Optically Active Cyclophane Receptors for Mono- and Disaccharides: The Role of Bidentate Ionic Hydrogen Bonding in Carbohydrate Recognition

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A new family of optically active cyclophane receptors for the complexation of mono- and disaccharides in competitive protic solvent mixtures is described. Macrocycles (−)-(*R*,*R*,*R*,*R*)-**1**–**4** feature preorganized binding cavities formed by four 1,1′-binaphthalene-2,2′-diyl phosphate moieties bridged in the 3,3′-positions by acetylenic or phenylacetylenic spacers. The four phosphodiester groups converge towards the binding cavity and provide efficient bidentate ionic H-bond acceptor sites (*Fig. 2*). Benzyloxy groups in the 7,7′-positions of the 1,1′-binaphthalene moieties ensure solubility of the nanometer-sized receptors and prevent undesirable aggregation. The construction of the macrocyclic framework of the four cyclophanes takes advantage of Pd^0-catalyzed aryl—acetylene cross-coupling by the *Sonogashira* protocol, and oxidative acetylenic homo-coupling methodology (*Schemes 2* and *8*–*10*). Several cleft-type receptors featuring one 1,1′-binaphthalene-2,2′-diyl phosphate moiety were also prepared (*Schemes 1*, *6*, and *7*). An undesired side reaction encountered during the synthesis of the target compounds was the formation of naptho[*b*]furan rings from 3-ethynylnaphthalene-2-ol derivatives, proceeding *via* 5-*endo-dig* cyclization (*Schemes 3*–*5*). Computer-assisted molecular modeling indicated that the macrocycles prefer nonplanar puckered, cyclobutane-type conformations (*Figs. 7* and *8*). According to these calculations, receptor (−)-(*R*,*R*,*R*,*R*)-**1** has, on average, a square binding site, which is complementary in size to one monosaccharide. The three other cyclophanes (−)-(*R*,*R*,*R*,*R*)-**2**–**4** feature, on average, wider rectangular cavities, providing a good fit to one disaccharide, while being too large for the complexation of one monosaccharide. This substrate selectivity was fully confirmed in ^{1}H-NMR binding titrations. The chiroptical properties of the cyclophanes and their nonmacrocyclic precursors were investigated by circular dichroism (CD) spectroscopy. The CD spectra of the acyclic precursors showed a large dependence from the number of 1,1′-binaphthalene moieties (*Fig. 9*), and those of the cyclophanes were remarkably influenced by the nature of the functional groups lining the macrocyclic cavity (*Fig. 11*). Profound differences were also observed between the CD spectra of linear and macrocyclic tetrakis(1,1′-binaphthalene) scaffolds, which feature very different molecular shapes (*Fig. 10*). In ^{1}H-NMR binding titrations with mono- and disaccharides (*Fig. 13*), concentration ranges were chosen to favor 1:1 host–guest binding. This stoichiometry was experimentally established by the curve-fitting analysis of the titration data and by *Job* plots. The titration data demonstrate conclusively that the strength of carbohydrate recognition is enhanced with an increasing number of bidentate ionic host–guest H-bonds (*Table 1*) in the complex formed. As a result of the formation of these highly stable H-bonds, carbohydrate complexation in competitive protic solvent mixtures becomes more favorable. Thus, cleft-type receptors (−)-(*R*)-**7** and (−)-(*R*)-**38** with one phosphodiester moiety form weak 1:1 complexes only in CD_3CN. In contrast, macrocycle (−)-(*R*,*R*,*R*,*R*)-**1** with four phosphodiester groups undergoes stable inclusion complexation with monosaccharides in CD_3CN containing 2% CD_3OD. With their larger number of H-bonding sites, disaccharide substrates bind even more strongly to the four phosphodiester groups lining the cavity of (−)-(*R*,*R*,*R*,*R*)-**2** and complexation becomes efficient in CD_3CN containing 12% CD_3OD. Finally, the introduction of two additional methyl ester residues further enhances the receptor capacity of (−)-(*R*,*R*,*R*,*R*)-**3**, and efficient disaccharide complexation occurs already in CD_3CN containing 20% CD_3OD.

1. Introduction. – Molecular recognition of carbohydrates is a critical event in a wide range of biological phenomena and the first step in numerous processes based on cell-cell interactions, including the transmission of diseases and the operation of the immune system [1]. The structural factors of protein–carbohydrate complexation have

been displayed in a large number of X-ray crystal structures [2][3]. Despite a huge body of biological data [1–4], many questions remain open concerning the contribution of individual bonding interactions to selective recognition and, in particular, the role of apolar association and hydrophobic desolvation [5]. This situation has initiated a variety of studies with artificial receptors, with the aim of complementing the biological investigations in the search for a molecular-level understanding of the principles governing carbohydrate recognition (for a review, see [6]; for other recent reports on synthetic carbohydrate receptors, see [7]).

Quiocho and co-workers have reported a large series of high-resolution X-ray crystal structures of bacterial carbohydrate-transport proteins bound to various sugar substrates [2]. An examination of these remarkable structures readily reveals that bidentate ionic H-bonds play an important role in protein–carbohydrate recognition. Such H-bonds are formed between the charged side chains of the amino acids Asp, Glu, and Arg in the receptor, and neighboring OH groups in the sugar substrate (*Fig. 1*). The formation of these strong H-bonds [8] presumably makes a large contribution to the association free energy of protein–carbohydrate complexes in aqueous solution [3][9]. On the one hand, bidentate bonding generates a favorable 'chelate effect' [10] and on the other, weaker, neutral H-bonds between sugar and solvating H_2O molecules are replaced by stronger, ionic ones in the complex.

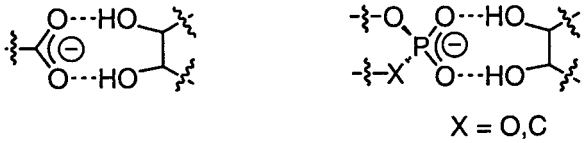
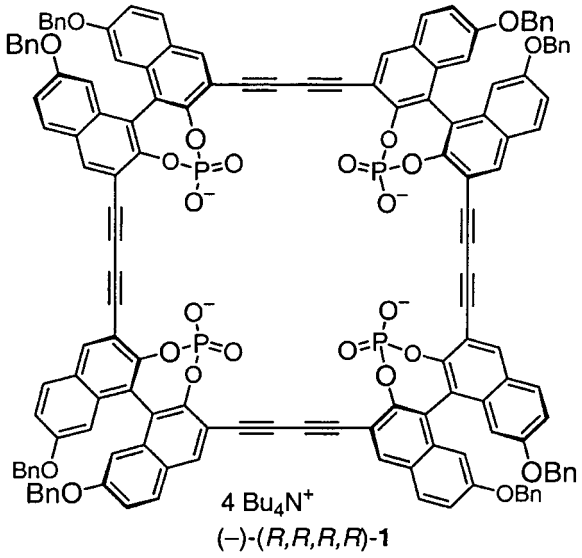
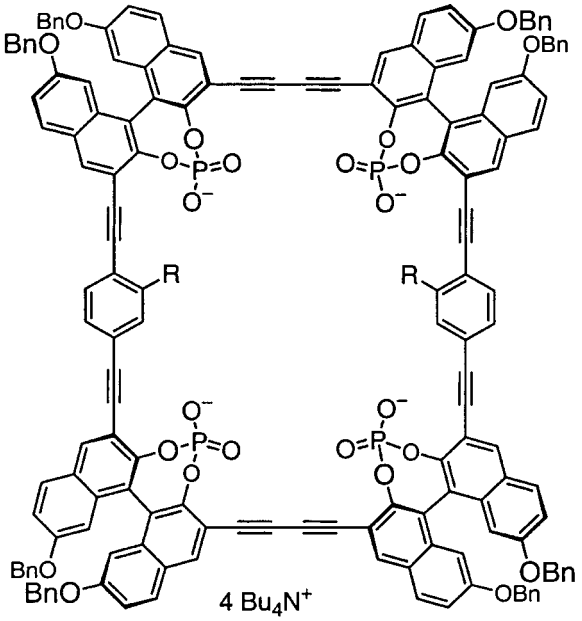


Fig. 1. *Bidentate ionic H-bonding of carbohydrates by Asp and Glu side chains in biological recognition* (left), *and by phosphodiesters and phosphonate esters in synthetic receptors* (right)

We had previously reported the synthesis and carbohydrate-recognition properties of a family of optically active cyclophane receptors, in which three 1,1′-binaphthalene-2,2′-diol moieties are interconnected by three buta-1,3-diynediyl linkers [11]. These macrocycles contain highly preorganized cavities lined with six convergent OH groups for H-bonding complexation of monosaccharides. These substrates were indeed bound with substantial diastereo- and enantioselectivity; however, the association was only efficient in apolar solvents such as $CDCl_3$, which do not compete for the H-bonding sites of the binding partners. To strengthen carbohydrate complexation in more competitive solvents, *Hamilton* and co-workers [12], and *Diederich* and co-workers [11a] independently introduced phosphonate ester and phosphodiester groups as bidentate ionic H-bond acceptor sites into synthetic receptors. Bidentate ionic H-bonding between backbone phosphodiester groups and vicinal diol moieties had previously been proposed as an important association mode in the complexation of fructose to DNA [13]. The strategy to improve sugar binding in more competitive solvents proved correct, and *Hamilton* and co-workers reported stable complexation of octyl glucosides by cleft-type bis-phosphonate receptors in CD_3CN [12]. In preliminary work [11a], we showed that receptor (–)-(*R*,*R*,*R*,*R*)-**1** (*Fig. 2*), with a cyclic array of phosphodiester sites for bidentate ionic H-bonding, complexes monopyranosides in CD_3CN containing a few percent of CD_3OD as competitive protic co-solvent.



(–)-(*R*,*R*,*R*,*R*)-**1**



(–)-(*R*,*R*,*R*,*R*)-**2** R = H
(–)-(*R*,*R*,*R*,*R*)-**3** R = CO_2Me
(–)-(*R*,*R*,*R*,*R*)-**4** R = CO_2^- K^+

Fig. 2. *Synthetic receptors for monosaccharides and disaccharides prepared and investigated in this work*

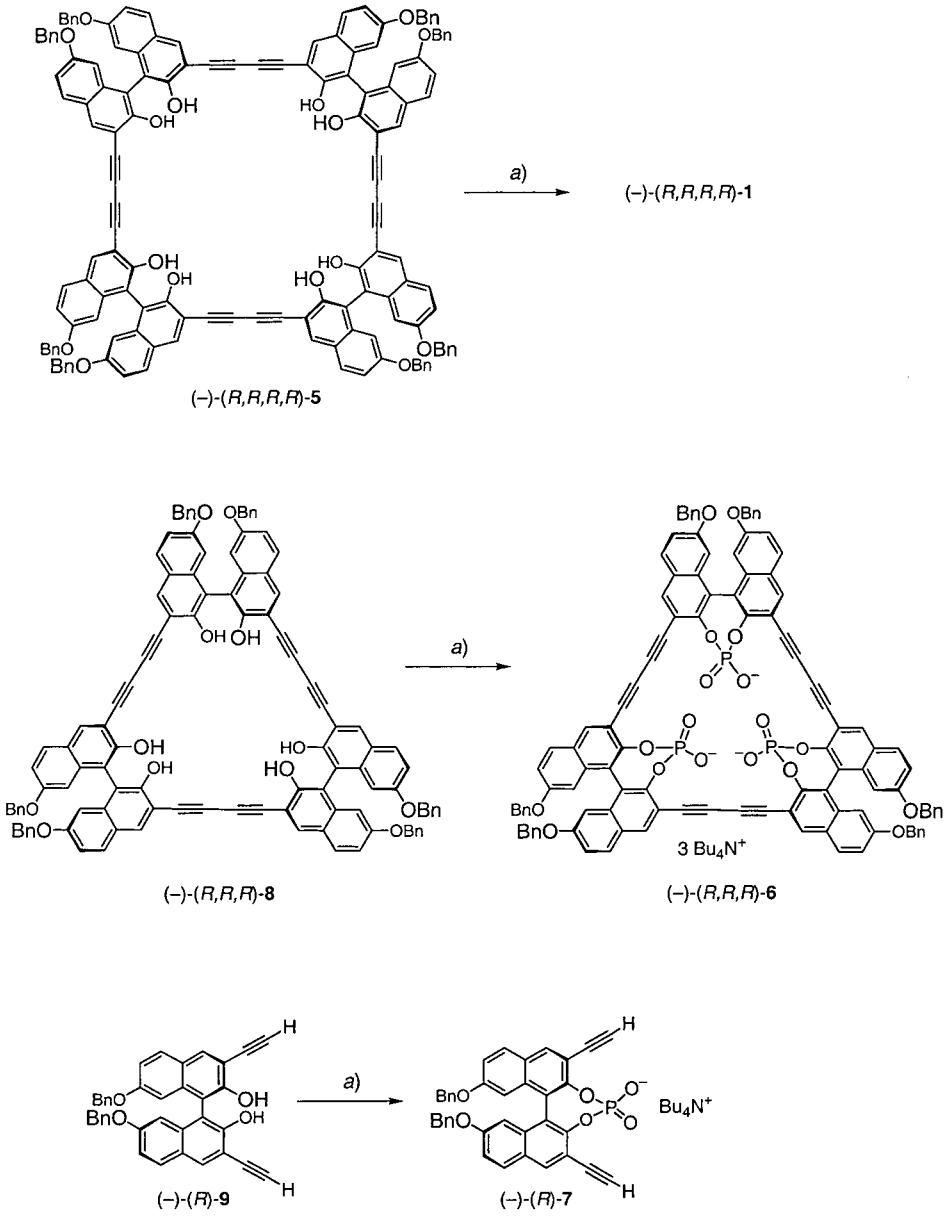
Here, we report the synthesis and carbohydrate-binding properties of a series of optically active receptors (−)-(*R*,*R*,*R*,*R*)-**1**, (−)-(*R*,*R*,*R*,*R*)-**2**, (−)-(*R*,*R*,*R*,*R*)-**3**, and (−)-(*R*,*R*,*R*,*R*)-**4** (*Fig. 2*) that feature central-cavity-binding sites with four convergent anionic phosphodiester groups for carbohydrate complexation in competitive protic solvent environments (for dendritic carbohydrate receptors with a central 1,1′-binaphthalene-2,2′-diylphosphate recognition site, see [14]). Whereas the first receptor in the series features a binding-cavity complementary in size to a monosaccharide, the three other macrocycles (for preliminary communications, see [15][16]) provide larger recognition sites for the preferential accommodation of disaccharides. The assembly of these highly functionalized receptors elegantly takes advantage of oxidative acetylenic homo- [17] and Pd^0-catalyzed aryl−alkyne cross-coupling [18]. We conclusively show that the strength of carbohydrate recognition becomes enhanced with an increasing number of bidentate ionic host−guest H-bonds, and that, with increasing number of these interactions, complexation in competitive protic solvent mixtures becomes more favorable.

2. Results and Discussion. – 2.1. *Synthesis of Receptor (−)-(*R,R,R,R*)-***1**. Octol (−)-(*R*,*R*,*R*,*R*)-**5** [11b] was converted into the tetraanionic receptor (−)-(*R*,*R*,*R*,*R*)-**1** by reaction with $POCl_3$ in dry CH_2Cl_2 in the presence of Et_3N, followed by hydrolysis of the formed chlorophosphates with THF/H_2O and counterion exchange (*Scheme 1*). The spectral data fully supported the formation of the D_4-symmetrical tetrakis(phosphodiester). The ^{31}P-NMR spectrum (121.5 MHz, CD_3CN) showed the phosphodiester resonance at 2.9 ppm. In the FAB (fast-atom bombardment) mass spectrum, the prominent peaks correspond to the Na complex of the molecular ion after loss of one to four Bu_4N^+ counterions (*e.g.*, $m/z = 3173$ ($[M + H + Na - 1\ Bu_4N]^+$, $^{13}C_2{}^{12}C_{198}H_{197}N_3O_{24}P_4Na^+$; calc. 3173.32). As controls for the binding experiments, macrocycle (−)-(*R*,*R*,*R*)-**6** lacking a binding cavity and mono-phosphodiester (−)-(*R*)-**7** were prepared in a similar way, starting from (−)-(*R*,*R*,*R*)-**8** [11b] and (−)-(*R*)-**9** [11b], respectively.

2.2. *Synthesis of Receptor (−)-*(R,R,R,R*)-***2**. Bis(silylethynylated) 1,1′-binaphthalene (+)-(*R*)-**10** [11b] was mono-deprotected to give (+)-(*R*)-**11**, which was cross-coupled [19] to 1,4-diiodobenzene under formation of (−)-(*R*,*R*)-**12** (*Scheme 2*). Alkyne-deprotection to (−)-(*R*,*R*)-**13**, followed by *Glaser-Hay* coupling [20], afforded (−)-(*R*,*R*,*R*,*R*)-**14**. Benzoyl ester hydrolysis led to (−)-(*R*,*R*,*R*,*R*)-**15**, which was transformed into the target tetrakis(phosphodiester) (−)-(*R*,*R*,*R*,*R*)-**2** under the conditions described in *Sect. 2.1* for the preparation of (−)-(*R*,*R*,*R*,*R*)-**1**. The average D_2 symmetry of (−)-(*R*,*R*,*R*,*R*)-**2** was supported by ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy. The ^{31}P-NMR spectrum (121.5 MHz, CD_3CN) displayed one single resonance at 4.6 ppm. In the FAB mass spectrum, the prominent peaks corresponded to the molecular ion or its Na complex after loss of two to four Bu_4N^+ counterions, with the base peak observed at m/z 2820.65 ($[M + 4\ H - 3\ Bu_4N]^+$).

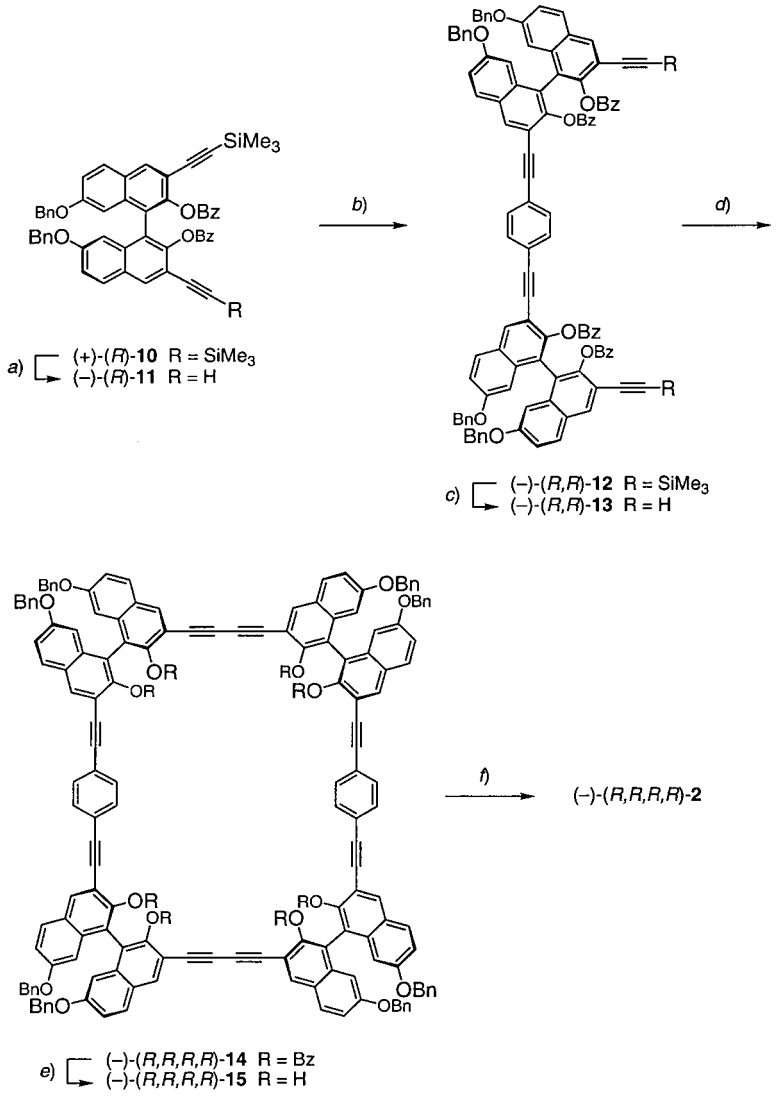
2.3. *Synthesis of Cleft-Shaped Receptors.* A strong motivation for the synthesis of cyclophane (−)-(*R*,*R*,*R*,*R*)-**4** with two carboxylate residues was the desire to potentially mimic, in a suitable pH range, the catalytic function of the corresponding residues in the active site of glycosidases [21]. We considered the synthesis of this cyclophane as a first step towards a template for catalytic disaccharide cleavage. To

Scheme 1. *Synthesis of Monosaccharide Receptor (−)-(*R,R,R,R*)-***1** *and Comparison Compounds (−)-(*R,R,R*)-***6** *and (−)-(*R*)-***7**



a) $POCl_3$, Et_3N, CH_2Cl_2, r.t., 3 h; then THF/H_2O, 40°, 12 h; then *Dowex*® (Bu_4N^+), CH_2Cl_2/MeCN 1:1; 67% ((−)-(*R*,*R*,*R*,*R*)-**1**); 65% ((−)-(*R*,*R*,*R*)-**6**); 68% ((−)-(*R*)-**7**). Bn = $PhCH_2$.

Scheme 2. *Synthesis of Disaccharide Receptor (−)-(*R,R,R,R*)-***2**



a) $Na_2B_4O_7 \cdot 10\ H_2O$, THF/$H_2O$ 1:1, r.t., 24 h; 37%. *b*) [$Pd_2(dba)_3$], PPh_3, Et_3N, 4-I-C_6H_4I, PhMe, 40°, 12 h; 50%. *c*) K_2CO_3, THF/MeOH, r.t., 2 h; 91%. *d*) CuCl, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), air, CH_2Cl_2, r.t., 10 min; 20%. *e*) KOH, MeOH, r.t., 30 min; 89%. *f*) $POCl_3$, Et_3N, CH_2Cl_2, r.t., 3 h; then THF/H_2O, 40°, 12 h; then *Dowex*® (Bu_4N^+), $CHCl_3$/MeCN 1:1; 63%. Bz = PhCO. dba = Dibenzylideneacetone.

explore methods for the introduction of the various functional groups into (−)-(*R*,*R*,*R*,*R*)-**4** and to obtain suitable nonmacrocyclic control compounds for the projected recognition and catalysis studies, the two cleft-type receptors (±)-**16** and (−)-(*R*)-**17** were prepared (*Fig. 3*).

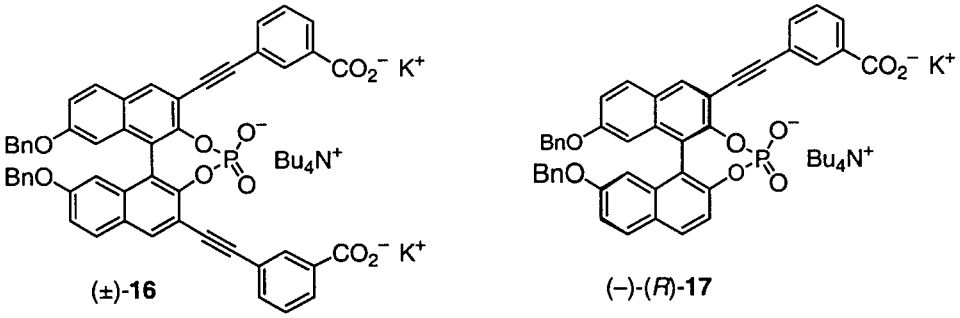
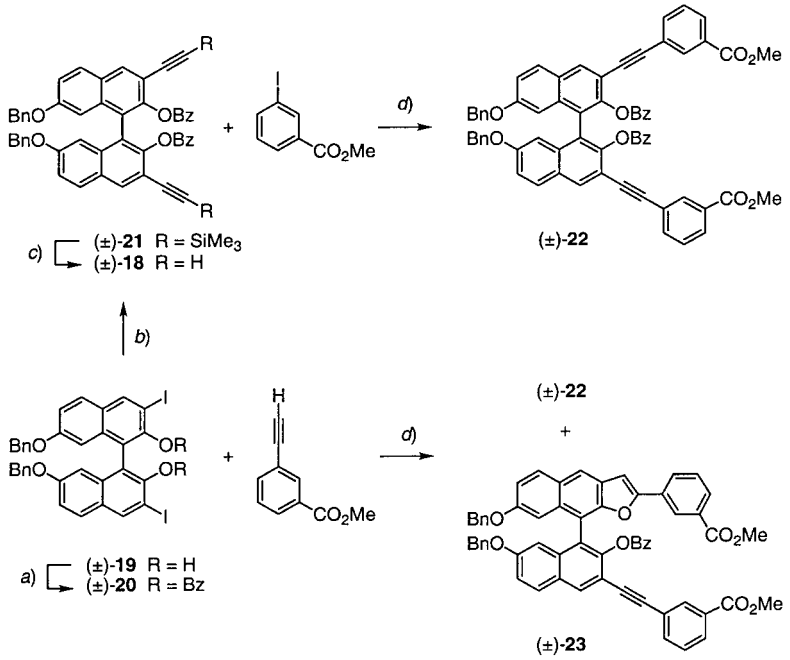


Fig. 3. *Cleft-type receptors with anionic recognition sites*

The projected synthesis of receptor (±)-**16** started from diethynylated (±)-**18**, which was prepared from the known diiodide (±)-**19** [11b] by benzoylation to give (±)-**20**, cross-coupling [19] with $Me_3Si-C\equiv CH$ under formation of (±)-**21** (98%; for a lower-yielding preparation of (±)-**21** by a *Stille* coupling, see [11b]), and alkyne deprotection (*Scheme 3*). Cross-coupling of (±)-**18** to methyl 3-iodobenzoate (2 equiv.) [22] under *Sonogashira* conditions readily afforded (±)-**22** in high yield.

Scheme 3. *Synthesis of the Protected Cleft-Type Receptor (±)-***22**



a) BzCl, DMAP (4-(dimethylamino)pyridine), pyridine, CH_2Cl_2, r.t., 2 h; 98%. *b*) $Me_3Si-C\equiv CH$, $[PdCl_2(dppf)]\cdot CH_2Cl_2$, CuI, Et_2NH, PhMe, 40°, 4 h; 98%. *c*) K_2CO_3, THF/MeOH, r.t., 2 h; 91%. *d*) $[PdCl_2(dppf)]\cdot CH_2Cl_2$, CuI, Et_2NH, PhMe, 40°, 5 h; 84% (±)-**22** (from (±)-**18**); < 20% (±)-**22** (from (±)-**19**). dppf = 1,1′-bis(diphenylphosphino)ferrocene.

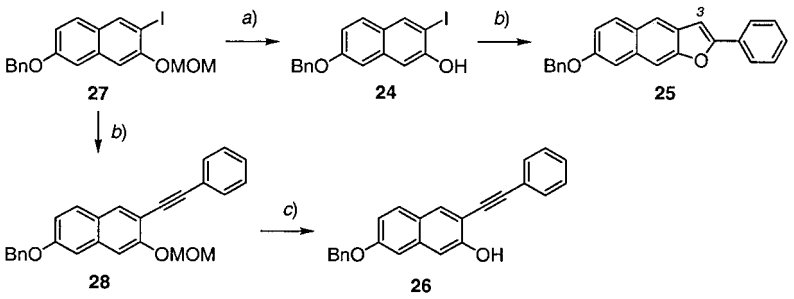
On the other hand, cross-coupling between diiodo derivative (±)-**20** and methyl 3-ethynylbenzoate (2 equiv.) [23] under the same conditions gave an inseparable mixture of the desired product (±)-**22**, naphtho[*b*]furan (±)-**23**, and the corresponding bis-furan analog. Formation of products containing naphtho[*b*]furan rings, initiated by benzoyl ester cleavage in (±)-**22**, was deduced from the presence of sharp *singlets* in the ^{1}H-NMR spectrum ($CDCl_3$) of the crude product mixture between 6.0 and 7.0 ppm, corresponding to the H–C(3) resonance of the furan ring.

The combination of palladium and cuprous catalysts is actually known to promote the 5-*endo-dig* cyclization of homopropargylic alcohols [24][25], as governed by the *Baldwin* ring-closure rules [26]. This route has been efficiently exploited for the preparation of functionalized benzo[*b*]furan-ring systems by reaction of 2-hydroxyaryl halides with a variety of alkynes in the presence of a Pd^0 catalyst and CuCl under mild conditions [25b]. Syntheses of indoles from alkynylanilines *via* a similar strategy have been reported as well [24][27].

An indication of the facile formation of naphtho[*b*]furan rings from 3-ethynyl-naphthalen-2-ol derivatives was also derived from a model study (*Scheme 4*). Submission of 3-iodonaphthalen-2-ol (**24**) [11b] to the standard *Sonogashira* cross-coupling with phenylacetylene afforded naphtho[*b*]furan **25** in 66% yield. The structure of **25** was established by X-ray crystallography (*Fig. 4*). The intermediacy of phenylethynylated naphthol **26** in the conversion of **24** to **25** was demonstrated through TLC comparison with an authentic sample obtained in two steps from **27** [11b] *via* **28**.

A similar cyclization was observed during attempts to cleave the benzoate protecting groups in compound (±)-**22** under mild conditions (3.6M NaOH in THF/MeOH at 20°) [11a][28] (*Scheme 5*). Product isolation afforded predominantly the mononaphtho[*b*]furans (±)-**29** and (±)-**30**. The constitution of both compounds was inferred from a combination of NMR spectroscopy and mass spectrometric analysis of the crude product mixture. The ^{1}H-NMR spectrum ($CDCl_3$) demonstrated the loss of C_2 symmetry in the two compounds, and the phenolic OH proton in (±)-**30** gave a broad *singlet* at 6.48 ppm. The FAB mass spectrum depicted the two molecular ion peaks at *m*/*z* 918 ((±)-**29**) and 814 ((±)-**30**). The formation of the desired 1,1′-

Scheme 4. *Synthesis of Naphtho[*b*]furan* **25**



a) Conc. aq. HCl soln., THF/MeOH, Δ, 3 h; 97% [11b]. *b*) Ph–C≡CH, $[PdCl_2(dppf)]\cdot CH_2Cl_2$, CuI, Et_2NH, PhMe, 40°, 3 h; 66% (**25**, **28**). *c*) Conc. aq. HCl soln., THF/MeOH, r.t., 72 h; 99%.

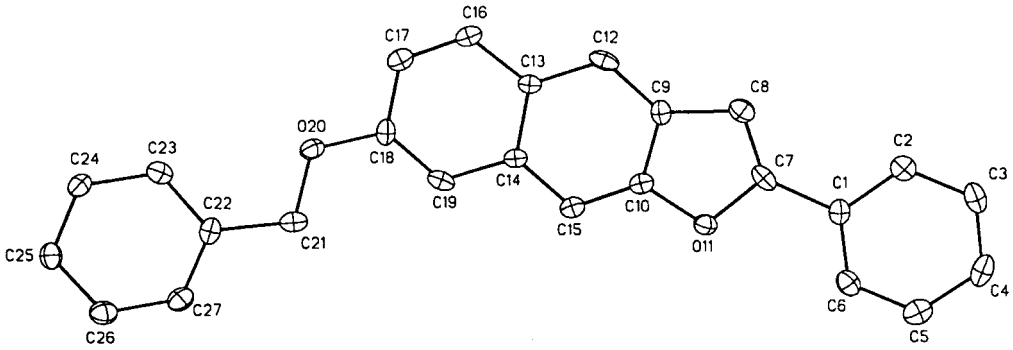
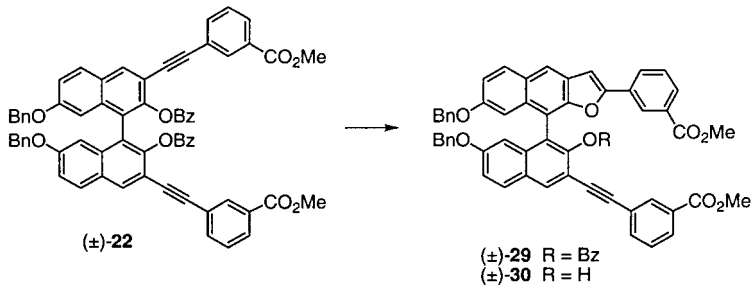


Fig. 4. *X-Ray crystal structure of naphtho[*b*]furan* **25**. Vibrational ellipsoids obtained at 153 K are shown at the 30% probability level. Torsional angle C(6)–C(1)–C(7)–O(11) = 1.2(3)°.

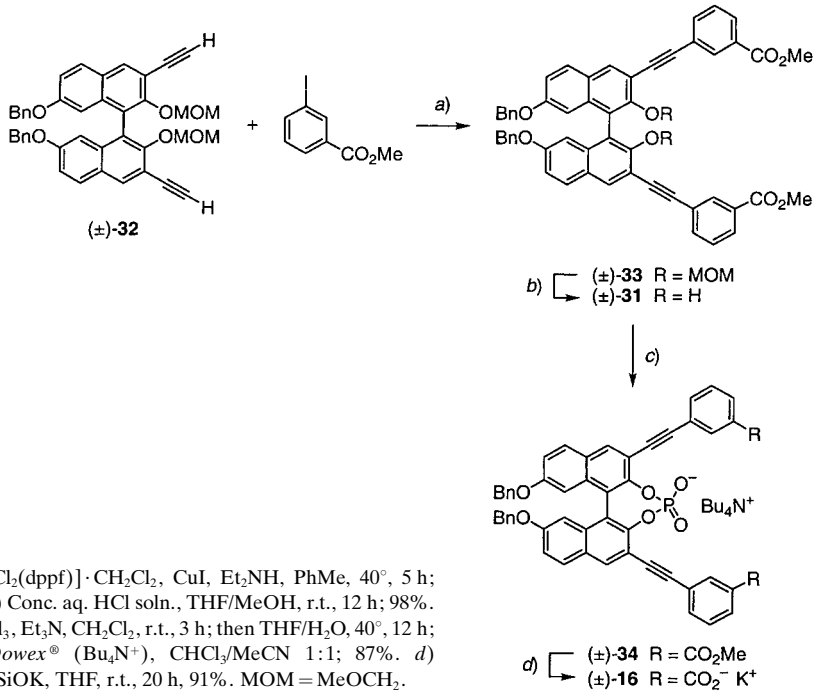
Scheme 5. *Naphtho[*b*]furan Formation During Cleavage of the Benzoyl Ester Moieties in (±)-***22***



binaphthalene-2,2′-diol (±)-**31** (*Scheme 6*) was not detected in the product mixture. These observations were reproduced under strict anhydrous conditions. Deprotection of 2-ethynylphenols under basic conditions is indeed known to be frequently followed by an intramolecular cyclization reaction [25d].

