# Thermotropic and Lyotropic Liquid Crystalline Phases of Rigid Aromatic Amphiphiles

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*Dedicated to Professor Ralf Miethchen on the occasion of his 60th birthday*

**Abstract:** Rodlike amphiphilic molecules that contain exclusively aromatic building-blocks and no flexible alkyl chains have been synthesized and their mesomorphic properties investigated. These novel compounds bear diol head groups of different size (2,3-dihydroxypropyloxy or 5,6-dihydroxy-3-oxahexyloxy groups) at one end of a biphenyl unit, various aromatic segments (benzyloxy, 4-, 3-, or 2-methylbenzyloxy, phenoxy groups) at the other, and additional methyl substituents in different positions. They were synthesized by using Suzuki cross-coupling reactions as the key steps. Their thermotropic mesomorphism was investigated by means of polarized light optical microscopy, differential scanning calorimetry, and, for enantiotropic phases, by X-ray scattering. The liquid crystallinity of this class of compounds is influenced by protic solvents, such as water and glycerol. Dependent on the temperature and the solvent content, different $S_A$ phases were found. Several mesophases resulting from the frustration of these layer structures (e.g., different columnar phases, optical isotropic mesophases, and nematic phases) were also present. The smectic phases have different degrees of intercalation ($S_{Ad}$, $S_{A2}$). The columnar phases are supposed to be ribbon structures that result from the collapse of the smectic layers. They occur in some pure compounds or they are induced upon the addition of protic solvents. The particular phase sequences of the different compounds depend mainly on the position of the methyl substituents at the biphenyl cores and are largely determined by the degree of intercalation of the aromatic cores.

**Keywords:** amphiphiles · biaryls · liquid crystals · mesophases · phase diagrams

## Introduction

Liquid crystalline phases represent well-ordered, self-assembled states of soft matter combining order and mobility on a supermolecular level. Low molecular mass materials which are able to form liquid crystalline phases are usually anisometric (rod-shaped or disc-shaped) molecules or amphiphilic molecules.[1] In most cases these molecules contain flexible alkyl- or polyether chains that are regarded as responsible for the mobility within these ordered systems. The parallel alignment of their anisometric rigid units on the other hand gives rise to an orientational order leading to nematic phases (N), whereas the microsegregation[2] of incompatible molecular parts is important for the formation of mesophases with a positional long-range order in one dimension (layer structures = smectic phases, S), in two dimensions (regular arrangements of cylinders = columnar mesophases, Col), or even in three dimensions (e.g., cubic mesophases, Cub).

Few attempts have been made so far to completely abstain from flexible chains. Some large rodlike or disclike rigid molecules without flexible chains can form (predominately nematic) liquid crystalline phases.[3] However, as a consequence of the lack of flexible chains, they have stable crystalline phases with very high melting points and mesomorphic properties occur only at elevated temperatures; this complicates investigation of their properties and limits their practical application. Nevertheless, some recent observations indicated that alkyl chains are not necessary for columnar liquid crystallinity in the case of some disclike molecules with peripheral chloro substituents.[4] Furthermore, chromonic liquid crystals, which represent aromatic molecules surrounded by a periphery of hydrophilic groups, have a rich lyotropic mesomorphism in dilute aqueous solutions covering different types of lamellar, columnar, and nematic phases.[5] Here, the

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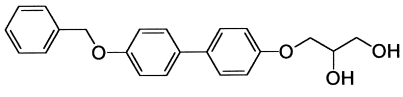
mobility is provided by the solvent. However, few amphiphilic aromatic molecules without alkyl chains can form liquid crystalline phases in the absence of a solvent. These are the potassium salt of 2-benzyl-3-phenylpropionic acid, which has a thermotropic columnar phase,[6] and some salts of 2-(3-phenoxyphenyl)propionic acid, for which lyotropic and/or thermotropic smectic and columnar phases have been reported.[7] Interestingly, the latter represent important non-steroidal anti-inflammatory drugs ("fenoprofens"), and there is discussion regarding the extent to which their pharmacological activity is related to their ability to form liquid crystalline phases. Therefore, it was an interesting challenge for us to synthesize rodlike amphiphiles[8] without flexible chains and to carry out fundamental studies on their self-organization.

The semi-rigid benzyloxybiphenyl unit was chosen as central core structure as the three linearly connected aromatic rings should provide a sufficiently large molecular anisometry, whereas the benzyl ether units provide a certain degree of flexibility.[9] To introduce amphiphilicity, a 2,3-dihydroxypropyloxy unit[10] was fixed to one of the ends. As expected, the parent amphiphile without additional substituents (**0**) is a



**0**: M.p. 230 °C

high-melting solid which readily crystallizes.[11] Therefore, no liquid crystalline properties can be detected for this molecule. To disturb the packing of the molecules in a crystal lattice, we have grafted one, two, or even three methyl groups in different positions along the aromatic core of this amphiphile.

The notation of these molecules is explained in Figure 1. The expressions ***x*** or ***x.y*** describe the position(s) of the methyl group(s) located at the central biphenyl core (**0** = no methyl

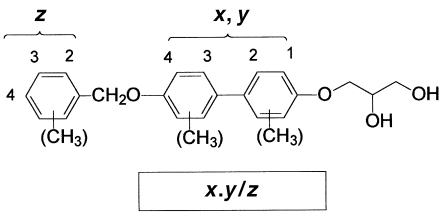
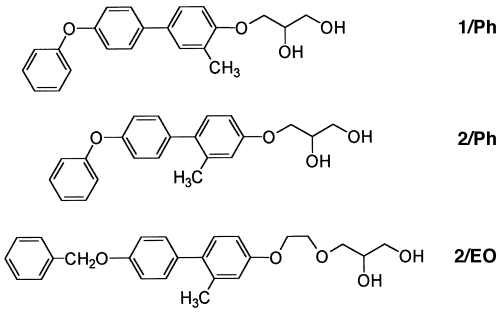



Figure 1. Structures and notation of the molecules under investigation.

group, only ***x*** = one methyl group, ***x.y*** = two methyl groups). The numbers ***x*** and ***y*** increase with the distance from the polar group, starting with the C-atom in the position *ortho* to the polar group.[12] This expression is followed by a number indicating the position of the methyl group at the terminal benzyl ether unit ***z*** (**0** = no methyl group) after a slash.

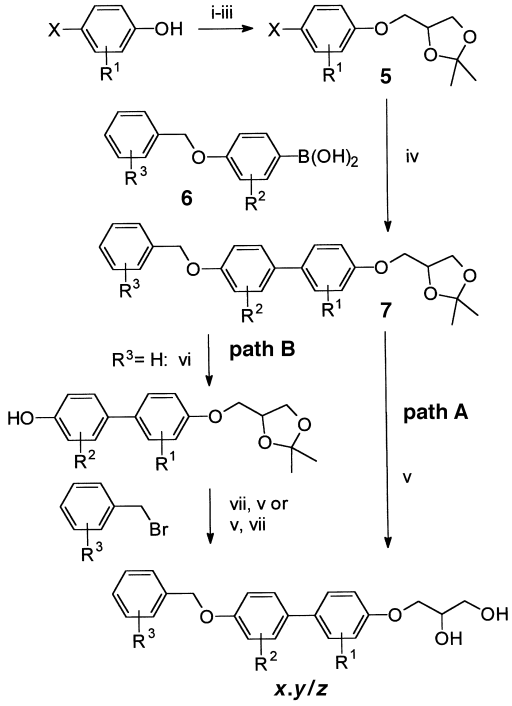
Because these molecules represent amphiphiles, their mesomorphic properties should be influenced by the addition of protic solvents. Glycerol and water were used for these investigations.

Finally, in order to generalize the results obtained, an additional compound with the larger 5,6-dihydroxy-3-oxahexyloxy group (**2/EO**) as the polar group and two molecules with a phenoxy group instead of the benzyloxy groups (**1/Ph** and **2/Ph**) have been synthesized and investigated.




## Results and Discussion

**Syntheses**: In Scheme 1, the synthetic pathways are shown. The compounds ***x.y/z*** were synthesized from different 4-halophenols.[13–17] Williamson etherification with allyl bromide,




Scheme 1. Synthesis of the amphiphiles ***x.y/z***; reagents and conditions: i) $CH_2$=CH−$CH_2Br$, $K_2CO_3$, acetone, reflux, 3 h; ii) $OsO_4$, *N*-methylmorpholine-*N*-oxide, $H_2O$, acetone, 20 °C, 20 h; iii) $Me_2C(OMe)_2$, Py · TosOH, 20 °C, 20 h; iv) $[Pd(PPh_3)_4]$, $NaHCO_3$, glyme, $H_2O$, reflux, 6 h; v) $H_2O$, MeOH, Py · TosOH, reflux, 3 h; vi) $H_2$, Pd−C, EtOAc or THF, 20 °C; vii) $K_2CO_3$, acetone, reflux, 8 h.

followed by dihydroxylation of the allylic double bond by employing the van Rheenens method[18]. Protection of the 1,2-diol unit[19] yielded the aryl halides **5** (X = Br, I), which were coupled in a Suzuki reaction[20, 21] with appropriate 4-benzyloxyphenyl boronic acids[21] **6** to give the biphenyl derivatives **7**. Cleavage of the acetonide protecting groups by acidic



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hydrolysis[22] yielded the desired diols (Path A). Alternatively, the benzyl ethers **7** with $R^3 = H$ can be cleaved hydrogenolytically, followed by etherification of the obtained phenols with appropriately substituted aryl methyl bromides and removal of the acetonide protecting group (Path B). In some cases the acetonide group was deprotected before benzylation.

The benzyl ether **2/EO** was synthesized from 4-bromo-3-methylphenol[15] and 1-(4-toluylsulfonyloxy)-2-oxa-5-hexene.[23] To obtain the phenyl ethers **1/Ph** and **2/Ph** 4-phenoxyphenyl boronic acid was used instead of the benzyloxyphenyl boronic acids. The products were purified by repeated crystallization from *n*-hexane/ethyl acetate mixtures in most cases.

**Thermotropic mesophases of the benzyl ethers *x/z*:** The thermotropic behavior of the compounds was investigated by means of polarized light optical microscopy, differential scanning calorimetry, and, in the case of enantiotropic phases, by X-ray diffraction. The thermotropic transition temperatures of the compounds ***x/z*** incorporating one or two methyl groups are summarized in Table 1.

*Molecules with one methyl group*: Liquid crystalline properties were found for all monomethyl substituted compounds **1/0** – **4/0**. The influence of the position of this methyl group on the mesomorphic properties (see Table 1, first row) can be summarized as follows. Compounds **1/0** and **4/0** with a methyl group in one of the peripheral positions at the biphenyl core (neighboring the hydrophilic group or the terminal benzyl ether unit, respectively) display more stable liquid crystalline phases than **2/0** and **3/0** with the methyl groups in the central positions neighboring the connection between the phenyl rings of the biphenyl units. This is in accordance with observations made for non-amphiphilic calamitic mesogens[24] and can be explained by the larger disturbance of a parallel alignment of the molecules in layers by the central methyl groups. Interestingly, the mesophase type strongly depends on the position of the methyl group. Compounds **1/0** and **3/0**, in which the methyl groups are directed towards the polar groups exclusively, have monotropic $S_A$ phases, whereas non-smectic phases were found for compounds **2/0** and **4/0**, in which the methyl groups are turned away from the diol group. Hence, a monotropic nematic phase was found for **2/0**. On further cooling, the transition to an $S_A$ phase and, simultaneously, the formation of circular, optical isotropic domains can be observed. These rapidly grow and fuse to form a homogeneous optical isotropic phase of high viscosity (Iso). The appearance of these is very similar to that of cubic phases.[25] Unfortunately, no X-ray investigations of this phase were possible due to its monotropic nature.

Compound **4/0** with the methyl substituent neighboring the terminal benzyl group is especially interesting. On cooling from the isotropic liquid state, the formation of an unusual texture is observed; this consists of coexisting regions with a spherulitic texture and regions with a broken fan-shaped texture as shown in Figure 2. By X-ray diffraction a columnar mesophase was found (see below). Thus, simply by shifting the methyl group along the rigid biphenyl core a wide variety of quite different mesophases can be obtained.

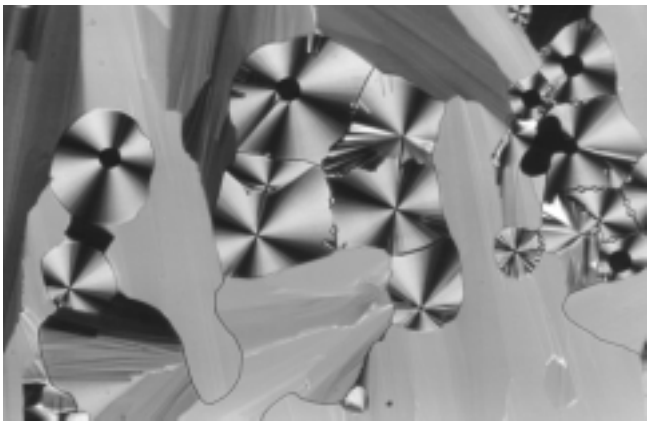
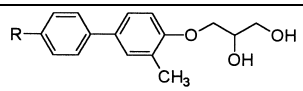
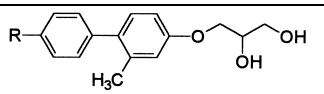
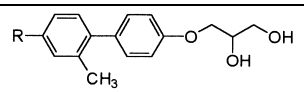
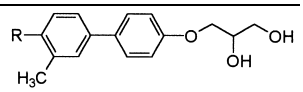


Figure 2. Polarized optical photomicrograph of the texture of the thermotropic mesophase of **4/0** at 150 °C as obtained by cooling from the isotropic liquid (a colored version of this texture can be found at http://www.chemie.uni-halle.de/org/ak/tschierske/index.html).

Table 1. Phase transition temperatures $T$ [°C] and corresponding enthalpy values $\Delta H$ [kJ mol$^{-1}$] (lower lines in italics) of the compounds **1/*z*** – **4/*z*** as obtained by DSC (peak temperatures in the heating scans, heating rate: 10 K min$^{-1}$). Abbreviations: K = crystalline solid state; $S_A$ = smectic A phase; Col = columnar phase; Iso = optical isotropic phase; N = nematic phase; I = isotropic liquid state.

| R |  Comp. | Phase transitions |  Comp. | Phase transitions |  Comp. | Phase transitions |  Comp. | Phase transitions |
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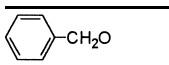
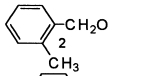
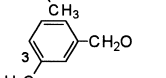
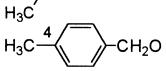
|  | **1/0** | K 147 ($S_A$ 127) I<br>*48.8 6.2* | **2/0** | K 102 (Iso 70 $S_A$ 70 N 72)[a] I<br>*29.6* | **3/0** | K 96 ($S_A$ 62)[a] I<br>*28.8* | **4/0** | K 130 Col 151 I<br>*24.4 8.5* |
|  | | | **2/2** | K 100 I<br>*25.1* | | | | |
|  | **1/3** | K 137 I<br>*46.1* | **2/3** | K 95 (Iso 70)[a] I<br>*24.0* | **3/3** | K 88 ($S_A$ 55) I<br>*26.2* | **4/3** | $K_1$ 88 $K_2$ 116 Col 151 I<br>*13.0 8.5 8.3* |
|  | **1/4** | K 150 $S_A$ 156 I<br>*37.1 9.4* | **2/4** | K 131 (Iso 95[a] $S_A$ 115) I<br>*33.3 1.7* | **3/4** | K 95 $S_A$ 104 I<br>*19.1 2.3* | **4/4** | $K_1$ 97 $K_2$ 133 Col 171 I<br>*6.8 22.8 9.1* |

[a] These transitions cannot be investigated by DSC due to rapid crystallization. They were obtained from polarized light microscopy alone.

*Molecules with two methyl groups*: All compounds with two methyl groups, one positioned on the biphenyl segment and the other grafted on to different positions of the benzyl group, are also included in Table 1. With the exception of **2/2** and **1/3**, all compounds are mesogenic. Interestingly, the mesophase type does not significantly change upon introduction of the additional methyl group; in other words, all mesogenic compounds **1/*z*** and **3/*z*** show smectic A phases, the optically isotropic mesophase Iso is observed for all mesogenic compounds **2/*z***, and all compounds **4/*z*** with the methyl group beside the benzyloxy unit have columnar mesophases with exactly the same highly characteristic texture as **4/0** (see Figure 2).

However, the methyl groups at the terminal benzyloxy group substantially influence the mesophase stability. Methyl groups in *ortho* and *meta* positions represent a second lateral disturbance and reduce the stability of smectic phases. In contrast to the smectic phases, the stability of non-smectic phases is not significantly changed. Thus, the clearing temperature of the columnar mesophase of **4/0** is not influenced by the additional *m*-methyl group in compound **4/3**. Also the optically isotropic phases of **2/0** and **2/3** have the same stability.

Elongation of the molecules by a methyl group in the *para* position has a stabilizing effect on all mesophases, especially smectic phases. Hence, the mesophases of **1/4, 2/4**, and of all compounds **4/*z*** are enantiotropic; this enabled us to study them by X-ray diffraction.

