Dendritic, 1,1′-Binaphthalene-Derived Cleft-Type Receptors (*Dendroclefts*) for the Molecular Recognition of Pyranosides

by **Anja Bähr**, **Béatrice Felber**, **Katharina Schneider**, and **François Diederich***

Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich

Two series of optically active, cleft-type dendritic receptors (*dendroclefts*) for carbohydrate recognition were prepared by attaching *Fréchet*-type dendrons *via* ethynediyl linkers to a core consisting of one or two 1,1′-binaphthalene-2,2′-diyl phosphate moieties. Sugar substrates were expected to bind *via* bidentate ionic H-bonding of two OH groups to the phosphodiester core and, additionally, to undergo *van der Waals* and CH$\cdots\pi$ interactions with the aromatic rings of the surrounding dendritic wedges. The synthesis of the dendritic receptors *G-1*-(*S*)-**1**, *G-2*-(*S*)-**2**, and *G-3*-(*S*)-**3** (*Fig. 1*; *G-x* = dendritic generation) with a single binaphthalene core started from 3,3′-diethynylated MOM-protected (MOM = methoxymethyl) 1,1′-binaphthalene-2,2′-diol (*S*)-**13** to which the *Fréchet*-type dendrons of generations 1–3 were attached *via Sonogashira* cross-coupling (*Scheme 3*). MOM-Ether deprotection followed by phosphodiester formation and ion exchange provided the targeted receptors. By a similar route, receptor *G-1*-(*S*)-**23** with dendritic wedges capped with oligoether groups was obtained (*Scheme 4*). In receptor *G-1*-(*S*)-**26**, the ethynediyl linker was omitted, and, in its synthesis, the dendritic wedges were attached to MOM-protected 3,3′-diiodo-1,1′-binaphthalene-2,2′-diol by *Suzuki* cross-coupling (*Scheme 5*). The synthesis of the dendritic receptors *G-2*-(*S*,*S*)-**42** and *G-1*-(*S*,*S*)-**43** with two binaphthalene moieties at the core (*Fig. 3*) started from diethynylated (*S*,*S*)-**39** and (*S*,*S*)-**33**, which contain two MOM-protected 1,1′-binaphthalene-2,2′-diol moieties bridged by *p*-phenylene or buta-1,3-diynediyl linkers, respectively, and was completed by attachment of the dendritic wedges by *Sonogashira* coupling, MOM-ether deprotection, phosphodiester formation, and ion exchange (*Schemes 9* and *10*). By an alternative route, the C-frame of receptor *G-2*-(*S*,*S*)-**41** was prepared by coupling the dendron to dialkynylated 1,1′-binaphthalene (*S*)-**44**, followed by oxidative *Glaser-Hay* coupling (*Scheme 8*). For control studies, the non-dendritic reference receptors (*S*)-**4** and (*S*)-**5** (*Fig. 1*) with one and (*S*,*S*)-**31** and (*S*,*S*)-**32** (*Fig. 2*) with two 1,1′-binaphthalene-2,2′-diyl phosphate moieties were also prepared. ^{1}H-NMR Complexation studies with the dendritic receptors containing one binaphthalene core and octyl glycosides **53**–**55** in CD_3CN and $CDCl_3$ (*Tables 2–4*) revealed that ionic H-bonding between the phosphodiester core in the dendritic receptors and the sugar OH groups provides the major driving force for stoichiometric 1:1 host-guest association. A smaller, yet significant contribution to the binding free enthalpy was also provided by interactions between the sugar guests and the dendritic wedges. Binding selectivity was weak in all cases, and only small changes in association strength were observed as a function of dendritic generation. In studies with the dendritic receptors, which contain two binaphthalene moieties at the core, higher-order complex stoichiometries prevented the determination of quantitative binding data. As a result of unfavorable steric interactions between the dendritic wedges, these flexible receptor systems apparently avoid adopting the '*syn*'-conformation with convergent phosphodiester sites that is required for efficient 1:1 host-guest complexation.

1. Introduction. – Molecular recognition between two or more complementary binding partners is extremely sensitive to the polarity of the surrounding environment. For example, the hydrophobic (or solvatophobic) effect is almost worthless in benzene [1] and solvent-exposed H-bonds count for little in H_2O [2]. Even binding selectivity can change with solvent environment [3][4]. It is, therefore, not surprising that the microenvironment at biological recognition sites is carefully controlled in order to achieve strong and selective complexation. Thus, small-molecule binding sites in

proteins are usually buried within a polypeptide superstructure that precisely controls the environmental micropolarity, the position of the convergent amino-acid residues participating in the recognition process, and even the number of solvent molecules present [5].

In the early 90s, researchers recognized the ability of dendritic branching to mimic functions of biological polypeptide superstructures and to create specific microenvironmental effects in the interior of dendrimers [6][7] (for surveys on dendrimer chemistry, see [8–12]). Dendritic iron porphyrins were found to be valid models of cytochromes: the dendritic branches create a unique local microenvironment around the isolated electroactive core, and this shielding from solvent profoundly alters the redox potential of the Fe^{III}/Fe^{II} couple [13]. Other investigations addressed the modulation of binding affinity and selectivity at cyclophane [14] and cleft-type [15] binding sites buried at the dendritic core (for general surveys on supramolecular dendrimer chemistry, see [16]).

Efficient and selective complexation of carbohydrates by synthetic receptors in aqueous solution remains a true frontier in supramolecular chemistry [17][18]. In biological carbohydrate recognition [5][19], the interplay of H-bonding and apolar as well as hydrophobic interactions is still poorly understood. It has, however, become clear that both modes of interactions are essential for stable and selective complexation in protic solvents. Therefore, we became interested in developing receptors featuring an efficient ionic H-bonding site buried inside a lipophilic dendritic shell. The novel dendritic hosts described in this paper contain a core that consists of one or two optically active 1,1′-binaphthalene-2,2′-diyl phosphate moieties. These phosphodiester groups had previously been found to provide highly efficient ionic H-bonding sites – even in protic solvent mixtures – when introduced into macrocyclic receptors for mono- and disaccharides [20][21]. As dendritic surrounding, we chose *Fréchet*-type wedges, which consist of resorcinol-ether repeating units [22][23]. We hoped that the sugar guests, which dock at the phosphodiester core, would form a large number of *van der Waals* contacts with these branches and undergo efficient $CH\cdots\pi$ interactions [24] with their aromatic rings. The latter interactions have been observed in numerous X-ray crystal structures of protein-carbohydrate complexes [5][25] and they have also been shown to contribute to sugar binding by artificial receptors [26]. At the same time, we expected that the lipophilic dendritic branching would shield the internal binding site from bulk polar solvent, thereby enhancing the strength of the host-guest H-bonds. Here, we describe the synthesis of these novel dendritic cleft-type receptor systems (*dendroclefts* [15]) and investigations of their sugar-binding ability in different solvents on the basis of ^{1}H-NMR binding titrations and extraction experiments.

2. Results and Discussion. – 2.1. *Synthesis of Receptors with a Single 1,1′-Binaphthalene-2,2′-diyl Phosphate Core.* We first prepared receptors *G-1*-(*S*)-**1**, *G-2*-(*S*)-**2**, and *G-3*-(*S*)-**3** of first to third generation together with comparison compounds (*S*)-**4** and (*S*)-**5** (*Fig. 1*). By their general shape – featuring a H-bonding site surrounded by two dendrons – they resemble two series of dendritic hosts previously prepared for sugar [15] and amidinium salt complexation [23], respectively.

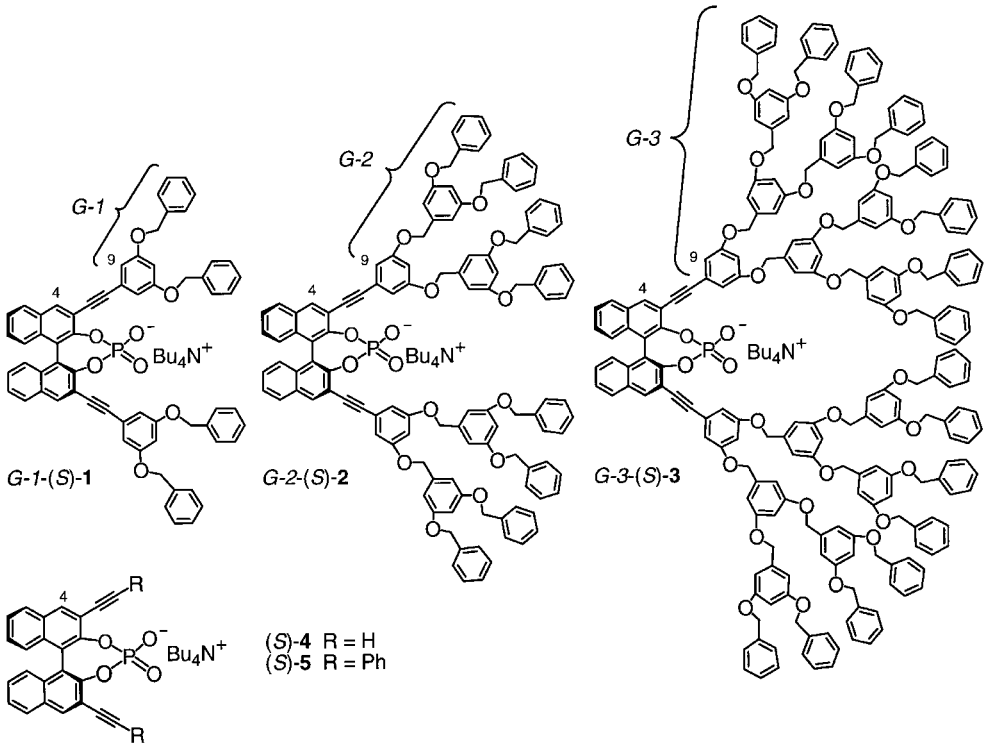


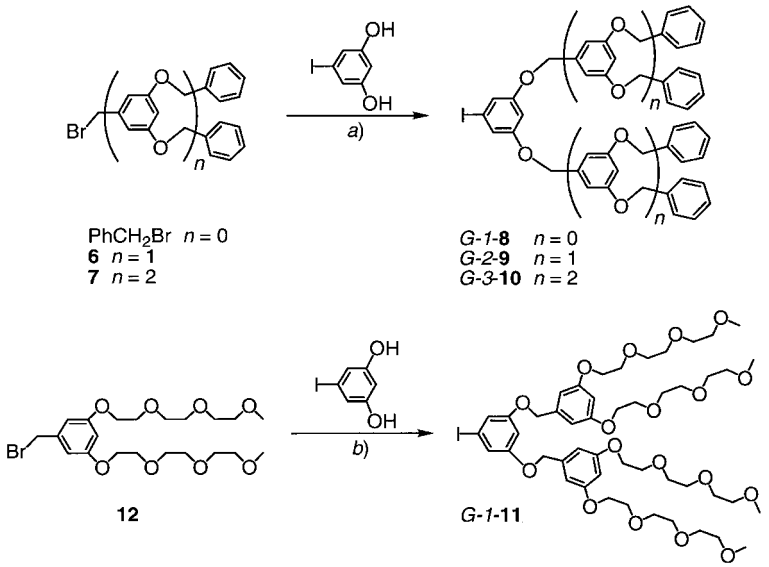
Fig. 1. *Dendritic hosts with a single 1,1′-binaphthalene-2,2′-diyl phosphate core and reference compounds*

For the synthesis of the *Fréchet*-type dendrons, 4-iodoresorcinol (5-iodobenzene-1,3-diol) [23] was prepared by *Sandmeyer* reaction [27] of 3,5-dimethoxyaniline to give 5-iodo-1,3-dimethoxybenzene, followed by methyl-ether cleavage. Subsequent *Williamson* ether synthesis with $PhCH_2Br$, **6** [22], or **7** [22] afforded dendrons *G-1*-**8**, *G-2*-**9**, and *G-3*-**10**, respectively (*Scheme 1*). We also prepared the dendritic wedge *G-1*-**11** starting from benzyl-bromide derivative **12** [28].

The non-dendritic reference compounds were prepared starting from (*S*)-**13** [29] (*Scheme 2*) (for ethynylated 1,1′-binaphthalene-2,2′-diol derivatives, see [30]). MOM-Ether cleavage (MOM = methoxymethyl) afforded (*S*)-**14**, and the cyclic phosphodiester (*S*)-**4** was obtained using $POCl_3$ and Et_3N [21b], followed by ion-exchange chromatography (*Dowex* (Bu_4N^+)). *Sonogashira* cross-coupling [31] of (*S*)-**13** with PhI gave (*S*)-**15** in excellent yield (97%). MOM-Ether deprotection provided (*S*)-**16**, and formation of the cyclic phosphodiester, followed by ion-exchange chromatography, led to the second reference compound (*S*)-**5**.

A protocol similar to that used in the synthesis of (*S*)-**5** was applied to the synthesis of the dendritic target molecules. Thus, the sequence *Sonogashira* cross-coupling → MOM-ether deprotection → phosphodiester formation and ion-exchange provided the first-generation ((*S*)-**13** and *G-1*-**8** → *G-1*-(*S*)-**17** → *G-1*-(*S*)-**18** → *G-1*-(*S*)-**1**), second-

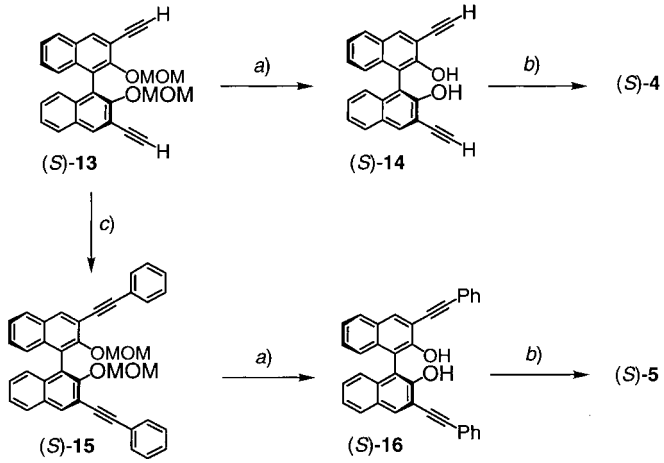
Scheme 1. *Syntheses of Dendritic Wedges*



a) K_2CO_3, acetone or acetone/MeCN 1:1, [18]crown-6, 55°, 24–60 h; 95% (*G-1*-**8**); 90% (*G-2*-**9**); 79% (*G-3*-**10**). *b*) K_2CO_3, acetone, [18]crown-6, 60°, 20 h; 43%.

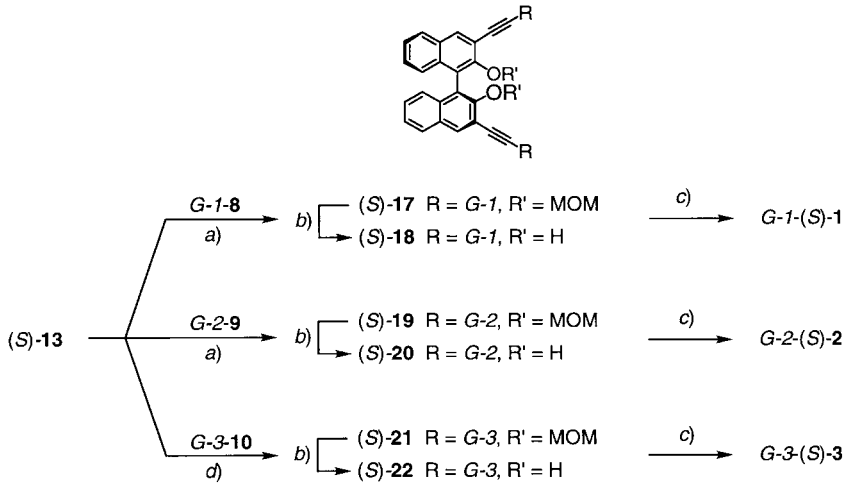
generation ((*S*)-**13** and *G-2*-**9** → *G-2*-(*S*)-**19** → *G-2*-(*S*)-**20** → *G-2*-(*S*)-**2**), and third-generation dendroclefts ((*S*)-**13** and *G-3*-**10** → *G-32*-(*S*)-**21** → *G-3*-(*S*)-**22** → *G-3*-(*S*)-**3**) (*Scheme 3*).

Scheme 2. *Synthesis of Non-dendritic Reference Compounds*



a) Conc. HCl (cat.), THF/MeOH, 20°, 4–12 h; 99% ((*S*)-**14**); 75% ((*S*)-**16**). *b*) $POCl_3$, Et_3N, CH_2Cl_2, 20°, 3–6 h; then THF/H_2O, 30-40°, 12 h, then *Dowex* (Bu_4N^+), CH_2Cl_2/MeCN 1:1; 38% ((*S*)-**4**); 54% ((*S*)-**5**). *c*) PhI, [$PdCl_2(PPh_3)_2$], CuI, THF/(i-Pr)$_2$NH, 40°; 2 h, 97%.

Scheme 3. *Synthesis of the Dendritic Receptors with One Phosphodiester Core*



a) $[PdCl_2(PPh_3)_2]$, CuI, THF/(i-Pr)$_2$NH, 40°, 12 h, 85% ((*S*)-**17**); 71% ((*S*)-**19**). *b*) Conc. HCl (cat.), THF/MeOH, 20°, 12 h; 79% ((*S*)-**18**); 85% ((*S*)-**22**). *c*) $POCl_3$, Et_3N, CH_2Cl_2, 20°, 3 h; then THF/H_2O, 40°, 12 h; then *Dowex* (Bu_4N^+), CH_2Cl_2/MeCN 1:1; 71% (*G-1*-(*S*)-**1**); 54% (*G-2*-(*S*)-**2** from (*S*)-**19**); 52% (*G-1*-(*S*)-**3**). *d*) $[PdCl_2(dppf)]$, CuI, THF/(i-Pr)$_2$NH, 40°, 2 h; 57% (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene). For *G-1* to *G-3*, see *Fig. 1*.

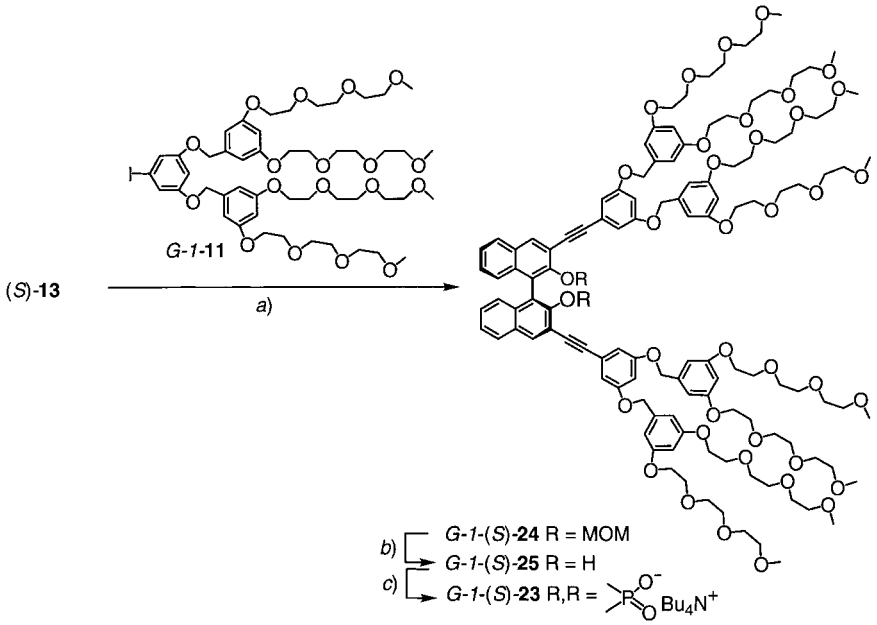
We examined different cross-coupling conditions and observed the best yield when (*S*)-**13** was added slowly over a period of 30 min to a suspension of catalyst and iodoaryl dendron. Both catalysts, $[PdCl_2(PPh_3)_2]$ and $[PdCl_2(dppf)]$, gave good results for the coupling of the first- and second-generation dendrons. With the third-generation derivative *G-3*-**10**, we observed a superior performance for $[PdCl_2(dppf)]$ over $[PdCl_2(PPh_3)_2]$. The coupling yields decreased from 85% (for *G-1*-**8**) to 57% (for *G-3*-**10**) due to the increased steric hindrance of the dendron. In all cases, the formation of homo-coupled products occurred as major side reaction, but purification could be easily achieved by GPC (gel-permeation chromatography).

For MOM-ether deprotection, it was necessary to use very mild acidic conditions to avoid *5-endo-dig* cyclization [32] of the free OH groups with the adjacent ethynyl moieties [29]. Following formation of the phosphodiester and prior to the ion-exchange chromatography, purification by column chromatography (SiO_2; CH_2Cl_2 containing 1–3% Et_3N) was required to obtain analytically pure target receptors.

Receptor *G-1*-(*S*)-**23** with polyether capping groups was prepared by an analogous sequence ((*S*)-**13** and *G-1*-**11** → *G-1*-(*S*)-**24** → *G-1*-(*S*)-**25** → *G-2*-(*S*)-**23**) (*Scheme 4*).

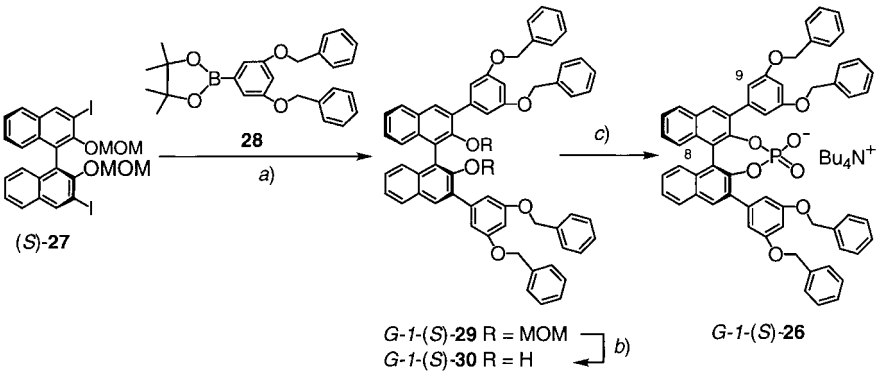
To investigate the influence of different distances between the first aromatic rings of the dendritic branches and the core phosphodiester group – the docking point for the sugar guest – receptor *G-1*-(*S*)-**26**, which lacks the acetylenic linker between binaphthalene and dendritic wedges, was prepared (*Scheme 5*). The synthesis started from diiodinated (*S*)-**27** [29], which was cross-coupled under *Suzuki* conditions [33] to the boronate dendron **28**. This reaction was best conducted in 1,2-dimethoxyethane

Scheme 4. *Synthesis of the Dendritic Receptor* G-1-(S)-**23**



a) [$PdCl_2$(dppf)], CuI, THF/(i-Pr)$_2$NH, 40°, 12 h; 65%. *b*) Conc. HCl (cat.), THF/MeOH, 20°, 12 h. *c*) $POCl_3$, Et_3N, CH_2Cl_2, 20°, 3 h; then THF/H_2O, 40°, 12 h; then *Dowex* (Bu_4N^+), CH_2Cl_2/MeCN 1:1; 61% (from *G-1*-(*S*)-**24**).

