar*H*), 6.80 (d, 1H, Ar*H*), 6.77 (d, 1H, Ar*H*), 6.69 (t, 1H, Ar*H*), 6.67 (t, 1H, Ar*H*), 6.61 (d, 2H, Ar*H*), 6.48 (t, 1H, Ar*H*), 5.49 (s, 1H, OC*H*O), 4.75 (d, 1H, *J* = 3.7 Hz, OC*H*O), 5.03 (d, 1H, *J* = 11.4 Hz, OCH_2), 4.92 (d, 1H, *J* = 11.4 Hz, OCH_2), 4.27 (dd, 1H, OCH_2), 4.07 (m, 1H, OCH_2), 3.98 (m, 1H, OCH_2), 3.94 (m, 2H, OCH_2), 3.92 (m, 1H, OCH_2), 3.90 (m, 1H, OCH_2), 3.81 (m, 2H, OCH_2), 3.79 (m, 2H, OCH_2), 3.74 (m, 2H, OCH_2), 3.73 (m, 2H, OCH_2), 3.68 (m, 2H, OCH_2), 3.66 (m, 1H, OCH_2), 3.60 (m, 1H, OCH_2), 3.48 (m, 1H, OCH_2), 3.80 (t, 1H, OC*H*), 3.79 (t, 1H, OC*H*), 3.32 (t, 1H, *J* = 9.3 Hz, OC*H*), 3.15 (t, 1H, OC*H*), 3.45 (s, 3H, OCH_3), 4.34 (d, 1H, *J* = 12.8 Hz, ArCH_2Ar), 4.17 (d, 1H, *J* = 12.5 Hz, ArCH_2Ar), 3.88 (d, 2H, ArCH_2Ar), 3.84 (d, 2H, ArCH_2Ar), 3.12 (d, 1H, *J* = 12.8 Hz, ArCH_2Ar), 2.98 (d, 1H, *J* = 12.8 Hz, ArCH_2Ar); ^{13}C NMR: δ 37.5, 37.3, 31.2, 31.1 (Ar*C*H$_2$Ar); FAB MS *m*/*z*: 1049.4 $[M+Na]^+$ (calcd 1049.5). Anal. calcd for $C_{64}H_{66}O_{12}$ (1027.22): C, 74.83; H, 6.48; found: C, 74.41; H, 6.40%.

Compound (*rac*)-**6c** (1,3-*alt*). Yield: 30%; mp 85–88°C; ^{1}H NMR: δ 8.10 (d, 2H, *J* = 9.0, Hz Ar*H*), 7.89 (d, 2H, *J* = 8.1 Hz, Ar*H*), 7.56 (d, 2H, *J* = 9.0 Hz, Ar*H*), 7.34 (t, 2H, Ar*H*), 7.23 (m, 2H, Ar*H*), 7.15 (d, 2H, *J* = 8.5 Hz, Ar*H*), 7.12 (d, 2H, *J* = 7.3 Hz, Ar*H*), 6.94 (m, 6H, Ar*H*), 6.66 (t, 2H, Ar*H*), 6.55 (t, 2H, Ar*H*), 5.66 (m, 2H, =C*H*), 5.00 (dd, 2H, *J* = 10.3 Hz, *J* = 1.3 Hz, =CH_2), 4.86 (dd, 2H, *J* = 17.3 Hz, *J* = 1.3 Hz, =CH_2), 3.10–4.10 (m, 28H, OCH_2, ArCH_2Ar). Anal. calcd for $C_{62}H_{52}O_8$ (925.09): C, 80.50; H, 5.67; found: C, 80.26; H, 5.61%.

4.3.3. Method (c). Similarly carried out to method (b) but $BrCH_2COOEt$ (10 mmol) and K_2CO_3 (10 mmol) were used in a 24 h reaction (eluents: hexane–EtOAc = 1:1 for **2f** and hexane–EtOAc = 8:2 for **6b**).