*X-ray investigations—Smectic phases*: Between crossed polarizers, the mesophases of **1/4** and **3/4** are characterized by focal conic fan-textures, which easily align homeotropically to give large pseudoisotropic areas. These textures are typical for $S_A$ phases: mesophases consisting of layers of more or less parallel-aligned molecules organized, on average, perpendicular to the layer planes. Nevertheless, the two smectic A phases of compounds **1/4** and **3/4** are quite different as indicated by X-ray scattering. The smectic phase of **1/4** is characterized by four equidistant sharp reflexes in the small-angle region and the diffuse scattering in the wide-angle region. The same diffuse scattering is found in the X-ray pattern of the $S_A$ phase of **3/4**; however, only one sharp reflex is found in the small-angle region indicating a reduced interlayer correlation. Also, the layer thickness is quite different. In the $S_A$ phase of **1/4** a $d$ value of 4.2 nm was obtained at 153 °C; this corresponds to 1.83 molecular lengths ($L = 2.3$ nm from CPK models). The layer thickness in this $S_A$ phase is in good agreement with the length of a dimer in which a slight overlap of the diol units takes place, as required by the hydrogen bonding between neighboring molecules (see Figure 3a). Therefore we designate this phase as $S_{A2}$ phase.

The layer thickness of **3/4** was found to be significantly smaller than that of **1/4**. It amounts $d = 3.52$ nm at 102 °C; this is only 1.5 molecular lengths ($L = 2.3$ nm). Hence, a significant intercalation should take place in the case of **3/4**, which has a methyl group in the center of the biphenyl unit. The most efficient packing of these molecules seems possible if a complete intercalation of the 4-methylbenzyl groups and also a partial overlapping of the diol groups is assumed ($S_{Ad}$ phase, see Figure 3b). For this arrangement, a layer thickness of 3.5 nm can be estimated, which agrees very well with the experimentally determined layer thickness.

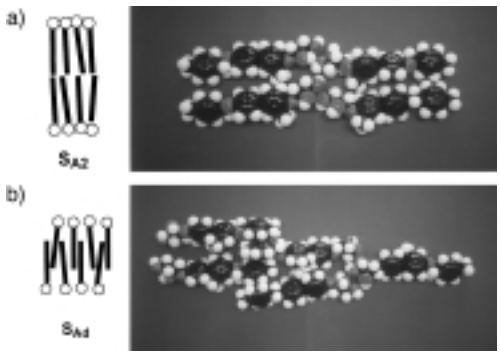



Figure 3. CPK models showing the arrangements of the molecules a) of compound **1/4** in the non-intercalated $S_{A2}$ phase and b) of compound **3/4** in the intercalated $S_{Ad}$ phase.

No X-ray data were available for the monotropic $S_A$ phase of **2/4**. However, miscibility studies indicate a complete and uninterrupted miscibility with the $S_{Ad}$ phase of compound **3/4**, whereas in the contact region with the $S_{A2}$ phase of **1/4** a nematic phase is induced and a phase boundary separates the $S_A$ phases of both compounds. This shows that the $S_A$ phase of **2/4** should be different from that of **1/4**. The $S_A$ phase of **2/4** should, therefore, be a strongly intercalated $S_{Ad}$ phase, similar to that of **3/4**.

Hence, the position of the methyl group at the biphenyl unit significantly influences the degree of intercalation. It seems that the peripheral methyl group of compound **1/4** allows a dense packing of the aromatic cores, whereas the central methyl groups of compounds **2/4** and **3/4** significantly hinder close packing, and space becomes available for intercalation.

*Columnar phases*: The X-ray investigations of the columnar phases of compounds **4/*z*** also produce diffuse scattering in the wide-angle region, indicating a short-range order of the molecules typical for liquid crystalline phases. In the small-angle region there are three sharp, non-equidistant reflections pointing to a two-dimensional lattice characteristic of columnar mesophases. Because the textures of all compounds **4/*z*** are highly characteristic and identical, and their mesophases have an uninterrupted miscibility with each other, we can assume that their columnar phases have the same structure. Indeed, the relative positions of the reflections are almost identical in all columnar mesophases. They can be related either to an oblique[26] or to a rectangular cell as shown in Table 2. Though both structures cannot be unambiguously distinguished, a rectangular cell seems to be more likely for two reasons. Firstly, in the rectangular cells of all compounds the parameter $b$ is in good agreement with the corresponding molecular length $L$ (**4/0**: $b/L = 3.86/2.2 = 1.75$; **4/4**: $b/L = 4.14/2.3 = 1.80$) and this parameter increases as expected upon elongation of the molecule. This contrasts with the case of an oblique lattice in which all parameters are strongly reduced in the order **4/0** > **4/3** > **4/4** (i.e., upon elongation of the molecule), which is hard to explain with a uniform model. Secondly, in other compounds, for which it was possible to



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Table 2. Observed Bragg reflections ($\theta$ [°]) and calculated lattice parameters of the columnar mesophases of the compounds **4/*z*** assuming a rectangular or an oblique cell.

| | Reflections | Rectangular cell | | Oblique cell | |
|---|---|---|---|---|---|
| | $\theta$ | *hk* | lattice parameter | *hk* | lattice parameter |
| **4/0** | 1.24 | 11 | $a = 9.02$ nm | 10 | $a = 9.91$ nm |
| | 2.28 | 02 | $b = 3.86$ nm | 01 | $b = 5.41$ nm |
| | 3.47 | 13 | | 11 | $\gamma = 159°$ |
| **4/3** | 1.20 | 11 | $a = 9.06$ nm | 10 | $a = 9.02$ nm |
| | 2.19 | 02 | $b = 4.04$ nm | 01 | $b = 4.94$ nm |
| | 3.32 | 13 | | 11 | $\gamma = 156°$ |
| **4/4** | 1.18 | 11 | $a = 8.72$ nm | 10 | $a = 6.42$ nm |
| | 2.15 | 02 | $b = 4.14$ nm | 01 | $b = 3.53$ nm |
| | 3.19 | 13 | | 11 | $\gamma = 144°$ |

prove a rectangular lattice by investigation of oriented samples, the 11, 02, and 13 reflections have been found to be the most intense reflections[27] and, therefore, this labeling seems reasonable.

A possible model of such a rectangular columnar phase is shown in Figure 4a. The values of the parameter *b* lie in between the *d* values of the smectic phases of **1/4** and **3/4**.

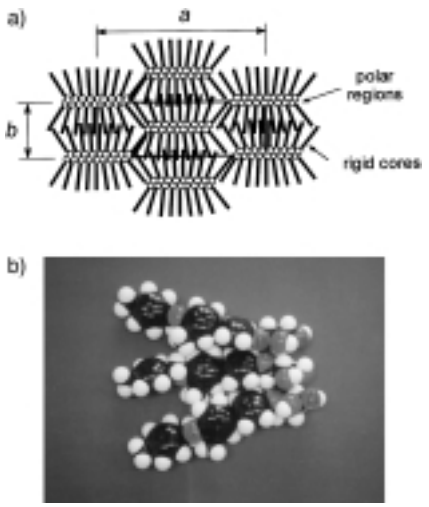



Figure 4. a) Cross-section of the proposed ribbon model of the thermotropic columnar phases of compounds **4/*z*** assuming a rectangular two-dimensional lattice. The ribbons are extended perpendicular to the projection plane. b) CPK models of **4/4** showing the splayed packing arrangement of the molecules in the columnar mesophase.

Thus, a ribbon structure seems likely for this columnar phase. In this case the parameter *b* can be attributed to the thickness of the ribbons, whereas the parameter *a* indicates a periodicity perpendicular to it. Because the value of *b* in the columnar phase of compound **4/4** is only slightly smaller than the *d* value of the $S_{A2}$ phase of **1/4**, the ribbons should represent fragments of a double layer structure or of a bilayer structure with only a slight degree of intercalation. From the parameter *a*, it can be calculated that about 8–10 molecules should be arranged side by side in the lateral diameter of the ribbons.

The occurrence of this columnar phase can be explained as follows: in compounds **4/*z***, the methyl groups are located in peripheral positions neighboring the benzyl groups. This causes these molecules to have a tapered shape. Dense packing of the aromatic units and the diol groups could lead to a splayed arrangement as shown in Figure 4b. The free space between the benzyl groups can be filled by bending the benzyl ether groups or by their intercalation. Hence, the tapered shape provides an increased diameter of the molecules at their lipophilic ends. This arrangement should lead to a significant steric frustration of the smectic bilayer structure which could result in a collapse and the formation of ribbonlike segments. These ribbons arrange in a two-dimensional lattice giving rise to the thermotropic columnar phases (Col).

### Mesophases of the benzyl ethers *x*/*z* in the presence of protic solvents

*General remarks*: Because all compounds are amphiphilic in nature, their mesomorphic properties should be influenced by protic solvents that specifically interact with the diol groups by hydrogen bonding. Water and glycerol were chosen for these investigations. Due to their extended lipophilic parts, all compounds do not dissolve in excess water or glycerol, but take up only a limited amount of these solvents. Compound **3/3**, as a representative example, takes up a maximum amount of approximately 1 mol water/mol mesogen in a closed, water-saturated atmosphere. Therefore, one can speak of a guest–host relationship or thermotropic mesomorphism of solvent complexes instead of a lyotropic polymorphism in the traditional sense.

The mesomorphic properties of the solvent-saturated samples are summarized in Tables 3, 4 and 5.[28] Furthermore the contact regions of these amphiphiles with excess solvent were investigated by polarized light microscopy. The results are summarized in the phase diagrams shown in Figure 5, Figure 7, Figure 9, Figure 13 and Figure 16. Due to experimental difficulties, we were not able to obtain well-defined and homogenous binary mixtures. Therefore, the phase diagrams are not quantitative, which means that the particular concentration of the solvents is unknown. As the investigations were done in the presence of excess solvents, the amount of solvent taken up may also have changed with temperature. It was also not possible to carry out X-ray diffraction investigations with the mesophases of the solvent-containing amphiphiles, either owing to their monotropic nature and tendency to crystallize, or the general difficulty in obtaining homogeneous mixtures and transferring them into glass capillaries without crystallization, separation of the components, or solvent loss. So the phase assignment to date is based on polarized light optical microscopic investigations. Nevertheless, these investigations have shown that the influence of these protic solvents on the mesophases is quite varied and strongly dependent on the structure of the amphiphiles.

*Compounds **1/z***: All solvent-saturated samples of molecules **1/*z***, with methyl groups neighboring the hydrophilic group, show exclusively $S_A$ phases. The development of these $S_A$ phases from the $S_A$ phases of the pure compounds is, however, not continuous. As an example, the binary phase diagram of compound **1/0** with glycerol is shown in Figure 5a. The

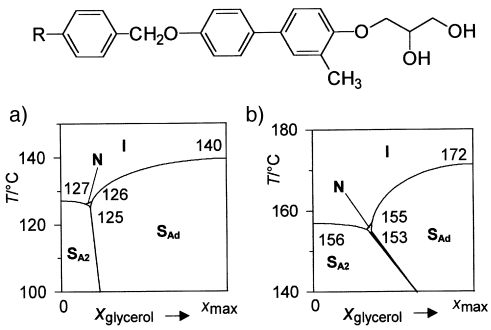



Figure 5. Qualitative phase diagrams of the systems a) **1/0**-glycerol (R = H) and b) **1/4**-glycerol (R = $CH_3$) as obtained by polarized light microscopy of the contact regions with the solvent; crystalline phases are not shown; $x_{max}$ corresponds to the solvent-saturated state.

thermotropic $S_A$ phase evidently takes up only a very limited amount of solvent, and its clearing temperature is only marginally influenced. In a small temperature and concentration range, a nematic phase can be seen. Below this nematic phase a sharp borderline separates two different $S_A$ phases, the thermotropic $S_A$ phase and the solvent-rich $S_A$ phase. The latter is further stabilized on increase of the glycerol content. The same type of phase diagram can be observed for **1/4**, but in this case a small region of a nematic phase separates the two $S_A$ phases (Figure 5b). Thus, the $S_A$ phases of the pure compounds **1/0** and **1/4** should be different from those of their solvent-saturated samples.

This could be explained by taking into account the results of the X-ray investigations of the thermotropic phase of **1/4**. For this compound an $S_{A2}$ phase without intercalation of the aromatic parts was found. The incorporation of the solvent molecules into the head-group regions should increase their volume, and space becomes available between the aromatic cores. In this way intercalation should become possible. Hence, the induced $S_A$ phases should represent strongly intercalated $S_{Ad}$ phases, and the two different subtypes of $S_A$ phases are incompatible with each other due to their different layer thickness (see Figure 6). The nematic phases that occur

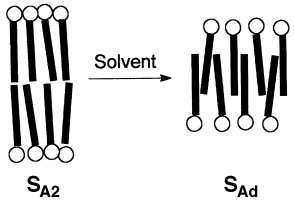


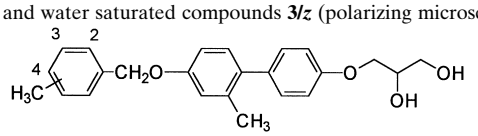

Figure 6. Transition from the $S_{A2}$ phases to the $S_{Ad}$ phases of compounds **1/*z***.

in the contact regions between the two $S_A$ phases could be cybotactic nematic phases and should be the result of the competition between the two different length scales.

Only an induced smectic A phase could be detected on addition of glycerol to the non-mesogenic compound **1/3**. It becomes visible at a certain solvent concentration and is further stabilized on increase of the solvent content. The glycerol-saturated sample has a clearing point of 118 °C. It can be assumed that this induced phase is the same $S_{Ad}$ phase as found in the solvent-rich systems **1/0**-glycerol and **1/4**-glycerol. Therefore, it seems that the substitution pattern of the benzyl group has only a marginal influence on the principal phase behavior of the compounds **1/*z***.

*Compounds **3/z***: For all investigated **3/*z***-solvent systems a further stabilization of the $S_A$ phases on increasing the solvent content was observed[29] and only one $S_A$ phase was found over the whole concentration range (see Table 3 and Figure 7). Hence, in these systems, the structure of the $S_A$ phases

Table 3. Mesophases and transition temperatures $T$ [°C] of the glycerol saturated and water saturated compounds **3/*z*** (polarizing microscopy).




| | Position | Water | Glycerol |
|---|---|---|---|
| **3/0** | – | $S_A$ 95 Col > 100 I | $S_A$ 70 I |
| **3/3** | 3 | $S_A$ 84 Col > 100 I | $S_A$ 60 Col 69 I |
| **3/4** | 4 | $S_A$ > 100 I | K 75 $S_A$ 127[a] I |

[a] The maximum of the mesophase stability in the contact region is 137 °C.

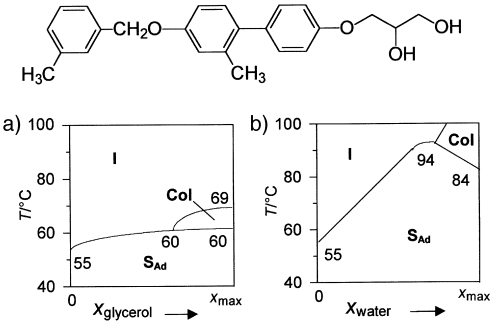



Figure 7. Phase diagrams of the systems a) **3/3**-glycerol and b) **3/3**-water.

should not change significantly with the solvent content. As proven by X-ray scattering, the mesophase of the pure compound **3/4** is a strongly intercalated $S_{Ad}$ phase. The similarity of the behavior of all compounds **3/*z*** suggests that the $S_A$ phases of the other compounds **3/*z*** should be also $S_{Ad}$ phases. It seems that hydration of the head groups does not significantly change the degree of intercalation. Therefore, only one $S_A$ subtype ($S_{Ad}$) is observed over the whole concentration range, in contrast to compounds **1/*z*** for which intercalation is possible only after the addition of solvent. In the systems **3/0**-water, **3/3**-glycerol, and **3/3**-water additional mesophases are induced in the solvent-rich samples above the $S_{Ad}$ phases (see Figure 7a and b). These mesophases have well-developed spherulitic textures typical for columnar mesophases, similar to that of the system **2/0**-glycerol, which is shown in Figure 11.

Remarkably, all columnar phases occur as high-temperature phases above $S_{Ad}$ phases. If one assumes that enhancing the temperature can either reduce the number of coordinated solvent molecules and/or increase the effective size of the aromatic regions by enhancing the mobility of the lipophilic units, then the effective diameter of the lipophilic regions can become larger than that of the polar regions with rising



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temperature. This could disturb the packing of the molecules in the planar $S_{Ad}$ structure thereby leading to the collapse of the layers into ribbonlike fragments (see Figure 8). Hence, these columnar phases should represent ribbon phases in which the intercalated lipophilic regions have a larger cross-section area than the polar regions. In this respect they are

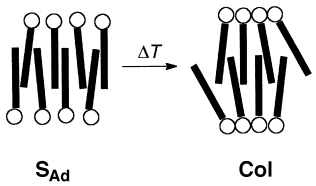



Figure 8. Proposed model for the transition from the $S_{Ad}$ phases to the columnar mesophases by changing the temperature.

similar to the thermotropic columnar phases of compounds **4/*z***, but they should differ in the degree of intercalation.

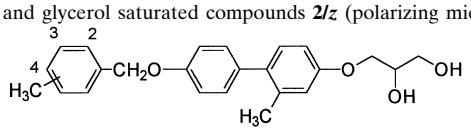
Remarkably, no columnar phase can be found for compound **3/4** with either glycerol or water. This reveals a certain influence of the substitution pattern of the benzyl group, which is even more pronounced for the compounds **2/*z***.

*Compounds **2/z***: The behavior of these compounds is more complicated. In all cases the isotropic mesophases (Iso) were destabilized on increasing solvent content and they cannot be found in the solvent-saturated systems.