In view of the problems associated with the removal of the benzoyl groups, the MOM-protected compound (±)-**32** [11b] was selected as the starting material for the synthesis of target cleft (±)-**16** (*Scheme 6*). Cross-coupling of (±)-**32** with methyl 3-iodobenzoate (2 equiv.) [22] gave (±)-**33**, and hydrolysis under acidic conditions provided – without naphtho[*b*]furan formation – the desired 1,1′-binaphthalene-2,2′-diol derivative (±)-**31**, the structure of which was confirmed by X-ray crystallography (*Fig. 5*). Transformation into phosphodiester (±)-**34** as described in *Sect. 2.1* was followed by methyl ester cleavage, which was conveniently accomplished with Me_3SiOK under anhydrous conditions [29] to yield (±)-**16** as a very hygroscopic compound. Evidence for the trianionic nature of (±)-**16** was obtained by negative electrospray-ionization mass spectrometry (NESI-MS), which showed the base peak at *m*/*z* 281.7, corresponding to $[M - 2\,K - Bu_4N]^{3-}$. The ^{1}H-NMR spectrum recorded at room temperature depicted only broad resonances; however, sharp signals were obtained at 374 K in $CDCl_2CDCl_2$, allowing full spectral assignment in support of the proposed structure (±)-**16**.

Scheme 6. *Synthesis of the* C_2*-Symmetrical Cleft-Type Receptor* (±)-**16**



a) $[PdCl_2(dppf)]\cdot CH_2Cl_2$, CuI, Et_2NH, PhMe, 40°, 5 h; 81%. *b*) Conc. aq. HCl soln., THF/MeOH, r.t., 12 h; 98%. *c*) $POCl_3$, Et_3N, CH_2Cl_2, r.t., 3 h; then THF/H_2O, 40°, 12 h; then *Dowex*® (Bu_4N^+), $CHCl_3$/MeCN 1:1; 87%. *d*) Me_3SiOK, THF, r.t., 20 h, 91%. MOM = $MeOCH_2$.

According to the methodology that led to the successful preparation of (±)-**16**, the optically active, C_1-symmetrical cleft-type receptor (−)-(*R*)-**17** (*Fig. 3*) was subsequently targeted (*Scheme 7*). Its synthesis started from monoiodo derivative (−)-(*R*)-**35**, which had been obtained as a side-product in the previously described preparation of the corresponding 3,3′-diodo compound ((−)-(*R*)-7,7′-bis(benzyloxy)-3,3′-diiodo-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene) [11b]. Cross-coupling afforded (+)-(*R*)-**36**, and MOM-ether deprotection gave (+)-(*R*)-**37**. Transformation into phosphodiester (−)-(*R*)-**38** followed by methyl ester hydrolysis with Me_3SiOK finally provided the dianionic cleft (−)-(*R*)-**17**, for which the NESI mass spectrum depicted the base peak at *m*/*z* 351.2, corresponding to $[M - K - Bu_4N]^{2-}$.

2.4. *Synthesis of Receptors (−)-(*R,R,R,R*)-***3** *and (−)-(*R,R,R,R*)-***4**. With the experience gained in the preparation of the cleft-type control compounds (±)-**16** and (−)-(*R*)-**17**, the synthesis of the highly functionalized macrocyclic receptors (−)-(*R*,*R*,*R*,*R*)-**3** and (−)-(*R*,*R*,*R*,*R*)-**4** was approached. A first key intermediate was bis(1,1′-binaphthalene) derivative (−)-(*R*,*R*)-**39** (*Scheme 8*). Its synthesis takes advantage of the elegant protocols developed by *Moore* and co-workers for the controlled synthesis of phenylacetylene sequences [30]. Slow removal of one Me_3Si-alkyne protecting group in (−)-(*R*)-**40** [11b] with borax in aqueous THF afforded (−)-(*R*)-**41** in 31% yield, together with unreacted starting material (67%), which was resubmitted to the deprotection in an iterative fashion, ultimately allowing good overall conversion. For the subsequent cross-coupling, diethyltriazenyl-benzoate **42** was prepared starting

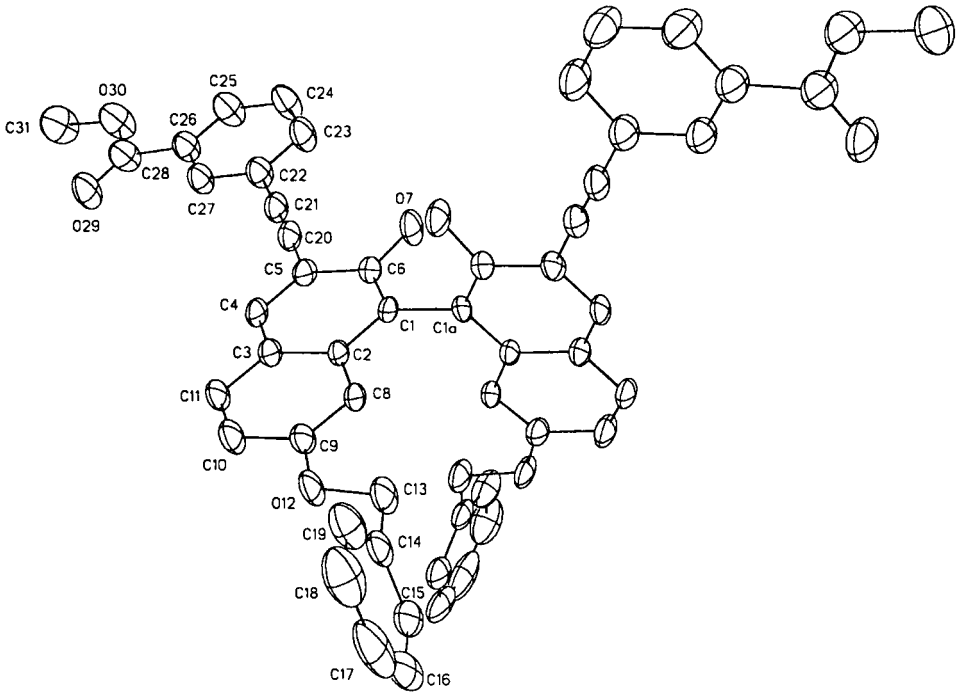


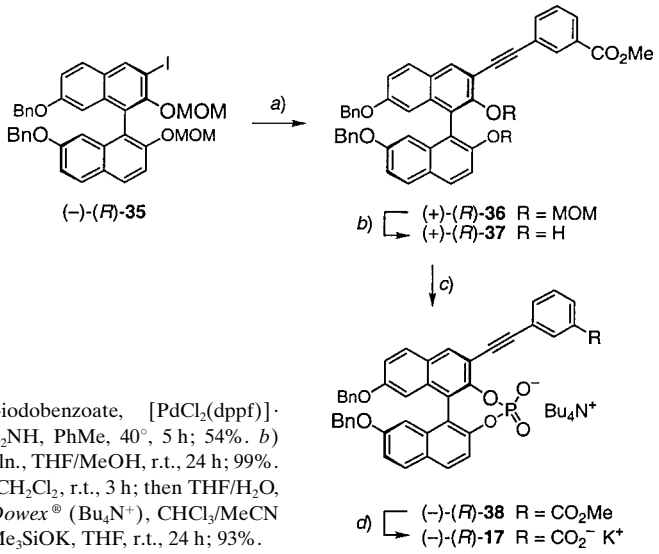
Fig. 5. *X-Ray crystal structure of 1,1′-binaphthalene-2,2′-diol (±)-***31**. Vibrational ellipsoids obtained at 238 K are shown at the 30% probability level.

from 2-amino-5-iodobenzoic acid *via* the corresponding methyl ester [31], according to published procedures [32]. Coupling of (−)-(*R*)-**41** to **42** under *Sonogashira* conditions [19] provided (−)-(*R*)-**43** in 76% yield, together with the diacetylene by-product (−)-(*R*,*R*)-**44** (16%) resulting from competing oxidative dimerization of (−)-(*R*)-**41** (under *Glaser-Hay* conditions, (−)-(*R*)-**41** can be quantitatively converted into (−)-(*R*,*R*)-**44**).

MeI-Promoted decomposition of the 3,3-diethyltriazenyl group [30] in (−)-(*R*)-**43** gave iodo derivative (−)-(*R*)-**45**, which was transformed by protodesilylation (to (−)-(*R*)-**46**) and *Glaser-Hay* homo-coupling in high overall yield (91%) to the targeted bis(1,1′-binaphthalene) (−)-(*R*)-**39**. Alternatively, diacetylene by-product (−)-(*R*,*R*)-**44** could also be converted into (−)-(*R*,*R*)-**39**, which improved the efficiency of the overall synthesis. Alkyne deprotection gave (−)-(*R*,*R*)-**47**, and double cross-coupling with diethyltriazenyl-benzoate **42** yielded (−)-(*R*,*R*)-**48**, which was transformed with MeI to (−)-(*R*,*R*)-**39**. The overall yield starting from diacetylene (−)-(*R*,*R*)-**44** was 54%.

The next key intermediate in the synthesis of the macrocyclic receptors was acyclic tetrakis(1,1′-binaphthalene) (−)-(*R*,*R*,*R*,*R*)-**49** featuring the entire C-backbone of the target macrocyclic receptors (*Scheme 9*) (for other 1,1′-binaphthalene-3,3′-diol-acetylene scaffolding, see [33]). Slow addition of an excess (3.8 equiv.) of (−)-(*R*)-**41** to a solution of bis(1,1′-binaphthalene) (−)-(*R*,*R*)-**39** and the *Sonogashira* catalyst mixture

Scheme 7. *Synthesis of the* C_1*-Symmetrical Cleft-Type Receptor (−)-(*R*)-***17***

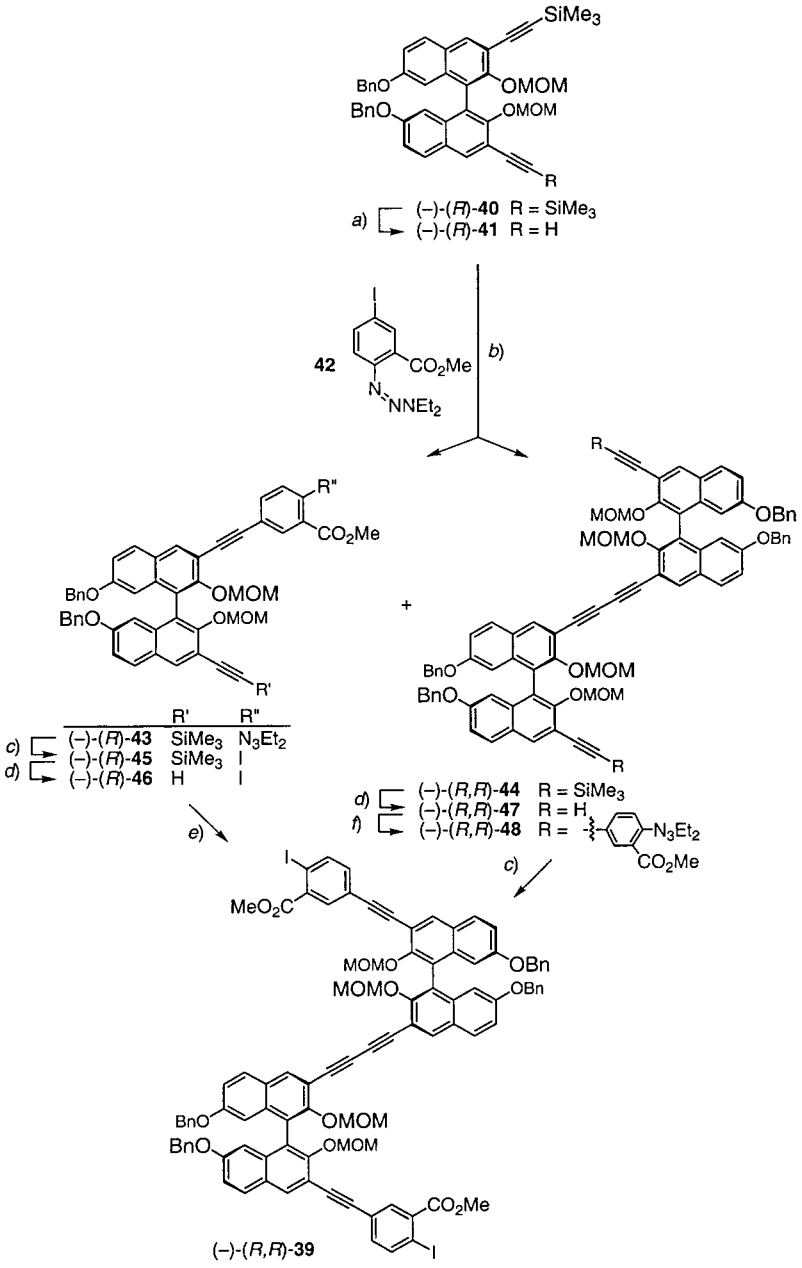


a) Methyl 3-iodobenzoate, $[PdCl_2(dppf)]\cdot CH_2Cl_2$, CuI, Et_2NH, PhMe, 40°, 5 h; 54%. *b*) Conc. aq. HCl soln., THF/MeOH, r.t., 24 h; 99%. *c*) $POCl_3$, Et_3N, CH_2Cl_2, r.t., 3 h; then THF/H_2O, 40°, 12 h; then *Dowex*® (Bu_4N^+), $CHCl_3$/MeCN 1:1; 91%. *d*) Me_3SiOK, THF, r.t., 24 h; 93%.

afforded the desired linear scaffold (−)-(*R*,*R*,*R*,*R*)-**49** as the major product (61% based on (−)-(*R*,*R*)-**39**), in addition to side-products resulting from incomplete cross-coupling ((−)-(*R*,*R*,*R*)-**50**; 11%) or competing oxidative homo-coupling ((−)-(*R*,*R*)-**44**; 22%). Complete conversion of (−)-(*R*,*R*)-**39** was observed, and the yield of oxidative homo-coupling was minimized by slow addition of alkyne (−)-(*R*)-**41**, which keeps its concentration in the reaction mixture low [34]. Because of large size differences, the three products were readily separated by gel-permeation chromatography (GPC, *Bio-Rad Bio-Beads S-X1*; CH_2Cl_2; retention times (analytical GPC) t_R 12.76 ((−)-(*R*,*R*,*R*,*R*)-**49**), 13.30 ((−)-(*R*,*R*,*R*)-**50**), and 13.98 min ((−)-(*R*,*R*)-**44**)). The C_2-symmetrical structure of (−)-(*R*,*R*,*R*,*R*)-**49** was confirmed by its ^{1}H-NMR spectrum (500 MHz, $CDCl_3$), which depicted four *singlets* of equal intensity between 2.69 and 2.50 ppm for the MeO protons of the MOM protecting groups. In contrast, C_1-symmetrical (−)-(*R*,*R*,*R*)-**50** gave six *singlets* for MOM MeO groups. The matrix-assisted laser-desorption-ionization time-of-flight (MALDI-TOF) mass spectrum depicted the Na complexes of the molecular ion as the most intense peaks at *m*/*z* 2968.8 ($[M+Na]^+$, $^{13}C_2{}^{12}C_{188}H_{158}NaO_{28}Si^+$; calc. 2968.0) and *m*/*z* 2388.9 ($[M+Na]^+$, $^{13}C^{12}C_{144}H_{117}INaO_{22}Si^+$; calc. 2388.7), corresponding to (−)-(*R*,*R*,*R*,*R*)-**49** and (−)-(*R*,*R*,*R*)-**50**, respectively.

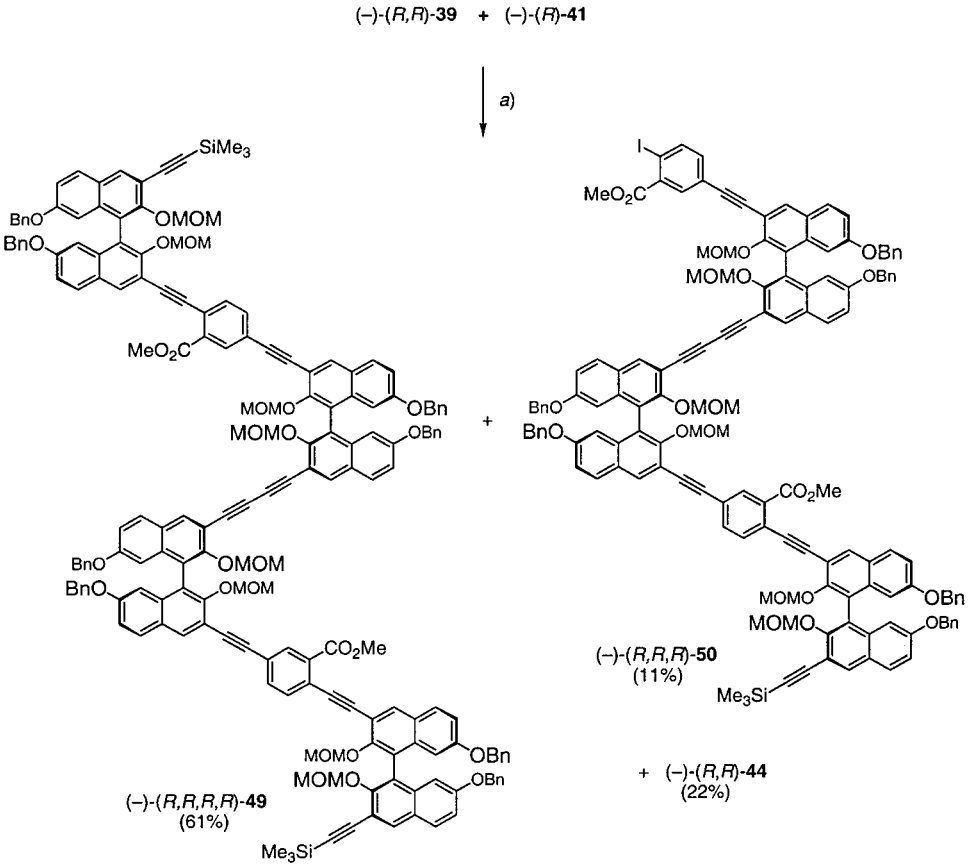
Protodesilylation of (−)-(*R*,*R*,*R*,*R*)-**49** afforded bis(ethynylated) (−)-(*R*,*R*,*R*,*R*)-**51**, and subsequent *Glaser-Hay* macrocyclization in dilute solution (CH_2Cl_2) furnished the 48-membered cyclophane (−)-(*R*,*R*,*R*,*R*)-**52** in a remarkable yield of 77% after preparative GPC (*NovoGROM GPC 1000*, 10 μm; CH_2Cl_2; retention times (analytical GPC) t_R 15.94 ((−)-(*R*,*R*,*R*,*R*)-**51**) and 16.30 min ((−)-(*R*,*R*,*R*,*R*)-**52**)) (*Scheme 10*). This large difference in retention time on GPC columns is remarkable for two compounds of nearly identical molecular weight and reflects their drastically different

Scheme 8. *Synthesis of Intermediate Bis(1,1′-binaphthalene) (−)-(*R,R*)-***39**



a) $Na_2B_4O_7 \cdot H_2O$, THF/H_2O, r.t., 4 h; 31% (98% based on reacted (−)-(*R*)-**40**). *b*) **42**, $[PdCl_2(dppf)] \cdot CH_2Cl_2$, CuI, Et_2NH, PhMe, 40°, 3.5 h; 76% ((−)-(*R*)-**43**); 16% ((−)-(*R*,*R*)-**44**). *c*) MeI, 130°, 14 h; 99%. *d*) K_2CO_3, THF/MeOH, r.t., 3 h; 93% ((−)-(*R*)-**46**); 94% ((−)-(*R*,*R*)-**47**). *e*) CuCl, O_2, TMEDA, CH_2Cl_2, r.t., 15 min; 99%. *f*) **42**, $[PdCl_2(dppf)] \cdot CH_2Cl_2$, CuI, Et_2NH, PhMe, 40°, 2 h; 58%.

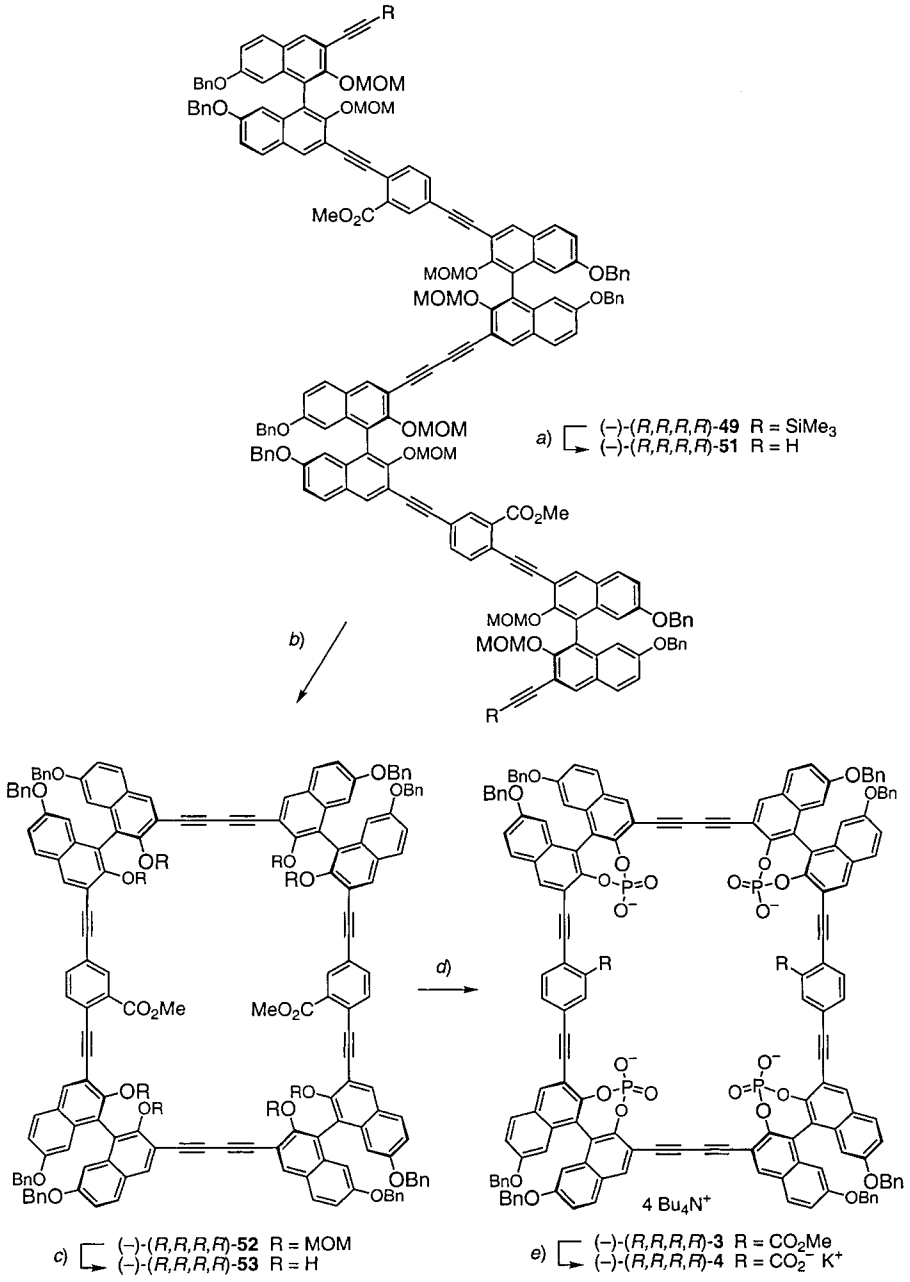
Scheme 9. *Synthesis of Tetrakis(1,1′-binaphthalene) (−)-(*R,R,R,R*)-***49**



a) $[PdCl_2(dppf))]\cdot CH_2Cl_2$, CuI, Et_2NH, PhMe, 35°, 3.5 h. Yields based on (−)-(*R*,*R*)-**39**.

molecular shapes. Extensive optimization of the reaction conditions was required to obtain the high yield. Use of freshly prepared CuCl (200 equiv.) [35] was crucial for good conversion. In addition, careful drying of the reagents, starting material, and solvent was necessary, as well as vigorous stirring, which reduces the particle size of CuCl and thus accelerates the reaction upon TMEDA addition [35]. High dilution ($c =$ 0.3 to 0.5 mM) was expectedly beneficial for the outcome of the macrocyclization. Even if not complete, the reaction is known to stop [35] after *ca*. 40 min. Addition of fresh CuCl and/or base did not allow further conversion of the starting material. Slow addition of the bis(ethynylated) precursor to a mixture of active reagents resulted in predominant formation of higher oligomers. Moreover, cyclization under homogenous *Eglinton* conditions ($Cu(OAc)_2$, pyridine) [36], generally recommended for the formation of macrocyclic buta-1,3-diynes [17][37–40], was unsuccessful, yielding higher oligomers and unreacted starting material.

Scheme 10. *Synthesis of Receptors (−)-(*R,R,R,R*)-**3** and (−)-(*R,R,R,R*)-**4***



a) K_2CO_3, THF/MeOH, r.t., 2.5 h; 99%. *b*) CuCl, dry air, TMEDA, CH_2Cl_2, 25°, 40 min; 77%. *c*) Conc aq. HCl soln., THF/MeOH, r.t., 15 h; 95%. *d*) $POCl_3$, Et_3N, CH_2Cl_2, r.t., 3 h; then THF/H_2O, 40°, 12 h; then *Dowex*® (Bu_4N^+), $CHCl_3$/MeCN 1:1, 86%. *d*) Me_3SiOK, THF, r.t., 20 h; 96%.

The MALDI-TOF mass spectrum of (−)-(*R*,*R*,*R*,*R*)-**52** depicted the Na complex of the molecular ion as the base peak at *m*/*z* 2822.3 ($[M+Na]^+$, $^{13}C_2{}^{12}C_{182}H_{140}NaO_{28}$; calc. 2821.9). In the ^{1}H-NMR spectrum (500 MHz, $CDCl_3$), the terminal alkyne resonances of the linear precursor had disappeared. In support of the C_2-symmetrical structure, the MeO protons of the MOM groups appeared as four *singlets* of equal intensity.

MOM-Ether deprotection under very dilute acidic conditions afforded macrocycle (−)-(*R*,*R*,*R*,*R*)-**53**, and subsequent treatment with $POCl_3$, followed by hydrolysis and counterion exchange, led to the targeted tetrakis(phosphodiester) (−)-(*R*,*R*,*R*,*R*)-**3**, which was obtained in 78% yield as a bright-yellow microcrystalline solid that fluoresces strongly in solution. Its NESI mass spectrum showed several dianionic species as the most intense peaks resulting from loss of the four Bu_4N groups followed by recombination of the tetraanion with various cations in the spectrometer (*e.g.*, $[M-4\ Bu_4N+2\ H]^{2-}$, $[M-4\ Bu_4N+H+Na]^{2-}$, $[M-4\ Bu_4N+NH_4+Na]^{2-}$, or $[M-4\ Bu_4N+2\ Na]^{2-}$). The ^{31}P-NMR spectrum (121.5 MHz, $CDCl_3$) displayed one resonance at 4.0 ppm, and a {^{1}H,^{1}H}-COSY spectrum allowed assignment of all proton resonances. In contrast, the increased fine structure due to long-range ^{31}P,^{13}C couplings did not allow a reliable assignment of many of the resonances in the ^{13}C-NMR spectrum (125.8 MHz, $CDCl_3$), which depicted the ester C=O resonance at 167.15 ppm.

Methyl-ester cleavage with Me_3SiOK under anhydrous conditions finally led to target molecule (−)-(*R*,*R*,*R*,*R*)-**4**, which was isolated as a hygroscopic orange-brown microcrystalline solid. Evidence for the hexaanionic structure was again obtained by NESI mass spectrometry, which showed dianionic and trianionic species such as $[M-4\ Bu_4N+H]^{3-}$, $[M-4\ Bu_4N+Na]^{3-}$, or $[M-4\ Bu_4N+2\ H]^{2-}$ as the most prominent ions. ^{1}H-NMR spectra recorded at room temperature consistently showed strongly broadened resonances, possibly due to conformational effects (see *Sect. 2.6*) and/or slow counterion (Bu_4N^+/K^+) exchange between the two different anionic (phosphate and carboxylate) sites in the cyclophane. A spectrum recorded at high temperature (500 MHz, 394 K, $(CD_3)_2SO$), however, produced sharper signals, enabling further characterization of the macrocycle. In particular, integration allowed confirmation of the salt stoichiometry, thereby supporting the presence of $4\ Bu_4N^+$ counterions. The chemical shifts of the receptor resonances are strongly dependent on solvent polarity and on residual traces of H_2O, which can be readily explained by ionic H-bonding to the phosphate and carboxylate acceptor sites [41].

Compound (−)-(*R*,*R*,*R*,*R*)-**4** is highly soluble in $CDCl_3$, dissolves satisfactorily in CD_3OD/CD_3CN mixtures in the concentration ranges needed for ^{1}H-NMR binding titrations, but is insoluble in H_2O. Efforts to isolate the macrocycle as a homogenous salt (with six identical countercations) by cation-exchange chromatography or various aqueous workups proved to be extremely tedious. Some success towards the preparation of the hexapotassium salt was obtained by double cation-exchange chromatography on a *Dowex® DR-2030* resin, with MeCN/MeOH as the eluent. In this experiment, the column was loaded in its upper half with H^+ ions and in its lower half, separated by a 1-cm layer of sand, with K^+ ions. The strategy of double counterion-exchange ($Bu_4N^+ \rightarrow H^+ \rightarrow K^+$) was chosen, since the direct exchange ($Bu_4N^+ \rightarrow K^+$) *via* ion chromatography was found to be a rather unfavorable process. Quantitative displacement of the Bu_4N^+ ions by the double-exchange protocol was confirmed by ^{1}H-NMR spectroscopy (500 MHz, $CDCl_3$), which showed the complete disappearance

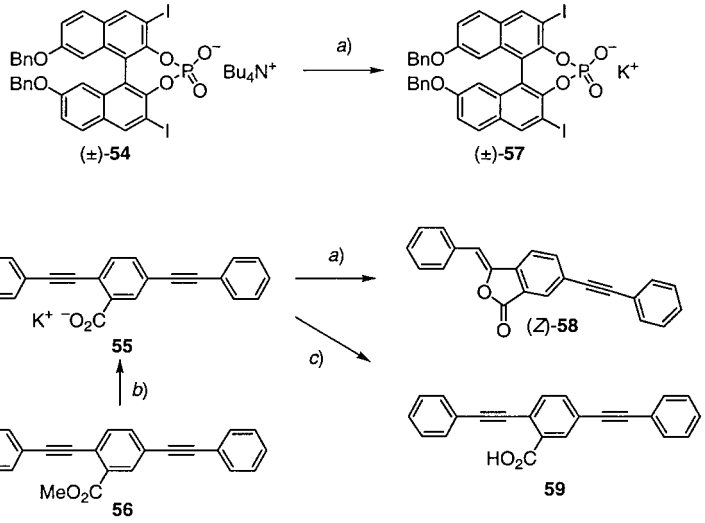
of the Bu_4N^+ resonances; however, further NMR-spectral characterization of the putative hexapotassium salt was prevented by strong spectral broadening. The solubility properties of this salt remained unchanged as compared to those of (−)-(*R*,*R*,*R*,*R*)-**4**.

To evaluate the stability of the macrocycle during cation-exchange, compounds (±)-**54** (prepared from the corresponding 3,3′-diiodo-1,1′-binaphthalene-2,2′-diol [11b]) and **55** (prepared from methyl ester **56**) were subjected to the double (H^+ then K^+) ion-exchange resin (*Scheme 11*). Phosphodiester (±)-**54** proved to be stable, and the structure of the formed potassium salt (±)-**57** was confirmed by ^{1}H- and ^{31}P-NMR spectroscopy, as well as NESI mass spectrometry. On the other hand, compound **55** underwent intramolecular 5-*exo-dig* cyclization [26] on the ion-exchange resin, yielding lactone (*Z*)-**58** as confirmed by X-ray crystallography (*Fig. 6*).

The formation of lactone (*Z*)-**58** is rather unexpected. Upon treatment with an acidic aqueous solution, **55** did not undergo cyclization but rather afforded formation of benzoic acid **59**. Intramolecular 5-*exo-dig* cyclizations of 2-alkynylbenzoic acids generally occur under metal-ion catalysis (*e.g.*, in the presence of Ag salts [42]) or under harsh acidic conditions [43]. Skeletal rigidification of (−)-(*R*,*R*,*R*,*R*)-**4** should prevent such cyclization on the ion-exchange resin, although the spectral data obtained for the putative hexapotassium salt do not entirely allow exclusion of this undesirable side reaction.

2.5. *Synthesis of α,α-Trehalose Derivative* **60**. This compound was used in ^{1}H-NMR binding studies (see *Sect. 2.8*) and was prepared in two steps starting from known hexa-*O*-benzyl-α,α-trehalose (**61**; *Scheme 12*) [44]. Etherification of the primary OH groups

Scheme 11. *Model Reactions to Probe the Stability of (−)-(*R,R,R,R*)-***4** *under Double Ion-Exchange* (H^+ then K^+) *Conditions*



a) *Dowex® DR-2030* (H^+), then *Dowex® DR-2030* (K^+), MeCN/MeOH 1:1. *b*) Me_3SiOK, THF, r.t., 18 h; 68%. *c*) 5% aq. HCl soln.

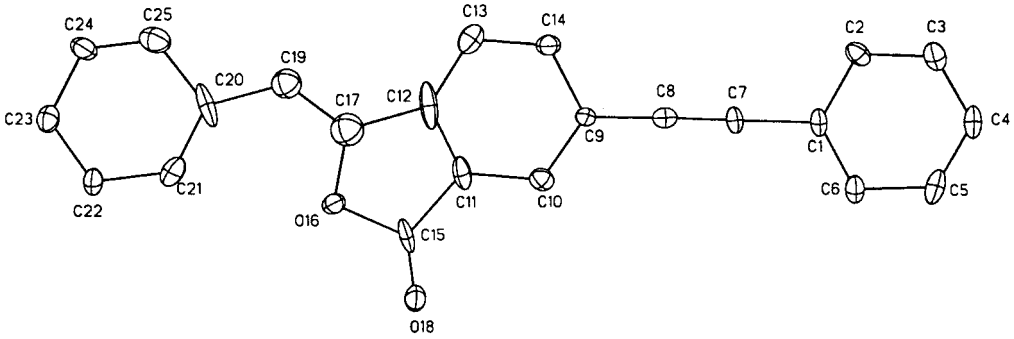
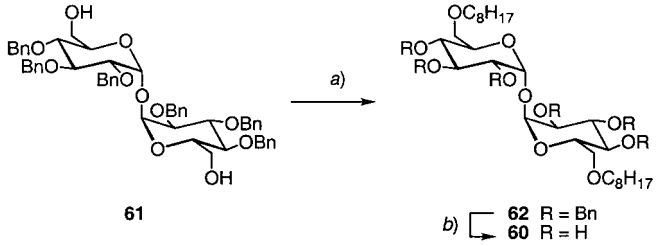


Fig. 6. *X-Ray crystal structure of phthalide (Z)-***58**. Vibrational ellipsoids obtained at 98 K are shown at the 30% probability level.

