Synthesis and mesophase characterization of non-conventional polyphilic block molecules with perfluorinated chains

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Thanks are due to my family and my friends for their support and encouragement.

Abbreviations

Chemical material

AcOH	Acetic acid
Ar	Aromatic
n-Bu	n-Butyl group
Bzl	Benzyl
CMC	*N*-Cyclohexyl-*N*′-(2-morpholinoethyl)carbodiimide methyl-p-toluenesulfonate
DMAP	4-Dimethylaminopyridine
DMF	*N*,*N*-Dimethylformanide
EtOAc	Ethyl acetate
Et	Ethyl
EtOH	Ethanol
MeOH	Methanol
NBS	*N*-Bromosuccinimide
NMMNO	*N*-Methylmorpholine-*N*-oxide
Ph	Phenyl
PPTS	Pyridiniumtosylate
THF	Tetrahydrofuran

Spectroscopy

DSC	Differential scanning calorimetry
δ	Chemical shift
Ms	Mass spectroscopy
NMR	Nuclear magnetic resonance
prim	Primary
sec	Secondary
d	Doublet
dd	Doubled doublet
m	Complex multiplet
q	Quartet
t	Triplet
J	Coupling constant
s	Singlet
br s	Broad singlet

Phase Name

Col	Columnar mesophase
Col_r	Rectangular columnar phase
Col_{rc}	Centered rectangular columnar phase (*c*2*mm*)
Col_{rp}	Non-centered rectangular columnar phase (*p*2*gg*)
Col_t	Tetragonal columnar phase (*p4mm*)
Col_h	Hexagonal columnar phase (*p6mm*)
Col_{rpm}	Non-centered rectangular columnar phase (*p*2*mg*)
Col_{ob}	Oblique columnar phase
Col(L)	Tentative assignment of Mesophases with a typical texture of a columnar phase, showing a well defined layer structure in X-ray investigations
$L_{Sm}(Col_r)$	Laminated smectic phase, in which adjacent layers have a positional and orientational correlation
$L_{Sm}(Col_L)$	Laminated smectic phase, in which adjacent layers have only an orientational correlation (sliding laminated smectic phase or lamellar columnar phase)
$L_{Sm\sim}$	Laminated modulated smectic phase
L_N	Laminated nematic phase
Cr	Crystalline phase
Cub_V	Bicontinuous cubic phase
Cub_I	Discontinuous cubic phases
Iso	Isotropic liquid phase
N	Nematic phase
SmA or S_A	Smectic A phase
SmA^+	Disordered SmA-phase (typical SmA texture, but in the small angle region of the X-ray pattern a diffuse reflection is found instead or beside the layer reflection)
Smb	Optically biaxial smectic phase

Others

a	Lattice parameter of columnar or cubic mesophases
d	Layer periodicity
T	Temperature
TLC	Thin-layer chromatography
RT	Room temperature (25 °C)

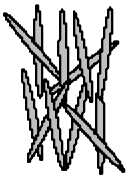
Contents

1 General introduction

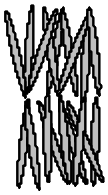
1.1 The concept of liquid crystalline mesophases

Liquid crystalline phases are formed as intermediate phases (mesophases) during the transition from the highly ordered crystalline solid to the disordered isotrop liquid states.[1] This state of mater combines order and mobility on a molecular level.
According to classic concepts, molecules being able to produce liquid crystalline phases are divided into two main classes: anisometric (rod-like or disc-like) molecules and amphiphilic molecules (surfactants).

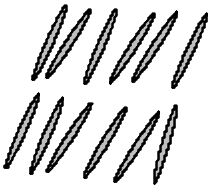
Rod-like molecule



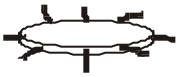
Nematic phase (N)



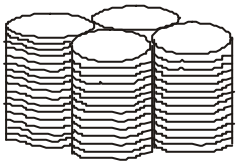
Smectic A phase (SmA)



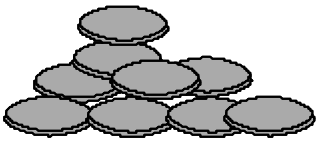
Smectic C phase (SmC)



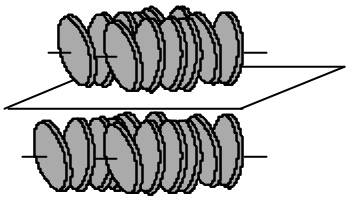
Disc-like molecule



Columnar phase (Col)



Discotic nematic phase (N_D)



Lamellar columnar phase (Col_L)

Figure 1.1 *Mesophases formed by rod-like molecules and disc-like molecules.*

In most cases, anisometric molecules form exclusively thermotropic mesophases whose mesomorphic properties are dependent on temperature.[2] Calamitic (rod-like) molecules can form nematic and/or smectic phases. In the nematic phase, the molecules maintain an orientational direction, while they do not have positional order. In smectic phases, besides the orientational order, the molecules are arranged in layers; if the long axes of the molecules are in average perpendicular to the plane of the layers, it is called smectic A

mesophase; if the molecules are uniformly tilted, it is a smectic C phase; if the smectic phase involves a hexagonal positional order in the plane of the layers, it is called smectic B phase. The most common mesophases formed by discotic molecules are columnar mesophases,[3] in which the molecules stack into columns which can further arrange into different lattices corresponding to hexagonal, rectangular and oblique columnar phases, sometimes discotic molecules can form nematic phases (in which the positional order is lost and the short axes of the molecules preferably align parallel) and smectic phases namely, the discotic lamellar and the lamellar columnar phases (see Figure 1.1).[4,5]

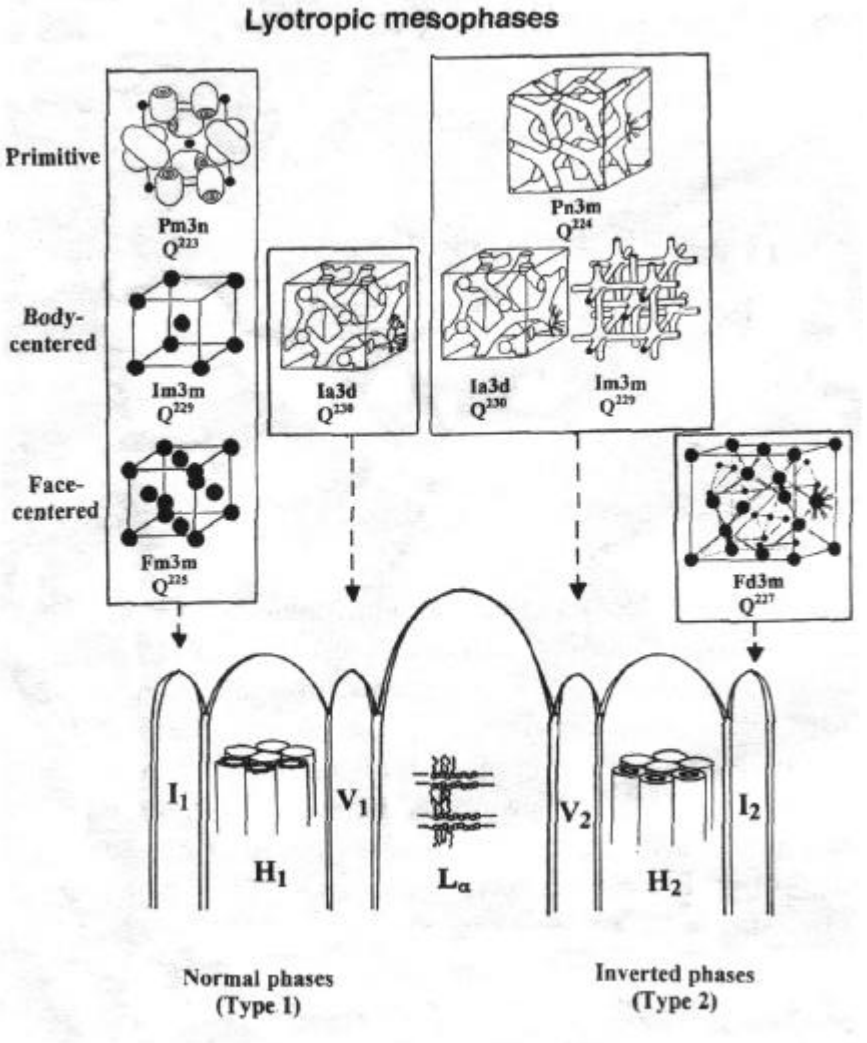


Figure 1.2 *Mesophases formed in lyotropic system.*

Amphiphilic molecules consisting of a hydrophilic headgroup and a hydrophobic part can form thermotropic and/or lyotropic mesophases whose mesomorphic properties change with the concentration of an additional solvent and the temperature.[6] The driving forces for the formation of liquid crystalline phases of amphiphilic molecules are the micro-segregation[7] of hydrophilic and the lipophilic molecular parts into different regions, as well as the strong attractive forces between the hydrophilic headgroups, such as intermolecular hydrogen bonding and coulomb force. Apart from the lamellar (smectic) and columnar mesophases,

different cubic phases have been detected in thermotropic and lyotropic phase sequences of amphiphilic molecules.[8,9] The mesophases formed in lyotropic system are schematically shown in Figure 1.2.

According to the sign of the interface curvature between hydrophilic and lipophilic regions, normal phases (type 1, in which the interface curvature between hydrophilic regions and lipophilic regions is directed away from the regions with stronger cohesive interaction) and inverted phases (type 2, in which the interface curvature is directed towards the regions with stronger cohesive interaction) are distinguished in lyotropic systems. At zero interface curvature the lamellar (Smectic A) phase occurs. As the absolute value of the curvature increases, the formation of cylindrical aggregates of the columnar mesophase takes place via bicontinuous cubic mesophases. As the interface curvature is further increased, the transition from the hexagonal columnar to a micellar cubic mesophase takes place.

Hence, cubic phases can occur as intermediate phases between lamellar and hexagonal columnar phases (bicontinuous cubic phase, V-phases), or between hexagonal columnar phases and micellar solutions (discontinuous cubic phases, I-phases). Bicontinuous cubic phases can be regarded as interwoven networks of branched columns, while the discontinuous cubic phases consist of closed spherical or nonspherical micelles.[10] Several different types of micellar cubic phases have been found in lyotropic system. In type 1-systems, *Pm*3*n* cubic phases are most common, however, it has been recently reported, that by increasing the content of water the *Pm*3*n* can be replaced by a body centered cubic phase of space group *Im*3*m* and a face centered cubic I_1-phase (space group *Fm*3*m*).[11] Exclusively micellar cubic phases of the space group *Fd*3*m* have been observed in lyotropic type 2 systems.[12]

Bolaamphiphilic molecules represent a special type of amphiphilic molecules, which have hydrophilic headgroups at both ends of the hydrophobic molecular part.[13] Unlike the conventional amphiphilic molecules which form bilayer smectic phases, these molecules. form monolayer smectic phases. Only few reports on columnar and cubic phases of bolaamphiphiles have occurred.[14]

1.2 Block copolymers and block molecules

Block copolymers consisting of chemically or structurally different blocks (Figure 1.3), can form the same mesophase types as those found for low molecular weight amphiphiles, but on a significantly larger lengths scale.[15,16,17] The microsegregation of the incompatible blocks into different regions, which are separated by interfaces is the main driving force for their mesogenity. The microsegregation itself depends on the size of the blocks and the degree of the chemical and structural differences among the blocks. Important parameters that govern the microsegregation of AB diblock-copolymer are the total degree of the polymerization $N = N_A+N_B$, the segment interaction parameter $\chi = V_R (\delta_A-\delta_B)^2 / RT$ (V_R, a reference volume, δ_A, δ_B are the different solubility parameters) and the volume fraction of the components f.[18]

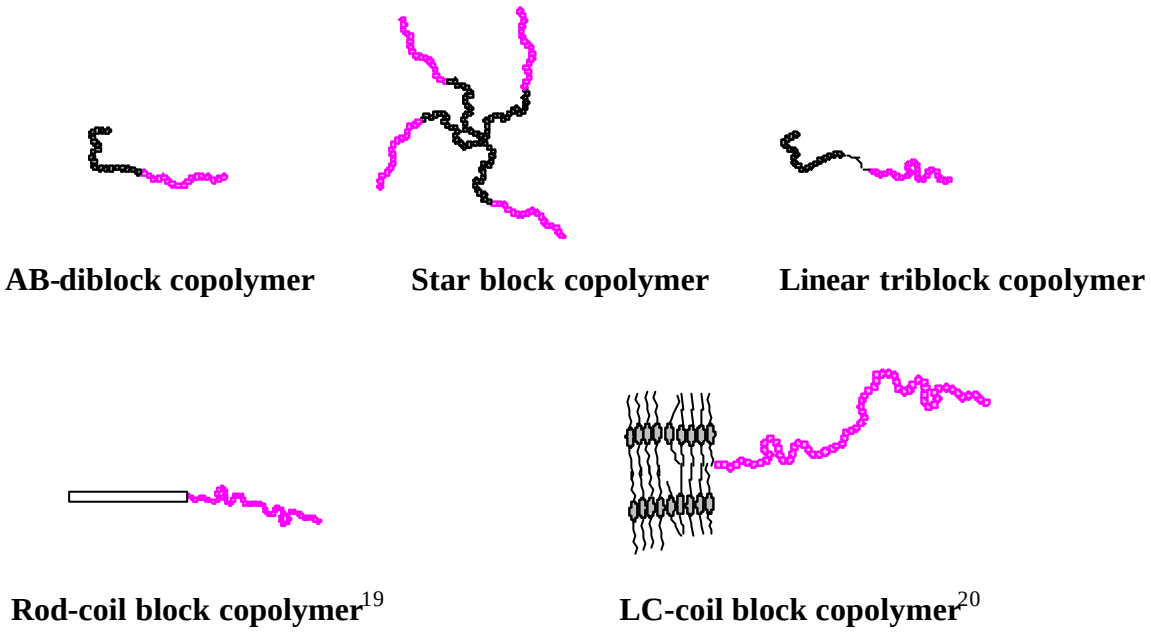


Figure 1.3 *Some examples of block copolymers.*

The product of N and χ decides the occurrence of the microsegregation. Since χ depends on temperature, microsegregation is temperature dependent and occurs below a certain order-disorder transition temperature. The parameter f determines the morphology of the formed structures, namely the curvature of the interface between the different regions.

The mesophases formed by the block copolymers are striking analogous to those formed by amphiphilic and anisometric molecules.[21] Actually, most liquid crystalline molecules can be regarded as low molecular weight analogues of block copolymers consisting of chemical or structural different building blocks (hydrophilic / lipophilic, polar / non-polar, hydrocarbon / fluorocarbon, oligosiloxane / hydrocarbon or rigid / flexible). The thermotropic and

lyotropic mesophases can be regarded as the consequence of the division of space into different regions separated by interfaces, generated by the aggregation of the blocks with different affinities. The stability of the mesophase depends on the degree of the chemical and structural difference and the size of the different building blocks. If the different units are very large as in block copolymers, even very small differences in chemical structure can give rise to microsegregation; if the blocks are small, the chemical difference between the blocks has to be increased.

The mesophase type depends on the interfacial curvature separating the different regions: Planar interfaces in smectic phases, cylindrical interfaces in columnar phases and three dimensionally bent interfaces in the cubic phases and other 3D-mesophases.

If the molecules are rigid, the formation of flat (calamitic molecules) and cylindrical (disc-like molecules) interfaces is favored; if the molecules are flexible (amphiphiles, blockcopolymers), then different mesophases can be found.

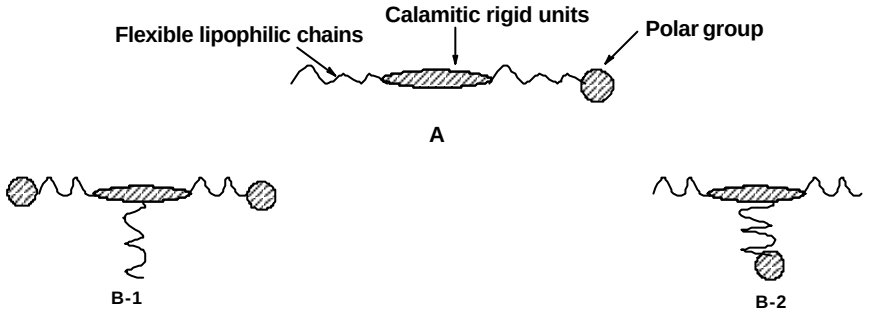


Figure 1.4 *Different topologies obtained by the combination of the rigid units, flexible chains and polar groups.*

Recently, in order to design new types of mesogens, different molecular structures have been combined. For example, hydrophobic parts of amphiphilic molecules have been replaced by anisometric rigid units.[22,23]In this way, there are two driving forces for their self-organization. One is the parallel arrangement of the anisometric rigid units, the other is the micro-segregation of incompatible molecular parts. If these two driving forces are combined in such a way that they act in the same direction, they can enhance each other. This cooperative combination of microsegregation and rigidity is found in calamitic molecules, where the polar groups are fixed in a terminal position (see Figure 1.4: A).[24,55a] Another designing principle makes use of the combination of micro-segregation and rigidity in a competitive manner. For example, the lipophilic chains can be connected in lateral positions to bolaamphilphilic molecules (Figure1.4: B-1)[25] or polar groups can be located in the lateral position of a calamitic core (Figure 1.4: B-2).[26] This could lead to novel block-molecules, which are able to build up novel non-conventional supramolecular structure, related to those of multiblock-copolymers.[27]

1.3 Liquid crystals with perfluorinated chains

Because of the unique thermal, mechanic and dielectric properties of fluorinated materials, as for example Teflon and polyvinylidenfluoride, they have many technical applications. Liquid crystals containing fluorinated aromatic segments or trifluoromethyl groups have attracted much attention owing to their excellent properties for liquid crystal display application.[28,29]

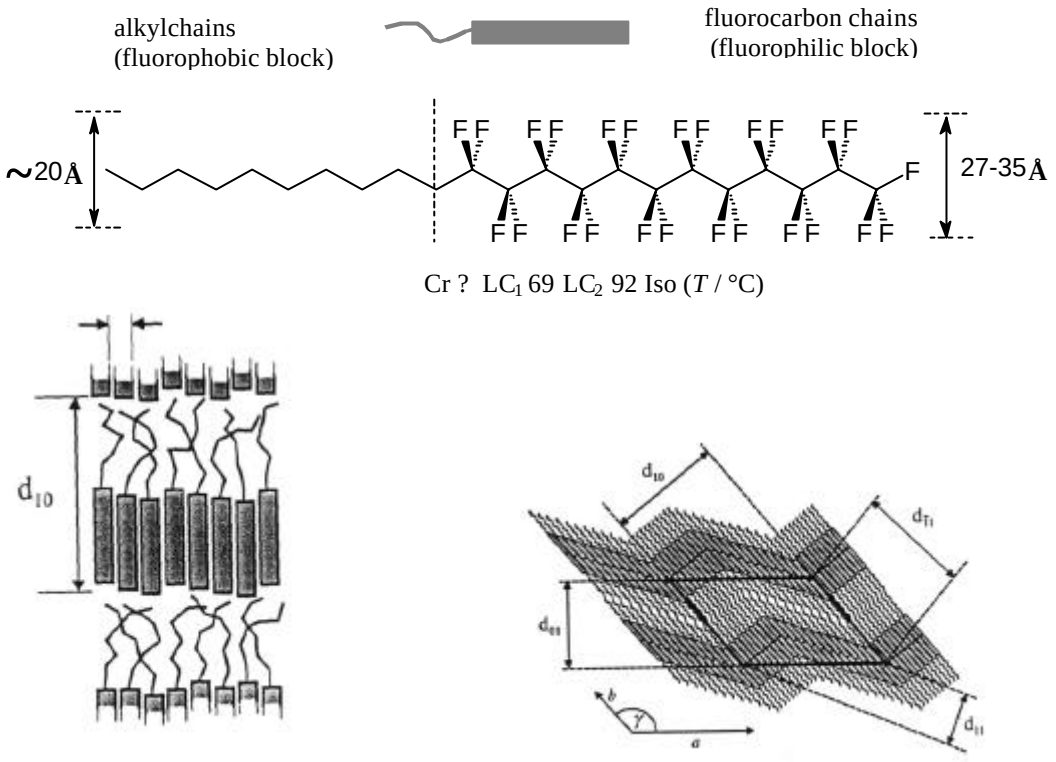


Figure 1.5 *Mesophases formed by partly fluorinated alkanes F-$(CF_2)_m$-$(CH_2)_n$-H: (a) model of the lamellar high-temperature phase; (b) undulated bilayer model of the low-temperature phase.*[32]

But only recently, liquid crystals containing longer perfluorinated chains were studied. Generally, liquid crystals incorporating perfluoroalkyl chains are known to show smectic properties.[30] Even very simple molecules as for example diblock molecules combining a hydrocarbon and a fluorocarbon chain form smectic liquid-crystalline phases (Figure 1.5).[31,32]

Also molecules with only one aromatic ring and fluorinated segments represented smectic mesophases, while their related hydrocarbon compounds are non- mesomorphic.[33]

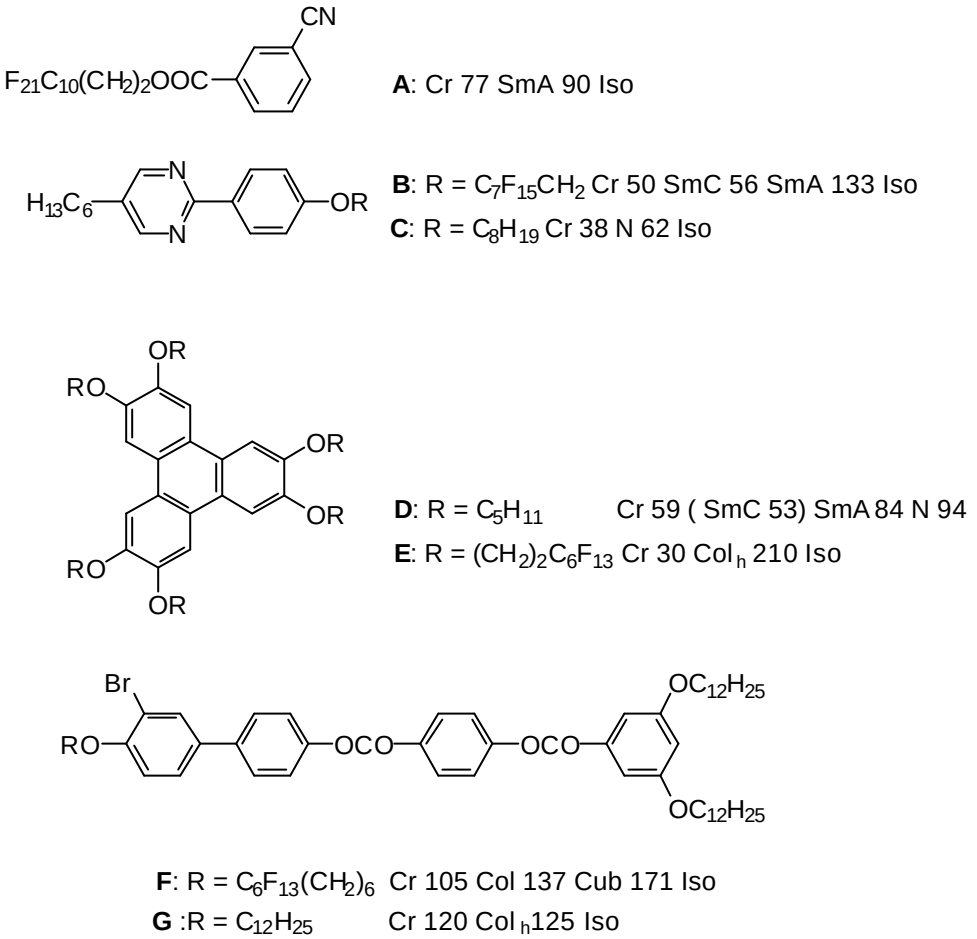


Figure 1.6 *Representative examples for the influence of the perfluorinated segments on the liquid crystalline properties of calamitic molecules (**A**, **B**, **C**),*[35a] *disk-like molecules (**D**, **E**)*[36] *and polycatenar molecules (**F**, **G**).*[34]

Attachment of fluorinated alkyl chains to rod like mesogens leads to an enhanced stability of their smectic phases.[35] Replacing the alkyl chains of disc-like molecules,[36] taper-shaped molecules and copolymers built up of tapered units by perfluorinated chains, stabilizes their columnar phases too.[37] Perfluorinated chains not only cause a phase stabilization, but also a variation of the mesophase structure. So nematic phases are replaced by smectic ones, and a diversity of mesophases was observed in polycatenar molecules with perfluorinated chains; as for example two-dimensional modulated smectic phases (SmA, SmC), columnar and cubic mesophases (Figure 1.6).[38]

These influences can be due to some special properties of the perfluorinated chains.[39]

1. The van der Waals radius of fluorine (0.147 nm) is larger than that of hydrogen (0.12 nm). Therefore the cross-section area of a perfluorinated chain (0.27-0.35 nm^2) is much larger than those of alkyl chains (0.18-0.20 nm^2) and biphenyl moieties (ca. 0.22 nm^2).
2. The energy barrier between *trans* and *gauche* conformation, as well as between different *gauche* conformations are 3-5 times higher than those in the linear hydrocarbons.