Compound **2f** (*cone*). Yield: 40%; $[\alpha]_D = +21.2$ (*c* 1, THF). ^{1}H NMR: δ 7.49 (d, 2H, Ar*H*), 7.37 (t+t, 2+1H, Ar*H*), 7.14 (d, 4H, *m*-Ar*H*), 6.95 (t, 2H, *p*-Ar*H*), 6.25 (t, 2H, *p*-Ar*H*), 6.13 (d, 2H, *m*-Ar*H*), 6.11 (d, 2H, *m*-Ar*H*), 5.55 (s, 1H, OC*H*O), 4.85 (d, 1H, *J* = 3.6 Hz, OC*H*O), 4.44 (m, 4H, OCH_2), 4.35 (m, 1H, OCH_2), 4.30 (m, 1H, OCH_2), 4.27 (m, 4H, OCH_2CH$_3$), 4.26 (m, 1H, OCH_2), 4.24 (m, 2H, OCH_2), 4.07 (m, 2H, OCH_2), 4.05 (m, 1H, OCH_2), 3.93 (m, 3H, OCH_2), 3.86 (m, 2H, OCH_2), 3.85 (m, 1H, OCH_2), 3.79 (m, 1H, OCH_2), 3.74 (m, 3H, OCH_2), 3.81 (m, 1H, OC*H*), 3.80 (m, 1H, OC*H*), 3.58 (t, 1H, *J* = 9.3 Hz, OC*H*), 3.49 (m, 1H, OC*H*), 3.45 (s, 3H, OCH_3), 4.50 (d, 2H, ArCH_2Ar), 4.48 (d, 2H, ArCH_2Ar), 3.23 (d, 1H, *J* = 13.1 Hz, ArCH_2Ar), 3.22 (d, 1H, *J* = 13.5 Hz, ArCH_2Ar), 3.21 (d, 1H, *J* = 13.5 Hz, ArCH_2Ar), 3.20 (d, 1H, *J* = 13.1 Hz, ArCH_2Ar), 1.34 (t, 3H, CH$_2$CH_3), 1.33 (t, 3H, CH$_2$CH_3); ^{13}C NMR: δ 31.2, 31.1, 31.0 (Ar*C*H$_2$Ar),); FAB-MS *m*/*z*: 1057.4 $[M+K]^+$ (calcd 1057.4). Anal. calcd for $C_{58}H_{66}O_{16}$ (1019.15): C, 68.35; H, 6.53; found: C, 68.62; H, 6.44%.

Compound (*S*)-**6b**. (31%), $[\alpha]_D = -54.7$ (*c* 1, THF), (*R*)-**6b** (28%), $[\alpha]_D = +55.7$ (*c* 1, THF); mp 132–134°C. ^{1}H NMR: δ 8.01 (d, 2H, *J* = 9.0 Hz, binaphthyl), 7.91 (d, 2H, *J* = 7.5 Hz, binaphthyl), 7.61 (d, 2H, *J* = 9.0 Hz, binaphthyl), 7.36 (t, 2H, *J* = 7.5 Hz, binaphthyl), 7.24 (t, 2H, *J* = 7.5 Hz, binaphthyl), 7.16 (d, 2H, *J* = 7.5 Hz, binaphthyl), 7.13 (d, 2H, *J* = 2.4 Hz, Ar*H*), 7.12 (d, 2H, *J* = 2.4 Hz, Ar*H*), 6.58 (d, 2H, *J* = 2.6 Hz, Ar*H*), 6.57 (d, 2H, *J* = 2.6 Hz, Ar*H*), 4.54 and 4.48 (m, 2+2H, OCH_2), 4.46 and 4.15 (m, 2+2H, OCH_2), 4.31 and 4.21 (m, 2+2H, OCH_2), 4.14 and 4.07 (m, 2+2H, OCH_2), 3.77 and 3.73 (m, 2+2H, OCH_2), 4.45 and 3.23 (d, 2+2H, *J* = 12.8 Hz, ArCH_2Ar), 4.45 and 3.19 (d, 2+2H, *J* = 12.7 Hz, ArCH_2Ar), 4.16 (q, 4H, OCH_2CH$_3$), 1.20 (t, 6H, OCH$_2$CH_3), 1.36 (s, 18H, C(CH_3)$_3$), 0.92 (s, 18H, C(CH_3)$_3$); ^{13}C NMR: δ 169.5 (*C*O), 154.3, 1342, 129.3, 129.1, 127.8, 126.2, 125.5, 123.5, 120.4, 115.6 (binaphthyl), 154.3, 152.0, 145.1, 144.8, 135.1, 132.0, 131.8, 125.5, 125.4, 124.8, 124.7 (Ar), 72.4, 72.1, 69.9, 69.4, 68.3 (O*C*H$_2$), 60.7 (O*C*H$_2$CH$_3$), 34.0, 33.6 (*C*(CH$_3$)$_3$), 31.6, 31.1 (C(*C*H$_3$)$_3$), 31.1, 31.0 (Ar*C*H$_2$Ar), 14.1 (OCH$_2$*C*H$_3$). Anal. calcd for $C_{80}H_{94}O_{12}$ (1247.62): C, 77.02; H, 5.67; found: C, 76.44; H, 5.62%.