Scheme 12. *Synthesis of α,α-Trehalose Derivative* **60**



a) Iodooctane, 2,6-di(*tert*-butyl)-4-methylpyridine, $AgOSO_2CF_3$, CH_2Cl_2, 0°, 4 h; 31%. *b*) H_2, 10% Pd/C, EtOH, r.t., 20 h; 79%.

in **61** with iodooctane in the presence of 2,6-di(*tert*-butyl)-4-methylpyridine and $AgOSO_2CF_3$ [45] afforded **62** in 31% yield, together with monoalkylated product (52%). The latter was resubmitted to the reaction conditions, ultimately allowing good conversion. Removal of the Bn groups by catalytic hydrogenolysis gave the targeted bis-*O*-octyl disaccharide **60** in 79% yield as a microcrystalline solid.

2.6. *Conformational Analysis.* Molecular-dynamics (MD) simulations (300 K, 55 ps) were performed in the gas phase on the tetraprotonated forms of (−)-(*R*,*R*,*R*,*R*)-**1** and (−)-(*R*,*R*,*R*,*R*)-**2** [46]. The ^{1}H- and ^{13}C-NMR spectra had suggested a time-averaged D_4-symmetrical geometry for the former and a D_2-symmetrical geometry for the latter macrocycle. The modeling of the two systems, however, revealed a rapid equilibration between nonplanar, lower-symmetry conformers, which prefer a puckered macrocyclic frame, resembling in its overall shape the preferred conformation of cyclobutane (*Figs. 7,a*, and *8,a*). In all conformers generated throughout the MD simulation, the cavities of both receptors remained open. The dihedral angle about the chirality axis in the 1,1′-binaphthalene moieties in both receptors amounts to $65 \pm 5°$.

Figs. 7,b, and *8,b*, show macrocyclic conformations obtained by averaging over all low-energy structures (within 10 kcal · mol^{-1}) generated during the molecular-dynamics simulations. The averaged structure of (−)-(*R*,*R*,*R*,*R*)-**1** features a square cavity with

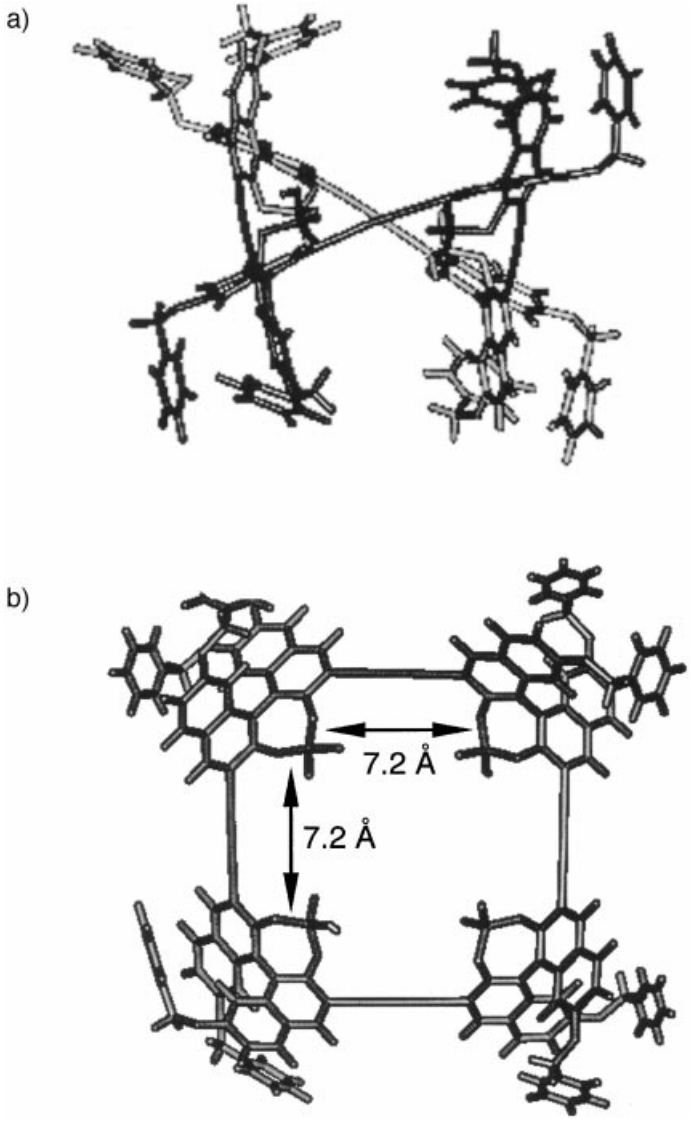


Fig. 7. *Molecular-dynamics simulation of receptor (–)-(*R,R,R,R*)-***1*** (*55 ps, 300 K, tetraprotonated receptor). *a*) One of the rapidly equilibrating, puckered low-energy conformers of the receptor. *b*) Macrocyclic conformation obtained by averaging over all low-energy structures (within 10 kcal · mol^{-1}) generated during the simulation.

the four P-atoms nearly located within a plane. The distance between neighboring P-atoms in this geometry amounts to 7.2 Å, and qualitative docking experiments indicate that the cavity is complementary in size to a monosaccharide that, upon inclusion complexation, can make contacts with all four phosphodiester groups. A good complementarity is also found between individual puckered receptors conformers and

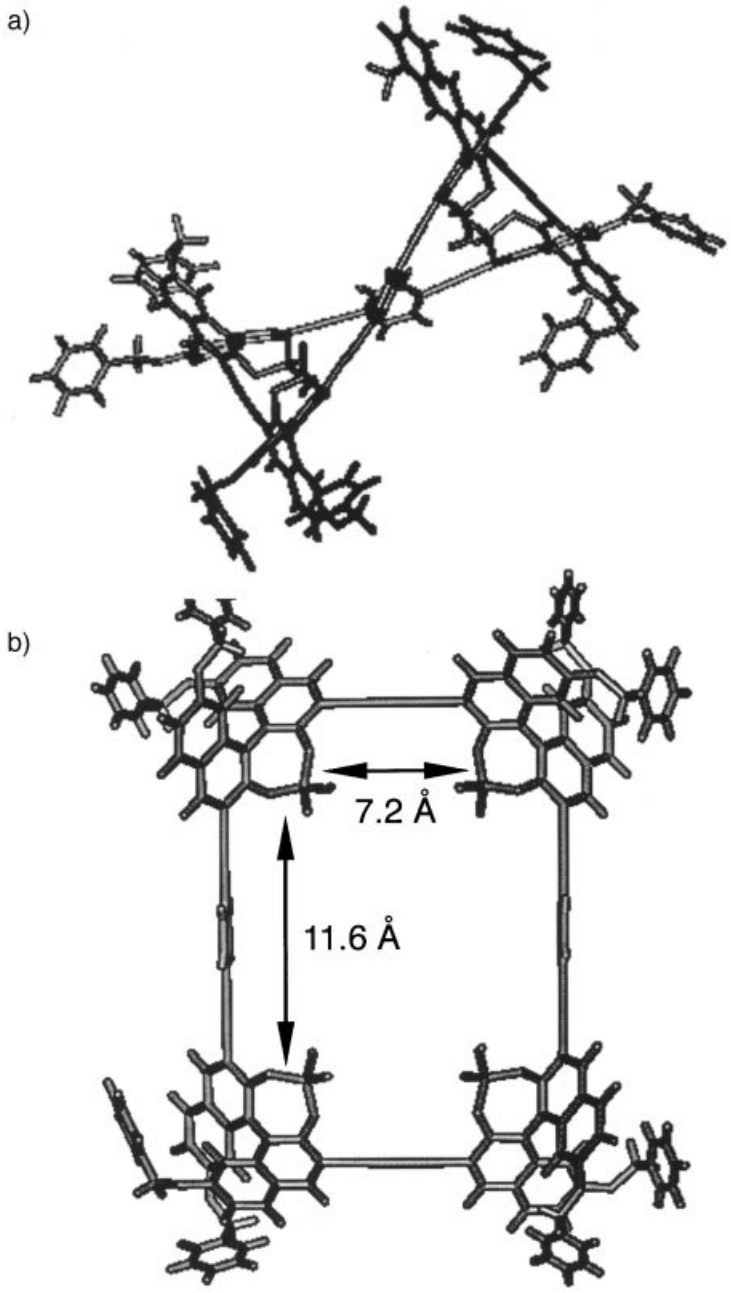


Fig. 8. *Molecular-dynamics simulation of receptor (−)-(*R,R,R,R*)-***2*** (55 ps, 300 K, tetraprotonated receptor). *a*) One of the rapidly equilibrating, puckered low-energy conformers of the receptor. *b*) Macrocyclic conformation obtained by averaging over all low-energy structures (within 10 kcal · mol^{-1}) generated during the simulation.

monosaccharide guests. The averaged structure of (−)-(*R*,*R*,*R*,*R*)-**2** contains a rectangular cavity with all four P-atoms again nearly located within a plane. The insertion of the two phenylene moieties produces a substantial enlargement of the cavity with distances between the rectangularly aligned P-atoms of 11.6 and 7.2 Å. According to qualitative docking experiments, this cavity is nicely complementary to disaccharides that, upon inclusion complexation, can make contacts to all four phosphodiester groups. The modeling also indicates that monosaccharides are too small to bind with a good fit into the rectangular cavity of (−)-(*R*,*R*,*R*,*R*)-**2**. These observations also hold for puckered conformers.

In contrast, the cavity of the planar macrocyclic (−)-(*R*,*R*,*R*)-**6** is nearly completely filled by the three phosphodiester groups (P···P distance: 5.8 Å). Therefore, sugar substrates can only bind to this receptor by docking onto one of the two receptor faces.

2.7. *Chiroptical Studies.* The chiroptical properties of some of the 1,1′-binaphthalene derivatives prepared during this study were investigated by circular dichroism (CD) spectroscopy in $CHCl_3$ at 20° [47][48]. We first investigated how the extension of linear oligomers influences the shape of the CD spectra and the magnitude of the *Cotton* effects (*Fig. 9*). Whereas the UV/VIS ($CHCl_3$) and CD spectra of 1,1′-binaphthalene (+)-(*R*)-**36** extend only to *ca.* 360 nm, the spectra of the three larger systems feature additional bands with maxima around 380 nm and reaching beyond 400 nm, in agreement with the more extended π-electron delocalization in these systems. With increasing oligomeric length, the intensity of the band near 380 nm in both UV/VIS and CD spectra increases strongly. In contrast, the two *Cotton* effects below 300 nm do not change much in strength in the progression from bis- to tetrakis(1,1′-binaphthalene), whereas the intensity of the corresponding UV absorptions increases.

CD Spectra are much more sensitive to differences in molecular shapes between chiral chromophores of similar constitution and configuration than UV/VIS spectra. This is impressively demonstrated by the comparison between the linear and macrocyclic tetrakis(1,1′-binaphthalene) derivatives (−)-(*R*,*R*,*R*,*R*)-**49** and (−)-(*R*,*R*,*R*,*R*)-**52** (*Fig. 10*). Whereas the UV/VIS spectra of the two compounds do resemble each other quite closely, the CD spectra differ strongly. In particular, the linear derivative gives a strong negative *Cotton* effect at 302 nm, whereas the *Cotton* effect of the macrocycle at this wavelength is of similar intensity but of opposite sign.

The functional groups lining the interior of the macrocyclic cavity also have quite a remarkable influence on the chiroptical properties but less on the electronic absorptions (*Fig. 11*). Thus, introduction of the phosphodiester groups in (−)-(*R*,*R*,*R*,*R*)-**3** changes the sign of the *Cotton* effect around 305 nm, compared to (−)-(*R*,*R*,*R*,*R*)-**52** and (−)-(*R*,*R*,*R*,*R*)-**53** with MOM-protected and free OH groups, respectively. Hexaanionic receptor (−)-(*R*,*R*,*R*,*R*)-**4** shows a significant loss in vibrational fine structure in the UV/VIS spectrum and a nearly complete loss of the chiroptical properties, which still remains to be explained.

2.8. *Complexation Studies.* ^{1}H-NMR titrations (500 MHz, 300 K) were performed to determine the binding of macrocyclic receptors and cleft comparison compounds to mono- and disaccharides **60** and **63**–**68** (*Fig. 12*). Titrations were usually run at constant guest concentration (*ca.* 0.25 mM) with the receptor concentration varied to obtain *ca.* 20–80% saturation binding. During the titrations, the complexation-induced change in chemical shift of the anomeric proton H–C(1) of the sugar was monitored

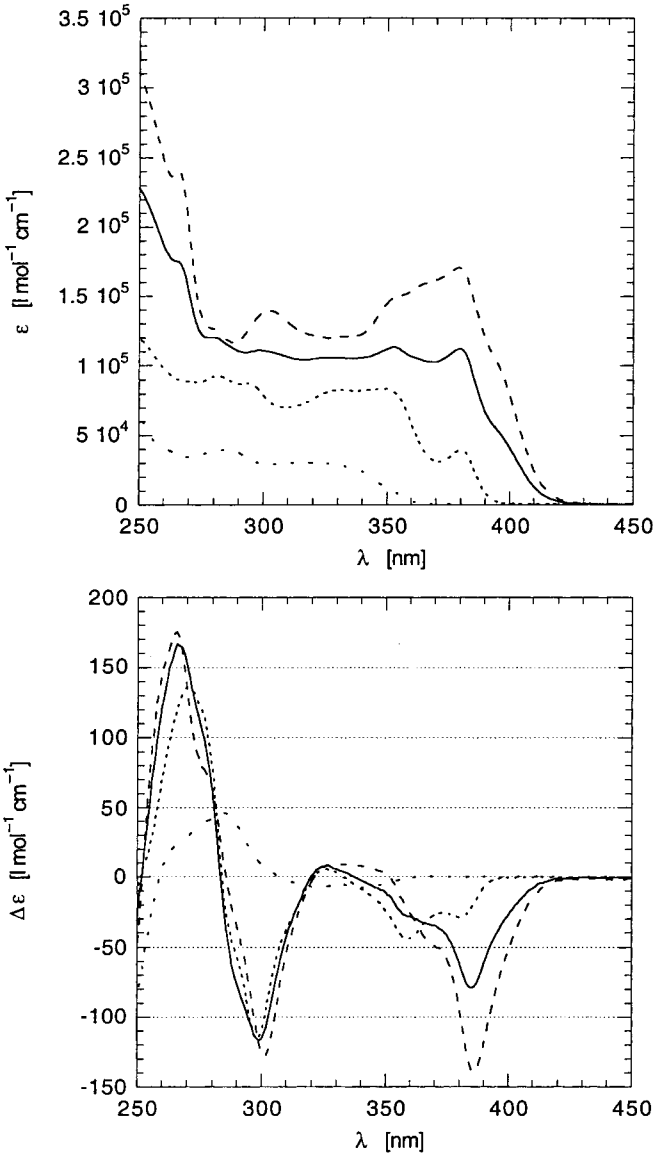


Fig. 9. *UV/VIS* (top) *and CD* (bottom) *spectra* ($CHCl_3$, 20°) *of a series of linear oligomers containing one* ((+)-(*R*)-**36**), *two* ((−)-(*R*,*R*)-**39**), *three* ((−)-(*R*,*R*,*R*)-**50**), *and four* ((−)-(*R*,*R*,*R*,*R*)-**49** *1,1′-binaphthalene moieties.* – – – –: (−)-(*R*,*R*,*R*,*R*)-**49**, ——: (−)-(*R*,*R*,*R*)-**50**, - - - - -: (−)-(*R*,*R*)-**39**, - - - - -: (+)-(*R*)-**36**.

and evaluated. The association constants K_a [$1 \cdot mol^{-1}$] and the binding free enthalpies ΔG^0 [$kcal \cdot mol^{-1}$] were obtained by nonlinear least-squares curve-fitting of the titration data [49].

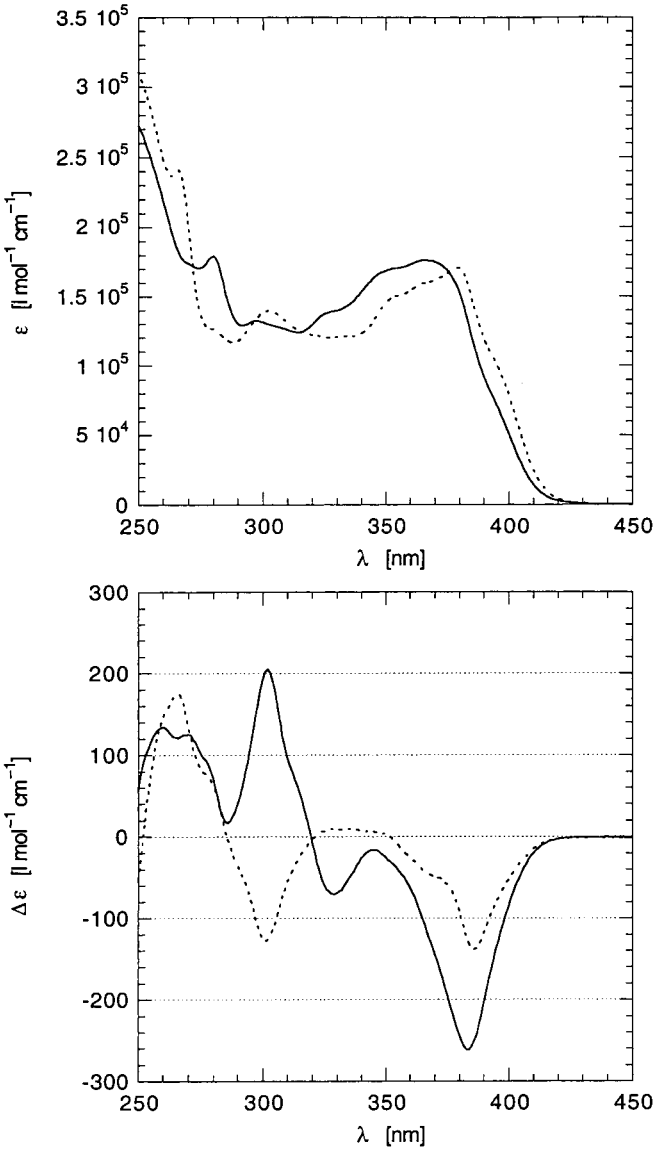


Fig. 10. *UV/VIS* (top) *and CD* (bottom) *spectra* ($CHCl_3$, 20°) *of linear* ((−)-(*R*,*R*,*R*,*R*)-**49**) *and macrocyclic* ((−)-(*R*,*R*,*R*,*R*)-**52**) *tetrakis(1,1′-binaphthalenes)*. ——: (−)-(*R*,*R*,*R*,*R*)-**52**, - - - - -: (−)-(*R*,*R*,*R*,*R*)-**49**.

The cleft-type mono-phosphodiester receptors did not show detectable binding to monosaccharides in the presence of a competitive protic co-solvent such as CD_3OD. However, weak 1:1 compexation between (−)-(*R*)-**7** and octyl β-D-glucoside (**63**) was found in pure CD_3CN (*Table*). Association strength increases upon further receptor functionalization: the complex formed by cleft (−)-(*R*)-**38** and **63** is additionally

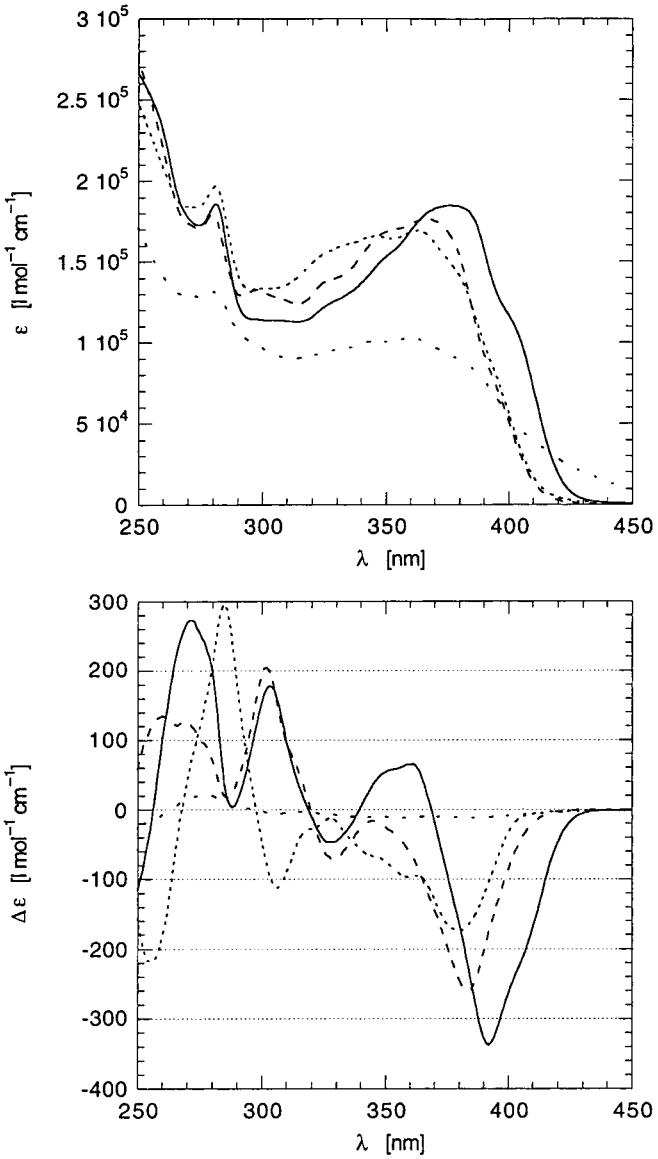


Fig. 11. *UV/VIS* (top) *and CD* (bottom) *spectra* ($CHCl_3$, 20°) *of macrocyclic tetrakis(1,1′-binaphthalenes).* – – – –: (–)-(*R*,*R*,*R*,*R*)-**52**, ——: (–)-(*R*,*R*,*R*,*R*)-**53**, - - - - -: (–)-(*R*,*R*,*R*,*R*)-**3**, - - - - -: (–)-(*R*,*R*,*R*,*R*)-**4**.

stabilized by favorable interactions between sugar and both phenyl [14] and methyl ester moieties. Unfortunately, cleft (–)-(*R*)-**17** with two anionic recognition sites proved to be insoluble in CD_3CN, which prevented the determination of its receptor properties in this environment. In the more polar mixture CD_3CN/CD_3OD 88:12, in

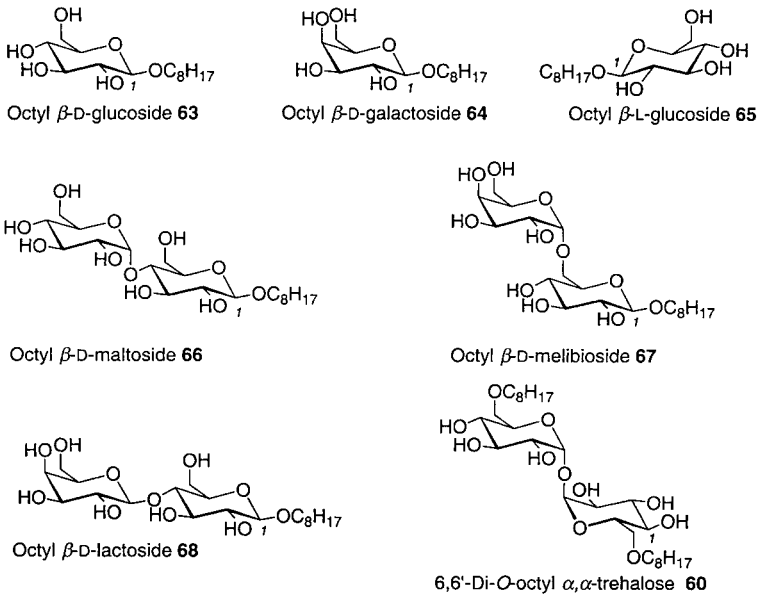


Fig. 12. *Mono- and disaccharides used as substrates in ^{1}H-NMR binding titrations*

Table. *Association Constants* K_a [M^{-1}] *and Complexation Free Enthalpies* ΔG^0 [kcal mol^{-1}] *from ^{1}H-NMR Binding Titrations* (500 MHz) *for 1:1 Complexes of Cleft-Type and Macrocyclic Receptors with Mono- and Disaccharides* (300 K). Also shown are the calculated and, in parenthesis, the maximum observed complexation-induced shifts ([ppm], – = upfield) $\Delta\delta_{sat}$ and $\Delta\delta_{max\ obs}$ of the anomeric proton H–C(1) resonance of the sugar substrate, which was monitored during the titration.

Receptor[a])	Substrate[a])	Solvent	K_a[b]) [$l \cdot mol^{-1}$]	ΔG^0 [kcal $\cdot mol^{-1}$]	$\Delta\delta_{sat}$ ($\Delta\delta_{max\ obs}$) [ppm]
(–)-(*R*)-**7**	**63**	CD_3CN	170	– 3.1	
(–)-(*R*)-**38**	**63**	CD_3CN	420	– 3.6	– 0.08 (– 0.030)
(–)-(*R*,*R*,*R*)-**6**	**63**	CD_3CN	3500	– 4.7	– 0.20 (– 0.129)
(–)-(*R*,*R*,*R*)-**6**	**64**	CD_3CN	2500	– 4.6	– 0.09 (– 0.057)
(–)-(*R*,*R*,*R*)-**6**	**65**	CD_3CN	2800	– 4.7	– 0.18 (– 0.111)
(–)-(*R*,*R*,*R*,*R*)-**1**	**63**	CD_3CN/CD_3OD 98 : 2	5200	– 5.1	– 0.19 (– 0.146)
(–)-(*R*,*R*,*R*,*R*)-**1**	**64**	CD_3CN/CD_3OD 98 : 2	5800	– 5.1	– 0.30 (– 0.237)
(–)-(*R*,*R*,*R*,*R*)-**1**	**65**	CD_3CN/CD_3OD 98 : 2	4500	– 5.0	– 0.07 (– 0.054)
(–)-(*R*,*R*,*R*,*R*)-**2**	**66**	CD_3CN/CD_3OD 88 : 12	11000	– 5.5	– 0.11 (– 0.077)
(–)-(*R*,*R*,*R*,*R*)-**2**	**67**	CD_3CN/CD_3OD 88 : 12	12500	– 5.6	– 0.11 (– 0.085)
(–)-(*R*,*R*,*R*,*R*)-**2**	**68**	CD_3CN/CD_3OD 88 : 12	10700	– 5.5	– 0.18 (– 0.127)
(–)-(*R*,*R*,*R*,*R*)-**3**	**67**	CD_3CN/CD_3OD 88 : 12	41000	– 6.3	– 0.09 (– 0.084)
(–)-(*R*,*R*,*R*,*R*)-**3**	**60**	CD_3CN/CD_3OD 80 : 20	20800	– 5.9	– 0.02 (– 0.018)
(–)-(*R*,*R*,*R*,*R*)-**3**	**67**	CD_3CN/CD_3OD 80 : 20	21700	– 5.9	– 0.05 (– 0.041)

[a]) During the titrations, the guest concentration usually was held constant at *ca.* 0.25 mM. The macrocyclic receptor concentration varied between *ca.* 0.03 – 0.8 mM, whereas the cleft receptor concentration varied between *ca.* 0.1 and 6 mM. [b]) Uncertainty in K_a estimated at ± 20% from duplicate and triplicate runs.

which (−)-(*R*)-**17** could be solubilized, no significant complexation of monosaccharides was observed.

Although macrocyclic tris-phosphodiester (−)-(*R*,*R*,*R*)-**6** does not have an open cavity binding site (see *Sect. 2.6*), its complexes with monosaccharides in CD_3CN are significantly more stable than those formed by the simple cleft-type receptors (*Table*). Presumably, the substrates dock onto one of the two receptor faces, thereby interacting with more than one anionic phosphodiester residue. At higher concentration ranges ($[receptor]_0 > 2.5$ mM), the binding titrations can no longer be evaluated according to the 1:1 complexation model, and complexes of higher host–guest stoichiometry presumably do form. In competitive CD_3CN/CD_3OD solvent mixtures, binding between (−)-(*R*,*R*,*R*)-**6** and monosaccharides was too weak to be evaluated.

The potential for formation of ionic host–guest H-bonds between the four convergent phosphodiester residues of receptor (−)-(*R*,*R*,*R*,*R*)-**1** and the OH groups of monosaccharides dramatically increases complexation strength, which becomes too large to be evaluated by ^{1}H-NMR titrations in pure CD_3CN. Complexation of octyl β-D-glucoside (**63**) occurred even in the presence of a protic co-solvent, and host–guest binding was observed in CD_3CN solutions containing up to 10% (*v*/*v*) of CD_3OD. The ^{1}H-NMR signals of all sugar protons were considerably shifted upfield due to complexation. For example, at $[host]_0 = [guest]_0 = 1.0$ mM, the resonance of the anomeric proton H–C(1) of **63** moved upfield from $\delta = 4.197$ to $\delta = 3.787$ ppm in pure CD_3CN, to $\delta = 3.903$ ppm in CD_3CN/CD_3OD 98:2, and to $\delta = 4.116$ ppm in CD_3CN/CD_3OD 90:10. Attempts at quantitative binding titrations in CD_3CN/CD_3OD 98:2 rapidly showed that the receptor tends to form complexes with higher, presumably 1:2 host–guest stoichiometry. In particular, at higher concentration ranges, with **63** present in excess over the receptor, higher complexation stoichiometry clearly predominated as indicated by the shape of the ^{1}H-NMR titration curves. 1:2 Host–guest complexation can be readily rationalized by the eight phosphodiester O-

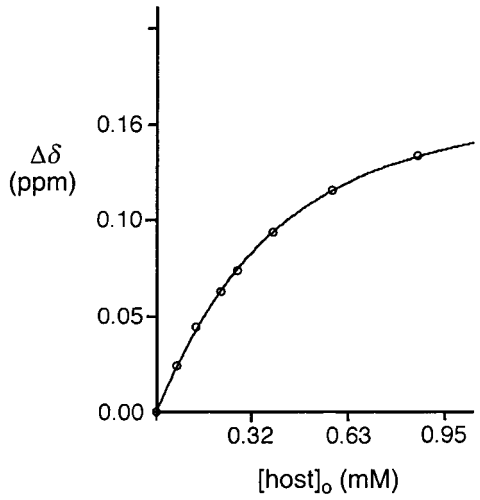


Fig. 13. *Nonlinear least-squares curve fit to the experimental data of the ^{1}H-NMR binding titration* (500 MHz, 300 K, CD_3CN/CD_3OD 98:2) *with [(−)-(*R,R,R,R*)-**1**] = 0.06 to 0.85 mM and* [**63**] = *0.25 mM*

atoms forming H-bonds to four OH groups of two sugar molecules that presumably dock from opposite faces onto the receptor. At low-concentration ranges of both binding partners ($[host]_0 = 0.06$ to 0.85 mM, $[guest]_0 = 0.25$ mM) in CD_3CN/CD_3OD 98:2, however, a good fit of the experimental data to a 1:1 host–guest binding model was eventually obtained (*Fig. 13*); the reproducibility of the calculated K_a values was ±20% (*Fig. 13*). The 1:1 stoichiometry in this concentration range was confirmed by *Job*-plot analysis [50]. Complexes of similar stability were formed with the three monosaccharides considered in the investigation: whereas association strength in the presence of the competitive co-solvent CD_3OD is quite appealing, the receptor does not show any binding diastereo- or enantioselectivity (*Table*).

Macrocycle (–)-(*R*,*R*,*R*,*R*)-**2** had been designed to selectively bind disaccharides over monosaccharides, and ^{1}H-NMR binding titrations in the competitive solvent mixture CD_3CN/CD_3OD 88:12 confirmed these expectations. The receptor exhibited a high binding affinity ($K_a \approx 10^4\ l \cdot mol^{-1}$, $\Delta G^0 = -5.5\ kcal \cdot mol^{-1}$) for disaccharides **66**–**68**. For all three substrates, an excellent fit of the titration data to a 1:1 host–guest binding model was obtained, and this stoichiometry was further corroborated by *Job*-plot analyses. Whereas no selectivity among these substrates was observed, the selectivity over monosaccharides was remarkably high. Upon addition of more than 2 equiv. of the receptor to a 0.25 mM solution of octyl β-D-glucoside (**63**), no change in chemical shift of its anomeric proton H–C(1) was observed within the error range ($\Delta\delta \pm 0.001$ ppm), while disaccharides **66**–**68** produced 60–80% saturation binding under these conditions. This high selectivity ($\Delta(\Delta G^0) > 3\ kcal \cdot mol^{-1}$) is readily explained by the size of the cavity binding site of (–)-(*R*,*R*,*R*,*R*)-**2**, which fits disaccharides well but, unlike the cavity of (–)-(*R*,*R*,*R*,*R*)-**1**, is much too spacious for incorporating a monosaccharide under formation of ionic H-bonds to all four convergent phosphodiester groups. Apparently, ionic H-bonding of **63** to only two phosphodiester groups in (–)-(*R*,*R*,*R*,*R*)-**2**, which are separated by 7.2 Å, is not sufficient to establish stable complexation in the competitive protic solvent mixture used. In pure CD_3CN, (–)-(*R*,*R*,*R*,*R*)-**2** was found to bind monosaccharide **63**, but with a host–guest stoichiometry higher than 1:1 and presumably 2:1 as suggested by *Job*-plot analysis. In a control run, octyl β-D-maltoside (**66**) displayed no binding to monophosphodiester cleft (–)-(*R*)-**7** in CD_3CN/CD_3OD 88:12 in concentration ranges below 10 mM. This experiment additionally supports that simultaneous ionic H-bonding between the substrate and the four encircling phosphodiester moieties of (–)-(*R*,*R*,*R*,*R*)-**2** is necessary for stable complexation to occur in the competitive solvent mixture.

The two extra methyl carboxylate groups in (–)-(*R*,*R*,*R*,*R*)-**3** further enhance the disaccharide binding affinity by additional H-bonding interactions, as well as by possibly providing an overall tighter host–guest fit. Thus, the binding free enthalpy measured for the complex with **67** in CD_3CN/CD_3OD 88:12 is significantly higher than that determined for the corresponding complex of receptor (–)-(*R*,*R*,*R*,*R*)-**2**, which lacks the two CO_2Me groups ($\Delta G^0 = -6.5$ *vs.* $-5.6\ kcal \cdot mol^{-1}$). With its additional interaction sites, receptor (–)-(*R*,*R*,*R*,*R*)-**3** complexes disaccharides efficiently even in the competitive solvent mixture CD_3CN/CD_3OD 80:20 (*Table*).

Interestingly, we observed, throughout the entire study, that increasing amounts of protic co-solvents helped to prevent undesired higher-stoichiometry association. Thus,

trehalose derivative **60** showed a strong tendency for binding with higher (presumably 1:2) stoichiometry to (−)-(*R*,*R*,*R*,*R*)-**3** in CD_3CN/CD_3OD 88:12, whereas exclusive 1:1 host–guest complexation was observed in CD_3CN/CD_3OD 80:20 according to *Job* plot and titration-data analysis. Again, the selectivity for disaccharide over monosaccharides was very high, and no binding of **63** could be detected under conditions that produced 81% and 90% saturation binding of **67** and **60**, respectively.