For compound **2/4** with a 4-methylbenzyloxy unit, only the continuous stabilization of the $S_A$ phase on increasing glycerol content was found, indicating that the structure of the $S_A$ phase ($S_{Ad}$) should not change significantly with solvent content.

A different behavior was found for all other compounds **2/*z*** (see Table 4 and Figure 9). As an example, the phase diagram of the system **2/0**-water is shown in Figure 9b. With increasing water content, the isotropic mesophase and the nematic phase of the pure compound are replaced by the $S_A$ phase, which is further stabilized. At a certain water concentrations a sharp phase boundary separates the $S_A$ phase of the pure compound from a second, water-rich $S_A$ phase; this indicates that the occurrence of the two different $S_A$ phases depends on the water concentration. Therefore, we assume that, in analogy to the systems **1/0**-glycerol and **1/4**-glycerol, a transition from a non-intercalated $S_{A2}$ phase to a strongly intercalated $S_{Ad}$ phase takes place in this system. This would mean that the thermotropic $S_A$ phase of **2/0** should be an $S_{A2}$ phase, in contrast to that of **2/4** which was proven to be an $S_{Ad}$ phase.

Table 4. Mesophases and transition temperatures $T$ [°C] of the water saturated and glycerol saturated compounds **2/*z*** (polarizing microscopy).




| | Position | Water | Glycerol |
|---|---|---|---|
| **2/0** | – | $S_A$ 83 Col > 100 I | Col 82 I |
| **2/2** | 2 | $S_A$ 69 Col > 100 I | Col 73 I |
| **2/3** | 3 | $S_A$ 68 Col > 100 I | Col 67 I |
| **2/4** | 4 | – | $S_A$ 140 I |

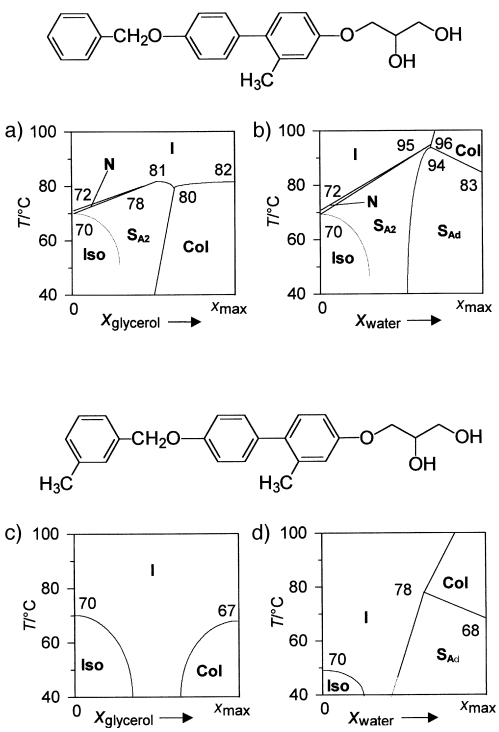



Figure 9. Phase diagrams of the systems a) **2/0**-glycerol, b) **2/0**-water, c) **2/3**-glycerol, and d) **2/3**-water (Iso = optically isotropic mesophase).

Hence, it seems that in the series of compounds **2/*z***, the substitution pattern of the benzyl group determines which $S_A$ subtype is found, whereby 4-methylbenzyl groups seem to induce $S_{Ad}$ phases. Additionally, above the $S_{Ad}$ phase a columnar phase with a typical spherulitic texture occurs.

The phase diagrams of the systems **2/2**-water and **2/3**-water (Figure 9d) are rather similar to that one of the **2/0**-water system, with the difference that the $S_{A2}$ phases are missing and only the induced phases ($S_{Ad}$ and Col) can be observed. However, in all three cases, the columnar phases occur as high-temperature phases in the solvent-rich parts of the phase diagrams above the $S_{Ad}$ phases. Therefore we assume that they should have essentially the same structures as those found in the lyotropic systems of compounds **3/*z***.

The observed phase sequence can be explained as shown in Figure 10. If it is assumed that the isotropic mesophase Iso represents a disturbed double layer structure in which the

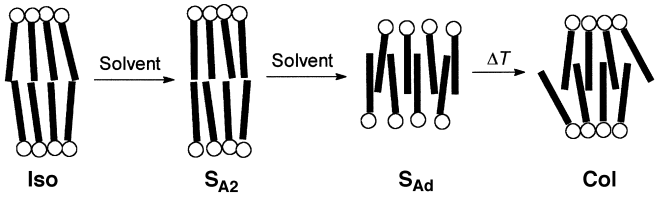



Figure 10. Proposed model for the transition from the isotropic mesophase Iso via different $S_A$ phases to the lyotropic columnar mesophase of compound **2/0**.

aromatic parts have a slightly larger space requirement than the polar regions, then the addition of water enhances the space-filling in the polar regions and allows the formation of

an $S_{A2}$ phase with an equal space-filling of both regions. On further increasing water content intercalation should become possible giving rise to the $S_{Ad}$ phase. The transition to the columnar phase can be explained in the same way as for the **3/*z***-solvent systems.

The phase diagrams of compounds **2/*z*** with glycerol are slightly different as no induced $S_{Ad}$ phases can be found. In the system **2/0**-glycerol, for example, (Figure 9a) the $S_A$ phase is at first stabilized, then slightly destabilized, and finally replaced by a columnar phase whose texture is shown in Figure 11. For

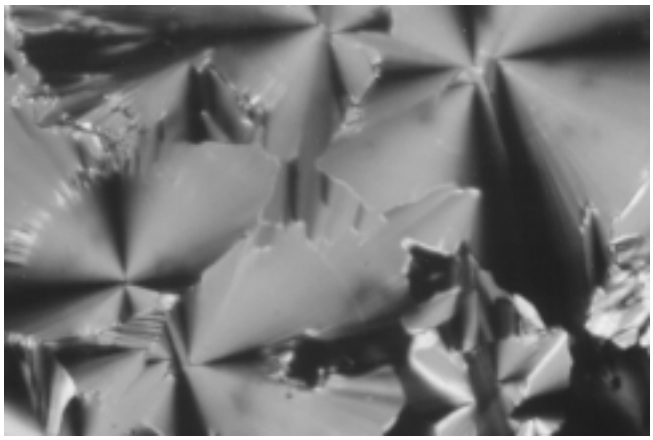


Figure 11. Polarized light optical photomicrograph of the texture of the induced columnar phase in the system **2/0** glycerol at 80 °C.

the systems **2/2**-glycerol and **2/3**-glycerol, only the induced columnar phases and no smectic phases were found (see, for example, Figure 9c). Probably, the induced smectic phases cannot be observed because the transition temperatures of the glycerol-containing systems are generally lower than those of the related systems with water.

*Compounds **4/z***: It was also of interest to investigate, how protic solvents influence the columnar phases of compounds **4/*z***. Figure 12 shows a polarized light optical photomicrograph of the contact region between **4/3** and glycerol at 126 °C. Additionally, the development of the mesomorphic properties of **4/3** in the contact region with glycerol and its dependence on the temperature is shown in the phase diagram in

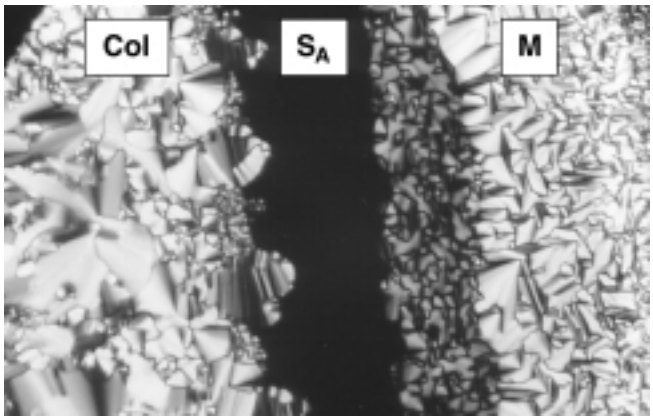



Figure 12. Polarized light optical photomicrograph of the contact region of **4/3** (left-hand side) with glycerol (right-hand side) at 128 °C.

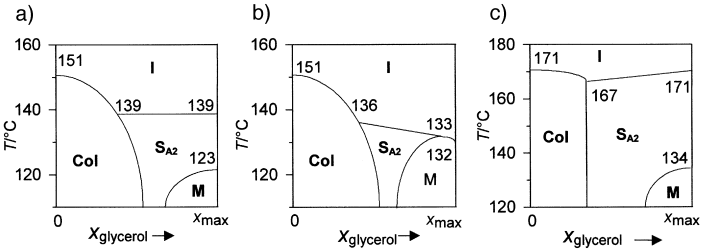



Figure 13. Phase diagrams of the systems a) **4/0**-glycerol, b) **4/3**-glycerol, and c) **4/4**-glycerol (M = mesophases with spherulitic textures, probably columnar mesophases).

Figure 13b. With increasing solvent content, the columnar phase of the pure compound (Col) is destabilized and a smectic A phase is induced. On further increasing the glycerol content an additional mesophase (M) appears below this induced $S_A$ phase and finally replaces the $S_A$ phase. This solvent-induced mesophase has a spherulitic texture (see Figure 12, right-hand side), which cannot be homeotropically aligned. Hence, it is most probably a columnar phase. However, the texture of this induced mesophase is not so well developed as those of compounds **2/*z*** and **3/*z***. Therefore, and because we presently cannot completely exclude other "intermediate" phases, such as rhomboedric and tetragonal mesh-phases,[30] for lack of X-ray results, we designate this phase as mesophase M.

The same principal types of phase diagrams were also obtained for the related compounds **4/0** (see Figure 13a) and **4/4** (see Figure 13c) with glycerol. Here, the $S_A$ phases were not completely replaced by the induced M phases. Remarkably, in contrast to the induced columnar phases of compounds **2/0, 3/0, 2/3**, and **3/3** which are high-temperature mesophases, these induced mesophases occur below the $S_A$ phases.

The observed phase sequence can be explained on the basis of the model of the columnar thermomesophases of the compounds **4/*z***. As explained above, these columnar phases should be ribbon phases that result from the collapse of a smectic bilayer structure due to the larger space required by the lipophilic regions in comparison with the polar regions (see Figure 4). This is in accordance with the fact that $S_A$ phases can be induced upon the addition of glycerol. The increased diameter of the hydrated polar ends should inhibit a splayed arrangement of the molecules giving rise to a parallel alignment of the molecules as shown in Figure 14. Hence, the induced $S_A$ phases should be non-intercalated $S_{A2}$ phases. A further increase of the solvent content can additionally enlarge the polar regions. It seems, however, that in these systems a deep intercalation of the aromatic cores is not possible, probably for steric reasons. Therefore no transition to an intercalated $S_{Ad}$ phase can be found. Instead, frustration occurs and gives rise to the formation of the induced mesophases in the solvent-rich regions. Consequently, these induced phases should represent disturbed double-layer structures (segments of the $S_{A2}$ phases) with larger cross-sectional areas of the polar regions (see Figure 15). In other words, the size ratio of head groups and aromatic units should be the reverse of those of the ribbons in the columnar phases



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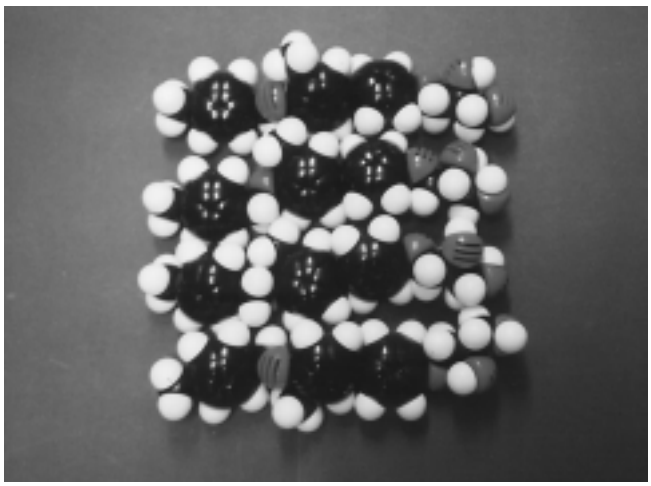


Figure 14. CPK models showing a non-intercalated parallel arrangement of the molecules of compound **4/4**.

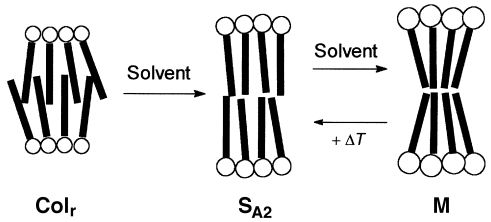



Figure 15. Proposed model for the transition from the thermotropic Col phases, via the $S_{A2}$ phases to the lyotropic M phases of compounds **4/*z***.

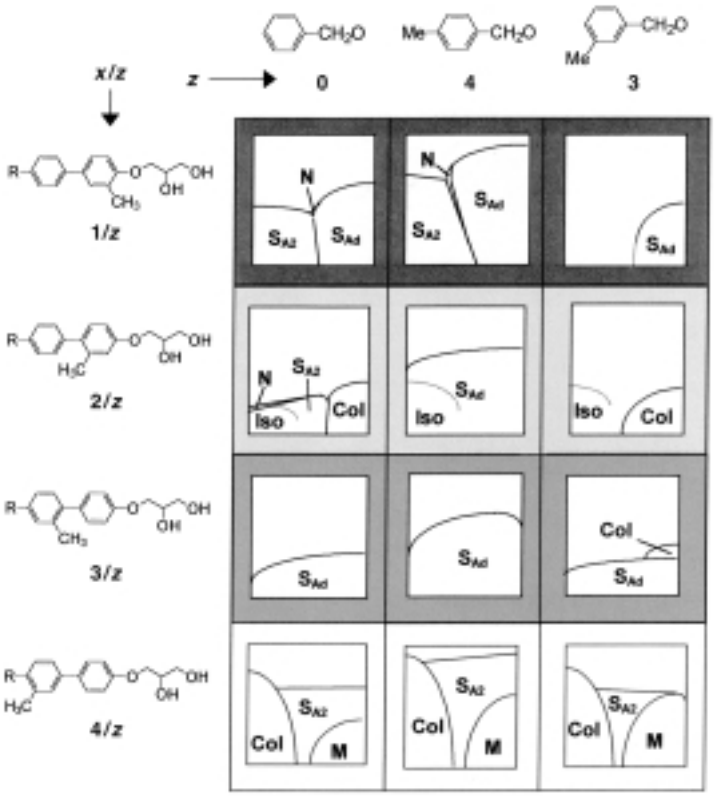



Figure 16. Comparison of the phase behavior of the investigated compounds in the presence of glycerol. In each diagram the solvent content increases from the left to the right.

of the pure compounds **4/*z*** and also the reverse of the induced high-temperature-columnar phases in the lyotropic systems of compounds **2/0, 2/3, 3/0**, and **3/3**. This assumption is supported by the fact that the induced M phases of compounds **4/*z*** have an inverted temperature dependence (i.e., they occur as low-temperature mesophases below smectic phases). As the aromatic regions can expand with rising temperature (enhanced mobility), the diameter of the polar and lipophilic regions can become equivalent as the temperature increases, thereby explaining the observed phase sequence (see Figure 15).

*Comparison of the systems*: These investigations have shown that the change of the mesophase, brought about by shifting the methyl group along the biphenyl rigid core, is largely caused by the varying degree of intercalation that modifies the effective diameter of the lipophilic parts with respect to the polar molecular parts. For the glycerol-containing systems the phase behavior is schematically summarized in Figure 16. It seems that the mesophase behavior is mainly determined by the substituent at the biphenyl unit.

In the series **1/*z*** and **4/*z*** in which the methyl groups are located in peripheral positions, the substituents at the benzyl group were found to have no significantly influence on the principal phase behavior. However, in the series of compounds **2/*z*** and **3/*z*** with methyl groups in central positions at the biphenyl core, the 4-methylbenzyl derivatives behave quite differently from the other compounds. Generally, the position of the methyl group at the biphenyl core mainly determines the type of thermotropic $S_A$ phase: $S_{A2}$ is dominantfor compounds **1/*z*** and $S_{Ad}$ is dominant for **3/*z***. It seems that compounds **2/*z*** are located at the borderline, so that here the substitution pattern of the benzyl group decides which $S_A$ subtype is preferred.

It is remarkable that no cubic phase can be detected as an intermediate phase between the smectic and columnar mesophases as typical for thermotropic[25a] and lyotropic systems[31] of classical amphiphiles. However, the optical isotropic mesophases (Iso), which can be found exclusively in the series of the compounds **2/*z***, could represent cubic phases. Unfortunately, all isotropic mesophases were metastable, so that we were not able to study their microstructure by X-ray scattering.

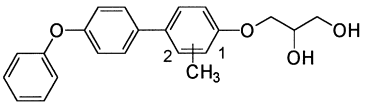
Comparison of the phase behavior of compounds **2/0** with compounds **4/*z*** (see Figure 16) suggests some degree of similarity, as in both systems the thermotropic non-lamellar phases (Iso and Col, respectively) are completely replaced by $S_{A2}$ phases, and novel mesophases are induced on further increasing solvent concentration. There is also a certain structural similarity between the compounds **2/*z*** and **4/*z***, as both types of molecules have the methyl groups directed towards their lipophilic ends. This leads to a certain degree of tapering in shape, with enlarged lipophilic ends. It seems that the less-defined taper shape of compounds **2/*z***, with their methyl groups in a more central position, yields only isotropic (probably cubic) thermomesophases, instead of the columnar phases that were found for compounds **4/*z***, which have a more pronounced taper shape.