4.4. Synthesis of 2,4-dinitrophenylazo derivatives 1e and 2g

To the mixture of $Tl(NO_3)_3 \cdot 3H_2O$ (2.0 g, 4.5 mmol) in dry MeOH (18 ml) and EtOH (54 ml) was added compound (*S*)-**1a** or **2a** (0.75 mmol) in $CHCl_3$ (15 ml) then stirred for 1 h at ambient temperature. After that the solution was diluted with water (70 ml), acidified with 10% aqueous HCl and extracted with 3×50 ml $CHCl_3$. The organic phase was washed with water, dried (Na_2SO_4) and evaporated to give **9a** (0.64 g, 0.73 mmol, *cone*) and **9b** (0.66g, 0.70 mmol, mixture of conformers) crude diquinones (the analytical samples were purified by chromatography with toluene/MeOH = 9:1). These compounds without purification were allowed to react overnight at ambient temperature with 2,4-dinitrophenyl hydrazine (0.3 g, 1.5 mmol for **9a** and 0.44 g, 2.2 mmol for **9b**) in a mixture of CH_2Cl_2 (15 ml), EtOH (5 ml) and *p*-TsOH (0.02 g) resulting in the formation of compounds **1e** (0.3 g 48%) and **2g** (0.48 g, 56%) as red crystals after column chromatography on silica (toluene/MeOH = 8:2).

Compound (*S*)-**9a** (*cone*). Mp 139–141°C. ^{1}H NMR: δ 7.88 (d, 2H, *J* = 9.0 Hz, binaphthyl), 7.44 (d, 2H, *J* = 9.0 Hz, binaphthyl), 7.83 (d, 2H, *J* = 8.2 Hz, binaphthyl), 7.31 (t, 2H, *J* = 7.7 Hz, binaphthyl), 7.20 (t, 2H, *J* = 8.2

Hz, binaphthyl), 7.16 (d, 2H, $J=8.3$ Hz, binaphthyl), 6.81 (d, 2H, Ar*H*), 6.79 (d, 2H, $J=2.4$ Hz, Ar*H*), 6.65 (t, 2H, $J=7.5$ Hz, Ar*H*), 6.76 (s, 2H, quinone), 6.60 (s, 2H, quinone), 4.15 (m, 2H, OCH_2), 3.80 (m, 4H, OCH_2), 3.71 (m, 2H, OCH_2), 3.64 (m, 4H, OCH_2), 3.52 (m, 4H, OCH_2), 4.15 and 3.23 (d, 2+2H, $J=13.0$ Hz, ArCH_2Ar), 3.98 and 3.23 (d, 2+2H, $J=13.0$ Hz, ArCH_2Ar); ^{13}C NMR: $\delta=188.6$, 185.9 (CO), 155.6, 154.8, 148.2, 134.3, 132.8, 132.5, 130.6, 130.4, 129.8, 129.6, 129.3, 127.9, 126.3, 125.8, 123.8, 123.6, 121.1, 116.8 (Ar), 74.0, 71.3, 70.7, 70.0 (O*C*H$_2$), 32.0, 31.8 (Ar*C*H$_2$Ar). Anal. calcd for $C_{68}H_{54}N_8O_{16}$ (1239.22): C, 65.91; H, 4.39, N 9.04; found: C, 65.08; H, 4.45, N 8.90%δ.