Complexation studies with the hexaanionic cyclophane receptor (−)-(*R*,*R*,*R*,*R*)-**4** were severely hampered by experimental difficulties and so far provided only qualitative evidence for saccharide binding. At $[host]_0 = [\mathbf{67}]_0 = 0.25$ mM in CD_3CN/CD_3OD 80:20, the resonance of the anomeric proton H–C(1) of the disaccharide was shifted upfield by −0.06 ppm. Comparable complexation-induced ^{1}H-NMR signal shifts were observed in CD_3CN solutions containing up to 40% CD_3OD. However, a linear relationship between $\Delta\delta$ and $[host]_0$ was observed over the entire ^{1}H-NMR titration range, and attempted quantitative interpretations of the suggested complexation event failed, *i.e.*, a qualitative distinction between either very strong binding or, conversely, poor complexation was impossible. Also, no conclusive information could be obtained from *Job*-plot analysis.

3. Conclusions. – A wide range of molecular-recognition studies with synthetic receptors had shown [6] that carbohydrate complexation based on neutral host–guest H-bonds was not very effective in competitive protic solvent mixtures. The aim of this work was to explore, whether bidentate, ionic host–guest H-bonding would make carbohydrate recognition by synthetic receptors more efficient in competitive protic solvent environments. To test this hypothesis, which was derived from examinations of X-ray crystal structures of protein–carbohydrate complexes, a new family of conformationally preorganized cyclophane receptors was prepared. These optically active macrocycles were obtained by 1,1′-binaphthalene-acetylene scaffolding, taking advantage of modern Pd^0-catalyzed aryl–acetylene cross-coupling and oxidative acetylenic homo-coupling methodology. They feature a binding cavity lined with four convergent anionic phosphodiester residues as bidentate ionic H-bond acceptor sites. Outwards-pointing benzyl ether moieties were attached to the major grooves of the 1,1′-binaphthalene moieties in the cyclophane skeleton, in order to enhance the solubility of the receptors and to prevent undesirable aggregation [11b].

Molecular-modeling examinations suggested that the, on average, square binding site in (−)-(*R*,*R*,*R*,*R*)-**1** was complementary in size to one monosaccharide, whereas the, on average, wider rectangular cavity in (−)-(*R*,*R*,*R*,*R*)-**2**–**4** provided a good fit to one disaccharide, but was too large for the efficient complexation of monosaccharides. These hypotheses were fully confirmed in ^{1}H-NMR binding-titration studies. Sugar binding to cleft-type receptors with one anionic phosphodiester moiety was much weaker, which demonstrated that simultaneous ionic H-bonding between the substrate and the four encircling phosphodiester residues in the cyclophanes is necessary for stable complexation to occur. The investigation demonstrates conclusively that the strength of carbohydrate recognition is enhanced with an increasing number of bidentate ionic host–guest H-bonds. The formation of these highly stable H-bonds clearly makes carbohydrate complexation more efficient in competitive solvent mixtures (*Table*). Cleft-type receptors (−)-(*R*)-**7** and (−)-(*R*)-**38** form weak 1:1

complexes only in CD_3CN. Similarly, cyclophane (−)-(*R*,*R*,*R*)-**6**, which lacks an open binding cavity, thereby preventing the sugar guest from becoming encircled by its three anionic phosphodiester residues, forms stable complexes only in the absence of CD_3OD. In contrast, macrocycle (−)-(*R*,*R*,*R*,*R*)-**1** undergoes stable inclusion complexation with monosaccharides in CD_3CN containing 2% CD_3OD. With their larger number of H-bonding sites, disaccharide substrates bind even more strongly to the four phosphodiester groups lining the cavity of (−)-(*R*,*R*,*R*,*R*)-**2**, and complexation becomes efficient in CD_3CN containing 12% CD_3OD. Finally, the introduction of two methyl ester residues further enhances the receptor capacity of (−)-(*R*,*R*,*R*,*R*)-**3**, and efficient disaccharide complexation is measured in CD_3CN containing 20% CD_3OD.

With this study, the objective of optimizing sugar-receptor H-bonding interactions has been reached. In future work, the diastereo- and enantioselectivity of carbohydrate complexation by members of this new family of cyclophane receptors needs to be improved. Furthermore, sandwiching the bound carbohydrate guest between aromatic rings located atop of and below the H-bonding cavity should greatly increase the number of host–guest dispersion and CH$\cdots\pi$ interactions, as well as enhance favorable hydrophobic desolvation processes, thereby enabling stable carbohydrate complexation in aqueous solution [5].

This work was supported by the *Swiss National Science Foundation* (*CHiral 2*) and *F. Hoffmann-La Roche AG*, Basel. *S. A.* thanks the *Royal Society*, London, for a *European Science Exchange Programme* postdoctoral fellowship and *Trinity College*, Cambridge, for a research fellowship. A doctoral fellowship from the *Stipendienfonds der Basler Chemischen Industrie* and from *Novartis AG* for *A. S. D.* is gratefully acknowledged.

Experimental Part

General. Reagent-grade solvents and chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Compounds (−)-(*R*,*R*,*R*,*R*)-**8**, (−)-(*R*)-**9**, (−)-(*R*)-**10**, (±)-(*R*)-**19**, **24**, **27**, (±)-**32**, and (−)-(*R*)-**40** were prepared as described in [11b]; methyl 3-ethynylbenzoate [23], methyl 2-amino-5-iodobenzoate [31], **61** [44], methyl 2,5-diiodobenzoate [51], $[PdCl_2(dppf)]\cdot CH_2Cl_2$ [52], and CuCl [53] were synthesized according to literature procedures. The octyl glycosides **63**–**65**, **67** [54], and **68** [55] were prepared according to known protocols [56]. Octyl β-D-maltoside (**66**) [57] was purchased from *Calbiochem*. THF was freshly distilled from Na/benzophenone ketyl, CH_2Cl_2 from CaH_2, and PhMe from Na; pyridine was dried over 4-Å molecular sieves; Et_3N was distilled from CaH_2 and stored over KOH; Et_2NH was distilled from BaO and stored over KOH; air was dried over $CaCl_2$. Moisture-sensitive reactions were performed under Ar in dried glassware. Org. extracts were dried over $MgSO_4$ or Na_2SO_4, and evaporated below 50° at water-aspirator pressure (*in vacuo*), followed by drying of the residue at 0.1 Torr. TLC: aluminum sheets precoated with *Fluka* SiO_2, with fluorescent indicator (254 nm), layer thickness 0.2 mm; aromatic compounds were visualized by 254- or 366-nm light; sugar derivatives were detected by treatment with an ethanolic soln. of H_2SO_4 (10%), or an aq. soln. of H_2SO_4 (10%), $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$ (5%), and $Ce(SO_4)_2\cdot 4\ H_2O$ (0.1%) followed by heating to *ca.* 200°. Column chromatography (CC): *Fluka* SiO_2 *60* (0.04–0.063 mm, 230–400 mesh) or SiO_2 *H* from *Fluka* (particle size 5–40 μm); distilled technical-grade solvents. Flash chromatography (FC): SiO_2 or SiO_2 *H*; head pressure of *ca.* 0.3 bar. Ion-exchange chromatography: *Dowex® 50 W X 8* resin (H^+ form; 200–400 mesh), or *Dowex® DR-2030* resin (H^+ form; 20–50 mesh). Anal. GPC: *Shodex* columns with a *Merck-HITACHI* column oven *L-7360* thermostatted at 40° and driven by a *Merck-HITACHI* pump *L-7100*, *Merck-HITACHI* UV detector *L-7400* ($\lambda = 366$ nm), *Merck-HITACHI* chromato-integrator *D-2500*; solvent: THF (HPLC-grade); flow rate fixed at 1 ml min^{-1}. Prep. GPC purification of (−)-(*R*,*R*,*R*,*R*)-**49** and (−)-(*R*,*R*,*R*)-**50** (mixture of 100–150 mg): glass-column (4.5 × 155 cm), filled with *Bio-Rad Bio-Beads® S-X1* (200–400 mesh), elution with CH_2Cl_2 (technical grade, distilled prior to use) at 20°; flow rate: *ca.* 40 drops (*ca.* 0.84 ml) min^{-1} (gravity). Purification of (−)-(*R*,*R*,*R*,*R*)-**52** by prep. scale high-performance GPC (8–15 mg/

injection): *NovoGROM GPC 1000* column, 10 μm (300 × 8 mm) at 20°, *Merck-HITACHI* intelligent pump *L-6250*, *Merck-HITACHI* UV detector *L-4000A* ($\lambda = 366$ nm); elution with PhMe (HPLC-grade); flow rate: 0.5 ml min^{-1}; the purity of each collected fraction was checked by analytical GPC. M.p.: *Büchi 510* apparatus; uncorrected. Optical rotations ($[\alpha]_D^{r.t.}$): *Perkin-Elmer 241 MC* polarimeter with a 10-cm cell at $\lambda = 589$ nm (Na-D band) at r.t.; concentrations (*c*) are in g/100 ml; $CHCl_3$ was filtered through neutral Al_2O_3 (*Woelm*, activity grade I) prior to use. CD Spectra (λ_{max} [nm], $\Delta\varepsilon$ [$l \cdot mol^{-1} \cdot cm^{-1}$]): *JASCO J-715* spectropolarimeter with a 1-cm cell at r.t.; shoulders are indicated by sh. UV/VIS (λ_{max} [nm], ε [$l \cdot mol^{-1} \cdot cm^{-1}$]): *Varian-CARY 5* spectrophotometer with a 1-cm cell at r.t.; shoulders are indicated by sh. IR ([cm^{-1}], KBr or $CHCl_3$): *Perkin-Elmer-FT1600* spectrometer. NMR (^1H, ^{13}C, ^{31}P; δ [ppm], *J* [Hz]): *Varian Gemini-200* and *-300* spectrometers, *Bruker AMX-500* spectrometer; residual solvent signals as internal reference; ^{31}P-NMR reference: H_3PO_4; all spectra were recorded at r.t. unless specified otherwise. MS (*m*/*z* (% relat. intensity)): EI and DEI spectra were measured at 70 eV on a *VG TRIBRID* spectrometer; FAB spectra were measured in the positive- or negative-ion mode with 3-nitrobenzyl alcohol (NOBA) as a matrix on a *VG ZAB2-SEQ* spectrometer; MALDI-TOF spectra were measured in the positive ion mode on a *Bruker REFLEX* spectrometer with 2-(4-hydroxyphenylazo)benzoic acid (HABA) as matrix; ESI spectra were measured in the negative (NESI) mode on a *Finnigan TSQ-7000* spectrometer. The experimentally observed highest peak in the molecular-ion cluster is given followed by the isotopic molecular formula corresponding to the most intense calculated peak in the cluster. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH-Zürich. The IUPAC nomenclature and numbering system has been used to name the new compounds. Compounds (−)-(*R*,*R*,*R*,*R*)-**1**, (−)-(*R*,*R*,*R*,*R*)-**2**, (−)-(*R*,*R*,*R*,*R*)-**5**, (−)-(*R*,*R*,*R*)-**6**, (−)-(*R*,*R*)-**12**, (−)-(*R*,*R*)-**13**, (−)-(*R*,*R*,*R*,*R*)-**14** and (−)-(*R*,*R*,*R*,*R*)-**15** have been named by the *Chemical Abstract Service*; the names of macrocycles (−)-(*R*,*R*,*R*,*R*)-**3**, (−)-(*R*,*R*,*R*,*R*)-**4**, (−)-(*R*,*R*,*R*,*R*)-**52**, and (−)-(*R*,*R*,*R*,*R*)-**53** were derived from the *Chemical Abstract Index Names* of parent compounds.

^{1}H-NMR Binding Titrations. The receptors and sugars were dried under high vacuum (10^{-7} Torr; turbopump: *Turbotronik NT 340 M*; *Combivac CM 31*) before the titration experiments. For the preparation of the stock solns., the compounds were weighed on a microbalance (*Mettler AT20*) and diluted by means of *Gilson Pipetman* pipettes (200 and 1000 μl). To obtain reproducible binding results, the NMR solvents (purchased from *Cambridge Isotope Laboratories, Inc.* and *Dr. Glaser AG*, Basel) were carefully dried over 3- or 4-Å molecular sieves prior to utilization. ^{1}H-NMR Titrations (*Bruker AMX-500* spectrometer) were performed at 300 K. The guest concentration was kept constant at 0.25 mM, and a soln. of host (and 0.25 mM guest) was added in portions *via* microsyringe to the septum-capped NMR tube containing the host. After each addition, a ^{1}H-NMR spectrum was recorded. Nonlinear least-squares curve-fitting analysis of the ^{1}H-NMR titration data yielded quantitative binding data (K_a, ΔG^0, $\Delta\delta_{sat}$) [49]. The K_a and ΔG^0 values reported are averages calculated from multiple runs.

*(−)-(*R,R,R,R*)-13,14,15,16,31,32,33,34,49,50,51,52,67,68,69,70-Hexadecadehydro-3,8,21,26,39,44,57,62-octakis(phenylmethoxy)-5,71:6,12:17,23:24,30:35,41:42,48:53,59:60,66-octamethenooctabenzo[*a,e,o,c$_l$,g$_l$,q$_l$,u$_l$*]-cyclohexapentacontene-73,74,75,76,77,78,79,80-octol* ((−)-(*R*,*R*,*R*,*R*)-**5**). To a soln. of the tetrabenzoate precursor (tetrakis[2,2′-bis(benzoyloxy)-7,7′-bis(benzyloxy)-1,1′-binaphthalene-3,3′-diylbis(ethynyl)] [11b]; 30 mg, 0.01 mmol) in THF (20 ml), a soln. of KOH in MeOH (3.6M, 0.2 ml) was slowly added. The resulting yellow soln. was stirred at r.t. for 30 min, then CH_2Cl_2 (250 ml) was added. The org. phase was washed with H_2O, dried ($MgSO_4$), and evaporated *in vacuo* to yield (−)-(*R*,*R*,*R*,*R*)-**5** (20 mg, 92%). M.p. 199° (CH_2Cl_2/hexane). $[\alpha]_D^{r.t.} = -759.6$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3689*w*, 3522*w*, 3056*w*, 2211*w*, 2133*w*, 1617*s*, 1500*m*, 1456*m*, 1378*m*, 1267*m*, 1217*m*, 1156*m*, 1011*m*, 911*m*, 700*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.11 (*s*, 8 H); 7.75 (*d*, *J* = 8.6, 8 H); 7.33–7.06 (*m*, 48 H); 6.36 (*d*, *J* = 2.2, 8 H); 4.76 (*d*, *J* = 12.0, 8 H); 4.70 (*d*, *J* = 12.0, 8 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 69.8; 78.3; 79.3; 104.9; 108.2; 112.0; 117.7; 124.1; 127.5; 128.0; 128.5; 130.1; 135.0; 135.7; 136.2; 159.0; 163.7. FAB$^+$-MS: 2178 (100, MH^+, $^{13}C^{12}C_{151}H_{97}O_{16}$; calc. 2178.77), 2088 (28, $[M - Bn]^+$, $^{13}C^{12}C_{144}H_{90}O_{16}$; calc. 2088.30). Anal. calc. for $C_{152}H_{96}O_{16}$ (2178.77): C 83.81, H 4.44, O 11.75; found: C 83.99, H 4.68, O 11.71.

*(−)-*N,N,N*-Tributyl-1-butanaminium (*R,R,R,R*)-13,14,15,16,31,32,33,34,49,50,51,52,67,68,69,70-Hexadecadehydro-75,80,85,90-tetrahydroxy-3,8,21,26,39,44,57,62-octakis(phenylmethoxy)-5,71,6,12:17,23,24,30:35,41,42,48:53,59,60,66-tetrakis(methynoxyphosphinidenoxymethyno)octabenzo[*a,e,o,s,c$_l$,g$_l$,q$_l$,u$_l$*]cyclohexapentacontene-75,80,85,90-tetraoxide (4:1)* ((−)-(*R*,*R*,*R*,*R*)-**1**). To (−)-(*R*,*R*,*R*,*R*)-**5** (30 mg, 0.014 mmol) in anh. CH_2Cl_2 (5 ml), a soln. of $POCl_3$ in anh. CH_2Cl_2 (0.16M, 1 ml) was added dropwise, followed by anh. Et_3N (0.3 ml). The soln. was stirred for 3 h at r.t., and the solvent was evaporated *in vacuo*. The residual oil was dissolved in THF/H_2O 5:4 (18 ml), and the soln. was stirred at 40° for 12 h. After addition of CH_2Cl_2 (100 ml), the org. phase was washed with H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. The residual solid was recrystallized from CH_2Cl_2 with layered addition of hexane to give, after centrifugation, a yellow solid, which was subjected to ion-exchange

chromatography (*Dowex® 50WX8*, Bu_4N^+, MeCN/$CHCl_3$ 1:1) to give (−)-(*R*,*R*,*R*)-**1** (132 mg, 67%). M.p. 252° (CH_2Cl_2/hexane). $[\alpha]_D^{r.t.} = -554.9$ ($c = 1.0$, MeCN). IR ($CHCl_3$): 3656*w*, 3322*m*, 2967*m*, 2922*m*, 2878*m*, 2211*w*, 2144*w*, 1722*w*, 1672*w*, 1617*s*, 1494*s*, 1450*m*, 1378*m*, 1244*s*, 1194*s*, 1094*s*, 1017*m*, 889*m*, 884*m*, 811*m*, 689*m*. ^{31}P-NMR (121 MHz, CD_3CN): 2.90. ^{1}H-NMR (500 MHz, CD_3CN): 8.26 (*s*, 8 H); 7.87 (*d*, $J = 9.2$, 8 H); 7.23–7.04 (*m*, 48 H); 6.62 (*s*, 8 H); 4.68 (*d*, $J = 12.2$, 8 H); 4.64 (*d*, $J = 12.2$, 8 H); 3.06–3.03 (*m*, 32 H); 1.55–1.41 (*m*, 32 H); 1.33–1.26 (*m*, 32 H); 0.91 (*t*, $J = 7.3$, 48 H). ^{13}C-NMR (50 MHz, CD_3CN): 159.6; 138.2; 136.4; 135.1; 131.5; 129.8; 129.2; 128.5; 127.0; 123.0; 119.7; 116.5; 115.0; 108.4; 80.6; 78.1; 71.1; 59.5; 24.5; 20.5; 14.1. FAB$^+$-MS: 3173 (25, $[M + Na + H - Bu_4N]^+$, $^{13}C_2{}^{12}C_{198}H_{197}N_3O_{24}P_4Na$; calc. 3173.32), 2932 (100, $[M + Na + 2\,H - 2\,Bu_4N]^+$, $^{13}C_2{}^{12}C_{182}H_{162}N_2O_{24}P_4Na$; calc. 2932.04), 2690 (98, $[M + Na + 3\,H - 3\,Bu_4N]^+$, $^{13}C^{12}C_{167}H_{127}NO_{24}P_4Na$; calc. 2689.76), 2448 (49, $[M + Na + 4\,H - 4\,Bu_4N]^+$, $^{13}C^{12}C_{151}H_{92}O_{24}P_4Na$; calc. 2448.49). Anal. calc. for $C_{216}H_{232}N_4O_4O_{24}P_4 \cdot 8\,H_2O$ (3536.3): C 73.37, H 7.07, N 1.58; found: C 73.24, H 6.97, N 1.53.

*(−)-*N,N,N-*Tributyl-1-butanaminium* (R,R,R*)-7,8,9,10,25,26,27,28,43,44,45,46-Dodecadehydro-57,62,67-trihydroxy-2,15,20,33,38,51-hexakis(phenylmethoxy)-6,54,47,53:11,17,18,24:29,35,36,42-tris(methynoxyphosphinidenoxymethyno)hexabenzo[*a,e,o,s,c_1,g_1*]cyclodotetracontene-57,62,67-trioxide (3:1)* ((−)-(*R*,*R*,*R*)-**6**). To (−)-(*R*,*R*,*R*)-**8** [11b] (30 mg, 0.018 mmol) in anh. CH_2Cl_2 (5 ml), a soln. of $POCl_3$ in anh. CH_2Cl_2 (0.16M, 1 ml) was added dropwise, followed by anh. Et_3N (0.3 ml). The soln. was stirred for 3 h at r.t., and the solvent was evaporated *in vacuo*. The residual oil was dissolved in THF/H_2O 5:4 (18 ml), and the soln. was stirred at 40° for 12 h. After addition of CH_2Cl_2 (100 ml), the org. phase was washed with H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. The residual solid was recrystallized from CH_2Cl_2 with layered addition of hexane to give, after centrifugation, a yellow solid, which was submitted to ion-exchange chromatography (*Dowex® 50WX8*, Bu_4N^+, MeCN/$CHCl_3$ 1:1) to give (−)-(*R*,*R*,*R*)-**6** (30 mg, 65%). M.p. 240° (CH_2Cl_2/hexane). $[\alpha]_D^{r.t.} = -469.4$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3689*m*, 3533*w*, 3311*w*, 2956*w*, 1617*s*, 1611*s*, 1494*m*, 1450*w*, 1372*w*, 1194*m*, 1100*s*, 1006*m*, 894*m*, 672*s*. ^{31}P-NMR (121 MHz, CD_3CN): 4.10. ^{1}H-NMR (300 MHz, CD_3CN): 8.25 (*s*, 6 H); 7.92 (*d*, $J = 9.4$, 6 H); 7.28–7.04 (*m*, 36 H); 6.67 (*m*, 6 H); 4.67 (*m*, 12 H); 3.07–3.01 (*m*, 24 H); 1.60–1.25 (*m*, 48 H); 0.93 (*t*, $J = 7.2$, 36 H). ^{13}C-NMR (100 MHz, (D_8)THF): 158.93; 137.87; 134.65; 134.44; 130.82; 129.09; 128.47; 128.09; 126.82; 122.58; 119.04; 115.71; 108.17; 79.29; 70.54; 59.04; 24.63; 20.43; 14.14. FAB$^+$-MS: 2341 (51, $[M + K + H - Bu_4N]^+$, $^{13}C^{12}C_{145}H_{139}N_2O_{18}P_3K$; calc. 2340.89), 2099 (100, $[M + K + 2\,H - 2\,Bu_4N]^+$, $^{13}C^{12}C_{129}H_{104}NO_{18}P_3K$; calc. 2099.61), 1858 (82, $[M + K + 3\,H - 3\,Bu_4N]^+$, $^{13}C^{12}C_{113}H_{69}O_{18}P_3K$; calc. 1858.34). Anal. calc. for $C_{162}H_{174}N_3O_{18}P_3 \cdot 6\,H_2O$ (2652.2): C 73.37, H 7.07, N 1.58; found: C 73.37, H 6.78, N 1.59.

(−)-Tetrabutylammonium (R*)-[7,7′-Bis(benzyloxy)-3,3′-diethynyl-1,1′-binaphthalene-2,2′-diyl]phosphate* ((−)-(*R*)-**7**). To (−)-(*R*)-**9** [11b] (40 mg, 0.073 mmol) in anh. CH_2Cl_2 (20 ml), a soln. of $POCl_3$ in anh. CH_2Cl_2 (0.16M, 1 ml) was added dropwise, followed by anh. Et_3N (0.3 ml). The soln. was stirred for 3 h at r.t., and the solvent was evaporated *in vacuo*. The residual oil was then dissolved in THF/H_2O 5:4 (18 ml), and the soln. was stirred at 40° for 12 h. After addition of CH_2Cl_2 (100 ml), the org. phase was washed with H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. The residual solid was recrystallized from CH_2Cl_2 with layered addition of hexane to give, after centrifugation, a yellow solid, which was submitted to ion-exchange chromatography (*Dowex® 50WX8*, Bu_4N^+, MeCN/$CHCl_3$ 1:1) to give (−)-(*R*)-**7** (42 mg, 68%). M.p. 80° (CH_2Cl_2/hexane). $[\alpha]_D^{r.t.} = -53.3$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3306*m*, 3067*w*, 3033*w*, 2989*m*, 2878*w*, 2578*w*, 2451*m*, 2107*w*, 1620*s*, 1498*m*, 1454*m*, 1248*s*, 1204*s*, 1165*m*, 1142*m*, 1092*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.00 (*s*, 2 H); 7.67 (*d*, $J = 9.3$, 2 H); 7.27–7.04 (*m*, 12 H); 6.55 (*d*, $J = 2.5$, 2 H); 4.54 (*d*, $J = 1.8$, 2 H); 4.49 (*d*, $J = 1.8$, 2 H); 3.20 (*s*, 2 H); 2.93–2.85 (*m*, 8 H); 1.28–1.09 (*m*, 16 H); 0.77 (*t*, $J = 7.2$, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 157.53; 150.88; 136.36; 134.05; 133.48; 129.55; 128.50; 127.96; 127.25; 125.41; 121.75; 118.19; 114.47; 106.89; 80.72; 80.52; 69.88; 57.95; 23.70; 19.51; 13.74. FAB$^-$-MS: 607 (76, $[M - Bu_4N]^-$, $C_{38}H_{24}O_6P$; calc. 607.59). Anal. calc. for $C_{54}H_{60}NO_6P \cdot 1.5\,H_2O$ (859.4): C 73.95, H 7.24, N 1.60; found: C 73.94, H 7.51, N 1.64.

*(−)-(*R*)-7,7′-Bis(benzyloxy)-3-ethynyl-3′-[(trimethylsilyl)ethynyl]-1,1′-binaphthalene-2,2′-diyl Dibenzoate* ((−)-(*R*)-**11**). A soln. of (+)-(*R*)-**10** [11b] (0.9 g, 1.0 mmol) and borax (2.0 g, 5.2 mmol) in THF (500 ml) and H_2O (460 ml) was stirred at r.t. for 24 h. The org. solvent was evaporated *in vacuo* at r.t., the aq. phase was extracted with CH_2Cl_2, and the combined org. extracts were dried (Na_2SO_4). After evaporation *in vacuo*, purification of the residual solid by CC (SiO_2 *H*, PhMe/hexane 7:3) gave (−)-(*R*)-**11** (308 mg, 37%) and starting material, which was resubmitted to the reaction conditions in an iterative fashion. M.p. 80°. $[\alpha]_D^{r.t.} = -23.8$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3312*m*, 3066*w*, 2961*m*, 2156*m*, 1745*s*, 1622*s*, 1495*m*, 1452*m*, 1388*m*, 1230*s*, 1178*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.11 (*s*, 1 H); 8.05 (*s*, 1 H); 7.82 (*m*, 2 H); 7.80 (*m*, 2 H); 7.74 (*d*, $J = 9.0$, 1 H); 7.71 (*d*, $J = 9.0$, 1 H); 7.55–7.10 (*m*, 18 H); 6.70 (br. *s*, 1 H); 6.64 (br. *s*, 1 H); 4.95–4.72 (*m*, 4 H); 3.10 (*s*, 1 H); −0.06 (*s*, 9 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 164.35; 164.17; 158.13; 158.08; 148.34; 148.06; 136.48; 134.75; 134.48; 134.36; 133.65; 133.45; 133.21; 130.17; 130.05; 129.81; 129.50; 129.45; 129.29; 129.11; 128.43; 128.31; 127.88; 127.82; 127.76; 126.60; 125.62; 123.61; 123.38; 119.97; 119.81; 114.26; 113.37; 106.16; 100.62; 99.16; 81.37;

79.65; 69.94; −0.42 (40 out of 45 resonances because of signal overlap). FAB$^+$-MS: 827 (8, MH$^+$, $C_{55}H_{42}O_6Si$; calc. 827.03). Anal. calc. for $C_{22}H_{22}O_4$ (827.03): C 79.88, H 5.12; found: C 79.46, H 5.19.

*(−)-(*R,R*)-3,3″-(1,4-Phenylenedi-2,1-ethynediyl)bis{7,7′-bis(phenylmethoxy)-3′-[(trimethylsilyl)ethynyl]}-1,1′-binaphthalene-2,2′-diol Tetrabenzoate* ((−)-(*R*,*R*)-**12**). A soln. of PhMe (5 ml) and Et_2NH (5 ml) was carefully degassed and Ar-saturated by several freeze-pump-thaw cycles, then (−)-(*R*)-**11** (220 mg, 0.27 mmol), PPh_3 (10 mg, 0.038 mmol), CuI (5 mg, 26.3 mmol), [Pd_2(dba)$_3$] (5 mg, 0.006 mmol), and 1,4-diiodobenzene (35 mg, 0.105 mmol) were added, and the mixture was stirred at 40° for 12 h. H_2O was added, and the product was extracted into CH_2Cl_2. CC (hexane/AcOEt 5:2) gave (−)-(*R*,*R*)-**12** (91 mg, 50%). M.p. 126°. $[\alpha]_D^{r.t.} = -90.1$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3689*w*, 3067*w*, 2944*w*, 2156*w*, 1739*s*, 1622*s*, 1494*m*, 1450*m*, 1383*m*, 1256*s*, 1244*s*, 1178*m*, 1133*w*, 1056*m*, 1017*m*, 894*m*, 844*m*, 694*m*, 672*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.08 (*s*, 4 H); 7.89–7.70 (*m*, 12 H); 7.51–7.13 (*m*, 36 H); 6.68 (*m*, 8 H); 4.96–4.73 (*m*, 8 H); −0.06 (*s*, 18 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 164.81; 164.54; 158.44; 148.72; 148.32; 136.86; 134.91; 134.00; 133.51; 131.31; 130.52; 129.84; 129.71; 128.97; 128.74; 128.59; 128.15; 128.05; 127.07; 126.93; 123.92; 123.75; 122.93; 120.17; 114.60; 114.40; 106.60; 106.48; 100.98; 99.43; 93.89; 87.90; 70.18; −0.31 (34 out of 38 resonances due to signal overlap). FAB$^+$-MS: 1728 (100, M^+, $^{13}C^{12}C_{115}H_{86}O_{12}Si_2$; calc. 1728.14). HR-FAB$^+$-MS: 1726.5726 ($M^+$, $^{13}C^{12}C_{115}H_{86}O_{12}Si_2$; calc. 1726.5657).

*(−)-(*R,R*)-3,3″-(1,4-Phenylenedi-2,1-ethynediyl)bis[3′-ethynyl-7,7′-bis(phenylmethoxy)]-1,1′-binaphthalene-2,2′-diol Tetrabenzoate* ((−)-(*R*,*R*)-**13**). To a soln. of (−)-(*R*,*R*)-**12** (180 mg, 0.104 mmol) in THF/MeOH 1:1 (40 ml), K_2CO_3 (100 mg, 0.72 mmol) was added, and the mixture was stirred at r.t. for 2 h. After addition of $CHCl_3$, the org. phase was washed with H_2O and dried (Na_2SO_4). The solvent was removed *in vacuo* to yield (−)-(*R*,*R*)-**13** (150 mg, 91%). M.p. 104°. $[\alpha]_D^{r.t.} = -48.4$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3689*w*, 3300*w*, 3022*w*, 2956*w*, 2911*w*, 2856*w*, 2111*w*, 1738*s*, 1622*s*, 1494*m*, 1450*m*, 1384*m*, 1056*m*, 1022*m*, 894*w*, 700*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.14 (*s*, 2 H); 8.08 (*s*, 2 H); 7.90–7.72 (*m*, 12 H); 7.52–7.21 (*m*, 36 H); 6.79–6.72 (*m*, 8 H); 4.99–4.76 (*m*, 8 H); 3.13 (*s*, 2 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 164.73; 164.66; 158.53; 158.48; 148.40; 148.27; 136.80; 135.04; 134.79; 134.69; 133.53; 131.32; 130.51; 130.35; 129.81; 129.59; 128.74; 128.63; 128.16; 128.03; 127.04; 126.94; 123.90; 123.84; 122.93; 120.32; 120.20; 114.38; 113.69; 106.42; 93.89; 87.81; 81.60; 79.87; 70.18 (35 out of 47 resonances due to signal overlap). FAB$^+$-MS: 1583 (100, M^+, $^{13}C^{12}C_{109}H_{70}O_{12}$; calc. 1583.78). HR-FAB$^+$-MS: 1582.4921 ($M^+$, $^{13}C^{12}C_{109}H_{70}O_{12}$; calc. 1582.4867).

*(−)-(*R,R,R,R*)-13,14,19,20,35,36,37,38,53,54,59,60,75,76,77,78-Hexadecadehydro-3,8,25,30,43,48,65,70-octakis(phenylmethoxy)-15,18:55,58-dietheno-5,79:6,12:21,27:28,34:39,45:46,52:61,67:68,74-octamethenooctabenzo[*a,e,o,s,g$_1$,k$_1$,u$_1$,y$_1$*]cyclotetrahexacontene-81,82,83,86,87,88,89,92-octol Octabenzoate* ((−)-(*R*,*R*,*R*,*R*)-**14**). A mixture of (−)-(*R*,*R*)-**13** (180 mg, 0.114 mmol) and CuCl (2.54 g, 25.7 mmol) in CH_2Cl_2 (1 l, freshly distilled from CaH_2) was vigorously stirred in open air at r.t. for 10 min. After addition of TMEDA (3.84 ml, 25.5 mmol), the dark-green mixture was vigorously stirred in open air for 30 min. H_2O (1 l) was added, and the biphasic mixture was stirred until the blue color of the org. layer had disappeared (*ca.* 1 h). The org. phase was separated, washed with H_2O, and dried (Na_2SO_4). After evaporation *in vacuo*, purification of the residual solid by CC (cyclohexane/AcOEt 5:3) gave (−)-(*R*,*R*,*R*,*R*)-**14** (36 mg, 20%). M.p. 157°. $[\alpha]_D^{r.t.} = -476$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3689*m*, 3022*w*, 1739*s*, 1622*s*, 1489*m*, 1444*m*, 1383*w*, 1261*s*, 1239*s*, 1172*w*, 1061*w*, 1022*m*, 894*w*, 700*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.03 (*s*, 4 H); 7.93 (*s*, 4 H); 7.83–7.65 (*m*, 24 H); 7.47–7.08 (*m*, 72 H); 6.78–6.61 (*m*, 16 H); 4.93–4.68 (*m*, 16 H). ^{13}C-NMR (50 MHz, CD_2Cl_2): 165.09; 165.00; 159.29; 158.97; 149.03; 148.78; 148.66; 137.28; 137.20; 135.59; 135.06; 134.16; 134.05; 133.63; 131.68; 130.64; 130.37; 130.21; 129.83; 129.36; 129.11; 128.86; 128.58; 128.30; 127.45; 127.30; 124.41; 124.09; 123.24; 120.62; 120.47; 114.61; 113.49; 106.92; 93.87; 87.84; 78.94; 77.95; 70.59 (39 out of 47 resonances due to signal overlap). FAB$^+$-MS: 3164 (100, M^+, $^{13}C_2{}^{12}C_{218}H_{136}O_{24}$; calc. 3163.52), 3073 (33, [M − Bn]$^+$, $^{13}C_2{}^{12}C_{211}H_{129}O_{24}$; calc. 3072.35).