3. Due to steric reasons, the perfluoroalkyl chains are more rigid than alkyl chains,[38,39] and they adapt a helical conformation.[40]
4. The dipole moment of the CF_2 group (2-3 D) is larger than that of CH_2 group, this may induce local dipolar repulsion between the perfluoroalkyl chains of the neighboring molecules.
5. The cohesive energy between perfluoroalkyl chains (10-15 mN/m) is lower than between hydrocarbon chains (30 mN/m) and between water molecules (72 mN/m). This leads to an incompatibility of perfuoroalkyl chains with water, with aliphatic and with aromatic hydrocarbon.[41]

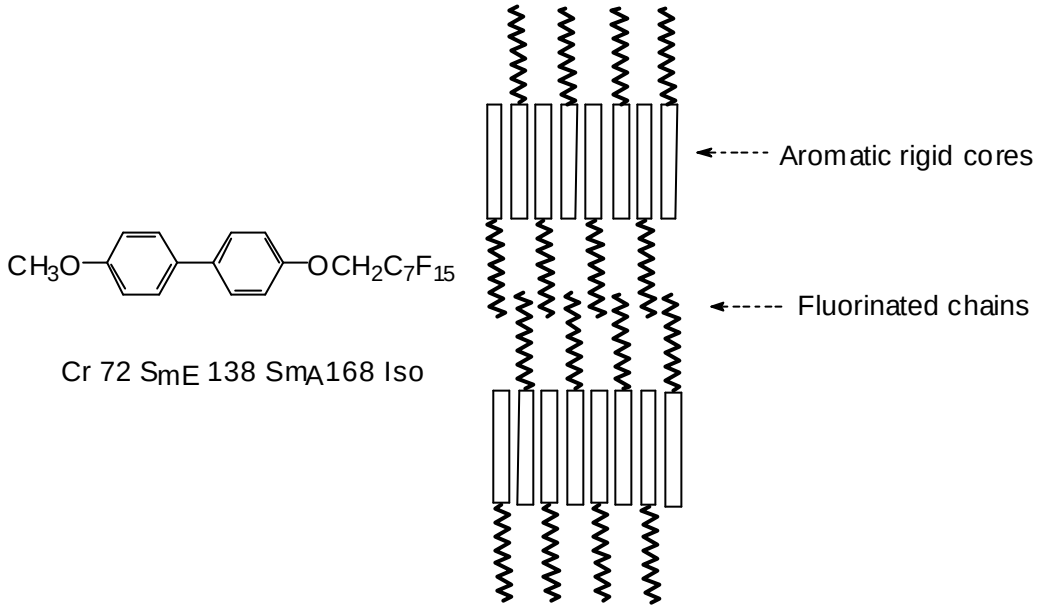
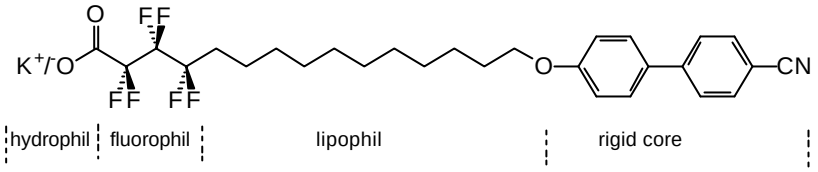


Figure 1.7 *A complete segregation of fluorinated chains and aromatic segments.*[43]

The incompatibility of perfluorinated hydrocarbons (R_F) and non-fluorinated hydrocarbons (R_H) is denoted as fluorophobic effect. Because of the fluorophobic effect, R_F-R_H diblock molecules (see Figure 1.5) represent amphiphiles, which can form micelles and bilayer aggregates in both hydrocarbon and fluorinated solvents.[42] The incompatibility between the perfluorinated block and the alkyl block is also responsible for the formation of separate alternating sublayers leading to mesophases.

Combination of the fluorinated chains with calamitic segments, such as biphenyl units leads to smectic phases with enhanced mesophase stabilities. In the calamitic compounds, shown in Figure 1.7, for example, the aromatic segments are completely interdigitated and ordered in an orthorhombic cell, while the fluorinated chains remain liquid-like disordered. Here, the stress caused by the different space filling of the intercalated aromatic cores (2×0.22 nm^2) and the non-intercalated perfluoroalkyl chains (0.27-0.36 nm^2) is released by folding the perfluoroalkyl chains.[43] The recently reported semifluorinated carboxylate **H**[44] is the

first example of an amphotropic molecule consisting of four different incompatible segments (Figure 1.8). These molecules represent amphiphilic block molecules in which rigid segments and micro-segregation enhance each other, leading to predominately smectic phases.



Cr 135 (SmC 135) SmA 190 Iso

Figure 1.8 *Four block semifluorinated carboxylate **H**.*

It should also be emphasized that, not in all cases, the influence of the perfluorinated chain on the liquid crystalline properties is in line with the properties expected from the special features of fluorinated chains. For example, despite of the incompatibility between the fluorinated and non-fluorinated segments, several diblockmolecules form monolayer structure, in which the perfluorinated chains and the alkyl chains are not separated.[45] Furthermore, it was reported, that in LB-films, the perfluorinated chains can adapt a non-helical conformation.[46] In this way, the influence of the perfluorinated chains on molecular self-organization is very complicated. Hence, the syntheses of new low molecules comprising fluorinated chains and their systematic investigation are of contemporary scientific interest.

1.4 Objectives

Therefore, the aim of this work is to introduce perfluorinated chains into several classes of non conventional low molecular weight block molecules shown in Figure 1.9, which were firstly studied in our laboratories.[48,55,57,25,61]

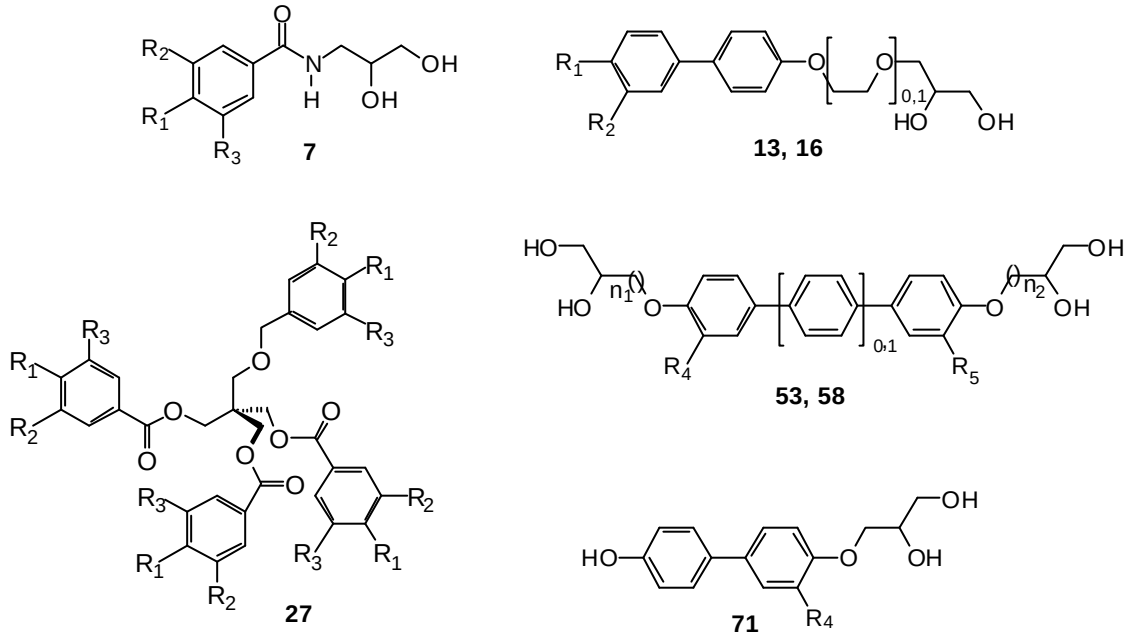
Our interest will be focused on the following key points:

1) Replacement of alkyl chains in the polyhydroxy amphiphiles **7**[48] by perfluorinated chains. Here, we want to know, whether it would be possible to change the cubic lattice type of the thermotropic inverted (type 2) micellar cubic phases from *Pm*3*n* to *Im*3*m* or *Fm*3*m* by increasing the size of the lipophilic molecular parts in the same way as the cubic lattice of the type 1 micellar cubic phases of the lyotropic $C_{12}EO_{12}$-system has been changed from *Pm*3*n via Im*3*m* to *Fm*3*m* by increasing the water concentration, i.e. on enlarging the polar region.[47]

2) As only columnar phases have been observed for the pentaerythritol benzoates with alkyl chains **27**,[57,59b] we want to know, whether it would be possible to realize other mesophase types by replacing the alkyl chains by perfluorinated chains.

3) Finally, the lateral alkylchains of the bolaamphiphiles **53**, **58**, **71**[25,61] will be replaced by lateral perfluorinated chains, which could possibly change the mesophase morphologies of such molecules.

We will compare the perfluorinated compounds with their corresponding hydrocarbon derivatives, and evaluate the influence of the fluorophobic effect and of steric effects on the mesophobic behavior of these new molecules.



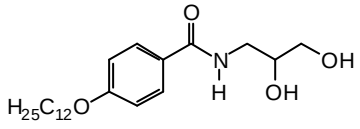
$R_1 = OC_nH_{2n+1}$; R_2, R_3 = H, $OC_nH_{2n+}1$; $R_4 = C_nH_{2n+1}$; R_5 = H, C_nH_{2n+1}

Figure 1.9 *Non conventional mesogens recently studied: polyhydroxyamphiphiles (**7**),*[48] *calamitic amphiphiles (**13**, **16**),*[55] *pentaerythritoltetrabenzoates (**27**);* [57,59b] *Bolaamphiphiles with lateral chains (**53**, **58**, **71**).* [25,61]

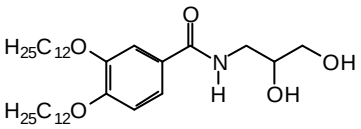
2 Thermotropic mesophases of simple amphilpilic molecules – polyhydroxy amphiphiles

2.1 Introduction

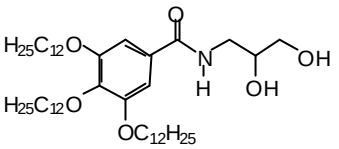
In the series of 1-benzoylaminopropane-2,3-diols, smectic, columnar and cubic mesophases can be formed depending on the number of alkyl chains attached to the diol moiety: the single chain compounds form exclusively SmA-phases, while double chain compounds can form smectic (SmA), bicontinuous cubic (Cub_{V2}) and columnar phases (Col_{h2}) depending on the chain length and the size of the polar headgroup. Triple chain compounds can form columnar (Col_{h2}) and in some cases even micellar cubic mesophases consisting of closed spheroidal micelles (Cub_{I2}). In this way, all main types of inverted (type 2) lyotropic mesophases have been realized by variation of the relative size of the lipophilic and the polar regions.[48,49] It should be emphasized that, in thermotropic phase sequences micellar cubic phases are extremely rare, besides these polyhydroxy amphiphiles only cone shaped dendritic aromatic polyethers decorated with lipophilic alkyl chains[50] can exhibit micellar cubic mesophases. Remarkably, all inverse micellar cubic thermotropic mesophases have the *Pm*3*n* lattice. Only in one case an *Im*3*n* phase was very recently reported. [50c]



Cr 89 SmA 132 Iso



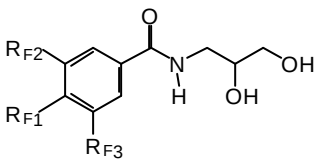
Cr 98 Col_{h2} 148 Iso



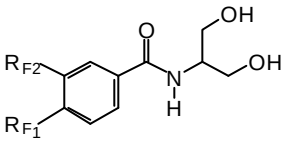
Cr 69 Cub_{I2} 121 Iso

Figure 2.1 *Thermotropic mesophases found in polyhydroxy amphiphiles **7** (phase transitions: T / °C).*

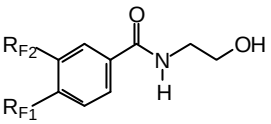
In order to design new compounds with thermotropic micellar cubic mesophases, we have synthesized the novel polyhydroxy amphiphiles with semifluorinated chains shown below:



7

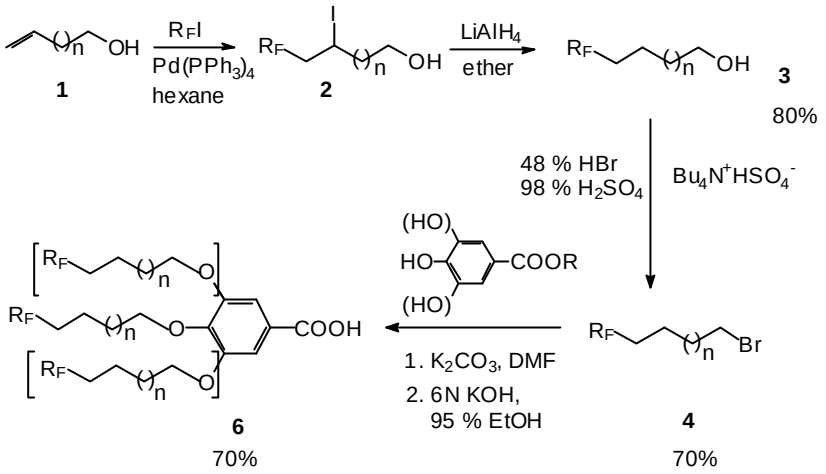


8-2F$_{4/6}$



9-2F$_{4/6}$

2.2 Synthesis

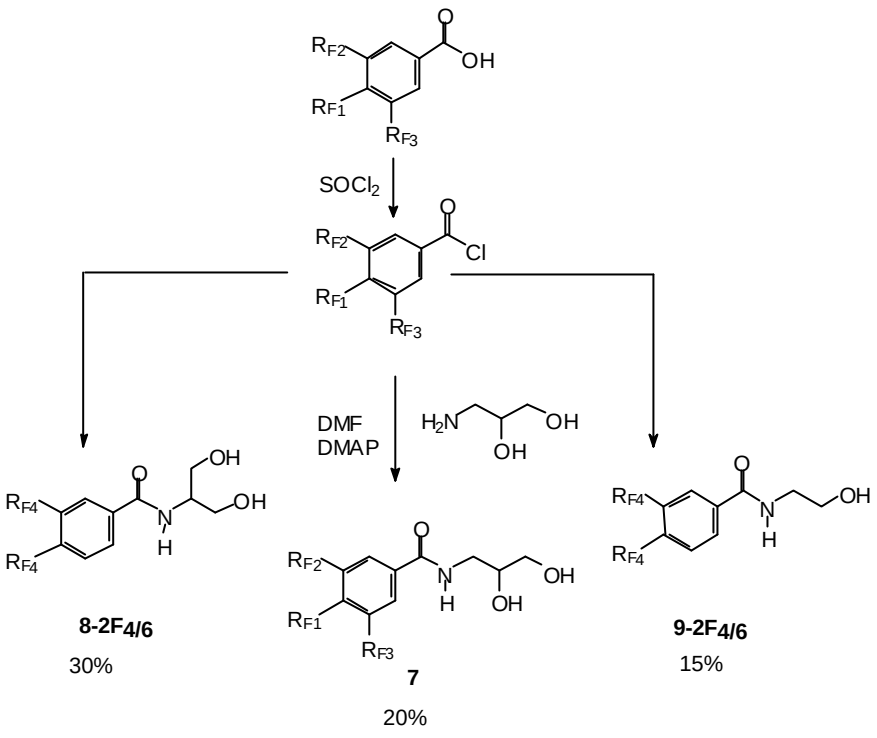


Scheme 2.1 *Synthesis of the alkoxybenzoic acids with semifluorinated chains.*

The alkoxybenzoic acids **6** with semifluorinated chains were synthesized according to Scheme 2.1. At first semifluorinated alkylbromides **4** with variable chain lengths were prepared from commercially available ω-alken-1-ols **1** and 1-iodoperfluoroalkanes. The key step is the Pd°-catalyzed radical addition of 1-iodoperfluoroalkanes to ω-alken-1-ols, followed by reduction of the obtained iodides **2** with $LiAlH_4$ to afford the semifluorinated alcohols **3**. Bromination of the semifluorinated alcohols **3** with 48 % aqueous HBr, n-$Bu_4N^+HSO_4^-$ as a phase transfer catalyst in the presence of catalytic amount of 98 % H_2SO_4 gave the semifluorinated alkylbromides **4**. The etherification of ethyl or methyl hydroxybenzoate by the semifluorinated alkyl bromides **4** was accomplished in DMF with K_2CO_3 as base, followed by basic hydrolysis in ethanolic KOH. The resulting perfluoroalkoxybenzoic acids **6** were purified by repeated crystallization from petroleum ether or ethanol.[51]

The benzamides **7**, **8** and **9** were synthesized according to Scheme 2.2. The benzoic acids **6** were treated with $SOCl_2$. The crude acid chlorides were aminolyzed with 1-aminopropane-2,3-diol, 2-aminopropane-1,3-diol, and 2-aminoethanol in the presence of DMAP to give the benzamides **7**, **8** and **9**.[9]

The purification of the final compounds was done by means of preparative centrifugal thin layer chromatrography with a Chromatotron (Harrison Research), followed by repeated crystallization.



R_{F1} = $O(CH_2)_mC_nF_{2n+1}$, n = 4, 6, m = 6, 4

R_{F2} = R_{F3} = H, $O(CH_2)_mC_nF_{2n+1}$, n = 4, 6, m = 6, 4

R_{F4} = $O(CH_2)_6C_4F_9$

Scheme 2.2 *Synthesis of the benzamides **7**, **8** and **9**.*

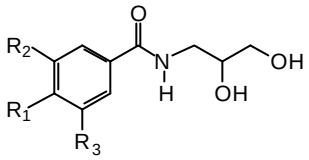
2.3 Liquid crystalline properties

2.3.1 1-Benzoylaminopropane-2,3-diols: 7

The mesomorphic properties of the synthesized compounds are collected in Table 2.1. In the notation of compounds **7**, the number of chains is given first, followed by the type of chains (H = hydrocarbon, F = semifluorinated chains). The following subscript numbers described the number of CF_2-units and CH_2-units in the semifluorinated chains.

Gernerally, the fluorinated compounds have a significantly enhanced stability of the mesophases in comparison to the hydrocarbon analogues. This increased mesophase stability should mainly be due to the increased intramolecular polarity contrast on replacing the alkyl chains by the more lipophilic semifluorinated chains.

Table 2.1 *Comparison of the transition temperatures and associated enthalpy values (lower lines, in italics) of the semifluorinated 1-benzoylaminopropane-2,3-diols with those of the related hydrocarbon derivatives.*



Comp.	R_1	R_2	R_3	Phase transitions (T / °C) ΔH/KJ mol^{-1}
7-1H	$OC_{12}H_{25}$	H	H	Cr 89 SmA 132 Iso *36.6 0.8*
7-1F$_6$/$_4$	$O(CH_2)_4C_6F_{13}$	H	H	Cr 79 SmA 223 Iso *28.9 1.05*
7-2H	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H	Cr 98 Col_{h2} 148 Iso *60.4 1.4*
7-2F$_4$/$_6$	$O(CH_2)_6C_4F_9$	$O(CH_2)_6C_4F_9$	H	Cr 47 Cub_{I2} 162 Iso *20.8 0.16*
7-2F$_6$/$_4$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	H	Cr 86 Cub_{I2} 208 Iso *27.5 0.63*
7-3H	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$	Cr 69 Cub_{I2} 121 Iso *11.5 0.7*
7-3F$_4$/$_4$	$O(CH_2)_4C_4F_9$	$O(CH_2)_4C_4F_9$	$O(CH_2)_4C_4F_9$	Cr 49 Cub_{I2} 154 Iso *37.1 0.80*
7-3F$_6$/$_4$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	Cr 59 Cub_{I2} 188 Iso *25.8 0.84*
7-3F$_7$/$_4$	$O(CH_2)_4C_7F_{15}$*	$O(CH_2)_4C_7F_{15}$	$O(CH_2)_4C_7F_{15}$	Cr <20 Cub_{I2} 193 Iso *0.86*

* $O(CH_2)_4C_7F_{15} = (CH_2)_4(CF_2)_4CF(CF_3)_2$

Table 2.2 *Lattice parameter of the smectic phases (d), hexagonal columnar mesophases (a_{hex}), and the cubic mesophases (a_{cub}) of the 1-benzoylaminopropane-2,3-diols 7.*

Comp.	d/nm (T / °C)	a_{hex}/nm (T/ °C)	a_{cub}/nm (T / °C)
7-1H	4.03 (85)		
7-1F$_6$/$_4$	4.2 (90)		
7-2H		3.48 (84)	
7-2F$_4$/$_6$			7.05 (75)
7-2F$_6$/$_4$			7.40 (75)
7-3H			7.94 (75)
7-3F$_4$/$_4$			5.45 (75)
7-3F$_6$/$_4$			7.40 (90)
7-3F$_7$/$_4$			7.40 (60), 7.6 (100)

The mesophase type can be the same or quite different for the fluorinated amphiphiles. The semifluorinated single chain compound **7-1F$_{6/4}$**, just like its hydrocarbon analogue **7-1H**,[9] exhibits a SmA mesophase with focal-conic fan textures. They can be homeotropically aligned giving pseudo-isotropic regions separated by oily streaks. The X-ray diffraction pattern of this compound exhibits a strong reflection in the small angle region corresponds to d = 4.2 nm and a diffuse scattering in the wide-angle region, indicating a layer structure. The layer spacing is larger than the length of the molecule (L = 2.7 nm as estimated from CPK models). Therefore, a bilayer structure with a partial intercalation of the polar moieties must be assumed.