Compound **9b**. Mp 104–106°C. ^{1}H NMR: δ 7.50 (d, 2H, Ph), 7.36 (t+t, 3H, Ph), 6.81 (m, 4H, Ar*H*), 6.68 (t, 2H, Ar*H*), 6.64 (s, 4H, quinone), 5.50 (s, 1H, OC*H*O), 4.82 (s, 1H, OC*H*O), 4.27 (m, 1H, OCH_2), 4.09–3.52 (m, 16H, OCH_2), 3.78 (m, 1H, OC*H*), 3.77 (m, 1H, OC*H*), 3.52 (m, 1H, OC*H*), 3.43 (t, 1H, OC*H*), 3.42 (s, 3H, OCH_3), 4.02 and 3.23 (d+d, 2+2H, $J=13.0$ Hz, ArCH_2Ar), 3.90 (d+d, 2+2H, $J=13.0$ Hz, ArCH_2Ar); ^{13}C NMR: δ 155.5, 155.3, 130.3, 129.9, 129.6, 123.5 (Ar), 137.5, 129.2, 128.3, 126.2 (Ph) 188.4, 185.7, 185.4, 148.2, 148.0, 132.7, (quinone), 101.4, 99.4 (O*C*HO), 81.9, 79.7, 79.5, 62.3 (O*C*H), 74.3, 73.8, 72.6, 71.9, 70.9, 70.7, 70.5, 70.2, 69.2 (O*C*H$_2$), 55.3 (O*C*H$_3$), 32.2, 31.8 (Ar*C*H$_2$Ar). Anal. calcd for $C_{66}H_{82}O_{14}$ (1099.36): C, 72.11; H, 7.52; found: C, 72.44; H, 7.46%.

Compound (*S*)-**1e**. Mp 173–175°C; ^{1}H NMR: δ 9.20 (s, 2H, OH), 8.76 (d, 2H, $J=2.0$ Hz, Ph), 8.47 (dd, 2H, $J=2.0$; 8.8 Hz, Ph), 7.82 (d, 2H, $J=8.8$ Hz, Ph), 7.97 (d, 2H, $J=9.3$ Hz, binaphthyl), 7.44 (d, 2H, $J=9.3$ Hz, binaphthyl), 7.87 (d, 2H, $J=7.8$ Hz, binaphthyl), 7.33 (t, 2H, $J=7.7$ Hz, binaphthyl), 7.25 (t, 2H, $J=7.6$ Hz, binaphthyl), 7.22 (d, 2H, binaphthyl), 7.86 (d, 2H, Ar*H*), 7.76 (d, 2H, $J=2.4$ Hz, Ar*H*), 7.01 (d, 2H, $J=7.7$ Hz, Ar*H*), 6.95 (d, 2H, $J=7.7$ Hz, Ar*H*), 6.79 (t, 2H, $J=7.7$ Hz, Ar*H*), 4.42 and 4.22 (m, 2+2H, OCH_2), 3.83 (m, 4H, OCH_2), 3.81 and 3.68 (m, 2+2H, OCH_2), 3.68 and 3.10 (m+d, 2+2H, OCH_2), 4.42 and 3.51 (d, 2+2H, $J=13.8$ Hz, ArCH_2Ar), 4.42 and 3.50 (d, 2+2H, $J=12.6$ Hz, ArCH_2Ar); ^{13}C NMR: δ 160.1, 159.2, 154.3, 151.7, 149.5, 146.9, 146.6, 134.5, 133.1, 132.0, 130.3, 130.0, 129.7, 129.6, 129.3, 128.4, 128.0, 127.8, 126.8, 126.0, 125.7, 125.3, 124.1, 120.9, 120.3, 120.2, 115.2 (Ar), 76.6, 70.5, 70.4, 70.3 (O*C*H$_2$), 31.1 (Ar*C*H$_2$Ar). Anal. calcd for $C_{56}H_{46}O_{10}$ (878.97): C, 76.52; H, 5.27; found: C, 76.08; H, 5.19%.