*(−)-(*R,R,R,R*)-13,14,19,20,35,36,37,38,53,54,59,60,75,76,77,78-Hexadecadehydro-3,8,25,30,43,48,65,70-octakis(phenylmethoxy)-15,18:55,58-dietheno-5,79:6,12:21,27:28,34:39,45:46,52:61,67:68,74-octamethenooctabenzo[*a,e,o,s,g$_1$,k$_1$,u$_1$,y$_1$*]cyclotetrahexacontene-81,82,83,86,87,88,89,92-octol* ((−)-(*R*,*R*,*R*,*R*)-**15**). To (−)-(*R*,*R*,*R*,*R*)-**14** (25 mg, 0.008 mmol) in THF (20 ml), a soln. of KOH in MeOH (3.6M, 0.2 ml) was added. The yellow mixture was stirred for 30 min at r.t., and CH_2Cl_2 (250 ml) was added. The org. phase was washed with H_2O, dried ($MgSO_4$) and evaporated *in vacuo* to give (−)-(*R*,*R*,*R*,*R*)-**15** (16 mg, 89%). M.p. 133° (CH_2Cl_2/hexane). $[\alpha]_D^{r.t.} = -555.8$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3689*w*, 3511*w*, 3011*w*, 2211*w*, 2144*w*, 1622*s*, 1494*m*, 1456*m*, 1378*m*, 1267*m*, 1189*m*, 1011*w*, 894*w*, 839*w*, 806*w*, 694*m*. ^{1}H-NMR (300 MHz, CD_2Cl_2): 8.12 (*m*, 8 H); 7.82–7.73 (*m*, 8 H); 7.54 (*m*, 8 H); 6.43–6.37 (*m*, 8 H); 7.31–7.07 (*m*, 48 H); 5.72–5.54 (br. *s*, 8 H); 4.84–4.66 (*m*, 16 H). ^{13}C-NMR (50 MHz, CD_2Cl_2): 159.72; 159.49; 153.45; 153.30; 152.61; 137.25; 136.53; 136.21; 135.66; 134.11; 132.46; 132.37; 130.81; 129.17; 128.61; 128.21; 125.03; 124.90; 123.63; 118.22; 113.59; 112.34; 110.10; 108.80; 105.64; 95.75; 86.80; 79.34; 79.19; 78.23; 70.47. FAB$^+$-MS: 2331 (100, MH$^+$, $^{13}C^{12}C_{163}H_{105}O_{16}$; calc.

2331.66), 2240 (20, $[M\mathrm{H}-\mathrm{Bn}]^+$, $^{13}C^{12}C_{156}H_{99}O_{16}$; calc. 2241.50). HR-FAB$^+$-MS: 2328.7301 ($M^+$, $^{13}C^{12}C_{163}H_{104}O_{16}$; calc. 2328.7324).

*(−)-*N,N,N-*Tributyl-1-butanaminium (*R,R,R,R*)-13,14,19,20,35,36,37,38,53,54,59,60,75,76,77,78-Hexadecadehydro-83,88,95,100-tetrahydroxy-3,8,25,30,43,48,65,70-octakis(phenylmethoxy)-15,18:55,58-dietheno-5,79,6,12:21,27,28,34:39,45,46,52:61,67,68,74-tetrakis(methynoxyphosphinidenoxymethyno)octabenzo[*a,e,o,s,g_1,k_1,u_1,y_1*]cyclotetrahexacontene-83,88,95,100-tetraoxide (4:1)* ((−)-(*R,R,R,R*)-**2**). To (−)-(*R,R,R,R*)-**15** (25 mg, 0.011 mmol) in anh. CH_2Cl_2 (10 ml), a soln. of $POCl_3$ in anh. CH_2Cl_2 (0.16M, 1 ml) was added dropwise, followed by anh. Et_3N (0.3 ml). The soln. was stirred for 3 h at r.t., and the solvent was evaporated *in vacuo*. The residual oil was dissolved in THF/H_2O 5:4 (18 ml) and the soln. stirred at 40° for 12 h. After addition of CH_2Cl_2 (100 ml), the org. phase was washed with H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. The residual solid was recrystallized from CH_2Cl_2 with layered addition of hexane to give, after centrifugation, a yellow solid which was submitted to ion exchange chromatography (*Dowex® 50WX8*, Bu_4N^+, MeCN/$CHCl_3$ 1:1) to give (−)-(*R,R,R,R*)-**2** (25 mg, 63%). M.p. 220° (CH_2Cl_2/hexane). $[\alpha]_D^{rt} = -388.1$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3667*w*, 3333*w*, 2967*s*, 2878*m*, 2211*w*, 2144*w*, 1750*w*, 1617*s*, 1494*s*, 1450*m*, 1372*m*, 1267*s*, 1244*s*, 1100*s*, 1022*m*, 894*m*, 844*m*, 811*m*, 700*m*. ^{31}P-NMR (121 MHz, CD_3CN): 4.6. ^{1}H-NMR (500 MHz, CD_3CN): 8.26 (*s*, 4 H); 8.18 (*s*, 4 H); 7.91–7.89 (*m*, 8 H); 7.67–7.65 (*m*, 8 H); 7.25–7.04 (*m*, 48 H); 6.65–6.55 (*m*, 8 H); 4.69–4.59 (*m*, 16 H); 3.08–3.05 (*m*, 32 H), 1.59–1.53 (*m*, 32 H), 1.35–1.12 (*m*, 32 H); 0.92 (*t*, $J = 7.3$, 48 H). ^{13}C-NMR (125 MHz, CD_2Cl_2): 157.94; 157.62; 151.04; 150.59; 136.68; 136.56; 133.91; 133.43; 131.60; 129.71; 129.60; 129.00; 128.38; 127.85; 127.82; 127.25; 126.60; 125.68; 125.58; 124.81; 123.58; 122.22; 121.69; 118.21; 118.03; 115.10; 114.15; 107.08; 92.12; 88.66; 79.82; 77.27; 69.95; 58.57; 23.84; 19.62; 13.46 (37 out of 41 resonances due to signal overlap). FAB$^+$-MS: 3083.9 (91, $[M - 2\,Bu_4N + 2\,H + Na]^+$, $^{13}C_2^{12}C_{194}H_{170}N_2O_{24}P_4Na$; calc. 3084.11), 3061.7 (96, $[M - 2\,Bu_4N + 3\,H]^+$, $^{13}C_2^{12}C_{194}H_{171}N_2O_{24}P_4$; calc. 3062.12), 2842.4 (85, $[M - 3\,Bu_4N + 3\,H + Na]^+$, $^{13}C_2^{12}C_{178}H_{135}NO_{24}P_4Na$; 2842.83), 2820.65 (100, $[M - 3\,Bu_4N + 4]^+$, $^{13}C_2^{12}C_{178}H_{136}NO_{24}P_4$; calc. 2820.85), 2600.9 (97, $[M - 4\,Bu_4N + 4\,H + Na]^+$, $^{13}C^{12}C_{163}H_{100}O_{24}P_4Na$; calc. 2600.54), 2578.61 (71, $[M - 4\,Bu_4N + 5\,H]^+$, $^{13}C^{12}C_{163}H_{101}O_{24}P_4$; calc. 2578.56). Anal. calc. for $C_{228}H_{240}N_4O_{24}P_4 \cdot 12\,H_2O$ (3760.6): C 72.82, H 7.08, N 1.49; found: C 72.87, H 7.11, N 1.60.

(±)-7,7′-Bis(benzyloxy)-3,3′-diiodo-1,1′-binaphthalene-2,2′-diyl Dibenzoate ((±)-**20**). To (±)-**19** [11b] (500 mg, 0.67 mmol) in anh. CH_2Cl_2 (40 ml), anh. pyridine (0.54 ml, 530 mg, 6.70 mmol), DMAP (82 mg, 0.67 mmol), and C_6H_5COCl (0.27 ml, 328 mg, 2.33 mmol) were added at 0°. The soln. was stirred at r.t. for 2 h, then washed with 0.02M aq. $CuSO_4$ soln., 20% aq. $NaHCO_3$ soln., and H_2O. Evaporation *in vacuo* yielded a colorless oil, which was purified by FC (hexane/AcOEt 5:1) to afford (±)-**20** (631 mg, 98%). White solid. M.p. 185°. IR (KBr): 3060*m*, 3022*m*, 2956*w*, 2889*w*, 1746v*s*, 1733v*s*, 1620v*s*, 1583*m*, 1567*s*, 1494v*s*, 1451*s*, 1428*m*, 1384*s*, 1356*m*, 1312*w*, 1256v*s*, 1214v*s*, 1178v*s*, 1150*s*, 1083*s*, 1078v*s*, 1056v*s*, 1022v*s*, 1000v*s*. ^{1}H-NMR (500 MHz, $CDCl_2CDCl_2$, 374 K): 8.25 (*s*, 2 H); 7.72 (*d*, $J = 7.6$, 4 H); 7.57 (*d*, $J = 9.0$, 2 H); 7.45 (*t*, $J = 7.6$, 2 H); 7.29 (*t*, $J = 7.6$, 4 H); 7.30–7.27 (*m*, 12 H); 6.57 (*s*, 2 H); 4.85 (*d*, *AB*, $J = 12.2$, 2 H); 4.71 (*d*, *AB*, $J = 12.2$, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 163.98; 157.92; 147.66; 139.51; 136.64; 134.25; 133.67; 130.27 (2×); 129.28; 128.93; 128.60 (2×); 128.08; 127.79; 124.75; 120.38; 106.31; 86.31; 70.04. FAB$^+$-MS: 958 (100, M^+), 832 (70, $[M\mathrm{H}-\mathrm{I}]^+$), 105 (86, $[C_6H_5CO]^+$). Anal. calc. for $C_{48}H_{32}I_2O_6$ (958.58): C 60.14, H 3.36, I 26.48; found: C 60.28, H 3.20, I 26.26.

(±)-7,7′-Bis(benzyloxy)-3,3′-bis[(trimethylsilyl)ethynyl]-1,1′-binaphthalene-2,2′-diyl Dibenzoate ((±)-**21**). A soln. of (±)-**20** (300 mg, 0.31 mmol) in anh. Et_2NH (6 ml) and anh. PhMe (6 ml) was carefully degassed and Ar-saturated by three freeze-pump-thaw cycles. After addition of CuI (30 mg, 0.16 mmol) and $[PdCl_2(dppf)] \cdot CH_2Cl_2$ (10 mg, 0.013 mmol), another degassing cycle was carried out. (Trimethylsilyl)acetylene (0.3 ml, 209 mg, 2.12 mmol) was added at 40°, and the mixture was stirred at this temp. for 4 h. The solvent was evaporated *in vacuo*, and the residual solid was dissolved in CH_2Cl_2. The org. phase was washed with sat. aq. NH_4Cl soln. and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. FC (hexane/AcOEt 5:1) yielded (±)-**21** (275 mg, 98%). White solid. M.p. 170–172° (CH_2Cl_2/pentane). For an alternative, lower-yield synthesis and complete characterization of (±)-**21**, see [11b].

(±)-7,7′-Bis(benzyloxy)-3,3′-diethynyl-1,1′-binaphthalene-2,2′-diyl Dibenzoate ((±)-**18**). To (±)-**21** (310 mg, 0.35 mmol) in THF/MeOH 1:1 (64 ml), K_2CO_3 (320 mg, 2.32 mmol) was added and the mixture stirred at r.t. for 2 h. After addition of CH_2Cl_2 (160 ml), the org. phase was washed with H_2O and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield (±)-**18** (237 mg, 91%). White solid. M.p. 95–97° (CH_2Cl_2/hexane). For complete characterization of (±)-**18**, see [11b].

(±)-7,7′-Bis(benzyloxy)-3,3′-bis[[3-(methoxycarbonyl)phenyl]ethynyl]-1,1′-binaphthalene-2,2′-diyl Dibenzoate ((±)-**22**). A soln. of (±)-**18** (240 mg, 0.32 mmol) and methyl 3-iodobenzoate [22] (250 mg, 0.95 mmol) in anh. Et_2NH (4.5 ml) and anh. PhMe (4.5 ml) was carefully degassed and Ar-saturated by several freeze-pump-thaw cycles. After addition of CuI (25 mg, 0.13 mmol) and $[PdCl_2(dppf)] \cdot CH_2Cl_2$ (10 mg, 0.013 mmol),

another degassing cycle was carried out. The mixture was stirred at 40° for 5 h, and the solvent was evaporated *in vacuo*. The residual solid was dissolved in CH_2Cl_2, the org. phase was washed with sat. aq. NH_4Cl soln. and H_2O, dried (Na_2SO_4), and evaporated *in vacuo*. CC (hexane/AcOEt 7:5) yielded (±)-**22** (272 mg, 84%). Slightly yellow solid. M.p. 172–173° (CH_2Cl_2/hexane). IR (KBr): 3067*w*, 3022*w*, 2944*w*, 2200*w*, 1733v*s*, 1721v*s*, 1620*s*, 1572*s*, 1494*s*, 1450*m*, 1434*m*, 1422*w*, 1389*m*, 1367*w*, 1322*w*, 1291v*s*, 1256v*s*, 1207v*s*, 1178v*s*, 1150*m*, 1133*m*, 1106*m*, 1089*m*, 1079*s*, 1056v*s*, 1022*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.15 (*s*, 2 H); 7.89–7.86 (br. *m*, 4 H); 7.87 (*dt*, *J* = 7.6, 1.5, 2 H); 7.82 (br. *m*, 2 H); 7.78 (*d*, *J* = 8.9, 2 H); 7.50 (*tt*, *J* = 7.5, 1.3, 2 H); 7.34 (*tm*, *J* = 7.5, 4 H); 7.22–7.15 (*m*, 16 H); 6.73 (br. *s*, 2 H); 4.95 (*d*, *AB*, *J* = 11.8, 2 H); 4.80 (*d*, *AB*, *J* = 11.8, 2 H); 3.86 (*s*, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 166.24; 164.40; 158.10; 148.41; 148.16; 136.45; 135.38; 134.57; 133.34; 133.17; 132.36; 130.30; 130.10; 129.49; 129.27; 129.14; 128.36; 128.24; 127.78; 127.65; 126.71; 123.54; 123.40; 119.91; 113.95; 106.19; 92.69; 86.53; 69.92; 52.13. FAB$^+$-MS: 1023 (100, *M*H$^+$), 1022 (73, *M*$^+$), 918 (39, [*M*H – Bz]$^+$), 105 (44, Bz$^+$). HR-FAB$^+$-MS: 1023.3203 (*M*H$^+$, $C_{68}H_{47}O_{10}$; calc. 1023.3169).

*7-Benzyloxy-2-phenylnaphtho[2,3-*b*]furan* (**25**). A suspension of **24** [11b] (70 mg, 0.19 mmol) in anh. Et_2NH (4 ml) and anh. PhMe (4 ml) was carefully degassed and Ar-saturated by several freeze-pump-thaw cycles. After addition of CuI (7 mg, 0.04 mmol) and [$PdCl_2$(dppf)]·CH_2Cl_2 (6 mg, 0.01 mmol), another degassing cycle was carried out. Phenylacetylene (0.04 ml, 37 mg, 0.36 mmol) was added at 40°, and the mixture was stirred at this temp. for 3 h. Evaporation *in vacuo* left a solid, which was dissolved in CH_2Cl_2. The org. phase was washed with sat. aq. NH_4Cl soln. and H_2O, dried (Na_2SO_4), and evaporated *in vacuo*. CC (hexane/AcOEt 23:1 → 5:1) afforded **25** (43 mg, 66%). Colorless plates. M.p. 220–221° (AcOEt). IR (KBr): 3057*w*, 3031*w*, 2894*w*, 1751*w*, 1635*w*, 1621*m*, 1605*w*, 1587*w*, 1564*w*, 1502*w*, 1458*m*, 1448*s*, 1404*m*, 1378*m*, 1332*w*, 1321*w*, 1306*w*, 1276*w*, 1264*s*, 1232v*s*, 1210*m*, 1196*m*, 1142*m*, 1107*w*, 1101*w*, 1072*w*, 1040*s*, 1019*s*, 874v*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.96 (*s*, 1 H); 7.94–7.92 (*m*, 2 H); 7.84 (*d*, *J* = 9.2, 1 H); 7.79 (*s*, 1 H); 7.53–7.51 (*m*, 2 H); 7.49–7.46 (*m*, 2 H); 7.44–7.34 (*m*, 4 H); 7.30–7.29 (*m*, 1 H); 7.19 (*dd*, *J* = 9.2, 2.5, 1 H); 7.11 (*d*, *J* = 1.0, 1 H); 5.22 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 157.54; 156.49; 154.91; 137.24; 132.95; 130.58; 129.77; 129.10; 129.07; 128.88; 128.63; 128.28; 127.89; 126.84; 125.42; 118.80; 118.18; 106.86; 105.76; 101.04; 70.20. EI-MS: 350 (50, *M*$^+$), 259 (100, [*M* – Bn]$^+$), 91 (14, Bn$^+$). Anal. calc. for $C_{25}H_{18}O_2$ (350.42): C 85.69, H 5.18; found: C 85.46, H 5.46. X-Ray: see *Fig. 4*.

6-Benzyloxy-3-(methoxymethoxy)-2-(phenylethynyl)naphthalene (**28**). A soln. of **27** [11b] (95 mg, 0.23 mmol) in anh. Et_2NH (2 ml) and anh. PhMe (1 ml) was carefully degassed and Ar-saturated by several freeze-pump-thaw cycles. After addition of CuI (5 mg, 0.03 mmol) and [$PdCl_2$(dppf)]·CH_2Cl_2 (7 mg, 0.01 mmol), another degassing cycle was carried out. Phenylacetylene (0.04 ml, 37 mg, 0.36 mmol) was added at 40°, and the mixture was stirred at this temp. for 3 h. Evaporation *in vacuo* gave a solid, which was dissolved in CH_2Cl_2. The org. phase was washed with sat. aq. NH_4Cl soln. and H_2O, dried (Na_2SO_4), and evaporated *in vacuo*. CC (hexane → hexane/AcOEt 5:1) provided **28** (59 mg, 66%). Colorless needles. M.p. 126–127° (hexane). IR (KBr): 3050*w*, 3028*w*, 2994*w*, 2945*w*, 2931*w*, 2913*w*, 2902*w*, 2873*w*, 2822*w*, 2210*w*, 1625v*s*, 1604*s*, 1502*s*, 1473*m*, 1464*m*, 1455*m*, 1444*m*, 1430*s*, 1390v*s*, 1371*m*, 1287*m*, 1246*m*, 1221v*s*, 1206v*s*, 1194v*s*, 1178*m*, 1167*s*, 1150v*s*, 1139v*s*, 1102*s*, 1072v*s*, 1006v*s*, 994v*s*. ^{1}H-NMR (300 MHz, CD_2Cl_2): 7.96 (*s*, 1 H); 7.69 (*d*, *J* = 8.7, 1 H); 7.60–7.54 (*m*, 2 H); 7.52–7.48 (*m*, 2 H); 7.45–7.35 (*m*, 7 H); 7.16–7.10 (*m*, 2 H); 4.96 (*s*, 2 H); 4.90 (*s*, 2 H); 3.58 (*s*, 3 H). ^{13}C-NMR (75 MHz, CD_2Cl_2): 158.76; 155.78; 137.58; 136.29; 133.94; 132.16; 129.73; 129.22; 129.07; 128.89; 128.68; 128.26; 125.09; 124.20; 118.36; 112.85; 109.95; 107.10; 95.84; 93.13; 86.65; 70.56; 56.72. EI-MS: 394 (35, *M*$^+$), 363 (3, [*M* – OMe]$^+$), 303 (100, [*M* – Bn]$^+$), 91 (67, Bn$^+$). Anal. calc. for $C_{27}H_{22}O_3$ (394.47): C 82.21, H 5.62; found: C 81.68, H 5.73.

7-Benzyloxy-3-(phenylethynyl)naphthalen-2-ol (**26**). To **28** (14 mg, 0.04 mmol) in THF (15 ml), a soln. of conc. HCl (37%, 60 mg) in MeOH (15 ml) was added. After stirring at r.t. for 72 h, H_2O (20 ml) was added, and the product was extracted into CH_2Cl_2 (3 × 15 ml). Evaporation *in vacuo* yielded **26** (12 mg, 99%). White solid. M.p. 174–175° (PhMe). IR (KBr): 3523*s* (br.), 3495*s* (br.), 3428*s* (br.), 2960*m*, 2924*s*, 2852*m*, 1632*s*, 1610*s*, 1571*w*, 1499*m*, 1474*m* (sh), 1452*s*, 1442*m*, 1427*m*, 1392*s*, 1274*s*, 1261v*s*, 1221v*s*, 1205v*s*, 1180*m*, 1167*m*, 1154*m*, 1130*m*, 1091v*s*, 1036v*s*, 1023v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.90 (*s*, 1 H); 7.64 (*d*, *J* = 9.3, 1 H); 7.59–7.33 (*m*, 10 H); 7.20 (*s*, 1 H); 7.09–7.05 (*m*, 2 H); 6.01 (br. *s*, 1 H); 5.17 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 158.45; 153.65; 136.97; 136.59; 132.24; 131.90; 129.57; 129.09; 128.89; 128.78; 128.33; 127.84; 124.19; 122.67; 117.62; 109.59; 108.66; 106.16; 96.20; 83.68; 70.17. EI-MS: 350 (26, *M*$^+$), 259 (16, [*M* – Bn]$^+$), 91 (100, Bn$^+$). HR-EI-MS: 350.1308 (*M*$^+$,$C_{25}H_{18}O_2$; calc. 350.1307).

(±)-Dimethyl 3,3′-{[7,7′-Bis(benzyloxy)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene-3,3′-diyl]bis(ethyne-1,2-diyl)} Bis(benzoate) ((±)-**33**). A soln. of methyl 3-iodobenzoate [22] (186 mg, 0.71 mmol) in anh. Et_2NH (3 ml) was carefully degassed and Ar-saturated by several freeze-pump-thaw cycles. After addition of CuI (25 mg, 0.13 mmol) and [$PdCl_2$(dppf)]·CH_2Cl_2 (10 mg, 0.013 mmol), another degassing cycle was carried out. A

soln. of (±)-**32** [11b] (150 mg, 0.24 mmol) in anh. PhMe (3 ml, freshly distilled from Na), which had been carefully degassed and Ar-saturated by several freeze-pump-thaw cycles, was added at 40°, and the mixture was stirred at this temp. for 5 h. Evaporation *in vacuo* gave a solid that was dissolved in CH_2Cl_2. The org. phase was washed with sat. aq. NH_4Cl soln. and H_2O, dried (Na_2SO_4), and evaporated *in vacuo*. CC (hexane/AcOEt 7:5) yielded (±)-**33** (172 mg, 81%). Yellow foam. IR (KBr): 3056*w*, 3033*w*, 2989*w*, 2949*m*, 2900*w*, 2822*w*, 2200*w*, 1723v*s*, 1619v*s*, 1578*m*, 1493*s*, 1436*s*, 1381*s*, 1322*m*, 1287v*s*, 1250*s*, 1217v*s*, 1206v*s*, 1157v*s*, 1111*s*, 1100*m*, 1078*m*, 1068*s*, 1017*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.24 (*t*, *J* = 1.4, 2 H); 8.16 (*s*, 2 H); 8.01 (*dt*, *J* = 7.8, 1.4, 2 H); 7.79 (*d*, *J* = 8.7, 2 H); 7.72 (*dt*, *J* = 7.8, 1.4, 2 H); 7.44 (*t*, *J* = 7.8, 2 H); 7.19–7.17 (*m*, 8 H); 7.10–7.09 (*m*, 4 H); 6.50 (*d*, *J* = 2.2, 2 H); 4.96 (*d*, *AB*, *J* = 5.9, 2 H); 4.90 (*d*, *AB*, *J* = 5.9, 2 H); 4.73 (*d*, *AB*, *J* = 12.5, 2 H); 4.67 (*d*, *AB*, *J* = 12.5, 2 H); 3.94 (*s*, 6 H); 2.61 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.73; 158.16; 153.89; 136.71; 135.77; 135.45; 134.26; 132.87; 130.82; 129.51; 128.85; 128.70; 128.52; 127.55; 126.09; 125.03; 124.14; 119.17; 114.66; 106.71; 99.05; 92.14; 87.92; 77.40; 69.99; 56.32; 52.40. FAB$^+$-MS: 902 (100, M^+), 871 (33, [M – OMe]$^+$), 858 (18, [MH – MOM]$^+$), 841 (10, [M – OMOM]$^+$), 826 (20, [M – OMOM – Me]$^+$), 749 (10, [M – 2 OMOM – OMe]$^+$), 735 (10, [M – 2 OMOM – OMe – Me + H]$^+$), 721 (10, [M – 2 OMOM – CO_2Me]$^+$), 703 (10, [M – 2 OMOM – OMe – O_2Me + H]$^+$). DEI-MS (CH_2Cl_2): 902 (9, M^+), 826 (2, [M – OMOM – Me]$^+$), 721 (1, [M – 2 OMOM – CO_2Me]$^+$), 91 (100, Bn$^+$). HR-DEI-MS (CH_2Cl_2): 902.3116 (M^+, $C_{58}H_{46}O_{10}$; calc. 902.3091).

(±)-Dimethyl 3,3′-{[7,7′-Bis(benzyloxy)-2,2′-dihydroxy-1,1′-binaphthalene-3,3′-diyl]bis(ethyne-1,2-diyl)} Bis(benzoate) ((±)-**31**). To (±)-**33** (100 mg, 0.11 mmol) in THF/MeOH 1:1 (100 ml), conc. HCl (0.1 ml) was added, and the mixture was stirred at r.t. for 12 h. Evaporation *in vacuo* left a solid, which was dissolved in AcOEt. The org. phase was washed with sat. aq. $NaHCO_3$ soln. and H_2O, dried, and evaporated *in vacuo* to yield (±)-**31** (88 mg, 98%). Slightly yellow solid. M.p. 86° (dec., CH_2Cl_2/hexane). IR (KBr): 3421*m* (br.), 3067*w*, 3033*w*, 3009*w*, 2954*w*, 2922*w*, 2867*w*, 2200*w*, 1716v*s*, 1707*s*, 1619v*s*, 1572*m*, 1499*s*, 1450*m*, 1440*s*, 1425*s*, 1400*w*, 1376*s*, 1322*w*, 1293v*s*, 1261*s*, 1222v*s*, 1207v*s*, 1183*s*, 1156*s*, 1135*s*, 1111*s*, 1078*m*, 1022*m*, 1009*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.23 (*t*, *J* = 1.5, 2 H); 8.11 (*s*, 2 H); 8.01 (*dt*, *J* = 7.8, 1.5, 2 H); 7.76 (*d*, *J* = 9.0, 2 H); 7.72 (*dt*, *J* = 7.8, 1.5, 2 H); 7.44 (*t*, *J* = 7.8, 2 H); 7.24–7.08 (*m*, 12 H); 6.45 (*d*, *J* = 2.5, 2 H); 5.84 (br. *s*, 2 H); 4.80 (*d*, *AB*, *J* = 12.1, 2 H); 4.72 (*d*, *AB*, *J* = 12.1, 2 H); 3.90 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.60; 158.90; 151.83; 136.63; 135.83; 135.58; 133.63; 133.02; 130.90; 130.20; 129.85; 128.72; 128.10; 127.75; 124.48; 123.46; 117.71; 112.54; 109.40; 105.06; 94.51; 85.49; 77.59; 69.94; 52.42. FAB$^+$-MS: 814 (100, M^+), 724 (15, [M – CO_2Me – OMe]$^+$). HR-DEI-MS (CH_2Cl_2): 814.2579 (M^+, $C_{54}H_{38}O_8$; calc. 814.2566). X-Ray: see *Fig. 5*.

(±)-Tetrabutylammonium (7,7′-Bis(benzyloxy)-3,3′-bis{[3-(methoxycarbonyl)phenyl]ethynyl}-1,1′-binaphthalene-2,2′-diyl)phosphate ((±)-**34**). To a soln. of (±)-**31** (160 mg, 0.15 mmol) in anh. CH_2Cl_2 (32 ml), $POCl_3$ (52 mg, 0.34 mmol) in anh. CH_2Cl_2 (2.5 ml) was added dropwise, followed by anh. Et_3N (0.63 ml, 457 mg, 4.52 mmol). After stirring for 3 h at r.t., evaporation *in vacuo* gave an oil, which was dissolved in THF/H_2O 5:4 (44 ml). After stirring at 40° for 12 h and addition of CH_2Cl_2 at r.t., the org. phase was washed with H_2O, dried (Na_2SO_4), and evaporated *in vacuo*. The residual solid was recrystallized from CH_2Cl_2 with layered addition of hexane to give a beige powder, which was submitted to ion-exchange chromatography (*Dowex® 50WX8*, Bu_4N^+, MeCN/$CHCl_3$ 1:1) to give (±)-**34** (150 mg, 87%). Yellow foam. IR ($CHCl_3$): 3330*w* (br.), 3226*w* (br.), 3064*w*, 2996*m* (sh), 2965*s*, 2877*m*, 2215*w*, 1720v*s*, 1621v*s*, 1601*m*, 1577*w*, 1497*s*, 1485*m*, 1455*m*, 1439*s*, 1428*m*, 1405*w*, 1380*m*, 1328*m*, 1289v*s*, 1258*s*, 1198*s*, 1168*w*, 1156*w*, 1137*w*, 1024*m*. ^{31}P-NMR (121.5 MHz, $CDCl_3$): 4.26. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.23 (*t*, *J* = 1.4, 2 H); 8.03 (*s*, 2 H); 7.95 (*dt*, *J* = 7.8, 1.4, 2 H); 7.89 (*dt*, *J* = 7.8, 1.4, 2 H); 7.74 (*d*, *J* = 9.0, 2 H); 7.40 (*t*, *J* = 7.8, 2 H); 7.23–7.06 (*m*, 12 H); 6.62 (*d*, *J* = 2.2, 2 H); 4.59 (*d*, *AB*, *J* = 12.0, 2 H); 4.48 (*d*, *AB*, *J* = 12.0, 2 H); 3.91 (*s*, 6 H); 2.99 (br. *s*, 8 H); 1.34 (br. *s*, 8 H); 1.24–1.17 (*m*, 8 H); 0.75 (*t*, *J* = 7.2, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.98; 157.80; 150.76 (*d*, ^2J(C,P) = 10.9); 136.90; 136.79; 133.89; 133.76; 132.73; 130.41; 129.85; 128.99; 128.63; 128.15; 127.55; 125.97; 125.08; 122.20 (*d*, ^3J(C,P) = 2.4); 118.43; 115.14 (*d*, ^3J(C,P) = 2.4); 107.34; 91.41; 88.61; 77.37; 70.05; 58.68; 52.29; 23.93; 19.63; 12.61. NESI-MS (MeOH, CH_2Cl_2): 875.3 (100, [M – Bu_4N]$^-$, $C_{54}H_{36}O_{10}P$; calc. 875.2). FAB$^+$-MS: 1360 (77, [M + Bu_4N]$^+$), 1119 (5, MH$^+$), 242 (100, Bu_4N^+). HR-FAB$^+$-MS: 876.2129 ([MH – Bu_4N]$^+$, $C_{54}H_{37}O_{10}P$; calc. 876.2124).

(±)-Dipotassium Tetrabutylammonium (7,7′-Bis(benzyloxy)-3,3′-bis{[3-(carboxylato)phenyl]ethynyl}-1,1′-binaphthalene-2,2′-diyl)phosphate ((±)-**16**). A slurry of Me_3SiOK (18 mg, 0.138 mmol) in anh. THF (3.5 ml) was added to a soln. of (±)-**34** (22 mg, 0.020 mmol) in anh. THF (1 ml). After stirring the suspension at r.t. for 20 h, the solvent was removed by flushing with N_2. After addition of CH_2Cl_2 (3 ml), the solvent was again removed by flushing with N_2. The residual solid was dissolved in CH_2Cl_2, and addition of hexane led to the precipitation of (±)-**16** (21 mg, 91%), which was isolated by centrifugation. Light-brown hygroscopic solid. M.p. > 202° (dec.). IR (KBr): 3422*w* (br.), 3058*w*, 2958*m*, 2931*m*, 2871*m*, 2209*w*, 1670*m* (sh), 1655*m*, 1619v*s*, 1596*s*, 1586*s* (sh), 1564v*s*, 1495*m*, 1453*m*, 1422*m*, 1380v*s*, 1274*s*, 1260v*s*, 1224*s*, 1205*s*, 1107v*s*, 1022*m*. ^{31}P-NMR

(121.5 MHz, $CDCl_2CDCl_2$): 4.55 (br.). ^{1}H-NMR (500 MHz, $CDCl_2CDCl_2$, 374 K): 8.32 (*s*, 2 H); 8.11 (*s*, 2 H); 7.79 (*d*, *J* = 9.0, 2 H); 7.56–7.52 (*m*, 4 H); 7.19–7.06 (*m*, 14 H); 6.71 (*s*, 2 H); 4.64 (*s*, 4 H); 3.03 (*t*, *J* = 7.7, 8 H); 1.44 (*s*, 8 H); 1.28–1.23 (*m*, 8 H); 0.84 (*t*, *J* = 7.3, 12 H). FAB$^+$-MS: 1612 (13, $[M - K + 2\,Bu_4N]^+$), 1408 (25, $[M + Bu_4N]^+$), 963 (21, $[M - Bu_4N + K + H]^+$), 925 (17, $[M - Bu_4N + 2\,H]^+$), 242 (100, Bu_4N^+). NESI-MS (MeOH, CH_2Cl_2): 885.3 (10, $[M - K - Bu_4N + H]^-$, $C_{52}H_{31}PKO_{10}$; calc. 885.1), 847.2 (9, $[M - 2\,K - Bu_4N + 2\,H]^-$, $C_{52}H_{32}O_{10}P$; calc. 847.2), 543.8 (24, $[M - 2\,K]^{2-}$, 1/2($C_{68}H_{66}O_{10}NP$); calc. 543.7), 423.2 (95, $[M - 2\,K - Bu_4N + H]^{2-}$, 1/2($C_{52}H_{31}O_{10}P$); calc. 423.1), 281.7 (100, $[M - 2\,K - Bu_4N]^{3-}$, 1/3($C_{52}H_{30}O_{10}P$); calc. 281.7).