**Further variations of the molecular structure**: In order to prove the generality of the concept of rigid aromatic

amphiphiles, selected molecules with slightly changed molecular structures were also investigated.[32]

*Variation of the terminal aromatic segment*: As expected, the phenyl ethers **1/Ph** and **2/Ph**, which have a more bent structure than the corresponding benzyl ethers **1/0** and **2/0**, do not form thermotropic mesophases (Table 5). They do, however, show mesomorphism in the solvent-containing state.

Table 5. Transition temperatures $T$ [°C] of the pure, water-saturated, and glycerol-saturated compounds **1/Ph** and **2/Ph** as obtained by polarizing microscopy.



| | Position | Pure comp. | Water | Glycerol |
|---|---|---|---|---|
| **1/Ph** | 1 | K 110 I | $S_A$ 97 I | $S_A$ 67 I |
| **2/Ph** | 2 | K 80 I | $S_A$ 63 Col 92 I | $S_A$ 28 I |

Compound **1/Ph**, with the methyl group in a peripheral position at the biphenyl core, exclusively forms an $S_A$ phase, whereas for the isomeric compound **2/Ph**, with the methyl group in a central position, an $S_A$ phase and a high-temperature columnar phase are induced in the presence of water (see Figure 17). Thus, their properties are related to those of the corresponding benzyl ethers **1/*z*** and **2/*z***, respectively (see Figure 16).

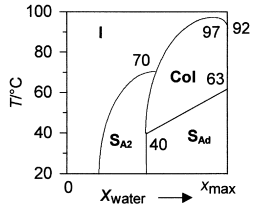
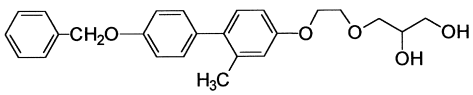



Figure 17. Phase diagram of the system **2/Ph**-water.

*Variation of the head group*: To investigate the influence of the head-group size we have replaced the 2,3-dihydroxypropyloxy head group of **2/0** by the larger 5,6-dihydroxy-3-oxahexyloxy moiety. The thermotropic transition temperatures of **2/EO** are



**2/EO**

Pure comp.: K 60 ($S_A$ 23) I
Water: $S_A$ 73 Col >100 I
Glycerol: Col 60 I

considerably reduced and, in contrast to the diols **2/*z***, no isotropic mesophase can be detected. This observation is in agreement with the assumption that these phases should represent disturbed layer structures due to a deficit in the space-filling of the polar regions. The introduction of the larger hydrophilic unit also has a destabilizing influence on the lyotropic mesophases, but the principal phase sequence is the same as found for the **2/0**-glycerol system (Figure 18).

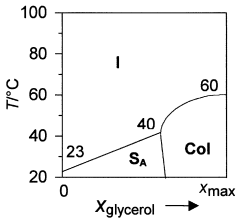
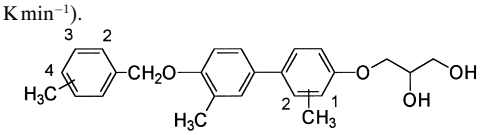



Figure 18. Phase diagram of the system **2/EO**-glycerol.

*Molecules with three methyl groups*: Compounds **4/*z*** are especially interesting with respect to the occurrence of thermotropic columnar phases. Therefore, it was of interest to see how the introduction of additional methyl groups can influence their phase behavior. The molecules ***x*.4/*z*** with three methyl groups (see Table 6) have only monotropic mesophases, with exception of **2.4/3** which is non-mesogenic. The mesophases are $S_A$ phases and for compound **1.4/4** an additional nematic phase was found. However, no columnar thermomesophase could be detected, as is typical for the parent compounds **4/*z***. This observation is in agreement with the proposed model of these columnar phases. Because the additional substituents near the diol group should increase the diameter of the polar ends, they reduce their taper shape and the thermotropic columnar phases are lost.

Table 6. Thermotropic transition temperatures $T$ [°C] of the compounds ***x*.4/*z*** as obtained by DSC (peak temperatures in the heating scans, heating rate: 10 K min$^{-1}$).



| | Phase transitions |
|---|---|
| **1.4/3** | K 113 ($S_A$ 73) I<br>*48.5* *3.3* |
| **2.4/3** | K 95 I<br>*24.4* |
| **1.4/4** | K 121 ($S_A$ 109 N 113) I<br>*38.3* *2.9* *0.8* |
| **2.4/4** | K 97 ($S_A$ 93) I<br>*24.6* *0.6*[a] |

[a] Despite of the low transition enthalpy, this mesophase is clearly identified as an $S_A$ phase by the typical optical texture.

The binary phase diagrams of the amphiphiles ***x*.4/*z*** with glycerol are compared in Figure 19. These phase diagrams appear to be quite different from each other, which shows that the influence of the substituents cannot simply be analyzed by an incremental approach. Nevertheless, they seem to be more or less related to those of compounds **4/*z***, characterized by the induction of novel mesophases on solvent addition. Induced mesophases (M) can be found for **1.4/3**, **2.4/3**, and **2.4/4**. According to their microscopic textures they most probably represent columnar phases, related to those found for the **4/*z***-glycerol systems. For compound **1.4/4** alone no such induced phase could be detected, probably because the methyl group neighboring the diol group and the 4-methyl group at the benzyl ether unit strongly favor $S_A$ phases.

Another interesting point is the occurrence of optically isotropic mesophases in the solvent saturated regions of the binary systems **1.1/4**-glycerol and **2.4/4**-glycerol. The isotropic phase occurring in the system **1.4/4**-glycerol (Is, see Figure 19b) is rather fluid and seems to be an isotropic liquid phase, whereas the isotropic phase of the glycerol-saturated compound **2.4/4** is highly viscous (plastic) and behaves like a cubic mesophase (Cub, see Figure 19d).[25] The position of this cubic phase in the phase sequence $S_A$–M (Col?)–Cub is quite unusual and requires further investigation.



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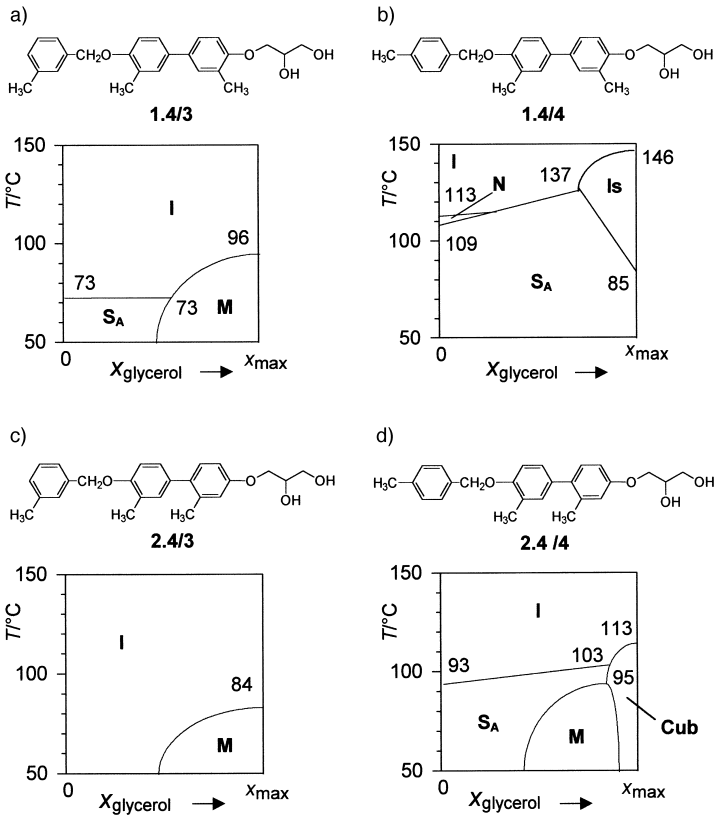


Figure 19. Phase diagrams of the systems a) **1.4/3**-glycerol, b) **1.4/4**-glycerol, c) **1.3/3**-glycerol, and d) **1.3/4**-glycerol [Is = fluid optically isotropic phase; Cub = highly viscous and optically isotropic, probably cubic mesophase, M = mesophases with spherulitic textures (most probably representing columnar phases, but other noncubic "intermediate" phases cannot be excluded)].

## Conclusion

Calamitic amphiphilic compounds with all-aromatic segments and methyl substituents in lateral positions are able to form different thermotropic liquid crystalline phases that can be modified by the addition of protic solvents. Thus, these compounds represent a novel class of amphotropic liquid crystalline materials,[33] combining structural features of classical amphiphiles and calamitic mesogens. Columnar phases, $S_A$ polymorphism, nematic phases, and optical isotropic phases can be observed for certain representatives of this class of compounds. Thus, the same diversity of different mesophases as, for example, in polycatenar compounds,[34] was found. In contrast to classical flexible amphiphilic molecules, in which the mesophase type is mainly determined by the size of the (hydrated) head groups relative to the lipophilic chains, here the rigid segments favor the formation of layer structures. Beside $S_{Ad}$ and $S_{A2}$ phases, various phases resulting from the frustration of these layers (Col, M, N, Iso) were found. The occurrence of the different mesophases is sensitive to the number and position of the methyl groups and the concentration of protic solvents. Depending on their positions, the lateral substituents can disturb the packing of the rigid cores, which can be partly compensated by intercalation. The degree of intercalation depends on the positions of the methyl groups and is additionally influenced by hydration. Hence, the self-organization of these nonconventional amphiphiles is determined by a delicate balance of microsegregation, space-filling, and interdigitation.

## Experimental Section

**General remarks**: 4-Benzyloxybromobenzene,[35, 36] 4-bromo-3-methylphenol,[15] 1-allyloxy-4-bromobenzene,[37] 1-(4-toluylsulfonyloxy)-3-oxa-5-hexene,[23] and 4-benzyloxyphenylboronic acid[21] (**6a**) were prepared according to literature procedures. Allyl bromide, benzyl bromide, 4-bromophenol, palladium on charcoal (5% Pd), 2,2-dimethoxypropane, trimethylborate, and *N*-bromosuccinimide (NBS) were used as obtained from Merck. 4-Iodo-2-methylphenol, 2-methylbenzyl bromide, 3-methylbenzyl bromide, 4-methylbenzyl bromide, 4-bromodiphenyl ether, *N*-methyl morpholine-*N*-oxide (50 or 60 wt% aq. solutions), and *n*-butyllithium (1.6 M solution in hexane) were used as obtained from Aldrich. Osmium tetroxide (Berlin Chemie) was used as a solution (0.1 g dissolved in 100 mL *tert*-butyl alcohol, stabilized with 2 mL *tert*-butylhydroperoxide). Confirmation of the structures and purity of intermediates and products was obtained by $^1$H NMR spectroscopy (VARIAN Unity 500, VARIAN Gemini 200 and VARIAN Gemini 2000 spectrometers) and mass spectrometry (EI: AMD 402, electron impact 70 eV; ESI: Finnigan Mat LCQ). Microanalyses were performed by using a Carlo Erba 1102 or a CHNS-932 elemental analyzer. The purity of all compounds was also checked by thin-layer chromatography (TLC, Merck, silica gel 60 $F_{254}$). Hexane/ethyl acetate mixtures and chloroform/methanol mixtures were used as eluents and the spots were detected by UV radiation. Glycerol used for the investigations of the lyotropic behavior was distilled in vacuo and stored over a molecular sieve. Transition temperatures were measured by using a Boetius hotstage and confirmed by differential scanning calorimetry (Perkin–Elmer DSC-7). Polarized optical photomicrographs were taken by means of a Nikon Optiphot polarizing microscope with Linkam LTS 350 hotstage and control unit. X-ray investigations were carried out with a Guinier-Goniometer (Huber). Lyotropic mesophases were studied by the penetration technique. A drop of pure amphiphile was surrounded by the solvent between two glass cover slides. The concentration gradient at the amphiphile/solvent boundary allows the phases to develop as bands. Their sequence was monitored as a function of temperature. Solvent-saturated samples were obtained by mixing the compounds with excess solvent between two cover slips. As glycerol takes up water very rapidly during sample preparation, special care was taken to avoid contamination with moisture. For the preparation of the contact samples the amphiphile was melted at the edge of a cover slip which was placed on top of a microscopy slide. The sample was allowed to spread between slide and cover slip by means of capillary forces. A drop of glycerol was placed at a certain distance to the cover slip on the slide and heated to approximately 260 °C for several seconds. Thus, excess water and some glycerol were allowed to evaporate. At the same temperature, the glycerol was forced to reach the edge of the cover slip beside the region of the amphiphile and to spread until the area around the amphiphile was completely covered with glycerol. Excess glycerol was carefully removed. Solvent-saturated samples with glycerol were obtained by heating a small sample and a drop of glycerol side by side on a microscopy slide to 260 °C for several seconds. Afterwards, the drops were rapidly covered with a glass slide and mixed by grinding the slides together.

**Synthesis of the compounds *x.y/z***

**4-Bromo-2-methylphenol:**[13, 17] HBr (48% aqueous solution, 100 mL) and DMSO (100 mL) were added dropwise to a stirred solution of *o*-cresol (20.3 g, 28.8 mmol) in AcOH (200 mL). The reaction was monitored by TLC. After the reaction was complete (ca. 1 h), saturated aqueous $NaHCO_3$ (200 mL) was added cautiously. After the addition of diethyl ether (200 mL) the phases were separated, and the aqueous phase was extracted with diethyl ether (100 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ ($4 \times 100$ mL) and water (100 mL). The solution was dried with $Na_2SO_4$ and the solvent was removed. The product was crystallized from hexane. Yield: 24.8 g (70%); m.p. 63 °C (62.5–63.5 °C [13]); $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.22$ (s, 1H; Ar–H), 7.15 (dd, $^3J(H,H) = 8.6$ Hz, $^4J(H,H) = 2.6$ Hz, 1H; Ar–H), 6.62 (d, $^3J(H,H) = 8.6$ Hz, 1H; Ar–H), 4.76 (br s, 1H; OH), 2.20 (s, 3H; $CH_3$).

**1-Benzyloxy-4-bromobenzenes**

**General procedure**: 4-Bromophenol (133 mmol) and the appropriate benzylbromide (146 mmol) were dissolved in acetone (200 mL). $K_2CO_3$ (55 g, 400 mmol) was added and the mixture was stirred under reflux (monitored by TLC, ca. 8 h). After the reaction was complete, the mixture was poured into ice-water (150 mL) and extracted with diethyl ether (3 × 50 mL). The combined extracts were washed with $Na_2CO_3$ solution (2 M, 50 mL), water (50 mL), and brine (50 mL). After drying with $Na_2SO_4$ and evaporation of the solvent, the product was purified by crystallization from methanol.

**1-Benzyloxy-4-bromo-2-methylbenzene**:[14] Synthesized from 4-bromo-2-methylphenol (24.8 g, 133 mmol) and benzylbromide (17.7 mL, 146 mmol). Yield: 26.5 g (73 %); m.p. 57 °C (62 °C [14]); $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.42 - 7.28$ (m, 6H; Ar–H), 6.86 (d, $^4J$(H,H) = 2.9 Hz, 1H; Ar–H), 6.66 (dd, $^3J$(H,H) = 8.8 Hz, $^4J$(H,H) = 2.9 Hz, 1H; Ar–H), 5.01 (s, 2H; Ar–$CH_2$), 2.34 (s, 3H; Ar–$CH_3$).

**1-Benzyloxy-4-bromo-3-methylbenzene**:[16] Synthesized from 4-bromo-3-methylphenol (25.0 g, 134 mmol) and benzylbromide (17.5 mL, 147 mmol). Yield: 28.5 g (77 %); m.p. 68 – 71 °C (70.5 – 71.5 °C [16]); $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.44 - 7.29$ (m, 6H; Ar–H), 6.89 (d, $^4J$(H,H) = 2.9 Hz, 1H; Ar–H), 6.70 (dd, $^3J$(H,H) = 8.6 Hz, $^4J$(H,H) = 2.9 Hz, 1H; Ar–H), 5.03 (s, 2H; Ar–$CH_2$), 2.37 (s, 3H; Ar–$CH_3$); elemental analysis calcd (%) for $C_{14}H_{13}OBr$ (277.2): C 60.67, H 4.73, Br 28.83; found C 60.61, H 4.82, Br 28.85.

**4-Bromo-2-methyl-1-(3-methylbenzyloxy)benzene**: Synthesized from 4-bromo-2-methylphenol (25.0 g, 134 mmol) and 3-methylbenzylbromide (25.4 g, 147 mmol). Yield: 31.6 g (81 %) of a pale yellow oil; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.3 - 7.1$ (m, 6H; Ar–H), 6.72 (d, $^3J$(H,H) = 8.8 Hz, 1H; Ar–H), 5.00 (s, 2H; Ar–$CH_2$), 2.36 (s, 3H; Ar–$CH_3$), 2.24 (s, 3H; Ar–$CH_3$).

**4-Bromo-2-methyl-1-(4-methylbenzyloxy)benzene**:[14] Synthesized from 4-bromo-2-methylphenol (25.0 g, 134 mmol) and 4-methylbenzylbromide (25.4 g, 147 mmol). Yield: 29.2 g (75 %); m.p. 82 – 83 °C (83 °C [14]).