Interestingly and remarkably, the semifluorinated two-chain compounds **7-2F$_{4/6}$** and **7-2F$_{6/4}$** do not display columnar mesophases as usually observed for the two chain hydrocarbon analogues (for example **7-2H**[9]). As shown below, they display micellar cubic phases. It seems that, the mesophase behavior of the two-chain compounds **7-2F** is similar to that of the related three-chain hydrocarbon analogue **7-3H**[9].

The semifluorinated three-chain compounds **7-3F$_{4/4}$**, **7-3F$_{6/4}$** and **7-3F$_{7/4}$** represented cubic mesophases as expected, but in comparison with their hydrocarbon analogues (for example **7-3H**[9]), a significant mesophase stabilization and a decrease of the melting point, and therefore a significantly broader liquid crystalline range is found.

The X-ray diffraction pattern of the cubic phases of the two-chain compounds **7-2F$_{4/6}$**, **7-2F$_{6/4}$** and the three-chain compounds **7-3F$_{4/4}$**, **7-3F$_{7/4}$** can all be indexed on the basis of a *Pm*3*n* lattice. The lattice parameter are collected in Table 2.2.

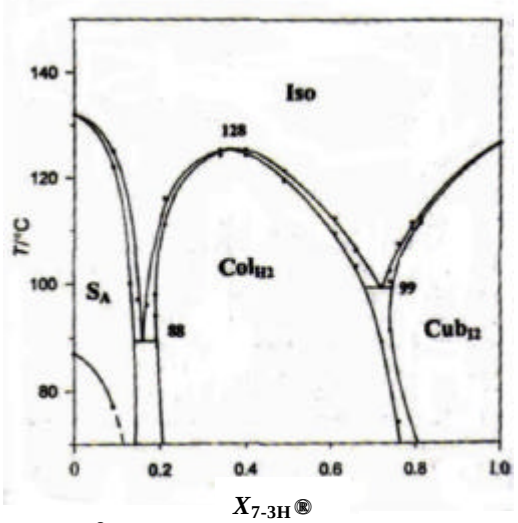
The inverse micellar structure of the cubic phases of compounds **7-2F$_{6/4}$**, **7-3F$_{6/4}$** and **7-3F$_{7/4}$** was confirmed by miscibility experiments. The binary phase diagrams of the systems **7-1F$_{6/4}$ + 7-2F$_{6/4}$**, **7-1F$_{6/4}$** + **7-3F$_{6/4}$** and **7-1F$_{6/4}$** + **7-3F$_{7/4}$** are shown in Figure 2.2b, 2.2c and 2.2d, respectively. As shown in Figure 2.2b, as the concentration of the two-chain amphiphile **7-2F$_{6/4}$** increases in the mixture with the single chain compound **7-1F$_{6/4}$**, the value of the polar-apolar interface curvature becomes increasingly negative. Because the phase sequence SmA-Cub$_{V2}$-Col$_{h2}$-Cub$_{I2}$ can be observed in the contact region between the SmA-phase of **7-1F$_{6/4}$** and the cubic phase of **7-2F$_{6/4}$**, the cubic phase of **7-2F$_{6/4}$** cannot be a bicontinuous one. A similar phase diagram was found in the systems of the single chain compound **7-1F$_{6/4}$** with the three chain compounds **7-3F$_{6/4}$** (Figure. 2.2c) and **7-3F$_{7/4}$** (Figure 2.2d), but the region of the Cub$_{I2}$-phase in these two binary systems is much broader than that in the system **7-1F$_{6/4}$** + **7-2F$_{6/4}$**.

These results indicate that, due to the larger cross-section area of perfluoroalkyl chains, compounds **7-2F$_{4/6}$** and **7-2F$_{6/4}$** with two semifluorinated chains form Cub$_{I2}$ phases, instead of the smectic, bicontinuous cubic and columnar phase of the hydrocarbon analogues. Interestingly, not only the lamellar phase, but also mesophases, which require curved polar-apolar interface curvatures (Cub$_{V2}$, Col$_{h2}$, Cub$_{I2}$) are significantly stabilized by introduction of the semifluorinated chains (Figure 2.2b, Figure 2.2c and Figure 2.2d). This is contrary to

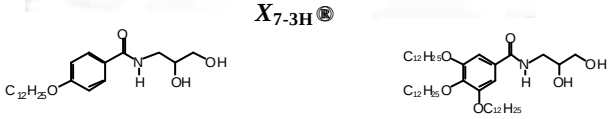
the general assumption, that perfluoroalkyl chains are more rigid than alkyl chains. Therefore, the influence of rigidity, which is often used to explain the increased smectic mesophase stability of perfluorinated calamitic liquid crystals,[43] seems to be less important here. Another remarkable phenomenon is that the induced Cub_{V2} phase, which does not occur in the binary phase diagram of the hydrocarbon analogues (see Figure 2.2a), occurred in all three binary phase diagrams of semifluorinated compounds in a certain concentration and temperature region. This leads to the unconventional themotropic phase sequences Col_{h2}-Cub_{V2}-Col_{h2}, SmA-Cub_{V2}-SmA and SmA-Cub_{V2}-SmA-Col_{h2} for certain mixtures (re–entrant behavior). The reason may be, that the average conformation of the semifluorinated chains changes in dependence on the temperature.

It should be pointed out that **7-2F$_{6/4}$** and **7-2F$_{4/6}$** were the first fluorinated molecules which exhibit the thermotropic micellar cubic mesophase.[52] Simultaneously, they are the first amphiphiles with only two lipophilic chains showing this mesophase.

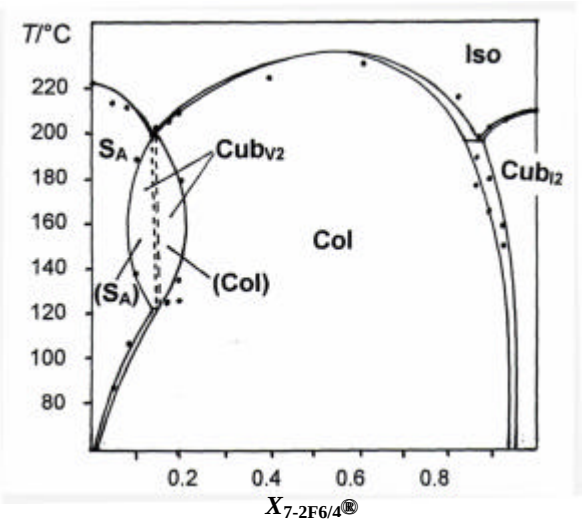
The three chain compound **7-3F$_{7/4}$**, in which the perfluorinated chains have the same length as in compound **7-3F$_{6/4}$**, but they are branched, has a *Pm*3*n* lattice too. This means that, by branching the perfluorinated chains, the structure of the cubic phase cannot be changed. However, the binary phase diagram (Figure. 2.2d) of the system **7-1F$_{6/4}$** + **7-3F$_{7/4}$** shows the broadest concentration region of the Cub_{I2} phase, which means that branching the chains can stabilize the cubic phase.



$X_{7\text{-}3H}$ ®

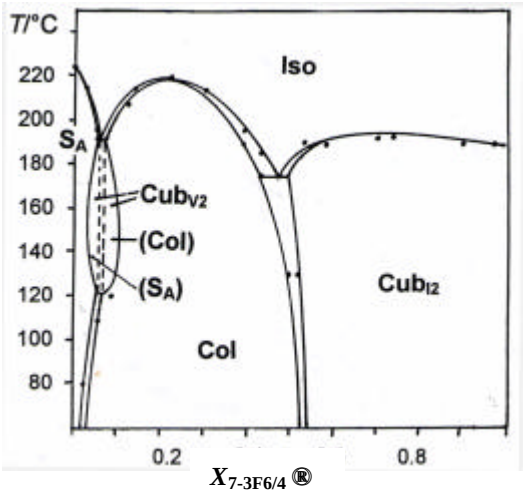


a *Phase diagram of the binary system* ***7-1H + 7-3H***



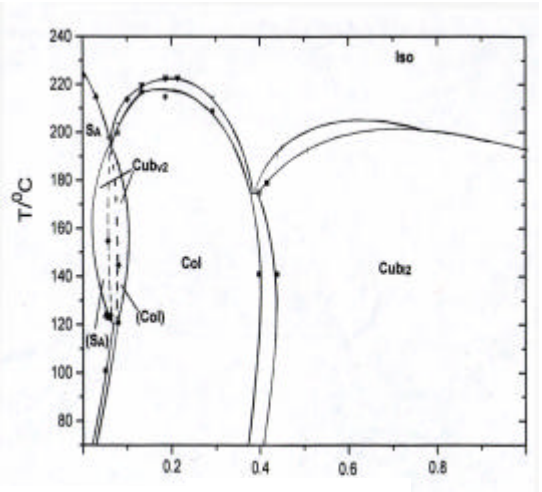
$X_{7\text{-}2F6/4}$®

b *Phase diagram of the binary system* ***7-1F$_{6/4}$ + 7-2F$_{6/4}$***

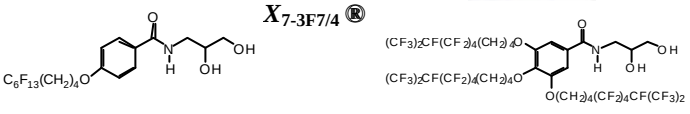


$X_{7\text{-}3F6/4}$ ®

c *Phase diagram of the binary system* ***7-1F$_{6/4}$ + 7-3F$_{6/4}$***



$X_{7\text{-}3F7/4}$ ®



d *Phase diagram of the binary system* ***7-1F$_{6/4}$ + 7-2F$_{7/4}$***

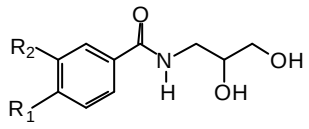
Figure 2.2 *Phase diagrams of binary system of different fluorinated compounds (b-d) and binary phase diagram of a related system of two hydrocarbon derivatives* ***7-1H + 7-3H*** *(a).*

2.3.2 The influence of the size of the hydrophilic parts of the amphiphilic molecules on their mesophase behaviors

It was reported that the mesophase behavior of polyhydroxy amphihiles with hydrocarbon chains can be changed by changing the position and number of the hydroxy groups (Table 2.3).[9,53]

A similar influence was observed for the series of fluorinated two chain amphiphiles **7-2F$_{4/6}$**, **8-2$_{4/6}$** and **9-2F$_{4/6}$**. The two chain propane-1,2-diol **7-2F$_{4/6}$** displays the Cub$_{I2}$ phase, whereas the related propane-1,3-diol **8-2F$_{4/6}$** displays exclusively a Col$_{h2}$ phase. It means that the 1,3-diol group represents a significantly larger hydrophilic group than the corresponding 1,2-diol group.[9] By decreasing the number of the hydroxy groups from two to one (compound **9-2F$_{4/6}$**), a Cub$_{V2}$ phase is obtained despite of the fact that this head group should be smaller than the propane-1,2-diol unit. It seems that reduction of the cohesive forces can also reduce the interface curvature. However also in these two cases, the perfluorinated chains enhance the stability of the mesophases. Therefore, the columnar mesophase is more stable in the fluorinated compound **8-2F$_{4/6}$**, and mesophase behavior can be observed for the fluorinated compound **9-2F$_{4/6}$**.

Table 2.3 *Comparison of the transition temperatures, the corresponding lattice parameter of the hexagonal columnar (a_{hex}), and cubic mesophases (a_{cub}) and associated enthalpy values (lower lines, in italics) of the semifluorinated amphiphilic 1-benzoylaminopropane-2,3-diols **7**, benzoylaminopropane-1,3-diol **8** and benzoylamino ethan-2-ol **9**.*



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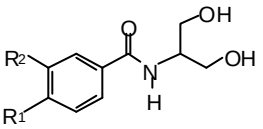

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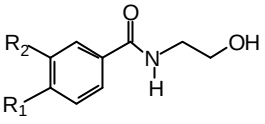
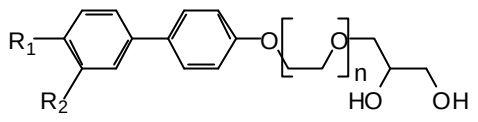


9

Comp.	$R_1 = R_2$	Phase transitions (T / °C) *ΔH/KJ mol^{-1}*	a_{hex}/nm (T / °C)	a_{cub}/nm (T / °C)
7-2F$_{4/6}$	$O(CH_2)_6C_4F_9$	Cr 47 Cub$_{I2}$ 162 Iso *20.8 0.46*		7.05 (75)
8-2F$_{4/6}$	$O(CH_2)_6C_4F_9$	Cr 71 Col$_{h2}$ 177 Iso *32.6 1.15*	3.8 (150)	
8-2H	OC_6H_{13}	Cr$_1$ 64 Cr$_2$ 108 [(Cub$_{V2}$ 50 (Col$_{h2}$ 50)] Iso *4.5 31.6*		
9-2F$_{4/6}$	$O(CH_2)_6C_4F_9$	Cr 71 Cub$_{V2}$[54] 112 Iso *49.2 0.42*		6.5 (25)

3 Linear combination of micro - segregation and rigidity: amphiphilic biphenyl derivatives

3.1 Introduction

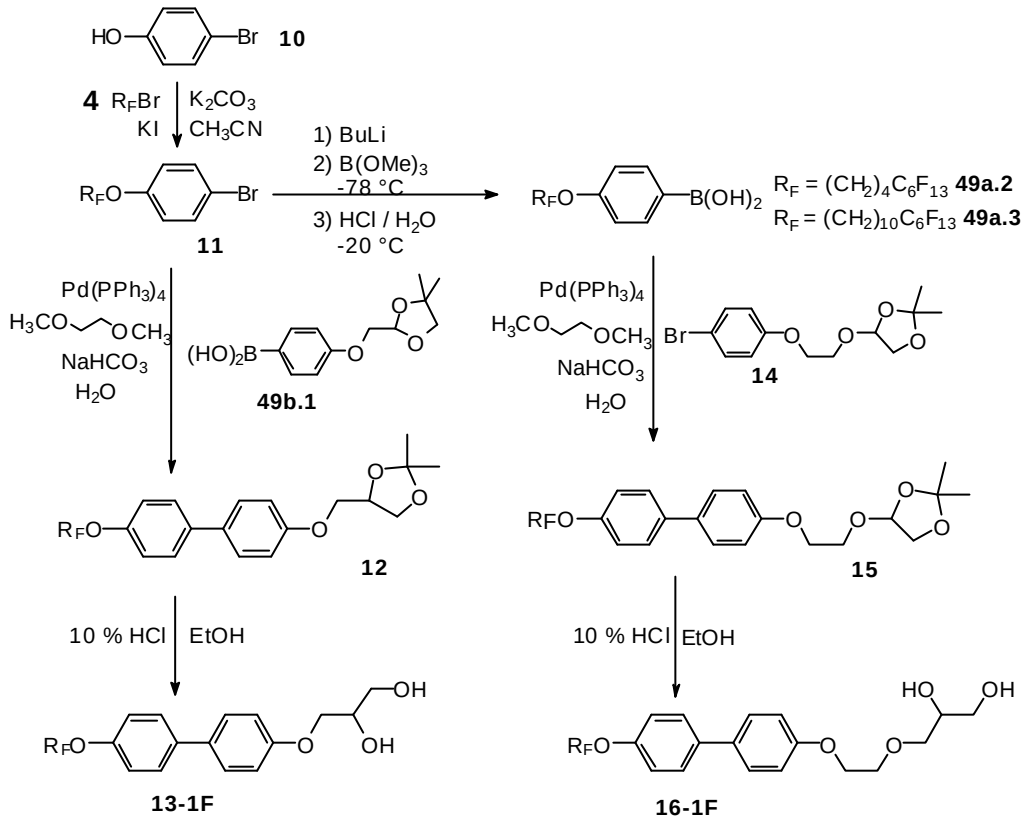


n = 0, **13-1H$_m$** $R_1 = OC_mH_{2m+1}$, $R_2 = H$
n = 1, **16-1H$_m$** $R_1 = OC_mH_{2m+1}$, $R_2 = H$
16-2H$_m$ $R_1 = R_2 = OC_mH_{2m+1}$
n = 10, 12, 16

Calamitic single chain amphiphilic biphenyl derivatives with the general formula **13-1H$_m$** and **16-1H$_m$** (R_2 = H) form not only SmA and SmC phase but also oblique columnar mesophases, despite the fact that they are neither disc-like nor taper shaped and the parallel arrangment of the individual molecules should favor smectic layer structures. Therefore, the columnar mesophases of these rod-like molecules are supposed to result from the collapse of the smectic layer structure into ribbons, which arrange in an oblique 2D-lattice. The related double chain compounds **16-2H$_m$** form hexagonal columnar mesophases, which are regarded as consisting of cylindrical aggregates. Hence, the same diversity of mesophases as in the thermotropic phase sequence of polycatenar compounds was detected for these compounds.[55] In order to further investigate the relationship between phase behavior and molecular structure in such molecules, we have synthesized their fluorinated analogues.

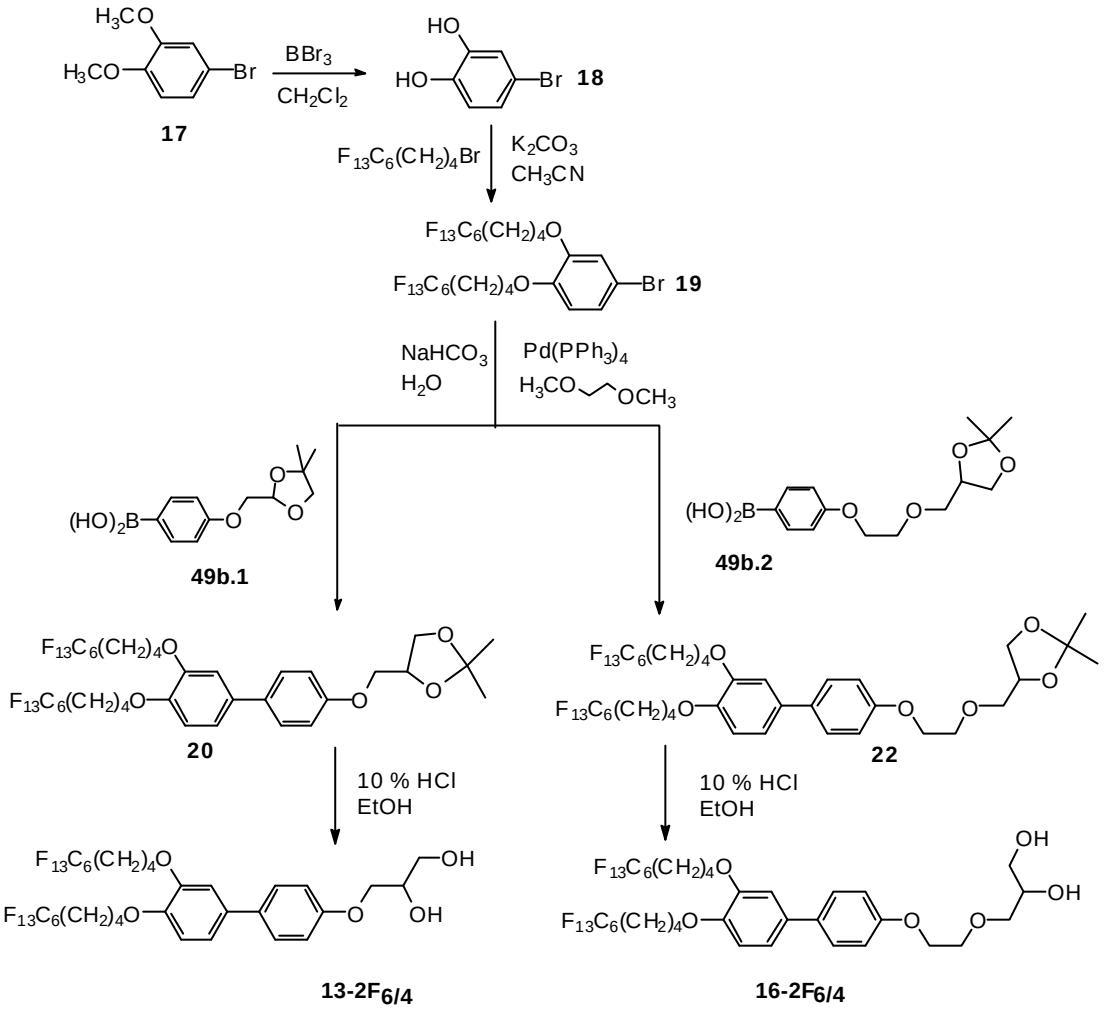
3.2 Synthesis

The single chain biphenyl derivative **13-1F** and **16-1F** were synthesized according to Scheme 3.1. At first, 4-bromophenol **10** was etherified with the semifluorinated alkylbromides **4**. The resulting bromobenzene derivative **11** was coupled with the boronic acid **49b.1** (synthesis according to Scheme 5.6b, see chapter 5) to afford the acetonide **12**. Acidic hydrolysis[41] of **12** gave the diols **13-1F**. From **11**, the boronic acids **49a** were synthesized by the standard method of halogen-metal-exchange. The coupling reaction of the boronic acids **49a** with the bromobenzene derivative **14** afforded the acetonide **15**, acidic hydrolysis[56] gave the diols **16-1F** with an additional oxyethylene unit.



Scheme 3.1 *Synthesis of the biphenyl derivatives **13-1F** and **16-1F**. [**13-1F$_{6/4}$**, **16-1F$_{6/4}$**: $R_F = (CH_2)_4C_6F_{13}$; **13-1F$_{6/10}$**,**16-1F$_{6/10}$**: $R_F = (CH_2)_{10}C_6F_{13}$].*

The double-chain derivatives **13-2F$_{6/4}$** and **16-2F$_{6/4}$** were synthesized according to Scheme 3.2. At first, the ether groups of the commercially available 4-bromoveratrole **17** were cleaved with boron tribromide. Etherification of the phenolic hydroxyl groups of **18** with the semifluorinated alkylbromide **4.2** afforded the bromobenzene derivative **19**. Coupling reaction between **19** and the boronic acid **49b.1** gave the acetonide **20**, the acetonide protecting group of **20** was removed by acidic hydrolysis in ethanol using 10 % HCl as catalyst to give the double chain derivative **13-2F$_{6/4}$**. If **19** was coupled with the boronic acid **49b.2**, then **22** was obtained, which was hydrolyzed to give **16-2F$_{6/4}$**.

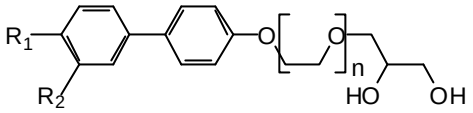


Scheme 3.2 *Synthesis of the amphiphilic biphenyl derivatives* ***13-2F$_{6/4}$*** *and* ***16-2F$_{6/4}$***.