*(−)-(*R*)-7,7′-Bis(benzyloxy)-3-iodo-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene* ((−)-(*R*)-**35**). This compound was obtained in 3% yield as a side product during the preparation of the corresponding 3,3′-diodo derivative as described in [11b]. M.p. 88–90°. $[\alpha]_D^{rt} = -58.8$ (*c* = 1.00, $CHCl_3$). IR (KBr): 3058*w*, 3028*w*, 2998*w*, 2956*m*, 2926*m*, 2896*m*, 2823*m*, 2781*w*, 1618v*s*, 1572*m*, 1555*m*, 1508v*s*, 1492v*s*, 1451*s*, 1445*s*, 1427*m*, 1376v*s*, 1348*m*, 1318*m*, 1300*w*, 1270*m*, 1258*s*, 1238v*s*, 1220v*s*, 1207v*s*, 1196v*s*, 1154v*s*, 1089*s*, 1068*s*, 1033v*s*, 1012v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.41 (*s*, 1 H); 7.87 (*d*, *J* = 9.0, 1 H); 7.77 (*d*, *J* = 9.0, 1 H); 7.70 (*d*, *J* = 9.0, 1 H); 7.38 (*d*, *J* = 9.0, 1 H); 7.22–7.06 (*m*, 12 H); 6.48 (*d*, *J* = 2.5, 1 H); 6.40 (*d*, *J* = 2.5, 1 H); 5.03 (*d*, *AB*, *J* = 6.9, 1 H); 4.95 (*d*, *AB*, *J* = 6.9, 1 H); 4.76–4.65 (*m*, 4 H); 4.58 (*d*, *AB*, *J* = 5.0, 1 H); 4.45 (*d*, *AB*, *J* = 5.0, 1 H); 3.18 (*s*, 3 H); 2.74 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 157.67 (2×); 153.78; 152.22; 139.07 (2×); 136.98; 136.77; 135.38; 135.28; 129.95; 129.75; 128.72 (2×); 128.63; 128.10; 128.52; 127.70 (2×); 125.82; 125.40; 119.43; 118.99; 117.63; 114.03; 106.21; 106.21; 105.78; 94.90; 89.74; 69.99; 69.91; 56.97; 56.09. DEI-MS (CH_2Cl_2): 712 (49, M^+), 636 (13, $[M - OMOM - Me]^+$), 91 (100, Bn^+). HR-DEI-MS (CH_2Cl_2): 712.1306 (M^+, $C_{38}H_{33}IO_6$; calc. 712.1324).

*(+)-Methyl (*R*)-3-{[7,7′-Bis(benzyloxy)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalen-3-yl]ethynyl}benzoate* ((+)-(*R*)-**36**). A soln. of (−)-(*R*)-**35** (361 mg, 0.51 mmol) in anh. Et_2NH (4 ml) and anh. PhMe (4 ml) was carefully degassed and Ar-saturated by several freeze-pump-thaw cycles. After addition of CuI (4 mg, 0.021 mmol) and $[PdCl_2(dppf)] \cdot CH_2Cl_2$ (17 mg, 0.020 mmol), another degassing cycle was carried out. A soln. of methyl 3-iodobenzoate (162 mg, 1.01 mmol) in anh. Et_2NH (4 ml) and anh. PhMe (4 ml), which had been carefully degassed and Ar-saturated by several freeze-pump-thaw cycles, was slowly added at 40°, and the mixture was stirred at this temp. for 5 h. Evaporation *in vacuo* gave a solid that was dissolved in $CHCl_3$. The org. phase was washed with sat. aq. NH_4Cl soln. and H_2O, dried (Na_2SO_4), and evaporated *in vacuo*. CC (hexane/AcOEt 5:1 → 2:1) yielded (+)-(*R*)-**36** (202 mg, 54%). Foam. UV/VIS ($CHCl_3$): 275 (sh, 35800), 287 (40400), 315 (30400), 329 (29800). $[\alpha]_D^{rt} = +36.4$ (*c* = 1.00, $CHCl_3$). CD ($CHCl_3$): 266 (sh, +23), 285 (+46), 323 (−7), 340 (−8). IR ($CHCl_3$): 3086*w*, 3064*w*, 3007*m*, 2951*w*, 2929*w*, 2907*w*, 2825*w*, 2394*w*, 2207*w*, 1721v*s*, 1622v*s*, 1601*m*, 1579*w*, 1509*s*, 1494*m*, 1453*m*, 1437*s*, 1422*w*, 1403*w*, 1381*m*, 1351*w*, 1324*m*, 1283*s*, 1272*s*, 1240*s*, 1198v*s*, 1155*s*, 1111*m*, 1100*m*, 1080*m*, 1052*m*, 1026*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.26 (*t*, *J* = 1.5, 1 H); 8.16 (*s*, 1 H); 8.01 (*dt*, *J* = 7.8, 1.5, 1 H); 7.88, 7.80, 7.79 (3*d*, *J* = 9.0, 3 H); 7.74 (*dt*, *J* = 7.8, 1.5, 1 H); 7.45 (*t*, *J* = 7.8, 1 H); 7.41 (*d*, *J* = 9.0, 1 H); 7.22–7.08 (*m*, 12 H); 6.51 (*d*, *J* = 2.5, 1 H); 6.49 (*d*, *J* = 2.5, 1 H); 5.07 (*d*, *AB*, *J* = 6.8, 1 H); 4.93 (*d*, *AB*, *J* = 6.8, 1 H); 4.87 (*d*, *AB*, *J* = 5.4, 1 H); 4.84 (*d*, *AB*, *J* = 5.4, 1 H); 4.80–4.69 (*m*, 4 H); 3.94 (*s*, 3 H); 3.17 (*s*, 3 H); 2.74 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.77; 158.16; 157.50; 153.78; 153.50; 137.00; 136.72; 135.83 (2×); 135.58; 135.38; 133.97; 132.86; 130.80; 129.69; 129.62; 129.43; 128.83; 128.68; 128.65; 128.08; 127.96; 127.73; 127.68; 126.29; 125.54; 125.52; 124.30; 119.61; 118.83; 117.57; 114.92; 114.41; 106.21; 105.86; 98.95; 95.16; 91.81; 88.29; 69.88 (2×); 56.45; 56.01; 52.40. FAB$^+$-MS: 744 (100, M^+), 713 (12, $[M - OMe]^+$), 700 (11, $[M - CHOMe]^+$), 669 (16, $[M - OMOM - CH_2]^+$), 91 (34, Bn^+). HR-FAB$^+$-MS: 744.2721 (M^+, $C_{48}H_{40}O_8$; calc. 744.2723).

*(+)-Methyl (*R*)-3-{[7,7′-Bis(benzyloxy)-2,2′-dihydroxy-1,1′-binaphthalen-3-yl]ethynyl}benzoate* ((+)-(*R*)-**37**). To (*R*)-**36** (202 mg, 0.27 mmol) in THF (80 ml), a soln. of conc. HCl (37%, 320 mg) in MeOH (80 ml) was added, and the mixture was stirred at r.t. for 24 h. After evaporation *in vacuo* to half of the original volume, the product was extracted with CH_2Cl_2 (3 × 25 ml). Evaporation *in vacuo* yielded (+)-(*R*)-**37** (178 mg, 99%). Foam. $[\alpha]_D^{rt} = +61.5$ (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 3525*m*, 3063*w*, 3033*w*, 3006*w*, 1953*m*, 2928*m*, 2854*w*, 2202*w*, 1722v*s*, 1621v*s*, 1578*w*, 1514*m*, 1498*s*, 1454*m*, 1440*s*, 1426*m*, 1378*m*, 1294*s* (sh), 1284*s*, 1272*s*, 1260*s*, 1197v*s*, 1153*m*, 1137*m*, 1113*m*, 1079*w*, 1023*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.26 (*t*, *J* = 1.4, 1 H); 8.14 (*s*, 1 H); 8.02 (*dt*, *J* = 7.9, 1.4, 1 H); 7.87, 7.80, 7.78 (3*d*, *J* = 8.9, 3 H); 7.74 (*dt*, *J* = 7.9, 1.4, 1 H); 7.45 (*t*, *J* = 7.9, 1 H); 7.24–7.09 (*m*, 13 H); 6.49 (*d*, *J* = 1.9, 1 H); 6.48 (*d*, *J* = 2.2, 1 H); 5.66 (br. *s*, 2 H); 4.83–4.72 (*m*, 4 H); 3.91 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.62; 159.15; 158.13; 152.97; 152.59; 136.85; 136.46; 136.87 (2×); 135.61; 134.83; 134.26; 133.05; 130.96; 130.87; 130.24; 130.17; 129.85; 128.93; 128.70 (2×); 128.18; 128.04; 127.87; 127.75; 125.01; 124.56; 123.49; 117.97; 116.66; 115.40; 111.21; 109.56; 105.05; 104.85; 94.31; 85.52; 69.99; 69.89; 52.44. FAB$^+$-MS: 656 (100, M^+), 566 (15, $[MH - Bn]^+$), 91 (34, Bn^+). HR-FAB$^+$-MS: 656.2202 (M^+, $C_{44}H_{32}O_6$; calc. 656.2199).

*(−)-Tetrabutylammonium ((*R*)-7,7′-Bis(benzyloxy)-3-{[3-(methoxycarbonyl)phenyl]ethynyl}-1,1′-binaphthalene-2,2′-diyl)phosphate* ((−)-(*R*)-**38**). To a soln. of (−)-(*R*)-**37** (134 mg, 0.20 mmol) in anh. CH_2Cl_2

(41 ml), $POCl_3$ (69 mg, 0.45 mmol) was added dropwise, followed by anh. Et_3N (0.85 ml, 617 mg, 6.10 mmol). After stirring for 3 h at r.t., evaporation *in vacuo* gave an oil which was dissolved in THF/H_2O 5:4 (58 ml). After stirring at 40° for 12 h, the soln. was evaporated *in vacuo* to half of its original volume and CH_2Cl_2 (25 ml) was added. The org. phase was washed with H_2O, dried (Na_2SO_4), and evaporated *in vacuo*. The residual solid was recrystallized from CH_2Cl_2 with layered addition of hexane to give, after centrifugation, a yellow solid, which was submitted to ion-exchange chromatography (*Dowex® 50WX8*, Bu_4N^+, MeCN/$CHCl_3$ 1:1). The isolated solid was dissolved in AcOEt (2 ml) and hexane was added (20 ml) to precipitate (−)-(*R*)-**38** (178 mg, 91%), which was isolated by centrifugation. Beige solid. M.p. >157° (dec.). $[\alpha]_D^{r.t.} = -253.0$ ($c = 1.01$, $CHCl_3$). IR (KBr): 3423*m* (br.), 3060*w*, 3030*w*, 2958*s*, 2933*m*, 2871*m*, 2213*w*, 1720*s*, 1621v*s*, 1599*m*, 1577*w*, 1510*m*, 1495*m*, 1453*m*, 1439*s*, 1381*m*, 1327*m*, 1296v*s*, 1287v*s* (sh), 1257*m*, 1234*s*, 1225*s*, 1205v*s*, 1104v*s*, 1012*m*. ^{31}P-NMR (121.5 MHz, $CDCl_3$): 5.43. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.26 (*t*, *J* = 1.4, 1 H); 8.05 (*s*, 1 H); 7.95 (*dt*, *J* = 7.8, 1.4, 1 H); 7.84 (*dt*, *J* = 7.8, 1.4, 1 H); 7.80, 7.76, 7.72 (3*d*, *J* = 8.8, 3 H); 7.42 (*d*, *J* = 8.8, 1 H); 7.39 (*t*, *J* = 7.8, 1 H); 7.22–7.05 (*m*, 12 H); 6.71 (*d*, *J* = 2.4, 1 H); 6.69 (*d*, *J* = 2.4, 1 H); 4.59 (*d*, *AB*, *J* = 11.5, 1 H); 4.55 (*s*, 2 H); 4.54 (*d*, *AB*, *J* = 11.5, 1 H); 3.91 (*s*, 3 H); 2.96 (*t*, *J* = 7.7, 8 H); 1.33–1.25 (*m*, 8 H); 1.19–1.14 (*m*, 8 H); 0.79 (*t*, *J* = 7.2, 12 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 166.55; 157.43; 156.72; 151.41 (*d*, ^2J(C,P) = 9.3); 150.47 (*d*, ^2J(C,P) = 9.5); 136.70; 136.53; 136.48; 133.66; 133.62; 133.36; 133.00; 132.33; 130.18; 129.92; 129.69; 129.49; 128.71; 128.41; 128.36; 127.85; 127.80; 127.34; 127.26; 126.30; 125.64; 124.81; 122.55 (*d*, ^3J(C,P) = 1.9); 121.13 (*d*, ^3J(C,P) = 1.7); 120.62 (*d*, ^3J(C,P) = 1.3); 118.43; 117.23; 115.03 (*d*, ^3J(C,P) = 1.9); 107.42; 107.07; 91.07; 88.61; 69.97; 69.85; 58.21; 52.16; 23.73; 19.52; 13.58. FAB$^+$-MS: 1202 (100, $[M + Bu_4N]^+$), 960 (30, MH^+), 719 (21, $[M - Bu_4N + 2\,H]^+$), 242 (74, Bu_4N^+). HR-FAB$^+$-MS: 960.4601 (MH^+, $C_{60}H_{67}NO_8P$; calc. 960.4604).

*(−)-Potassium Tetrabutylammonium ((*R*)-7,7′-Bis(benzyloxy)-3-[[3-(carboxylato)phenyl]ethynyl]-1,1′-binaphthalene-2,2′-diyl)phosphate* ((−)-(*R*)-**17**). A slurry of Me_3SiOK (4.7 mg, 36.5 μmol) in anh. THF (1 ml) was added to a soln. of (−)-(*R*)-**38** in anh. THF (1 ml). The resulting suspension was stirred at r.t. for 24 h, and the solvent was removed by flushing with N_2. After addition of CH_2Cl_2 (3 ml), the solvent was again removed by flushing with N_2. The residual solid was dissolved in CH_2Cl_2, and the product was precipitated by addition of hexane to give (−)-(*R*)-**17** (13 mg, 93%) after centrifugation. Beige solid. M.p. >107° (dec.). $[\alpha]_D^{r.t.} = -191.2$ ($c = 0.50$, $CHCl_3$). IR (KBr): 3422*m* (br.), 3061*w*, 3030*w*, 2958*s*, 2934*w*, 2872*m*, 2212*w*, 1951*w* (br.), 1700*m*, 1620v*s*, 1508*m*, 1494*m*, 1454*m*, 1442*m*, 1381*m*, 1264*s*, 1224v*s* (sh), 1205v*s*, 1100*s*, 1087*s*, 1025*m*. ^{31}P-NMR (121.5 MHz, CD_3CN): 4.79. ^{1}H-NMR (500 MHz, CD_3CN): 8.18 (*s*, 1 H); 8.10 (br. *s*, 1 H); 7.97, 7.92, 7.90 (3*d*, *J* = 8.8, 3 H); 7.68–7.65 (*m*, 2 H); 7.34 (*d*, *J* = 8.8, 1 H); 7.30 (*t*, *J* = 7.8, 1 H); 7.22–7.02 (*m*, 12 H); 6.68 (*d*, *J* = 2.5, 1 H); 6.67 (*d*, *J* = 2.3, 1 H); 4.68 (*d*, *AB*, *J* = 12.2, 1 H); 4.67 (*s*, 2 H); 4.64 (*d*, *AB*, *J* = 12.2, 1 H); 3.07 (*m*, 8 H); 1.60–1.54 (*m*, 8 H); 1.37–1.29 (*m*, 8 H); 0.95 (*t*, *J* = 7.4, 12 H). NESI-MS (MeOH): 944.7 (8, $[M - K]^-$, $C_{59}H_{63}O_8NP$; calc. 944.4), 703.2 (50, $[M - K - Bu_4N + H]^-$, $C_{43}H_{28}O_8P$ requires 703.2), 351.2 (100, $[M - K - Bu_4N]^{2-}$, 1/2($C_{43}H_{27}O_8P$); calc. 351.1).

*(−)-(*R*)-7,7′-Bis(benzyloxy)-3-ethynyl-2,2′-bis(methoxymethoxy)-3′-[(trimethylsilyl)ethynyl]-1,1′-binaphthalene* ((−)-(*R*)-**41**). A soln. of (−)-(*R*)-**40** [11b] (619 mg, 0.79 mmol) and borax (1.52 g, 3.99 mmol) in THF/H_2O 11:10 (670 ml) was stirred at r.t. for 4 h. The org. solvent was evaporated *in vacuo* at r.t., the aq. phase was extracted with CH_2Cl_2 (3 × 80 ml), and the combined org. extracts were dried (Na_2SO_4). After evaporation *in vacuo*, CC (hexane/AcOEt 5:1 with 0.5% Et_3N) gave starting material (−)-(*R*)-**40** (413 mg, 67%) and product (−)-(*R*)-**41** (175 mg, 31%; 98% based on reacted (−)-(*R*)-**40**). White solid, which precipitated out of the concentrated pure fractions. M.p. 99–100°. $[\alpha]_D^{r.t.} = -48.7$ ($c = 1.00$, $CHCl_3$). IR (KBr): 3244*m*, 3056*w*, 3033*w*, 2944*m*, 2900*w*, 2822*w*, 2144*m*, 1619v*s*, 1492*s*, 1450*m*, 1400*m*, 1378*s*, 1356*m*, 1317*w*, 1283*w*, 1242v*s*, 1217v*s*, 1189*s*, 1157v*s*, 1144*s*, 1094*m*, 1069*s*, 1022*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.09 (*s*, 1 H); 8.07 (*s*, 1 H); 7.75 (*d*, *J* = 9.0, 1 H); 7.72 (*d*, *J* = 9.0, 1 H); 7.19–7.17 (*m*, 6 H); 7.15 (*dd*, *J* = 9.0, 2.5, 1 H); 7.13 (*dd*, *J* = 9.0, 2.5, 1 H); 7.08–7.06 (*m*, 4 H); 6.43 (*d*, *J* = 2.5, 1 H); 6.41 (*d*, *J* = 2.5, 1 H); 4.94 (*d*, *AB*, *J* = 5.9, 1 H); 4.83 (*d*, *AB*, *J* = 5.9, 1 H); 4.83 (*d*, *AB*, *J* = 5.9, 1 H); 4.79 (*d*, *AB*, *J* = 5.9, 1 H); 4.70 (*d*, *AB*, *J* = 12.1, 1 H); 4.69 (*d*, *AB*, *J* = 12.1, 1 H); 4.65 (*d*, *AB*, *J* = 12.1, 1 H); 4.64 (*d*, *AB*, *J* = 12.1, 1 H); 3.29 (*s*, 1 H); 2.59 (*s*, 3 H); 2.55 (*s*, 3 H); 0.27 (*s*, 9 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 157.77; 157.75; 153.85; 153.78; 136.42; 136.40; 135.28; 135.06; 134.64; 134.49; 129.14; 129.12; 128.40 (2×); 127.76; 127.75; 127.30; 127.27; 125.63 (2×); 124.81; 124.46; 118.88; 118.76; 114.58; 113.71; 106.37 (2×); 102.20; 98.70; 98.51; 98.20; 80.87; 80.76; 69.79; 69.73; 56.17; 55.99; −0.10. DEI-MS (CH_2Cl_2): 706 (100, M^+), 676 (9, $[M - 2\,Me]^+$), 630 (21, $[M - OMOM - Me]^+$), 584 (4, $[M - 2\,OMOM]^+$), 539 (20), 511 (16, $[M - 2\,OMOM - SiMe_3]^+$), 91 (79, Bn^+). Anal. calc. for $C_{45}H_{42}O_6Si$ (706.91): C 76.46, H 5.99; found: C 76.28, H 6.12.

Methyl 2-(3,3-Diethyltriaz-1-enyl)-5-iodobenzoate (**42**). A suspension of methyl 2-amino-5-iodobenzoate [31] (5.0 g, 18.1 mmol) in 6M aq. HCl soln. (10 ml) and MeCN (20 ml) was cooled to 0°, and a soln. of $NaNO_2$ (1.4 g, 20.3 mmol) in H_2O (5 ml) was added dropwise. The mixture was stirred at 0° for 2 h and subsequently

added to an ice-cold soln. of K_2CO_3 (3.7 g, 26.8 mmol) and Et_2NH (2.8 ml, 2.0 g, 27.07 mol) in H_2O (40 ml). The mixture was stirred at 0° for 30 min and extracted with Et_2O (2 × 30 ml). The combined org. extracts were washed with H_2O (3 × 20 ml), dried ($MgSO_4$), and evaporated *in vacuo*. CC (hexane/AcOEt 5:1) provided **42** (6.3 g, 97%). Orange liquid. IR ($CHCl_3$): 2980*m*, 2933*m*, 2878*w*, 1724v*s*, 1606*w*, 1578*w*, 1465*s*, 1452v*s*, 1435v*s*, 1413v*s*, 1389v*s*, 1351v*s*, 1342v*s*, 1331v*s*, 1293v*s*, 1265v*s*, 1254v*s*, 1140*m*, 1112*s*, 1083v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.91 (*d*, *J* = 2.2, 1 H); 7.68 (*dd*, *J* = 8.7, 2.2, 1 H); 7.17 (*d*, *J* = 8.7, 1 H); 3.85 (*s*, 3 H); 3.74 (*q*, *J* = 7.0, 4 H); 1.27 (br. *s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.95; 150.01; 140.44; 138.12; 128.36; 121.26; 87.92; 52.23; 49.33; 41.79; 14.50; 11.22. DEI-MS (CH_2Cl_2): 361 (20, M^+), 330 (4, $[M - OMe]^+$), 289 (60, $[M - NEt_2]^+$), 261 (100, $[M - N_3Et_2]^+$), 246 (13, $[M - N_3Et_2 - Me]^+$), 231 (11, $[M - N_3Et_2 - OMe + H]^+$), 203 (25, $[M - N_3Et_2 - CO_2Me + H]^+$). Anal. calc. for $C_{12}H_{16}IN_3O_2$ (361.18): C 39.91, H 4.46, N 11.63, I 35.14; found: C 40.09, H 4.67, N 11.62, I 35.04.

*(−)-Methyl (*R*)-5-({7,7′-Bis(benzyloxy)-2,2′-bis(methoxymethoxy)-3′-[(trimethylsilyl)ethynyl]-1,1′-binaphthalen-3-yl}ethynyl)-2-(3,3-diethyltriaz-1-enyl)benzoate* ((−)-(*R*)-**43**). A soln. of **42** (115 mg, 0.32 mmol) in anh. Et_2NH (4 ml) was carefully degassed and Ar-saturated by several freeze-pump-thaw cycles. After addition of CuI (11 mg, 0.058 mmol) and $[PdCl_2(dppf)] \cdot CH_2Cl_2$ (10 mg, 0.012 mmol), another degassing cycle was carried out. A soln. of (−)-(*R*)-**41** (149 mg, 0.21 mmol) in anh. PhMe (4 ml, freshly distilled from Na) was carefully degassed and Ar-saturated by several freeze-pump-thaw cycles and then slowly added at 40°. After stirring at this temp. for 3.5 h, the solvent was evaporated *in vacuo*, and the residual solid was dissolved in $CHCl_3$. The org. phase was washed with sat. aq. NH_4Cl soln. and H_2O, dried (Na_2SO_4), and evaporated *in vacuo*. CC (hexane/AcOEt 5:1 with 0.5% Et_3N) yielded dimer (−)-(*R*,*R*)-**44** (24 mg, 16%; see below for characterization) in addition to the desired product (−)-(*R*)-**43** (151 mg, 76%). Yellow foam. $[\alpha]_D^{r.t.} = -76.2$ (*c* = 1.01, $CHCl_3$). IR ($CHCl_3$): 3022*w*, 3008*m*, 2953*m*, 2822*w*, 2152*w*, 1724*s*, 1620v*s*, 1493*s*, 1461*s*, 1450*s*, 1436*s*, 1382v*s*, 1344*s*, 1330*s*, 1289*m*, 1244v*s*, 1158*s*, 1139*m*, 1111*s*, 1075*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.11 (*s*, 1 H); 8.08 (*s*, 1 H); 7.81 (*d*, *J* = 1.9, 1 H); 7.76 (*d*, *J* = 9.3, 1 H); 7.73 (*d*, *J* = 9.3, 1 H); 7.57 (*dd*, *J* = 8.3, 1.9, 1 H); 7.43 (*d*, *J* = 8.3, 1 H); 7.20–7.05 (*m*, 12 H); 6.46 (*d*, *J* = 2.5, 1 H); 6.45 (*d*, *J* = 2.5, 1 H); 4.98–4.83 (*m*, 4 H); 4.73–4.62 (*m*, 4 H); 3.88 (*s*, 3 H); 3.78 (*q*, *J* = 7.2, 4 H); 2.59 (*s*, 3 H); 2.56 (*s*, 3 H); 1.42–1.04 (br. *m*, 6 H); 0.27 (*s*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.74; 158.08; 157.97; 154.20; 153.84; 149.91; 136.77; 136.74; 135.43; 135.28; 134.72; 134.49; 133.92; 132.86; 129.40 (2×); 128.67 (2×); 128.00 (2×); 127.57; 127.53; 126.87; 126.13; 125.92; 124.99; 124.95; 119.62; 119.36; 119.04; 115.06; 114.85; 106.70 (2×); 102.52; 98.95; 98.79; 98.35; 92.85; 87.43; 77.42; 69.96; 69.91; 56.27; 56.17; 52.13; 49.33 (br.); 41.84 (br.); 14.53 (br.); 11.20 (br.); −0.06. FAB$^+$-MS: 940 (100, MH^+), 939 (87, M^+), 908 (15, $[M - OMe]^+$), 733 (15, $[M - N_3Et_2 - OEt - Et]^+$), 91 (71, Bn^+). HR-FAB$^+$-MS: 940.3983 (MH^+, $C_{57}H_{58}N_3O_8Si$; calc. 940.3993).

*(−)-(*R,R*)-3,3′-(Buta-1,3-diynediyl)bis{7,7′-bis(benzyloxy)-2,2′-bis(methoxymethoxy)-3′-[(trimethylsilyl)ethynyl]-1,1′-binaphthalene}* ((−)-(*R*,*R*)-**44**). A mixture of (*R*)-**41** (120 mg, 0.17 mmol) and CuCl (1.01 g, 10.19 mmol) in CH_2Cl_2 (500 ml; freshly distilled from CaH_2) was vigorously stirred in open air for 15 min. After addition of TMEDA (1.6 ml, 1.22 g, 10.52 mmol), the dark-green mixture was vigorously stirred in open air at r.t. for 3 h. Addition of H_2O (500 ml) gave a biphasic mixture that was stirred until all blue color had disappeared in the org. layer (*ca.* 1 h). The org. phase was separated, washed with sat. aq. NH_4Cl soln. and H_2O, and dried (Na_2SO_4). Evaporation *in vacuo* gave (−)-(*R*,*R*)-**44** (119 mg, 99%). White solid. M.p. 84–85° (CH_2Cl_2/hexane). UV/VIS ($CHCl_3$): 252 (160200), 267 (166200), 279 (84400), 296 (60000), 351 (53400), 380 (50400). $[\alpha]_D^{r.t.} = -72.9$ (*c* = 1.0, $CHCl_3$). CD ($CHCl_3$): 265 (+260), 280 (−200), 294 (sh, −82), 318 (+48), 354 (−18), 380 (−10). IR (KBr): 3067*w*, 3034*w*, 2945*m*, 2911*m*, 2145*w*, 1722*w*, 1618v*s*, 1492*s*, 1450*m*, 1379*s*, 1243v*s*, 1222*s*, 1206*s*, 1189*s*, 1156*s*, 1095*m*, 1072*s*, 1011*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.13 (*s*, 2 H); 8.08 (*s*, 2 H); 7.74 (*d*, *J* = 9.0, 2 H); 7.73 (*d*, *J* = 9.0, 2 H); 7.20–7.18 (*m*, 12 H); 7.15 (*dd*, *J* = 9.0, 2.5, 2 H); 7.14 (*dd*, *J* = 9.0, 2.5, 2 H); 7.08–7.05 (*m*, 8 H); 6.43 (*d*, *J* = 2.5, 2 H); 6.41 (*d*, *J* = 2.5, 2 H); 4.97–4.78 (*m*, 8 H); 4.73–4.61 (*m*, 8 H); 2.68 (*s*, 6 H); 2.55 (*s*, 6 H); 0.26 (*s*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 158.34; 158.13; 154.44; 154.16; 136.71; 136.63; 135.80; 135.51; 135.28; 134.83; 129.49; 129.43; 128.67 (2×); 128.04; 127.55; 127.50; 125.96; 125.88; 125.14; 124.56; 119.24; 119.04; 114.82; 113.83; 106.70; 106.58; 102.34; 99.13; 98.77; 98.46; 79.76; 77.84; 77.35; 69.99; 69.93; 56.45; 56.16; −0.08. FAB$^+$-MS: 1411 (31, M^+), 91 (100, Bn^+). Anal. calc. for $C_{90}H_{82}O_{12}Si_2$ (1411.81): C 76.57, H 5.85; found: C 76.56, H 5.97.

*(−)-Methyl (*R*)-5-({7,7′-Bis(benzyloxy)-2,2′-bis(methoxymethoxy)-3′-[(trimethylsilyl)ethynyl]-1,1′-binaphthalen-3-yl}ethynyl)-2-iodobenzoate* ((−)-(*R*)-**45**). A soln. of (−)-(*R*)-**43** (39 mg, 0.04 mmol) in MeI (2 ml) in a *Schlenk* tube was carefully degassed and Ar-saturated by several freeze-pump-thaw cycles. The tube was sealed and the soln. heated for 14 h at 130°. The mixture was then filtered at r.t. and concentrated by distillation. The residual solid was filtered through a short plug of SiO_2 (hexane/AcOEt 5:1 with 0.5% of Et_3N) to give (−)-(*R*)-**45** (40 mg, 99%). Yellow foam. $[\alpha]_D^{r.t.} = -67.3$ (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 3056*w*, 3011*w*, 2956*s*, 2928*s*, 2856*m*,

2431*w*, 2389*w*, 2211*w*, 2144*w*, 1731*s*, 1620v*s*, 1494*s*, 1460*m*, 1450*m*, 1438*m*, 1406*m*, 1378*s*, 1283*s*, 1247v*s*, 1158*s*, 1138*m*, 1099*m*, 1065*m*, 1010*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.13 (*s*, 1 H); 8.09 (*s*, 1 H); 7.99 (*d*, *J* = 8.1, 1 H); 7.98 (*d*, *J* = 2.2, 1 H); 7.77 (*d*, *J* = 9.0, 1 H); 7.74 (*d*, *J* = 9.0, 1 H); 7.29 (*dd*, *J* = 8.1, 2.2, 1 H); 7.20–7.05 (*m*, 12 H); 6.45 (*d*, *J* = 3.1, 1 H); 6.44 (*d*, *J* = 3.1, 1 H); 4.96 (*d*, *AB*, *J* = 5.9, 1 H); 4.89 (*d*, *AB*, *J* = 5.9, 1 H); 4.84 (*d*, *AB*, *J* = 5.9, 1 H); 4.82 (*d*, *AB*, *J* = 5.9, 1 H); 4.71 (*d*, *AB*, *J* = 12.1, 1 H); 4.71 (*d*, *AB*, *J* = 12.1, 1 H); 4.64 (br. *d*, *AB*, *J* = 12.1, 2 H); 3.95 (*s*, 3 H); 2.60 (*s*, 3 H); 2.53 (*s*, 3 H); 0.27 (*s*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.57; 158.18; 158.13; 154.20; 153.76; 141.80; 136.71; 136.68; 135.62; 135.53; 135.32; 135.03; 134.83; 134.20; 133.94; 129.48; 129.44; 128.67 (2×); 128.02 (2×); 127.52 (2×); 126.05; 125.92; 125.16; 124.70; 123.94; 119.24; 119.03; 114.84; 114.35; 106.73; 106.62; 102.38; 99.03; 98.80; 98.48; 93.85; 91.15; 89.44; 69.96; 69.93; 56.35; 56.14; 52.73; −0.08. FAB$^+$-MS: 966 (100, M^+), 935 (53, $[M-OMe]^+$), 890 (29, $[M-OMOM-Me]^+$). HR-FAB$^+$-MS: 966.2088 (M^+, $C_{53}H_{47}IO_8Si$; calc. 966.2087).

*(−)-Methyl (*R*)-5-{[7,7′-Bis(benzyloxy)-3′-ethynyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthalen-3-yl]ethynyl}-2-iodobenzoate* ((−)-(*R*)-**46**). To a soln. of (−)-(*R*)-**45** (108 mg, 0.11 mmol) in THF/MeOH 1:1 (20 ml), K_2CO_3 (103 mg, 0.75 mmol) was added, and the mixture was stirred at r.t. for 3 h. After addition of $CHCl_3$ (20 ml), the org. phase was washed with H_2O and dried (Na_2SO_4). The solvent was evaporated *in vacuo* to yield (−)-(*R*)-**46** (93 mg, 93%). White solid. M.p. 143° (dec.; $CHCl_3$/hexane). UV/VIS ($CHCl_3$): 260 (72300), 289 (39300), 315 (31100), 328 (30900), 342 (28600). $[\alpha]_D^{rt} = -32.0$ (*c* = 1.01, $CHCl_3$). IR (KBr): 3233*m*, 3056*w*, 3033*w*, 2956*m*, 2911*m*, 2211*w*, 1728*s*, 1618v*s*, 1544*w*, 1494*s*, 1467*m*, 1456*m*, 1450*m*, 1433*m*, 1378v*s*, 1283*m*, 1239v*s*, 1205v*s*, 1189*s*, 1156v*s*, 1139*s*, 1100*m*, 1061*s*, 1028*s*, 1017*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.13 (*s*, 1 H); 8.11 (*s*, 1 H); 7.99 (*d*, *J* = 8.7, 1 H); 7.98 (*d*, *J* = 2.2, 1 H); 7.77 (*d*, *J* = 9.0, 1 H); 7.75 (*d*, *J* = 9.0, 1 H); 7.29 (*dd*, *J* = 8.7, 2.2, 1 H); 7.20–7.06 (*m*, 12 H); 6.45 (br. *s*, 2 H); 4.90–4.81 (*m*, 4 H); 4.70–4.64 (*m*, 4 H); 3.95 (*s*, 3 H); 3.30 (*s*, 1 H); 2.62 (*s*, 3 H); 2.59 (*s*, 3 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 166.16; 157.87; 157.83; 153.80; 153.40; 141.48; 136.32; 136.31; 135.23; 135.18; 135.15; 134.71; 133.96; 133.61; 129.23; 129.18; 128.36 (2×); 127.74; 127.72; 127.21 (2×); 125.71; 125.59; 125.45; 124.69; 124.57; 123.59; 118.94; 118.84; 114.08; 113.69; 106.43; 106.30; 98.74; 98.71; 93.68; 90.98; 89.14; 80.88; 80.76; 69.78; 69.74; 56.13; 56.09; 52.57. DEI-MS (CH_2Cl_2): 894 (2, M^+), 127 (3, I^+), 91 (100, Bn^+). FAB$^+$-MS: 894 (74, M^+), 863 (22, $[M-OMe]^+$), 850 (21, $[MH-MOM]^+$), 819 (24, $[M-OMOM-Me+H]^+$), 91 (41, Bn^+). HR-FAB$^+$-MS: 894.1690 (M^+, $C_{50}H_{39}IO_8$, calc. 894.1691).