Compound **2g**. Mp 145–147°C; ^{1}H NMR: δ 8.95 (s, 1H, O*H*), 8.83 (s, 1H, O*H*), 8.77 (s, 2H, dinitro-Ph), 8.49 (d, 2H, dinitro-Ph), 7.82 (d, 2H, dinitro-Ph), 7.78 (s, 2H, Ar*H*), 7.47 (s, 2H, Ar*H*), 7.00 (d, 4H, Ar*H*), 6.82 (t, 2H, Ar*H*), 4.79 (d, 1H, $J=3.0$ Hz, OC*H*O), 4.30 (m, 1H, OCH_2), 4.23 (m, 2H, OCH_2), 4.15 (m, 1H, OCH_2), 4.14 (m, 2H, OCH_2), 4.05 (m, 2H, OCH_2), 4.03 (m, 2H, OCH_2), 3.92 (m, 2H, OCH_2), 3.87 (m, 2H, OCH_2), 3.84 (m, 2H, OCH_2), 3.56 (m, 2H, OCH_2), 4.23 (m, 1H, OC*H*), 3.77 (m, 1H, OC*H*), 3.61 (m, 1H, OC*H*), 3.40 (t, 1H, OC*H*), 3.35 (s, 3H, OCH_3), 4.57 (d, 1H, $J=13.0$ Hz, ArCH_2Ar), 4.48 (d, 1H, $J=13.0$ Hz, ArCH_2Ar), 4.41 (d, 1H, $J=12.5$ Hz, ArCH_2Ar), 4.34 (d, 1H, $J=13.0$ Hz, ArCH_2Ar), 3.56 (d, 2H, ArCH_2Ar), 3.55 (d, 2H, ArCH_2Ar); ^{13}C NMR: δ 159.9, 159.7, 151.8, 146.2, 132.6, 132.4, 132.2, 132.1, (Ar), 149.4, 146.8, 146.4, 127.8, 120.3, 120.2 (dinitro-Ph), 98.3 (O*C*HO), 81.8, 81.1, 62.9 (O*C*H), 77.2, 76.4, 72.5, 72.4, 71.8, 71.2, 70.8, 70.7, 69.8, 69.7 (O*C*H$_2$), 55.2 (O*C*H$_3$), 31.2 (Ar*C*H$_2$Ar). Anal. calcd for $C_{55}H_{54}N_8O_{20}$ (1147.07): C, 57.59; H, 4.74, N 9.77; found: C, 57.28; H, 4.65, N 9.62%.

4.5. Synthesis of indophenols 2h and 3e

To the MeCN (80 ml) solution of **2a** or **3a** (1 mmol), 4-amino-*m*-cresol (0.5 g, 4 mmol) and DBU (3 ml, 20 mmol) was added $K_3Fe(CN)_6$ (2.64 g, 8 mmol) dissolved in 8 ml water and stirred for 48 h at rt. Then the solvent was removed under reduced pressure, the residue was dissolved in $CHCl_3$, thoroughly washed with water, dried to afford **2h** (0.34 g, 31%) or **3e** (0.25 g 22%) as dark red crystals after column chromatography on silica (toluene/MeOH = 8:2).