**4-Benzyloxyphenylboronic acids 6**

**General procedure**: The appropriate 1-benzyloxy-4-bromobenzene (23.6 mmol) was dissolved in THF (50 mL). The solution was cooled to −78 °C and *n*BuLi (1.6 M solution in hexane, 21.4 mL, 34.5 mmol) was added dropwise. After stirring at −78 °C for an additional 2 h, trimethylborate (8 mL, 71 mmol) dissolved in THF (8 mL) was added dropwise at the same temperature. The mixture was allowed to warm to ambient temperature overnight. Then hydrochloric acid (10 %, 30 mL) was added at 0 °C. After stirring for an additional hour, diethyl ether (75 mL) was added, and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with water (2 × 50 mL) and dried with $Na_2SO_4$. After evaporation of the solvent, a solid was formed on the addition of *n*-pentane. It was purified by crystallization from hexane/ethyl acetate 5:1 (50 mL). The products were used without further purification.

**4-Benzyloxy-2-methylphenylboronic acid (6b)**:[21]: Synthesized from 1-benzyloxy-4-bromo-3-methylbenzene (6.5 g, 23.6 mmol). Yield: 3.2 g (56 %); m.p. 140 °C; $^1$H NMR (200 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta =$ 7.5 – 6.7 (m, 8H; Ar–H), 6.49 (s, 2H; OH), 5.06 (s, 2H; $CH_2$), 2.26 (s, 3H; $CH_3$).

**4-Benzyloxy-3-methylphenylboronic acid (6c)**:[21] Synthesized from 1-benzyloxy-4-bromo-2-methylbenzene (19.0 g, 72 mmol). Yield: 4.8 g (29 %); m.p. 130 °C.

**3-Methyl-4-(3-methylbenzyloxy)phenylboronic acid (6d)**: Synthesized from 4-bromo-2-methyl-1-(3-methylbenzyloxy)benzene (7.7 g, 35 mmol). Yield: 7.6 g (85 %); m.p. 155 °C; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.03$ (d, $^3J$(H,H) = 8.0 Hz, 1H; Ar–H), 7.98 (s, 1H; Ar–H), 7.3 – 7.2 (m, 3H; Ar–H), 7.13 (m, 1H; Ar–H), 6.98 (d, $^3J$(H,H) = 8.3 Hz, 1H; Ar–H), 5.13 (s, 2H; $CH_2$), 2.37 (s, 6H; $CH_3$).

**3-Methyl-4-(4-methylbenzyloxy)phenylboronic acid (6e)**: Synthesized from 4-bromo-2-methyl-1-(4-methylbenzyloxy)benzene (7.7 g, 35 mmol). Yield: 7.0 g (68 %); m.p. 160 °C; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.02$ (d, $^3J$(H,H) = 8.0 Hz, 1H; Ar–H), 7.98 (s, 1H; Ar–H), 7.5 – 7.1 (m, 8H; Ar–H), 6.98 (d, $^3J$(H,H) = 8.2 Hz, 1H; Ar–H), 5.12 (s, 2H; $CH_2$), 2.35 (s, 6H; $CH_3$).

**1-Allyloxy-4-halobenzenes**

**General procedure**: The appropriate 4-halophenol (85.5 mmol) and allyl bromide (7.9 mL; 94 mmol) were dissolved in acetonitrile (200 mL). $K_2CO_3$ (35 g, 250 mmol) was added, and the mixture was stirred under reflux (monitored by TLC, ca. 2 h). After the reaction was complete, the mixture was poured into ice – water (150 mL) and extracted with diethyl ether (3 × 50 mL). The combined extracts were washed with $Na_2CO_3$ solution (2 M, 50 mL), water (50 mL), and brine (50 mL). After drying with $Na_2SO_4$ and evaporation of the solvent, the compounds were used as the crude products.

**1-Allyloxy-4-iodo-2-methylbenzene**:[23] Synthesized from 4-iodo-2-methylphenol (20.0 g, 85.5 mmol). Yield: 22.0 g (94 %) of a pale yellow oil; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.44 - 7.38$ (m, 2H; Ar–H), 6.55 (d, $^3J$(H,H) = 8.4 Hz, 1H; Ar–H), 6.13 – 5.94 (m, 1H; C*H*=$CH_2$), 5.46 – 5.35 (dd, $^2J$(H,H) = 7.2 Hz, $^3J$(H,H) = 1.6 Hz, 1H; *trans*-CH=C$H_2$), 5.29 – 5.23 (dd, $^2J$(H,H) = 10.5 Hz, $^3J$(H,H) = 1.6 Hz, 1H; *cis*-CH=C$H_2$), 4.50 (m, 2H; $CH_2$), 2.19 (s, 1H; Ar–$CH_3$).

**1-Allyloxy-4-bromo-2-methylbenzene**: Synthesized from 4-bromo-2-methylphenol (11.2 g, 60 mmol). Yield: 13.2 g (97 %) of a of a pale yellow oil; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.3 - 7.2$ (m, 2H; Ar–H), 6.68 (d, $^3J$(H,H) = 8.3 Hz, 1H; Ar–H), 6.2 – 5.95 (m, 1H; C*H*=$CH_2$), 5.48 – 5.25 (m, 2H; CH=C$H_2$) 4.52 (m, 2H; $CH_2$), 2.24 (s, 3H; Ar–$CH_3$).

**1-Allyloxy-4-bromo-3-methylbenzene**: Synthesized from 4-bromo-3-methylphenol (25.0 g, 135 mmol). Yield: 27 g (89 %) pale yellow oil; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.42$ (d, $^3J$(H,H) = 8.7 Hz, 1H; Ar–H), 6.95 (d, $^4J$(H,H) = 3.1 Hz, 1H; Ar–H), 6.63 (dd, $^3J$(H,H) = 8.7 Hz, $^4J$(H,H) = 3.1 Hz, 1H; Ar–H), 6.15 – 5.95 (m, 1H; C*H*=$CH_2$), 5.48 – 5.25 (m, 2H; CH=C$H_2$) 4.50 (m, 2H; $CH_2$), 2.24 (s, 3H; Ar–$CH_3$).

**3-Aryloxypropane-1,2-diols**

**General procedure**: *N*-methylmorpholine-*N*-oxide (20 mL of a 60 wt % aqueous solution, 115 mmol) and $OsO_4$ (15 mL of a 4 mM solution in *tert*-butyl alcohol) were added to a solution of the appropriate 1-allyloxy-4-halobenzene (107 mmol) in dry acetone (120 mL). The mixture was stirred at 20 °C. After the reaction was complete (TLC), a saturated aqueous $Na_2SO_3$ solution (5 mL) was added, and the mixture was stirred for additional 30 minutes. Then the mixture was withdrawn using suction over silica gel (ca. 50 g). The silica gel was rinsed with acetone (50 mL). The solvent was removed and the residue was taken up in ethyl acetate (100 mL). The solution was washed with dilute $H_2SO_4$ (10 %, 30 mL), saturated $NaHCO_3$ solution (30 mL), water (30 mL), and brine (30 mL), and dried with $Na_2SO_4$. The solvent was removed. Crystallization from *n*-hexane or hexane/ethyl acetate yielded the pure products.

**3-(4-Bromophenyloxy)propane-1,2-diol**: Synthesized from allyloxy-4-bromobenzene (12.0 g, 56 mmol). Purified by crystallization from hexane/ethyl acetate 10:3 (65 mL). Yield: 10.8 g (81 %); m.p. 82 °C; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.36$ (d, $^3J$(H,H) = 9.0 Hz, 2H; Ar–H), 6.78 (d, $^3J$(H,H) = 9.0 Hz, 2H; Ar–H), 4.07 (m, 1H; sec. CH), 4.0 – 3.7 (m, 4H; $OCH_2$).

**3-(4-Iodo-2-methylphenyloxy)propane-1,2-diol**: Synthesized from 1-allyloxy-4-iodo-2-methylbenzene (10.2 g, 37 mmol). Purified by crystallization from hexane/ethyl acetate 2:1 (60 mL). Yield: 9 g (79 %); m.p. 109 °C; $^1$H NMR (200 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta = 7.5 - 7.4$ (m, 2H; Ar–H), 6.77 (d, $^3J$(H,H) = 9.2 Hz, 1H; Ar–H), 4.92 (d, $^3J$(H,H) = 5.0 Hz, 1H; sec. OH), 4.65 (t, $^3J$(H,H) = 5.7 Hz, 1H; prim. OH), 4.03 – 3.72 (m, 3H; $ArOCH_2$, sec. CH), 3.48 (dd, $^3J$(H,H) = 5.5 Hz, $^3J$(H,H) = 5.5 Hz, 2H; C$H_2$OH), 2.14 (s, 3H; Ar–$CH_3$).

**3-(4-Bromo-2-methylphenyloxy)propane-1,2-diol**: Synthesized from 1-allyloxy-4-bromo-2-methylbenzene (24.2 g, 107 mmol). Crystallization from *n*-hexane/ethyl acetate 4:1 (100 mL). Yield: 18.3 g (66 %); m.p. 91 – 93 °C; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.26$ (m, 2H; Ar–H), 6.88 (d, $^3J$(H,H) = 9.2 Hz, 1H; Ar–H), 4.10 (m, 1H; sec. CH), 4.00 (m, 2H; $ArOCH_2$), 3.84 (dd, $^2J$(H,H) = 10.8 Hz $^3J$(H,H) = 2.7 Hz, 1H; C$H_a$H$_b$OH), 3.75 (dd, $^2J$(H,H) = 11.4 Hz $^3J$(H,H) = 5.4 Hz, 1H; CH$_a$H$_b$OH), 2.18 (s, 3H; Ar–$CH_3$).

**3-(4-Bromo-3-methylphenyloxy)propane-1,2-diol**: Synthesized from 1-allyloxy-4-bromo-3-methylbenzene (24.2 g, 107 mmol). Crystallization from *n*-hexane (100 mL). Yield: 23.6 g (85 %); m.p. 98 °C; $^1$H NMR (200 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta = 7.45$ (d, $^3J$(H,H) = 8.8 Hz, 1H; Ar–H), 6.98 (d, $^4J$(H,H) = 2.8 Hz, 1H; Ar–H), 6.74 (dd, $^3J$(H,H) = 8.8 Hz, $^4J$(H,H) = 3.0 Hz, 1H; Ar–H), 4.94 (d, $^3J$(H,H) = 4.9 Hz, 1H; sec. OH), 4.67 (t,



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$^3J$(H,H) = 5.6 Hz, 1H; prim. OH), 4.03–3.72 (m, 3H; ArOC$H_2$, sec. CH), 3.45 (dd, $^3J$(H,H) = 5.5 Hz, $^3J$(H,H) = 5.5 Hz, 2H; C$H_2$OH), 2.32 (s, 3H; Ar–C$H_3$); $^{13}$C NMR (50 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta$ = 158.2, 138.3, 132.6, 117.3, 114.4, 112.2, 69.9, 62.8, 22.6.

**4-(4-Bromophenyloxymethyl)-2,2-dimethyl-1,3-dioxolanes 5**

**General procedure**: The appropriate 3-aryloxypropane-1,2-diol (46 mmol) and pyridinium-*p*-toluene sulfonate (100 mg) in 2,2-dimethoxypropane (70 mL) were stirred at 20 °C. After the reaction was complete (TLC), the 2,2-dimethoxypropane was removed by using an evaporator, and the residue was taken up in diethyl ether (100 mL) and washed with saturated $NaHCO_3$ solution (30 mL), water (30 mL), and brine (30 mL). After drying with $Na_2SO_4$ and evaporation of the diethyl ether, the product was purified by distillation in vacuo or by crystallization from hexane.

**4-(4-Bromophenyloxymethyl)-2,2-dimethyl-1,3-dioxolane (5a)**: Synthesized from 3-(4-bromophenyloxy)propane-1,2-diol (24.7 g, 100 mmol). Yield: 25.5 g (89 %); m.p. 70 °C; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.37 (d, $^3J$(H,H) = 8.9 Hz, 2H; Ar–H), 6.80 (d, $^3J$(H,H) = 9.0 Hz, 2H; Ar–H), 4.46 (m, 1H; sec. CH), 4.20–3.85 (m, 4H; OC$H_2$), 1.46 (s, 3H; C$H_3$), 1.40 (s, 3H; C$H_3$); elemental analysis calcd (%) for $C_{12}H_{15}O_3Br$ (287.2): C 50.19, H 5.26, Br 27.58; found C 50.06, H 5.17, Br 27.58.

**4-(4-Iodo-2-methylphenyloxymethyl)-2,2-dimethyl-1,3-dioxolane (5b)**: Synthesized from 3-(4-iodo-2-methylphenyloxy)propane-1,2-diol (18.4 g, 60 mmol). Purified by distillation in vacuo. Yield: 17.6 g (85 %) pale yellow oil; b.p. 120 °C/0.008 Torr; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.41–7.36 (m, 2H; Ar–H), 6.55 (dd, $^3J$(H,H) = 9.2 Hz, $^4J$(H,H) = 2.9, 1H; Ar–H), 4.47 (m, 1H; sec. CH), 4.17–3.85 (m, 4H; OC$H_2$), 2.14 (s, 3H; Ar–C$H_3$), 1.43 (s, 3H; C$H_3$), 1.38 (s, 3H; C$H_3$).

**4-(4-Bromo-2-methylphenyloxymethyl)-2,2-dimethyl-1,3-dioxolane (5c)**: Synthesized from 3-(4-bromo-2-methylphenyloxy)propane-1,2-diol (15.6 g, 60 mmol). Yield: 17.3 g (96 %) of a pale yellow oil which was used without further purification; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.18–7.25 (m, 2 Ar–H), 6.67 (d, $^3J$(H,H) = 9.3 Hz, 1H; Ar–H), 4.45 (m, 1H; sec. CH), 4.20–3.85 (m, 4H; OC$H_2$), 2.17 (s, 3H; Ar–C$H_3$), 1.44 (s, 3H; C$H_3$), 1.38 (s, 3H; C$H_3$).

**4-(4-Bromo-3-methylphenyloxymethyl)-2,2-dimethyl-1,3-dioxolane (5d)**: Synthesized from 3-(4-bromo-3-methylphenyloxy)propane-1,2-diol (14.5 g, 46 mmol). The product was purified by distillation in vacuo followed by crystallization from hexane. Yield: 11.4 g (82 %); b.p. 80 °C/0.001 Torr; m.p. 55–57 °C; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.37 (d, $^3J$(H,H) = 8.8 Hz, 1H; Ar–H), 6.79 (d, $^4J$(H,H) = 2.9 Hz, 1H; Ar–H), 6.60 (dd, $^3J$(H,H) = 8.8 Hz, $^4J$(H,H) = 2.9 Hz, 1H; Ar–H), 4.43 (m, 1H; sec. CH), 4.17–3.82 (m, 4H; OC$H_2$), 2.33 (s, 3H; Ar–C$H_3$), 1.44 (s, 3H; C$H_3$), 1.38 (s, 3H; C$H_3$).

**4-(4′-Benzyloxybiphenyl-4-yloxymethyl)-2,2-dimethyl-1,3-dioxolanes (7)**

**Preparation by a Suzuki cross-coupling reaction**

**General procedure**: The reaction was completed under an argon atmosphere. The appropriate 4-(4-bromophenyloxymethyl)-2,2-dimethyl-1,3-dioxolane **5** (26.3 mmol), the appropriate benzyloxyphenylboronic acid **6** (22.9 mmol), and [Pd(PPh$_3$)$_4$](0.5 g) were dissolved in glyme (160 mL) and stirred under reflux for 6 h after addition of saturated aqueous $NaHCO_3$ solution (100 mL). The product precipitated almost quantitatively when the mixture was let to stand overnight at ambient temperature. It was filtered off by suction and dissolved in $CHCl_3$ (50 mL). The solution was dried with $Na_2SO_4$. In order to remove catalyst residues, the solution was filtered over silica gel with suction. The silica gel was carefully rinsed with $CHCl_3$ (100 mL). The combined organic solutions were evaporated. If not specially mentioned, the products were purified by crystallization from methanol/ethyl acetate mixtures (1:1–5:1).

**4-(4′-Benzyloxybiphenyl-4-yloxymethyl)-2,2-dimethyl-1,3-dioxolane (7a)**: Synthesized from **5a** (5.0 g, 18.3 mmol) and 4-benzyloxyphenylboronic acid (**6a**, 4.2 g, 18.5 mmol). Yield: 4.4 g (62 %); m.p. 162 °C; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.48–7.32 (m, 9H; Ar–H), 7.03 (d, $^3J$(H,H) = 8.6 Hz, 2H; Ar–H), 6.97 (d, $^3J$(H,H) = 8.4 Hz, 2H; Ar–H), 5.11 (s, 2H; Ar–C$H_2$), 4.51 (m, 1H; sec. CH), 4.20 (m, 1H; sec. CH), 4.10–3.90 (m, 4H; OC$H_2$), 1.48 (s, 3H; C$H_3$), 1.42 (s, 3H; C$H_3$); elemental analysis calcd (%) for $C_{25}H_{26}O_4$ (390.5): C 76.90, H 6.71; found C 76.61, H 6.55.