Scheme 5. *Synthesis of Dendritic Receptor* G-1-(S)-**26**



a) [$PdCl_2$(dppf)], DME, aq. Na_2CO_3 soln., 85°, 3 h; 80%. *b*) Conc. HCl (cat.), THF/MeOH, 20°, 20 h. *c*) $POCl_3$, Et_3N, CH_2Cl_2, 20°, 4 h; then THF/H_2O, 40°, 12 h; then *Dowex* (Bu_4N^+), CH_2Cl_2/MeCN 1:1; 93% (from *G-1*-(*S*)-**29**).

(DME) with [$PdCl_2$(dppf)] as the catalyst and aq. Na_2CO_3 solution as the base, providing *G-1*-(*S*)-**29** in 80% yield.

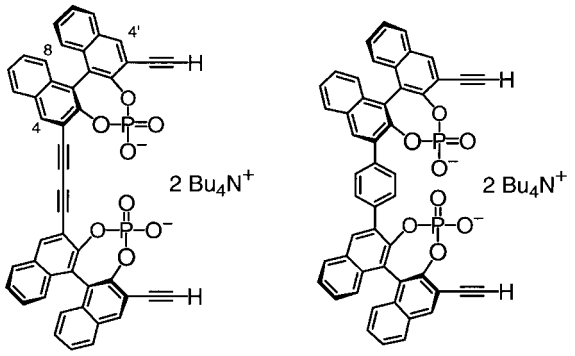
Boronate **28** was prepared by cross-coupling of (pinacolato)boron with *G-1*-**8** in dioxane with [$PdCl_2$(dppf)] and Et_3N [34]. In the Pd-catalyzed cross-coupling of

(pinacolato)boron (or bis(pinacolato)diboron) with either an iodo- or bromoaryl substrate to give the corresponding boronate, reduction is frequently observed as a major side reaction [34]. According to the ^{1}H-NMR spectra of the crude product, the desired compound **28** was formed as the major product (*ca.* 65%) together with the reduction product 1,3-bis(benzyloxy)benzene (*ca.* 35%). Decomposition of **28** during column chromatography (SiO_2) could be suppressed by adding Et_3N (0.5%) to the eluent (hexane/AcOEt 10:1), and pure **28** was then obtained in 54% yield. When the same reaction was performed with the dendritic wedge *G-2*-**9**, the desired product was formed in *ca.* 50% yield (^{1}H-NMR spectrum of the crude product), but here decomposition could not be avoided during the subsequent column chromatography.

The inverse approach towards *G-1*-(*S*)-**29**, namely coupling of the iodoaryl dendron *G-1*-**8** with a 1,1′-binaphthalenediboronic acid or ester, was less successful. When we attempted to transform 3,3′-diiodinated 1,1′-binaphthalene (*S*)-**27** into the bis(boronic acid) or the corresponding diester by lithiation and quenching with trimethoxyborane [35][36], complex product mixtures were isolated. The same result was obtained by the above-described Pd-catalyzed cross-coupling reaction with (pinacolato)boron or bis(pinacolato)diboron. The synthesis of *G-1*-(*S*)-**26** was finally completed *via* the sequence *G-1*-(*S*)-**29** → *G-1*-(*S*)-**30** → *G-1*-(*S*)-**26** (*Scheme 5*).

2.2. *Synthesis of Receptors with a Bis(1,1′-binaphthalene-2,2′-diyl Phosphate) Core.* We first prepared the two non-dendritic reference compounds (*S*,*S*)-**31** and (*S*,*S*)-**32** (*Fig. 2*). For the synthesis of the former, buta-1,3-diynediyl-bridged (+)-(*S*,*S*)-**33** was obtained by the route described in [29] for its antipode (−)-(*R*,*R*)-**33** (*Scheme 6*). MOM-Ether deprotection (→(*S*,*S*)-**34**) and phosphodiester formation, followed by ion-exchange, afforded (*S*,*S*)-**31**.

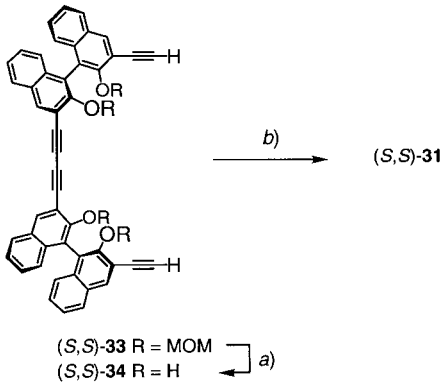
The synthesis of the reference compound (*S*,*S*)-**32** with a *p*-phenylene-spacer started with the unsymmetrically functionalized 1,1′-binaphthalene derivatives (*S*)-**35** or (*S*)-**36**, which were prepared from symmetrical diiodinated (*S*)-**27** by single *Sonogashira* cross-coupling under carefully controlled conditions (*Scheme 7*). When 2.0 equiv. of $R_3Si-C\equiv CH$ (R = Me or i-Pr) in very dilute solution at 40° were used, and the reaction was immediately quenched after the appearance of dialkynylated product



(*S*,*S*)-**31** (*S*,*S*)-**32**

Fig. 2. *Non-dendritic reference compounds (*S,S*)-***31*** *and (*S,S*)-***32***

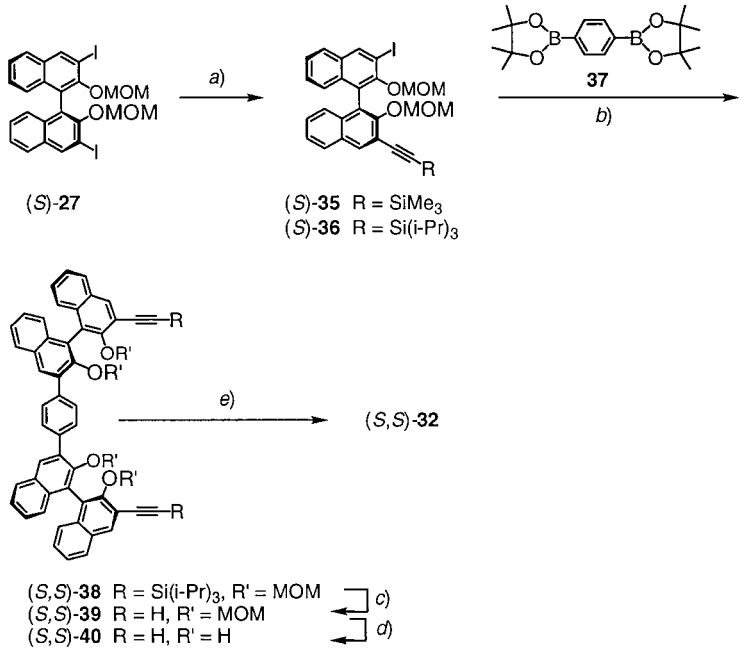
Scheme 6. *Synthesis of the Buta-1,3-diyne-1,4-diyl-Linked Reference Compound (*S,S*)-***31**



a) Conc. HCl (cat.), THF/MeOH, 20°, 10 h. *b*) $POCl_3$, Et_3N, CH_2Cl_2, 20°, 3 h; then THF/H_2O, 30°, 12 h; then *Dowex* (Bu_4N^+), CH_2Cl_2/MeCN 1:1; 52% (from (*S,S*)-**33**).

(generally after 3–5 h; TLC), (*S*)-**35** and (*S*)-**36**, respectively, were obtained in 30% yield. Other conditions (such as ambient temperature, 0.5–1.0 equiv. of $R_3Si-C\equiv CH$) gave worse results, with chromatographic product separation becoming very tedious

Scheme 7. *Synthesis of the* p*-Phenylene-Linked Reference Compound (*S,S*)-***32**



a) $R_3Si-C\equiv CH$, [$PdCl_2(PPh_3)_2$], CuI, Et_3N, toluene, 40°, 3–4 h; 30%. *b*) [$PdCl_2$(dppf)], aq. Na_2CO_3 soln., benzene, EtOH, 80°, 12 h; 74% (from (*S*)-**36**). *c*) Bu_4NF, THF, 20°, 1 h; 97%. *d*) Conc. HCl (cat.), THF/MeOH, 20°, 10 h. *e*) $POCl_3$, Et_3N, CH_2Cl_2, 20°, 3 h; then THF/H_2O, 30°, 12 h; then *Dowex* (Bu_4N^+), CH_2Cl_2/MeCN 1:1; 55% (from (*S*)-**39**).

and difficult. Due to greater differences in polarity, the (i-Pr)$_3$Si-protected derivative (*S*)-**36** was more readily separated from dialkynylated side product than the Me$_3$Si-protected analog.

For the subsequent *Suzuki* cross-coupling to build the C-skeleton of (*S*,*S*)-**32**, bis[boronate] **37** was prepared by Pd-catalyzed cross-coupling [34], starting from (pinacolato)boron and 1,4-diiodobenzene. The second coupling occurred only after heating the mixture for 12 h to 80°. In this conversion, the monosubstituted reduction product, 2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxoborolane, was also formed in significant yields (up to 50%). Partial decomposition occurred during column chromatography, but purification could be achieved by recrystallization from hexane to provide pure **37** as white needles in 44% yield. Compound **37** is an interesting new building block that can be applied to diverse molecular scaffolding.

The *Suzuki* cross-coupling required strongly basic conditions and protic solvent mixtures and could, therefore, not be conducted with (*S*)-**35**. The Me$_3$Si alkyne protecting group is too labile under these conditions, and cleavage, followed by undesirable homo-coupling, became the predominant reaction channel.

The cross-coupling between (i-Pr)$_3$Si-protected (*S*)-**36** and **37** under formation of (*S*,*S*)-**38** was examined under various conditions. It was found that the reaction was best conducted with [PdCl$_2$(dppf)] as catalyst in a mixture of benzene, EtOH, and aq. Na$_2$CO$_3$ solution. After 3 h at 80°, the product had been already formed in good yields. Repeated addition of catalyst over 12 h finally afforded (*S*,*S*)-**38** after GPC in 74% yield (*Scheme 7*). Removal of the (i-Pr)$_3$Si groups with Bu$_4$NF proceeded smoothly and gave (*S*,*S*)-**39** in 75% yield. MOM Deprotection (→(*S*,*S*)-**40**) and phosphodiester formation, followed by ion-exchange, completed the synthesis of (*S*,*S*)-**32**.

The three dendroclefts *G-2*-(*S*,*S*)-**41**, *G-2*-(*S*,*S*)-**42**, and *G-1*-(*S*,*S*)-**43** with bis(1,1′-binaphthalene-2,2′-diyl phosphate) cores (*Fig. 3*) were prepared as described below.

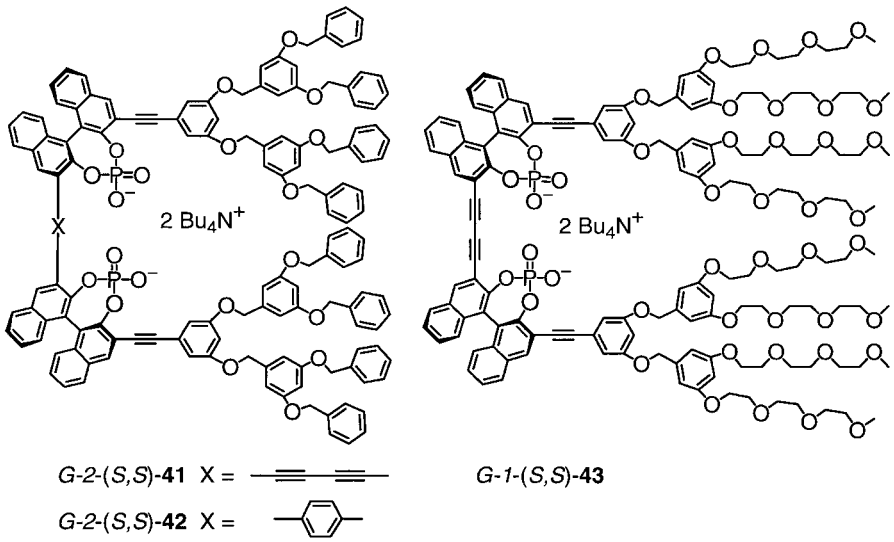


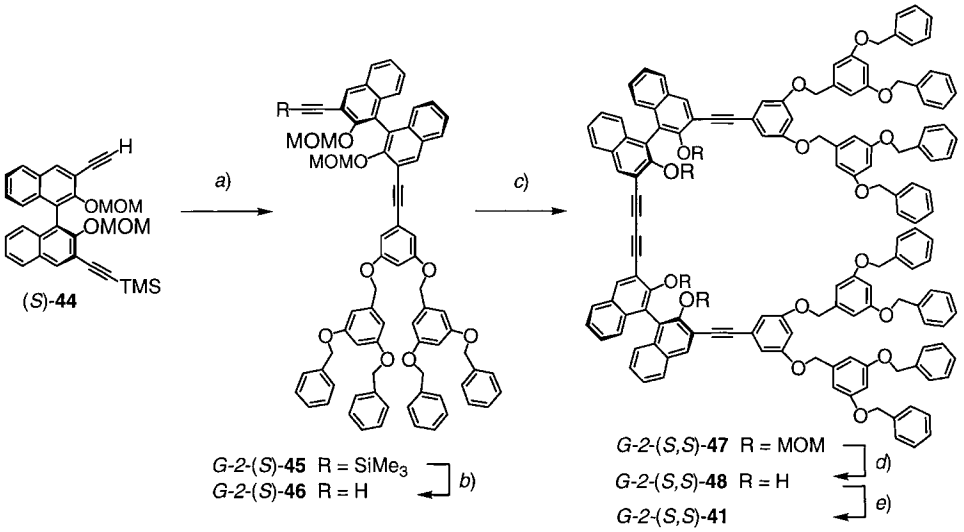
Fig. 3. *Dendritic receptors with bis(1,1′-binaphthalene-2,2′-diyl phosphate) cores*

For the synthesis of *G-2-*(*S,S*)-**41**, mono-deprotected bis-alkynylated (*S*)-**44** [29] was subjected to the *Sonogashira* cross-coupling with *G-2-***9** to give *G-2-*(*S*)-**45** (*Scheme 8*). The best yield (67%) was obtained when the alkyne was added slowly to the mixture of iodinated dendron, catalysts, and base; under these conditions homo-coupling of the alkyne was largely avoided. Purification of *G-2-*(*S*)-**45** was best accomplished by GPC. Alkyne deprotection provided *G-2-*(*S*)-**46**, which was subjected to *Glaser-Hay* homo-coupling to give *G-2-*(*S,S*)-**47** in 81% yield after GPC. Finally, the standard sequence of MOM-ether deprotection (→ *G-2-*(*S,S*)-**48**) and phosphodiester formation, followed by ion-exchange, led to dendrocleft *G-2-*(*S,S*)-**41** in a high overall yield of 13% starting from (*S*)-1,1′-binaphthalene-2,2′-diol [29].

The synthesis of dendritic receptor *G-2-*(*S,S*)-**42** with a *p*-phenylene linker between the two 1,1′-binaphthalene moieties started from (*S,S*)-**39** that was cross-coupled with iododendron *G-2-***9** to give *G-2-*(*S,S*)-**49** (*Scheme 9*). MOM-Ether deprotection (→*G-2-*(*S,S*)-**50**), phosphodiester formation, and ion-exchange afforded the desired target compound.

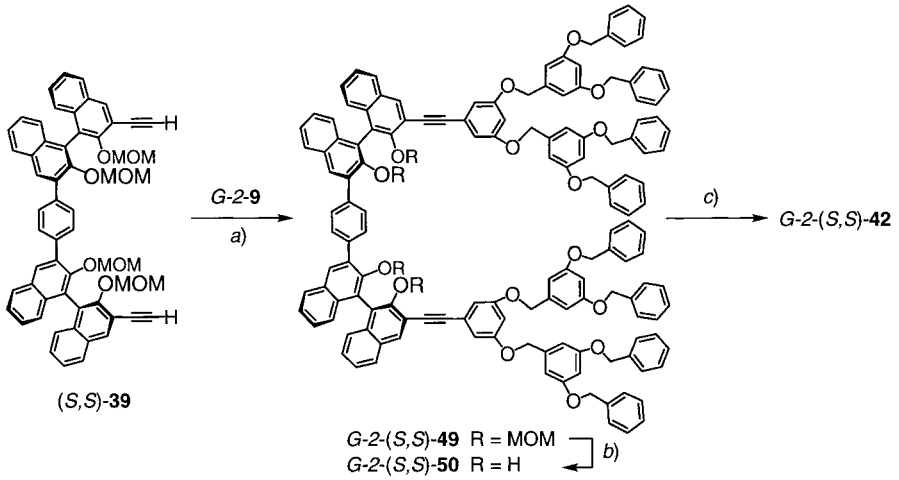
A similar sequence led from diethynylated (*S,S*)-**33** to the third dendrocleft *G-1-*(*S,S*)-**43** with a bis[1,1′-binaphthalene] core and polyether capping groups (*Scheme 10*). *Sonogashira* cross-coupling with iodo dendron **14** (→ *G-1-*(*S,S*)-**51**), MOM-ether deprotection (→ *G-1-*(*S,S*)-**52**), and phosphodiester formation, followed by ion-exchange, afforded the desired target compound. Due to the high polarity of *G-1-*(*S,S*)-**43**, with its polyether branching, chromatography (SiO_2) required a very polar solvent mixture (CH_2Cl_2/Et_3N 95:5). Under these conditions, however, some SiO_2 was

Scheme 8. *Synthesis of the Dendritic Bis(1,1′-binaphthalene-2,2′-diyl Phosphate) Receptor* G-2-(S)-**41**



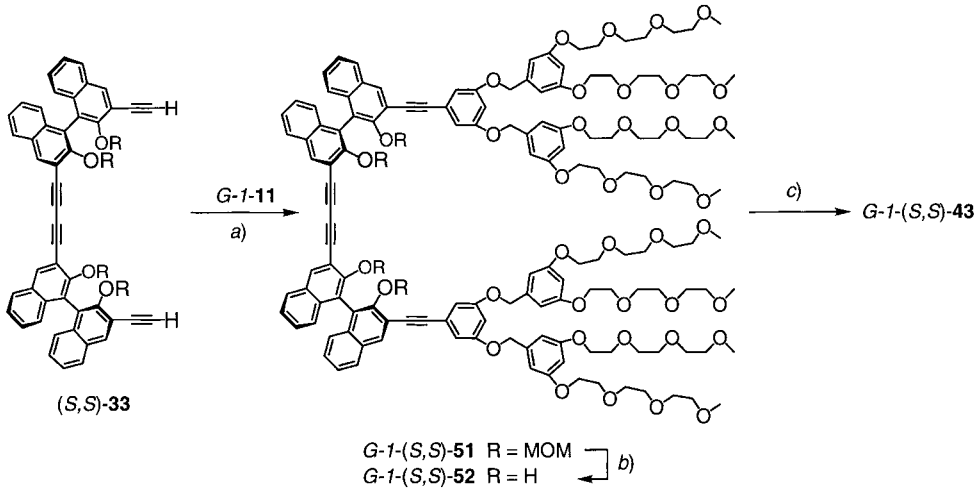
a) [$PdCl_2(PPh_3)_2$], CuI, THF/(i-Pr)$_2$NH, 45°, 5 h; 69%. *b*) K_2CO_3, THF, MeOH, 20°, 2 h. *c*) CuCl, TMEDA (*N,N,N′,N′*-tetramethylethylenediamine), air, CH_2Cl_2, 20°, 1.5 h; 81%. *d*) Conc. HCl (cat.), THF/MeOH, 20°, 10 h. *e*) $POCl_3$, Et_3N, CH_2Cl_2, 20°, 3 h; then THF/H_2O, 30°, 12 h; then *Dowex* (Bu_4N^+), CH_2Cl_2/MeCN 1:1; 82% (from *G-2-*(*S,S,*)-**47**).

Scheme 9. *Synthesis of the Dendritic Bis(1,1′-binaphthalene-2,2′-diyl Phosphate) Receptor* G-2-(S)-**42**



a) [$PdCl_2$(dppf)], CuI, THF/(i-Pr)$_2$NH, 40°, 4 h; 48%. *b*) Conc. HCl (cat.), THF/MeOH, 20°, 10 h. *c*) $POCl_3$, Et_3N, CH_2Cl_2, 20°, 3 h; then THF/H_2O, 30°, 12 h; then *Dowex* (Bu_4N^+), CH_2Cl_2/MeCN 1:1; 79% (from *G-2-*(*S,S*)-**48**).

Scheme 10. *Synthesis of the Dendritic Bis(1,1′-binaphthalene-2,2′-diyl Phosphate) Receptor* G-1-(S)-**43**

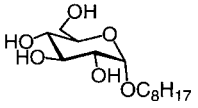


a) [$PdCl_2(PPh_3)_2$], CuI, THF/(i-Pr)$_2$NH, 40°, 4 h; 34%. *b*) Conc. HCl (cat.), THF/MeOH, 20°, 12 h. *c*) $POCl_3$, Et_3N, CH_2Cl_2, 20°, 4.5 h; then THF/H_2O, 40°, 12 h; then *Dowex* (Bu_4N^+), CH_2Cl_2/MeCN 1:1; 35% (from *G-1-*(*S,S*)-**51**).

dissolved, which necessitated subsequent extractions with CH_2Cl_2/H_2O and led to a low yield (35%) in the last step of the synthesis.

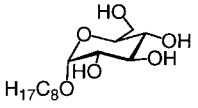
2.3. *Sugar Complexation with the Dendritic Receptors.* Binding studies with the octyl glucosides **53**–**55** were performed by 500-MHz ^{1}H-NMR titrations at 300 K. In most cases, the complexation-induced downfield shifts of the proton signals of the receptor,

held at constant concentration, were monitored as a function of guest concentration. Some inverse titrations (constant guest concentration and variable receptor concentration), following the upfield shifts of signals of the monosaccharides, were also undertaken for comparison. The standard solvent for the titrations was CD_3CN, although some studies were also executed in less polar ($CDCl_3$, favoring host-guest H-bonding) or more polar solvent systems (CD_3CN/MeOD (98:2), $(CD_3)_2SO$, and even D_2O, which favor apolar interactions and hydrophobic desolvation) [1]. In several titrations, the evaluation of the thermodynamic quantities K_a [M^{-1}] and ΔG^0 [kcal mol^{-1}] for 1:1 host-guest complexation was hampered by the formation of complexes with higher stoichiometry.



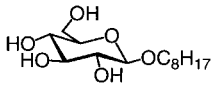
Octyl α-D-glucoside

53



Octyl α-L-glucoside

54



Octyl β-D-glucoside

55

2.3.1. *[1]H-NMR Binding Studies with Receptors Featuring One 1,1′-Binaphthalene-2,2-diyl-Phosphate Recognition Site.* By comparing the sugar-binding ability of dendroclefts *G-1*-(*S*)-**1**, *G-2*-(*S*)-**2**, and *G-3*-(*S*)-**3** to that of reference compounds (*S*)-**4** and (*S*)-**5**, which lack the dendritic shell, we hoped to identify the contributions to the binding free enthalpy resulting from the *Fréchet*-type dendrons in the former. The dendritic shell could provide an environment of reduced polarity around the phosphodiester site, thereby strengthening the bidentate ionic H-bonding to two OH groups of the sugar substrate. Furthermore, the apolar regions of the sugar substrates could interact favorably with the aromatic rings in the dendritic wedges. Therefore, we expected increasing host-guest binding strength with enhanced dendritic coverage.