Compound **2h**. Mp 152–154°C; ^{1}H NMR: δ 8.37 (s, 1H, O*H*), 8.16 (s, 1H, O*H*), 7.44 (d, 2H, Ar*H*), 7.35 (t, 1H, Ar*H*), 7.33 (t, 2H, Ar*H*), 7.12 (dd, 2H, quinone), 6.96 (t, 2H, *p*-Ar*H*), 6.77 (d, 4H, *m*-Ar*H*), 6.73 (s, 4H, *m*-Ar*H*), 6.55 (d, 1H, quinone), 6.53 (d, 1H, quinone), 6.45 (dd, 1H, quinone), 6.40 (dd, 1H, quinone), 5.20 (s, 1H, OC*H*O), 4.90 (d, 1H, $J=3.0$ Hz, OC*H*O), 4.19 (m, 1H, OCH_2), 4.16 (m, 2H, OCH_2), 4.14 (m, 2H, OCH_2), 4.13 (m, 2H, OCH_2), 4.11 (m, 1H, OCH_2), 4.05 (m, 1H, OCH_2), 4.04 (m, 2H, OCH_2), 4.00 (m, 2H, OCH_2), 3.95 (m, 1H, OCH_2), 3.79 (m, 4H, OCH_2), 3.80 (m, 1H, OC*H*), 3.76 (m, 1H, OC*H*), 3.71 (m, 1H, OC*H*), 2.93 (t, 1H, OC*H*), 3.44 (s, 3H, OCH_3), 4.73 (d, 1H, $J=13.0$ Hz, ArCH_2Ar), 4.48 (d, 1H, $J=13.0$ Hz, ArCH_2Ar), 4.37 (d, 1H, $J=12.5$ Hz, ArCH_2Ar), 4.32 (d, 1H, $J=13.0$ Hz, ArCH_2Ar), 3.42 (d, 2H, ArCH_2Ar), 3.39 (d, 2H, ArCH_2Ar), 2.26 (s, 6H, CH_3); ^{13}C NMR: δ 153.4, 152.9, 152.1, 151.9, 141.9, 141.7, 138.0, 137.8, 133.5, 133.2, 132.9, 129.3, 129.2, 128.4, 126.3, 123.0, 122.7 (Ar), 188.4, 156.7, 156.5, 150.2, 131.9, 130.3, 129.3 (quinone), 101.3, 99.7 (O*C*HO), 81.7, 80.7, 78.9, 62.2 (O*C*H), 76.3, 76.1, 72.9, 71.9, 71.2, 70.5, 69.0 (O*C*H$_2$), 55.3 (O*C*H$_3$), 31.2 (Ar*C*H$_2$Ar), 18.3 (*C*H$_3$); FAB-MS m/z: 1107.1 [M+Na]$^+$ (calcd 1107.4). Anal. calcd for $C_{64}H_{64}N_2O_{14}$ (1085.21): C, 70.83; H, 5.94, N 2.58; found: C, 70.41; H, 6.02, N 2.50%.

Compound **3e**. Mp 137–140°C; ^{1}H NMR: δ 7.64 (s, 2H, O*H*), 7.42 (d, 4H, Ar*H*), 7.33 (m, 6H, Ar*H*), 7.10 (d, 2H, quinone), 6.89 (t, 2H, *p*-Ar*H*), 6.78 (s, 4H, *m*-Ar*H*), 6.76 (d, 4H, *m*-Ar*H*), 6.56 (s, 2H, quinone), 6.33 (d, 2H, quinone), 5.30 (s, 1H, OC*H*O), 4.61 and 3.39 (d+d, 1+1H, ArCH_2Ar),), 4.51 and 3.45 (d+d, 1+1H, ArCH_2Ar), 4.33 (m, 2H, OC*H*), 3.90 (m, 2H, OC*H*), 4.33 (m, 2H, OCH_2), 4.19 (m, 2H, OCH_2), 4.16 (m, 4H, OCH_2), 3.95 (m, 2H, OCH_2), 3.83 (m, 2H, OCH_2), 3.74 (m, 2H, OCH_2), 3.72 (m, 2H, OCH_2), 3.59 (m, 2H, OCH_2), 3.53 (t, 2H, OCH_2), 2.32 (s, 6H, CH_3); ^{13}C NMR: δ 153.0, 152.0, 141.9, 138.0, 133.2, 132.5, 129.4,

129.3, 128.3, 126.3, 125.4, 122.8 (Ar), 188.4, 156.8, 150.1, 132.0, 130.4, 129.2 (quinone), 101.0 (O*C*HO), 69.2, 67.2 (O*C*H), 77.5, 76.0, 70.8, 70.2, 69.6 (O*C*H_2), 31.3, 30.9 (Ar*C*H_2Ar), 18.4 (*C*H_3); FAB-MS m/z: 1183.2 $[M+Na]^+$ (calcd 1183.5). Anal. calcd for $C_{70}H_{68}N_2O_{14}$ (1161.31): C, 72.40; H, 5.90, N 2.41; found: C, 71.86; H, 5.83, N 2.32%.

Acknowledgements

Financial supports by the Ministry of Education (FKFP Project no. 0348/1997) and the Hungarian Scientific Research Found (OTKA No. T 34347, T 25561 and T 32180) are gratefully acknowledged. The authors thank Dr Gy. Parlagh for taking the FAB-MS spectra. One of the authors (B.B.) thanks the Z. Magyary fellowship.