**4-(4′-Benzyloxy-3-methylbiphenyl-4-yloxymethyl)-2,2-dimethyl-1,3-dioxolane (7b)**: Synthesized from **5b** (5.0 g, 14.5 mmol) and **6a** (3.3 g, 14.5 mmol). Work-up procedure: The product precipitated almost quantitatively when the mixture was let to stand overnight at ambient temperature. It was drawn off by suction and dissolved in ethyl acetate (50 mL). The solution was dried with $Na_2SO_4$ and the solvent evaporated. The residue was dissolved in hot hexane (50 mL) and filtered. On cooling, the product was precipitated again. It was filtered off by suction and purified by two crystallizations from isopropanol (30 mL). Yield: 3.1 g (53 %); m.p. 114 °C; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.60–7.25 (m, 9H; Ar–H), 7.03 (d, $^3J$(H,H) = 8.8 Hz, 2H; Ar–H), 6.87 (d, $^3J$(H,H) = 8.0 Hz, 1H; Ar–H), 5.11 (s, 2H; Ar–C$H_2$), 4.50 (m, 1H; sec. CH), 4.25–3.95 (m, 4H; OC$H_2$), 2.29 (s, 3H; Ar–C$H_3$), 1.49 (s, 3H; C$H_3$), 1.43 (s, 3H; C$H_3$).

**4-(4′-Benzyloxy-2-methylbiphenyl-4-yloxymethyl)-2,2-dimethyl-1,3-dioxolane (7c)**: Synthesized from **5d** (7.9 g, 26.3 mmol) and **6a** (5.2 g, 22.9 mmol). Yield: 7.2 g (68 %); m.p. 114 °C; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.49 (d, $^3J$(H,H) = 7.2 Hz, 2H; Ar–H), 7.39 (m, 2H; Ar–H), 7.31 (m, 1H; Ar–H), 7.18 (d, $^3J$(H,H) = 8.7 Hz, 2H; Ar–H), 7.05 (d, $^3J$(H,H) = 8.3 Hz, 1H; Ar–H), 7.00 (d, $^3J$(H,H) = 8.7 Hz, 2H; Ar–H), 6.81 (d, $^3J$(H,H) = 2.7 Hz, 1H; Ar–H), 6.77 (dd, $^3J$(H,H) = 8.3 Hz, $^4J$ 2.7 Hz, 1H; Ar–H), 5.12 (s, 2H; Ar–C$H_2$), 4.49 (m, 1H; sec. CH), 4.20 (dd, $^2J$(H,H) = 8.4 Hz, $^3J$(H,H) = 6.3 Hz, 1H; OC$H_a$H$_b$), 4.12 (dd, $^2J$(H,H) = 9.5 Hz, $^3J$(H,H) = 4.7 Hz, 1H; OC$H_a$H$_b$), 3.99 (m, 2H; 2 OCH$_a$H$_b$), 2.18 (s, 3H; Ar–C$H_3$); elemental analysis calcd (%) for $C_{26}H_{28}O_4$ (404.5): C 77.20, H 6.98; found C 77.65, H 7.17.

**4-(4′-Benzyloxy-2′-methylbiphenyl-4-yloxymethyl)-2,2-dimethyl-1,3-dioxolane (7d)**: Synthesized from **5a** (3.54 g, 12.3 mmol) and **6b** (3.0 g, 12.3 mmol). Work-up procedure: The solvent was removed in vacuo and the aqueous residue was extracted with $CHCl_3$ (3 × 30 mL). After drying with $Na_2SO_4$, the solution was filtered over silica gel with suction, and the silica gel was rinsed carefully with additional $CHCl_3$ (100 mL). The solvent was removed under reduced pressure. The oily residue crystallized when allowed to stand overnight and was crystallized from *n*-hexane (30 mL). Yield: 2.0 g (41 %); m.p. 78 °C; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.48–6.82 (m, 12H; Ar–H), 5.09 (s, 2H; Ar–C$H_2$), 4.51 (m, 1H; sec. CH), 4.23–3.90 (m, 4H; OC$H_2$), 2.25 (s, 3H; Ar–C$H_3$), 1.48 (s, 3H; C$H_3$), 1.42 (s, 3H; C$H_3$).

**4-(4′-Benzyloxy-3′-methylbiphenyl-4-yloxymethyl)-2,2-dimethyl-1,3-dioxolane (7e)**: Synthesized from **5a** (6.0 g, 21 mmol) and **6c** (4.8 g, 20.8 mmol). Yield: 4.6 g (55 %); m.p. 115 °C; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.50–7.26 (m, 9H; Ar–H), 6.99–6.91 (m, 3H; Ar–H), 5.13 (s, 1H; Ar–C$H_2$), 4.51 (m, 1H; sec. CH), 4.23–3.89 (m, 4H; OC$H_2$), 2.18 (s, 3H; Ar–C$H_3$), 1.49 (s, 3H; C$H_3$), 1.43 (s, 3H; C$H_3$); elemental analysis calcd (%) for $C_{26}H_{28}O_4$ (404.5): C 77.20, H 6.98; found C 77.25, H 7.23.

**4-[3′-Methyl-4′-(3-methylbenzyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolane (7f)**: Synthesized from **5a** (2.0 g, 7.0 mmol) and **6d** (1.6 g, 6.4 mmol). Yield: 0.7 g (27 %); m.p. 93–95 °C; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.45 (d, $^3J$(H,H) = 8.6 Hz, 2H; Ar–H), 7.40–7.10 (m, 6H; Ar–H), 6.94 (d, $^3J$(H,H) = 8.6 Hz, 2H, Ar–H), 6.91 (d, $^3J$(H,H) = 8.2 Hz, 1H; Ar–H), 5.06 (s, 1H; Ar–C$H_2$), 4.47 (m, 1H; sec. CH), 4.20–3.90 (m, 4H; OC$H_2$), 2.37 (s, 3H; Ar–C$H_3$), 2.33 (s, 3H; Ar–C$H_3$), 1.46 (s, 3H; C$H_3$), 1.40 (s, 3H; C$H_3$).

**4-[3′-Methyl-4′-(4-methylbenzyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolane (7g)**: Synthesized from **5a** (2.0 g, 7.0 mmol) and **6e** (1.6 g, 6.4 mmol). Yield: 0.90 g (34 %); m.p. 118–120 °C; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.44 (d, $^3J$(H,H) = 8.8 Hz, 2H; Ar–H), 7.40–7.10 (m, 6H; Ar–H), 6.93 (d, $^3J$(H,H) = 8.8 Hz, 2H; Ar–H), 6.90 (d, $^3J$(H,H) = 8.2 Hz, 1H, Ar–H), 5.05 (s, 1H; Ar–C$H_2$), 4.46 (m, 1H; sec. CH), 4.20–3.80 (m, 4H; OC$H_2$), 2.35 (s, 3H; Ar–C$H_3$), 2.30 (s, 3H; Ar–C$H_3$), 1.45 (s, 3H; C$H_3$), 1.39 (s, 3H; C$H_3$).

**4-[3,3′-Dimethyl-4′-(4-methylbenzyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolane (7h)**: Synthesized from **5c** (2.6 g, 8.8 mmol) and **6e** (2.0 g, 8.0 mmol). Yield: 1.3 g (38 %); m.p. 74–76 °C; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.40–7.20 (m, 8H; Ar–H), 6.92 (d, $^3J$(H,H) = 8.4 Hz, 1H; Ar–H), 6.86 (d, $^3J$(H,H) = 9.2 Hz, 1H; Ar–H), 5.08 (s, 1H; Ar–C$H_2$), 4.51 (m, 1H; sec. CH), 4.25–3.90 (m, 4H; OC$H_2$), 2.38 (s, 3H; Ar–C$H_3$), 2.33 (s, 3H; Ar–C$H_3$), 2.28 (s, 3H; Ar–C$H_3$), 1.49 (s, 3H; C$H_3$), 1.43 (s, 3H; C$H_3$).

**4-[2,3′-Dimethyl-4′-(4-methylbenzyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolane (7i)**: Synthesized from **5d** (2.6 g, 8.8 mmol) and **6e** (2.0 g, 8.0 mmol). Yield: 0.5 g (15 %); m.p. 73–75 °C; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ = 7.40–6.70 (m, 10H; Ar–H), 5.06 (s, 1H; Ar–C$H_2$), 4.46 (m, 1H; sec. CH), 4.20–3.85 (m, 4H; OC$H_2$), 2.36 (s, 3H; Ar–C$H_3$),

2.29 (s, 3H; Ar−$CH_3$), 2.24 (s, 3H; Ar−$CH_3$), 1.46 (s, 3H; $CH_3$), 1.40 (s, 3H; $CH_3$).

**4-[2,3′-Dimethyl-4′-(3-methylbenzyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolane (7k)**: Synthesized from **5d** (2.0 g, 6.5 mmol) and **6d** (2.5 g, 5.9 mmol). Purified by crystallization at −20 °C. Yield: 0.8 g (33%); pale yellow oil; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.40-6.60$ (m, 10H; Ar−H), 5.06 (s, 1H; Ar−$CH_2$), 4.47 (m, 1H; sec. CH), 4.20–3.80 (m, 4H; $OCH_2$), 2.38 (s, 3H; Ar−$CH_3$), 2.30 (s, 3H; Ar−$CH_3$), 2.24 (s, 3H; Ar−$CH_3$), 1.46 (s, 3H; $CH_3$), 1.40 (s, 3H; $CH_3$).

**4-[3,3′-Dimethyl-4′-(3-methylbenzyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolane (7l)**: Synthesized from **5c** (2.0 g, 6.5 mmol) and **6d** (1.5 g, 5.9 mmol). Yield: 0.8 g (40%); m.p. 50–51 °C; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.40-7.10$ (m, 8H; Ar−H), 6.90 (d, $^3J$(H,H) = 8.4 Hz, 1H; Ar−H), 6.84 (d, $^3J$(H,H) = 9.2 Hz, 1H; Ar−H), 5.06 (s, 1H; Ar−$CH_2$), 4.49 (m, 1H; sec. CH), 4.20–3.90 (m, 4H; $OCH_2$), 2.37 (s, 3H; Ar−$CH_3$), 2.33 (s, 3H; Ar−$CH_3$), 2.26 (s, 3H; Ar−$CH_3$), 1.47 (s, 3H; $CH_3$), 1.40 (s, 3H; $CH_3$).

**Synthesis by exchange of the benzyl ether unit (Path B, Scheme 1)**

**General procedure**: The appropriate benzyl ether **7** (8.6 mmol) was dissolved in ethyl acetate (50 mL), and palladium on charcoal (0.25 g) was added. The mixture was shaken under a $H_2$ atmosphere at 20 °C and normal pressure (TLC). After the reaction was complete, the catalyst was removed by filtration and the solvent evaporated. (The acidity of the charcoal may cause a partial cleavage of the acetonide protecting group, so that re-protection according to procedure for the formation of **5** might be necessary.) The products were used without further purification.

A mixture of the obtained 4-(4′-hydroxybiphenyl-4-yloxymethyl)-2,2-dimethyl-1,3-dioxolane (1.59 mmol), the appropriate methylbenzylbromide (1.73 mmol) and $K_2CO_3$ (2.5 g, 18 mmol) in dry acetone (25 mL) was stirred under reflux (TLC, ca. 5 h). After the reaction had finished, water (20 mL) was added and the mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined extracts were washed with $Na_2CO_3$ solution (2M, 30 mL), water (30 mL), and brine (30 mL), dried with $Na_2SO_4$, and the solvent was removed under reduced pressure.

**4-[3-Methyl-4′-(4-methylbenzyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolane (7m)**: Synthesized from **7b** and 4-methylbenzylbromide. Purified by repeated crystallization from 20 mL ethanol. Yield: 50%; transitions/°C: K 134 ($S_C$ 76 $S_A$ 96 N 106) I; $^1$H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.43$ (d, $^3J$(H,H) = 8.7 Hz, 2H; Ar−H), 7.34–7.28 (m, 4H; Ar−H), 7.18 (d, $^3J$(H,H) = 7.8 Hz, 2H; Ar−H), 6.95 (d, $^3J$(H,H) = 8.7 Hz, 2H; Ar−H), 6.85 (d, $^3J$(H,H) = 8.7 Hz, 1H; Ar−H), 5.04 (s, 2H; Ar−$CH_2$), 4.48 (m, 1H; sec. CH), 4.20–3.78 (m, 4H; $OCH_2$), 2.27 (s, 3H; Ar−$CH_3$), 2.26 (s, 3H; Ar−$CH_3$), 1.46 (s, 1H; $CH_3$), 1.40 (s, 1H; $CH_3$).

**4-[2′-Methyl-4′-(4-methylbenzyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolane (7n)**: Synthesized from **7d** and 4-methylbenzylbromide. Yield 73%. The crude product was used without further purification.

**4-[3-Methyl-4′-(3-methylbenzyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolane (7o)**: Synthesized from **7b** and 3-methylbenzylbromide. Purified by repeated crystallization from ethanol (20 mL). Yield: 0.38 g (57%); m.p. 64 °C; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.44$ (d, $^3J$(H,H) = 8.8 Hz, 2H; Ar−H), 7.38–7.26 (m, 4H; Ar−H), 7.20 (s, 1H; Ar−H), 7.16 (s, 1H; Ar−H), 6.99 (d, $^3J$(H,H) = 8.6 Hz, 2H; Ar−H), 6.85 (d, $^3J$(H,H) = 9.2 Hz, 1H; Ar−H), 5.04 (s, 2H; Ar−$CH_2$), 4.48 (m, 1H; sec. CH), 4.20–3.74 (m, 4H; $OCH_2$), 2.35 (s, 3H; Ar−$CH_3$), 2.26 (s, 3H; Ar−$CH_3$), 1.46 (s, 1H; $CH_3$), 1.40 (s, 1H; $CH_3$).

**4-[2′-Methyl-4′-(3-methylbenzyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolane (7p)**: Synthesized from **7d** and 3-methylbenzylbromide. Yield 82%. The product was used without further purification.

**3-(4′-Benzyloxybiphenyl-4-yloxy)propane-1,2-diols x.y/z**

**Hydrolytic deprotection of 4-(4′-benzyloxybiphenyl-4-yloxymethyl)-2,2-dimethyl-1,3-dioxolanes (Path A, Scheme 1)**

**General procedure**: A mixture of the appropriate 4-(4′-benzyloxybiphenyl-4-yloxy)methyl-2,2-dimethyl-1,3-dioxolane **7** (4 mmol), methanol (25 mL), water (3 mL), and pyridinium-*p*-toluene sulfonate (0.1 g) was heated at reflux for 3 h. The reaction was monitored by TLC. After the reaction had finished, the solvent was removed in vacuo. The residue was taken up in ethyl acetate (30 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL), water (20 mL), and brine (20 mL), and then dried with $Na_2SO_4$. The solvent was distilled off and the product purified by repeated crystallization from *n*-hexane/ethyl acetate mixtures (5:4–3:1). The yields refer to the purified products.

**3-(4′-Benzyloxybiphenyl-4-yloxy)propane-1,2-diol (0)**: Obtained from **7a** (2.0 g, 5.1 mmol). Yield: 1.37 g (80%); m.p. 230 °C; $^1$H NMR (400 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta = 7.55-7.27$ (m, 9H; Ar−H), 7.04 (d, $^3J$(H,H) = 8.8, 2H; Ar−H), 6.97 (d, $^3J$(H,H) = 8.8 Hz, 2H; Ar−H), 5.12 (s, 2H; Ar−$CH_2$), 4.00 (dd, $^2J$(H,H) = 9.8 Hz, $^3J$(H,H) = 4.2 Hz, 1H; ArOC$H_a$H$_b$), 3.87 (m, 1H; ArOC$H_a$$H_b$), 3.78 (m, 1H; sec. CH), 3.66 (d, $^3J$(H,H) = 5.5 Hz, 2H; C$H_2$OH); $^{13}$C NMR (100 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta = 158.1$, 157.6, 137.3, 132.7, 128.6, 127.9, 127.7, 127.3, 115.3, 115.0, 70.0, 69.7, 69.3, 62.7.

**3-(4′-Benzyloxy-3-methylbiphenyl-4-yloxy)propane-1,2-diol (1/0)**: Obtained from **7b** (1.5 g, 3.8 mmol) Yield: 0.90 g (62%); transitions/°C: K 147 ($S_A$ 127) I; $^1$H NMR (500 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta = 7.51$ (d, $^3J$(H,H) = 8.5 Hz, 2H; Ar−H), 7.45 (d, $^3J$(H,H) = 8.8 Hz, 2H; Ar−H), 7.42–7.30 (m, 5H; Ar−H), 7.04 (d, $^3J$(H,H) = 8.5 Hz, 2H; Ar−H), 6.94 (d, $^3J$(H,H) = 8.6 Hz, 1H; Ar−H), 5.12 (s, 2H; Ar−$CH_2$), 4.83 (d, $^3J$(H,H) = 5.1 Hz, 1H; sec. OH), 4.60 (t, $^3J$(H,H) = 5.6 Hz, 1H; prim. OH), 4.00 (dd, $^2J$(H,H) = 9.8 Hz, $^3J$(H,H) = 4.6 Hz, 1H; ArOC$H_a$H$_b$), 3.90 (dd, $^2J$(H,H) = 9.8 Hz, $^3J$(H,H) = 5.9 Hz, 1H; ArOC$H_a$$H_b$), 3.82 (m, 1H; sec. CH), 3.47 (m, 2H; C$H_2$OH), 2.20 (s, 3H; Ar−$CH_3$); $^{13}$C NMR (50 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta = 157.3$, 156.0, 137.1, 132.7, 131.8, 128.4, 128.3, 127.7, 127.1, 126.2, 124.5, 115.1, 111.7, 70.0, 69.6, 69.2, 62.8, 16.1; MS (ESI): *m*/*z* (%): 387.1 (32) [*M*+Na]$^+$, 750.9 (100) [2*M*+Na]$^+$; elemental analysis calcd (%) for $C_{23}H_{24}O_4$ (364.4): C 75.80, H 6.68; found C 75.76, H 6.62.