3.3 Mesophase behavior

The transition temperatures of the fluorinated compounds **13-F**, **16-F** and the non-fluorinated compounds **13-H**, **16-H** are shown in Table 3.1. Just like the hydrocarbon analogue **16-1H$_{10}$**, [55a] the single chain compound **16-1F$_{6/4}$** shows a SmA phase, a SmC phase and two phases with textures typical for columnar mesophases (Figure 3.1). However, the textures of these two columnar phases are different from those of the Col$_{ob}$ phase of **16-1H$_{10}$**. Because until now, only a layer period was detected by means of X-ray diffraction experiments. The specific structures of these two columnar mesophases remain unknown.

Table 3.1 *Comparison of the phase transition temperatures and associated enthalpy values (lower lines, in italics) of the semifluorinated amphiphilic biphenyl derivatives with the related hydrocarbon analogues.*



Comp.	R_1	R_2	n	Phase transition (T / °C) ΔH/KJ mol^{-1}
16-1H$_{16}$	$OC_{16}H_{33}$	H	1	Cr 136 Col$_{ob1}$ 145 Cub 146 Col$_{ob2}$ 148 SmA 170 Iso
16-1F$_{6/4}$	$O(CH_2)_4C_6F_{13}$	H	1	Cr 147 Colx$_1$ 152 Colx$_2$ SmC 158 SmA 219 Iso *14.9* *6.1*
16-1F$_{6/10}$	$O(CH_2)_{10}C_6F_{13}$	H	1	Cr 149 (Colx$_1$ 148) Colx$_2$ 168 SmA 203 Iso *32.9* *1.6* *2.2*
16-1H$_{10}$	$OC_{10}H_{21}$	H	1	Cr 143 Col$_{ob}$ 146 SmC 147 SmA 171 Iso
13-1F$_{6/4}$	$O(CH_2)_4C_6F_{13}$	H	0	Cr 175 SmA 242 Iso *35.9* *5.3*
13-1F$_{6/10}$	$O(CH_2)_{10}C_6F_{13}$	H	0	Cr 168 SmA 225 Iso *36.7* *2.0*
16-2H$_{12}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$	1	Cr$_1$ 83 Cr$_2$ 87 Col$_h$ 135 Iso
13-2F$_{6/4}$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	0	Cr 87 Col 137 Iso *220* *1.2*
16-2F$_{6/4}$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	1	Cr < 20 Col 145 Iso *1.33*

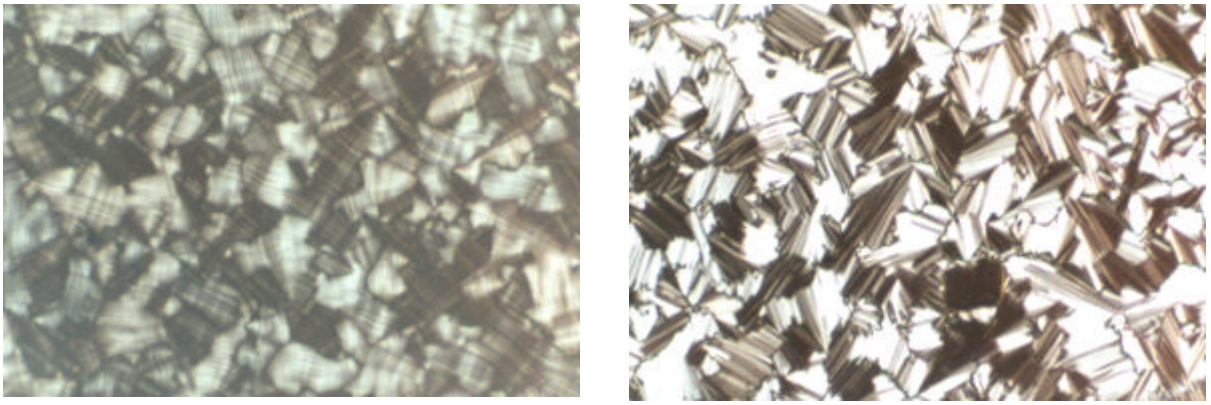
Another compound with an interesting polymorphism is **16-1H$_{16}$**.[55c] It has a phase sequence Col$_{ob1}$-Cub-Col$_{ob2}$ below the SmA phase. We have synthesized its fluorinated analogue **16-1F$_{6/10}$**. It exhibits two columnar phases too (Figure 3.2), but they are not separated by a cubic phase. Also, the structures of these columnar phases could not be determined till now.

The single chain compounds **13-1F$_{6/4}$**, **13-1F$_{6/10}$**, in which the size of the polar units is reduced (n = 0) in comparison with compounds **16** exhibit only smectic phases. It seems that the oxyethylene unit is essential for the occurrence of the columnar mesophases. Probably the polar units must have a critical size or have some flexibility in order to disturb the layer arrangement and to induce the columnar phase.

The fluorinated double-chain derivatives **16-2F$_{6/4}$** and **13-2F$_{6/4}$** exhibit hexagonal columnar phases, as shown by their typical spherulitic textures.

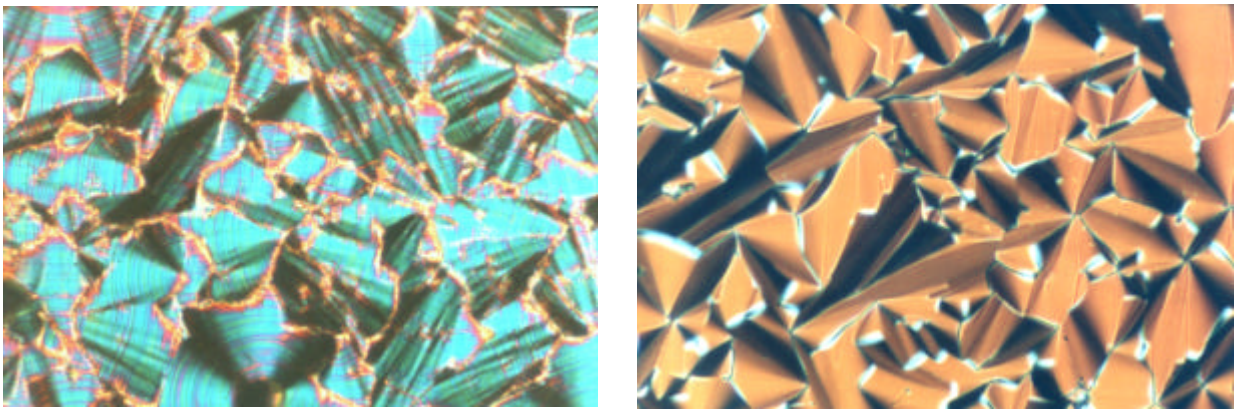
Compared with the hydrocarbon analogues, the columnar mesophase of the fluorinated compounds are stabilized. The same explanations we used for the mesophase behavior of the polyhydroxy amphipiles **7** (see Chapter 2) could apply here. Namely the second semifluorinated chain induces a taper shaped molecular structure, leading to circular cylindrical aggregates, which can organize to hexagonal columnar phases. The enhanced mesophase stabilities are due to the fluorophobic effect. Accordingly, the introduction of the

perfluorinated segment in such biphenyl derivatives influences the liquid crystalline behavior, but no unexpected effects have been observed.



a b

Figure 3.1 *Texture of the columnar phases formes by compound* ***16-1F$_{6/4}$****: (a) Col$_{x1}$ at 148 °C; (b) Col$_{x2}$ at 153 °C.*



a b

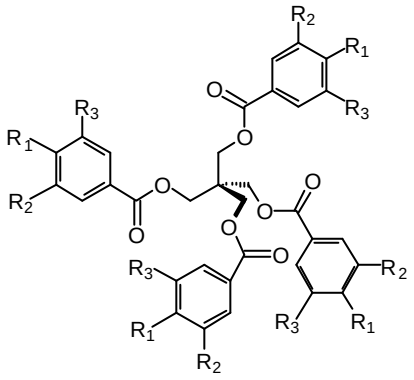
Figure 3.2 *Texture of the columnar phases formed by compound* ***16-1F$_{6/10}$****: (a) Col$_{x1}$ at 148 °C; (b) Col$_{x2}$ at 167 °C.*

4 Semifluorinated pentaerythritol derivatives

4.1 Introduction

Recently, star-shaped pentaerythritol tetrabenzoates,[57] have been reported as a novel type of liquid crystals. Contrary to the classical liquid crystalline material, the mesogenity of these molecules is not based on an anisometric shape (rod-like or disc-like segments) or on a strong amphiphilicity. Their mesogenity was assumed to be caused solely by microsegregation of the polar central units from the peripheral lipophilic alkyl chains. If this assumption is valid, then it should be possible to change the mesophase type by changing the relative size of the lipophilic parts with respect to the polar parts, as known for lyotropic liquid crystalline systems. However, efforts, which have been directed to check this assumption by changing the number of alkyl chains attached to the benzoate units, have failed so far. The columnar phases of 3,4-dialkoxybenzoates were significantly destabilized on grafting additional alkyl chains and were completely lost by reducing their number (see Table 4.1). Because perfluorinated chains can stabilize smectic as well as columnar mesophases, we hoped, that the analogous compounds **27-1F** and **27-3F** with semifluorinated chains instead of alkyl chains could be mesogenic.

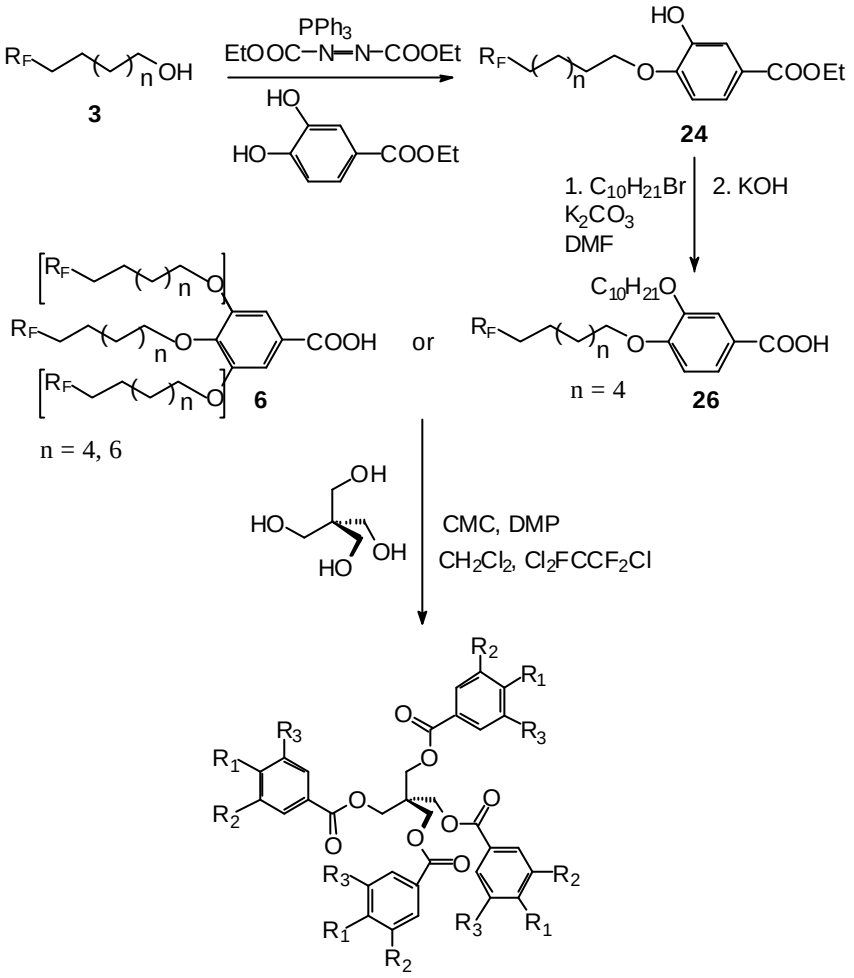
Table 4.1 *Influence of the number of the hydrocarbon chains on the transition temperatures of the pentaerythritol benzoates **27-1H**, **27-2H** and **27-3H**.*



Comp.[49b]	R_1	R_2	R_3	Phase transitions (T / °C)
27-1H	$OC_{10}H_{21}$	H	H	Cr 42 Iso
27-2H	$OC_{10}H_{21}$	$OC_{10}H_{21}$	H	Cr 54 (Col_{h2} 47) Iso
27-3H	$OC_{10}H_{21}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$	Cr 41 (Col_{h2} 8) Iso

4.2 Synthesis

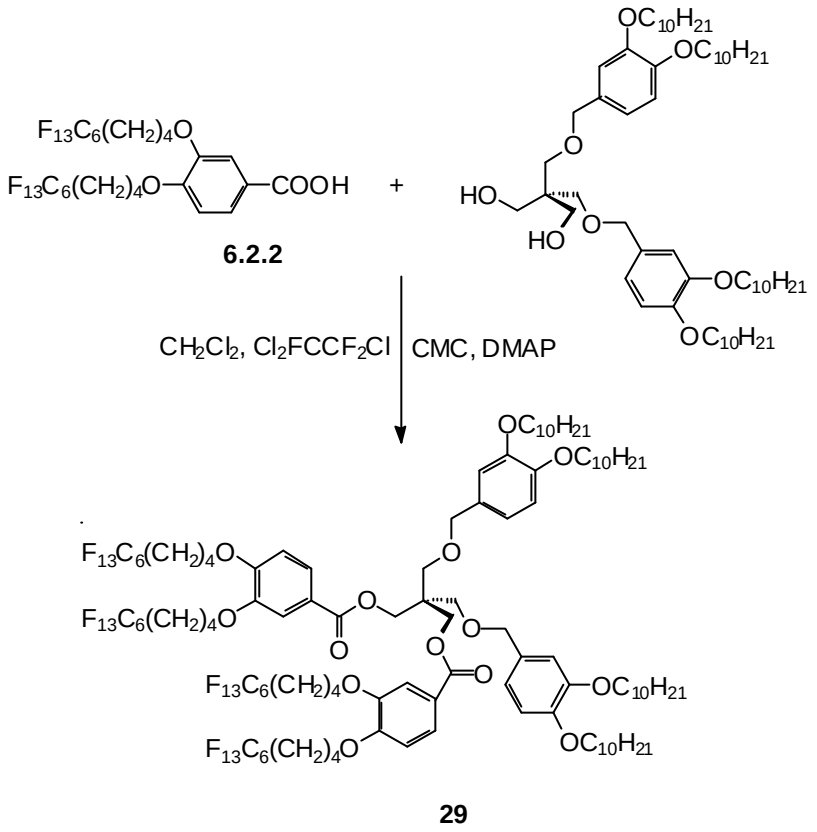
The synthetic route starts with the benzoic acids **6** and **26**. The benzonic acids **6** were synthesized according to Scheme 2.1 (see Chapter 2.2). The benzoic acid **26**, with one semi-fluorinated and one non-fluorinated chain, was prepared *via* Mitsunobu etherification[58] of



Scheme 4.1 *Synthesis of the pentaerythritoltetralbenzoates **27** and **28**.*

ethyl 3,4-dihydroxybenzoate with the semifluorinated alcohol **3** to yield the monoalkylated benzoate **24**. Etherification of the OH-group of **24** with 1-bromodecane yielded the benzoic acid **26** after saponificaion of the ethyl ester group with ethanolic KOH. Acylation of pentaerythritol was achieved with the water soluble *N*-cyclohexyl-*N′*-(2-morpholinoethyl)carbodiimide methyl-p-toluenesulfonate (CMC) in the mixed solvent system methylene chloride / Freon 113 (1:1)[59] in the presence of 4-(dimethylamino)pyridine (DMAP), with an excess of the semifluorinated benzoic acids **6** or **26**. Because of the poor

solubility of the semifluorinated benzoic acids in methylene chloride, it was necessary to add Freon 113 (1,1,2-trichlorotrifluoroethane) as a cosolvent (Scheme 4.1).



6.2.2

29

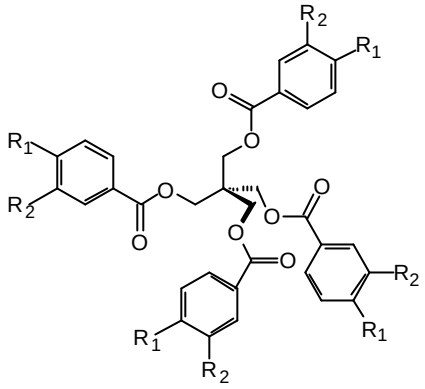
Scheme 4.2 *Synthesis of desymmetrized compound **29**.*

The desymmetrized pentaerythritol derivatives **29** was obtained according to Scheme 4.2. Accordingly, 2,2-bis(3,4-didecyloxybenzyloxymethyl)-1,3-propanediol[59b] was acylated with excess benzoic acid **6** under the same condition as described for the synthesis of **27** and **28.**

4.3 Liquid crystalline properties

The mesomorphic properties of the pentaerythritol derivatives comprising eight lipophilic chains are shown in Table 4.2. The liquid crystalline phases of all fluorinated compounds have spherulitic textures, as typical for columnar phases. The columnar phase of compound **27-2F$_{6/4}$**[59b] is a hexagonal one (a_{hex} = 3.4 nm, at T = 130 ^{o}C). As the optical textures of all these pentaerythritol derivatives are identical and a complete miscibility was found, we assume that also the columnar phases of all other compounds are hexagonal phases.

Table 4.2 *Columnar mesophases formed by the pentaerythritol derivatives **27**.*



Comp.	R^1	R^2	Phase transition (T / °C) *DH/KJ mol^{-1}*	CF_2 : CH_2
27-2H	$C_{10}H_{21}$	$C_{10}H_{21}$	Cr 54 (Col_h 47) Iso *102.3* *5.4*	0 : 1
27-2F$_{4/6}$	$C_4F_9(CH_2)_6$	$C_4F_9(CH_2)_6$	Cr < 20 Col_h 100 Iso[3b] *4.1*	0.67 : 1
27-2F$_{6/4}$	$C_6F_{13}(CH_2)_4$	$C_6F_{13}(CH_2)_4$	Cr 88 Col_h 131 Iso[3b] *86.5* *5.6*	1.5 : 1
28	$C_6F_{13}(CH_2)_4$	$C_{10}H_{21}$	Cr < 20 Col_h 108 Iso *5.6*	0.43 : 1

Abbreviation: CF_2:CH_2 = ratio of fluorinated to hydrogenated carbon atoms in the chains.

The stacking of the molecules into the hexagonal columnar mesophase should be driven by microsegregation of the polar central blocks from the semifluorinated chains. The central polar units aggregate into extended cylinders which are surrounded by the semifluorinated alkyl chains (Figure 4.1-a). However, due to the tetrahedral preorganisation of the taper-shaped units around the tetrahedral central cores (see Figure 4.1-c), a disc-like geometry is not provided by the molecular shape. Instead, an average disc-like molecular shape is the result of the self assembly process which overrides the unfavorable effect of the molecular geometry.

The mesophase stabilization in the order **27-2H**, **27-2F$_{6/4}$**, **27-2F$_{4/6}$**, i.e. with an increasing degree of the fluorination, is again due to the fluorophobic effect, which increases the intramolecular contrast and thus forces micro-segregation.

Most interestingly, however, compound **28**, in which the semifluorinated and non-fluorinated chains are covalenly fixed side by side, also has a significantly enhanced mesophase stability of the columnar phase in comparison to **27-2H**. Here, fluorinated and non-fluorinated chains cannot segregate into separated regions. However, the columnar phase of this compound is even more stable than expected from its degree of fluorination (see CF_2:CH_2 in Table 4.2). This shows, that micro-segregation of the perfluorinated and hydrogenated segments is not so important for mesophase stabilization and that the

mesophase stabilization should mainly result from the enhanced incompatibility between the lipophilic chains (i.e. the mixed system alkyl chains + perfluoroalkyl chains) and the polar regions on increasing the degree of fluorination.

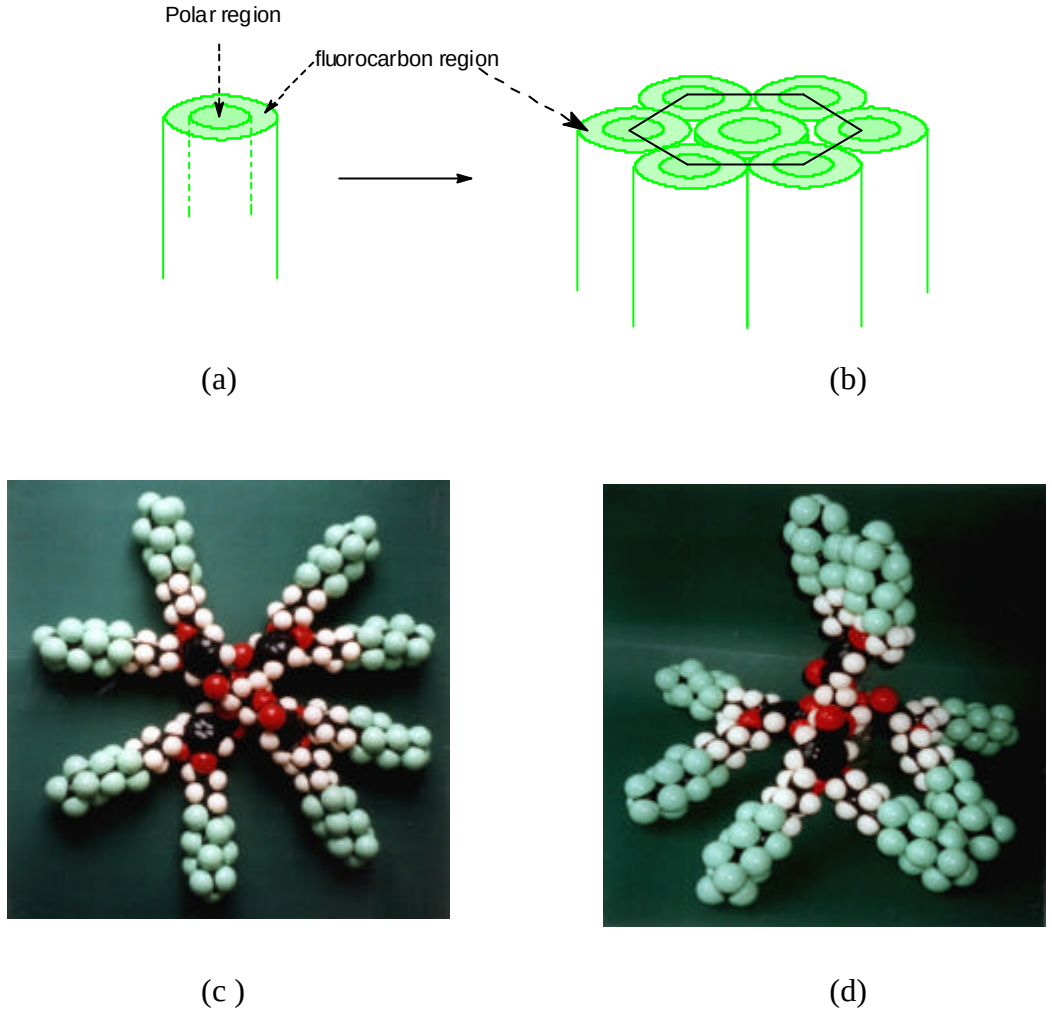
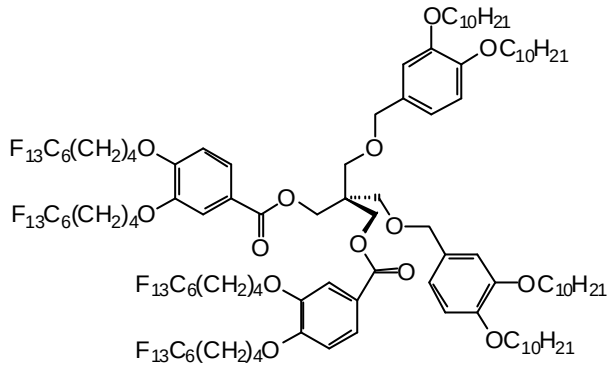


Figure 4.1 *Schematic presentation of the arrangement of the molecules* ***27-2F$_{4/6}$****,* ***27-2F$_{6/4}$*** *and* ***28*** *in the columnar mesophase: (a) cylindrical aggregate; (b) arrangement of the aggregates in the Col$_h$-phase; CPK models of two possible conformers of compound* ***27-2F$_{6/4}$****; (c) conformer with a rather flat disk-like shape; (d) conformer with a tetrahedral organization of the benzoate units.*



29

Compound **29** consists of two different halves: one half consisting of two 3,4-dialkoxybenzyl units, the other one of two 3,4-bis(tridecafluorodecyloxy)benzoyl units. By cooling to 59 °C, a spherulitic texture as typical for columnar phases was observed. On further cooling to 31 °C, the texture changed to another spherulitic one. Calorimetric measurements show three transition processes: at 15 °C (glass transition), at 31 °C and at 59 °C (see Figure 4.2, cooling trace).