2.3.1.1. *Studies with the Reference Receptors.* For the small cleft-type receptors (*S*)-**4** and (*S*)-**5**, it could not be excluded that two such molecules would bind to one sugar molecule, thereby forming complexes with 2:1 host-guest stoichiometry. The analysis of the ^{1}H-NMR data (300 K), by *Job*'s method of continuous variation [39], however, clearly confirmed the exclusive formation of a complex with 1:1 host-guest stoichiometry between (*S*)-**5** and **55** in CD_3CN. In this experiment at a total concentration of the binding partners of 2.0 mM, the complexation-induced upfield shift $\Delta\delta$ of the sugar resonance H–C(1) was monitored as a function of the mole fraction of the sugar x_{sugar}. The plot of $\Delta\delta/x_{sugar}$ as a function of x_{sugar} gave a clear maximum at 0.5, indicating a 1:1 host-guest stoichiometry.

The same experiment with (*S*)-**4** and **55** in CD_3CN led to insignificant changes in both $\Delta\delta/x_{sugar}$ and $\Delta\delta/x_{receptor}$, which prevented an accurate determination of the complex stoichiometry. In $CDCl_3$, the *Job* plot for this association gave a flat curve without a clear maximum, thereby preventing any precise analysis, too.

In ^{1}H-NMR binding titrations with (*S*)-**5**, the receptor exhibited small ($\Delta\delta_{sat} <$ 0.1 ppm) but highly reproducible complexation-induced downfield shifts of the sharp resonances for the binaphthalene proton H–C(4) and the phenyl proton H–C(9) (for the arbitrary numbering, see *Fig. 1*). In studies with (*S*)-**4**, the small downfield shifts

($\Delta\delta_{sat} < 0.1$ ppm) of the binaphthalene resonance H–C(4) and the ethynyl signal were followed. *Table 1* gives the averaged association constants K_a [M^{-1}] and complexation free enthalpies ΔG^0 [kcal mol^{-1}] calculated by nonlinear least-square curve-fitting analysis of the titration data with the program *Associate V.1.6* [40].

Reference receptor (*S*)-**4** binds octyl glucosides **53**–**55** in CD_3CN with low affinity ($K_a = 70–150\ M^{-1}$, $\Delta G^0 = -2.5$ to -2.9 kcal mol^{-1}). With the Ph-substituted receptor (*S*)-**5**, the association constants increase ($K_a = 160–200\ M^{-1}$, $\Delta G^0 = -3.0$ to -3.1 kcal mol^{-1}), presumably as a result of favorable interactions (dispersion and CH $\cdots\pi$) between the two Ph rings and apolar regions of the sugar. An inverse titration of (*S*)-**5** and **55** gave a slightly higher association constant ($K_a = 300\ M^{-1}$, $\Delta G^0 = -3.4$ kcal mol^{-1}). The strength of H-bonding interactions is extremely sensitive to the environment [3], and such a discrepancy between thermodynamic data obtained from standard and inverse titrations may well originate from the differences in the experimental conditions. Also, the data are not corrected for possible self-association between the binding partners that can interfere differentially in both titration modes.

As expected, a significant enhancement in the value of the association constant ($K_a = 1220\ M^{-1}$, $\Delta G^0 = -4.2$ kcal mol^{-1} for the complex of (*S*)-**5** with **55**) was obtained when the studies were carried out in the less competitive solvent $CDCl_3$.

All titration data discussed so far were in good agreement with a 1:1 host-guest complexation mode. However, the binding curve that resulted from the titration of (*S*)-**4**

Table 1. *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 Receptors* (S)-**4** *and* (S)-**5** *with Monosaccharides* **53**–**55** *in* CD_3CN *or* $CDCl_3$ (300 K). Also shown are the calculated and, in parentheses, the maximum observed complexation-induced shifts ([ppm], + = downfield), $\Delta\delta_{sat}$ and $\Delta\delta_{max\,obs}$, of the receptor signals monitored during the titration.

Sugar/Solvent [a])	Receptor	K_a [b]) [M^{-1}]	ΔG^0 [kcal mol^{-1}]	$\Delta\delta_{sat}$ ($\Delta\delta_{max\,obs}$) [ppm]
53/CD_3CN	(*S*)-**4**	70	−2.5	H–C(4): +0.047 (+0.026)
				≡C–H: +0.100 (+0.056)
54/CD_3CN	(*S*)-**4**	120	−2.8	H–C(4): +0.032 (+0.020)
				≡C–H: +0.087 (+0.044)
55/CD_3CN	(*S*)-**4**	150	−2.9	H–C(4): +0.035 (+0.024)
				≡C–H: +0.082 (+0.043)
55/$CDCl_3$	(*S*)-**4** [c])	960	−4.1	H–C(4): +0.046 (+0.042)
		260	−3.2	≡C–H: +0.38 (+0.27)
55/$CDCl_3$ [d])	(*S*)-**4**	2060	−4.5	H–C(1): −0.049 (−0.045) [e])
53/CD_3CN	(*S*)-**5**	160	−3.0	H–C(4): +0.038 (+0.025)
				H–C(9): +0.080 (+0.051)
54/CD_3CN	(*S*)-**5**	200	−3.1	H–C(4): +0.042 (+0.028)
				H–C(9): +0.074 (+0.053)
55/CD_3CN	(*S*)-**5**	180	−3.1	H–C(4): +0.034 (+0.023)
				H–C(9): +0.078 (+0.054)
55/CD_3CN [d])	(*S*)-**5**	300	−3.4	H–C(1): −0.088 (−0.055) [e])
55/$CDCl_3$	(*S*)-**5**	1220	−4.2	H–C(4): +0.053 (+0.048)
				H–C(9): +0.064 (+0.058)

[a]) Host concentration was constant at 1.0 mM, guest concentration varied between 0.3 and 12.5 mM. [b]) Uncertainty in K_a estimated at 10%. [c]) Strongly different results for the two signals H–C(4) and H–C(10) indicate higher-order stoichiometries. [d]) Inverse titration with constant sugar concentration (0.5 mM) and host concentration varied between 0.2 and 6.3 mM. [e]) $\Delta\delta_{sat}$ ($\Delta\delta_{max\,obs}$) of the sugar resonance H–C(1).

with **55** in $CDCl_3$ exhibited only a poor fit to the 1:1 stoichiometry model. Furthermore, the thermodynamic quantities calculated from the downfield shifts of the binaphthalene resonance H–C(4) and the ethynyl resonance differed strongly, and an inverse titration gave a significantly higher association constant (see *Table 1*). These observations can be rationalized by the formation of complexes with higher stoichiometries, which was not further investigated in the course of this work. These findings are in agreement with results from *Job*-plot analyses (see above), which had remained inconclusive with respect to the host-guest stoichiometry.

2.3.1.2. *Studies with the Dendroclefts.* Compounds *G-1*-(*S*)-**1**, *G-2*-(*S*)-**2**, and *G-3*-(*S*)-**3** do not aggregate appreciably in CD_3CN at concentrations below 5.0 mM, as was confirmed by ^{1}H-NMR dilution experiments. In binding titrations with *G-1*-(*S*)-**1** and *G-2*-(*S*)-**2**, the receptors exhibited small but highly reproducible downfield shifts ($\Delta\delta_{sat} < 0.1$ ppm) of the sharp binaphthalene signal (H–C(4)) and the phenyl resonance (H–C(9)) (for numbering, see *Fig. 1*) upon addition of the monosaccharide guests **53**–**55**. In titrations with *G-3*-(*S*)-**3**, the shifts of the H–C(4) signal were negligible and could not be evaluated. All data could be nicely fitted to the 1:1 host-guest binding model (*Table 2*). This stoichiometry was confirmed by *Job*-plot analysis for the complex formed between *G-1*-(*S*)-**1** and **55**.

The complexes formed by the first-generation dendrocleft *G-1*-(*S*)-**1** were significantly more stable ($K_a = 260-350$ M^{-1}) than those of reference compound (*S*)-**4** ($K_a = 70-150$ M^{-1}). A further, slight enhancement in binding strength was observed with the second-generation receptor *G-2*-(*S*)-**2**, whereas host-guest affinity started decreasing at the third-generation level. It can be assumed that steric hindrance by

Table 2. *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 Receptors* G-1-(S)-**1**, G-2-(S)-**2**, *and* G-3-(S)-**3** *with Monosaccharides* **53**–**55** *in* CD_3CN *or* $CDCl_3$ (300 K). Also shown are the calculated and, in parentheses, the maximum observed complexation-induced shifts ([ppm], + = downfield), $\Delta\delta_{sat}$ and $\Delta\delta_{max\,obs}$, of the receptor signal H–C(9) monitored during the titration.

Sugar/Solvent[a])	Receptor	K_a[b]) [M^{-1}]	ΔG^0 [kcal mol^{-1}]	$\Delta\delta_{sat}$ ($\Delta\delta_{max\,obs}$) [ppm]
53/CD_3CN	*G-1*-(*S*)-**1**	260	−3.3	+0.074 (0.055)
54/CD_3CN	*G-1*-(*S*)-**1**	240	−3.2	+0.068 (+0.051)
55/CD_3CN	*G-1*-(*S*)-**1**	350	−3.5	+0.063 (+0.050)
55/$CDCl_3$	*G-1*-(*S*)-**1**	1160	−4.2	+0.058 (+0.053)
53/CD_3CN	*G-2*-(*S*)-**2**	270	−3.3	+0.067 (+0.055)
54/CD_3CN	*G-2*-(*S*)-**2**	330	−3.4	+0.064 (+0.050)
55/CD_3CN	*G-2*-(*S*)-**2**	370	−3.5	+0.059 (+0.047)
55/$CDCl_3$	*G-2*-(*S*)-**2**	2280	−4.6	+0.065 (+0.060)
55/CD_3CN[c])	*G-2*-(*S*)-**2**	740	−3.9	−0.125 (−0.084)[d])
53/CD_3CN	*G-3*-(*S*)-**3**	180	−3.1	+0.052 (+0.034)
54/CD_3CN	*G-3*-(*S*)-**3**	220	−3.2	+0.055 (+0.039)
55/CD_3CN	*G-3*-(*S*)-**3**	290	−3.4	+0.052 (+0.040)
55/$CDCl_3$	*G-3*-(*S*)-**3**	760	−3.9	+0.066 (+0.058)

[a]) Host concentration was constant at 1.0 mM (0.5 mM for *G-3*-(*S*)-**3**, guest concentration varied between 0.3 and 12.5 mM. [b]) Uncertainty in K_a estimated at 10%. Similar K_a values were obtained when the complexation-induced shift of the binaphthalene resonance (H–C(10)) could be evaluated. [c]) Inverse titration with constant sugar concentration (0.5 mM) and host concentration varied between 0.1 and 3.1 mM. [d]) $\Delta\delta_{sat}$ ($\Delta\delta_{max\,obs}$) determined for the upfield shift of the sugar resonance H–C(1).

the bulky dendritic wedges starts interfering with the docking of the sugar at the buried phosphodiester H-bonding site inside *G-3*-(*S*)-**3**. Substrate selectivity is low in all cases, with a slight preference being observed for the complexation of octyl β-D-glucoside **55**. From an inverse titration (at constant sugar concentration) of *G-2*-(*S*)-**2** with **55**, a higher binding constant ($K_a = 740\ M^{-1}$, $\Delta G^0 = -3.9$ kcal mol^{-1}) with respect to that obtained in the standard titration (at constant receptor concentration; $K_a = 370\ M^{-1}$, $\Delta G^0 = -3.5$ kcal mol^{-1}) was calculated. The same phenomenon had already been observed in the inverse titration of reference receptor (*S*)-**4** with **55** and confirms the sensitivity of H-bonding interactions towards different experimental conditions.

In titrations in CD_3CN/CD_3OD 98:2, the maximum observed changes in chemical shift of the receptor protons decreased as did the values of the association constants (K_a in all cases *ca.* $100\ M^{-1}$) calculated for the formed 1:1 complexes. This decrease in host-guest affinity was independent of dendritic generation. Attempted titrations between *G-2*-(*S*)-**2** and **55** in $(CD_3)_2SO$ – a solvent which competes effectively for the H-bonding donor sites in the sugar substrate – could not be evaluated, since complexation strength was too low. In the noncompetitive solvent $CDCl_3$, however, binding strength was enhanced significantly, with the second-generation receptor forming the most stable complex with guest **55** ($K_a = 2280\ M^{-1}$, $-\Delta G^0 = 4.6$ kcal mol^{-1}). These solvent-dependent studies clearly show that bidentate ionic H-bonding is by far the most important interaction in the complexes formed by the dendroclefts, and that dispersion interactions and solvophobic effects make much smaller contributions to the measured binding free enthalpies.

When the acetylenic spacer between the 1,1′-binaphthalene core and the dendritic shell was removed, an interesting solvent dependency of the association strength was observed. A comparison of the complexation of the octyl glycosides by the first-generation dendroclefts *G-1*-(*S*)-**1** (*Table 2*) and *G-1*-(*S*)-**26** (*Table 3*) in CD_3CN reveals a significant decrease in association strength upon removal of the ethynediyl spacers. Thus, the complex of **55** with *G-1*-(*S*)-**26** is 0.7 kcal mol^{-1} less stable than the complex formed by *G-1*-(*S*)-**1**. On the other hand, the association strength remains identical ($\Delta G^0 = -4.2$ kcal mol^{-1}) in $CDCl_3$. The origin of this substantial solvent effect

Table 3. *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 Receptor* G-1-(S)-**26** *with Monosaccharides* **53**–**55** *in* CD_3CN *and* $CDCl_3$ (300 K). Also shown are the calculated and, in parentheses, the maximum observed complexation-induced shifts ([ppm], + = downfield), $\Delta\delta_{sat}$ and $\Delta\delta_{max\,obs}$, of the receptor signals H–C(8) and H–C(9) monitored during the titration (for the numbering, see *Scheme 5*).

Sugar/Solvent[a])	K_a[b]) [M^{-1}]	ΔG^0 [kcal mol^{-1}]	$\Delta\delta_{sat}$ ($\Delta\delta_{max\,obs}$) H–C(8) [ppm]	$\Delta\delta_{sat}$($\Delta\delta_{max\,obs}$) H–C(9) [ppm]
53/CD_3CN	90	−2.7	−0.069 (−0.035)	+0.178 (+0.093)
54/CD_3CN	80	−2.6	−0.072 (−0.035)	+0.207 (+0.104)
55/CD_3CN	110	−2.8	−0.075 (−0.043)	+0.203 (+0.119)
55/CD_3CN[c])	40	−2.2	−0.113 (−0.040)	no significant shift
55/$CDCl_3$	1230	−4.2	−0.056 (−0.053)	+0.167 (+0.155)

[a]) Host concentration was constant at 1.0 mM, guest concentration varied between 0.3 and 12.5 mM. [b]) Uncertainties in K_a estimated at ±10%. [c]) Addition of 2% MeOD.

remains unclear at present. It could result both from differences in the solvation of the H-bonding groups of the binding partners and solvent-dependent interactions between the sugar and the dendritic Ph groups of the two receptors.

The effect of solvent on association strength again changes when receptor *G-1*-(*S*)-**23** with ethynediyl spacers and oligoether capping groups is used. In $CDCl_3$, the introduction of the oligoether groups does not affect the measured binding free enthalpy, and monosaccharide **55** forms complexes of nearly identical stability with the first-generation receptors *G-1*-(*S*)-**1** (*Table 2*) and *G-1*-(*S*)-**23** (*Table 4*). In CD_3CN, however, the oligoether receptor is more effective by 0.2–0.3 kcal mol^{-1}. Dendritic oligoether wedges have previously been shown to participate in carbohydrate recognition, presumably through O···H–O H-bonding [15b]. In this present case, such interactions seem to make a larger contribution to the binding in CD_3CN than in $CDCl_3$.

Table 4. *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 Receptor* G-1-(S)-**23** *with Monosaccharides* **53**–**55** *in* CD_3CN *and* $CDCl_3$ (300 K). Also shown are the calculated and, in parentheses, the maximum observed complexation-induced shifts ([ppm], + = downfield), $\Delta\delta_{sat}$ and $\Delta\delta_{max\,obs}$, of the receptor H–C(4) and H–C(9) signals monitored during the titration (for the numbering, see *Fig. 1*).

Sugar/Solvent[a])	K_a[b]) [M^{-1}]	ΔG^0 [kcal mol^{-1}]	$\Delta\delta_{sat}$ ($\Delta\delta_{max\,obs}$) H–C(4) [ppm]	$\Delta\delta_{sat}$ ($\Delta\delta_{max\,obs}$) H–C(9) [ppm]
53/CD_3CN	370	−3.5	+0.040 (+0.032)	+0.054 (+0.043)
54/CD_3CN	310	−3.4	+0.042 (+0.033)	+0.054 (+0.043)
55/CD_3CN	570	−3.8	+0.041 (+0.033)	+0.050 (+0.044)
55/CD_3CN[c])	130	−2.9	+0.022 (+0.012)	+0.024 (+0.013)
55/$CDCl_3$	1090	−4.1	+0.048 (+0.043)	+0.056 (+0.051)

[a]) Host concentration was constant at 1.0 mM, guest concentration varied between 0.5 and 12.5 mM. [b]) Uncertainties in K_a estimated at ±10%. [c]) Addition of 2% MeOD.

2.3.2. *^{1}H-NMR Binding Studies with Receptors Featuring Two 1,1′-Binaphthalene-2,2-diyl-Phosphate Recognition Sites.* Dendritic receptors with two ionic H-bonding sites were expected to exhibit higher association strength and substrate selectivity [21]. On the other hand, nearly free rotation about the buta-1,3-diynediyl or *p*-phenylene spacer between the two 1,1′-binaphthalene moieties enables these systems to adopt a large number of conformations. Cooperative binding of one sugar molecule to both phosphodiester sites – with formation of a 1:1 host-guest complex – can only take place in the '*syn*'-conformation, in which the two 1,1′-binaphthalene moieties are oriented in the same direction. Computer modeling [41] and CPK (*Corey-Pauling-Koltum*) model examinations indicated that the '*syn*'-conformers of the receptors with a buta-1,3-diynediyl bridge feature an appropriately sized cleft to accommodate monosaccharide guests through ionic H-bonding to both phosphodiester moieties. Previous studies with macrocyclic receptors, in which the buta-1,3-diynediyl-bridged 1,1′-binaphthalene-2,2′-diyl-phosphate sites are forced into the '*syn*'-conformation, further corroborated these expectations [21a]. In contrast, '*anti*'-type conformations, with the two phosphodiester sites pointing in opposite directions, could favor formation of 1:2 host-guest complexes. Even the formation of complexes in which two receptor molecules surround one guest molecule could not be excluded *a priori*.

2.3.2.1. *Binding Studies with Reference Receptors.* In ^{1}H-NMR binding titrations at constant concentration of receptors (*S*,*S*)-**31** and (*S*,*S*)-**32**, the resonance of the acetylenic H-atom was conveniently monitored (*Table 5*). In some titrations, complexation-induced downfield shifts of the binaphthalene resonances (H–C(4), H–C(4′), and H–C(8); for numbering, see *Fig. 2*) could also be evaluated, providing similar thermodynamic quantities.

Table 5. *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 Receptors* (S,S)-**31** and (S,S)-**32** *with Monosaccharides* **53**–**55** *in* CD_3CN (300 K). Also shown are the calculated and, in parentheses, the maximum observed complexation-induced shifts ([ppm], + = downfield), $\Delta\delta_{sat}$ and $\Delta\delta_{max\,obs}$, of the ethynyl resonance of the receptor which was monitored during the titration.

Sugar[a])	Receptor	K_a[b]) [M^{-1}]	ΔG^0 [kcal mol^{-1}]	$\Delta\delta_{sat}$ ($\Delta\delta_{max\,obs}$) [ppm]
53	(*S*,*S*)-**31**	200	– 3.1	+ 0.065 (+ 0.044)
54	(*S*,*S*)-**31**	150	– 3.0	+ 0.076 (+ 0.045)
55	(*S*,*S*)-**31**	350	– 3.5	+ 0.066 (+ 0.054)
53	(*S*,*S*)-**32**	210	– 3.2	+ 0.059 (+ 0.042)
54	(*S*,*S*)-**32**	260	– 3.3	+ 0.065 (+ 0.051)
55	(*S*,*S*)-**32**	280	– 3.4	+ 0.057 (+ 0.038)

[a]) Host concentration was constant at 0.5 mM, guest concentration varied between 0.3 and 12.5 mM. [b]) Uncertainty in K_a estimated at 10%.

The two receptors (*S*,*S*)-**31** and (*S*,*S*)-**32** form 1:1 complexes of comparable stability with octyl glucosides in CD_3CN ($K_a = 150–350\ M^{-1}$, $\Delta G^0 = -3.0$ to -3.5 kcal mol^{-1}; *Table 5*). The association constants are increased by a factor of about two, as compared to those determined for the corresponding complexes of the non-dendritic receptor (*S*)-**4** featuring only one phosphodiester site (*Table 1*). The substrate selectivity remained low in all cases. Competing higher-order complexation prevented the determination of the stability of 1:1 host-guest complexes in $CDCl_3$.

2.3.2.2. *Binding Studies with the Dendritic Receptors.* The dendritic receptors *G-2*-(*S*,*S*)-**41** and *G-1*-(*S*,*S*)-**43** with buta-1,3-diynediyl spacers showed good solubility in CD_3CN (up to 5 mM) and did not aggregate appreciably at concentrations below 5 mM (^{1}H-NMR dilution experiment with *G-2*-(*S*)-**41**). Complexation-induced shifts observed in the ^{1}H-NMR spectra in CD_3CN indicated that the receptors were interacting with the octyl glucosides. *Job*-plot analyses were subsequently performed with receptor *G-2*-(*S*,*S*)-**41** and octyl glucoside **55** in order to shed light on the stoichiometry of the associations formed. Due to only very modest changes of $\Delta\delta/x_{sugar}$ or $\Delta\delta/x_{host}$, the curves exhibited flat shapes weakly indicating a maximum around 0.5. This result was considered to be a first, yet inconclusive, indication for a 1:1 host-guest complexation mode.

Liquid-liquid extractions with receptor *G-2*-(*S*,*S*)-**41** (1.0 mM in $CDCl_3$ or CD_3CN) and D-glucose (40 mM in H_2O), in which the mixture was exposed for 15 min to an ultrasonic bath at 20°, resulted in no extraction of the sugar into the organic phase (^{1}H-NMR). Under the same experimental conditions (receptor concentration 1.0 mM), however, solid D-glucose was solubilized in both $CDCl_3$ and CD_3CN. A strong broadening of all signals was observed in the ^{1}H-NMR spectra of the organic solutions

after extraction, which prevented any analysis of stoichiometry and host-guest bonding. Therefore, the solvent was evaporated, and the resulting solid was redissolved in $(CD_3)_2SO$. In this solvent, the interaction between host and guest that caused the signal broadening became very weak, and the amount of extracted sugar could be determined by integration of the ^{1}H-NMR resonances of the binding partners. The results indicated that 1.0 equiv. of D-glucose was extracted into the CD_3CN solution, whereas, under the same conditions, 2.0 equiv. of the sugar were extracted into the $CDCl_3$ solution.