**3-(4′-Benzyloxy-2-methylbiphenyl-4-yloxy)propane-1,2-diol (2/0)**: Obtained from **7c** (1.6 g, 4.0 mmol). Yield: 1.1 g (76%); transitions/°C: K 102 (Iso 70 $S_A$ 70 N 72) I; $^1$H NMR (500 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta = 7.47$ (d, $^3J$(H,H) = 7.1 Hz, 2H; Ar−H), 7.40 (m, 2H; Ar−H), 7.30 (m, 1H; Ar−H), 7.20 (d, $^3J$(H,H) = 8.8 Hz, 2H; Ar−H), 7.06 (d, $^3J$(H,H) = 8.3 Hz, 2H; Ar−H), 7.03 (d, $^3J$(H,H) = 8.8 Hz, 2H; Ar−H), 6.83 (d, $^4J$(H,H) = 2.7 Hz, 1H; Ar−H), 6.78 (dd, $^3J$(H,H) = 8.3 Hz, $^4J$(H,H) = 2.7 Hz, 1H; Ar−H), 5.12 (s, 2H; Ar−$CH_2$), 4.88 (d, $^3J$(H,H) = 5.1 Hz, 1H; sec. OH), 4.60 (t, $^3J$(H,H) = 5.6 Hz, 1H; prim. OH), 3.99 (dd, $^2J$(H,H) = 9.8 Hz, $^3J$(H,H) = 4.3 Hz, 1H; ArOC$H_a$H$_b$), 3.85 (dd, $^2J$(H,H) = 10.0 Hz, $^3J$(H,H) = 6.1 Hz, 2H; ArOCH$_a$$H_b$), 3.78 (m, 1H; sec. CH), 3.44 (m, 2H; C$H_2$OH), 2.19 (s, 3H; Ar−$CH_3$); MS (70 eV, EI): *m*/*z* (%): 364 (92) [*M*]$^+$, 273 (86), 199 (72), 91 (100); elemental analysis calcd (%) for $C_{23}H_{24}O_4$ (364.4): C 75.80, H 6.68; found C 75.57, H 6.59.

**3-(4′-Benzyloxy-2′-methylbiphenyl-4-yloxy)propane-1,2-diol (3/0)**: Obtained from **7d** (0.50 g, 1.24 mmol). Yield: 0.29 g (65%); transitions/°C: K 96 ($S_A$ 62) I; $^1$H NMR (200 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta = 7.51-7.34$ (m, 5H; Ar−H), 7.22 (d, $^3J$(H,H) = 8.6 Hz, 2H; Ar−H), 7.10 (d, $^3J$(H,H) = 8.4 Hz, 1H; Ar−H), 7.00–6.86 (m, 4H; Ar−H), 5.14 (s, 2H; Ar−$CH_2$), 4.95 (d, $^3J$(H,H) = 4.9 Hz, 1H; sec. OH), 4.67 (t, $^3J$(H,H) = 5.6 Hz, 1H; prim. OH), 4.10–3.81 (m, 3H; ArO$CH_2$, sec. CH), 3.48 (dd, $^3J$(H,H) = 5.5 Hz, $^3J$(H,H) = 5.5 Hz, 2H; C$H_2$OH), 2.22 (s, 3H; Ar−$CH_3$); $^{13}$C NMR (50 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta = 157.5$, 157.2, 137.2 , 136.1, 133.8, 133.1, 130.5, 130.1, 128.4, 127.7, 127.5, 116.5, 114.1, 112.1, 69.9, 69.5, 69.1, 62.7, 20.5; MS (70 eV, EI): *m*/*z* (%): 364 (100) [*M*]$^+$, 273 (91), 199 (72), 171 (8), 153 (5), 91 (90); elemental analysis calcd (%) for $C_{23}H_{24}O_4$ (364.4): C 75.80, H 6.68; found C 75.41, H 6.43.

**3-(4′-Benzyloxy-3′-methylbiphenyl-4-yloxy)propane-1,2-diol (4/0)**: Obtained from **7e** (0.4 g, 1.1 mmol). Yield: 0.13 g (36%); transitions/°C: K 130 Col 151 I; $^1$H NMR (200 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta = 7.56-7.30$ (m, 9H; Ar−H), 7.10–6.97 (m, 3H; Ar−H), 5.18 (s, 2H; Ar−$CH_2$), 4.95 (d, $^3J$(H,H) = 4.9 Hz, 1H; sec. OH), 4.67 (t, $^3J$(H,H) = 5.6 Hz, 1H; prim. OH), 4.10–3.70 (m, 3H; ArO$CH_2$, sec. CH), 3.47 (dd, $^3J$(H,H) = 5.5 Hz, $^3J$(H,H) = 5.5 Hz, 2H; C$H_2$OH), 2.28 (s, 3H; Ar−$CH_3$); MS (70 eV, EI): *m*/*z* (%): 364 (62) [*M*]$^+$, 273 (100), 199 (95), 91 (43); elemental analysis calcd (%) for $C_{23}H_{24}O_4$ (364.4): C 75.80, H 6.68; found C 75.54, H 6.38.

**3-[3-Methyl-4′-(3-methylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol (1/3)**: Obtained from **7o** (0.30 g, 0.71 mmol). Yield: 0.12 g (45%); m.p. 137 °C; $^1$H NMR (200 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta = 7.54$ (d, $^3J$(H,H) = 8.6 Hz, 2H; Ar−H), 7.41–7.10 (m, 6H; Ar−H), 7.07 (d, $^3J$(H,H) = 8.7 Hz, 2H; Ar−H), 6.98 (d, $^3J$(H,H) = 8.4 Hz, 1H; Ar−H), 5.11 (s, 2H; Ar−$CH_2$), 4.92 (br s, 1H; sec. OH), 4.66 (br s, 1H; prim. OH), 4.10–3.80 (m, 3H; ArO$CH_2$, sec. CH), 3.52 (br s, 2H; C$H_2$OH), 2.35 (s, 3H; Ar−$CH_3$), 2.24 (s, 3H; Ar−$CH_3$); elemental analysis calcd (%) for $C_{24}H_{26}O_4$ (378.5): C 76.17, H 6.92; found C 76.03, H 6.84.



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**3-[3-Methyl-4′-(4-methylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol (1/4)**: Obtained from **7m** (0.64 g, 1.5 mmol). Yield: 0.11 g (19%); transitions/°C: K 150 $S_A$ 156 I; $^1$H NMR (200 MHz, [D$_6$]DMSO, 25°C, TMS): $\delta$ = 7.53 (d, $^3J$(H,H) = 8.8 Hz, 2H; Ar–H), 7.50–7.30 (m, 4H; Ar–H), 7.20 (d, $^3J$(H,H) = 7.9, 2H; Ar–H), 7.05 (d, $^3J$(H,H) = 8.8 Hz, 2H; Ar–H), 6.97 (d, $^3J$(H,H) = 8.5 Hz, 1H; Ar–H), 5.10 (s, 2H; Ar–C$H_2$), 4.91 (d, $^3J$(H,H) = 5.0 Hz, 1H; sec. OH), 4.65 (t, $^3J$(H,H) = 5.7 Hz, 1H; prim. OH), 4.10–3.80 (m, 3H; ArOC$H_2$, sec. CH), 3.60–3.45 (m, 2H; C$H_2$OH), 2.32 (s, 3H; Ar–C$H_3$), 2.23 (s, 3H; Ar–C$H_3$); MS (ESI): *m*/*z* (%): 401.2 (18) [*M*+Na]$^+$, 778.9 (100) [2*M*+Na]$^+$; elemental analysis calcd (%) for $C_{24}H_{26}O_4$ (378.5): C 76.17, H 6.92; found C 76.16, H 6.84.

**3-[2′-Methyl-4′-(3-methylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol (3/3)**: Obtained from **7p** (0.84 g, 2.0 mmol). Yield: 0.11 g (35%); transitions/°C: K 88 ($S_A$ 55) I; $^1$H NMR (200 MHz, [D$_6$]DMSO, 25°C, TMS): $\delta$ = 7.36–6.87 (m, 11H; Ar–H), 5.1 (s, 1H; Ar–C$H_2$), 4.96 (d, $^3J$(H,H) = 5.0 Hz, 1H; sec. OH), 4.68 (t, $^3J$(H,H) = 5.6 Hz, 1H; prim. OH), 4.15–3.80 (m, 3H; ArOC$H_2$, sec. CH), 3.6–3.4 (m, 2H; C$H_2$OH), 2.36 (s, 3H; Ar–C$H_3$), 2.23 (s, 3H; Ar–C$H_3$); MS (ESI): *m*/*z* (%): 401.1 (25) [*M*+Na]$^+$, 778.9 (100) [2*M*+Na]$^+$; elemental analysis calcd (%) for $C_{24}H_{26}O_4$ (378.5): C 76.17, H 6.92; found C 76.11, H 7.26.

**3-[2′-Methyl-4′-(4-methylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol (3/4)**: Obtained from **7n** (0.64 g, 1.5 mmol). Yield: 0.21 g (36%); transitions/°C: K 95 $S_A$ 104 I; $^1$H NMR (200 MHz, [D$_6$]DMSO, 25°C, TMS): $\delta$ = 7.36 (d, $^3J$(H,H) = 8.0 Hz, 2H; Ar–H), 7.22 (d, $^3J$(H,H) = 8.4 Hz, 4H; Ar–H), 7.09 (d, $^3J$(H,H) = 8.4 Hz, 1H; Ar–H), 7.00 (s, 1H; Ar–H), 6.94 (m, 2H; Ar–H), 6.87 (dd, $^3J$(H,H) = 8.4 Hz, $^4J$ 2.5, 1H; Ar–H), 5.08 (s, 2H; Ar–C$H_2$), 4.97 (br s, 1H; sec. OH), 4.67 (br s, 1H; prim. OH), 4.08–3.84 (m, 3H; ArOC$H_2$, sec. CH), 3.48 (br s, 2H; C$H_2$OH), 2.33 (s, 3H; Ar–C$H_3$), 2.21 (s, 3H; Ar–C$H_3$); MS (ESI): *m*/*z* (%): 401.1 (26) [*M*+Na]$^+$, 778.9 (100) [2*M*+Na]$^+$; elemental analysis calcd (%) for $C_{24}H_{26}O_4$ (378.5): C 76.17, H 6.92; found C 75.80, H 6.86.

**3-[3′-Methyl-4′-(3-methylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol (4/3)**: Obtained from **7f** (0.4 g, 1.0 mmol). Yield: 95 mg (26%); transitions/°C: $K_1$ 88 $K_2$ 116 Col 151 I; $^1$H NMR (400 MHz, CDCl$_3$, 25°C, TMS):: $\delta$ = 7.46 (d, $^3J$(H,H) = 8.7 Hz, 2H; Ar–H), 7.35–7.10 (m, 6H; Ar–H), 6.94 (d, $^3J$(H,H) = 8.7 Hz, 2H; Ar–H), 6.91 (d, $^3J$(H,H) = 8.6 Hz, 1H; Ar–H), 5.06 (s, 1H; Ar–C$H_2$), 4.10–4.00 (m, 3H; ArOC$H_2$, sec. CH), 3.84 (dd, $^2J$(H,H) = 11.4 Hz, $^3J$(H,H) = 3.6 Hz, 1H; C$H_a$H$_b$OH), 3.75 (dd, $^2J$(H,H) = 11.4 Hz, $^3J$(H,H) = 5.2 Hz, 1H; CH$_a$H$_b$OH), 2.37 (s, 3H; Ar–C$H_3$), 2.32 (s, 3H; Ar–C$H_3$); EI-MS *m*/*z*, 70 EV (%): 378 (60) [*M*]$^+$, 273 (100), 199 (50), 105 (95); elemental analysis calcd (%) for $C_{24}H_{26}O_4$ (378.5): C 76.17, H 6.92; found C 76.18, H 6.90.

**3-[3′-Methyl-4′-(4-methylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol (4/4)**: Obtained from **7g** (0.7 g, 1.7 mmol). Yield: 0.36g (57%); transitions/°C: $K_1$ 97 $K_2$ 133 Col 171 I; $^1$H NMR (200 MHz, CDCl$_3$, 25°C, TMS): $\delta$ = 7.45 (d, $^3J$(H,H) = 8.8 Hz, 2H; Ar–H), 7.40–7.15 (m, 6H; Ar–H), 6.95–6.90 (m, 3H; Ar–H), 5.06 (s, 1H; Ar–C$H_2$), 4.10–4.00 (m, 3H; ArOC$H_2$, sec. CH), 3.70–3.90 (m, 2H; C$H_2$OH), 2.35 (s, 3H; Ar–C$H_3$), 2.30 (s, 3H; Ar–C$H_3$); MS (70 eV, EI): *m*/*z* (%): 378 (30) [*M*]$^+$, 273 (20), 199 (25), 105 (100); elemental analysis calcd (%) for $C_{24}H_{26}O_4$ (378.5) C 76.17, H 6.92; found C 76.71, H 6.86.

**3-[3,3′-Dimethyl-4′-(3-methylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol (1.4/3)**: Obtained from **7l** (0.4 g, 1.0 mmol). Yield: 160 mg (26%); transitions/°C: K 113 ($S_A$ 73) I; $^1$H NMR (200 MHz, CDCl$_3$, 25°C, TMS): $\delta$ = 7.40–7.05 (m, 8H; Ar–H), 6.90 (d, $^3J$(H,H) = 8.6 Hz, 1H; Ar–H), 6.86 (d, $^3J$(H,H) = 9.2 Hz, 1H; Ar–H), 5.06 (s, 1H; Ar–C$H_2$), 4.10–4.05 (m, 3H; ArOC$H_2$, sec. CH), 3.90–3.70 (m, 2H; C$H_2$OH), 2.37 (s, 3H; Ar–C$H_3$), 2.32 (s, 3H; Ar–C$H_3$), 2.27 (s, 3H; Ar–C$H_3$); MS (70 eV, EI): *m*/*z* (%): 392 (45) [*M*]$^+$, 287 (58), 213 (40), 105 (100); elemental analysis calcd (%) for $C_{25}H_{28}O_4$ (392.5): C 76.50, H 7.19; found C 77.52, H 7.18.

**3-[3,3′-Dimethyl-4′-(4-methylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol (1.4/4)**: Obtained from **7h** (0.8 g, 2.0 mmol). Yield: 0.42 g (54%); transitions/°C: K 121 ($S_A$ 109 N 113) I; $^1$H NMR (200 MHz, CDCl$_3$, 25°C, TMS): $\delta$ = 7.40–7.15 (m, 8H; Ar–H), 6.90 (d, $^3J$(H,H) = 8.6 Hz, 1H; Ar–H), 6.85 (d, $^3J$(H,H) = 9.2 Hz, 1H; Ar–H), 5.05 (s, 1H; Ar–C$H_2$), 4.10–4.05 (m, 3H; ArOC$H_2$, sec. CH), 3.90–3.70 (m, 2H; C$H_2$OH), 2.35 (s, 3H; Ar–C$H_3$), 2.31 (s, 3H; Ar–C$H_3$), 2,27 (s, 3H; Ar–C$H_3$); MS (70 eV, EI): *m*/*z* (%): 392 (45) [*M*]$^+$, 287 (58), 213 (40), 105 (100).

**3-[2,3′-Dimethyl-4′-(3-methylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol (2.4/3)**: Obtained from **7k** (0.7 g, 1.6 mmol). Yield: 180 mg (36%); m.p. 95°C; $^1$H NMR (200 MHz, CDCl$_3$, 25°C, TMS): $\delta$ = 7.30–7.00 (m, 6H; Ar–H), 6.89 (d, $^3J$(H,H) = 8.0 Hz, 2H; Ar–H), 6.85–6,70 (m, 3H; Ar–H), 5.06 (s, 1H; Ar–C$H_2$), 4.10–4.05 (m, 3H; ArOC$H_2$, sec. CH), 3.90–3.70 (m, 2H; C$H_2$OH), 2.38 (s, 3H; Ar–C$H_3$), 2.30 (s, 3H; Ar–C$H_3$). 2.25 (s, 3H; Ar–C$H_3$); MS (70 eV, EI): *m*/*z* (%): 392 (67) [*M*]$^+$, 287 (100), 213 (47), 105 (98); elemental analysis calcd (%) for $C_{25}H_{28}O_4$ (392.5) C 76.50, H 7.19; found C 76.40, H 7.34.

**3-[2,3′-Dimethyl-4′-(4-methylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol (2.4/4)**: Obtained from **7i** (0.53 g, 1.2 mmol). Yield: 0.30 g (66%); transitions/°C: K 97 ($S_A$ 93) I; $^1$H NMR (200 MHz, CDCl$_3$, 25°C, TMS): $\delta$ = 7.40–6.7 (m, 10H; Ar–H), 5.08 (s, 1H; Ar–C$H_2$), 4.10–4.05 (m, 3H; ArOC$H_2$, sec. CH), 3.90–3.70 (m, 2H; C$H_2$OH), 2.39 (s, 3H; Ar–C$H_3$), 2.31 (s, 3H; Ar–C$H_3$), 2.27 (s, 3H; Ar–C$H_3$); MS (70 eV, EI): *m*/*z* (%): 392 (45) [*M*]$^+$, 287 (45), 213 (25), 105 (100).