*(−)-(*R,R*)-3,3′-(Buta-1,3-diynediyl)bis[7,7′-bis(benzyloxy)-3′-ethynyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene]* ((−)-(*R*,*R*)-**47**). To a soln. of (−)-(*R*,*R*)-**44** (159 mg, 0.11 mmol) in THF/MeOH 1:1 (20 ml), K_2CO_3 (103 mg, 0.74 mmol) was added, and the mixture was stirred at r.t. for 3 h. After addition of AcOEt (20 ml), the org. phase was washed with H_2O and dried (Na_2SO_4). Evaporation *in vacuo* yielded (−)-(*R*,*R*)-**47** (134 mg, 94%). Yellow amorphous solid. $[\alpha]_D^{rt} = -17.6$ (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 3300*w*, 2945*m*, 2927*s*, 2856*m*, 1722*w*, 1619*m*, 1600*m*, 1464*w*, 1461*w*, 1456*w*, 1378*w*, 1262v*s*, 1239*m*, 1189*w*, 1156*m*, 1098v*s*, 1013v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.14 (*s*, 2 H); 8.10 (*s*, 2 H); 7.75 (*d*, *J* = 9.0, 2 H); 7.75 (*d*, *J* = 9.0, 2 H); 7.24–7.06 (*m*, 24 H); 6.43 (br. *s*, 4 H); 4.86–4.73 (*m*, 8 H); 4.71–4.64 (*m*, 8 H); 3.30 (*s*, 2 H); 2.69 (*s*, 6 H); 2.61 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 158.47; 158.24; 154.49; 154.16; 136.69; 136.63; 135.80; 135.61; 135.48; 135.11; 129.59; 129.51; 128.70 (2×); 128.08 (2×); 127.55 (2×); 125.97; 125.92; 125.03; 124.77; 119.28; 119.17; 113.99; 113.85; 106.73; 106.58; 99.13; 98.95; 81.10; 79.84; 77.88; 76.80; 70.02 (2×); 56.43; 56.30. FAB$^+$-MS: 1267 (39, M^+), 1191 (21, $[M-OMOM-Me]^+$), 91 (100, Bn^+). HR-FAB$^+$-MS: 1266.4551 (M^+, $C_{84}H_{66}O_{12}$; calc. 1266.4554).

*(−)-Dimethyl (*R,R*)-5,5′-({3,3′-(Buta-1,3-diynediyl)bis[7,7′-bis(benzyloxy)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene-3,3′-diyl]}bis(ethyne-1,2-diyl))-2,2′-bis(3,3′-diethyltriaz-1-enyl)dibenzoate* ((−)-(*R*,*R*)-**48**). A soln. of **42** (85 mg, 0.24 mmol) in anh. Et_2NH (3 ml) was carefully degassed and Ar-saturated by several freeze-pump-thaw cycles. After addition of CuI (9 mg, 0.047 mmol) and $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (8 mg, 0.009 mmol), another degassing cycle was carried out. A soln. of (−)-(*R*,*R*)-**47** (100 mg, 0.08 mmol) in anh. PhMe (3 ml, freshly distilled from Na), which had been carefully degassed and Ar-saturated by several freeze-pump-thaw cycles, was slowly added at 40°, and the mixture was stirred at this temp. for 2 h. Evaporation *in vacuo* gave a solid that was dissolved in $CHCl_3$. The org. phase was washed with sat. aq. NH_4Cl soln. and H_2O, dried (Na_2SO_4), evaporated *in vacuo*. CC (hexane/AcOEt 7:5 with 0.5% Et_3N), gave (−)-(*R*,*R*)-**48** (80 mg, 58%). Yellow amorphous solid. $[\alpha]_D^{rt} = -342.0$ (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 3056*w*, 3011*m*, 2956*m*, 2933*m*, 2856*w*, 2400*w*, 2356*w*, 2344*w*, 2211*w*, 2133*w*, 1722*m*, 1617v*s*, 1489*s*, 1467*s*, 1444*s*, 1433*s*, 1383*s*, 1333*m*, 1294*m*, 1261*s*, 1239v*s*, 1156*s*, 1106*m*, 1078*s*, 1011*m*, 994*m*, 944*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.15 (*s*, 2 H); 8.13 (*s*, 2 H); 7.82 (*d*, *J* = 1.9, 2 H); 7.77 (*d*, *J* = 9.0, 2 H); 7.76 (*d*, *J* = 9.0, 2 H); 7.57 (*dd*, *J* = 8.4, 1.9, 2 H); 7.44 (*d*, *J* = 8.4, 2 H); 7.20–7.07 (*m*, 24 H); 6.48 (*d*, *J* = 2.3, 2 H); 6.46 (*d*, *J* = 2.3, 2 H); 4.98–4.82 (*m*, 8 H); 4.75–4.67 (*m*, 8 H); 3.88 (*s*, 6 H); 3.78 (br. *q*, *J* = 6.4, 8 H); 2.72 (*s*, 6 H); 2.63 (*s*, 6 H); 1.28–1.26 (br. *s*, 12 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 168.36; 158.06; 157.70; 154.13; 153.49; 149.58; 136.41; 136.31; 135.50; 135.24; 134.84; 134.20; 133.75;

132.55; 129.24; 129.19; 128.39 (2×); 127.89 (2×); 127.25; 127.23; 126.53; 125.82; 125.68; 124.89; 124.36; 119.27; 119.08; 118.99; 118.79; 114.78; 113.60; 106.46; 106.37; 98.91; 98.71; 92.70; 87.11; 79.62; 77.66; 69.81; 69.79; 56.31; 56.12; 52.00; 49.18 (br.); 41.80 (br.); 14.41 (br.); 11.13 (br.). FAB$^+$-MS: 1734 (100, M^+, $^{13}C^{12}C_{107}H_{96}N_6O_{16}$), 91 (28, Bn^+). HR-FAB$^+$-MS: 1732.6885 (M^+, $C_{108}H_{96}N_6O_{16}$; calc. 1732.6882).

*(−)-Dimethyl (*R,R*)-5,5′-({3,3′-(Buta-1,3-diynediyl)bis[7,7′-bis(benzyloxy)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene-3,3′-diyl]}bis(ethyne-1,2-diyl))-2,2′-diiodo Dibenzoate* ((−)-(*R,R*)-**39**). a) *From (−)-(*R,R*)-**48***. A soln. of (−)-(*R,R*)-**48** (33 mg, 19.0 μmol) in MeI (2 ml), in a *Schlenk* tube was carefully degassed and Ar-saturated by several freeze-pump-thaw cycles. The tube was sealed and the soln. heated for 14 h at 130°. The mixture was filtered at r.t. and concentrated by distillation, and the residual solid was purified by filtration through a short plug of SiO_2 (hexane/AcOEt 7:5 with 0.5% of Et_3N) to give (−)-(*R,R*)-**39** (34 mg, 99%).

b) *From (−)-(*R*)-**46***. A mixture of (−)-(*R*)-**46** (120 mg, 0.17 mmol) and CuCl (1.01 g, 10.19 mmol) in CH_2Cl_2 (500 ml, freshly distilled from CaH_2) was vigorously stirred in open air at r.t. for 15 min. After addition of TMEDA (1.6 ml, 1.22 g, 10.52 mmol), the dark-green mixture was vigorously stirred in open air for 3 h. Addition of H_2O (500 ml) gave a biphasic mixture that was stirred until the blue color had disappeared in the org. layer (*ca.* 1 h). The org. phase was separated, washed with sat. aq. NH_4Cl soln. and H_2O, and dried (Na_2SO_4). Evaporation *in vacuo* gave (−)-(*R,R*)-**39** (120 mg, 99%). Amorphous yellow solid. UV/VIS ($CHCl_3$): 282 (92500), 293 (87100), 331 (82570), 348 (83600), 380 (39500). $[\alpha]_D^{r.t.} = -185.4$ ($c = 1.01$, $CHCl_3$). CD ($CHCl_3$): 270 (+136), 298 (−120), 325 (+5), 359 (−45), 380 (−29). IR ($CHCl_3$): 3061*w*, 3056*w*, 3015*w*, 2959*m*, 2915*m*, 2859*w*, 2395*w*, 2206*w*, 2139*w*, 1731*m*, 1619*s*, 1493*m*, 1464*m*, 1447*m*, 1436*m*, 1375*m*, 1286*m*, 1262v*s*, 1241*s*, 1192*m*, 1159*s*, 1099v*s*, 1016v*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.15 (*s*, 2 H); 8.13 (*s*, 2 H); 7.98 (*d*, $J = 8.4$, 2 H); 7.98 (*d*, $J = 2.2$, 2 H); 7.77 (*d*, $J = 9.0$, 2 H); 7.76 (*d*, $J = 9.0$, 2 H); 7.29 (*dd*, $J = 8.4, 2.2$, 2 H); 7.21–7.07 (*m*, 24 H); 6.45 (br. *s*, 4 H); 4.92–4.80 (*m*, 8 H); 4.75–4.68 (*m*, 8 H); 3.95 (*s*, 6 H); 2.68 (*s*, 6 H); 2.62 (*s*, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.22; 158.15; 157.96; 145.16; 143.44; 141.52; 136.34; 136.29; 135.45; 135.35; 135.21; 135.20; 134.76; 134.08; 133.67; 129.33; 129.31; 128.42 (2×); 127.81 (2×); 127.26; 127.23; 125.76; 125.71; 124.72; 124.55; 123.62; 119.02 (2×); 114.12; 113.57; 106.42 (2×); 98.96; 98.84; 93.73; 91.07; 89.11; 79.59; 77.71; 69.86; 69.82; 56.31; 56.22; 52.63. FAB$^+$-MS: 1787 (M^+, $^{13}C^{12}C_{99}H_{76}I_2O_{16}$). HR-FAB$^+$-MS: 1786.3222 ($M^+$, $C_{100}H_{76}I_2O_{16}$; calc. 1786.3226).

*(−)-Dimethyl (*R,R,R,R*)-2,2′-Bis({7,7′-bis(benzyloxy)-2,2′-bis(methoxymethoxy)-3′-[(trimethylsilyl)ethynyl]-1,1′-binaphthalen-3-yl}ethynyl)-5,5′-({3,3′-(buta-1,3-diynediyl)bis[7,7′-bis(benzyloxy)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene-3,3′-diyl]}bis(ethyne-1,2-diyl)) Dibenzoate* ((−)-(*R,R,R,R*)-**49**). A soln. of (−)-(*R,R*)-**39** (72 mg, 0.040 mmol) in anh. Et_2NH (1.5 ml) and anh. PhMe (1.5 ml) was carefully degassed and Ar-saturated by several freeze-pump-thaw cycles. After addition of CuI (1.6 mg, 0.008 mmol) and $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (3.5 mg, 0.005 mmol), another degassing cycle was carried out. A soln. of (−)-(*R*)-**41** (108 mg, 0.153 mmol) in anh. Et_2NH (2.5 ml) and anh. PhMe (2.5 ml), carefully degassed and Ar-saturated by several freeze-pump-thaw cycles, was then slowly added *via* syringe pump (2.25 ml·h^{-1}) at 35°. The mixture was further stirred at this temp. for another 3.5 h. Evaporation *in vacuo* gave a solid which was dissolved in $CHCl_3$. The org. phase was washed with sat. aq. NH_4Cl soln. and H_2O, dried (Na_2SO_4), and evaporated *in vacuo*. CC (hexane/AcOEt 5:1 → 7:5 with 0.5% Et_3N) afforded dimer (−)-(*R,R*)-**44** (24 mg, 22% based on (−)-(*R*)-**41**) in addition to a mixture of (−)-(*R,R,R*)-**50** and (−)-(*R,R,R,R*)-**49**. The above procedure was repeated and the combined mixtures of trimer and tetramer subjected to preparative GPC (*Bio-Rad Bio-Beads® S-X1*, 200–400 mesh; CH_2Cl_2), to afford the desired product (−)-(*R,R,R,R*)-**49** (144 mg, 61% based on (−)-(*R,R*)-**39**) together with (−)-(*R,R,R*)-**50** (21 mg, 11% based on (−)-(*R,R*)-**39**).

*Data of (−)-(*R,R,R,R*)-**49***: Amorphous bright-yellow solid. UV/VIS ($CHCl_3$): 266 (240600), 280 (sh, 126200), 302 (139800), 361 (sh, 155300), 355 (sh, 150300), 379 (170400). $[\alpha]_D^{r.t.} = -344.8$ ($c = 1.0$, $CHCl_3$). CD ($CHCl_3$): 266 (+175), 279 (sh, +170), 301 (−130), 371 (sh, −50), 386 (−140). IR ($CHCl_3$): 3056*w*, 3000*m*, 2956*m*, 2928*s*, 2856*m*, 2211*w*, 2144*w*, 1722*m*, 1619v*s*, 1492v*s*, 1450*m*, 1439*m*, 1406*w*, 1381*s*, 1289*m*, 1261*s*, 1244v*s*, 1189*s*, 1158v*s*, 1100*m*, 1078*m*, 1011*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.20, 8.152, 8.145, 8.07 (4*s*, 8 H); 8.18 (*s*, 2 H); 7.781, 7.779, 7.76, 7.72 (4*d*, $J = 9.5$, 8 H); 7.63 (*s*, 4 H); 7.20–7.17 (*m*, 24 H); 7.15 (*dd*, $J = 9.5, 2.5$, 8 H); 7.08–7.06 (*m*, 16 H); 6.46, 6.45, 6.44 (3*d*, $J = 2.5$, 4 H, 2 H, 2 H); 4.99–4.83 (*m*, 16 H); 4.71–4.66 (*m*, 16 H); 4.00 (*s*, 6 H); 2.69, 2.63, 2.56, 2.50 (4*s*, 24 H); 0.26 (*s*, 18 H). ^{13}C-NMR (125.8 MHz): 165.85; 158.15; 157.95; 157.82; 157.72; 154.16; 153.85; 153.49; 153.33; 136.42 (2×); 136.37; 136.32; 135.48; 135.45; 135.37; 135.34; 135.18; 135.13; 135.44; 134.41; 134.11; 134.08; 133.56; 131.67; 129.32 (2×); 129.10; 128.44 (2×); 128.41 (2×); 127.82 (2×); 127.76 (2×); 127.46 (2×); 127.32; 127.27; 125.83; 125.80; 125.72; 125.65; 124.78; 124.63; 124.54; 123.56; 123.09; 119.04; 118.99; 118.85; 118.82; 114.60; 114.56; 114.25; 113.60; 106.42 (4×); 102.25; 98.97; 98.89; 98.86; 98.55; 98.17; 93.91; 91.88; 91.75; 89.51; 79.61; 77.72; 70.56; 69.87; 69.86; 69.76 (2×); 68.47; 56.33; 56.23; 56.07; 56.03; 52.41; −0.09. FAB$^+$-MS: 2946 (100, MH^+, $^{13}C_2^{12}C_{188}H_{159}O_{28}Si_2$). MALDI-TOF-MS (HABA): 2968.8 (100, [*M* +

Na]$^+$, $^{13}C_2{}^{12}C_{188}H_{158}NaO_{28}Si_2$; calc. 2968.0), 2924.1 (9, [M + Na − 3 Me + H]$^+$, $^{13}C_2{}^{12}C_{185}H_{150}NaO_{28}Si_2$; calc. 2924.0), 2895.7 (7, [M + Na − $SiMe_3$ + H]$^+$, $^{13}C_2{}^{12}C_{185}H_{150}NaO_{28}Si$; calc. 2896.0).

*(−)-Methyl (*R,R,R*)-5-({3′-[({3′-[[4-({7,7′-Bis(benzyloxy)-2,2′-(methoxymethoxy)-3′-[(trimethylsilyl)ethynyl]-1,1′-binaphthalene-3-yl}ethynyl)-3-(methoxycarbonyl)phenyl]ethynyl]{7,7′-bis(benzyloxy)-2,2′-(methoxymethoxy)-1,1′-binaphthalene-3-yl})buta-1,3-diynyl]{7,7′-bis(benzyloxy)-2,2′-(methoxymethoxy)-1,1′-binaphthalen-3-yl}ethynyl)-2-iodobenzoate* (−)-((*R*,*R*,*R*)-**50**). Amorphous yellow solid. UV/VIS ($CHCl_3$): 265 (sh, 175200), 280 (120300), 298 (110800), 325 (105700), 353 (113500), 380 (112100). $[\alpha]_D^{rt} = -263.4$ ($c = 1.0$, $CHCl_3$). CD ($CHCl_3$): 266 (+170), 299 (−120), 327 (+8), 360 (sh, −28), 285 (−79). IR ($CHCl_3$): 3060*w*, 3008*m*, 2956*m*, 2926*m*, 2860*w*, 2204*w*, 2148*w*, 1729*s*, 1619v*s*, 1492v*s*, 1458*m*, 1449*s*, 1435*m*, 1381*s*, 1291*s*, 1258v*s*, 1244v*s*, 1191*s*, 1158v*s*, 1102*s*, 1079*s*, 1016*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.29–8.08 (*m*, 7 H); 7.98 (*d*, J = 8.2, 1 H); 7.98 (*d*, J = 2.1, 1 H); 7.79–7.72 (*m*, 6 H); 7.63 (*s*, 2 H); 7.29 (*dd*, J = 8.2, 2.1, 1 H); 7.20–7.16 (*m*, 18 H); 7.14 (*dd*, J = 8.8, 2.5, 6 H); 7.08–7.06 (*m*, 12 H); 6.47–6.44 (*m*, 6 H); 5.01–4.81 (*m*, 12 H); 4.74–4.66 (*m*, 12 H); 4.00, 3.94 (2*s*, 6 H); 2.69, 2.68, 2.634, 2.627, 2.57, 2.51 (6*s*, 18 H); 0.27 (*s*, 9 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 166.24; 165.85; 158.15 (2×); 157.97; 157.95; 157.82; 157.72; 154.17 (2×); 153.85; 153.50; 153.44; 153.33; 141.53; 136.42 (2×); 136.39; 136.37; 136.35; 136.31; 135.51; 135.49; 135.45; 135.36; 135.34; 135.21 (2×); 135.18; 135.13; 134.78; 134.44; 134.41; 134.10; 134.08; 133.68; 133.56; 131.67; 129.31 (2×); 128.43 (3×); 128.41 (3×); 127.81 (3×); 127.76 (3×); 127.32 (2×); 127.27 (4×); 125.82; 125.80; 125.77; 125.72 (2×); 125.65; 124.79 (2×); 124.72; 124.63; 124.61; 124.57; 124.53; 123.63; 123.56; 123.08; 119.03 (2×); 118.98 (2×); 118.85; 118.82; 114.59; 114.56; 114.25; 114.12; 113.60; 113.58; 106.44 (6×); 102.25; 98.97 (2×); 98.89; 98.86; 98.84; 98.71; 98.55; 98.16; 93.92; 93.73; 91.88; 91.74; 91.07; 89.50; 89.12; 79.63; 79.61; 79.58; 79.56; 77.74; 77.69; 77.43; 69.87 (2×); 69.83 (2×); 69.76 (2×); 68.45; 56.33 (2×); 56.23 (2×); 56.07; 56.03; 52.64; 52.41; −0.09. MALDI-TOF-MS (HABA): 2388.9 (100, [M + Na]$^+$, $^{13}C^{12}C_{144}H_{117}INaO_{22}Si$; calc. 2388.7), 2344.4 (33, [M + Na − 3 Me + H]$^+$, $^{13}C^{12}C_{141}H_{109}INaO_{22}Si$; calc. 2344.6), 2316.4 (34, [M + Na − $SiMe_3$ + H]$^+$, $^{13}C^{12}C_{141}H_{109}INaO_{22}$; calc. 2316.6), 2262.6 (43, [M + Na − I + H]$^+$, $^{13}C^{12}C_{144}H_{118}NaO_{22}Si$; calc. 2262.8).

*(−)-Dimethyl (*R,R,R,R*)-2,2′-Bis{[7,7′-bis(benzyloxy)-2,2′-bis(methoxymethoxy)-3′-ethynyl-1,1′-binaphthalene-3-yl]ethynyl}-5,5′-({3,3′-(buta-1,3-diynediyl)bis[7,7′-bis(benzyloxy)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene-3,3′-diyl]}bis(ethyne-1,2-diyl))dibenzoate* ((−)-(*R*,*R*,*R*,*R*)-**51**). To a soln. of (−)-(*R*,*R*,*R*,*R*)-**49** (30 mg, 0.010 mmol) in THF/MeOH 1:1 (4 ml), K_2CO_3 (10 mg, 0.072 mmol) was added, and the mixture was stirred at r.t. for 2.5 h. After addition of $CHCl_3$ (10 ml), the org. phase was washed with H_2O and dried (Na_2SO_4). Evaporation *in vacuo* yielded (−)-(*R*,*R*,*R*,*R*)-**51** (29 mg, 99%). Amorphous yellow solid. $[\alpha]_D^{rt} = -263.6$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3304*w*, 3065*w*, 3023*w*, 3246*w*, 2929*m*, 2201*w*, 1728*m*, 1619v*s*, 1492v*s*, 1449*m*, 1407*w*, 1291*m*, 1238v*s*, 1193*s*, 1158v*s*, 1137*m*, 1098*w*, 1079*m*, 1010*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.21, 8.16, 8.15, 8.11 (4*s*, 8 H); 8.19 (*s*, 2 H); 7.81–7.74 (*m*, 8 H); 7.64 (*s*, 4 H); 7.20–7.07 (*m*, 48 H); 6.48, 6.47, 6.46, 6.45 (4*d*, J = 2.5, 8 H); 5.02–4.83 (*m*, 16 H); 4.75–4.66 (*m*, 16 H); 4.00 (*s*, 6 H); 3.30 (*s*, 2 H); 2.70, 2.64, 2.63, 2.54 (4*s*, 24 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 165.82; 158.14; 157.94; 157.88; 157.80; 154.16; 153.79; 153.49; 153.35; 136.40; 136.38; 136.36; 136.31; 135.47; 135.34; 135.30; 135.28; 135.17; 134.65; 134.47; 134.09; 134.08; 133.55; 131.68; 129.35; 129.32; 129.13; 128.42 (2×); 128.40 (2×); 127.80 (2×); 127.77 (2×); 127.29; 127.26 (2×); 127.24; 125.80; 125.79; 125.71; 125.63; 124.79; 124.77; 124.59; 124.53; 123.51; 123.11; 119.02; 118.98; 118.90; 118.82; 114.62; 114.23; 113.71; 113.59; 107.07; 106.43; 106.39; 105.77; 98.96; 98.86 (2×); 98.70; 93.83; 91.86; 91.78; 89.52; 80.88; 80.77; 79.60; 77.71; 69.86; 69.83 (2×); 69.81 (2×); 69.76; 56.32; 56.21; 56.20; 55.99; 52.40. MALDI-TOF-MS (HABA): 2823.7 (100, [M + Na]$^+$, $^{13}C_2{}^{12}C_{182}H_{142}NaO_{28}$; calc. 2824.0), 2779.7 (12, [M + Na − 3 Me + H]$^+$, $^{13}C_2{}^{12}C_{179}H_{134}NaO_{28}$; calc. 2779.9).

*(−)-(*R,R,R,R*)-16,57-Bis(methoxycarbonyl)-13,14,19,20,35,36,37,38,53,54,59,60,75,76,77,78-hexadecadehydro-81,82,83,86,87,88,89,92-octakis(methoxymethoxy)-3,8,25,30,43,48,65,70-octakis(phenylmethoxy)-15,18:55,58-dietheno-5,79:6,12:21,27:28,34:39,45:46,52:61,67:68,74-octamethenooctabenzo[*a,e,o,s,g_1,k_1,u_1,y_1*]cyclotetrahexacontene* ((−)-(*R*,*R*,*R*,*R*)-**52**). To a mixture of (−)-(*R*,*R*,*R*,*R*)-**51** (23 mg, 8.03 μmol) and freshly prepared CuCl [53] (159 mg, 1.61 mmol), anh. CH_2Cl_2 (24 ml, freshly distilled over CaH_2 and sat. with dried air) was added. The mixture was vigorously stirred under dried air for 5 min (vigorous stirring at this stage reduces the particle size of CuCl, accelerating the rate of reaction upon addition of TMEDA). After addition of TMEDA (192 mg, 1.66 mmol), the mixture turned dark-green, and vigorous stirring under a weak flow of anh. air was continued for 40 min at 25°. H_2O (75 ml) was added to give a biphasic mixture, which was stirred until the blue color in the org. layer had disappeared (*ca.* 30 min). The org. phase was separated, washed with sat. aq. NH_4Cl soln. and H_2O, dried (Na_2SO_4), and evaporated *in vacuo*. Filtration through a short plug SiO_2 (hexane/AcOEt 1:1 with 0.5% of Et_3N), followed by prep. GPC (*NovoGROM GPC 1000* column, 10 μm, 300 × 8 mm; PhMe), gave a solid that was dissolved in AcOEt. Precipitation with hexane and centrifugation afforded (−)-(*R*,*R*,*R*,*R*)-**52** (18 mg, 77%). Light-yellow solid. M.p. >114° (dec.). UV/VIS ($CHCl_3$): 280 (179400), 298

(132500), 321 (sh, 131400), 341 (sh, 155200), 367 (175900). $[\alpha]_D^{rt} = -570.8$ ($c = 0.50$, $CHCl_3$). CD ($CHCl_3$): 260 (+130), 270 (+125), 302 (+205), 329 (−70), 383 (−260). IR ($CHCl_3$): 3088*w*, 3066*w*, 3034*w*, 3007*m*, 2958*m*, 2928*m*, 2868*w*, 2855*w*, 2212*w*, 2143*w*, 1729*w*, 1619v*s*, 1492*s*, 1448*m*, 1381*m*, 1293*m*, 1261v*s*, 1243*s*, 1193*m*, 1157*s*, 1142*m* (sh), 1098*s*, 1079*s*, 1071*s*, 1013*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.19, 8.133, 8.125 (3*s*, 2 H, 4 H, 2 H); 8.174–8.169 (*m*, 2 H); 7.79, 7.78, 7.75, 7.74 (4*d*, $J = 9.1$, 8 H); 7.63–7.62 (*m*, 4 H); 7.21–7.05 (*m*, 48 H); 6.46–6.45 (*m*, 8 H); 5.04–4.82 (*m*, 16 H); 4.73–4.62 (*m*, 16 H); 4.00 (*s*, 6 H); 2.69, 2.67, 2.58, 2.50 (4*s*, 24 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 165.86; 158.13; 158.05; 157.92; 157.90; 154.47; 154.45; 153.73; 153.60; 136.45; 136.42; 136.36; 136.35; 135.56; 135.49; 135.21; 135.18; 134.26; 134.19; 133.47; 131.66; 129.41; 129.36; 129.34; 129.27; 128.43 (4×); 127.81 (4×); 127.25 (4×); 125.81 (2×); 125.69 (2×); 124.92; 124.81; 124.58; 124.50; 123.53; 123.14; 119.04 (2×); 118.94; 118.84; 114.73; 114.34; 113.62 (2×); 106.51 (2×); 106.19; 106.47; 99.06; 99.02; 98.97; 98.92; 93.64; 91.86; 91.80; 89.35; 79.40; 79.35; 77.70; 77.66; 77.57; 77.42; 69.86 (4×); 69.79 (2×); 56.38; 56.35; 56.23; 56.06; 52.40. MALDI-TOF-MS (HABA): 2822.3 (100, $[M + Na]^+$, $^{13}C_2{}^{12}C_{182}H_{140}NaO_{28}$; calc. 2821.9), 2778.3 (21, $[M + Na - 3\ Me + H]^+$, $^{13}C_2{}^{12}C_{179}H_{132}NaO_{28}$; calc. 2777.9).

*(−)-(*R,R,R,R*)-16,57-Bis(methoxycarbonyl)-13,14,19,20,35,36,37,38,53,54,59,60,75,76,77,78-hexadecadehydro-3,8,25,30,43,48,65,70-octakis(phenylmethoxy)-15,18:55,58-dietheno-5,79:6,12:21,27:28,34:39,45:46,52:61,67:68,74-octamethenooctabenzo[*a,e,o,s,g_1,k_1,u_1,y_1*]cyclotetrahexacontene-81,82,83,86,87,88,89,92-octol* ((−)-(*R,R,R,R*)-**53**). To recrystallized (−)-(*R,R,R,R*)-**52** (18 mg, 6.43 μmol) in THF (12 ml), a soln. of conc. HCl (37%, 48 mg) in MeOH (12 ml) was slowly added at 0°. The mixture was stirred at r.t. for 15 h, then CH_2Cl_2 (15 ml) was added and the org. phase washed with H_2O. Evaporation *in vacuo* yielded (−)-(*R,R,R,R*)-**53** (15 mg, 95%). Yellow solid. M.p. >201° (dec.; AcOEt/hexane). UV/VIS ($CHCl_3$): 281 (185600), 324 (sh, 120600), 376 (184200), 400 (sh, 116800). $[\alpha]_D^{rt} = -933.6$ ($c = 0.50$, $CHCl_3$). CD ($CHCl_3$): 271 (+270), 303 (+180), 329 (−47), 349 (sh, +52), 361 (+65), 392 (−340). IR (KBr): 3500*s*, 3413*s*, 3061*w*, 3028*w*, 2950*w*, 2922*w*, 2861*w*, 2194*w*, 2128*w*, 1714*m*, 1620v*s*, 1494*s*, 1452*m*, 1434*m*, 1378*m*, 1265*s*, 1256*s*, 1220*s*, 1207v*s*, 1160*m*, 1138*m*, 1106*w*, 1076*w*, 1022*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.29 (*s*, 2 H); 8.12, 8.10, 8.090, 8.087 (4*s*, 8 H); 7.78–7.69 (*m*, 12 H); 7.24–7.04 (*m*, 48 H); 6.42–6.41 (*m*, 8 H); 5.61–5.57 (br. *m*, 8 H); 4.81–4.64 (*m*, 16 H); 3.86 (*s*, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 165.39; 158.92; 158.69; 158.62; 158.46; 154.02; 152.57; 152.40; 151.67; 136.46; 136.34; 136.30; 136.28; 136.24; 135.74; 135.71; 135.44; 134.77; 134.60 (2×); 134.20; 133.39; 133.23; 132.73 (2×); 130.06; 130.01; 129.99; 129.83; 128.47; 128.44 (2×); 128.37; 127.91; 127.89; 127.86; 127.78; 127.46 (2×); 127.44; 127.42; 124.70; 124.16; 124.09; 123.92; 123.84; 122.45; 117.66; 117.63; 117.37; 117.15; 114.46; 113.93; 112.43; 111.84; 109.40; 108.96; 108.39; 108.11; 105.26; 104.91 (3×); 95.20; 93.92; 93.06; 86.91; 79.17; 78.74; 78.66; 78.36; 69.83; 69.79; 69.75; 69.68; 52.08. MALDI-TOF-MS (HABA): 2490.9 (30, $[M + 2\ Na - 2\ H]^+$, $^{13}C_2{}^{12}C_{166}H_{106}Na_2O_{20}$; calc. 2490.7), 2468.9 (100, $[MH + Na]^+$, $^{13}C_2{}^{12}C_{166}H_{107}NaO_{20}$; calc. 2468.7), 2446.9 (19, M^+, $^{13}C_2{}^{12}C_{166}H_{108}O_{20}$; calc. 2446.8).

*(−)-*N,N,N-*Tributyl-1-butanaminium (*R,R,R,R*)-16,57-Bis(methoxycarbonyl)-13,14,19,20,35,36,37,38,53,54,59,60,75,76,77,78-hexadecadehydro-83,88,95,100-tetrahydroxy-3,8,25,30,43,48,65,70-octakis(phenylmethoxy)-15,18:55,58-dietheno-5,79,6,12:21,27,28,34:39,45,46,52:61,67,68,74-tetrakis(methynoxyphosphinidenoxymethyno)octabenzo[*a,e,o,s,g_1,k_1,u_1,y_1*]cyclotetrahexacontene-83,88,95,100-tetraoxide (4:1)* ((−)-(*R,R,R,R*)-**3**). To (−)-(*R,R,R,R*)-**53** (14 mg, 5.72 μmol) in anh. CH_2Cl_2 (5 ml), $POCl_3$ in anh. CH_2Cl_2 (1 ml, 50.35 mM soln., 7.7 mg, 50.35 μmol) was added dropwise, followed by anh. Et_3N (0.1 ml, 72.60 mg, 0.72 mmol). The soln. was stirred for 3 h at r.t., and the solvent was evaporated *in vacuo* to give an oil that was dissolved in THF/H_2O 15:8 (11.5 ml). After stirring at 40° for 12 h, the soln. was condensed *in vacuo* to half of its original volume, and CH_2Cl_2 (15 ml) was added. The org. phase was washed with H_2O, dried (Na_2SO_4), and evaporated *in vacuo*. Recrystallization from CH_2Cl_2 with layered addition of hexane, followed by centrifugation, gave a yellow solid, which was submitted to ion-exchange chromatography (*Dowex® 50WX8*, Bu_4N^+, MeCN/$CHCl_3$ 1:1) to give (−)-(*R,R,R,R*)-**3** (18 mg, 86%). Bright-yellow solid. M.p. >191° (dec.; CH_2Cl_2/hexane). UV/VIS ($CHCl_3$): 281 (196700), 346 (165500), 363 (169000). $[\alpha]_D^{rt} = -497.0$ ($c = 0.50$, $CHCl_3$). CD ($CHCl_3$): 256 (−220), 285 (+300), 306 (−110), 322 (sh, −27), 345 (sh, −67), 360 (−97), 379 (−175). IR (KBr): 3423*m* (br.), 3059*w*, 3030*w*, 2960*s*, 2933*m*, 2872*m*, 2204*w*, 2136*w*, 1728*w*, 1715*w* (sh), 1618v*s*, 1493v*s*, 1452*m*, 1444*m*, 1380*m*, 1292*s*, 1246*s*, 1205v*s*, 1160*w*, 1139*w*, 1100v*s*, 1023*m*. ^{31}P-NMR (121.5 MHz, $CDCl_3$): 3.98. ^{1}H-NMR (500 MHz, CD_3CN): 8.25, 8.22, 8.21 (3*s*, 4 H, 2 H, 2 H); 8.13 (*d*, $J = 2.1$, 2 H); 7.94–7.86 (*m*, 8 H); 7.79–7.74 (*m*, 4 H); 7.23–7.05 (*m*, 48 H); 6.64–6.62 (*m*, 8 H); 4.70–4.63 (*m*, 16 H); 4.03 (*s*, 6 H); 3.06 (*t*, $J = 8.3$, 32 H); 1.59–1.52 (*m*, 32 H); 1.33–1.26 (*m*, 32 H); 0.91 (*t*, $J = 7.3$, 48 H). ^{1}H-NMR (500 MHz, $CDCl_3$): 8.18–8.09 (*m*, 10 H); 7.78–7.71 (*m*, 12 H); 7.24–7.05 (*m*, 48 H); 6.63–6.62 (*m*, 8 H); 4.62–4.55 (*m*, 16 H); 4.05 (*s*, 6 H); 3.10 (br. *s*, 32 H); 1.46 (br. *s*, 32 H); 1.23 (br. *s*, 32 H); 0.81 (br. *s*, 48 H). NESI-MS (MeOH, 2,4,6-tris(perfluoroheptyl/nonyl)-1,3,5-triazine, NH_4^+): 1368.1 (18, $[M - 4\ Bu_4N + 2\ Na]^{2-}$, 1/2($^{13}C^{12}C_{167}H_{100}Na_2O_{28}P_4$); calc. 1367.8), 1366.2 (28, $[M - 4\ Bu_4N + Na + NH_4]^{2-}$, 1/2($^{13}C^{12}C_{167}H_{104}NNaO_{28}P_4$); calc. 1365.3), 1357.1 (77, $[M - 4\ Bu_4N + H + Na]^{2-}$, 1/2($^{13}C^{12}C_{167}H_{101}NaO_{28}$-

Pa); calc. 1356.8), 1346.1 (100, $[M-4\,Bu_4N+2\,H]^{2-}$, 1/2($^{13}C^{12}C_{167}H_{102}O_{28}P_4$); calc. 1345.8). MALDI-TOF-MS (HABA): 3661.8 (11, $[M+2\,H]^+$, $^{13}C_2{}^{12}C_{230}H_{246}N_4O_{28}$; calc. 3661.7), 3442.7 (25, $[M-Bu_4N+2\,H+Na]^+$, $^{13}C_2{}^{12}C_{214}H_{210}N_3NaO_{28}P_4$; calc. 3442.4), 3420.7 (100, $[M-Bu_4N+3\,H]^+$, $^{13}C_2{}^{12}C_{214}H_{211}N_3O_{28}P_4$; calc. 3420.4), 3178.0 (9, $[M-2\,Bu_4N+3\,H]^+$, $^{13}C_2{}^{12}C_{198}H_{175}N_2NaO_{28}P_4$; calc. 3178.1). FAB^+-MS: 3177 (8, $[M-2\,Bu_4N+2\,H]^+$, $^{13}C_2{}^{12}C_{198}H_{174}N_2NaO_{28}P_4$; calc. 3177), 242 (100, Bu_4N^+).