^{1}H-NMR Binding titrations with *G-2*-(*S*,*S*)-**41** and octyl glucosides **53**–**55** were subsequently carried out at 300 K in dry CD_3CN, $CDCl_3$, and CD_3CN/MeOD 98:2. Highly resolved spectra were obtained, and the complexation-induced downfield shift of the signals of the 1,1′-binaphthalene protons H–C(4) and H–C(4′) could be readily monitored during the titrations. However, nonlinear least-squares curve fitting to a 1:1 host-guest complexation model with *Associate V. 1.6* was not successful. It became clear that higher-order association occurred predominantly. Attempts to further analyze the situation with the program *Specfit V.2.10* [42], which is capable of fitting data from multiple binding equilibria, failed. Disappointingly, a similar situation was encountered in binding studies with *G-2*-(*S*,*S*)-**42** and *G-1*-(*S*,*S*)-**43**. All attempts to determine concentration conditions for standard or inverse titrations, under which one single defined host-guest complexation stoichiometry would prevail, failed. The absence of defined 1:1 host-guest association clearly contrasts with the preference of the non-dendritic reference compounds (*S*,*S*)-**31** and (*S*,*S*)-**32** to form 1:1 host-guest complexes (*Table 5*). It must, therefore, be concluded that the dendritic wedges prevent 1:1 host-guest complexation by the dendroclefts. We propose that the '*syn*'-conformations of these receptors, in which the two phosphodiester moieties can bind cooperatively to one sugar molecule, are strongly disfavored due to repulsive intramolecular interactions between the dendritic wedges.

3. Conclusions. – Two classes of optically active, cleft-type dendritic receptors (*dendroclefts*) for carbohydrate recognition were constructed by efficient, high-yielding routes. The first series contains a 1,1′-binaphthalene-2,2′-diyl phosphate core embedded into *Fréchet*-type dendrons of first to third generation. The second series features similar dendritic wedges (up to the second generation), whereas the core consists of two 1,1′-binaphthalene-2,2′-diyl phosphate moieties bridged by buta-1,3-diynediyl or *p*-phenylene spacers. ^{1}H-NMR Binding studies (300 K) showed that bidentate ionic H-bonding between the phosphodiester moieties and the OH-groups of octyl glucosides represents the predominant binding mode in the complexes that form in CD_3CN or less polar solvents such as $CDCl_3$. Interactions between the apolar surfaces of the sugar and the aromatic rings of the dendritic wedges provide a minor (up to a factor of *ca.* 3 in K_a) yet clearly identifiable contribution to the overall binding free enthalpy in CD_3CN. The dendritic receptors *G-1*-(*S*)-**1**, *G-2*-(*S*)-**2**, and *G-3*-(*S*)-**3** with a single 1,1′-binaphthalene core predominantly form complexes of 1:1 host-guest stoichiometry with octyl glucosides, and association strength was readily evaluated. Host-guest binding affinity increased upon changing from non-dendritic reference receptors to the first- and second-generation dendroclefts, but decreased at the third-generation level, due to steric hindrance of the core H-bonding site by the bulky dendritic wedges. The dendritic

receptors *G-2*-(*S*,*S*)-**41**, *G-2*-(*S*,*S*)-**42**, and *G-1*-(*S*,*S*)-**43** with two 1,1′-binaphthalene moieties at the core underwent complex higher-order association, and experimental conditions, under which 1:1 complexation would be predominant, could not be worked out. In contrast, the reference compounds (*S*,*S*)-**31** and (*S*,*S*)-**32**, which feature similar cores but lack the dendritic wedges, form defined 1:1 host-guest complexes. We, therefore, conclude that unfavorable intramolecular steric interactions between the dendritic wedges in *G-2*-(*S*,*S*)-**41**, *G-2*-(*S*,*S*)-**42**, and *G-1*-(*S*,*S*)-**43** prevent these receptors from adopting the '*syn*'-conformation, in which the two 1,1′-binaphthalene-2,2′-diyl phosphate sites converge to interact with a single sugar molecule under formation of a 1:1 complex. Overall, this study indicates that dendritic cleft-type receptors are too flexible to form high-affinity, high-selectivity complexes with monosaccharides. The dendritic wedges are not effective in providing apolar interactions and solvophobic driving forces required for binding carbohydrates in protic solvents. Therefore, our efforts aimed at achieving carbohydrate recognition by synthetic receptors in protic solvents, and in particular in H_2O, will be continued with the design and synthesis of more elaborate systems that feature multiple H-bonding sites converging into a spherical, highly preorganized macrocyclic recognition site of reduced polarity at the core of dendrimers.

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Experimental Part

General. All reactions were carried out under N_2. Solvents and reagents were reagent-grade and used without further purification unless otherwise stated. THF and Et_2O were freshly distilled from sodium benzophenone ketyl. Evaporation *in vacuo* was conducted at H_2O aspirator pressure. Column chromatography (CC): SiO_2 *60* (230–400 mesh, 0.040–0.063 mm) from *E. Merck* (for products containing MOM-ether protecting groups) or *Fluka*; visualization by UV light. Prep. gel-permeation chromatography (GPC): *Bio-Beads SX-1* or *SX-3* from *Bio-Rad*, eluent CH_2Cl_2 unless otherwise stated; detection at 300 nm by UV on an anal. GPC apparatus from *Merck Hitachi*. M.p.: *Büchi SMP-20*; uncorrected. Optical rotation ($[\alpha]_D^{r.t.}$): *Perkin-Elmer 241* polarimeter with a 1-dm cell at the Na-D line ($\lambda = 589$ nm) at r.t. The concentration c is given in g/100 ml. $CHCl_3$ was used as solvent unless otherwise stated. IR Spectra (cm^{-1}): *Perkin-Elmer 1600-FT IR*. NMR Spectra: *Bruker AMX 500* or *AMX 400*, and *Varian Gemini 300* or *200* at 296 or 300 K, with solvent peak as reference. MS (*m/z* (%)): EI: *VG TRIBRID* spectrometer at 70 eV; FAB: *VG ZAB2-SEQ* spectrometer with 3-nitrobenzyl alcohol (NOBA) as matrix; MALDI-TOF: *Bruker Reflex* spectrometer with 2-(4-hydroxyphenylazo)benzoic acid (HABA), α-cyano-4-hydroxycinnamic acid (CCA), 2,4,6-trihydroxyacetophenone/diammonium citrate (THA/citrate) 2:1 or 1,8,9-trihydroxyanthracene (dithranol) as matrix; positive-ion mode unless otherwise stated. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH-Zürich.

^{1}H-NMR Binding Titrations. Quantitative binding data (K_a, ΔG^0, $\Delta\delta_{sat}$) were determined by nonlinear least-squares curve-fitting of ^{1}H-NMR titration data (500 MHz, 300 K) with the program *Associate V.1.6* [40]. Commercially available guests **53** and **55** were used without further treatment. Octyl pyranoside **54** was prepared according to published procedures [43]. Titration samples were prepared by adding a soln. of guest in portions *via* microsyringe to the septum-capped NMR tube containing the host at constant concentration. After each addition, a ^{1}H-NMR spectrum was recorded. In inverse titrations, constant guest and variable host concentrations were applied. Specific concentrations used in the titrations are included in the footnotes to *Tables 1–5*.

1,3-Bis(benzyloxy)-5-iodobenzene (*G-1*-**8**). A mixture of 5-iodobenzene-1,3-diol (1.25 g, 5.3 mmol), $PhCH_2Br$ (1.81 g, 1.15 ml, 10.6 mmol), [18]crown-6 (0.42 g, 1.6 mmol), and K_2CO_3 (2.20 g, 15.9 mmol) in dry acetone (100 ml) was heated under N_2 and vigorous stirring to 55° for 24 h. The solvent was evaporated, and the

residue was dissolved in H_2O (40 ml) and CH_2Cl_2 (50 ml). The aq. layer was extracted with CH_2Cl_2 (2 × 50 ml), the combined org. phases were dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. CC (SiO_2; hexane/AcOEt 6:1) yielded *G-1*-**8** (2.1 g, 95%). White powder. M.p. 57°. IR (KBr): 3067*w*, 3032*m*, 2998*w*, 2930*w*, 2878*m*, 1592*s*, 1568*s*, 1491*m*, 1444*m*, 1425*m*, 1377*s*, 1341*w*, 1324*m*, 1277*s*, 1239*m*, 1215*m*, 1049*m*, 1028*m*, 986*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.08 (*s*, 4 H); 6.60 (*t*, *J* = 2.5, 1 H); 7.01 (*d*, *J* = 2.5, 2 H); 7.33–7.49 (*m*, 10 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 70.41; 94.26; 102.41; 117.28; 127.81; 128.42; 128.91; 136.63; 160.57. FAB-MS: 417 (100, MH^+). Anal. calc. for $C_{20}H_{17}IO_2$ (416.26): C 57.71, H 4.12, O 7.69; found: C 57.80, H 4.26, O 7.77.

1,3-Bis[3,5-bis(benzyloxy)benzyloxy]-5-iodobenzene (*G-2*-**9**). A mixture of 5-iodobenzene-1,3-diol (1.9 g, 7.8 mmol), **6** [22] (6.3 g, 16.5 mmol), [18]crown-6 (0.41 g, 1.6 mmol), and K_2CO_3 (4.3 g, 31.4 mmol) in dry acetone (140 ml) was heated under N_2 and vigorous stirring to 55° for 24 h. Workup as described for *G-1*-**8**, followed by CC (SiO_2; CH_2Cl_2/hexane 3:1) yielded *G-2*-**9** (6.0 g, 90%). White powder. M.p. 116°. IR (KBr): 3011*w*, 2889*w*, 1592*s*, 1450*m*, 1369*s*, 1328*m*, 1297*m*, 1156*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.90 (*s*, 4 H); 5.02 (*s*, 8 H); 6.50 (*t*, *J* = 2.2, 1 H); 5.56 (*t*, *J* = 2.2, 2 H); 6.62 (*d*, *J* = 2.2, 4 H); 6.92 (*d*, *J* = 2.2, 2 H); 7.26–7.42 (*m*, 20 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 70.09; 70.14; 94.03; 101.71; 102.15; 106.37; 117.04; 127.54; 128.02; 128.59; 136.73; 138.72; 160.11; 160.19. MALDI-TOF-MS (2,5-DHB): 880 (20, $[M+K]^+$), 864 (73, $[M+Na]^+$), 841 (100, MH^+). Anal. calc. for $C_{48}H_{41}IO_6$ (840.76): C 68.57, H 4.92; found: C 68.64, H 5.03.

1,3-Bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}-5-iodobenzene (*G-3*-**10**). A mixture of 5-iodobenzene-1,3-diol (0.47 g, 2.0 mmol), **7** (3.55 g, 4.4 mmol), [18]crown-6 (140 mg, 0.5 mmol), and K_2CO_3 (1.38 g, 9.0 mmol) in dry MeCN/acetone 1:1 (100 ml) was heated under N_2 and vigorous stirring to 55° for 3 d. Workup as described for *G-1*-**8**, followed by CC (SiO_2; CH_2Cl_2/hexane 3:1) yielded *G-3*-**10** (2.7 g, 79%). White solid. M.p. 53°. IR (KBr): 3027*m*, 2918*w*, 2864*m*, 1595*s*, 1449*m*, 1374*m*, 1342*w*, 1319*w*, 1292*m*, 1156*s*, 1051*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.90 (*s*, 4 H); 4.96 (*s*, 8 H); 5.01 (*s*, 16 H); 6.53–6.58 (*m*, 7 H); 6.62 (*d*, *J* = 2.4, 4 H); 6.67 (*d*, *J* = 2.1, 8 H); 6.95 (*d*, *J* = 2.1, 2 H); 7.26–7.42 (*m*, 40 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 70.01; 70.11 (2×); 94.04; 101.63; 101.73; 102.17; 106.38; 106.44; 117.05; 127.53; 127.98; 128.56; 136.77; 138.72; 139.17; 160.09; 160.13; 160.17. MALDI-TOF-MS (HABA): 1712 ($[M+Na]^+$). Anal. calc. for $C_{104}H_{89}IO_{14}$ (1689.74): C 73.93, H 5.31, O 13.26; found: C 73.77, H 5.15, O 13.04.

1,3-Bis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyloxy)-5-iodobenzene (*G-1*-**11**). To 5-iodobenzene-1,3-diol (0.30 g, 1.29 mmol) and **12** (1.11 g, 2.68 mmol) in acetone (63 ml), K_2CO_3 (0.457 g, 3.31 mmol), and [18]crown-6 (69 mg, 0.26 mmol) were added, and the mixture was heated under N_2 to 60°. After 20 h, the mixture was cooled to 20° and filtered through *Celite* and SiO_2. Evaporation *in vacuo* and GPC (*Bio-Beads SX-3*) afforded *G-1*-**11** (586 mg, 43%). Highly viscous oil. IR (neat): 3087*w*, 2938*s*, 2875*s*, 2724*w*, 1962*w*, 1754*w*, 1722*w*, 1684*w*, 1596*s*, 1572*m*, 1448*s*, 1374*m*, 1348*m*, 1321*m*, 1198*m*, 1172*s*, 1110*s*, 1070*s*, 1027*m*, 995*m*, 947*m*, 841*m*, 718*w*, 680*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.39 (*s*, 12 H); 3.54–3.59 (*m*, 8 H); 3.65–3.77 (*m*, 24 H); 3.84–3.88 (*m*, 8 H); 4.10–4.15 (*m*, 8 H); 4.92 (*s*, 4 H); 6.47 (*t*, *J* = 2.0, 2 H); 6.53–6.58 (*m*, 5 H); 6.95 (*d*, *J* = 2.2, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 59.15; 67.64; 69.80; 70.23; 70.72; 70.80; 70.96; 72.08; 94.19; 101.46; 102.35; 106.28; 117.18; 138.84; 160.44 (2×). FAB-MS: 1065 (100, M^+). Anal. calc. for $C_{48}H_{73}IO_{18}$ (1065.01): C 54.13, H 6.91; found: C 54.13, H 6.86.

(S)-3,3′-Diethynyl-1,1′-binaphthalene-2,2′-diol ((*S*)-**14**). To (*S*)-**13** (100 mg, 0.24 mmol) in THF/MeOH 1:1 (200 ml), conc. HCl (37%, 350 µl) was added. The soln. was stirred for 4 h under N_2 at 20°, then H_2O (200 ml) was added. The aq. phase was extracted with CH_2Cl_2 (2 × 100 ml), and the combined org. phases were dried (Na_2SO_4) and concentrated to give crude (*S*)-**14** (91 mg, 99%). ^{1}H-NMR (200 MHz, $CDCl_3$): 3.33 (*s*, 2 H); 5.75 (*s*, 2 H); 7.10–7.15 (*m*, 2 H); 7.31–7.41 (*m*, 4 H); 7.83–7.88 (*m*, 2 H); 8.21 (*s*, 2 H).

Tetrabutylammonium (+)-(S)-3,3′-Diethynyl-1,1′-binaphthalene-2,2′-diyl Phosphate ((+)-(*S*)-**4**). To (*S*)-**14** (0.11 g, 0.24 mmol) in dry CH_2Cl_2 (50 ml), $POCl_3$ (0.16M soln. in CH_2Cl_2, 4.8 ml, 0.53 mmol) and Et_3N (0.73 g, 1.0 ml, 7.2 mmol) were added at 20° under N_2, and the soln. was stirred for 3 h. After evaporation *in vacuo*, THF/H_2O 1:1 (40 ml) was added, and the mixture was stirred for 12 h at 40°. CH_2Cl_2 (80 ml) and H_2O (80 ml) were added, and the separated org. phase was washed with H_2O (2 × 60 ml), dried (Na_2SO_4), and concentrated. Recrystallization (toluene), followed by ion-exchange chromatography (*Dowex 50WX8*, Bu_4N^+; CH_2Cl_2/MeCN 1:1), provided (*S*)-**4** (58 mg, 38% starting from (*S*)-**13**). Yellow solid. M.p. >240°. $[\alpha]_D^{rt.} = +223.5$ (*c* = 0.5, $CHCl_3$). IR (KBr): 3310*w*, 3167*w*, 2956*m*, 2867*w*, 2100*m*, 1483*m*, 1306*s*, 1450*m*, 1236*m*, 1111*s*, 1097*s*, 903*m*, 767*m*. ^{1}H-NMR (200 MHz, CD_3CN): 0.93 (*t*, *J* = 7.2, 12 H); 1.22–1.63 (*m*, 16 H); 3.00 (*m*, 8 H); 3.60 (*s*, 2 H); 7.13–7.17 (*m*, 2 H); 7.23–7.31 (*m*, 2 H); 7.40–7.48 (*m*, 2 H); 7.91–7.95 (*m*, 2 H); 8.22 (*s*, 2 H). ^{13}C-NMR (50 MHz, CD_3CN): 13.88; 20.42; 24.43; 59.48; 81.65; 82.74; 117.94; 123.80; 126.43; 127.52; 128.33; 129.47; 131.14; 133.76; 135.82; 151.58 (*d*, $J(^{31}P,^{13}C) = 9.3$). ^{31}P-NMR (121 MHz, CD_3CN): 5.36. ESI-MS (negative-ion mode): 395 (100, $[M-Bu_4N]^-$). Anal. calc. for $C_{40}H_{48}NO_4P \cdot H_2O$ (655.82): C 73.26, H 7.68, N 2.14; found: C 73.16, H 7.67, N 2.25.

(+)-(S)-2,2′-Bis(methoxymethoxy)-3,3′-bis(2-phenylethynyl)-1,1′-binaphthalene ((+)-(*S*)-**15**). A degassed soln. of (*S*)-**13** (100 mg, 0.24 mmol) in abs. THF (2 ml) was added slowly (10 min) to a degassed soln. of PhI (0.10 ml, 0.92 mmol), $[PdCl_2(PPh_3)_2]$ (12 mg, 5 mol-%), and CuI (3 mg, 5 mol-%) in dry THF (4 ml) and dry (i-Pr)$_2$NH (3 ml) at 40°, and the mixture was stirred for 2 h at 40°. Sat. aq. NaCl soln. (20 ml) and CH_2Cl_2 (30 ml) were added, the phases were separated, and the aq. phase was extracted with CH_2Cl_2 (30 ml). The combined org. phases were dried (Na_2SO_4) and concentrated. CC (SiO_2; hexane/AcOEt 6:1, containing 0.5% Et_3N) yielded (*S*)-**15** (134 mg, 97%). White foam. M.p. 81°. $[\alpha]_D^{rt} = +197.1$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3058*m*, 2951*m*, 2925*m*, 2818*w*, 2216*w*, 1594*m*, 1492*s*, 1443*m*, 1426*m*, 1390*m*, 1359*m*, 1332*w*, 1257*w*, 1226*m*, 1199*m*, 1157*s*, 1097*m*, 1062*s*, 1013*m*, 972*s*, 916*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.53 (*s*, 6 H); 4.97 (*d*, *AB*, $J = 6.3$, 2 H); 5.21 (*d*, *AB*, $J =$ 6.3, 2 H); 7.29–7.37 (*m*, 10 H); 7.41–7.47 (*m*, 2 H); 7.55–7.58 (*m*, 4 H); 7.87 (*d*, $J = 8.1$, 2 H); 8.24 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 56.19; 86.65; 93.92; 99.07; 117.52; 123.46; 125.79; 126.13; 126.82; 127.47; 127.83; 128.68; 128.72; 130.59; 131.82; 134.05; 134.46; 153.35. FAB-MS: 574 (100, M^+). Anal. calc. for $C_{40}H_{30}O_4 \cdot 0.5\,H_2O$ (580.67): C 82.31, H 5.35; found: C 82.65, H 5.39.

(+)-(S)-3,3′-Bis(2-phenylethynyl)-1,1′-binaphthalene-2,2′-diol ((+)-(*S*)-**16**). To (*S*)-**15** (170 mg, 0.30 mmol) in THF (100 ml), conc. HCl (37%, 250 µl) in MeOH (100 ml) was added, and the soln. was stirred for 12 h under N_2 at 20°. H_2O (200 ml) and CH_2Cl_2 (200 ml) were added, the aq. phase was extracted with CH_2Cl_2 (100 ml), the combined org. phases were dried (Na_2SO_4), and concentration gave crude (*S*)-**16** (110 mg, 75%). Oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.91 (*s*, 2 H); 7.19 (*d*, $J = 8.4$, 2 H); 7.26–7.40 (*m*, 10 H); 7.57–7.60 (*m*, 4 H); 7.87 (*d*, $J = 7.5$, 2 H); 8.21 (*s*, 2 H).

Tetrabutylammonium (+)-(S)-3,3′-Bis(2-phenylethynyl)-1,1′-binaphthalene-2,2′-diyl Phosphate ((+)-(*S*)-**5**). To crude (*S*)-**16** (100 mg, 0.17 mmol) in dry CH_2Cl_2 (35 ml), $POCl_3$ (0.2M soln. in CH_2Cl_2, 1.9 ml, 0.38 mmol) and Et_3N (0.53 g, 0.73 ml, 5.2 mmol) were added at 20° under N_2, and the soln. was stirred for 6 h. After evaporation *in vacuo*, THF/H_2O 1:1 (30 ml) was added, and the mixture was stirred for 12 h at 30°. CH_2Cl_2 (50 ml) and H_2O (30 ml) were added, the separated org. phase was washed with H_2O (2×30 ml), dried (Na_2SO_4), and concentrated. CC (SiO_2; CH_2Cl_2/Et_3N 98:3, followed by ion-exchange chromatography (*Dowex 50WX8*, Bu_4N^+; CH_2Cl_2/MeCN 1:1), provided (*S*)-**5** (58 mg, 54%). M.p. 239°. $[\alpha]_D^{rt} = +287.1$ ($c = 0.5$, $CHCl_3$). IR (neat): 3389*m* (br.), 3056*m*, 2954*m*, 2934*m*, 2867*w*, 2211*w*, 1598*m*, 1490*s*, 1439*m*, 1420*m*, 1378*w*, 1361*w*, 1299*s*, 1213*m*, 1152*w*, 1109*s*, 1096*s*, 1091*w*, 963*w*, 918*m*. ^{1}H-NMR (500 MHz, CD_3CN): 0.91 (*t*, $J = 7.2$, 12 H); 1.25–1.32 (*m*, 8 H); 1.48–1.55 (*m*, 8 H); 2.98–2.01 (*m*, 8 H); 7.20 (*d*, $J = 8.2$, 2 H); 7.25–7.29 (*m*, 2 H); 7.40–7.46 (*m*, 8 H); 7.63–7.65 (*m*, 4 H); 7.95 (*d*, $J = 8.2$, 2 H); 8.23 (*s*, 2 H). ^{13}C-NMR (125 MHz, CD_3CN): 13.70; 20.21; 24.20; 59.12; 87.84; 93.71; 118.59; 123.52 (*d*, $J(^{31}P,^{13}C) = 2.3$); 124.41; 126.00; 127.24; 127.72; 129.14; 129.42; 129.57; 130.92; 132.48; 133.26; 134.22; 151.13 (*d*, $J(^{31}P,^{13}C) = 9.8$). ^{31}P-NMR (121 MHz, CD_3CN): 6.10. ESI-MS (negative-ion mode): 547 (100, $[M - Bu_4N]^-$). Anal. calc. for $C_{52}H_{56}NO_4P \cdot 0.5\,H_2O$ (799.01): C 78.17, H 7.19; N 1.75, O 9.01, P 3.88; found: C 78.11, H 7.37, N 1.77, O 8.48, P 3.91.