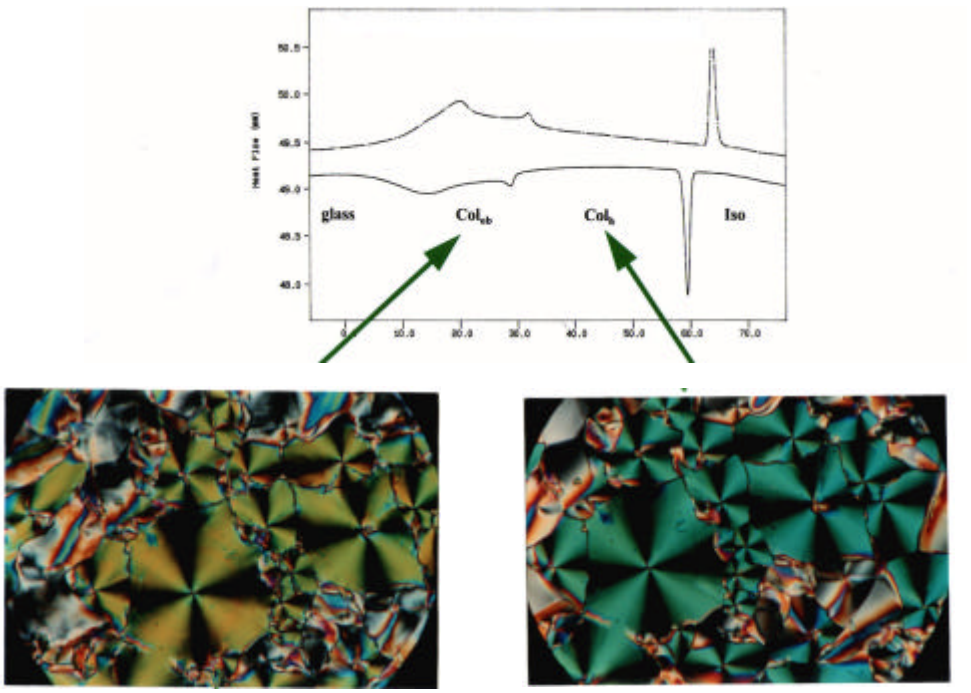


Figure 4.2 *DSC heating and cooling trace of compound **29** and textures of the different mesophases.*

X-ray investigations indicated the presence of both an oblique and a hexagonal columnar mesophases with the following lattice parameters: Col_{ob}: a = 4.19 nm, b = 3.59 nm, α = 115 °C at 25 °C; Col_h: a_{hex} = 3.73 nm at 50 °C, respectively. The formation of these two different columnar mesophases is explained as follows: **I**: at higher temperature, both the

alkyl chains and the semifluorinated chains are not segregated. Hence, a hexagonal columnar mesophase is formed (Figure 4.1-b); **II**: at lower temperature the alkyl chains and the semifluorinated chains may become incompatible, which may lead to a slight deviation from the hexagonal lattice to an oblique lattice, a possible model for this oblique columnar phase is shown in Figure 4.3.

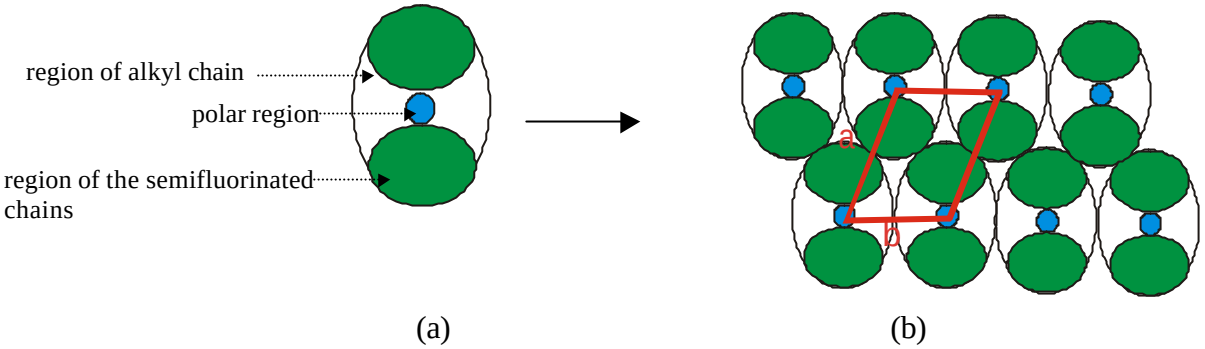
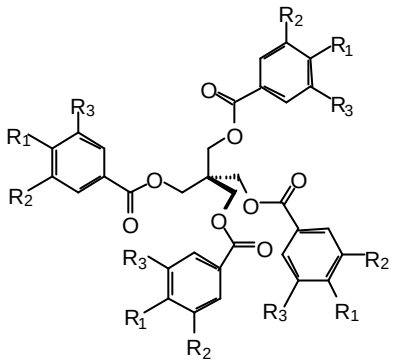


Figure 4.3 *Possible model of the oblique columnar mesophases of **29**: (a) cross-section of a cylindrical aggregate; (b) arrangement of the aggregates in the Col_{ob}-phase.*

The proposed structure can be regarded as a lamellar organization of columns, composed of fluorocarbon layers and hydrocarbon layers, whereby columns of the polar regions are regularly arranged within the hydrocarbon layer (Figure 4.3). It is however not clear, why an oblique instead of a rectangular lattice is found.

The liquid crystalline properties of the semifluorinated compounds in dependence on the numbers of semifluorinated chains is shown in Table 4.3. All semifluorinated compounds exhibit enantiotropic liquid crystalline phases, and most importantly they exhibit different mesophases. Compared with the hydrocarbon analogues, all fluorinated compounds exhibit broad regions of enantiotropic liquid crystalline phases, whereas, the hydrocarbon analogues are non-mesomorphic or their mesophases are only monotropic (see Table 4.1). These broad mesophase ranges result from a dramatic stabilization of the liquid crystalline state and a reduction of the melting points.

Table 4.3 *Thermotropic phase transition temperatures and associated enthalpy values (lower lines, in italics) of compounds **27**.*



Comp.	R_1	R_2	R_3	Phase transitions *ΔH/KJ mol^{-1}*
27-1F$_{4/6}$	$O(CH_2)_6C_4F_9$	H	H	Cr <20 Cub_{v2} 49 Iso *0.4*
27-1F$_{6/4}$	$O(CH_2)_4C_6F_{13}$	H	H	Cr 59 SmA 88 Iso *10.1 1.0*
27-2F$_{6/4}$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	H	Cr 88 Col_{h2} 131 Iso *8.5 5.6*
27-3F$_{4/6}$	$O(CH_2)_6C_4F_9$	$O(CH_2)_6C_4F_9$	$O(CH_2)_6C_4F_9$	Cr <20 Cub_{I2} 73 Iso *0.4*
27-3F$_{6/4}$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	Cr 36 Cub_{I2} 101 Iso *8.4 0.4*

By using optical microscopy between crossed polarizes, the formation of a birefringent fan-like texture was observed on cooling compound **27-1F$_{6/4}$**, with four semifluorinated chains to 88 °C. Shearing gave a typical "oily streaks" optical texture with homeotropic regions, which indicates a mesophase with a layer structure (SmA). X-ray scattering confirmed this phase assignment (one sharp reflex in the small angle region and a diffuse scattering in the wide angle region) with a layer periodicity of d = 3.2 nm. This periodicity is in agreement with an arrangement of these molecules in layers consisting of alternating sublayers of the microsegregated semifluorinated chains and sublayers of the polar benzoate units.

The other four chain compound **27-1F$_{4/6}$** with shorter fluorinated segments, has a Cub_{V2} phase. This was proven by the optical isotropy of this mesophase, its rather high viscosity and by miscibility studies: in the contact region of compound **27-1F$_{4/6}$** and the micellar cubic mesophase of **27-3F$_{4/6}$** a columnar mesophase was induced. The occurrence of a cubic phase is surprising, because the volume fraction of the lipophilic chains is reduced in compound **27-1F$_{4/6}$** in comparison to compound **27-1F$_{6/4}$** which has a SmA phase. It seems, that longer perfluorinated chains can also have a stabilizing effect on lamellar phases due to their rigidity.[52b]

Compound **27-2F$_{6/4}$**[59b] with eight semifluorinated chains has a hexagonal columnar mesophase as previously mentioned (Col_{h2}, a_{hex} = 3.4 nm at T = 130 °C). Here, the polar regions form circular cylinders surrounded by the semifluorinated chains.

No birefringence was found on cooling the compounds **27-3F$_{4/6}$** and **27-3F$_{6/4}$** having twelve chains. However, a significant increase of the viscosity was observed on cooling form the isotropic liquid state at 73 °C and 101 °C, respectively. Calorimetric measurements indicate a phase transition which occurs at 73 °C and 101 °C in the heating scans, but at 47 °C (**27-3F$_{4/6}$**) and 85 °C (**27-3F$_{6/4}$**) in the cooling scans (10 K min^{-1}), respectively. Obviously, the transition to this isotropic phase can be significantly supercooled and this is typical for three-dimensional ordered mesophases. Preliminary X-ray investigations of the isotropic mesophase of compound **27-3F$_{6/4}$** indicate a diffuse scattering in the wide angle region and three independent sharp reflexes in the small angle region. Together with the other observations (optical isotropy, viscosity, supercoolability), the existence of a cubic mesophase was confirmed. The cubic mesophase occurs in a phase sequence SmA→ Col_{h2} → Cub on increasing the number of semifluorinated chains while keeping the size of the polar central unit constant. Hence, the polar/apolar interface curvature becomes increasingly more curved in the order described above and therefore the cubic 3D lattice of compound **27-3F** should be built up by discrete spheroidic entities containing the polar parts of the molecules surrounded by a continuum of the nonpolar chains (inverted micellar cubic phases, Cub_{I2}).

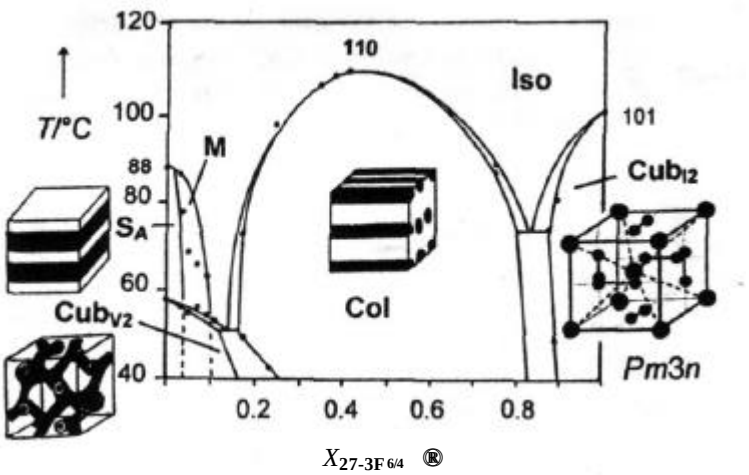


Figure 4.4 *Phase diagram of the binary system **27-1F$_{6/4}$** + **27-3F$_{6/4}$**.*

In order to prove this hypothesis, we investigated binary mixtures of different concentrations of compounds **27-1F$_{6/4}$** and **27-3F$_{6/4}$** by optical microscopy. The results are summarized in the phase diagram, shown in Figure 4.4. The most important observation is that a broad region ($X_{27\text{-}3F6/4}$ = 0.15-0.85) of a columnar mesophase, built up from cylindrical aggregates, is induced between the smectic phase of compound **27-1F$_{6/4}$** (planar aggregates)

and the cubic phase of **27-3F$_{6/4}$**. As the polar/apolar interface curvature is reduced on addition of **27-1F$_{6/4}$**, the aggregates forming the cubic phase must be more curved than the cylindrical aggregates in the induced columnar phase. This shows that the cubic phase must comprise closed spheroidic aggregates, which additionally confirms the proposed inverted micellar structure of the cubic mesophase of **27-3F$_{6/4}$** (Cub$_{I2}$ phase).

For such thermotropic Cub$_{I2}$ phases, *Pm*3*n* lattices have been found almost exclusively. Indeed, the relative positions of the small angle reflexes in the cubic phase of **27-3F$_{6/4}$** at α = 1.57° and 1.73° correspond to the most intensive reflexes found for other inverted micellar cubic mesophases of the *Pm*3*n* type. Assuming such a *Pm*3*n* lattice, the reflexes can be indexed to 200 and 210, and a cubic lattice parameter a_{cub} = 5.6 nm was calculated. The number of molecules per unit cell was calculated according to $n = a_{cub}^3 (N_A/M)\rho$ (N_A = Avogadro constant, M = molecular mass), assuming a density of ρ = 1.4 g cm^{-3} to give about 28 molecules per unit cell. [77]

Though, the precise shape of the micelles in *Pm*3*n* phases is still under debate, it is now accepted that the unit cells contain eight discrete micellar aggregates of two different types (see Figure 4.4).[9,48c,50a,60] Two aggregates of one type are located at the corners and in the center of the unit cell, forming a body centered sublattice, and six aggregates of the other type are located pairwise at the face bisectors of the cubes. Hence, the 28 molecules should be shared among eight entities forming the unit cell of the *Pm*3*n* lattice, and therefore, the cubic lattice should be built up by aggregates consisting of three to four molecules. The aggregates thus represent micelles built up by the selfassembly of molecules deformed, on average, to a cone like shape.

A closer inspection of the binary phase diagram, indicates in regions with a high concentration of **27-1F$_{6/4}$** ($X_{27\text{-}3F_{6/4}}$ = 0.10-0.15) another optically isotropic region. Below a temperature of about 50 °C, this isotropic phase is highly viscous and plastic, which again points to a cubic mesophase. As this phase occurs between a smectic and an inverted columnar phase it should be an inverted bicontinuous cubic phase consisting of interpenetrating networks of branched columns formed by the polar molecular parts within the apolar continuum of the semifluorinated chains (Cub$_{V2}$).

In regions of very low concentration of **27-3F$_{6/4}$** ($X_{27\text{-}3F_{6/4}}$ = 0.05-0.10), close to conditions for the smectic phase, an additional birefringent mesophase (M) is induced. Shearing the sample of this mesophase shows bright, homogeneous regions by optical microscopy. We assume, that this phase could probably be another intermediate phase with a two- or three-dimensional structure.

These results show, that a wide variety of completely different mesophases can be realized by the self-assembly of pure samples or binary system of molecules in which a star-like shape is provided by tetrahedral central cores. Because the flexibility of these molecules allows them to adopt different conformations, the actual average conformation changes

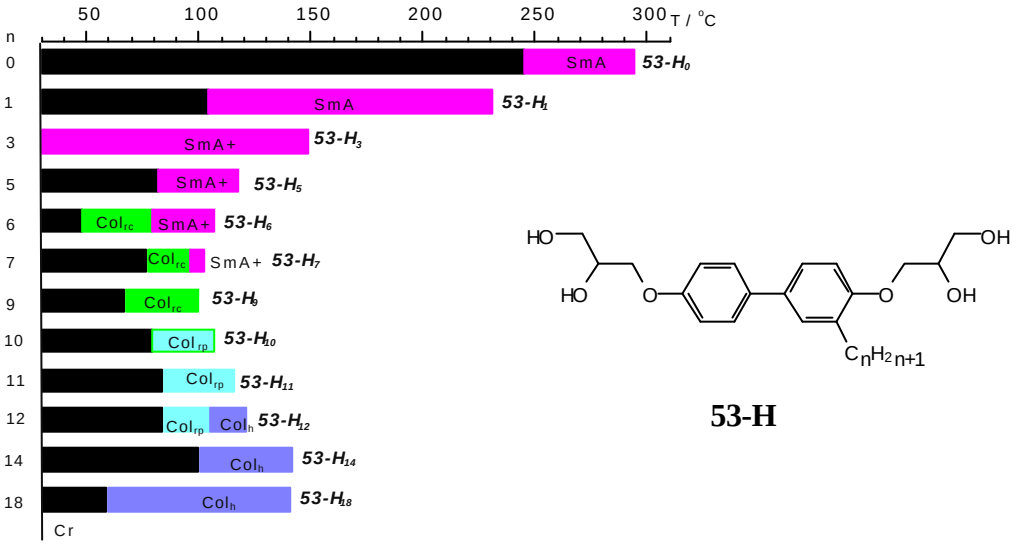
during the process of self-assembly, whereby, conformers which fit best the geometry provided by the interfaces are favored. The interface geometry itself can simply be tailored by changing the space required by the incompatible units. This is the main difference to classical thermotropic liquid crystals, and to the columnar and cubic mesophases formed by taper- or cone-shaped amphiphiles and dendrons. For these molecules, the self-assembly is facilitated by a complimentary shape provided by a special molecular architecture.

The increased mesophase stability of all fluorinated compounds **27-1F**, **27-2F** and **27-3F** in comparison to the related alkyl compounds **27-1H**, **27-2H** and **27-3H** should again arise largely from an increased intramolecular polarity contrast on replacing alkyl chains by the semifluoralkyl chains, which favors micro-segregation. The larger cross-section area of the fluorinated alkyl chain in comparison to the alkyl chains should be responsible for the transition from a columnar to a micellar cubic phase upon replacing the alkyl chains of **27-3H** by semifluorinated chains. It should be pointed out that **27-3F** and the amphiphilic diols **7-2F** and **7-3F** (see chapter 2) belong to the first fluorinated molecules which can form thermotropic micellar cubic mesophases. Furthermore, the phase sequence SmA $\leftrightarrow$ (M) $\leftrightarrow$ Cub_{V2} $\leftrightarrow$ Col_{h2} $\leftrightarrow$ Cub_{I2} represents the whole sequence of inverted lyotropic phases of surfactant solvent systems, which is first realized here in a binary systems of only two different low molecular weight block molecules in the absence of any solvent. This observation is of fundamental interest, because it shows that it is indeed possible to design all types of mesophases (smectic, columnar, bicontinuous cubic, and micellar cubic) without the classical concepts of rigidity/anisometry and strong amphiphilicity. Additionally, these novel compounds represent an interesting borderline case between low molecular weight amphiphiles (surfactants, lipids) and block copolymers.

5 Calamitic bolaamphiphiles with lateral semifluorinated chains

5.1 Introduction

Bolaamphiphiles with lateral alkyl chains **53-H** (R = C_nH_{2n+1}, n = 0-18)[61] can be regarded as low molecular weight block-molecules consisting of three distinct incompatible portions: a rigid, rod-like aromatic unit, two hydrophilic terminal groups and a lateral alkyl chain. Such molecules give rise to columnar mesophases. Their formation was explained as a consequence of the segregation of the liphophilic and flexible lateral chains from the rigid aromatic cores into separate cylindrical domains which lead to the collapse of the smectic monolayer structure of the parent nonsubstituted bolaamphiphiles.



53-H

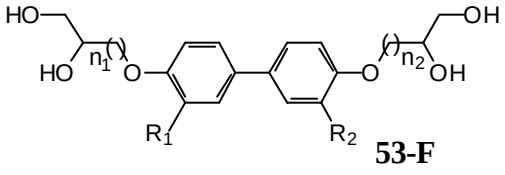
Figure 5.1 *Transition temperatures (T / °C) of compounds **53-H** in dependence on the length of the alkyl chains. SmA^+ = disordered SmA-phase (typical SmA texture, but in the small angle region of the X-ray pattern a diffuse reflection is found instead or beside the layer reflection), Col_{rc} = centered rectangular columnar phase* (*c*2*mm*); *Col_{rp} = non-centered rectangular columnar phase* (*p*2*gg*); *Col_h = hexagonal columnar phase* (*p*6*mm*).

The results obtained with these compounds up to now are summarized in Figure 5.1. Small lateral alkyl chains lead to a drastic lowering of the melting temperature and destabilize the monolayer SmA mesophase of the unsubstituted compounds **53-H_0**. Elongation of the lateral chain, firstly induces disordered SmA^+ phases characterized by the occurrence of a diffuse small angle scattering beside or instead of the sharp layer reflection. Homologues with longer lateral alkyl chains (n = 9-14) form columnar phases. Three different 2D-structures: Col_{rc}, Col_{rp}, Col_h were found.

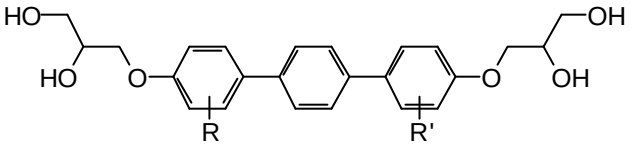
In order to further extend this designing principle, we decided to introduce an additional incompatible segment into these molecules. As perfluorinated chains are incompatible with aliphatic chains, aromatic units as well as polar groups, and they can in some cases enhance lipophilicity and micro-segregation, we have synthesized rigid bolaamphiphiles with fluorinated lateral chains.

5.2 Synthesis

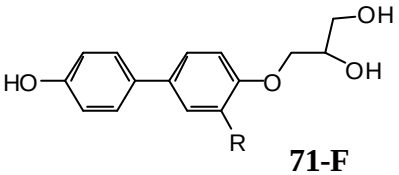
In this chapter, the synthesis of the bolaamphilic biphenyl derivatives **53-F** (see Scheme 5.7a and Scheme 5.7c), the terphenyl derivatives **58-F** (see Scheme 5.7b and Scheme 5.7d) and the triols **71-F** (see Scheme 5.10) is described. Two bolaamphiphilc compounds **53F.15** and **53F.16**, which have larger head groups (see Scheme 5.8 and Scheme 5.9) and compound **58-H_9F_6** with two different lateral chains were also synthesized (see Scheme 5.11). Pd°-catalyzed addition of perfluoralkyliodides to 2-allylphenol or 2-allylanisole, selective bromination and then Pd°-catalyzed cross-coupling with appropriate benzene boronic acids were the key steps and gave the final products **53-F**, **58-F** and **71-F** after acidolytic deprotection of the diol groups or dihydroxylation of the double bonds or after cleavage of the benzyl protecting group by palladium catalyzed hydrogenation reaction.