**Synthesis by exchange of the benzyl group**

**4-(4′-Hydroxy-2-methylbiphenyl-4-yloxymethyl)-2,2-dimethyl-1,3-dioxolane**: Obtained according to the procedure for Path B by hydrogenolysis of **7c** (3.5 g, 8.8 mmol). Yield: 2.0 g (75%) of a colorless oil which partially crystallizes on prolonged standing (M.p. 80°C). $^1$H NMR (200 MHz, CDCl$_3$, 25°C, TMS): $\delta$ = 7.17–7.10 (m, 3H; Ar–H), 6.88–6.75 (m, 4H; Ar–H), 5.15 (br s, 1H; OH), 4.51 (m, 1H; sec. CH), 4.23–3.89 (m, 4H; OC$H_2$), 2.24 (s, 1H; Ar–C$H_3$), 1.49 (s, 3H; C$H_3$), 1.42 (s, 3H; C$H_3$).

**3-(4′-Hydroxy-2-methylbiphenyl-4-yloxy)propane-1,2-diol**: Obtained from 4-(4′-hydroxy-2-methylbiphenyl-4-yloxymethyl)-2,2-dimethyl-1,3-dioxolane (3.0 g, 9.6 mmol) by hydrolysis according to the general procedure for Path A. Purified by crystallization from *n*-hexane/ethyl acetate 5:4 (90 mL). Yield: 1.5 (57%); transitions/°C: K 80 $S_A$ 89 I; $^1$H NMR (200 MHz, [D$_6$]DMSO, 25°C, TMS): $\delta$ = 9.40 (br s, 1H; Ar-OH), 7.12–7.04 (m, 3H; Ar–H), 6.86–6.76 (m, 4H; Ar–H), 4.9 (br s, 1H; sec. OH), 4.65 (br s, 1H; prim. OH), 4.04–3.84 (m, 3H; ArOC$H_2$, sec. CH), 3.49–3.39 (m, C$H_2$OH, overlapped by $H_2$O), 2.21 (s, 3H; Ar–C$H_3$); elemental analysis calcd (%) for $C_{16}H_{18}O_4$ (274.3): C 70.06, H 6.61; found C 70.29, H 6.69.

**3-[2-Methyl-4′-(2-methylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol (2/2)**: Synthesized according to the general procedure for Path B from 3-(4′-hydroxy-2-methylbiphenyl-4-yloxy)propane-1,2-diol (0.5 g, 1.8 mmol) and 2-methylbenzylbromide (0.25 mL, 1.9 mmol). Yield: 0.12 g (17%); m.p. 100°C; $^1$H NMR (200 MHz, [D$_6$]DMSO, 25°C, TMS): $\delta$ = 7.45 (m 1H; Ar–H), 7.25 (m, 5H; Ar–H), 7.19 (m, 3H; Ar–H), 6.85 (m, 2H; Ar–H), 5.13 (s, 2H; Ar–C$H_2$), 4.94 (d, $^3J$(H,H) = 4.9 Hz, 1H; sec. OH), 4.66 (t, $^3J$(H,H) = 5.6 Hz, 1H; prim. OH), 4.10–3.75 (m, 3H; ArOC$H_2$, sec. CH), 3.47 (dd, $^3J$(H,H) = 5.5 Hz, $^3J$(H,H) = 5.5 Hz, 2H; C$H_2$OH), 2.37 (s, 3H; Ar–C$H_3$), 2.23 (s, 3H; Ar–C$H_3$); MS (ESI): *m*/*z* (%): 401.2 (20) [*M*+Na]$^+$, 778.9 (100) [2*M*+Na]$^+$; elemental analysis calcd (%) for $C_{24}H_{26}O_4$ (378.5): C 76.17, H 6.92; found C 76.08, H 7.29.

**3-[2-Methyl-4′-(3-methylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol (2/3)**: Synthesized according to the general procedure for Path B from 3-(4′-hydroxy-2-methylbiphenyl-4-yloxy)propane-1,2-diol (0.65 g, 2.37 mmol) and 3-methylbenzylbromide (0.35 mL, 2.6 mmol). Yield: 0.28 g (31%); transitions/°C: K 95 (Iso 70) I; $^1$H NMR (200 MHz, [D$_6$]DMSO, 25°C, TMS): $\delta$ = 7.31–6.78 (m, 11H; Ar–H), 5.1 (s, 1H; Ar–C$H_2$), 4.93 (d, $^3J$(H,H) = 5.0 Hz, 1H; sec. OH), 4.66 (t, $^3J$(H,H) = 5.7, 1H; prim. OH), 4.10–3.75 (m, 3H; ArOC$H_2$, sec. CH), 3.48 (m, 2H; C$H_2$OH), 2.35 (s, 3H; Ar–C$H_3$), 2.22 (s, 3H; Ar–C$H_3$); MS (ESI): *m*/*z* (%): 401.2 (24) [*M*+Na]$^+$, 778.9 (100) [2*M*+Na]$^+$; elemental analysis calcd (%) for $C_{24}H_{26}O_4$ (378.5): C 76.17, H 6.92; found C 76.16, H 6.82.

**3-[2-Methyl-4′-(4-methylbenzyloxy)biphenyl-4-yloxy]propane-1,2-diol (2/4)**: Synthesized according to the general procedure for Path B from 3-(4′-hydroxy-2-methylbiphenyl-4-yloxy)propane-1,2-diol (0.27 g, 1.0 mmol) and 4-methylbenzylbromide (0.15 mL, 1.1 mmol). Yield: 0.15 g (54%); transitions/°C: K 131 (Iso 95 $S_A$ 115) I; $^1$H NMR (200 MHz, [D$_6$]DMSO, 25°C, TMS): $\delta$ = 7.37 (d, 2H; $^3J$(H,H) = 8.0 Hz, Ar–H), 7.22 (d, $^3J$(H,H) = 8.7 Hz, 4H; Ar–H), 7.10–7.01 (m, 3H; Ar–H), 6.90–6.70 (m, 2H; Ar–H), 5.1 (s, 1H; Ar–C$H_2$), 4.92 (d, $^3J$(H,H) = 5.0 Hz, 1H; sec. OH), 4.65 (t, $^3J$(H,H) = 5.7 Hz, 1H; prim. OH), 4.10–3.84 (m, 3H; ArOC$H_2$, sec. CH), 3.48 (dd, $^3J$(H,H) = 5.5 Hz, $^3J$(H,H) = 5.5 Hz, 2H; C$H_2$OH), 2.33 (s, 3H; Ar–C$H_3$), 2.21 (s, 3H; Ar–C$H_3$); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C, TMS): $\delta$ = 159.3, 158.8, 138.6, 137.6, 135.7, 135.1, 135.0, 132.1, 131.7, 130.6, 129.4, 117.8, 116.0, 113.5, 71.4, 71.0, 70.6, 64.2, 22.1, 21.9; MS (70 eV, EI): *m*/*z* (%): 378 (16) [*M*]$^+$, 279 (3), 199 (8), 105 (100).

**Synthesis of compounds 1/Ph and 2/Ph**

**4-Phenyloxyphenylboronic acid (8)**:[21] Synthesized according to the general procedure for compounds **6** from 4-bromodiphenyl ether (12.5 g, 50 mmol). The product was filtered off with suction from *n*-pentane, dissolved in ethyl acetate (40 mL), and precipitated with *n*-hexane (70 mL). The product was used without further purification. Yield: 8.3 g (78 %); m.p. 115 °C; $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 7.96$ (s, 2H; OH), 7.78 (d, $^3J$(H,H) = 8.6, 2H; Ar–H), 7.4 – 6.7 (m, 7H; Ar–H).

**4-(3-Methyl-4′-phenyloxybiphenyl-4-ylmethyl)-2,2-dimethyl-1,3-dioxolane (9)**: Synthesized according to the general procedure for the Suzuki cross-coupling reactions from **5b** (2.0 g, 6.6 mmol) and **8** (1.2 g, 6.0 mmol). The product was obtained as a pale yellow oil, which was used without further purification. Yield: 1.51 g (58 %).

**4-(2-Methyl-4′-phenyloxybiphenyl-4-ylmethyl)-2,2-dimethyl-1,3-dioxolane (9b)**: Synthesized according to the general procedure for the Suzuki cross-coupling reactions from **5d** (2.0 g, 6.6 mmol) and **8** (1.2 g, 6.0 mmol). The product was obtained as a pale yellow oil which was used without further purification. Yield: 1.75 g (67 %).

**3-(3-Methyl-4′-phenyloxybiphenyl-4-yloxy)propane-1,2-diol (1/Ph)**: Synthesized according to the general procedure for Path A from **9a** (1,0 g, 2.6 mmol). Purified by repeated crystallization from *n*-hexane/ethyl acetate 10:4 (20 mL, crystallization overnight at – 29 °C). Yield: 91 mg (10 %); m.p. 110 °C; $^1$H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 7.61$ (m, 2H; Ar–H), 7.43 – 7.36 (m, 4H; Ar–H), 7.14 (t, $^3J$(H,H) = 7.3 Hz, 1H; Ar–H), 7.06 – 7.01 (m, 4H; Ar–H), 6.97 (d, $^3J$(H,H) = 8.4 Hz, 1H; Ar–H), 4.90 (d, $^3J$(H,H) = 5.0 Hz, 1H; sec. OH), 4.63 (t, $^3J$(H,H) = 5.4 Hz, 1H; prim. OH), 4.03 – 3.77 (m, 3H; ArOCH$_2$, sec. CH), 3.57 – 3.50 (m, 2H; C*H*$_2$OH), 2.21 (s, 3H; Ar–CH$_3$); $^{13}$C NMR (100 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 158.4$, 158.0, 157.2, 137.0, 133.0, 131.6, 130.1, 129.2, 128.0, 126.4, 125.0, 120.5, 120.2, 113.2, 71.5, 71.1, 64.3, 17.5; MS (ESI): *m*/*z* (%): 373.1 (42) [*M*+Na]$^+$, 722.8 (100) [2*M*+Na]$^+$.

**3-(2-Methyl-4′-phenyloxybiphenyl-4-yloxy)propane-1,2-diol (2/Ph)**: Synthesized according to the general procedure for Path A from **9b** (1.5 g, 3.8 mmol). Purified by repeated crystallization from *n*-hexane/ethyl acetate 1:1 (20 mL, crystallization overnight at -29 °C ). Yield: 0.36 g (27 %); m.p. 80 °C; $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 7.50 – 6.80$ (m, 12H; Ar–H), 4.94 (d, $^3J$(H,H) = 5.1 Hz, 1H; sec. OH), 4.67 (t, $^3J$(H,H) = 5.7 Hz, 1H; prim. OH), 4.10 – 3.75 (m, 3H; ArOCH$_2$, sec. CH), 3.47 (m, 2H; C*H*$_2$OH), 2.25 (s, 3H; Ar–CH$_3$); elemental analysis calcd (%) for C$_{22}$H$_{22}$O$_4$ (350.4): C 75.41, H 6.33; found C 75.09, H 6.41.

**Synthesis of compound 2/EO**

**1-Bromo-2-methyl-4-(3-oxahex-5-enyloxy)benzene (10)**: A mixture of 4-bromo-3-methylphenol (21 g, 113 mmol), 1-(4-toluylsulfonyloxy)-3-oxa-5-hexene (32 g, 125 mmol), and $K_2CO_3$ (52 g, 377 mmol) in dry acetonitrile (300 mL) was stirred under reflux for 6 h (TLC). After the reaction was finished, water (200 mL) was added, and the mixture was extracted with ether (3 × 70 mL). The combined extracts were washed with water (2 × 75 mL). After drying with $Na_2SO_4$ and evaporation of the solvent, the product was purified by distillation in vacuo. Yield: 21.8 g (72 %); b.p. 122 °C/0.075 Torr; $^1$H NMR (200 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 7.37$ (d, $^3J$(H,H) = 8.6 Hz, 1H; Ar–H), 6.81 (d, $^4J$(H,H) = 2.9 Hz, 1H; Ar–H), 6.63 (dd, $^3J$(H,H) = 8.8 Hz, $^4J$(H,H) = 2.9 Hz, 1H; Ar–H), 6.03 – 5.83 (m, 1H; C*H*=CH$_2$), 5.36 – 5.25 (dd, $^2J$(H,H) = 7.2 Hz, $^3J$(H,H) = 1.7 Hz, 1H; *trans*–CH=C*H*$_2$), 5.24 – 5.17 (dd, $^2J$(H,H) = 10.3 Hz, $^3J$(H,H) = 1.7 Hz, 1H; *cis*–CH=C*H*$_2$), 4.07 (m, 4H; ArOCH$_2$-, OC*H*$_2$–CH=CH$_2$), 3.77 (m, 2H; ArOCH$_2$C*H*$_2$O), 2.35 (s, 3H; Ar–CH$_3$).

**6-(4-Bromo-3-methylphenyloxy)-4-oxahexane-1,2-diol (11)**: Synthesized according to the general procedure for the 3-aryloxypropane-1,2-diols from **10** (4.1 g, 15.2 mmol). Purified by flash chromatography (silica gel, 3 × 25 cm, starting with hexane/ethyl acetate 10:6 after all apolar impurities had been eluted, pure ethyl acetate was used. Yield: 1.4 g (38 %); $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 7.44$ (d, $^3J$(H,H) = 8.5 Hz, 1H; Ar–H), 6.90 (d, $^4J$(H,H) = 3.0 Hz, 1H; Ar–H), 6.75 (dd, $^3J$(H,H) = 8.8 Hz, $^4J$(H,H) = 3.0 Hz, 1H; Ar–H), 4.15 – 3.30 (m, 11H; OCH$_2$, OH), 2.31 (s, 3H; Ar–CH$_3$).

**4-[4-(4-Bromo-3-methylphenyloxy)-2-oxabutyl]-2,2-dimethyl-1,3-dioxolane (12)**: Acetalization was carried out according to the procedure for compounds **5** from **11** (19.0 g, 62.3 mmol). The product was used without further purification. Yield: 21 g (98 %) of a pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 7.36$ (d, $^3J$(H,H) = 8.7 Hz, 1H; Ar–H), 6.78 (d, $^4J$(H,H) = 2.5 Hz, 1H; Ar–H), 6.60 (dd, $^3J$(H,H) = 8.7 Hz, $^4J$(H,H) = 2.6 Hz, 1H; Ar–H), 4.28 (m, 2H; sec. CH), 4.10 – 3.50 (m, 8H; OCH$_2$), 2.33 (s, 3H; Ar–CH$_3$), 1.41 (s, 3H; CH$_3$), 1.34 (s, 3H; CH$_3$).

**4-[4-(4′-Benzyloxy-2-methylbiphenyl-4-yloxy)-2-oxabutyl]-2,2-dimethyl-1,3-dioxolane (13)**: Synthesized according to the procedure for the Suzuki cross-coupling reactions from **12** (14.0 g, 40.6 mmol) and 4-benzyloxyphenylboronic acid (**6a**, 8.5 g, 40 mmol). Work-up procedure: The solvent was removed in vacuo and the aqueous residue was extracted with ethyl acetate (2 × 100 mL). The solvent was again removed under reduced pressure, the residue taken up in CHCl$_3$ (50 mL), and filtered over silica gel with suction. The compound was used as the crude product. Yield: 17.3 g (95 %) pale yellow oil; $^1$H NMR (200 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 7.46 – 7.34$ (m, 5H; Ar–H), 7.26 – 7.11 (m, 3H; Ar–H), 7.02 (d, $^3J$(H,H) = 8.8 Hz, 2H; Ar–H), 6.84 (m, 2H; Ar–H), 5.11 (s, 2H; Ar–CH$_2$), 4.32 (m, 1H; sec. CH), 4.20 – 3.55 (m, 8H; OCH$_2$, sec. CH), 2.26 (s, 3H; Ar–CH$_3$), 1.45 (s, 3H; CH$_3$), 1.38 (s, 3H; CH$_3$).

**6-[4′-Benzyloxy-2-methylbiphenyl-4-yloxy)-4-oxahexane-1,2-diol (2/EO)**: Synthesized according to the general procedure for Path B from **13** (5.0 g 11.2 mmol). Purified by repeated crystallization from *n*-hexane/ethyl acetate 7:2 (90 mL) (crystallization with vigorous stirring at – 30 °C after hot filtration). Yield: 1.5 g (33 %); K 60 (S$_A$ 23) I; $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 7.55 – 7.30$ (m, 5H; Ar–H), 7.23 (d, $^3J$(H,H) = 8.8 Hz, 2H; Ar–H), 7.06 (m, 3H; Ar–H), 6.84 (m, 2H; Ar–H), 5.15 (s, 2H; Ar–CH$_2$), 4.66 (d, $^3J$(H,H) = 4.9 Hz, 1H; sec. OH), 4.50 (t, $^3J$(H,H) = 5.6 Hz, 1H; prim. OH), 4.12 (m, 2H; ArOCH$_2$), 3.76 (m, 2H; ArOCH$_2$-C*H*$_2$O), 3.70 – 3.30 (m, 5H; OC*H*$_2$C*H*(OH)C*H*$_2$OH), 2.22 (s, 3H; CH$_3$); MS (70 eV, EI): *m*/*z* (%): 408 (100) [*M*]$^+$, 317 (82), 243 (10), 199 (90), 91 (88), 75 (10); elemental analysis calcd (%) for C$_{25}$H$_{28}$O$_5$ (408.5): C 73.51, H 6.91; found C 73.45, H 7.03.

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