(+)-(S)-3,3′-Bis[2-[3,5-bis(benzyloxy)phenyl]ethynyl]-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene (*G-1*-(+)-(*S*)-**17**). A degassed soln. of (*S*)-**13** (50 mg, 0.12 mmol) in dry THF (2 ml) was added slowly (30 min) to a degassed soln. of *G-1*-**8** (110 mg, 0.26 mmol), $[PdCl_2(PPh_3)_2]$ (4.0 mg, 4 mol-%), and CuI (0.9 mg, 4 mol-%) in abs. THF (1 ml) and dry (i-Pr)$_2$NH (3 ml). After stirring at 40° for 5 h, sat. aq. NaCl soln. (10 ml) and CH_2Cl_2 (20 ml) were added. The phases were separated, and the aq. phase was extracted with CH_2Cl_2 (15 ml). The combined org. phases were dried (Na_2SO_4) and concentrated. CC (SiO_2; CH_2Cl_2/toluene $1:2 \rightarrow 1:1$, containing 0.5% Et_3N) afforded *G-1*-(+)-(*S*)-**17** (100 mg, 85%). White foam. M.p. 68°. $[\alpha]_D^{rt} = +82.1$ ($c = 0.5$, $CHCl_3$). IR (KBr): 3059*w*, 3033*w*, 2922*s*, 2846*m*, 2236*w*, 1585*s*, 1493*w*, 1454*m*, 1430*m*, 1373*m*, 1349*m*, 1318*w*, 1244*m*, 1211*w*, 1159*s*, 1100*w*, 1056*m*, 980*m*, 925*w*, 908*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 2.51 (*s*, 6 H); 4.93 (*d*, *AB*, $J = 6.3$, 2 H); 5.06 (*s*, 8 H); 5.17 (*d*, *AB*, $J = 6.3$, 2 H); 6.64 (*t*, $J = 2.4$, 2 H); 6.82 (*d*, $J = 2.3$, 4 H); 7.16–7.47 (*m*, 26 H); 7.86 (*d*, $J = 8.1$, 2 H); 8.23 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 56.19; 70.36; 86.36; 93.85; 93.85; 99.13; 103.87; 110.79; 117.36; 124.82; 125.82; 126.11; 126.82; 127.53; 127.75; 127.84; 128.31; 130.58; 134.09; 134.56; 136.89; 153.39; 160.08. FAB-MS: 999 (100, M^+). Anal. calc. for $C_{68}H_{54}O_8 \cdot 0.5\,H_2O$ (1008.19): C 81.08, H 5.50; found: C 80.92, H 5.59.

(+)-(S)-3,3′-Bis[2-[3,5-bis(benzyloxy)phenyl]ethynyl]-1,1′-binaphthalene-2,2′-diol (*G-1*-(+)-(*S*)-**18**). To *G-1*-(+)-(*S*)-**17** (90 mg, 0.09 mmol) in THF (35 ml), conc. HCl (37%, 100 µl) in MeOH (35 ml) was added, and the soln. was stirred under N_2 at 20° for 7 h. After addition of H_2O (60 ml), the aq. phase was extracted with CH_2Cl_2 (2×70 ml), and the combined org. phases were dried (Na_2SO_4) and concentrated. CC (SiO_2; CH_2Cl_2/toluene 1:5, containing 0.5% Et_3N) afforded *G-1*-(+)-(*S*)-**18** (65 mg, 79%). Foam. M.p. 88°. $[\alpha]_D^{rt} = +56.3$ ($c =$ 0.5, $CHCl_3$). IR (neat): 3491*s* (br.), 3063*w*, 3023*w*, 2924*w*, 2854*w*, 2219*w*, 1593*s*, 1586*s*, 1495*w*, 1451*w*, 1426*m*, 1376*w*, 1351*w*, 1262*m*, 1222*m*, 1152*s*, 1048*m*, 1022*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.06 (*s*, 8 H); 5.84 (*s*, 2 H); 6.68 (*t*, $J = 2.1$, 2 H); 6.85 (*d*, $J = 2.1$, 4 H); 7.20 (*d*, $J = 7.8$, 2 H); 7.28–7.47 (*m*, 24 H); 7.88 (*d*, $J = 7.5$, 2 H); 8.21 (*s*,

2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 70.38; 83.82; 96.33; 104.30; 110.90; 112.34; 113.70; 124.04; 124.66; 127.54; 127.76; 128.25; 128.36; 128.51; 128.91; 129.01; 133.70; 134.10; 136.84; 151.14; 160.15. FAB-MS: 911 (100, M^+). HR-FAB-MS: 911.3298 (M^+, $C_{64}H_{46}O_6$; calc. 911.3294).

Tetrabutylammonium (+)-(S)-3,3′-Bis{2-[3,5-bis(benzyloxy)phenyl]ethynyl}-1,1′-binaphthalene-2,2′-diyl Phosphate (*G-1*-(+)-(*S*)-**1**). To *G-1*-(+)-(*S*)-**18** (45 g, 0.05 mmol) in dry CH_2Cl_2 (10 ml), $POCl_3$ (0.2M soln. in CH_2Cl_2, 0.55 ml, 0.11 mmol) and Et_3N (135 mg, 195 µl, 1.4 mmol) were added at 20° under N_2, and the soln. was stirred for 3 h. Evaporation *in vacuo* and addition of THF/H_2O 1:1 (10 ml) provided a mixture, which was stirred for 12 h at 30°. CH_2Cl_2 (20 ml) and H_2O (30 ml) were added, the separated org. phase was washed with H_2O (2 × 20 ml), dried (Na_2SO_4), and concentrated. CC (SiO_2; CH_2Cl_2/Et_3N 99:1), followed by ion-exchange chromatography (*Dowex 50WX8*, Bu_4N^+, CH_2Cl_2/MeCN 1:1), afforded *G-1*-(+)-(*S*)-**1** (43 mg, 71%). Yellow foam. M.p. 87°. $[\alpha]_D^{r.t.} = +194.6$ ($c = 0.5$, $CHCl_3$). IR (neat): 3060*w*, 3025*w*, 2955*m*, 2217*w*, 1587*s*, 1492*w*, 1431*m*, 1374*m*, 1292*m*, 1253*w*, 1157*s*, 1101*m*, 1053*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.73 (*t*, *J* = 7.3, 12 H); 1.11–1.14 (*m*, 8 H); 1.23–1.28 (*m*, 8 H); 2.89 (*t*, *J* = 9.05, 8 H); 5.03 (*s*, 8 H); 6.59 (*t*, *J* = 2.4, 2 H); 6.94 (*d*, *J* = 2.4, 4 H); 7.17–7.23 (*m*, 2 H); 7.29–7.43 (*m*, 24 H); 7.81 (*d*, *J* = 8.2, 2 H); 8.13 (*s*, 2 H). ^{13}C-NMR (125 MHz, CD_3CN): 13.56; 19.46; 23.64; 58.16; 70.16; 86.85; 92.99; 103.02; 110.98; 117.72; 122.67; 122.68; 124.75; 125.52; 126.33; 126.79; 127.57; 127.88; 127.93; 128.50; 130.05; 132.51; 133.61; 136.71; 159.56. ^{31}P-NMR (121 MHz, $CDCl_3$): 4.71. FAB-MS: 1457 (49, $[M + Bu_4N]^+$), 1215 (21, MH^+), 973 (6, $[MH_2 - Bu_4N]^+$), 243 (100, Bu_4N^+). HR-FAB-MS: 972.2848 ($[MH - Bu_4N]^+$, $C_{64}H_{45}O_8P$; calc. 972.2852).

(+)-(S)-3,3′-Bis(2-{3,5-bis[3,5-bis(benzyloxy)benzyloxy]phenyl}ethynyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene (*G-2*-(+)-(*S*)-**19**). To a degassed soln. of (*S*)-**13** (0.2 g, 0.47 mmol) in abs. THF (12 ml) and dry (i-Pr)$_2$NH (6 ml), $[PdCl_2(PPh_3)_2]$ (16.6 mg, 5 mol-%), CuI (4.5 mg, 5 mol-%), and *G-2*-**9** (0.80 g, 0.95 mmol) were added, and the mixture was heated to 40° for 12 h. Sat. aq. NaCl soln. (60 ml) and CH_2Cl_2 (70 ml) were added, the phases were separated, and the aq. phase was extracted with CH_2Cl_2 (2 × 60 ml). The combined org. phases were dried (Na_2SO_4), filtered through SiO_2 and *Celite*, and concentrated. GPC (*Bio-Beads SX-1*) afforded *G-2*-(+)-(*S*)-**19** (0.62 g, 71%). Highly viscous oil. $[\alpha]_D^{r.t.} = +96.7$ ($c = 0.5$, $CHCl_3$). IR (KBr): 3031*w*, 2869*w*, 2214*w*, 1593*s*, 1506*s*, 1449*m*, 1152*s*, 1053*m*, 736*m*, 696*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.48 (*s*, 6 H); 4.92 (*d*, *AB*, *J* = 6.2, 2 H); 4.96 (*s*, 8 H); 5.01 (*s*, 16 H); 5.16 (*d*, *AB*, *J* = 6.2, 2 H); 6.55 (*t*, *J* = 2.3, 4 H); 6.58 (*t*, *J* = 2.3, 2 H); 6.66 (*d*, *J* = 2.3, 8 H); 6.78 (*d*, *J* = 2.3, 4 H); 7.21–7.42 (*m*, 46 H); 7.83–7.85 (*m*, 2 H); 8.21 (*s*, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 56.07; 70.12 (2×); 86.25; 93.65; 98.91; 101.65; 103.54; 106.32; 110.60; 117.11; 124.49; 124.58; 125.55; 125.86; 126.56; 127.27; 127.54; 127.99; 128.57; 130.31; 133.81; 134.31; 136.74; 139.00; 153.07; 159.65; 160.19. MALDI-TOF-MS (HABA): 1871 ($[M + Na]^+$). Anal. calc. for $C_{124}H_{102}O_{16} \cdot 2H_2O$ (1884.2): C 79.05, H 5.67; found: C 79.13, H 5.82.

(+)-(S)-3,3′-Bis(2-{3,5-bis[3,5-bis(benzyloxy)benzyloxy]phenyl}-ethynyl)-1,1′-binaphthalene-2,2′-diol (*G-2*-(+)-(*S*)-**20**). To *G-2*-(+)-(*S*)-**19** (0.60 g, 0.33 mmol) in THF/MeOH 1:1 (260 ml), conc. HCl (37%, 350 µl) was added, and the soln. was stirred under N_2 at 20° for 12 h. After addition of H_2O (200 ml), the aq. phase was extracted with CH_2Cl_2 (2 × 200 ml), and the combined org. phases were dried (Na_2SO_4) and concentrated to give crude *G-2*-(+)-(*S*)-**20** (0.58 g, 100%). Highly viscous oil. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.00 (*s*, 8 H); 5.05 (*s*, 16 H); 5.19 (*s*, 2 H); 6.61 (*t*, *J* = 2.0, 4 H); 6.66 (*t*, *J* = 2.0, 2 H); 6.71 (*d*, *J* = 2.0, 8 H); 6.85 (*d*, *J* = 2.0, 4 H); 7.20–7.46 (*m*, 46 H); 7.83–7.87 (*m*, 2 H); 8.21 (*s*, 2 H).

Tetrabutylammonium (+)-(S)-3,3′-Bis(2-{3,5-bis[3,5-bis(benzyloxy)benzyloxy]phenyl}ethynyl)-1,1′-binaphthalene-2,2′-diyl Phosphate (*G-2*-(+)-(*S*)-**2**). To *G-2*-(+)-(*S*)-**20** (0.59 g, 0.33 mmol) in dry CH_2Cl_2 (66 ml), $POCl_3$ (0.16M soln. in CH_2Cl_2, 6.6 ml, 0.72 mmol) and Et_3N (0.94 g, 1.3 ml, 9.33 mmol) were added at 20° under N_2, and the soln. was stirred for 3 h. Evaporation *in vacuo* and addition of THF/H_2O 1:1 (70 ml) gave a mixture, which was stirred for 12 h at 40°. CH_2Cl_2 (200 ml) and H_2O (200 ml) were added, and the separated org. phase was washed with H_2O (2 × 100 ml), dried (Na_2SO_4), and concentrated. CC (SiO_2; CH_2Cl_2, containing 1.5% Et_3N), followed by ion-exchange chromatography (*Dowex 50WX8*, Bu_4N^+; CH_2Cl_2/MeCN 1:1), afforded *G-2*-(+)-(*S*)-**2** (0.37 g, 54% from *G-2*-(+)-(*S*)-**19**). Yellow foam. M.p. 68° (dec.). $[\alpha]_D^{r.t.} = +101.8$ ($c = 0.5$, $CHCl_3$). IR (KBr): 3022*w*, 2867*w*, 2200*w*, 1594*s*, 1506*s*, 1450*m*, 1242*m*, 1156*s*, 1061*m*, 969*m*, 828*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.76–0.80 (*m*, 12 H); 1.13–1.34 (*m*, 16 H); 2.94 (*m*, 8 H); 4.99 (*s*, 8 H); 5.03 (*s*, 16 H); 6.55–6.58 (*m*, 6 H); 6.69 (*d*, *J* = 2.1, 8 H); 6.92 (*d*, *J* = 2.1, 4 H); 7.19–7.43 (*m*, 46 H); 7.81–7.84 (*m*, 2 H); 8.16 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.67; 19.61; 23.82; 58.46; 70.17; 70.31; 87.25; 93.17; 101.81; 103.22; 106.63; 111.31; 118.04; 122.99; 123.02; 125.06; 125.87; 126.68; 127.08; 127.83; 128.26; 128.83; 130.35; 132.86; 133.97; 137.08; 139.52; 150.20 (*d*, $J(^{31}P,^{13}C) = 9.8$); 159.83; 160.50. ^{31}P-NMR (121 MHz, $CDCl_3$): 4.82. MALDI-TOF-MS (HABA): 1821 (100, $[M - Bu_4N]^+$). Anal. calc. for $C_{136}H_{128}NO_{16}P \cdot 2H_2O$ (2099.5): C 77.80, H 6.34, N 0.67; found: C 77.74, H 6.60, N 0.92.

(+)-(S)-3,3′-Bis[2-(3,5-bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}phenyl)ethynyl]-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene (*G-3*-(+)-(*S*)-**21**). A soln. of (*S*)-**13** (67 mg, 0.16 mmol) in abs. THF (1 ml) and dry (i-Pr)$_2$NH (2 ml) was slowly added (30 min) to a degassed soln. of *G-3*-**10** (560 mg, 0.33 mmol), [PdCl$_2$(dppf)] (4.9 mg, 4 mol-%), and CuI (1.2 mg, 4 mol-%) in dry THF (2.5 ml) and dry (i-Pr)$_2$NH (4 ml) at 40°, and the mixture was stirred at 40° for 2 h. Sat. aq. NaCl soln. (20 ml) and CH_2Cl_2 (40 ml) were added, the phases were separated, and the aq. phase was extracted with CH_2Cl_2 (2 × 40 ml). The combined org. phases were dried (Na_2SO_4), filtered through SiO_2 and *Celite*, and concentrated. GPC (*Bio-Beads SX-1*) gave *G-3*-(+)-(*S*)-**21** (320 mg, 57%). Highly viscous oil. $[\alpha]_D^{r.t.} = +25.8$ ($c = 0.5$, $CHCl_3$). IR (KBr): 3060*w*, 3024*w*, 2933*m*, 2869*m*, 1596*s*, 1492*w*, 1446*m*, 1369*m*, 1346*w*, 1319*w*, 1292*w*, 1269*w*, 1246*w*, 1214*w*, 1156*s*, 1050*s*, 978*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.55 (*s*, 6 H); 4.95–4.99 (*m*, 26 H); 5.03 (*s*, 32 H); 5.21 (*d*, *AB*, $J = 6.3$, 2 H); 6.55–6.62 (*m*, 20 H); 6.67 (*t*, $J = 2.1$, 2 H); 6.71 (*d*, $J = 2.4$, 16 H); 6.86 (*d*, $J = 2.1$, 4 H); 7.27–7.47 (*m*, 86 H); 7.64 (*d*, $J = 8.4$, 2 H); 8.25 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 56.24; 70.18; 70.26; 86.57; 93.90; 99.14; 101.89; 103.74; 106.65; 110.87; 117.37; 124.91; 125.85; 126.14; 126.86; 127.58; 127.84; 128.07; 128.26; 128.44; 128.59; 128.65; 128.86; 130.59; 134.12; 134.69; 137.10; 139.31; 139.52; 153.40; 160.07; 160.46; 160.52. MALDI-TOF-MS (HABA): 3586 (100, $[M + K]^+$), 3569 (88, $[M + Na]^+$). Anal. calc. for $C_{236}H_{198}O_{32} \cdot 2\,H_2O$ (3582.21): C 79.13, H 5.68; found: C 79.07, H 6.12.

(+)-(S)-3,3′-Bis[2-(3,5-bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}phenyl)ethynyl]-1,1′-binaphthalene-2,2′-diol (*G-3*-(+)-(*S*)-**22**). To *G-3*-(+)-(*S*)-**21** (300 mg, 0.09 mmol) in THF (40 ml), conc. HCl (37%, 75 µl) in MeOH (30 ml) was added, and the soln. was stirred under N_2 at 20° for 24 h, then the reaction was quenched with H_2O (80 ml). The aq. phase was extracted with CH_2Cl_2 (2 × 80 ml), and the combined org. phases were dried (Na_2SO_4) and concentrated. CC (SiO_2; CH_2Cl_2/Et_3N 98 : 2) provided *G-3*-(+)-(*S*)-**22** (264 mg, 85%). Highly viscous oil. $[\alpha]_D^{r.t.} = +20.1$ ($c = 0.5$, $CHCl_3$). IR (neat): 3500*m* (br.), 3062*w*, 3034*w*, 2922*w*, 2866*w*, 1596*s*, 1497*m*, 1451*s*, 1374*m*, 1343*w*, 1325*w*, 1292*m*, 1264*m*, 1157*s*, 1054*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.96 (*s*, 24 H); 5.01 (*s*, 32 H); 5.84 (*s*, 2 H); 6.54–6.58 (*m*, 14 H); 6.66 (*d*, $J = 2.1$, 8 H); 6.68 (*d*, $J = 2.4$, 16 H); 6.83 (*d*, $J = 2.1$, 4 H); 7.19 (d, $J = 8.4$, 2 H); 7.27–7.45 (*m*, 84 H); 7.83 (*d*, $J = 7.5$, 2 H); 8.18 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 70.17; 70.25 (2 ×); 84.05; 96.23; 101.89; 101.93; 104.14; 106.62; 110.95; 112.36; 113.67; 124.12; 124.65; 124.95; 127.83; 128.25; 128.42; 128.52; 128.57; 128.85; 129.06; 133.83; 134.05; 137.03; 139.23; 139.49; 151.22; 160.05; 160.42; 160.49. MALDI-TOF-MS (HABA): 3482 ($[M + Na]^+$).

Tetrabutylammonium (+)-(S)-3,3′-Bis[2-(3,5-bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}phenyl)-ethynyl]-1,1′-binaphthalene-2,2′-diyl Phosphate (*G-3*-(+)-(*S*)-**3**). To a soln. of crude *G-3*-(+)-(*S*)-**22** (250 mg, 0.07 mmol) in dry CH_2Cl_2 (15 ml), $POCl_3$ (0.2M soln. in CH_2Cl_2, 0.8 ml, 0.16 mmol) and Et_3N (203 mg, 280 µl, 2.02 mmol) were added at 20° under N_2, and the soln. was stirred for 3 h at 20°. Evaporation *in vacuo* and addition of THF/H_2O 1 : 1 (16 ml) gave a mixture, which was stirred for 12 h at 30°. CH_2Cl_2 (20 ml) and H_2O (20 ml) were added, and the separated org. phase was washed with H_2O (2 × 30 ml), dried (Na_2SO_4), and concentrated. CC (SiO_2, CH_2Cl_2/Et_3N 98 : 2), followed by ion-exchange chromatography (*Dowex 50WX8*, Bu_4N^+; CH_2Cl_2/MeCN 1 : 1), afforded *G-3*-(+)-(*S*)-**3** (145 mg, 52%). Highly viscous oil. $[\alpha]_D^{r.t.} = +63.7$ ($c = 0.5$, $CHCl_3$). IR (neat): 3059*w*, 3033*w*, 1595*s*, 1493*w*, 1450*m*, 1373*m*, 1343*w*, 1321*w*, 1291*w*, 1205*w*, 1156*s*, 1098*w*, 1050*m*, 972*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.77 (*t*, $J = 6.9$, 12 H); 1.10–1.21 (*m*, 8 H); 1.23–1.38 (*m*, 8 H); 2.88–2.98 (*m*, 8 H); 4.96 (*s*, 16 H); 4.97 (*s*, 8 H); 5.00 (*s*, 32 H); 6.53–6.57 (*m*, 14 H); 6.60 (*t*, $J = 2.1$, 8 H); 6.69 (*d*, $J = 1.8$, 16 H); 6.83 (*d*, $J = 2.1$, 4 H); 7.18–7.40 (*m*, 86 H); 7.81 (*d*, $J = 8.1$, 2 H); 8.15 (*s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 13.64; 19.57; 23.76; 58.39; 70.01; 70.10 (2 ×); 87.26; 92.90; 103.05; 106.42; 110.99; 117.62; 122.78; 124.69; 125.31; 125.72; 126.33; 126.91; 127.55; 127:71; 127.98; 128.24; 128.40; 128.57; 129.05; 130.14; 132.68; 133.76; 136.79; 139.24; 159.51; 160.06; 160.16 (2 ×). ^{31}P-NMR (202 MHz, $CDCl_3$): 4.85. MALDI-TOF-MS (HABA): 3562 (61, $[M - Bu_4N + 2\,Na]^+$), 3540 (100, $[MH - Bu_4N + Na]^+$). Anal. calc. for $C_{248}H_{224}NO_{32}P \cdot 2\,H_2O$ (3797.54): C 78.44, H 6.05; N 0.37; found: C 78.13, H 6.16, N 0.52.