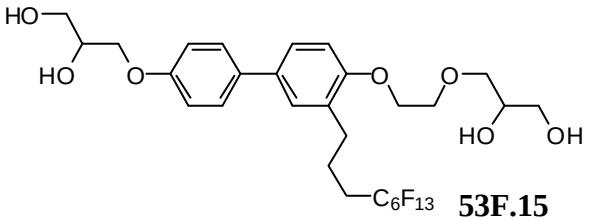
53-F



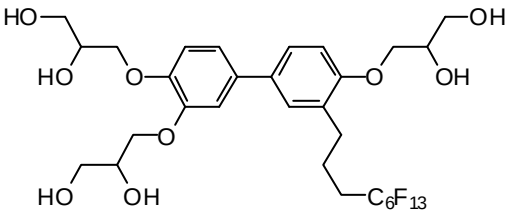
58-F



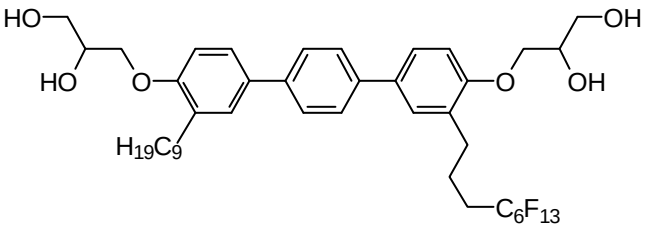
71-F



53F.15

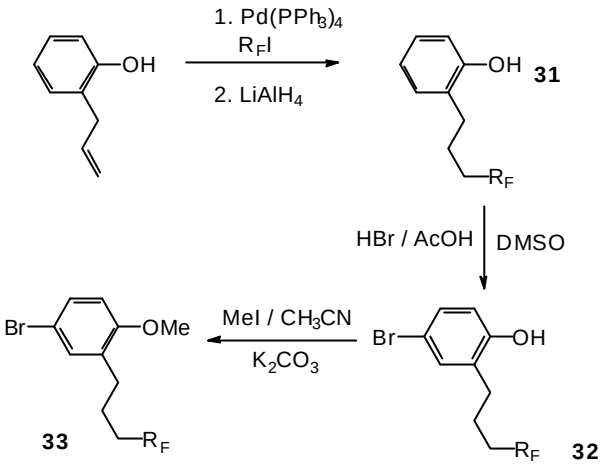


53F.16



58-H_9F_6

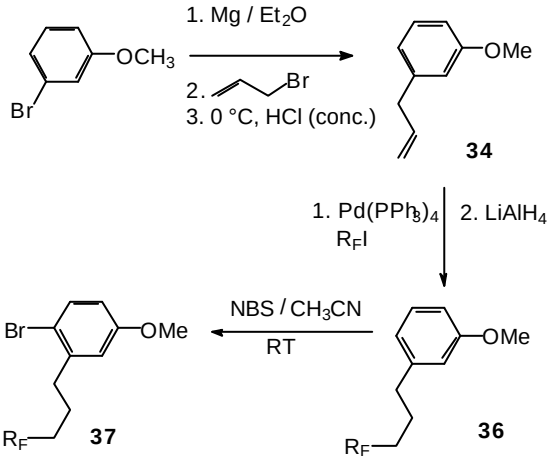
5.2.1 Synthesis of the 4-bromophenols 32 and the 4-bromoanisoles 33, 37, 41, 43



R_F	Comp.	Comp.	Comp.
C_3F_7	**31.1**	**32.1**	**33.1**
C_4F_9	**31.2**	**32.2**	**33.2**
C_6F_{13}	**31.3**	**32.3**	**33.3**
$(CF_2)_4CF(CF_3)_2$	**31.4**	**32.4**	**33.4**
C_8F_{17}	**31.5**	**32.5**	**33.5**
$C_{10}F_{21}$	**31.6**	**32.6**	**33.6**
$C_{12}F_{25}$	**31.7**	**32.7**	**33.7**

Scheme 5.1 *Synthesis of the 4-bromo-2-(semifluoroalkyl)phenols **32** and the 4-bromo-2-(semifluoroalkyl)anisoles **33**.*

The synthesis of the calamitic skeleton of all compounds starts with 2-allylphenol or 3-bromoanisole. The 4-bromophenols **32**, with a semifluorinated chain in 2-position, were prepared by palladium-catalyzed addition of 1-iodoperfluoroalkanes to 2-allylphenol, followed by reduction of the iodide group with $LiAlH_4$, and finally para-selective bromination of the resulting 2-(semifluoroalkyl)phenols **31** with HBr/AcOH/DMSO.[62] The 4-bromophenols **32** were etherified with methyliodide to give the 4-bromoanisoles **33** (scheme 5.1).



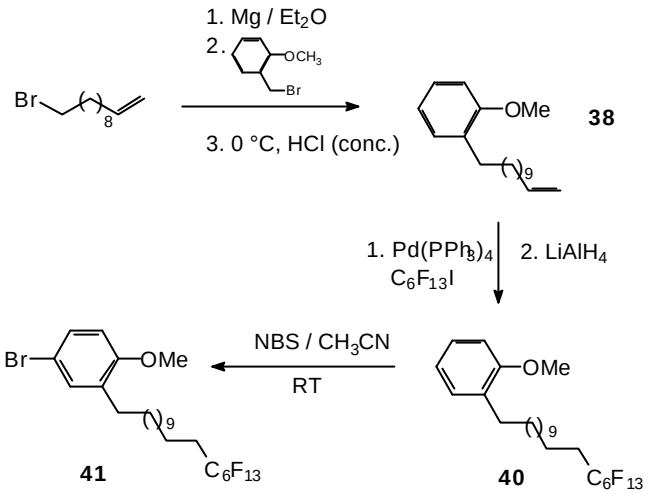
R_F	Comp.	Comp.
C_4F_9	**36.1**	**37.1**
C_6F_{13}	**36.2**	**37.2**
C_8F_{17}	**36.3**	**37.3**

Scheme 5.2 *Synthesis of 4-bromo-3-(semifluoroalkyl)anisoles **37**.*

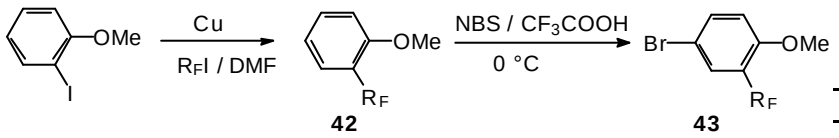
The 4-bromoanisoles **37** which have the semifluorinated chains in the 3-position, were prepared in an analogous way from **34**, which was synthesized by Grignard reaction between 3-methoxyphenylmagnesiumbromide and allylbromide.[63] In this case para-selective

bromination of the 3-substituted anisoles **36** was carried out with NBS/CH_3CN [64](Scheme 5.2).

4-Bromo-2-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H7H,7H,8H,8H,9H,9H,10H,10H, 11H,11H,12H,12H-perfluorooctadecyl)anisole **41** was prepared in a similar way, starting with C-C coupling between 2-methoxybenzylbromide and 11-undecene-1-yl magnesiumbromide (Scheme 5.3).



Scheme 5.3 *Synthesis of 4-bromo-2-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H, 7H,8H,8H,9H,9H,10H,10H,11H,11H,12H,12H-perfluorooctadecyl)anisole **41**.*

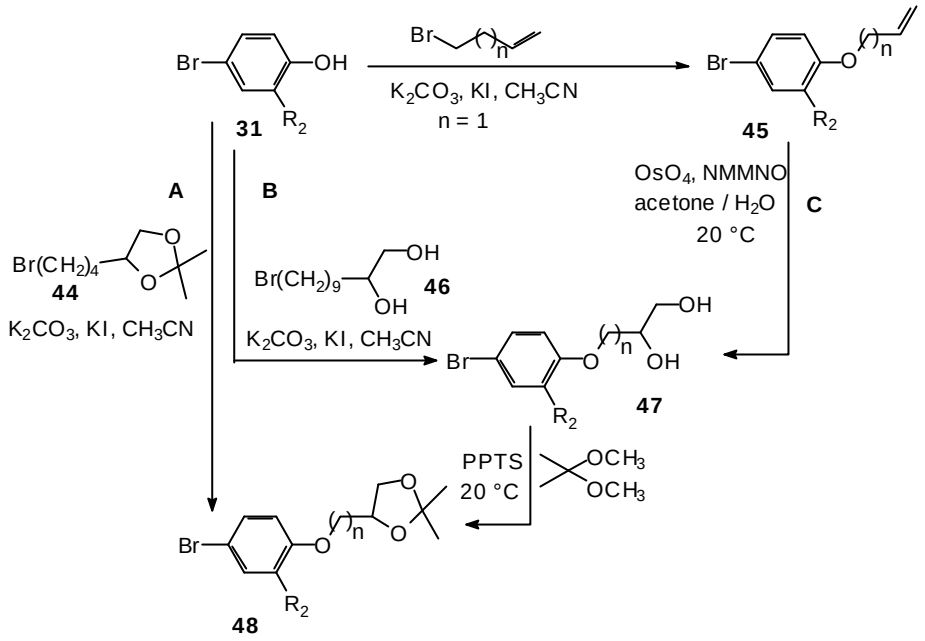


R_F	Comp.	Comp.
C_4F_9	**42.1**	**43.1**
C_8F_{17}	**42.2**	**43.2**

Scheme 5.4 *Synthesis of the 4-bromoanisoles **43**.*

Compounds **43** with perfluorinated chains directly attached to the aromatic core were prepared by coupling reaction of 2-iodoanisole with the appropriate 1-iodoperfluoroalkane in the present of active copper powder (produced in situ by reduction of $CuSO_4$ with zinc-dust),[65] followed by bromination with NBS in trifluoroacetic acid at 0 °C [66] (Scheme 5.4).

5.2.2 Synthesis of the 4-{w-[4-bromo-2-(semifluoroalkyl)phenoxy]alkyl}-2,2-dimethyl-1,3-dioxolanes 48

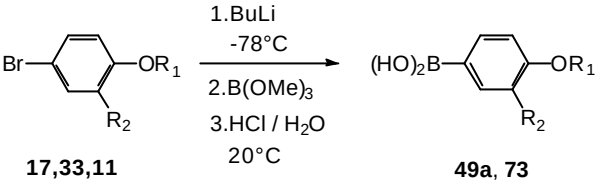


n	R_2	Comp.	Comp.	Comp.
1	$(CH_2)_3C_6F_{13}$	**45.1**	**47.1**	**48.1**
1	$(CH_2)_3C_8F_{17}$	**45.2**	**47.2**	**48.2**
1	$(CH_2)_3C_{10}F_{21}$	**45.3**	**47.3**	**48.3**
1	$(CH_2)_3C_{12}F_{25}$	**45.8**	**47.8**	**48.8**
4	$(CH_2)_3C_6F_{13}$			**48.4**
9	$(CH_2)_3C_6F_{13}$		**47.4**	**48.5**
4	$(CH_2)_3C_8F_{17}$			**48.6**
9	$(CH_2)_3C_8F_{17}$		**47.5**	**48.7**

Scheme 5.5 *Synthesis of 4-{ω-[4-bromo-2-(semifluoroalkyl)phenoxy]alkyl}-2,2-dimethyl-1,3-dioxolanes* ***48.***

The 4-{ω-[4-bromo-2-(semifluoroalkyl)phenoxy]alkyl}-2,2-dimethyl-1,3-dioxolanes **48** were produced by three different ways as shown in Scheme **5.5**. Etherification of the phenol **31** with 4-(4-bromobutyl)-2,2-dimethyl-1,3-dioxolane **44**[67] afforded compounds **48.4** and **48.6** (**A**). Etherification of the phenolic hydroxyl group of **31** with 11-bromoundecane-1,2-diol **46**,[68] afforded firstly the 11-(4-bromophenoxy)undecane-1,2-diols **47.4** and **47.5**. Protection of the diol structure of compounds **47** using 2,2-dimethoxypropane and catalytic amounts of pyridinium tosylate produced the acetonides **48.5** and **48.7** (**B**).[69] For the preparation of **48.1**, **48.2**, **48.3** and **48.8**, we used the etherification of the phenolic hydroxyl function of compounds **31** firstly with appropriate ω-bromoalkenes, followed by dihydroxylation of the double bond employing VAN RHEENEN method with catalytic amounts of osmiumtetroxide and NMMNO (*N*-methylmorpholine-*N*-oxide) as reoxydant in acetone / water,[70] and finally protection of the diol group (**C**).

5.2.3 Synthesis of boronic acids 49 and 73



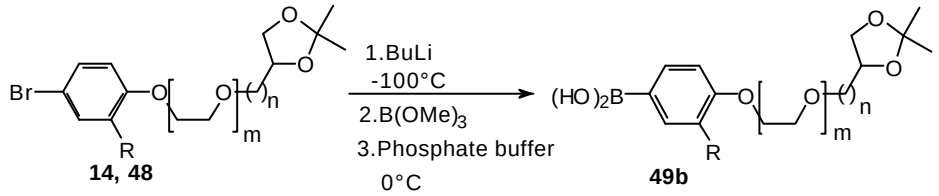
17,33,11 **49a**, **73**

R_1	R_2	Comp.	Comp.
CH_3	OCH_3	**17**	**49a.1**
CH_3	$(CH_2)_3C_4F_9$	**33.2**	**49a.4**
CH_3	$(CH_2)_3C_6F_{13}$	**33.3**	**49a.5**
CH_3	$(CH_2)_3(CF_2)_4CF(CF_3)_2$	**33.4**	**49a.6**
CH_3	C_9H_{19}	**33.7**	**73**

Scheme 5.6a *Synthesis of the boronic acids **49a** and **73**.*

The boronic acids **49** were synthesized from the corresponding aromatic bromo derivatives by the standard method of halogen-metal-exchange with n-BuLi,[71] followed by reaction with trimethylborate and acidic hydrolysis.

In the case of the bromobenzene derivatives **14** and **48**, the halogen-metal-exchange reaction was carried out at –100 °C, in order to avoid the occurrence of lithiation in ortho-position to the acetonide group. To avoid the cleavage of the acetonide protecting group during the acid hydrolysis, phosphate buffer (pH = 4.5-5) was used instead of 10 % HCl.

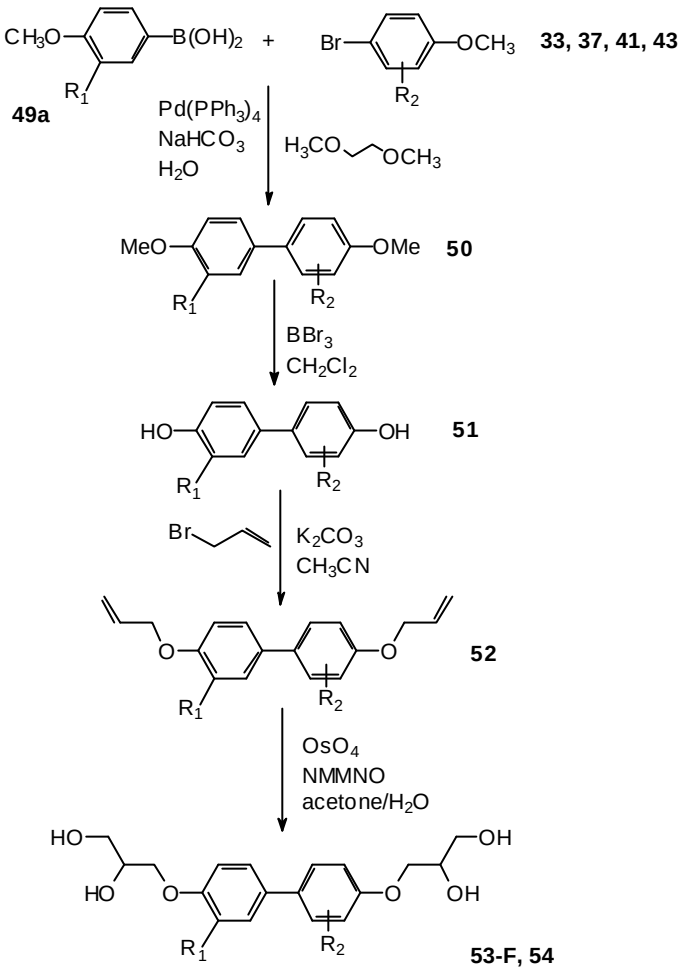


14, 48 **49b**

m	n	R	Comp.	Comp.
0	1	H	**48.9**	**49b.1**
1	1	H	**14**	**49b.2**
0	4	H	**48.10**	**49b.3**
1	1	C_6H_{13}	**48.11**	**49b.4**

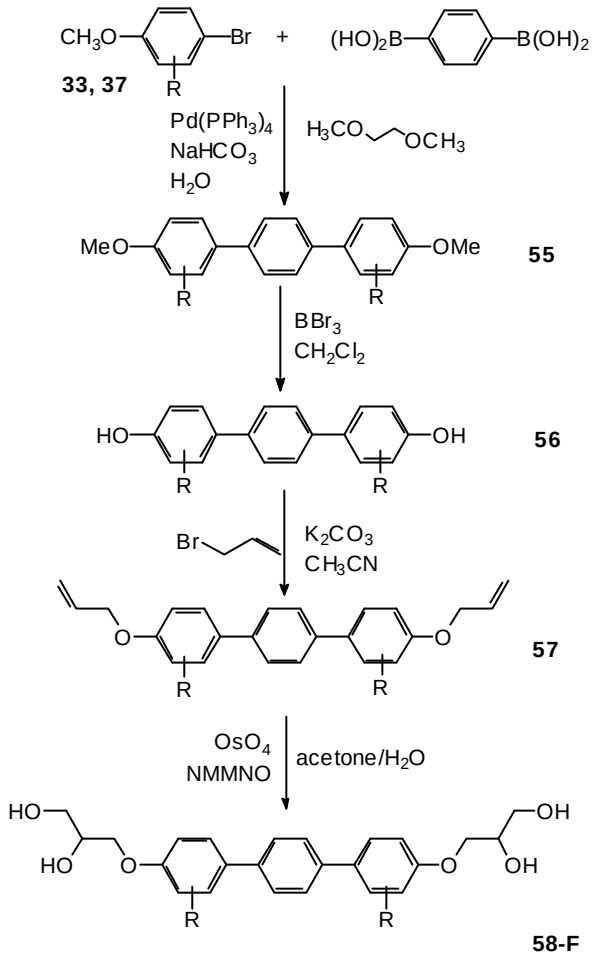
Scheme 5.6b *Synthesis of the boronic acids **49b**.*

5.2.4 Synthesis of bolaamphiphilic tetraols 53-F, 54 and 58-F with biphenyl and p-terphenyl rigid cores



R_1	R_2	Comp.	Comp.	Comp.	Comp.	Comp.
H	3-C_4F_9		**43.1**	**50.1**	**51.1**	**53-$F_{4/0}$**
H	3-$(CH_2)_3C_3F_7$		**33.1**	**50.2**	**51.2**	**53-F_3**
H	3-$(CH_2)_3C_4F_9$		**33.2**	**50.3**	**51.3**	**53-F_4**
H	2-$(CH_2)_3C_4F_9$		**37.1**	**50.8**	**51.8**	**53c-F_4**
H	3-C_8F_{17}		**43.2**	**50.4**	**51.4**	**53-$F_{8/0}$**
H	2-$(CH_2)_3C_6F_{13}$		**37.2**	**50.9**	**51.9**	**53c-F_6**
H	3-$(CH_2)_3(CF_2)_4CF(CF_3)_2$		**33.4**	**50.5**	**51.5**	**53-F_7**
H	2-$(CH_2)_3C_8F_{17}$		**37.3**	**50.10**	**51.10**	**53c-F_8**
H	3-$(CH_2)_3C_{10}F_{21}$		**33.6**	**50.6**	**51.6**	**53-F_{10}**
H	3-$(CH_2)_{12}C_6F_{13}$		**41**	**50.7**	**51.7**	**53-$F_{6/12}$**
3-$(CH_2)_3C_6F_{13}$	3′-$(CH_2)_3C_6F_{13}$	**49a.5**	**33.3**	**50.11**	**51.11**	**54-$F_{6,6}$**
3-$C_{12}H_{25}$	3′-$(CH_2)_{12}C_6F_{13}$	**49a.5**		**50.12**	**51.12**	**54-$H_{12}F_6$**
3-$(CH_2)_3(CF_2)_4CF(CF_3)_2$	3-$(CH_2)_3(CF_2)_4CF(CF_3)_2$	**49a.6**	**33.4**	**50.13**	**51.13**	**54-$F_{7,7}$**

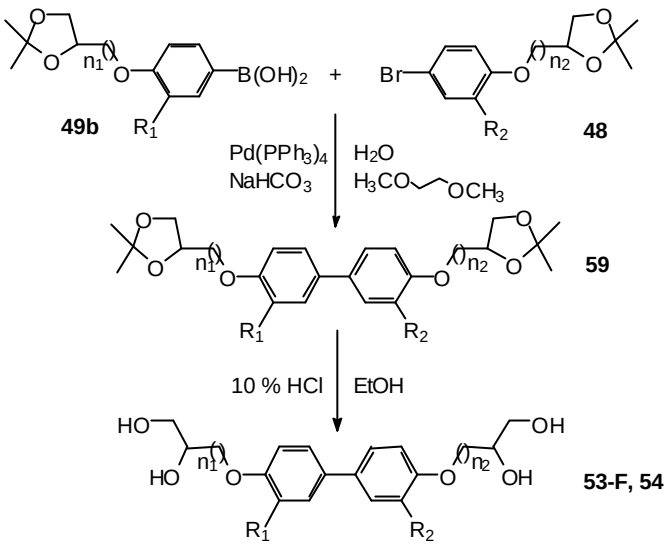
Schema 5.7a *Synthesis of biphenyl derivatives **53-F** (Path A).*



R	Comp.	Comp.	Comp.	Comp.	Comp.
3-$(CH_2)_3C_4F_9$	**33.3**	**55.1**	**56.1**	**57.1**	**58-F$_{4,4}$**
2-$(CH_2)_3C_6F_{13}$	**37.2**	**55.2**	**56.2**	**57.2**	**58-F$_{6,6}$**

Scheme 5.7b *Synthesis of terphenyl derivatives **58-F** (Path A).*

Several different synthetic pathways were used to synthesize the bolaamphiphilic biphenyl derivatives **53-F** and **54** and the terphenyl derivatives **58-F**. In path A (Scheme 5.7a and Scheme 5.7b), the coupling reaction[72] between the 4-bromoanisoles **33**, **37**, **41** and **43** and the 4-methoxybezeneboronic acid **49a** or the commercially available benzene diboronic acid **54** leads to the 4,4′-dimethoxybiphenylderivatives **50** and the 4,4″-dimethoxy-p-terphenylderivatives **55**, respectively. After deprotection of the methylethers with boron tribromide,[73] the resulting divalent phenols **51** or **56** were etherified with allylbromide followed by dihydroxylation of the allylic double bonds to give the biphenyl derivatives **53-F** and **54** and the terphenyl derivatives **58-F**.