(−)-Potassium N,N,N-*Tributyl-1-butanaminium (*R,R,R,R*)-16,57-Bis(carboxylato)-13,14,19,20,35,36,37,38, 53,54,59,60,75,76,77,78-hexadecadehydro-83,88,95,100-tetrahydroxy-3,8,25,30,43,48,65,70-octakis(phenylmethoxy)-15,18:55,58-dietheno-5,79,6,12:21,27,28,34:39,45,46,52:61,67,68,74-tetrakis(methynoxyphosphinidenoxymethyno)octabenzo[*a,e,o,s,g$_1$,k$_1$,u$_1$,y$_1$*]cyclotetrahexacontene-83,88,95,100-tetraoxide (2:4:1)* ((−)-(*R,R,R,R*)-**4**). A slurry of Me_3SiOK (2.2 mg, 17.15 μmol) in anh. THF (0.5 ml) was added to a soln. of (−)-(*R,R,R,R*)-**3** (8.0 mg, 2.19 μmol) in anh. THF (0.5 ml). The resulting suspension was stirred at r.t. for 20 h, and the solvent was removed by flushing with N_2. After addition of CH_2Cl_2 (3 ml), the solvent was again removed by flushing with N_2. The residual solid was dissolved in CH_2Cl_2, and the product was precipitated by addition of hexane to give (−)-(*R,R,R,R*)-**4** (7.8 mg, 96%) after centrifugation. Light-brown solid. M.p. >173° (dec.). UV/VIS ($CHCl_3$): 280 (131400), 346 (100900), 360 (102700). $[\alpha]_D^{rt.}=-346.0$ ($c=0.10$, $CHCl_3$). CD ($CHCl_3$): 252 (−21), 278 (+21), 293 (sh, +2), 306 (−6), 342 (−11), 358 (−12), 387 (−12), 409 (sh, −7). IR (KBr): 3416v*s*, 3059*w*, 3029*w*, 2960*s*, 2374*m*, 2204*w*, 2134*w*, 1174*w*, 1619v*s*, 1583*m*, 1495*s*, 1453*m*, 1431*m*, 1376*m*, 1265*s*, 1250*s*, 1217*s*, 1205*s*, 1156*w*, 1143*w*, 1101*s*, 1023*m*. ^{31}P-NMR (121.5 MHz, $(CD_3)_2SO$): 4.87. ^{1}H-NMR (500 MHz, $(CD_3)_2SO$, 394 K): 8.27–8.19 (*m*, 2 H); 8.25, 8.17, 8.03 (3*s*, 4 H, 2 H, 2 H); 7.96–7.88 (*m*, 8 H); 7.60–7.06 (*m*, 52 H); 6.82–6.58 (*m*, 8 H); 4.91–4.74 (*m*, 16 H); 3.18 (*t*, $J=8.3$, 32 H); 1.65–1.59 (*m*, 32 H); 1.39–1.32 (*m*, 32 H); 0.94 (*t*, $J=7.4$, 48 H). NESI-MS (MeOH): 1390 (57, $[M-4\,Bu_4N+Na+H_3O]^{2-}$, 1/2($^{13}C_2{}^{12}C_{164}H_{97}K_2NaO_{29}P_4$); calc. 1390.2), 1370 (64, $[M-4\,Bu_4N+2\,H]^{2-}$, 1/2($^{13}C_2{}^{12}C_{164}H_{96}K_2O_{28}P_4$); calc. 1370.2), 920 (57, $[M-4\,Bu_4N+Na]^{3-}$, 1/3($^{13}C_2{}^{12}C_{164}H_{94}K_2NaO_{28}P_4$); calc. 920.5), 913 (100, $[M-4\,Bu_4N+H]^{3-}$, 1/3($^{13}C_2{}^{12}C_{164}H_{95}K_2O_{28}P_4$); calc. 913.1), 901 (48, $[M-4\,Bu_4N-K+2\,H]^{3-}$, 1/3($^{13}C_2{}^{12}C_{164}H_{96}KO_{28}P_4$); calc. 900.5).

Methyl 2,5-Bis(phenylethynyl)benzoate (**56**). A soln. of methyl 2,5-diiodobenzoate [51] (obtained by esterification of commercially available 2,5-diiodobenzoic acid, 757 mg, 1.95 mmol) in anh. Et_2NH (10 ml) was carefully degassed and Ar-saturated by several freeze-pump-thaw cycles. After addition of CuI (8 mg, 0.04 mmol) and $[PdCl_2(dppf)]\cdot CH_2Cl_2$ (32 mg, 0.04 mmol), another degassing cycle was carried out. Phenylacetylene (0.65 ml, 605 mg, 5.92 mmol) was added at 40°, and the mixture was stirred at this temp. for 3 h. Evaporation *in vacuo* gave a solid which was dissolved in CH_2Cl_2 (25 ml). The org. phase was washed with sat. aq. NH_4Cl soln. and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. CC (hexane → hexane/AcOEt 50:1) afforded **56** (628 mg, 96%). Needle-shaped crystals. M.p. 74–76° (hexane). IR (KBr): 3053*m*, 2991*w*, 2946*w*, 2206*m*, 1735v*s*, 1721v*s*, 1594*w*, 1570*w*, 1535*w*, 1503*s*, 1440*s*, 1326*m*, 1284*s*, 1238v*s*, 1190*m*, 1179*m*, 1157*m*, 1133*m*, 1074v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.16–8.15 (*m*, 1 H); 7.63–7.53 (*m*, 6 H); 7.40–7.35 (*m*, 6 H); 3.99 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.36; 134.54; 134.28; 133.97; 132.27; 132.08; 131.98; 129.01; 128.73; 128.68 (2×); 123.55; 123.42; 123.37; 122.99; 96.40; 92.24; 88.38; 88.35; 52.46. FAB^+-MS: 336 (100, M^+), 321 (22, $[M-Me]^+$), 305 (22, $[M-OMe]^+$). Anal. calc. for $C_{24}H_{16}O_2$ (336.39): C 85.69, H 4.79; found: C 85.55, H 4.89.

Potassium 2,5-bis[(phenyl)ethynyl]benzoate (**55**) and *2,5-bis[(phenyl)ethynyl]benzoic acid* (**59**). A suspension of **56** (109 mg, 0.32 mmol) and Me_3SiOK (46 mg, 0.36 mmol) in anhydr. THF (12 ml) was stirred at r.t. for 18 h. The precipitate was filtered and washed with Et_2O (5 ml) to give **55** (79 mg, 68%). To the combined filtrates, 5% aq. HCl soln. (20 ml) was added and the formed carboxylic acid extracted with CH_2Cl_2 (3 × 15 ml). Evaporation *in vacuo* afforded **59** (30 mg, 29%).

Data of **55**: Hygroscopic white solid. M.p. >250°. IR (KBr): 3433*w* (br.), 3048*w*, 3029*w*, 1622v*s*, 1597*s*, 1580v*s*, 1500*m*, 1440*m*, 1404*s*, 1372v*s*. ^{1}H-NMR (300 MHz, CD_3OD): 7.72 (br. *s*, 1 H); 7.59–7.50 (*m*, 5 H); 7.46–7.43 (*m*, 1 H); 7.38–7.34 (*m*, 6 H). ^{13}C-NMR (75 MHz, CD_3OD): 175.97; 145.36; 134.07; 133.07; 132.92; 132.13; 131.95; 129.96; 129.89; 129.68 (2×); 125.33; 124.68; 124.25; 122.13; 95.12; 92.05; 90.00 (2×). NESI-MS (MeOH): 321.2 (100, $[M-K]^-$, $C_{23}H_{13}O_2$; calc. 321.1). Anal. calc. for $C_{23}H_{13}KO_2\cdot H_2O$ (378.47): C 72.99, H 4.00; found: C 73.65, H 3.91.

Data of **59**: White solid. M.p. 73–75°. IR (KBr): 3444*w* (br.), 3057*w*, 2968*w*, 2816*w*, 2633*w*, 2536*w*, 2210*m*, 1695v*s*, 1682v*s*, 1597*w*, 1536*w*, 1505v*s*, 1478*m*, 1439*m*, 1412*m*, 1391*w*, 1313*w*, 1312*w*, 1291*s*, 1250v*s*, 1157*w*, 1140*w*, 1070*w*. ^{1}H-NMR (300 MHz, $(CD_3)_2SO$): 13.36 (br. *s*, 1 H); 8.01–8.00 (*m*, 1 H); 7.74–7.66 (*m*, 2 H); 7.60–7.57 (*m*, 2 H); 7.54–7.51 (*m*, 2 H); 7.43–7.42 (*m*, 6 H). ^{13}C-NMR (75 MHz, $(CD_3)_2SO$): 167.98; 135.58 (2×); 135.24; 134.36; 133.13; 132.95; 130.82; 130.72; 130.38 (2×); 123.96; 123.85; 123.73; 123.31; 97.12; 93.45; 89.76; 89.55. NESI-MS (MeOH): 321.1 (100, $[M-H]^-$, $C_{23}H_{13}O_2$; calc. 321.1). Anal. calc. for $C_{23}H_{14}O_2\cdot 1/4\ H_2O$ (378.47): C 84.52, H 4.47; found: C 84.74, H 4.68.

(Z)-3-Benzylidene-1,3-dihydro-6-(phenylethynyl)isobenzofuran-1-one ((*Z*)-**58**). Compound **55** was chromatographed on a *Dowex® DR-2030* ion-exchange column (eluent: MeCN/MeOH 1:1) charged in its upper part with H^+ and in the lower with K^+ cations. Recrystallization from CD_3OD afforded (*Z*)-**58** as crystals suitable for X-ray analysis. The purity of the product was determined by ^{1}H-NMR to be *ca.* 85%. M.p. 169–170°. IR (KBr): 3084*w*, 3055*w*, 3021*w*, 2208*w*, 1778v*s*, 1720*m*, 1648*m*, 1614*w*, 1595*w*, 1571*w*, 1497*m*, 1475*w*, 1439*m*, 1320*w*, 1313*w*, 1275*w*, 1245*w*, 1177*w*, 1112*m*, 1068*w*, 1010*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.09–8.08 (*m*, 1 H); 7.88–7.84 (*m*, 3 H); 7.77–7.74 (*m*, 1 H); 7.59–7.56 (*m*, 2 H); 7.46–7.34 (*m*, 7 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.59; 139.81; 137.66; 133.21; 132.05; 130.48; 129.22; 129.10; 128.92; 128.83; 128.76; 126.27; 125.59; 125.51; 124.02; 122.68; 120.09; 92.54; 88.05. NESI-MS (MeOH): 321.2 (100, $[M-H]^-$, $C_{23}H_{13}O_2$; calc. 321.1). X-Ray: see *Fig. 6*.

2,2′,3,3′,4,4′-Hexa-O-*benzyl-6,6′-di*-O-*octyl-α,α-trehalose* (**62**). To a clear soln. of **61** [44] (93 mg, 0.11 mmol), iodooctane (162 mg, 0.67 mmol), and 2,6-di(*tert*-butyl)-4-methylpyridine (151 mg, 0.74 mmol) in anh. CH_2Cl_2 (2 ml), $AgSO_2CF_3$ (162 mg, 0.63 mmol) was added at 0°, and the suspension was stirred for 4 h in the dark [45]. Dilution with CH_2Cl_2 and filtration over *Celite®*, washing the filtrate with sat. aq. $NaHCO_3$ soln., drying ($MgSO_4$), and evaporation *in vacuo* afforded crude product, which was purified by CC (hexane/AcOEt 8:1 → 1:1) to give **62** (36 mg, 31%) and monoalkylated side product (55 mg, 52%). Viscous oil. IR ($CHCl_3$): 3089*w*, 3065*w*, 3008*m*, 2929v*s*, 2858*s*, 1602*w*, 1497*m*, 1454*s*, 1400*w*, 1360*m*, 1340*w*, 1328*w*, 1261*w*, 1241*w*, 1159*s*, 1139*m*, 1100v*s*, 1070v*s*, 1027*s*, 997v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.36–7.25 (*m*, 30 H); 5.22 (*d*, *J* = 3.4, 2 H); 4.99 (*d*, *AB*, *J* = 10.9, 2 H); 4.86 (*d*, *AB*, *J* = 10.9, 4 H); 4.69 (*s*, 4 H); 4.59 (*d*, *AB*, *J* = 10.9, 2 H); 4.09 (*dm*, *J* = 9.5, 2 H); 4.03 (*t*, *J* = 9.5, 2 H); 3.68 (*t*, *J* = 9.5, 2 H); 3.58 (*dd*, *J* = 9.5, 3.4, 2 H); 3.49–3.35 (*m*, 6 H); 3.30–3.22 (*m*, 2 H); 1.55 (*s*, 4 H); 1.23 (*s*, 20 H); 0.86 (*t*, *J* = 6.7, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 139.25; 138.89; 138.57; 128.65; 128.57 (2×); 128.17; 128.13 (2×); 127.92; 127.75 (2×); 94.68; 81.96; 79.60; 77.93; 75.77; 75.22; 72.84; 71.92; 70.81; 69.04; 31.91; 29.67; 29.53; 29.29; 26.26; 22.69; 14.11. FAB$^+$-MS: 1105 (50, $[M-2H]^+$), 1016 (3, $[M-Bn-H]^+$), 545 (6, $C_{35}H_{45}O_5^+$), 437 (30, $[C_{35}H_{45}O_5-Bn-OH]^+$), 329 (11, $[C_{35}H_{45}O_5-2\,Bn-2\,OH]^+$), 181 (74, $[2\,Bn-H]^+$), 91 (100, Bn^+).

6,6′-Di-O-*octyl-α,α-trehalose* (**60**). A soln. of **62** (97 mg, 0.088 mmol) in THF (16 ml) was added to a suspension of Pd/C (10% Pd, 160 mg) in EtOH (16 ml), and the mixture was hydrogenated for 20 h at r.t. under atmospheric pressure. After removal of the catalyst by filtration over *Celite®*, the filtrate was evaporated *in vacuo*. The residual solid was taken in AcOEt, Et_2O and hexane were added, and compound **60** (39 mg, 79%) was isolated by centrifugation. Soapy solid. M.p. > 136° (dec.). IR (KBr): 3381v*s*, 2926*m*, 2852*m*, 1149*m*, 1106*m*, 1081*m*, 1040*m*, 995*m*. ^{1}H-NMR (500 MHz, CD_3OD): 5.01 (*d*, *J* = 3.7, 2 H); 3.85 (*ddd*, *J* = 10.0, 5.2, 2.0, 2 H); 3.71 (*t*, *J* = 9.3, 2 H); 3.61 (*dd*, *J* = 11.1, 2.0, 2 H); 3.55 (*dd*, *J* = 11.1, 5.2, 2 H); 3.47 (*dt*, *J* = 9.5, 6.6, 2 H); 3.42–3.37 (*m*, 4 H); 3.25 (*dd*, *J* = 10.0, 9.3, 2 H); 1.53–1.47 (*m*, 4 H); 1.33–1.23 (*m*, 20 H); 0.88 (*t*, *J* = 7.0, 6 H). ^{13}C-NMR (125.8 MHz, CD_3OD): 95.04; 74.63; 73.17; 72.77; 72.64; 72.12; 71.18; 33.00; 30.70; 30.58; 30.41; 27.21; 23.71; 14.43. FAB$^+$-MS: 589 (100, $[M+Na]^+$). MALDI-MS: 589.4 (82, $[M+Na]^+$), 315.2 (100, $[C_{14}H_{28}O_5+Na+O]^+$). HR-MALDI-MS: 589.356 ($[M+Na]^+$, $C_{28}H_{54}NaO_{11}$; calc. 589.356).

Preparation of Monooctyl Glycosides. A soln. of mono- (1.8 g, 10 mmol) or disaccharide (3.6 g, 10 mmol) in Ac_2O (monosaccharides: 12.5 ml, 0.13 mol; disaccharides: 20 ml, 0.21 mol) and anh. AcONa (monosaccharides: 0.8 g, 10 mmol; disaccharides: 1.3 g, 16 mmol) was stirred for 4 h at 120°. After evaporation and general workup (extraction with H_2O/CH_2Cl_2, drying of the org. phase with $MgSO_4$, and evaporation *in vacuo*), the peracetylated sugar (10 mmol) was dissolved in dry CH_2Cl_2, and the soln. was stirred under Ar together with $SnCl_4$ (10 mmol, 10 ml of a 1M soln. in CH_2Cl_2) and octanol (1.6 g, 12 mmol) in the presence of molecular sieves (4 Å, 4 g) for 4 h at 20°. After general workup and CC (hexane/AcOEt 7:3), the octyl glycosides formed were heated to reflux with MeONa (1 g, 18.5 mmol) in MeOH (40 ml) until a clear soln. formed. After neutralization with an ion-exchange resin (*Dowex® 50X8*), the soln. was filtered, evaporated *in vacuo*, and the residue was dried first at 10^{-1} Torr, then at 10^{-7} Torr for 14 d.

X-Ray Crystal Structure of Compound **25**. X-Ray crystal data for $C_{25}H_{18}O_2$ (M_r 350.39): monoclinic space group $P2_1/n$ (No. 14), $D_c = 1.350$ g cm^{-3}, $Z = 4$, $a = 7.405(1)$, $b = 5.966(1)$, $c = 39.162(4)$ Å, $\beta = 94.61(1)°$, $V = 1724.5(4)$ Å^3, CuK_α radiation, $\lambda = 1.5418$ Å, $2.26° \le \theta \le 64.95°$, 2907 unique reflections, $T = 153(2)$ K. The structure was solved by direct methods (SIR92 [58]) and refined by full-matrix least-squares analysis (SHELXL-97 [59]), using an isotropic extinction correction. All heavy atoms were refined anisotropically (H-atoms isotropically, whereby H-positions are based on stereochemical considerations). Final $R(F) = 0.060$, $wR(F^2) = 0.153$ for 263 parameters and 2645 reflections with $I > 2\sigma(I)$. *Cambridge Crystallographic Data Centre* Deposition No. CCDC-162370.

*X-Ray Crystal Structure of Compound (±)-***31**. X-Ray crystal data for $C_{54}H_{38}O_8$ (M_r 814.84): monoclinic space group $P2/n$, $D_c = 1.025$ g cm^{-3}, $Z = 2$, $a = 11.126(2)$, $b = 13.556(3)$, $c = 17.716(4)$ Å, $\beta = 99.03(3)°$, $V =$

2638.9(10) Å^3, CuK_α radiation, $\lambda = 1.5418$ Å, $4.13^\circ \leq \theta \leq 54.96^\circ$, 3288 unique reflections, $T = 238$ K. The structure was solved by direct methods (SIR92 [58]) and refined by full-matrix least-squares analysis (SHELXL-97 [59]), using an isotropic extinction correction. All heavy atoms were refined anisotropically (H-atoms isotropically, whereby H-positions are based on stereochemical considerations). Final $R(F) = 0.0865$, $wR(F^2) = 0.249$ for 299 parameters and 2064 reflections with $I > 2\sigma(I)$. *Cambridge Crystallographic Data Centre* Deposition No. CCDC-162369.

*X-Ray Crystal Structure of Compound (Z)-***58**. X-Ray crystal data for $C_{23}H_{14}O_2$ (M_r 322.34): triclinic space group $P\bar{1}$, $D_c = 1.317$ g cm^{-3}, $Z = 3$, $a = 8.535(2)$, $b = 9.915(2)$, $c = 15.536(3)$ Å, $\alpha = 80.14(2)$, $\beta = 80.90(1)$, $\gamma = 71.33(2)^\circ$, $V = 1219.6(4)$ Å^3, CuK_α radiation, $\lambda = 1.5418$ Å, $2.90 \leq \theta \leq 69.93^\circ$, 4732 unique reflections, $T = 98(2)$ K. The structure was solved by direct methods (SIR92 [58]) and refined by full-matrix least-squares analysis (SHELXL-97 [59]), with an isotropic extinction correction and an exponentially modified weight factor $r = 3.0$ Å^2 [60]. The three independent molecules exhibit static disorder, in particular within the sub-units C(11)–C(12) until C(20) (see, *e.g.*, *Fig. 6*). As a result, the molecular geometry is much less accurate than the estimated standard deviations might suggest. The atoms C(17), C(19), C(12′), C(17′), C(19′), C(17″), and C(19″) were refined isotropically, all other heavy atoms were refined anisotropically (H-atoms isotropically, whereby H-positions are based on stereochemical considerations). Final $R(F) = 0.067$, $wR(F^2) = 0.177$ for 676 parameters, 3 restraints and 3984 reflections with $I > 2\sigma(I)$. *Cambridge Crystallographic Data Centre* Deposition No. CCDC-162371.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre.* Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

REFERENCES

[1] a) A. Varki, *Glycobiology* **1993**, *3*, 97; b) N. Sharon, H. Lis, *Sci. Am.* **1993**, *268* (1), 74; c) R. A. Dwek, *Chem. Rev.* **1996**, *96*, 683; d) R. A. Laine, *Glycobiology* **1994**, *4*, 759.

[2] a) F. A. Quiocho, *Pure Appl. Chem*. **1989**, *61*, 1293; b) N. K. Vyas, M. N. Vyas, F. A. Quiocho, *J. Biol. Chem*. **1991**, *266*, 5226; c) F. A. Quiocho, *Biochem. Soc. Trans.* **1993**, *21*, 442; d) M. N. Vyas, N. K. Vyas, F. A. Quiocho, *Biochemistry* **1994**, *33*, 4762; e) A. J. Sharff, L. E. Rodseth, S. Szmelcman, M. Hofnung, F. A. Quiocho, *J. Mol. Biol*. **1995**, *246*, 8.

[3] Y. C. Lee, R. T. Lee, *Acc. Chem. Res.* **1995**, *28*, 321; W. I. Weis, K. Drickamer, *Ann. Rev. Biochem*. **1996**, *65*, 441; H. Lys, N. Sharon, *Chem. Rev.* **1998**, *98*, 637.

[4] E. E. Simanek, G. J. Garvey, J. A. Jablonowski, C.-H. Wong, *Chem. Rev*. **1998**, *98*, 833; P. Sears, C.-H. Wong, *Angew. Chem*. **1999**, *111*, 2446; *Angew. Chem.*, *Int. Ed*. **1999**, *38*, 2300.

[5] R. U. Lemieux, in 'Carbohydrate Antigens', Eds. P. J. Garegg, A. A. Lindberg, American Chemical Society, Washington, D.C., 1993, Vol. 519, pp. 5–18; E. J. Toone, *Curr. Opin. Struct. Biol*. **1994**, *4*, 719; A. M. Davis, S. J. Teague, *Angew. Chem*. **1999**, *111*, 778; *Angew. Chem.*, *Int. Ed*. **1999**, *38*, 736.

[6] A. P. Davis, R. S. Wareham, *Angew. Chem*. **1999**, *111*, 3160; *Angew. Chem., Int. Ed*. **1999**, *38*, 2978.

[7] M. Inouye, K. Takahashi, H. Nakazumi, *J. Am. Chem. Soc*. **1999**, *121*, 341; D. K. Smith, A. Zingg, F. Diederich, *Helv. Chim. Acta* **1999**, *82*, 1225; M. Mazik, H. Bandmann, W. Sicking, *Angew. Chem*. **2000**, *112*, 562; *Angew. Chem., Int. Ed*. **2000**, *39*, 551; O. Rusin, V. Král, *Chem. Commun.* **1999**, 2367; V. Král, O. Rusin, J. Charvátová, P. Anzenbacher Jr., J. Fogl, *Tetrahedron Lett*. **2000**, *41*, 10147.

[8] G. A. Jeffrey, W. Saenger, 'Hydrogen Bonding in Biological Structures', Springer, Berlin, 1991; G. A. Jeffrey, 'An Introduction to Hydrogen Bonding', Oxford University Press, New York, 1997, G. R. Desiraju, T. Steiner, 'The Weak Hydrogen Bond', Oxford University Press, New York, 1999.

[9] N. K. Vyas, *Curr. Opin. Struct. Biol*. **1991**, *1*, 732.

[10] H.-J. Schneider, A. Yatsimirsky, 'Principles and Methods in Supramolecular Chemistry', John Wiley, Chichester, 2000.

[11] a) S. Anderson, U. Neidlein, V. Gramlich, F. Diederich, *Angew. Chem.* **1995**, *107*, 1722; *Angew. Chem., Int. Ed*. **1995**, *34*, 1596; b) A. Bähr, A. S. Droz, M. Püntener, U. Neidlein, S. Anderson, P. Seiler, F. Diederich, *Helv. Chim. Acta* **1998**, *81*, 1931.

[12] G. Das, A. D. Hamilton, *J. Am. Chem. Soc*. **1994**, *116*, 11139; G. Das, A. D. Hamilton, *Tetrahedron Lett*. **1997**, *38*, 3675.

[13] H. Pelmore, G. Eaton, M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, **1992**, 149.

[14] A. Bähr, B. Felber, K. Schneider, F. Diederich, *Helv. Chim. Acta* **2000**, *83*, 1346.

[15] U. Neidlein, F. Diederich, *Chem. Commun*. **1996**, 1493.
[16] A. S. Droz, F. Diederich, *J. Chem. Soc., Perkin Trans. 1* **2000**, 4224.
[17] P. Siemsen, R. C. Livingston, F. Diederich, *Angew. Chem*. **2000**, *112*, 2749; *Angew. Chem., Int. Ed*. **2000**, *39*, 2632.
[18] K. Sonogashira, in 'Metal-catalyzed Cross-Coupling Reactions', Eds. F. Diederich, P. J. Stang, Wiley-VCH, Weinheim, 1998, pp. 203–229.
[19] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, *Synthesis* **1980**, 627.
[20] A. S. Hay, *J. Org. Chem*. **1962**, *27*, 3320.
[21] T. D. Heightman, A. T. Vasella, *Angew. Chem*. **1999**, *111*, 794; *Angew. Chem., Int. Ed*. **1999**, *38*, 750.
[22] D. D. Tanner, D. W. Reed, B. P. Setiolane, *J. Am. Chem. Soc*. **1982**, *104*, 3917.
[23] W. B. Austin, N. Bilow, W. J. Kelleghan, K. S. Y. Lau, *J. Org. Chem.* **1981**, *46*, 2280.
[24] C. E. Castro, E. J. Gaughan, D. C. Owsley, *J. Org. Chem*. **1966**, *31*, 4071.
[25] a) D. R. Buckle, C. J. M. Rockell, *J. Chem. Soc., Perkin Trans. 1* **1985**, 2443; b) A. Arcadi, F. Marinelli, *Synthesis* **1986**, 749; c) S. Torii, L. H. Xu, H. Okumoto, *Synlett* **1992**, 515; d) A. Arcadi, S. Cacchi, M. Del Rosario, G. Fabrizi, F. Marinelli, *J. Org. Chem*. **1996**, *61*, 9280; e) N. G. Kundu, M. Pal, J. S. Mahanty, M. De, *J. Chem. Soc., Perkin Trans. 1* **1997**, 2815.
[26] J. E. Baldwin, *J. Chem. Soc., Chem. Commun*. **1976**, 734.
[27] Y. Kondo, F. Shiga, N. Murata, T. Sakamoto, H. Yamanaka, *Tetrahedron* **1994**, *50*, 11803; Y. Kondo, S. Kojima, T. Sakamoto, *J. Org. Chem.* **1997**, *62*, 6507.
[28] T. M. Greene, P. G. M. Wuts, 'Protective Groups in Organic Synthesis', Wiley, New York, 1991.
[29] E. D. Laganis, B. L. Chenard, *Tetrahedron Lett*. **1984**, *25*, 5831.
[30] J. Zhang, J. S. Moore, Z. Xu, R. A. Aguirre, *J. Am. Chem. Soc*. **1992**, *114*, 2273; J. S. Moore, E. J. Weinstein, Z. Wu, *Tetrahedron Lett*. **1991**, *32*, 2465; Z. Wu, J. S. Moore, *Tetrahedron Lett*. **1994**, *35*, 5539; J. K. Young, J. S. Moore, in 'Modern Acetylene Chemistry', Eds. P. J. Stang, F. Diederich, VCH, Weinheim, 1995, 415.
[31] H. Takalo, J. Kankare, E. Hänninen, *Acta Chem. Scand. B* **1988**, *42*, 448.
[32] H. Ku, J. R. Barrio, *J. Org. Chem*. **1981**, *46*, 5239.
[33] M. K. Ng, H.-F. Chow, T.-L. Chan, T. C. W. Mak, *Tetrahedron Lett*. **1996**, *37*, 2979; C.-J. Li, D. Wang, W. T. Slaven IV, *Tetrahedron Lett*. **1996**, *37*, 4469; C.-J. Li, W. T. Slaven IV, V. T. John, S. Banerjee, *Chem. Commun*. **1997**, 1569; K. Onitsuka, Y. Harada, F. Takei, S. Takahashi, *Chem. Commun*. **1998**, 643; L. Ma, Q.-S. Hu, D. Vitharana, C. Wu, C. M. S. Kwan, L. Pu, *Macromolecules* **1997**, *30*, 204; L. Pu, *Chem. Rev*. **1998**, *98*, 2405; W.-S. Huang, Q.-S. Hu, L. Pu, *J. Org. Chem*. **1999**, *64*, 7940; M. S. Gin, J. S. Moore, *J. Org. Chem*. **2000**, *2*, 135.
[34] S. Thorand, N. Krause, *J. Org. Chem*. **1998**, *63*, 8551.
[35] H. Anderson, Oxford University, personal communication.
[36] G. Eglinton, A. R. Galbraith, *Chem. Ind. (London)* **1956**, 737.
[37] R. Bürli, A. Vasella, *Angew. Chem*. **1997**, *109*, 1945; *Angew. Chem.*, *Int. Ed.* **1997**, *36*, 1852.
[38] D. O'Krongly, S. R. Denmeade, M. Y. Chiang, R. Breslow, *J. Am. Chem. Soc*. **1985**, *107*, 5544.
[39] S. Höger, K. Bonrad, L. Karcher, A.-D. Meckenstock, *J. Org. Chem.* **2000**, *65*, 1588; Ö. Unsal, A. Godt, *Chem. Eur. J.* **1999**, *5*, 1728.
[40] S. Anderson, H. L. Anderson, in 'Templated Organic Synthesis', Eds. F. Diederich, P. J. Stang, Wiley-VCH, Weinheim, 2000, pp. 1–38.
[41] R. P. Bonar-Law, J. K. M. Sanders, *J. Am. Chem. Soc*. **1995**, *117*, 259.
[42] Y. Ogawa, M. Maruno, T. Wakamatsu, *Heterocycles* **1995**, *41*, 2587.
[43] R. L. Letsinger, E. N. Oftedahl, J. R. Nazy, *J. Am. Chem. Soc*. **1965**, *87*, 742.
[44] J. M. Cotéron, C. Vicent, C. Bosso, S. Penadés, *J. Am. Chem. Soc*. **1993**, *115*, 10066; I. Azuma, T. Sakurai, H. Ishida, T. Kitajima, M. Yamazaki, *Carbohydr. Res.* **1991**, *212*, 47; S. R. Gilbertson, C.-W. T. Chang, *J. Org. Chem*. **1995**, *60*, 6226.
[45] R. M. Burk, T. S. Gac, M. B. Roof, *Tetrahedron Lett*. **1994**, *35*, 8111.
[46] *Insight II* V. 95.0 and *Discover* V. 95.0/3.00, CVFF forcefield, Biosym Technologies, San Diego, 1995.
[47] 'Circular Dichroism and the Conformational Analysis of Biomolecules', Ed. G. D. Fasman, Plenum Press, New York, 1996; D. A. Lightner, J. E. Gurst, 'Organic Conformational Analysis and Stereochemistry from Circular Dichroism Spectroscopy', Wiley-VCH, New York, 2000.
[48] G. Proni, P. G. Spada, P. Lustenberger, R. Welti, F. Diederich, *J. Org. Chem*. **2000**, *65*, 5522.
[49] B. Peterson, '*Associate V. 1.6*', Ph. D. thesis, University of California at Los Angeles, 1994; *Quantum Soft* '*Profit V. 5.01*', Cherwell Scientific Publishing, Frankfurt, 1996.

[50] K. A. Conners, 'Binding Constants: The Measurement of Molecular Complex Stability', John Wiley, New York, 1987; P. Job, *Ann. Chim. (10. Série)* **1928**, *9*, 113.
[51] J. A. Corkill, M. Joppich, S. H. Kuttab, R. W. Giese, *Anal. Chem*. **1982**, *54*, 481.
[52] T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, K. Hirotsu, *J. Am. Chem. Soc*. **1984**, *106*, 158.
[53] R. N. Keller, H. D. Wycoff, in 'Inorganic Syntheses', Vol. 2, Ed. W. C. Fernelius, McGraw-Hill, New York, 1946, pp. 1 – 4.
[54] L. M. Wingert, G. A. Jeffrey, D. Cabaret, M. Wakselman, *Carbohydr. Res.* **1995**, *275*, 25.
[55] G. Pohlenz, M. Trimborn, H. Egge, *Glycobiology* **1994**, *4*, 625.
[56] V. Vill, T. Böcker, J. Thiem, F. Fischer, *Liq. Crystals* **1989**, *6*, 349.
[57] H. Alpes, K. Allman, H. Plattner, J. Reichert, R. Riek, S. Schulz, *Biochim. Biophys. Acta* **1986**, *862*, 294.
[58] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr*. **1994**, *27*, 435.
[59] G. M. Sheldrick, '*SHELXL-97, Program for the Refinement of Crystal Structures*', University of Göttingen, Germany, 1997.
[60] J. D. Dunitz, P. Seiler, *Acta Crystallogr., Sect. B* **1973**, *29*, 589.

Received June 6, 2001