(+)-(S)-3,3′-Bis{2-[3,5-bis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyloxy)phenyl]ethynyl}-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene (*G-1*-(+)-(*S*)-**24**). A degassed soln. of (*S*)-**13** (50 mg, 0.12 mmol) in abs. THF (2 ml) was added to a degassed soln. of [PdCl$_2$(dppf)] (8.5 mg, 5 mol-%), CuI (1.1 mg, 5 mol-%), and *G-1*-**11** (0.30 g, 0.37 mmol) in dry (i-Pr)$_2$NH (2.5 ml) and THF (3.5 ml), and the mixture was warmed to 40° for 12 h. Sat. aq. NaCl soln. (20 ml) and CH_2Cl_2 (30 ml) were added, the phases were separated, and the aq. phase was extracted with CH_2Cl_2 (2 × 30 ml). The combined org. phases were dried (Na_2SO_4), filtered through SiO_2 and *Celite*, and concentrated. GPC (*Biobeads SX-1*) provided *G-1*-(+)-(*S*)-**24** (0.18 g, 65%). Highly viscous oil. $[\alpha]_D^{r.t.} = +64.4$ ($c = 1.0$, $CHCl_3$). IR (KBr): 2920*m*, 2869*s*, 2817*w*, 1596*s*, 1449*m*, 1350*m*, 1321*w*, 1296*w*, 1240*m*, 1171*s*, 1147*s*, 1107*s*, 1068*m*, 978*m*, 844*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 2.55 (*s*, 6 H); 3.36 (*s*, 24 H); 3.52–3.54 (*m*, 16 H); 3.63–3.68 (*m*, 32 H); 3.71–3.73 (*m*, 16 H); 3.83 (*t*, $J = 4.8$, 16 H); 4.11 (*t*, $J = 4.8$, 16 H); 4.94 (*d*, *AB*, $J = 6.2$, 2 H); 4.95 (*s*, 8 H); 5.17 (*d*, *AB*, $J = 6.2$, 2 H); 6.45 (*t*, $J = 2.2$, 4 H); 6.58 (*d*, $J = 2.2$, 8 H); 6.59 (*t*, $J = 2.3$,

2 H); 6.72 (*d*, *J* = 2.3, 4 H); 7.22 (*t*, *J* = 7.9, 2 H); 7.28–7.32 (*m*, 2 H); 7.41–7.44 (*m*, 2 H); 7.86 (*d*, *J* = 8.2, 2 H); 8.23 (*s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 56.05; 58.98; 67.47; 69.62; 70.03; 70.52; 70.61; 70.77; 71.89; 86.21; 93.59; 98.85; 101.17; 103.41; 106.03; 110.48; 117.08; 124.52; 125.51; 125.80; 126.51; 127.23; 127.54; 130.27; 133.77; 134.33; 138.79; 152.98; 159.65; 160.09. MALDI-TOF-MS (2,5-DHB): 2321 (100, $[M\mathrm{H} + \mathrm{Na}]^+$), 2277 (53, $[M\mathrm{H} + \mathrm{Na} - \mathrm{CH_2OMe}]^+$). Anal. calc. for $C_{124}H_{166}O_{40} \cdot H_2O$ (2314.64): C 64.21, H 7.32; found: C 64.21, H 7.45.

*(+)-(*S*)-3,3′-Bis{2-[3,5-bis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyloxy)phenyl]ethynyl}-1,1′-binaphthalene-2,2′-diol* (*G-1*-(+)-(*S*)-**25**). To *G-1*-(+)-(*S*)-**24** (150 mg, 0.065 mmol) in THF/MeOH 1:1 (40 ml), conc. HCl (37%, 60 µl) was added, and the soln. was stirred under N_2 at 20° for 12 h. After addition of H_2O (60 ml), the aq. phase was extracted with CH_2Cl_2 (2 × 80 ml), and the combined org. phases were dried (Na_2SO_4) and concentrated to give crude *G-1*-(+)-(*S*)-**25**. Highly viscous oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.35 (*s*, 24 H); 3.52–3.56 (*m*, 16 H); 3.62–3.69 (*m*, 32 H); 3.71–3.73 (*m*, 16 H); 3.81 (*t*, *J* = 4.8, 16 H); 4.10 (*t*, *J* = 4.8, 16 H); 4.96 (*s*, 8 H); 6.01 (*s*, 2 H); 6.44 (*t*, *J* = 1.8, 4 H); 6.58 (*d*, *J* = 1.8, 8 H); 6.61 (*t*, *J* = 2.1, 2 H); 6.80 (*d*, *J* = 2.1, 4 H); 7.17 (*d*, *J* = 8.1, 2 H); 7.26–7.39 (*m*, 4 H); 7.86 (*d*, *J* = 8.1, 2 H); 8.20 (*s*, 2 H).

*Tetrabutylammonium (+)-(*S*)-3,3′-Bis{2-[3,5-bis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyloxy)phenyl]ethynyl}-1,1′-binaphthalene-2,2′-diyl Phosphate* (*G-1*-(+)-(*S*)-**23**). To *G-1*-(+)-(*S*)-**25** (145 mg, 0.065 mmol) in dry CH_2Cl_2 (12 ml), $POCl_3$ (0.2M soln. in CH_2Cl_2, 0.7 ml, 0.14 mmol) and Et_3N (0.18 g, 0.26 ml, 1.85 mmol) were added at 20° under N_2, and the soln. was stirred for 3 h. After evaporation *in vacuo*, THF/H_2O 1:1 (20 ml) was added, and the mixture was stirred for 12 h at 40°. CH_2Cl_2 (50 ml) and H_2O (50 ml) were added, and the separated org. phase was washed with H_2O (2 × 50 ml), dried (Na_2SO_4), and concentrated. CC (CH_2Cl_2/AcOEt/Et_3N 50:47:3), followed by ion-exchange chromatography (*Dowex 50WX8*, Bu_4N^+; CH_2Cl_2/MeCN 1:1), afforded *G-1*-(+)-(*S*)-**23** (100 mg, 61%). Yellow foam. $[\alpha]_D^{r.t.} = +169.2$ (*c* = 1.0, $CDCl_3$). IR (KBr): 3070*w*, 2932*s*, 2874*s*, 2220*w*, 1597*s*, 1448*s*, 1351*m*, 1324*w*, 1297*m*, 1251*m*, 1168*s*, 1139*s*, 1109*s*, 1060*m*, 953*w*, 847*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.17–1.25 (*m*, 12 H); 1.34–1.39 (*m*, 8 H); 1.92–2.16 (*m*, 8 H); 3.00–3.34 (*m*, 8 H); 3.36 (*s*, 24 H); 3.52–3.54 (*m*, 16 H); 3.62–3.67 (*m*, 32 H); 3.70–3.72 (*m*, 16 H); 3.82 (*t*, *J* = 4.8, 16 H); 4.10 (*t*, *J* = 4.8, 16 H); 4.95 (*s*, 8 H); 6.44 (*t*, *J* = 2.2, 4 H); 6.56 (*t*, *J* = 2.3, 2 H); 6.58 (*d*, *J* = 2.2, 8 H); 6.89 (*d*, *J* = 2.3, 4 H); 7.17–7.24 (*m*, 4 H); 7.35 (*m*, 2 H); 7.82 (*d*, *J* = 8.4, 2 H); 8.16 (*s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 13.60; 19.56; 23.78; 58.47; 58.97; 67.49; 69.62; 70.02; 70.51; 70.60; 70.74; 71.89; 87.13; 92.73; 101.20; 102.99; 106.06; 110.91; 117.61; 122.74; 124.65; 125.64; 126.28; 126.86; 127.86; 130.09; 132.64; 133.78; 138.96; 149.82 (*d*, $J(^{31}P,^{13}C) = 9.4$); 159.47; 160.05. ^{31}P-NMR (121 MHz, $CDCl_3$): 4.79. MALDI-TOF-MS (HABA): 2316 (100, $[M\mathrm{H} - \mathrm{Bu_4N} + 2\,\mathrm{Na}]^+$), 2294 (17, $[M\mathrm{H_2} - \mathrm{Bu_4N} + \mathrm{Na}]^+$).

1-[3,5-Bis(benzyloxy)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**28**). To a soln. of *G-1*-**8** (1.00 g, 1.18 mmol) in dioxane (10 ml), $[PdCl_2(dppf)]$ (29 mg, 3 mol-%), Et_3N (0.36 mg, 0.49 ml, 3.56 mmol), and (pinacolato)boron (0.23 g, 0.25 ml, 1.78 mmol) were added, and the mixture was heated to 80° for 12 h. H_2O (30 ml), and CH_2Cl_2 (30 ml) were added, and, after filtration over *Celite*, the phases were separated. The aq. phase was extracted with CH_2Cl_2 (40 ml), the combined org. phases were dried (Na_2SO_4), and the solvent was evaporated *in vacuo*. CC (SiO_2; hexane/AcOEt 10:1, containing 0.5% Et_3N) provided **28** (540 mg, 54%). White solid. M.p. 128°. IR (KBr): 3068*w*, 3034*w*, 2975*m*, 2866*m*, 1587*s*, 1495*w*, 1474*m*, 1460*m*, 1430*m*, 1345*s*, 1359*s*, 1311*m*, 1276*w*, 1217*m*, 1159*s*, 1104*w*, 1053*m*, 1025*m*, 968*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.38 (*s*, 12 H); 5.08 (*s*, 4 H); 6.57 (*t*, *J* = 2.1, 1 H); 7.12 (*d*, *J* = 2.1, 2 H); 7.33–7.49 (*m*, 10 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.86; 70.07; 83.91; 105.84; 113.01; 127.54; 127.87; 128.51; 137.07; 159.66 (signal for the C-atom next to B-atom not visible). FAB-MS: 416 (100, M^+). HR-EI-MS: 416.2156 (M^+, $C_{26}H_{29}BO_4$; calc. 416.2159).

*(+)-(*S*)-3,3′-Bis[3,5-bis(benzyloxy)phenyl]-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene* (*G-1*-(+)-(*S*)-**29**). To a degassed soln. of (+)-(*S*)-**27** (290 mg, 0.46 mmol), **28** (400 mg, 0.96 mmol), and Na_2CO_3 (195 mg, 1.84 mmol) in H_2O (6.5 ml) and DME (14 ml), $[PdCl_2(PPh_3)_2]$ (45 mg, 8 mol-%) was added, and the mixture was warmed to 85° for 3 h. Sat. aq. NaCl soln. (20 ml) and CH_2Cl_2 (30 ml) were added, the phases were separated, and the aq. phase was extracted with CH_2Cl_2 (30 ml). The combined org. phases were dried (Na_2SO_4) and concentrated. CC (SiO_2; hexane/AcOEt 5:1, containing 0.5% Et_3N) afforded *G-1*-(+)-(*S*)-**29** (350 mg, 80%). White foam. M.p. 71°. $[\alpha]_D^{r.t.} = +24.5$ (*c* = 0.5, $CHCl_3$). IR (neat): 3059*m*, 3023*m*, 2924*m*, 2825*w*, 1593*s*, 1493*m*, 1452*m*, 1416*m*, 1371*m*, 1344*m*, 1267*m*, 1231*w*, 1120*w*, 1155*s*, 1082*m*, 1057*m*, 1028*m*, 970*m*, 916*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 2.33 (*s*, 6 H); 4.37 (*d*, *AB*, *J* = 5.9, 2 H); 4.39 (*d*, *AB*, *J* = 5.9, 2 H); 5.11 (*s*, 8 H); 6.67 (*t*, *J* = 2.3, 2 H); 7.02 (*d*, *J* = 2.3, 4 H); 7.28–7.47 (*m*, 26 H); 7.87 (*d*, *J* = 8.1, 2 H); 7.93 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 55.77; 70.22; 98.41; 101.28; 109.07; 125.12; 126.30; 126.47; 126.54; 127.62; 127.83; 127.96; 128.57; 130.41; 130.69; 133.64; 135.03; 136.94; 141.09; 151.29; 159.78. FAB-MS: 951 (4, M^+), 887 (100). Anal. calc. for $C_{64}H_{54}O_8 \cdot 1.5\,H_2O$ (978.16): C 78.59, H 5.87; found: C 78.88, H 6.03.

*(+)-(*S*)-3,3′-Bis[3,5-bis(benzyloxy)phenyl]-1,1′-binaphthalene-2,2′-diol* (*G-1*-(+)-(*S*)-**30**). To *G-1*-(+)-(*S*)-**29** (350 mg, 0.37 mmol) in THF (100 ml), conc. HCl (37%, 350 µl) in MeOH (100 ml) was added, and the soln.

was stirred for 20 h under N_2 at 20°. H_2O (100 ml) and CH_2Cl_2 (150 ml) were added, the aq. phase was extracted with CH_2Cl_2 (100 ml), and the combined org. phases were dried (Na_2SO_4) and concentrated. CC (SiO_2; hexane/AcOEt 5:1, containing 0.5% Et_3N) gave *G-1*-(+)-(*S*)-**30** (180 mg, 57%). Viscous oil. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.11 (*s*, 8 H); 5.44 (*s*, 2 H); 6.70 (*t*, *J* = 2.4, 2 H); 7.00 (*d*, *J* = 2.4, 4 H); 7.25–7.49 (*m*, 26 H); 7.92 (*d*, *J* = 8.0, 2 H); 8.02 (*s*, 2 H).

*Tetrabutylammonium (+)-(*S*)-3,3′-Bis[3,5-bis(benzyloxy)phenyl]-1,1′-binaphthalene-2,2′-diyl Phosphate* (*G-1*-(+)-(*S*)-**26**). To *G-1*-(+)-(*S*)-**30** (85 mg, 0.10 mmol) in dry CH_2Cl_2 (20 ml), $POCl_3$ (0.2M soln. in CH_2Cl_2; 2.2 ml, 0.22 mmol) and Et_3N (0.28 g, 0.39 ml, 2.8 mmol) were added at 20° under N_2, and the soln. was stirred for 4 h. After evaporation *in vacuo*, THF/H_2O 1:1 (20 ml) was added, and the mixture was stirred for 12 h at 30°. CH_2Cl_2 (30 ml) and H_2O (20 ml) were added, and the separated org. phase was washed with H_2O (30 ml), dried (Na_2SO_4), and concentrated. CC (SiO_2; CH_2Cl_2/Et_3N 98:3), followed by ion-exchange chromatography (*Dowex 50WX8*, Bu_4N^+; CH_2Cl_2/MeCN 1:1), afforded *G-1*-(+)-(*S*)-**26** (110 mg, 93%). M.p. 112°. $[\alpha]_D^{rt} = +80.7$ (*c* = 0.5, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.71 (*t*, *J* = 7.3, 12 H); 1.03–1.05 (*m*, 8 H); 1.11–1.18 (*m*, 8 H); 2.69–2.73 (*m*, 8 H); 5.13 (*d*, *AB*, *J* = 11.7, 4 H); 5.18 (*d*, *AB*, *J* = 11.7, 4 H); 6.64 (*t*, *J* = 2.2, 2 H); 7.15–7.18 (*m*, 4 H); 7.34–7.37 (*m*, 14 H); 7.46–7.48 (*m*, 12 H); 7.86 (*d*, *J* = 8.2, 2 H); 7.93 (*s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 13.53; 19.40; 23.61; 58.08; 70.18; 101.48; 109.78; 123.48; 124.37; 125.45; 126.97; 127.67; 127.73; 128.06; 128.37; 130.22; 130.51; 132.64; 135.07; 137.43; 141.00; 147.98 (*d*, $J(^{31}P,^{13}C) = 9.4$); 159.31. ^{31}P-NMR (121 MHz, $CDCl_3$): 4.86. FAB-MS: 1408 (10, $[MH + Bu_4N]^+$), 1166 (11, MH^+), 925 (23, $[MH - Bu_4N]^+$), 242 (100, Bu_4N^+). Anal. calc. for $C_{76}H_{80}NO_8P \cdot 2H_2O$ (1202.49): C 75.91, H 7.04, N 1.16; found: C 75.98, H 7.22, N 1.23.

*(+)-(*S,S*)-3,3′-(Buta-1,3-diynediyl)bis(3′-ethynyl-1,1′-binaphthalene-2,2′-diol)* ((+)-(*S*,*S*)-**34**). To (*S*,*S*)-**33** (80 mg, 0.11 mmol) in THF (100 ml), conc. HCl (37%, 300 µl) in MeOH (100 ml) was added, and the soln. was stirred for 10 h under N_2 at 20°. H_2O (200 ml) and CH_2Cl_2 (160 ml) were added, the aq. phase was extracted with CH_2Cl_2 (2 × 120 ml), and the combined org. phases were dried (Na_2SO_4) and evaporated *in vacuo* to give crude (+)-(*S*)-**34** (74 mg, 98%). Highly viscous oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.26 (*s*, 2 H); 5.63 (*s*, 2 H); 5.79 (*s*, 2 H); 7.08–7.14 (*m*, 4 H); 7.26–7.40 (*m*, 8 H); 7.83–7.86 (*m*, 4 H); 8.19 (*s*, 2 H); 8.23 (*s*, 2 H).

*Bis(tetrabutylammonium) (+)-(*S,S*)-3,3′-(Buta-1,3-diynediyl)bis(3′-ethynyl-1,1′-binaphthalene-2,2′-diyl Phosphate)* ((+)-(*S*,*S*)-**31**). To (*S*,*S*)-**34** (70 mg, 0.10 mmol) in dry CH_2Cl_2 (30 ml), $POCl_3$ (0.2M soln. in CH_2Cl_2, 2.2 ml, 0.44 mmol) and Et_3N (0.60 g, 0.82 ml, 6.0 mmol) were added at 20° under N_2, and the soln. was stirred for 3 h. After evaporation, THF (10 ml) and H_2O (10 ml) were added, and the mixture was stirred for 12 h at 30°. Evaporation *in vacuo*, addition of CH_2Cl_2 (25 ml) and H_2O (20 ml), and phase separation provided an org. phase, which was washed with H_2O (3 × 20 ml), dried over Na_2SO_4, and evaporated *in vacuo*. CC (SiO_2; CH_2Cl_2/Et_3N 97:3 → 95:5), followed by dissolving the product in CH_2Cl_2 (15 ml), washing with H_2O (10 ml), and ion-exchange chromatography (*Dowex 50WX8*, Bu_4N^+; CH_2Cl_2/MeCN 1:1), provided (+)-(*S*,*S*)-**31** (68 mg, 53%). Yellow foam. M.p. >250°. $[\alpha]_D^{rt} = +247.3$ (*c* = 0.5, $CHCl_3$). IR (KBr): 3422*s*, 2961*m*, 2922*w*, 2867*w*, 1617*w*, 1483*w*, 1451*w*, 1417*m*, 1306*m*, 1283*m*, 1250*w*, 1200*w*, 1150*w*, 1111*s*, 1097*s*, 1017*w*, 961*w*, 906*w*, 811*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.78 (*t*, *J* = 7.3, 24 H); 1.16–1.25 (*m*, 16 H); 1.41–1.47 (*m*, 16 H); 2.99–3.12 (*m*, 16 H); 3.28 (*s*, 2 H); 7.19–7.22 (*m*, 4 H); 7.30–7.38 (*m*, 8 H); 7.80 (*d*, *J* = 8.2, 2 H); 7.81 (*d*, *J* = 8.2, 2 H); 8.12 (*s*, 2 H); 8.16 (*s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 13.65; 19.56; 23.82; 58.48; 78.29; 79.95; 80.21; 81.51; 116.58; 117.06; 122.26; 123.07; 124.83; 125.09; 126.53; 126.59; 126.96; 127.02; 127.92; 128.04; 129.97 (2×); 132.51; 132.96; 134.53; 135.36; 150.26; 150.33. ^{31}P-NMR (121 MHz, $CDCl_3$): 4.76. FAB-MS: 1516 (10, $[M + Bu_4N]^+$), 1275 (12, MH^+), 242 (100, Bu_4N^+). Anal. calc. for $C_{80}H_{94}N_2O_8P_2 \cdot H_2O$ (1291.61): C 74.39, H 7.49, N 2.17; found: C 74.10, H 7.58, N 2.26.

*(+)-(*S*)-2,2′-Bis(methoxymethoxy)-3-iodo-3′-[2-(trimethylsilyl)ethynyl]-1,1′-binaphthalene* ((+)-(*S*)-**35**). To a degassed soln. of (+)-(*S*)-**27** (2.50 g, 3.99 mmol) in Et_3N (40 ml) and abs. toluene (40 ml), $[PdCl_2(PPh_3)_2]$ (79 mg, 5 mol-%), CuI (38 mg, 5 mol-%), and (trimethylsilyl)acetylene (0.79 g, 1.13 ml, 7.98 mmol) were added, and the mixture was heated to 40° for 4 h. Sat. aq. NaCl soln. (300 ml) and CH_2Cl_2 (250 ml) were added, the phases were separated, and the aq. phase was extracted with CH_2Cl_2 (2 × 250 ml). The combined org. phases were washed with sat. aq. $NaHCO_3$ soln., dried (Na_2SO_4), and evaporated *in vacuo*. CC (hexane/CH_2Cl_2 1:1, containing 0.5% Et_3N) provided (+)-(*S*)-**35** (0.70 g, 30%) besides dialkynylated product (0.43 g, 19%) and starting material (+)-(*S*)-**27** (0.59 g, 24%). M.p. 65°. $[\alpha]_D^{rt} = +13.3$ (*c* = 1.0, $CHCl_3$). IR (KBr): 3051*w*, 2997*w*, 2954*m*, 2900*w*, 2825*w*, 2145*w*, 1490*w*, 1447*w*, 1426*w*, 1383*m*, 1350*m*, 1245*m*, 1194*w*, 1159*s*, 1102*w*, 1081*w*, 1054*m*, 1026*w*, 979*s*, 930*s*, 908*m*, 876*m*, 844*s*, 779*w*, 751*m*, 714*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.27 (*s*, 9 H); 2.44 (*s*, 3 H); 2.63 (*s*, 3 H); 4.75 (*d*, *AB*, *J* = 5.6, 1 H); 4.78 (*d*, *AB*, *J* = 5.6, 1 H); 4.93 (*d*, *AB*, *J* = 6.2, 1 H); 5.14 (*d*, *AB*, *J* = 6.2, 1 H); 7.18 (*d*, *J* = 8.4, 2 H); 7.26–7.32 (*m*, 4 H); 7.39–7.44 (*m*, 2 H); 8.18 (*s*, 1 H); 8.53 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): −0.13; 55.98; 56.76; 92.59; 98.85; 99.55; 99.63; 101.91; 117.28; 125.82; 126.00 (2×); 126.43;

126.63; 126.86; 126.94; 127.11; 127.76; 127.89; 130.33; 132.53; 134.02; 134.18; 135.41; 140.04; 152.40; 153.69. FAB-MS: 596 (13, M^+), 565 (30, $[M-OCH_3]^+$), 521 (100, $[M-C_4H_{11}O]^+$). Anal. calc. for $C_{29}H_{29}IO_4Si$ (596.54): C 58.39, H 4.90; found: C 58.02, H 4.96.