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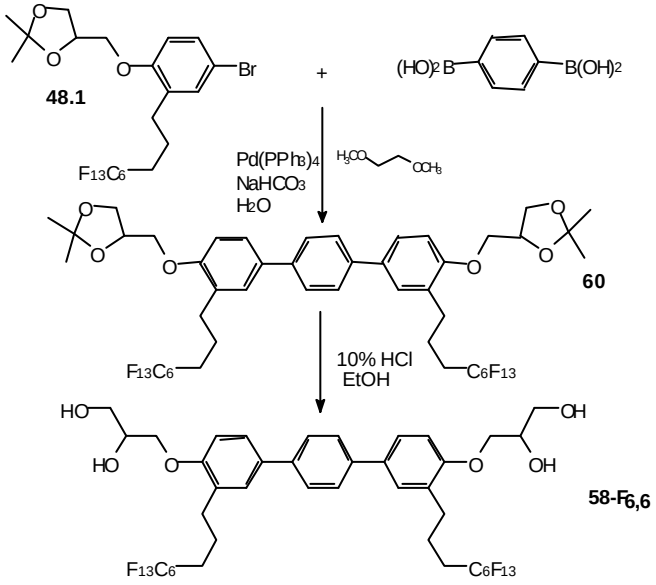
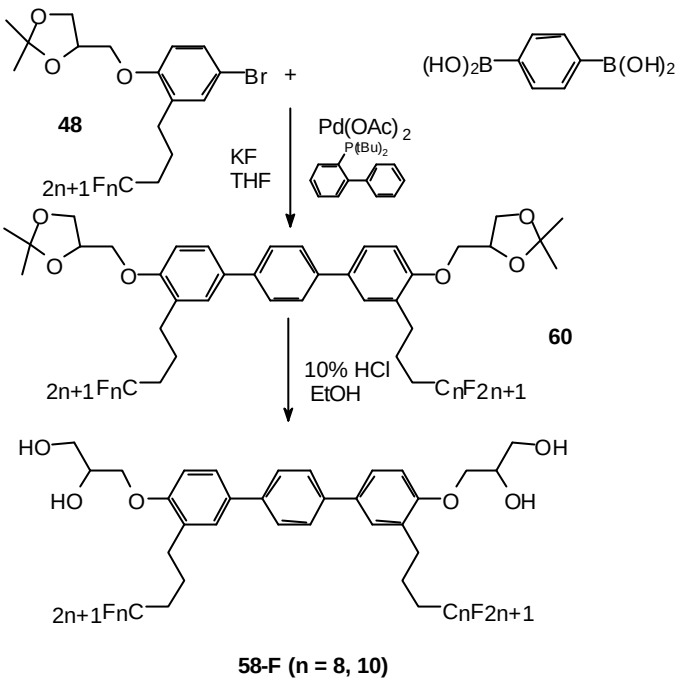
R_1	R_2	n_1	n_2	Comp.	Comp.	Comp.	Comp.
H	3-$(CH_2)_3C_8F_{17}$	1	1	**48.2**	**49b.1**	**59.1**	**53-F_8**
H	3-$(CH_2)_3C_6F_{13}$	1	4	**48.4**	**49b.1**	**59.2**	**$53^{1,4}$-F_6**
H	3-$(CH_2)_3C_6F_{13}$	1	9	**48.5**	**49b.1**	**59.3**	**$53^{1,9}$-F_6**
H	3-$(CH_2)_3C_6F_{13}$	4	4	**48.4**	**49b.3**	**59.4**	**$53^{4,4}$-F_6**
H	3-$(CH_2)_3C_8F_{17}$	4	1	**48.5**	**49b.3**	**59.5**	**$53^{4,1}$-F_8**
H	3-$(CH_2)_3C_8F_{17}$	1	4	**48.6**	**49b.1**	**59.6**	**$53F^{1,4}$-F_8**
H	3-$(CH_2)_3C_8F_{17}$	1	9	**48.7**	**49b.1**	**59.7**	**$53^{1,9}$-F_8**
3-CH_3	3′-$(CH_2)_3C_6F_{13}$	1	1	**48.1**		**59.8**	**54-H_1F_6**
3-C_6H_{13}	3′-$(CH_2)_3C_6F_{13}$	1	1	**48.1**	**49b.4**	**59.9**	**54-H_6F_6**

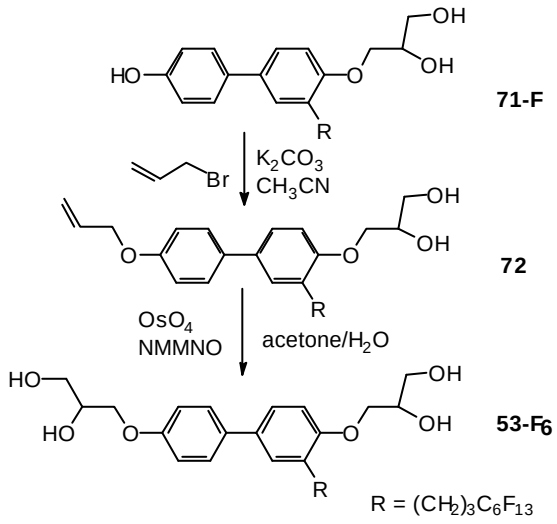
Schema 5.7c *Synthesis of the bolaamphiphilic biphenyl derivatives **53-F** and **54** (Path B).*



Schema 5.7d *Synthesis of the bolaamphiphilic tertraol **58-$F_{6,6}$** (Path B)..*



Schema 5.7e *Synthesis of the bolaamphiphilic tertraol* ***58-F$_{8,8}$*** *and .* ***58-F$_{10,10}$.***



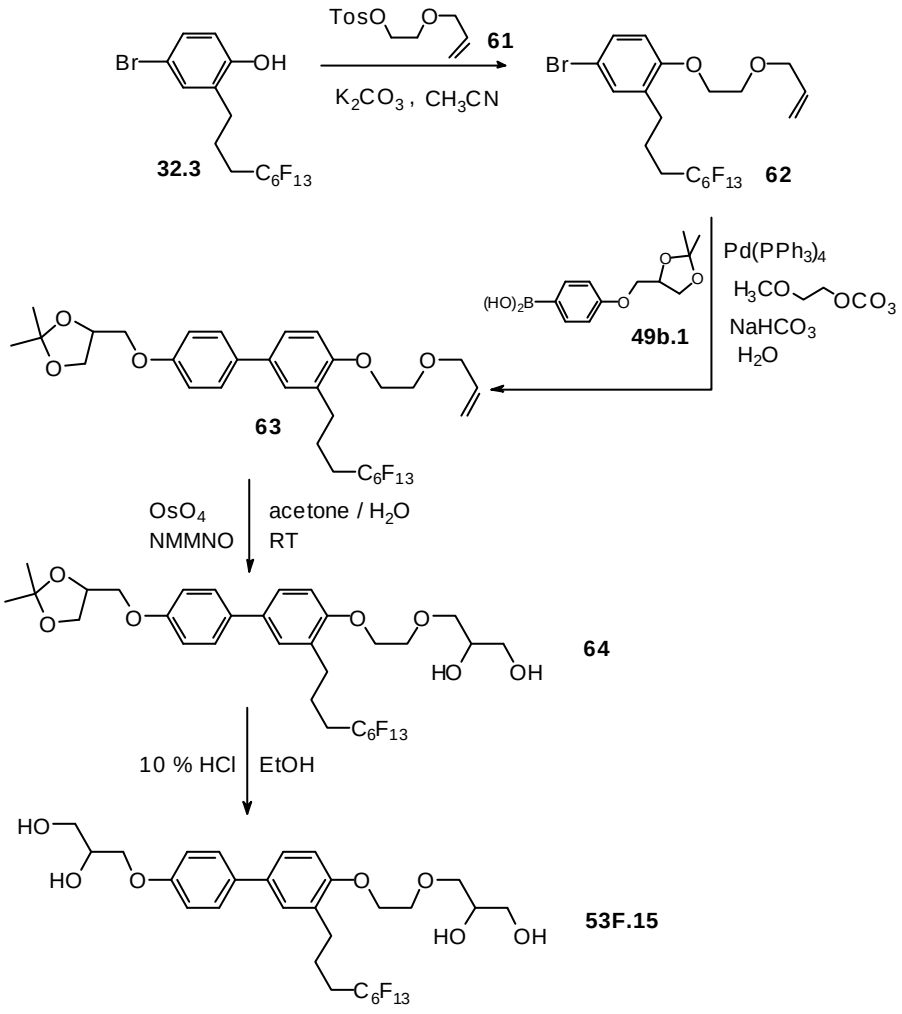
Scheme 5.7f *Synthesis of the bolaamphiphilic tetraols* ***53-F$_6$*** *(Path C).*

In the second synthetic path B (Scheme 5.7c, 5.7d) the coupling reaction was carried out between the 4-{ω-[4-bromo-2-(semifluoroalkyl)phenoxy]alkyl}-2,2-dimethyl-1,3-dioxolanes **48** and the boronic acids **49b**, or the benzene diboronic acid **54**. The resulting bisacetonides **59** and **60** were deprotected[56] to afford the tetraols **53-F, 54** or **58-F$_{6,6}$**. In the case of

compounds **58-F$_{8,8}$** and **58-F$_{10,10}$**, the coupling reaction was catalyzed by 2-(di-*tert*-butylphosphino)biphenyl, $Pd(OAc)_2$, KF in THF[74] instead with $Pd(PPh_3)_4$ in aqueous glyme and $NaHCO_3$, because of the poor solubility of compounds **48.2** and **48.3** in this solvent system (Scheme 5.7e).

Compound **53-F$_6$** was synthesized by etherification of the phenolic OH-group of compound **71-F** (see section **5.2.6**) with allylbromide, followed by dihydroxylation of the allylic double bond (Path C, see Scheme 5.7f).

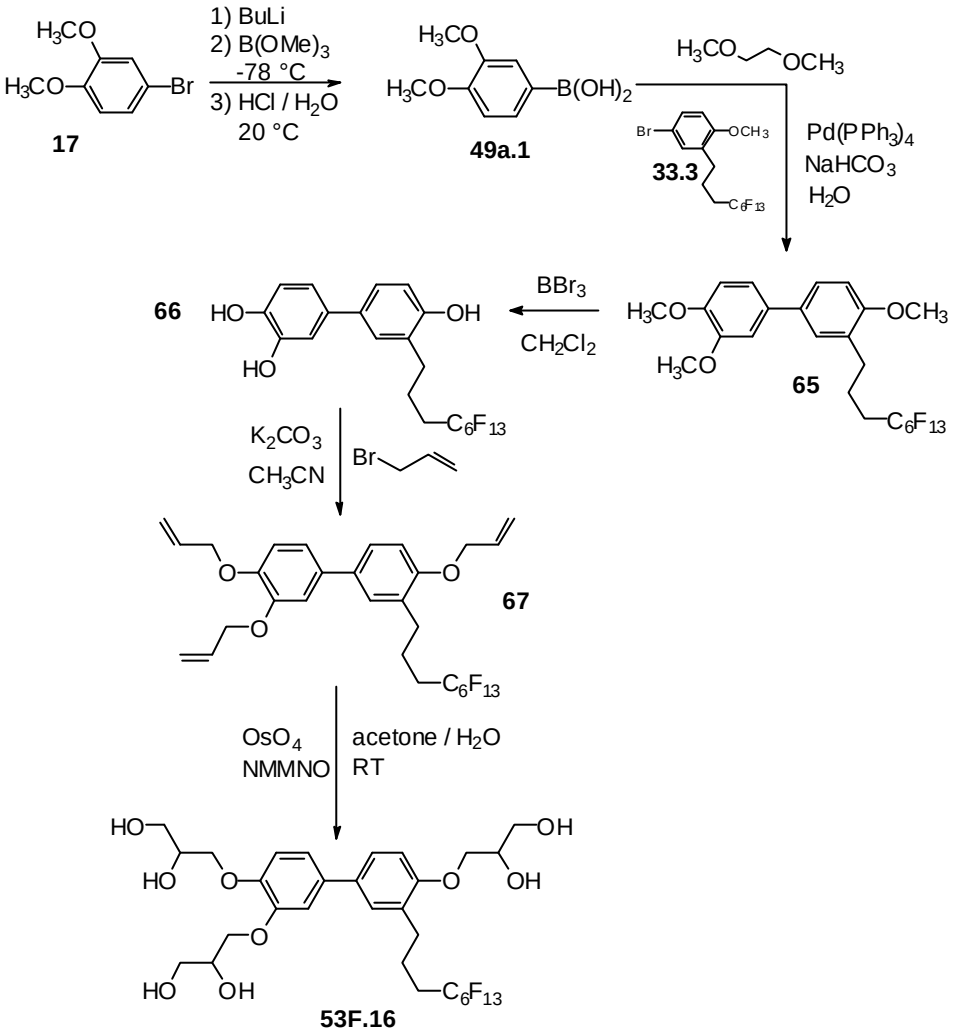
5.2.5 Synthesis of bolaamphiphiles with larger head groups (53F.15 and 53F.16)



Scheme 5.8 *Synthesis of the bolaamphiphile **53F.15**.*

6-[4′-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4-yloxy]-4-oxahexane-1,2-diol **53F.15** was synthesized according to Scheme 5.8. At first the 4-bromophenol derivative **32.3** was etherified with 1-toluenesulfonyloxy-3-oxa-5-hexene **61**[75]

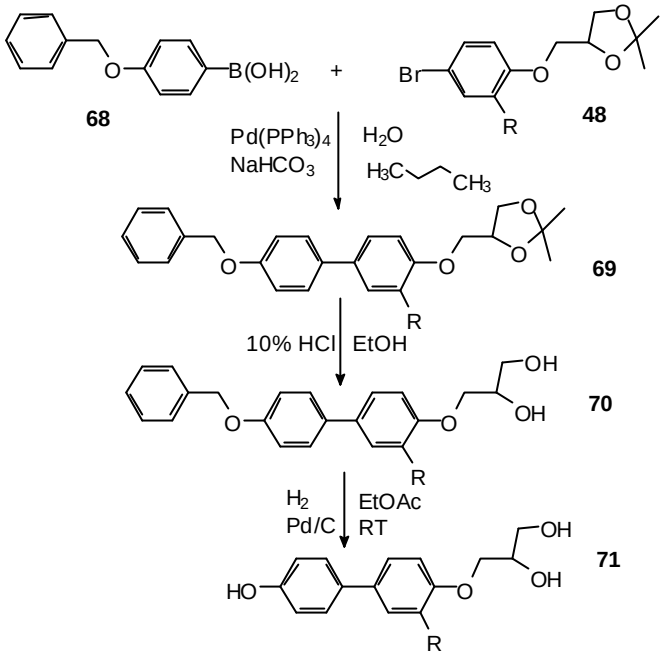
in the presence of K_2CO_3. The coupling reaction between the resulting allylether **62** and the boronic acid **49b.1** afforded **63**, dihydroxylation of the allylic double bond of **63** resulted **64**, which was deprotected to **53F.15**.



Scheme 5.9 *Synthesis of the bolaamphiphile **53F.16**.*

3-[3′,4′-Bis(2,3-dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4-yloxy]propane-1,2-diol **53F.16** was synthesized according to Scheme 5.9. At first the boronic acid **49a.1** was synthesized from commercially available 4-bromoveratrol (see Scheme 5.6a). Coupling reaction between **49a.1** and the 4-bromoanisole **33.3** yielded the trimethylether **65**. The ether groups of **65** were cleaved by borontribromide. Etherification of the resulting trivalent phenol **66** with allylbromide, followed by dihydroxylation yielded the product **53F.16**.

5.2.6 Synthesis of bolaamphiphilic triol derivatives 71



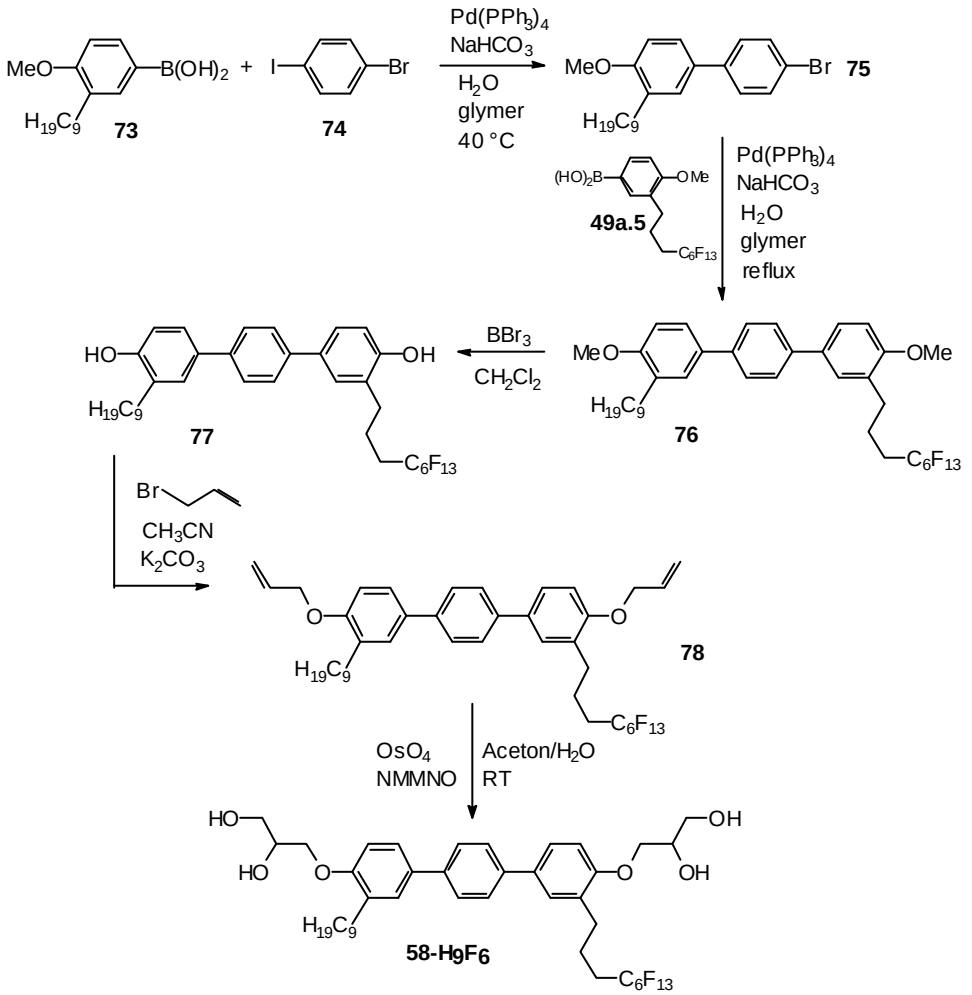
R	Comp.	Comp.	Comp.	Comp.
$C_{14}H_{29}$		**69H.3**	**70H.3**	**71-H_{14}**
$(CH_2)_3C_6F_{13}$	**48.1**	**69F.1**	**70F.1**	**71-F_6**
$(CH_2)_3C_8F_{17}$	**48.2**	**69F.2**	**70F.2**	**71-F_8**
$(CH_2)_3C_{10}F_{21}$	**48.3**	**69F.3**	**70F.3**	**71-F_{10}**
$(CH_2)_3C_{12}F_{25}$	**48.8**	**69F.4**	**70F.4**	**71-F_{12}**

Scheme 5.10 *Synthesis of bolaamphiphilic triols **71**.*

Under the same coupling conditions as described above, 4-benzyl benzeneboronic acid **68**[76] was coupled with the 4-(4-bromophenyloxy)methyl-2,2-dimethyl-1,3-dioxolanes **48** to afford the 4-(4′-benzyloxybiphenyl-4-yloxymethyl)-2,2-dimethyl-1,3-dioxolanes **69**, the acetonide protecting group of **69** was removed by acidic hydrolysis in ethanol using 10 % HCl. Finally the benzyl protecting group was cleaved by palladium catalyzed hydrogenation reaction in ethyl acetate to produce the triols **71**.

5.2.7 Synthesis of the bolaamphiphilic terphenyl derivative 58-H_9F_6 with two different lateral chains

A bolaamphiphilic terphenyl derivative with two different lateral chains, one fluorinated, the other one an alkyl chain, was synthesized according to Scheme 5.11. The synthesis started with the cross coupling reaction between 1-bromo-4-iodobenzene **74** and the boronic acid **73** (see Scheme 5.6a) at 40 °C. Because the reactivity of the aryl iodide is much higher than that of the aryl bromide, the coupling reaction occurred firstly with the iodide group to afford compound **75**. An additional coupling reaction between **75** and boronic acid **49a.5** afforded the terphenyl derivative **76**. After ether cleavage (BBr_3),[73] etherification with allylbromide and dihydroxylation, the tetraol **58-H_9F_6** was obtained.

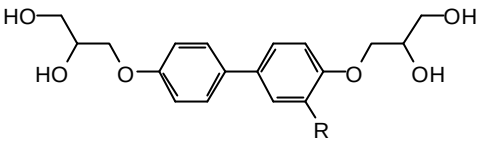


Scheme 5.11 *Synthesis of the bolaamphiphilic tetralol **58-H_9F_6** with two different lateral chains.*

5.3 Liquid crystalline behavior

5.3.1 Bolaamphilic tetraols with a biphenyl core substituted by one lateral fluorinated chain

Table 5.1 *Transition temperatures, associated enthalpy values (lower lines, in italics) and the volume fraction of the lateral chain (f_R) of the bolaamphiphiles* ***53-F*** *with one semifluorinated lateral chain.*



Comp.	R	Phase Transitions (T / °C)		f_R
		ΔH/KJ mol^{-1}		
53-F$_3$	$(CH_2)_3C_3F_7$	Cr 97 Col$_{rc}$	119 Iso	0.38
		26.3	*10.9*	
53-F$_4$	$(CH_2)_3C_4F_9$	Cr 47 Col$_{rp}$	135 Iso	0.42
		8.8	*9.2*	
53-F$_6$	$(CH_2)_3C_6F_{13}$	Cr 47 Col$_h$	171 Iso	0.49
		10.4	*14.4*	
53-F$_7$	$(CH_2)_3(CF_2)_4CF(CF_3)_2$	Cr 45 Col$_h$	179 Iso	0.52
		10.5	*13.9*	
53-F$_8$	$(CH_2)_3C_8F_{17}$	Cr 70 Col$_h$	188 Iso	0.54
		6.7	*15.7*	
53-F$_{10}$	$(CH_2)_3C_{10}F_{21}$	Cr 57 Col$_{rpm}$	180 Iso	0.58
		13.4	*9.6*	
53-F$_{6/12}$	$(CH_2)_{12}C_6F_{13}$	Cr < 20 Col	150 Iso	
			5.2	

The transition temperatures of compounds **53-F** are summarized in Table 5.1. In Figure 5.2, the dependence of the mesomorphic properties of the homologous series of compounds **53-F** on the length of the lateral semifluorinated-chain is shown graphically.

All compounds with semifluorinated chains have columnar mesophases. These columnar mesophases are stabilized by elongation of these lateral chains. In comparison to the corresponding hydrocarbon analogues **53-H** (see Figure 5.1) with the same chain length, most

fluorinated compounds **53-F** have reduced melting points and all have significantly enhanced mesophase stabilities.