References

1. Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495–2496 and 7017–7036.
2. Host–Guest Complex Chemistry, I. and II. *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1981; Vol. 98 and 1982; Vol. 101.
3. Lehn, J. M. *Supramolecular Chemistry*; VCH: Weinheim, 1995.
4. *Comprehensive Supramolecular Chemistry*; Lehn, J. M.; Atwood, J. L.; Davies, J. E.; McNicol, D. D., Eds.; Pergamon: New York, 1996.
5. Alberts, B.; Bray, D.; Lewis, J.; Raff, M.; Roberts, K.; Watson, J. D. *Molecular Biology of the Cell*; Garland: New York, 1983.
6. Stoddart, J. F. *Topics in Stereochemistry*; Wiley-Interscience: New-York, 1988; Vol. 17, pp. 207–288.
7. For reviews, see: Webb, T. H.; Wilcox, C. S. *Chem. Soc. Rev.* **1993**, *22*, 383–395; Chankvetadze, B.; Endresz, G.; Blaschke, G. *Chem. Soc. Rev.* **1996**, *25*, 141; Easton, C. J.; Lincoln, S. F. *Chem. Soc. Rev.* **1996**, *25*, 163.
8. Izatt, R. M.; Zhu, C. Y, Huszthy, P.; Bradshaw, J. S. In *Crown Compounds: Toward Future Applications*; Cooper, S. R., Ed. Enantiomeric Recognition in Macrocycle-Primary Ammonium Cation Systems. VCH: New York, 1992; Chapter 12.
9. Kyba, E. B.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 2692–2693.
10. Tőke, L.; Bakó, P.; Keserű, Gy. M.; Albert, M.; Fenichel, L. *Tetrahedron* **1998**, *54*, 213–222 and references cited therein.
11. For review, see: Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713–745.
12. For review, see: Ludwig, R. *Fresenius J. Anal. Chem.* **2000**, 103–128.
13. Kubo, Y. *Synlett* **1999**, 161–174.
14. Tóth, K.; Lan, B. T. T.; Jeney, J.; Horváth, M.; Bitter, I.; Grün, A.; Ágai, B.; Tőke, L. *Talanta* **1994**, *41*, 1041–1049.
15. Bitter, I.; Grün, A.; Tóth, G.; Szöllôsy, Á.; Horváth, Gy.; Ágai, B.; Tőke, L. *Tetrahedron* **1996**, *52*, 639–641.
16. Bitter, I.; Grün, A.; Tőke, L.; Tóth, G.; Balázs, B.; Mohammed-Ziegler, I.; Grofcsik, A.; Kubinyi, M. *Tetrahedron* **1997**, *53*, 16867–16876.
17. Balázs, B.; Tóth, G.; Horváth, Gy.; Grün, A.; Csokai, V.; Tőke, L.; Bitter, I. *Eur. J. Org. Chem.* **2001**, 61–70.
18. Grün, A.; Csokai, V.; Parlagh, Gy.; Bitter, I. *Tetrahedron Lett.* **2002**, *43*, 4153–4156.
19. Csokai, V.; Grün, A.; Parlagh, Gy.; Bitter, I. *Tetrahedron Lett.* **2002**, *43*, 4627–4629.
20. Reichwein, A. M.; Verboom, W.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 358–366.
21. Bitter, I.; Grün, A.; Tóth, G.; Balázs, B.; Tőke, L. *Tetrahedron* **1997**, *53*, 9799–9812.
22. Bitter, I.; Grün, A.; Balázs, B.; Tóth, G.; Horváth, Gy.; Tőke, L. *Synth. Commun.* **1999**, *29*, 3905–3917.
23. Bakó, P.; Tőke, L. *J. Incl. Phenom.* **1995**, *23*, 195–201.
24. Di Cesare, P.; Gross, B. *Synth. Commun.* **1979**, 4581.
25. Shimizu, H.; Iwamoto, K.; Fujimoto, K.; Shinkai, S. *Chem. Lett.* **1991**, 2147–2150.