*(+)-(*S*)-2,2′-Bis(methoxymethoxy)-3-iodo-3′-[2-(triisopropylsilyl)ethynyl]-1,1′-binaphthalene* ((+)-(*S*)-**36**). To a degassed soln. of (+)-(*S*)-**27** (1.50 g, 2.40 mmol) in Et_3N (24 ml) and abs. toluene (24 ml), $[PdCl_2(PPh_3)_2Cl_2]$ (47 mg, 5 mol-%), CuI (23 mg, 0.12 mmol, 5 mol-%), and (triisopropylsilyl)acetylene (0.87 g, 1.06 ml, 4.791 mmol) were added, and the mixture was heated to 40° for 3 h. Sat. aq. NaCl soln. (50 ml) and CH_2Cl_2 (100 ml) were added, the phases were separated, and the aq. phase was extracted with CH_2Cl_2 (2 × 100 ml). The combined org. phases were washed with sat. aq. $NaHCO_3$ soln., dried (Na_2SO_4), and evaporated *in vacuo*. CC (hexane/CH_2Cl_2 5:1, containing 0.5% Et_3N) yielded (+)-(*S*)-**36** (0.49 g, 30%), in addition to dialkynylated material (0.65 g, 37%). M.p. 53°. $[\alpha]_D^{r.t.} = +1.0$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3048*w*, 2941*m*, 2850*m*, 2146*m*, 1616*w*, 1589*w*, 1561*w*, 1490*w*, 1462*m*, 1446*m*, 1424*m*, 1385*m*, 1347*m*, 1242*m*, 1204*m*, 1160*s*, 1099*w*, 1077*m*, 1055*s*, 979*s*, 929*s*, 885*s*, 808*w*, 780*w*, 749*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.20 (*ms*, 21 H); 2.33 (*s*, 3 H); 2.72 (*s*, 3 H); 4.78 (*d*, *AB*, $J = 5.5$, 1 H); 4.83 (*d*, *AB*, $J = 5.5$, 1 H); 5.03 (*d*, *AB*, $J = 6.3$, 1 H); 5.32 (*d*, *AB*, $J = 6.3$, 1 H); 7.18–7.23 (*m*, 2 H); 7.28–7.31 (*m*, 2 H); 7.41–7.44 (*m*, 2 H); 7.78 (*d*, $J = 8.2$, 1 H); 7.85 (*d*, $J = 8.2$, 1 H); 8.22 (*s*, 1 H); 8.55 (*s*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.32; 18.66; 55.53; 56.58; 92.39; 95.89; 98.58; 99.18; 103.49; 117.18; 125.44; 125.64; 125.69; 126.20; 126.28; 126.45; 126.66; 126.73; 127.36; 127.43; 129.98; 132.17; 133.61; 133.95; 135.61; 139.57; 151.88; 153.16. FAB-MS: 681 (7, M^+), 461 (100, $[M-(i\text{-}Pr)_3Si-2\,MeO]^+$). Anal. calc. for $C_{35}H_{41}IO_4Si$ (680.70): C 61.76, H 6.07; found: C 61.61, H 5.88.

*Dialkynylated Side-Product (−)-(*S*)-2,2′-Bis(methoxymethoxy)-3,3′-bis[2-(triisopropylsilyl)ethynyl]-1,1′-binaphthalene.* M.p. 133°. $[\alpha]_D^{r.t.} = -0.4$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3051*w*, 2942*s*, 2864*s*, 2151*m*, 1622*w*, 1583*w*, 1491*w*, 1463*m*, 1426*m*, 1391*m*, 1352*w*, 1322*w*, 1287*w*, 1243*m*, 1202*w*, 1159*s*, 1099*w*, 1071*m*, 1017*w*, 977*s*, 915*m*, 883*m*, 786*w*, 750*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.16 (*ms*, 42 H); 2.34 (*s*, 6 H); 4.95 (*d*, *AB*, $J = 6.2$, 2 H); 5.34 (*d*, *AB*, $J = 6.2$, 2 H); 7.15 (*d*, $J = 8.33$, 2 H); 7.24–7.27 (*m*, 2 H); 7.38–7.41 (*m*, 2 H); 7.81 (*d*, $J = 8.2$, 2 H); 8.16 (*s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.41; 18.72; 55.76; 95.69; 98.60; 103.77; 117.19; 125.38; 125.97; 126.70; 127.01; 127.27; 130.12; 133.94; 135.40; 153.01. FAB-MS: 735 (17, M^+); 515 (100, $[M-(i\text{-}Pr)_3Si-2\,MeO]^+$). Anal. calc. for $C_{46}H_{62}O_4Si_2$ (735.2): C 75.15, H 8.50; found: C 75.21, H 8.44.

2,2′-(1,4-Phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxoborolane) (**37**). To 1,4-diiodobenzene (1.00 g, 3.0 mmol) in dioxane (24 ml) and Et_3N (0.92 g, 1.3 ml, 9.1 mmol), $[PdCl_2(dppf)]$ (74 mg, 3 mol-%) and (pinacolato)boron (1.16 g, 1.3 ml, 9.1 mmol) were added, and the mixture was heated to 80° for 12 h. After cooling, H_2O (20 ml) was added, and the mixture was extracted with CH_2Cl_2 (3 × 30 ml). The combined org. phases were washed with sat. aq. $NaHCO_3$ soln., dried (Na_2SO_4), and evaporated *in vacuo*. Recrystallization (hexane) yielded **37** (443 mg, 44%). Brown needles. M.p. 240° ([44]: 243–245°). IR (KBr): 2978*m*, 2942*w*, 1522*m*, 1463*w*, 1393*m*, 1352*s*, 1322*m*, 1273*w*, 1256*w*, 1213*w*, 1169*w*, 1142*s*, 1102*s*, 1120*m*, 962*w*, 857*m*, 826*w*, 799*w*, 669*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.35 (*s*, 24 H); 7.80 (*s*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 24.92; 84.02; 134.15 (signal for the C-atom next to B-atom not visible). FAB-MS: 330 (28, M^+), 231 (100, $[M-C_6H_{11}O]^+$). Anal. calc. for $C_{18}H_{28}B_2O_4$ (330.04): C 65.51, H 8.55; found: C 65.39, H 8.62.

*(+)-(*S,S*)-3,3′-(1,4-Phenylene)bis[2,2′-bis(methoxymethoxy)-3′-[2-(triisopropylsilyl)ethynyl]-1,1′-binaphthalene]* ((+)-(*S,S*)-**38**). To (+)-(*S*)-**36** (200 mg, 0.30 mmol) and **37** (48 mg, 0.15 mmol) in benzene (6.5 ml) and EtOH (1.8 ml), a soln. of Na_2CO_3 (62 mg, 0.59 mmol) in H_2O (5 ml) and $[PdCl_2(dppf)]$ (4.8 mg, 4 mol-%) were added, and the vigorously stirred mixture was heated to 80° under Ar for 4 h. A second portion of $[PdCl_2(dppf)]$ (4.8 mg, 4 mol-%) was added, and stirring was continued for another 4 h at 80°. After a third addition of $[PdCl_2(dppf)]$ (2.4 mg, 2 mol-%) and heating for 4 h, the mixture was cooled to 20° and evaporated *in vacuo*. The residue was extracted with CH_2Cl_2 (3 × 20 ml), and the combined org. phases were washed with sat. aq. $NaHCO_3$ and NaCl solns., dried (Na_2SO_4), and concentrated. GPC (*Bio-Beads SX-3*) afforded (+)-(*S,S*)-**38** (130 mg, 74%). M.p. 112°. $[\alpha]_D^{r.t.} = +124.8$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3056*w*, 2941*s*, 2853*s*, 2360*m*, 2137*w*, 1615*w*, 1588*w*, 1562*w*, 1540*w*, 1492*w*, 1460*m*, 1444*m*, 1423*m*, 1389*m*, 1353*m*, 1327*w*, 1241*m*, 1199*m*, 1159*s*, 1097*m*, 1078*m*, 1054*m*, 1022*w*, 988*s*, 965*s*, 942*m*, 916*m*, 884*m*, 841*w*, 814*w*, 782*w*, 749*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.19 (*ms*, 42 H); 2.30 (*s*, 6 H); 2.44 (*s*, 6 H); 4.40 (*d*, *AB*, $J = 6.2$, 2 H); 4.45 (*d*, *AB*, $J = 6.2$, 2 H); 5.06 (*d*, *AB*, $J = 6.2$, 2 H); 5.33 (*d*, *AB*, $J = 6.2$, 2 H); 7.20–7.31 (*m*, 8 H); 7.38–7.49 (*m*, 4 H); 7.84 (*d*, $J = 8.2$, 2 H); 7.89 (*s*, 4 H); 7.92 (*d*, $J = 8.2$, 2 H); 8.03 (*s*, 2 H); 8.19 (*s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.47; 18.80; 55.79; 56.04; 95.91; 98.75; 98.92; 104.09; 117.67; 125.53; 125.66; 126.42; 126.53; 126.81 (2×); 127.00; 127.37; 127.68; 128.00; 129.85; 130.46; 130.96; 131.11; 133.92; 134.25; 135.09; 135.69; 138.36; 151.61; 153.42. MALDI-TOF-MS (HABA): 1223 (13, $[MH+K]^+$), 1208 (61, $[MH_2+Na]^+$), 1207 (100, $[MH+Na]^+$), 1206 (98, $[M+Na]^+$).

*(+)-(*S,S*)-3,3′-(1,4-Phenylene)bis[2,2′-bis(methoxymethoxy)-3′-ethynyl-1,1′-binaphthalene]* ((+)-(*S,S*)-**39**). A soln. of (+)-(*S,S*)-**38** (130 mg, 0.13 mmol) and Bu_4NF (519 µl, 1.0M soln. in THF, 0.512 mmol) in THF (13 ml)

was stirred for 1 h at 20° under N_2. After addition of H_2O (30 ml), the mixture was extracted with CH_2Cl_2 (3 × 30 ml), and the combined org. phases were dried (Na_2SO_4). Evaporation *in vacuo* and CC (SiO_2; hexane/AcOEt 3:1, containing 0.5% Et_3N) provided (*S,S*)-**39** (115 mg, 97%). White powder. M.p. 68°. $[\alpha]_D^{r.t.} = +123.2$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3059*w*, 2945*m*, 2856*m*, 2106*w*, 2071*w*, 1617*w*, 1591*m*, 1490*m*, 1464*s*, 1424*s*, 1389*s*, 1354*s*, 1241*s*, 1201*m*, 1159*s*, 1096*m*, 1075*m*, 1044*m*, 986*s*, 974*s*, 934*m*, 912*m*, 881*w*, 838*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.23 (*s*, 6 H); 2.66 (*s*, 6 H); 3.35 (*s*, 2 H); 4.35 (*d*, *AB*, $J = 6.3$, 2 H); 4.40 (*d*, *AB*, $J = 6.3$, 2 H); 4.98 (*d*, *AB*, $J = 6.0$, 2 H); 5.07 (*d*, *AB*, $J = 6.0$, 2 H); 7.21 (*d*, $J = 8.1$, 4 H); 7.26–7.32 (*m*, 4 H); 7.40–7.46 (*m*, 4 H); 7.83–7.93 (*m*, 8 H); 8.02 (*s*, 2 H); 8.21 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 55.80; 56.16; 80.72; 81.53; 98.57; 98.97; 116.37; 125.32; 125.56; 125.79; 126.30; 126.50; 126.68; 126.72; 127.38; 127.58; 127.89; 129.58; 130.19; 130.86; 130.87; 133.46; 134.20; 134.80; 135.06; 138.02; 151.45; 153.27. MALDI-TOF-MS (2,5-DHB): 893 ($[M + Na]^+$).

*(+)-(*S,S*)-3,3′-(1,4-Phenylene)bis(3′-ethynyl-1,1′-binaphthalene-2,2′-diol)* ((+)-(*S,S*)-**40**). To (+)-(*S,S*)-**39** (35 mg, 0.046 mmol) in THF (50 ml), conc. HCl (37%, 150 µl) in MeOH (50 ml) was added, and the soln. was stirred for 10 h under N_2 at 20°. H_2O (100 ml) and CH_2Cl_2 (80 ml) were added, the aq. phase was extracted with CH_2Cl_2 (2 × 60 ml), and the combined org. phases were dried (Na_2SO_4) and evaporated *in vacuo* to give crude (+)-(*S,S*)-**40**. Highly viscous oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.26 (*s*, 2 H); 5.28 (*s*, 2 H); 5.81 (*s*, 2 H); 7.13 (*d*, $J = 7.8$, 4 H); 7.26–7.42 (*m*, 8 H); 7.83–7.93 (*m*, 8 H); 8.02 (*s*, 2 H); 8.21 (*s*, 2 H).

*Bis(tetrabutylammonium) (+)-(*S,S*)-3,3′-(1,4-Phenylene)bis(3′-ethynyl-1,1′-binaphthalene-2,2′-diyl Phosphate)* ((+)-(*S,S*)-**32**). To (+)-(*S,S*)-**40** (32 mg, 0.046 mmol) in dry CH_2Cl_2 (30 ml), $POCl_3$ (0.2M soln. in CH_2Cl_2, 1.0 ml, 0.20 mmol) and Et_3N (0.29 g, 0.40 ml, 2.8 mmol) were added at 20° under N_2, and the soln. was stirred for 3 h. After evaporation, THF (10 ml) and H_2O (10 ml) were added, and the mixture was stirred for 12 h at 30°. Evaporation *in vacuo*, followed by addition of CH_2Cl_2 (25 ml) and H_2O (20 ml), provided an org. phase, which was separated and washed with H_2O (3 × 20 ml), dried (Na_2SO_4), and evaporated *in vacuo*. CC (SiO_2; CH_2Cl_2/Et_3N 97:3) and ion-exchange chromatography (*Dowex 50WX8*, Bu_4N^+; CH_2Cl_2/MeCN 1:1) gave (+)-(*S,S*)-**32** (34 mg, 55% (from (*S,S*)-**39**)). Yellow foam. M.p. >250°. $[\alpha]_D^{r.t.} = +164.7$ ($c = 0.5$, $CHCl_3$). IR (KBr): 2961*m*, 2922*w*, 2874*w*, 2100*w*, 1617*w*, 1482*w*, 1461*w*, 1416*m*, 1386*w*, 1381*w*, 1351*w*, 1297*s*, 1245*m*, 1195*w*, 1150*w*, 1104*s*, 1054*w*, 1024*w*, 979*w*, 952*w*, 893*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.61 (*t*, $J = 7.3$, 24 H); 0.89–1.04 (*m*, 16 H); 1.07–1.25 (*m*, 16 H); 2.61–2.81 (*m*, 16 H); 3.28 (*s*, 2 H); 7.11–7.21 (*m*, 8 H); 7.31–7.41 (*m*, 4 H); 7.78 (*d*, $J = 8.2$, 2 H); 7.94 (*d*, $J = 8.2$, 2 H); 8.03 (*s*, 2 H); 8.08 (*s*, 2 H); 8.27 (*s*, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 13.51; 19.37; 23.52; 58.34; 80.28; 81.39; 116.91; 122.36; 123.09; 124.65; 125.62; 126.49; 126.66; 127.54; 127.91; 128.00; 128.21; 128.58; 129.89; 130.46; 130.76; 132.26; 132.67; 134.11; 135.85; 136.87; 148.49; 149.96. ^{31}P-NMR (121 MHz, $CDCl_3$): 4.61. FAB-MS: 1303 (8, MH^+), 1543 (13, $[M + Bu_4N]^+$), 242 (100, Bu_4N^+). HR-FAB-MS: 1300.6804 (M^+, $C_{82}H_{98}N_2O_8P_2$; calc. 1300.6798).

*(+)-(*S*)-3′-(2-{3,5-Bis[3,5-bis(benzyloxy)benzyloxy]phenyl}ethynyl)-2,2′-bis(methoxymethoxy)-3-[2-(trimethylsilyl)ethynyl]-1,1′-binaphthalene* (*G-2*-(+)-(*S*)-**45**). To a degassed soln. of *G-2*-**9** (338 mg, 0.40 mmol) in abs. THF (6 ml) and dry (i-Pr)$_2$NH (5 ml), $[PdCl_2(PPh_3)_2]$ (13.1 mg, 5 mol-%) and CuI (3.5 mg, 5 mol-%) were added. A degassed soln. of (+)-(*S*)-**44** (184 mg, 0.37 mmol) in abs. THF (4 ml) was slowly added, and the resulting mixture heated to 45° for 5 h. After addition of sat. aq. NaCl soln. (20 ml), the aq. phase was extracted with CH_2Cl_2 (2 × 100 ml), and the combined org. phases were dried (Na_2SO_4) and evaporated *in vacuo*. CC (SiO_2; hexane/AcOEt 7:1, containing 0.5% Et_3N) yielded *G-2*-(+)-(*S*)-**45** (308 mg, 69%). M.p. 73°. $[\alpha]_D^{r.t.} = +50.7$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3058*w*, 3024*w*, 2955*w*, 2922*w*, 2880*w*, 2820*w*, 2149*w*, 1596*s*, 1493*w*, 1450*m*, 1429*m*, 1373*m*, 1344*w*, 1323*w*, 1293*w*, 1245*m*, 1208*w*, 1158*s*, 1053*m*, 978*m*, 844*m*, 751*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.31 (*s*, 9 H); 2.50 (*s*, 3 H); 2.52 (*s*, 3 H); 4.94 (*d*, *AB*, $J = 6.3$, 1 H); 4.95 (*d*, *AB*, $J = 6.3$, 1 H); 5.02 (*s*, 4 H); 5.07 (*s*, 8 H); 5.21 (*d*, *AB*, $J = 6.3$, 1 H); 5.23 (*d*, *AB*, $J = 6.3$, 1 H); 6.62 (*t*, $J = 2.1$, 2 H); 6.65 (*t*, $J = 2.4$, 1 H); 6.73 (*d*, $J = 2.1$, 4 H); 6.85 (*d*, $J = 2.1$, 2 H); 7.22–7.47 (*m*, 26 H); 7.87 (*t*, $J = 6.9$, 2 H); 8.22 (*s*, 1 H); 8.26 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): −0.06; 56.11; 56.22; 70.23; 70.30; 86.51; 93.88; 98.96; 99.14; 99.39; 101.91; 102.14; 103.80; 106.55 (2×); 110.87; 117.33; 117.37; 124.90; 125.80; 125.84; 126.06; 126.18; 126.84 ; 127.53; 127.62 (2×); 127.86; 128.10; 128.30; 128.88; 130.45; 130.61; 134.15 (2×); 134.57; 135.24; 137.08; 139.36; 153.44; 153.73; 160.02; 160.57. MALDI-TOF-MS (CCA): 1247 (11, $[MH + K]^+$), 1231 (96, $[MH_2 + Na]^+$), 1230 (100, $[MH + Na]^+$). Anal. calc. for $C_{79}H_{70}O_{10}Si \cdot 0.4$ AcOEt (1242.76): C 77.90, H 5.94; found: C 77.81, H 5.95.

*(+)-(*S*)-3′-(2-{3,5-Bis[3,5-bis(benzyloxy)benzyloxy]phenyl}ethynyl)-3-ethynyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene* (*G-2*-(+)-(*S*)-**46**). A soln. of *G-2*-(+)-(*S*)-**45** (200 mg, 0.17 mmol) and K_2CO_3 (81 mg, 0.59 mmol) in THF/MeOH 1:1 (18 ml) was stirred for 2 h at 20°. After addition of H_2O (10 ml) and extraction with CH_2Cl_2 (3 × 70 ml), the combined org. phases were dried (Na_2SO_4) and evaporated *in vacuo* to give crude *G-2*-(+)-(*S*)-**46**. M.p. 65°. $[\alpha]_D^{r.t.} = +14.2$ ($c = 1.0$, $CHCl_3$). IR (neat): 3282*m*, 3066*m*, 3030*m*, 2931*m*, 2867*m*, 2822*w*, 2250*w*, 1595*s*, 1496*m*, 1450*s*, 1429*m*, 1373*s*, 1348*m*, 1321*m*, 1294*m*, 1242*m*, 1204*m*, 1157*s*, 1053*s*, 976*s*, 909*m*, 834*m*, 735*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.53 (*s*, 3 H); 2.56 (*s*, 3 H); 3.36 (*s*, 1 H); 4.92 (*d*, *AB*, $J = 6.5$,

1 H); 4.96 (*d*, *AB*, *J* = 6.5, 1 H); 5.02 (*s*, 4 H); 5.07 (*s*, 8 H); 5.14 (*d*, *AB*, *J* = 6.5, 1 H); 5.19 (*d*, *AB*, *J* = 6.5, 1 H); 6.60 (*t*, *J* = 2.4, 2 H); 6.62 (*t*, *J* = 2.7, 1 H); 6.70 (*d*, *J* = 2.1, 4 H); 6.82 (*d*, *J* = 2.4, 2 H); 7.21 – 7.50 (*m*, 26 H); 7.85 (*d*, *J* = 7.2, 2 H); 8.23 (*s*, 1 H); 8.26 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 53.36; 55.97; 56.03; 70.03; 70.09; 80.58; 81.56; 86.22; 93.68; 98.89; 98.97; 101.69; 103.58; 106.35; 110.65; 116.28; 117.17; 124.628; 125.65; 125.68; 125.78; 126.02; 126.57; 126.62; 127.38; 127.57 (2 ×); 127.65; 128.09; 128.67; 130.21; 130.37; 133.85; 134.09; 134.43; 135.29; 136.84; 139.11; 153.23; 153.49; 159.80; 160.33. FAB-MS: 1135 (34, M^+), 1104 (100, $[M - OMe]^+$). Anal. calc. for $C_{76}H_{62}O_{10} \cdot H_2O$ (1153.35): C 79.15, H 5.59; found: C 79.38, H 5.84.

*(+)-(*S,S*)-3,3′-(Buta-1,3-diynediyl)bis[3′-(2-{3,5-bis[3,5-bis(benzyloxy)benzyloxy]phenyl}ethynyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene]* (*G-2*-(+)-(*S*,*S*)-**47**). A soln. of *G-2*-(+)-(*S*)-**46** (180 mg, 0.16 mmol) and CuCl (190 mg, 1.9 mmol) in abs. CH_2Cl_2 (110 ml) was stirred under dry air for 15 min, and TMEDA (0.28 ml, 0.22 g, 1.9 mmol) was then added. After 1.5 h, H_2O (150 ml) was added, and the separated org. phase was washed with H_2O (4 × 150 ml), dried (Na_2SO_4), and evaporated *in vacuo*. GPC (*Bio-Beads SX-1*) yielded *G-2*-(+)-(*S*,*S*)-**47** (145 mg, 81%). M.p. 59°. $[\alpha]_D^{rt} = +280.8$ (*c* = 1.0, $CHCl_3$). IR (neat): 3057*m*, 3029*m*, 2984*m*, 2930*m*, 2875*m*, 2824*m*, 2215*w*, 1955*w*, 1708*w*, 1596*s*, 1497*m*, 1451*s*, 1429*s*, 1373*s*, 1347*s*, 1323*m*, 1294*m*, 1266*m*, 1240*m*, 1216*m*, 1202*m*, 1160*s*, 1100*m*, 1057*s*, 1027*m*, 978*m*, 925*m*, 908*m*, 834*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.52 (*s*, 6 H); 2.63 (*s*, 6 H); 4.89 (*d*, *AB*, *J* = 6.3, 2 H); 4.96 (*d*, *AB*, *J* = 6.3, 2 H); 4.99 (*s*, 8 H); 5.04 (*s*, 16 H); 5.10 (*d*, *AB*, *J* = 5.9, 2 H); 5.19 (*d*, *AB*, *J* = 5.9, 2 H); 6.58 (*t*, *J* = 2.1, 4 H); 6.61 (*t*, *J* = 2.1, 2 H); 6.69 (*d*, *J* = 2.1, 8 H); 6.81 (*d*, *J* = 2.1, 4 H); 7.21 – 7.44 (*m*, 52 H); 7.86 (*d*, *J* = 8.1, 4 H); 8.24 (*s*, 2 H); 8.26 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 56.21; 56.42; 70.22; 70.28; 78.31; 79.73; 86.35; 93.93; 99.13; 99.35; 101.88; 103.79; 106.54; 110.84; 116.31; 117.36; 124.80; 125.77; 125.87; 126.03; 126.35; 126.69; 126.87; 127.63; 127.83 (3 ×); 128.10; 128.28; 128.85; 130.45; 130.58; 133.97; 134.51; 134.72; 136.16; 137.03; 139.30; 153.42; 153.94; 159.99; 160.52. MALDI-TOF-MS (CCA): 2292 (100, $[M\text{H} + \text{Na}]^+$), 2248 (36, $[M\text{H} + \text{Na} - \text{MeOCH}_2]^+$), 2203 (13, $[M\text{H} + \text{Na} - 2\ \text{MeOCH}_2]^+$). Anal. calc. for $C_{152}H_{122}O_{20} \cdot 2H_2O$ (2304.69): C 79.22, H 5.51; found: C 79.23, H 5.67.

*(+)-(*S,S*)-3,3′-(Buta-1,3-diynediyl)bis[3′-(2-{3,5-bis[3,5-bis(benzyloxy)benzyloxy]phenyl}ethynyl)-2,2′-dihydroxy-1,1′-binaphthalene]* (*G-2*-(+)-(*S*,*S*)-**48**). To *G-2*-(+)-(*S*,*S*)-**47** (180 mg, 0.08 mmol) in THF (35 ml), conc. HCl (37%, 32 µl) in MeOH (35 ml) was added, and the soln. was stirred for 10 h under N_2 at 20°. After addition of H_2O (20 ml) and CH_2Cl_2 (30 ml), the aq. phase was extracted with CH_2Cl_2 (2 × 50 ml), and the combined org. phases were dried (Na_2SO_4) and evaporated *in vacuo* to give crude *G-2*-(+)-(*S*,*S*)-**48** (170 mg, 98%). Highly viscous oil. $[\alpha]_D^{rt} = +312.0$ (*c* = 1.0, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): 4.98 (s, 8 H); 5.03 (*s*, 16 H); 5.55 (*s*, 2 H); 5.84 (*s*, 2 H); 6.57 (*t*, *J* = 2.4, 4 H); 6.62 (*t*, *J* = 2.4, 2 H); 6.66 (*d*, *J* = 2.1, 8 H); 6.80 (*d*, *J* = 2.4, 4 H); 7.17 – 7.42 (*m*, 52 H); 7.86 (*m*, 4 H); 8.22 (*s*, 2 H); 8.24 (*s*, 2 H).

*Bis(tetrabutylammonium) (+)-(*S,S*)-3,3′-(Buta-1,3-diynediyl)bis[3′-(2-{3,5-bis[3,5-bis(benzyloxy)benzyloxy]phenyl}ethynyl)-1,1′-binaphthalene-2,2′-diyl Phosphate]* (*G-2*-(+)-(*S*,*S*)-**41**). To *G-2*-(+)-(*S*,*S*)-**48** (170 mg, 78 µmol) in dry CH_2Cl_2 (30 ml), $POCl_3$ (0.16M soln. in CH_2Cl_2, 2.14 ml, 0.34 mmol) and Et_3N (0.47 g, 0.33 g, 4.68 mmol) were added at 20° under N_2, and the soln. was stirred for 3 h. After evaporation *in vacuo*, THF (15 ml) and H_2O (15 ml) were added, and the mixture was stirred for 12 h at 30°. Evaporation *in vacuo*, followed by addition of CH_2Cl_2 (30 ml) and H_2O (15 ml) provided an org. phase, which was washed with H_2O (3 × 20 ml), dried (Na_2SO_4), and evaporated *in vacuo*. CC (SiO_2; CH_2Cl_2/Et_3N 97:3) and ion-exchange chromatography (*Dowex 50WX8*, Bu_4N^+; CH_2Cl_2/MeCN 1:1) afforded *G-2*-(+)-(*S*,*S*)-**41** (173 mg, 82%). Yellow foam. M.p. 92°. $[\alpha]_D^{rt} = +389.5$ (*c* = 1.0, $CHCl_3$). IR (KBr): 3068*w*, 3036*w*, 2961*m*, 2929*m*, 2865*m*, 1596*s*, 1498*w*, 1450*m*, 1429*w*, 1375*m*, 1343*w*, 1295*m*, 1253*w*, 1205*w*, 1155*s*, 1098*s*, 1050*m*, 1028*m*, 895*w*, 831*w*, 804*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.73 (*t*, *J* = 7.3, 24 H); 1.06 – 1.32 (*m*, 32 H); 2.81 – 2.91 (*m*, 16 H); 4.98 (*s*, 8 H); 5.03 (*s*, 16 H); 6.55 – 6.57 (*m*, 6 H); 6.70 (*d*, *J* = 2.2, 8 H); 6.91 (*d*, *J* = 2.3, 4 H); 7.17 – 7.42 (*m*, 52 H); 7.79 (*d*, *J* = 8.2, 2 H); 7.80 (*d*, *J* = 8.2, 2 H); 8.09 (*s*, 2 H); 8.13 (*s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 13.67; 19.51; 23.68; 58.19; 69.99; 70.11; 78.35; 79.72; 86.38; 93.42; 101.61; 103.07; 106.39; 111.04; 116.59; 118.27; 122.27; 123.08; 124.88; 125.05; 125.44; 126.40; 126.51; 126.97; 127.02; 127.54; 127.95; 128.53; 129.15; 129.20; 129.92; 130.01; 132.17; 132.97; 133.71; 135.09; 136.77; 139.26; 150.07; 150.15 (*d*, $J(^{31}P,^{13}C) = 9.1$); 159.38; 160.11. ^{31}P-NMR (121 MHz, $CDCl_3$): 4.47. ESI-MS (negative-ion mode): 2457 (8, $[M - Bu_4N]^-$), 2237 (3, $[M - 2\ Bu_4N + Na]^-$), 1107 (100, $[M - 2\ Bu_4N]^{2-}$). Anal. calc. for $C_{176}H_{174}N_2O_{20}P_2 \cdot 4H_2O$ (2771.36): C 76.28, H 6.62, N 1.01; found: C 76.29, H 6.70, N 1.10.

*(+)-(*S,S*)-3,3′-(1,4-Phenylene)bis[3′-(2-{3,5-bis[3,5-bis(benzyloxy)benzyloxy]phenyl}ethynyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene]* (*G-2*-(+)-(*S*,*S*)-**49**). To a degassed mixture of *G-2*-**9** (330 mg, 0.39 mmol), [$PdCl_2$(dppf)] (11 mg, 10 mol-%), and CuI (2 mg, 10 mol-%) in (i-Pr)$_2$NH (2 ml) and abs. THF (3 ml) at 40°, a soln. of (+)-(*S*,*S*)-**39** (100 mg, 0.13 mmol) in abs. THF (2 ml) was added slowly (30 min). After stirring for 4 h at 40°, sat. aq. NaCl soln. (10 ml) was added, and the mixture was extracted with CH_2Cl_2 (3 × 50 ml). The combined org. phases were dried (Na_2SO_4), and the solvent was evaporated *in vacuo*. GPC (*Bio-Beads SX-1*) yielded *G-2*-(+)-(*S*,*S*)-**49** (140 mg, 48%). Yellow foam. M.p. 100°. $[\alpha]_D^{rt} = +146.3$ (*c* = 1.0, $CHCl_3$). IR (neat):

3057*m*, 3033*m*, 2924*m*, 2875*m*, 2826*m*, 2215*w*, 1596*s*, 1494*w*, 1449*s*, 1428*m*, 1374*m*, 1345*m*, 1321*w*, 1296*m*, 1263*w*, 1242*m*, 1157*s*, 1101*w*, 1076*m*, 1056*s*, 1027*m*, 985*m*, 964*m*, 923*w*, 907*w*, 836*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 2.26 (*s*, 6 H); 2.65 (*s*, 6 H); 4.39 (*d*, *AB*, *J* = 6.2, 2 H); 4.43 (*d*, *AB*, *J* = 6.3, 2 H); 5.00 (*s*, 8 H); 5.05 (*s*, 16 H); 5.05 (*d*, *AB*, *J* = 6.0, 2 H); 5.18 (*d*, *AB*, *J* = 6.0, 2 H); 6.59 (*t*, *J* = 2.3, 4 H); 6.62 (*t*, *J* = 2.3, 2 H); 6.69 (*d*, *J* = 2.1, 8 H); 6.84 (*d*, *J* = 2.1, 4 H); 7.26 – 7.46 (*m*, 52 H); 7.87 (*d*, *J* = 8.1, 2 H); 7.89 (*s*, 4 H); 7.94 (*d*, *J* = 8.1, 2 H); 8.05 (*s*, 2 H); 8.25 (*s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 55.84; 56.12; 70.06; 70.12; 86.44; 93.59; 98.61; 98.92; 101.67; 103.52; 106.33; 110.65; 117.26; 124.64; 125.31; 125.50; 125.97; 126.37; 126.47; 126.59; 126.73; 127.16; 127.54 (2 ×); 127.86; 127.98; 128.56; 129.61; 130.36; 130.84; 130.87; 133.52; 134.02; 134.25; 134.81; 136.75; 138.04; 139.03; 151.40; 152.97; 159.66; 160.20. MALDI-TOF-MS (CCA): 2321 (100, $[M\mathrm{H}+\mathrm{Na}]^+$), 2337 (35, $[M\mathrm{H}+\mathrm{K}]^+$). Anal. calc. for $C_{154}H_{126}O_{20}\cdot 3H_2O$ (2350.76): C 78.69, H 5.66; found: C 78.47, H 5.74.

*(+)-(*S,S*)-3,3′-(1,4-Phenylene)bis[3′-(2-{3,5-bis[3,5-bis(benzyloxy)benzyloxy]phenyl}ethynyl)-1,1′-binaphthalene-2,2′-diol]* (*G-2*-(+)-(*S,S*)-**50**). To *G-2*-(+)-(*S,S*)-**49** (180 mg, 0.078 mmol) in THF (30 ml), conc. HCl (37%, 100 µl) in MeOH (30 ml) was added, and the soln. was stirred for 10 h under N_2 at 20°. H_2O (20 ml) and CH_2Cl_2 (30 ml) were added, the aq. phase was extracted with CH_2Cl_2 (2 × 50 ml), and the combined org. phases were dried (Na_2SO_4) and evaporated *in vacuo* to give crude *G-2*-(+)-(*S,S*)-**50** (170 mg, 100%). ^{1}H-NMR (300 MHz, $CDCl_3$): 4.98 (*s*, 8 H); 5.03 (*s*, 16 H); 6.58 (*t*, *J* = 2.1, 4 H); 6.63 (*t*, *J* = 2.1, 2 H); 6.68 (*d*, *J* = 2.1, 8 H); 6.83 (*d*, *J* = 2.1, 4 H); 7.18 (*d*, *J* = 8.0, 2 H); 7.26 – 7.43 (*m*, 50 H); 7.87 (*s*, 4 H); 7.89 (*d*, *J* = 8.0, 2 H); 7.94 (*d*, *J* = 8.0, 2 H); 8.07 (*s*, 2 H); 8.24 (*s*, 2 H) (OH signals are not visible).

*Bis(tetrabutylammonium) (+)-(*S,S*)-3,3′-(1,4-Phenylene)bis[3′-(2-{3,5-bis[3,5-bis(benzyloxy)benzyloxy]phenyl}ethynyl)-1,1′-binaphthalene-2,2′-diyl Phosphate]* (*G-2*-(+)-(*S,S*)-**42**). To *G-2*-(+)-(*S,S*)-**50** (170 mg, 0.078 mmol) in dry CH_2Cl_2 (30 ml), $POCl_3$ (0.2M soln. in CH_2Cl_2, 1.66 ml, 0.33 mmol) and Et_3N (0.46 g, 0.66 ml, 0.45 mmol) were added at 20° under N_2, and the soln. was stirred for 3 h. Evaporation *in vacuo*, followed by addition of THF (15 ml) and H_2O (15 ml), afforded a mixture, which was stirred for 12 h at 30°. After evaporation of THF *in vacuo*, CH_2Cl_2 (30 ml) and H_2O (15 ml) were added, and the phases were separated. The org. phase was washed with H_2O (3 × 20 ml), dried (Na_2SO_4), and evaporated *in vacuo*. CC (SiO_2; CH_2Cl_2/Et_3N 98:2) and ion-exchange chromatography (*Dowex 50WX8*, Bu_4N^+; CH_2Cl_2/MeCN 1:1) gave *G-2*-(+)-(*S,S*)-**42** (168 mg, 79%). Yellow foam. M.p. 120°. $[\alpha]_D^{rt} = +172.8$ (*c* = 0.5, $CHCl_3$). IR (KBr): 3059*w*, 3030*w*, 2960*m*, 2929*m*, 2871*m*, 1596*s*, 1493*w*, 1450*m*, 1426*w*, 1373*m*, 1344*w*, 1294*m*, 1252*w*, 1204*w*, 1155*s*, 1098*s*, 1050*m*, 988*w*, 964*w*, 887*w*, 834*m*, 810*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.57 (*t*, *J* = 7.3, 24 H); 0.90 – 0.99 (*m*, 16 H); 1.03 – 1.14 (*m*, 16 H); 2.59 – 2.72 (*m*, 16 H); 4.98 (*s*, 8 H); 5.03 (*s*, 16 H); 6.55 – 6.57 (*m*, 6 H); 6.69 (*d*, *J* = 2.2, 8 H); 6.92 (*d*, *J* = 2.3, 4 H); 7.14 – 7.42 (*m*, 52 H); 7.80 (*d*, *J* = 8.4, 2 H); 7.92 (*d*, *J* = 8.4, 2 H); 8.03 (*s*, 2 H); 8.13 (*s*, 2 H); 8.31 (*s*, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 13.67; 19.51; 23.68; 58.19; 69.99; 70.11; 78.35; 79.72; 86.38; 93.42; 101.61; 103.07; 106.39; 111.04; 116.59; 118.27; 122.27; 123.08; 124.88; 125.05; 125.44; 126.40; 126.51; 126.97; 127.02; 127.54; 127.95; 128.53; 129.15; 129.20; 129.92; 130.01; 132.17; 132.97; 133.71; 135.09; 136.77; 139.26; 150.07; 150.15 (*d*, $J(^{31}P, ^{13}C) = 9.1$); 159.38; 160.11. ^{31}P-NMR (121 MHz, $CDCl_3$): 4.68. MALDI-TOF-MS: 2972 (100, $[M\mathrm{H}_2+\mathrm{Bu}_4\mathrm{N}]^+$), 2730 (11, $M\mathrm{H}_2^+$). Anal. calc. for $C_{178}H_{178}N_2O_{20}P_2$ (2727.31): C 78.39, H 6.58, N 1.03; found: C 78.21, H 6.75, N 1.07.

*(+)-(*S,S*)-3,3′-(Buta-1,3-diynediyl)bis(3′-{2-[3,5-bis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyloxy)phenyl]ethynyl}-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene)* (*G-1*-(+)-(*S,S*)-**51**). To a degassed mixture of *G-1*-**11** (234 mg, 0.22 mmol), $[PdCl_2(PPh_3)_2]$ (6.4 mg, 10 mol-%), and CuI (1.7 mg, 10 mol-%) in (i-Pr)$_2$NH (2.3 ml) and abs. THF (3 ml), a soln. of (+)-(*S,S*)-**33** (84 mg, 0.1 mmol) in abs. THF (2.1 ml) was slowly added at 40°, and the mixture was stirred for 4 h at 40°. Sat. aq. NaCl soln. (10 ml) was added, and the mixture was extracted with CH_2Cl_2 (3 × 50 ml). The combined org. phases were dried (Na_2SO_4), and the solvent was evaporated *in vacuo*. GPC (*Bio-Beads SX-1*) yielded *G-1*-(+)-(*S,S*)-**51** (83 mg, 34%). Highly viscous, yellow oil. $[\alpha]_D^{rt} = +200.2$ (*c* = 1.0, $CHCl_3$). IR (neat): 3055*w*, 2928*s*, 2876*s*, 1596*s*, 1449*m*, 1351*m*, 1322*m*, 1297*m*, 1244*m*, 1157*s*, 1105*s*, 1073*m*, 977*m*, 929*w*, 843*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.54 (*s*, 6 H); 2.65 (*s*, 6 H); 3.37 (*s*, 24 H); 3.52 – 3.57 (*m*, 16 H); 3.63 – 3.76 (*m*, 48 H); 3.82 – 3.87 (*m*, 16 H); 4.10 – 4.15 (*m*, 16 H); 4.89 (*d*, *AB*, *J* = 6.2, 2 H); 4.94 – 4.97 (*m*, 10 H); 5.09 (*d*, *AB*, *J* = 6.2, 2 H); 5.18 (*d*, *AB*, *J* = 5.8, 2 H); 6.46 (*t*, *J* = 2.2, 4 H); 6.59 – 6.62 (*m*, 10 H); 6.79 (*d*, *J* = 2.0, 4 H); 7.19 – 7.37 (*m*, 8 H); 7.41 – 7.48 (*m*, 4 H); 7.87 (*d*, *J* = 7.8, 4 H); 8.24 (*s*, 2 H); 8.26 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 56.19; 56.42; 59.15; 67.66; 69.81; 70.22; 70.70; 70.80; 70.96; 72.08; 78.26; 79.73; 86.31; 93.90; 99.09; 99.32; 101.41; 103.70; 106.28; 110.74; 116.31; 117.36; 124.77; 125.71; 125.85; 126.01; 126.34; 126.66; 126.86; 127.62; 127.89 (2 ×); 128.08; 130.43; 130.56; 133.94; 134.49; 134.77; 136.16; 139.10; 153.35; 153.87; 160.00; 160.44. MALDI-TOF-MS (CCA): 2741 (100, $[M\mathrm{H}_2+\mathrm{Na}]^+$).

*(+)-(*S,S*)-3,3′-(Buta-1,3-diynediyl)bis(3′-{2-[3,5-bis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyloxy)phenyl]ethynyl}-1,1′-binaphthalene-2,2′-diol)* (*G-1*-(+)-(*S,S*)-**52**). To *G-1*-(+)-(*S,S*)-**51** (83 mg, 0.031 µmol) in THF (14 ml), conc. HCl (37%, 50 µl) in MeOH (14 ml) was added, and the mixture was stirred for 12 h under

N_2. After addition of H_2O (30 ml), the aq. phase was extracted with CH_2Cl_2 (3×50 ml), and the combined org. phases were dried ($MgSO_4$) and evaporated *in vacuo* to give crude *G-1*-(+)-(*S,S*)-**52** (77 mg, 98%). Highly viscous oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.35 (*s*, 24 H); 3.52–3.56 (*m*, 16 H); 3.63–3.76 (*m*, 48 H); 3.80–3.85 (*m*, 16 H); 4.09–4.14 (*m*, 16 H); 4.99 (*s*, 8 H); 6.01 (*s*, 2 H); 6.11 (*s*, 2 H); 6.46 (*t*, $J = 2.2$, 4 H); 6.60 (*d*, $J = 2.4$, 8 H); 6.64 (*t*, $J = 2.6$, 2 H); 6.81 (*d*, $J = 2.6$, 4 H); 7.15 (*d*, $J = 8.0$, 4 H); 7.32–7.43 (*m*, 8 H); 7.85–7.89 (*m*, 4 H); 8.23 (*s*, 2 H); 8.25 (*s*, 2 H).

*Bis(tetrabutylammonium) (+)-(*S,S*)-3,3′-(Buta-1,3-diynediyl)bis(3′-{2-[3,5-bis(3,5-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyloxy)phenyl]ethynyl}-1,1′-binaphthalene-2,2′-diyl Phosphate)* (*G-1*-(+)-(*S,S*)-**43**). To *G-1*-(+)-(*S,S*)-**52** (80 mg, 31 μmol) in dry CH_2Cl_2 (12 ml), $POCl_3$ (0.16M soln. in CH_2Cl_2, 0.86 ml, 0.136 mmol) and Et_3N (0.26 ml, 0.19 g, 1.89 mmol) were added at 20° under N_2, and the soln. was stirred for 4.5 h. Evaporation *in vacuo* was followed by addition of THF (6 ml) and H_2O (6 ml), and the resulting mixture was stirred for 12 h at 40°. THF was evaporated *in vacuo*, and the aq. phase was extracted with CH_2Cl_2 (3×20 ml). The combined org. phases were washed with H_2O (40 ml), dried ($MgSO_4$), and evaporated *in vacuo*. After CC (SiO_2; CH_2Cl_2/Et_3N 95:5), the product was dissolved in CH_2Cl_2 (15 ml), and the soln. was washed with H_2O (10 ml). The org. phase was dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Ion-exchange chromatography (*Dowex 50WX8*, Bu_4N^+; CH_2Cl_2/MeCN 1:1) afforded *G-1*-(+)-(*S,S*)-**43** (34 mg, 35%). Highly viscous, yellow oil. $[\alpha]_D^{r.t.} = +339.4$ ($c = 1.0$, $CHCl_3$). IR (neat): 3056*w*, 2922*s*, 2864*s*, 2214*w*, 2147*w*, 1596*s*, 1448*s*, 1351*m*, 1298*s*, 1250*m*, 1169*s*, 1140*s*, 1099*s*, 1064*s*, 896*m*, 858*m*, 805*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.76 (*t*, $J = 7.2$, 24 H); 1.13–1.27 (*m*, 16 H); 1.30–1.40 (*m*, 16 H); 2.96–2.99 (*m*, 16 H); 3.35 (*s*, 24 H); 3.51–3.54 (*m*, 16 H); 3.58–3.72 (*m*, 48 H); 3.82 (*t*, $J = 4.8$, 16 H); 4.10 (*t*, $J = 4.8$, 16 H); 4.94 (*s*, 8 H); 6.43 (*m*, 4 H); 6.55 (*t*, $J = 2.3$, 2 H); 6.58 (*d*, $J = 1.8$, 8 H); 6.88 (*d*, $J = 1.8$, 4 H); 7.18–7.24 (*m*, 8 H); 7.35–7.41 (*m*, 4 H); 7.81–7.85 (*m*, 4 H); 8.14 (*s*, 2 H); 8.15 (*s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 13.64; 19.54; 23.77; 58.41; 58.97; 67.49; 69.63; 70.02; 70.51; 70.59; 70.75; 71.88; 78.30; 79.88; 86.40; 93.34; 101.22; 103.09; 106.12; 110.91; 116.48; 118.05; 122.23; 123.10; 124.83; 125.06; 125.40; 126.38; 126.50; 126.95; 127.02; 127.91; 128.03; 129.95; 130.08; 132.25; 132.97; 133.83; 135.24; 139.02; 149.90; 150.10 (*d*, $J(^{31}P,^{13}C) = 9.4$); 149.93 (*d*, $J(^{31}P,^{13}C) = 8.7$); 160.03. ^{31}P-NMR (121 MHz, $CDCl_3$): 4.47. MALDI-TOF-MS (HABA): 3391 (65, $[M + Bu_4N]^+$), 3149 (100, MH^+), 2727 (46, $[MH + Na + K - 2\,Bu_4N]^+$), 2709 (48, $[MH + 2\,Na - 2\,Bu_4N]^+$), 2688 (75, $[MH_2 + Na - 2\,Bu_4N]^+$). MALDI-TOF-MS (HABA; negative-ion mode): 3146 (4, M^-); 2906 (72, $[MH - Bu_4N]^-$); 2687 (78, $[MH + Na - 2\,Bu_4N]^-$), 2664 (100, $[MH_2 - 2\,Bu_4N]^-$).

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