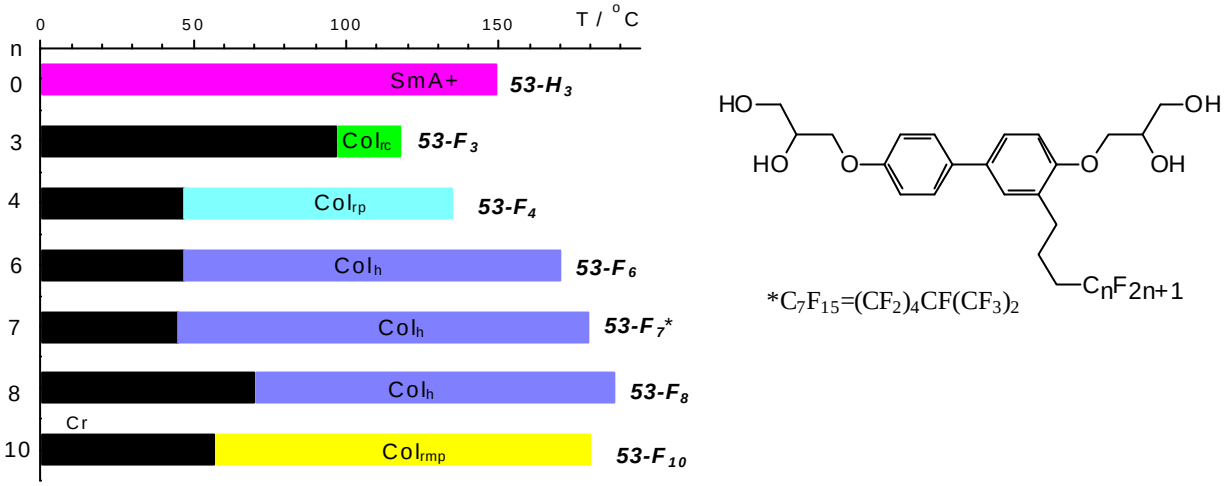


Figure 5.2 *Dependence of the transition temperatures of compounds **53-F** on the length of the semifluorinated chains. Col_{rmp} = non-centered rectangular columar phase with p2mg structure, for the other abbreviations see Figure 5.1.*

Interestingly, also compound **53-F$_7$**, which has a branched semifluorinated chain, exhibits a broad region of a columnar phase. The clearing temperature of this molecule with seven fluorinated C-atom is exactly intermediate between those of compounds **53-F$_6$** and **53-F$_8$** with six and eight C-atom in the non-branched lateral chains. This means, that branching has no influence on the stability of these mesophases.

The columnar phases of the bolaamphiphiles exhibit four different types of textures. A mosaic-like texture was detected for compound **53-F$_3$** with a relatively short lateral chain (Figure 5.3a). This texture is identical with those of the bolaamphiphiles **53-H$_6$**, **53-H$_7$** and **53-H$_9$** with lateral alkyl chains. For these compounds, a rectangular columnar mesophase with a *c*2*mm*-lattice has been found by X-ray diffraction. Also the powder X-ray diffraction pattern of the mesophase of **53-F$_3$** (Figure 5.3b) is nearly identical with those obtained for the related bolaamphiphiles **53-H$_6$**, **53-H$_7$** and **53-H$_9$** with hydrocarbon chains with respect to the relative positions and the intensities of the reflections. Therefore it can also be indexed on the basis of a centered rectangular columnar structure: *c*2*mm* with the lattice parameter a = 3.3 nm and b = 3.4 nm. The length of the molecule (L) in its most extended conformation from head group to head group is 2.1 nm. Hence, the values of the lattice parameters are between one and two molecular length ($L < a, b < 2L$). The number of molecules located in the hypothetical unit cell with a height of 0.45 nm (corresponding to the average distance between the aromatic cores) have been calculated by two different methods (see table 5.2),[77] yielding values of about eight molecules (Figure 5.3c). Therefore the model shown in Figure 5.3d, which was firstly proposed for the *c*2*mm*-phases of the alkylsubstituted bolaamphiphiles

53-H_6 - 53-H_9[61] can be used to explain the structure of the Col_r phase of **53-F_3**. The semifluorinated lateral chains segregate with formation of columns. Each column is surrounded by the rigid aromatic units, which are connected end-by-end and side-by-side by hydrogen bonding networks between the terminal diol groups. In this way, each column is enclosed by four bolaamphiphilic cores, and in average two biphenyl cores are arranged side by side within each of the cylinder walls separating the columns. The H-bonding networks at the ends of the biphenyl units are organized in separate ribbons where about eight diol groups are arranged in their cross-section. It seems, that this special organization allows an efficient space filling for molecules with a medium length of the lateral chain [C_6H_{13} to C_9H_{19} and $(CH_2)_3C_3F_7$]. However, there is an upper limit of the space available within these cylinders, enclosed between the four bolaamphiphilic cores. If the lateral chains are further elongated, the supramolecular organization is expected to change.

The columnar mesophase of compound **53-F_4**, which differs from **53-F_3** by one additional CF_2-group in the lateral chain, grows dendritically from the isotropic state and coalesces to a texture consisting of mosaic-like and spherulitic regions. Powder X-ray investigations confirms a noncentred rectangular columnar mesophase with a *p2gg* two dimensional lattice. The lattice parameter a = 5.9 nm and b = 5.4 nm are much larger than two molecular length (a, $b > 2L$), it can be calculated that about 20 molecules are arranged in average side by side in the cross section of each unit cell (see Table 5.2). These results are similar to those obtained with the bolaamphiphiles **53-H_{10}**, **53-H_{11}** and **53-H_{12}** with lateral alkyl chains of medium length. Therefore, the model shown in Figure 5.4c, which was proposed for the *p2gg*-phases of these hydrocarbon analogues[61] can also be used to explain the structure of the Col_r phase of **53-F_4**. In this model the molecules are organized in bilayer ribbons with about ten molecules in the cross-section, *i.e.* about five molecules are arranged in their lateral diameter. As a result, the lipophilc regions are significantly enlarged and simultaneously the diameter of the cylinders containing the H-bonding networks can remain rather large.

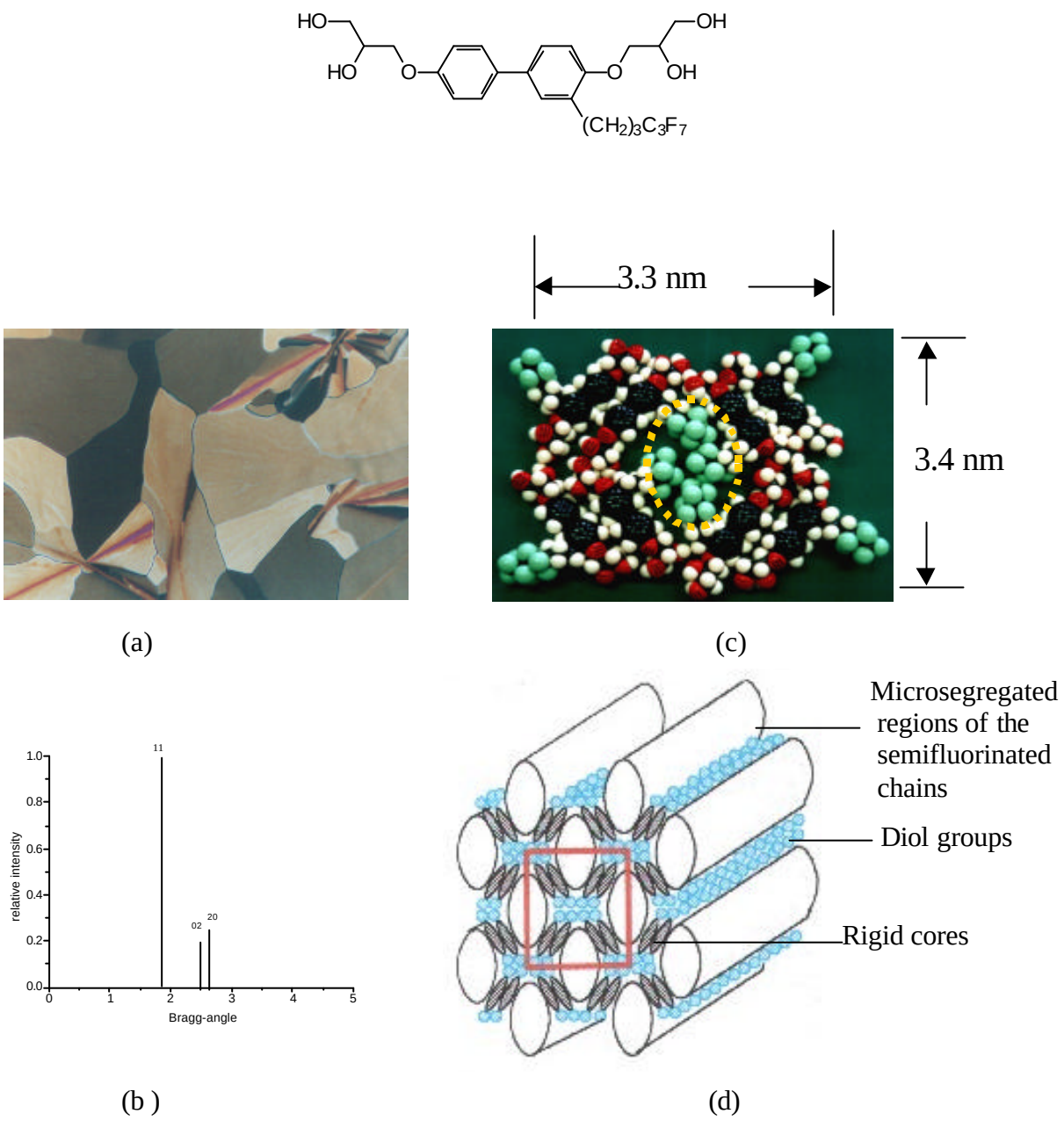


Figure 5.3 *(a) Mosaic texture of the rectangular columnar phase of* ***53-F₃*** *at 117 °C; (b) scheme of the powder X-ray diffraction pattern of the mesophase of* ***53-F₃****, lattice parameter of the centered rectangular columnar phase (c2mm), a = 3.3 nm, b = 3.4 nm; (c) CPK models showing an arrangement of eight molecules arranged in such a manner that the semifluorinated chains form a separated region surrounded by bolaamphiphilic cores; (d) model suggested for the organization of the molecules in the columnar phase of* ***53-F₃****.*

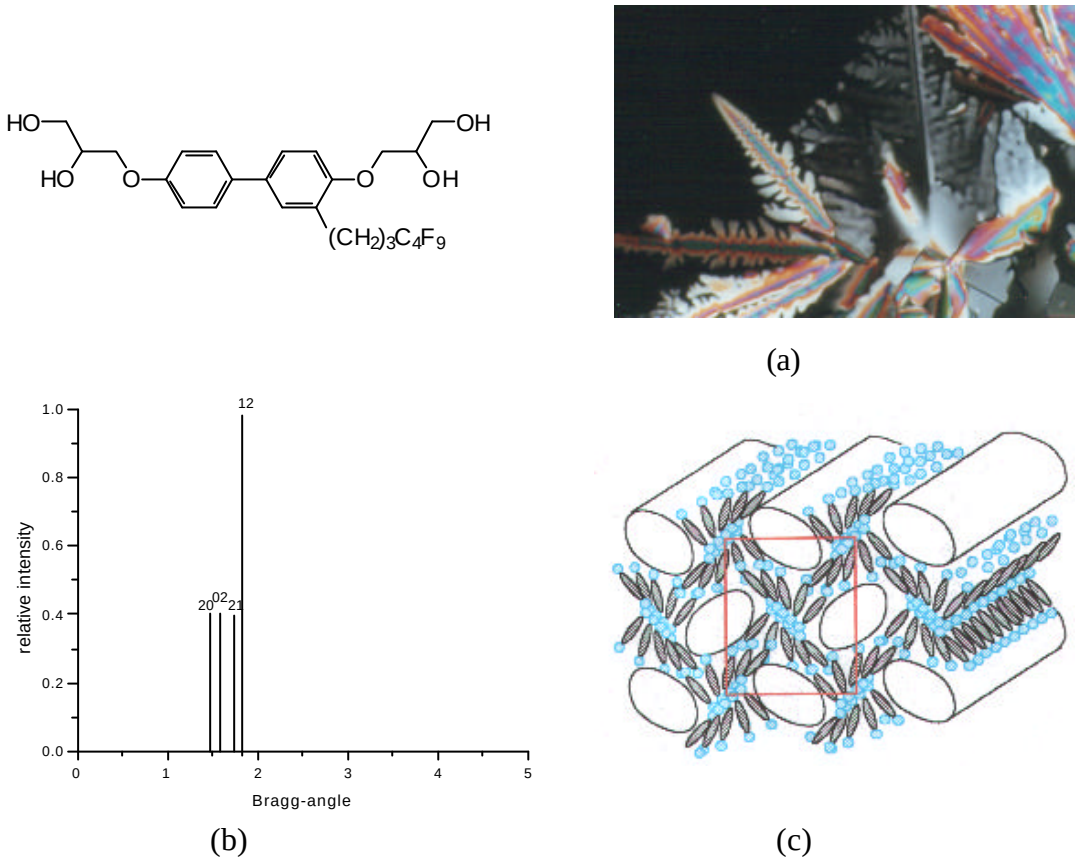
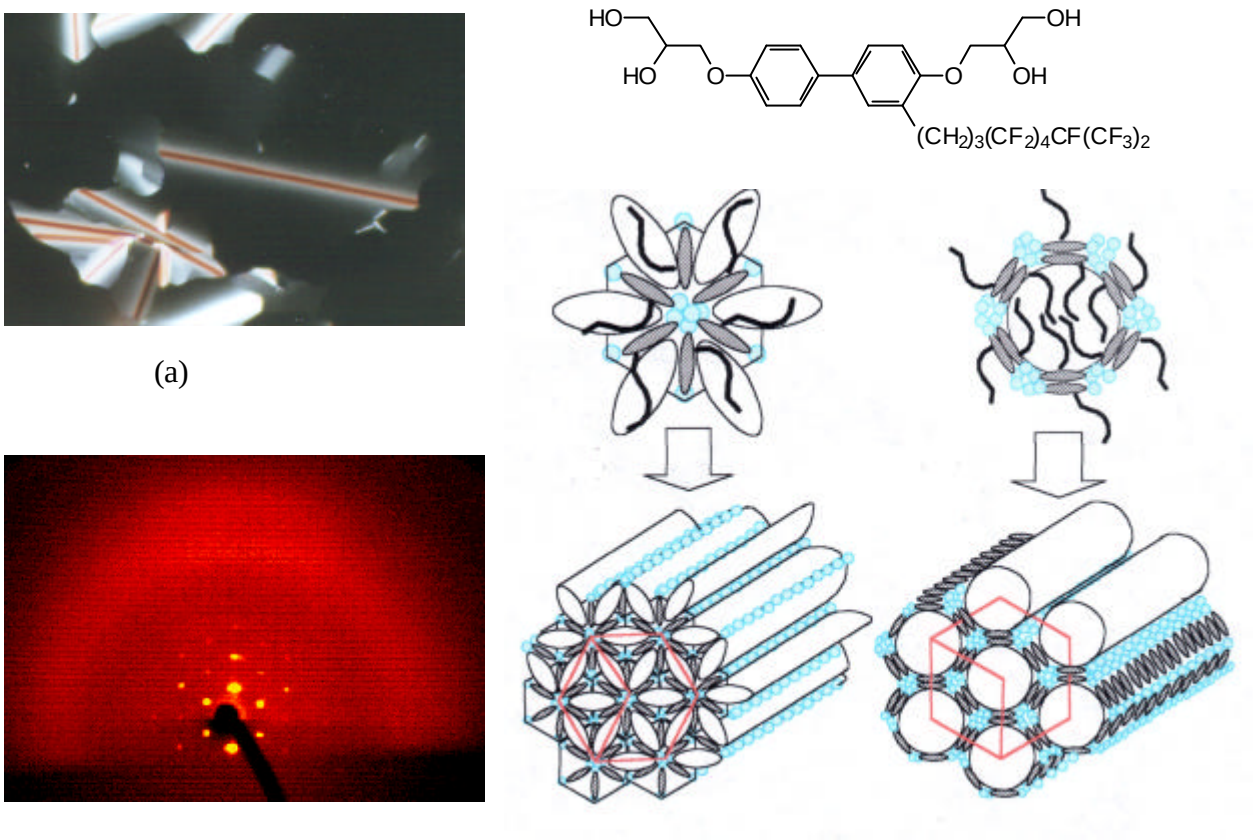


Figure 5.4 *(a) Texture of the columnar mesophase of compound* ***53-F₄*** *at 134 °C; (b) scheme of the powder X-ray diffraction pattern of the mesophase of* ***53-F₄*** *at 134 °C, lattice parameter of the non-centered rectangular columnar phase (p2gg): a = 5.9 nm, b = 5.4 nm; (c) model of the* Col_r *mesophase of* ***53-F₄****.*

The textures of the columnar mesophases of compounds **53-F$_6$**, **53-F$_7$** and **53-F$_8$** which have fluorinated segments incorporating 6 to 8 CF_2-group (see Figure 5.5) are quite different from those of the mesophases of compounds **53-F$_3$** and **53-F$_4$** with short fluorinated chains, but similar to one another. They all show large homeotropic regions with birefringent domains, as typical for hexagonal columnar phases. The observation of large homeotropically alinged regions indicates that these phases are optically uniaxial phases. Optically uniaxial phases are hexagonal columnar mesophases, tetragonal columnar phases and smectic A phases. Detailed X-ray investigations were carried out with well developed monodomains of the oriented sample of compound **53-F$_7$** [R = $(CH_2)_3(CF_2)_4CF(CF_3)_2$]. The diffraction pattern of compound **53-F$_7$** is shown in Figure 5.5. It displays a diffuse scattering in the wide angle region which indicates a liquid like disorder within this phase. In the small angle region a lot of spot-like reflections can be found. They can be indexed on the basis of a centred rectangular or hexagonal 2D lattice, because its texture shows large homeotropic areas, which means that the mesophase has an optically uniaxial structure, the centered rectangular structure, being

biaxial, can therefore be excluded. The mesophase of compound **53-F$_7$** should therefore be a hexagonal columnar one. The lattice parameter can be calculated to a_{hex} = 3.5 nm ($1L < a < 2L$). Also X-ray investigations for the mesophases of compounds **53-F$_6$** and **53-F$_8$** show the typical diffraction pattern of hexagonal columnar phases. The lattice parameter amount to a_{hex} = 3.47 nm for compound **53-F$_6$** and a_{hex} = 3.6 nm for compound **53-F$_8$**. The lattice parameter for these Col_h phases are slightly increased with elongation of the lateral semifluorinated chains. In all Col_h-phases about six molecules are arranged in average in the cross section of each cylinder (see Table 5.2). Two possible molecular arrangements are supposed for these Col_h phases (see Figure 5.5c-1, 5.5c-2).



(a) (b) (c-1) (c-2)

Figure 5.5 *(a) Texture of the columnar phase of compound **53-F$_7$** at 178 °C; (b) diffraction pattern of the mesophase of **53-F$_7$** (oriented sample at 160 °C); (c) models of the Col_h phase of **53-F$_7$**: (c-1) radial model; (c-2) cylinder model.*

I: In the radial model (see Figure 5.5c-1), only two semifluorinated chains are located side by side in the cross-section of the elliptical lipophilic cylinders. The cylinder walls have a

thickness of only one aromatic core. One half of the number of diol group is arranged in polar columnar with six diol groups in the cross-section, whereas the other halve is organized in polar cylinders which have only three diol groups in their diameter.

II: The cylinder model is shown in Figure 5.5c-2. In this model, the rigid aromatic units build up hexagonal cylinder shells around the circular lipophilic columns of the semifluorinated chains. This model shows quite a good space filling within the cylinders. The lipophilic chains segregated into regions with significantly larger and more circular-section areas, so that their interfaces to the aromatic regions are reduced. In this model each of the columns of the hydrogen bonding networks has six diol groups in the cross-section. Therefore the cylinder model seems more reasonable, but on the basis of our present experimental results, we cannot distinguish these two possible arrangements.

The mesophase of compoud **53-F$_{10}$** (see Figure 5.7), which has the longest semifluorinated lateral chain, exhibits a lancet-like texture with small spherulitic domains, but without any homeotropic regions. This texture is quite different from all those of the above discussed columnar phases, however it has remarkably similarities to the texture found for the mesophases of some Pd(II)-carbene complexes (**X**) (Figure 5.6).[78] It is however not yet clear if the mesophases of these carbene complexes are real liquid crystalline phases or soft crystals. Nevertheless, in the crystalline state, these molecules are organized in a layer structure in which the rigid cores are separated by the perpendicular alkyl chains, arranged in separated layers (see Figure 5.6). Such an arrangement could also be discussed as a possible structure of the mesophase of **53-F$_{10}$**

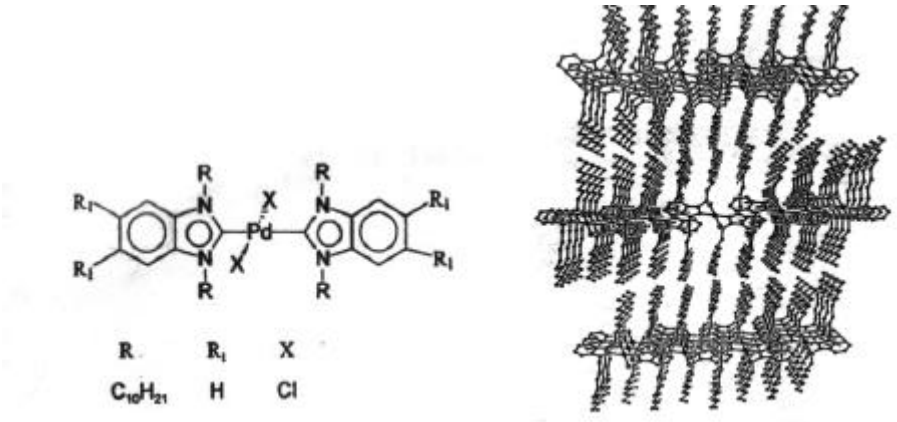
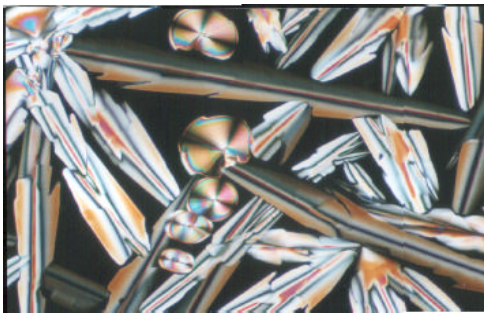
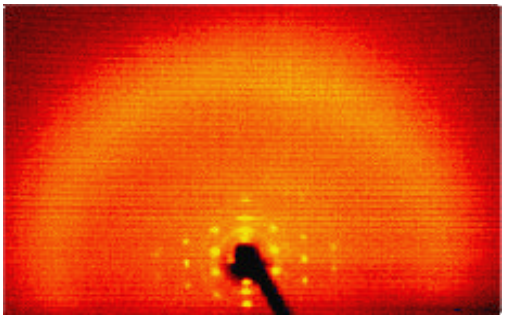


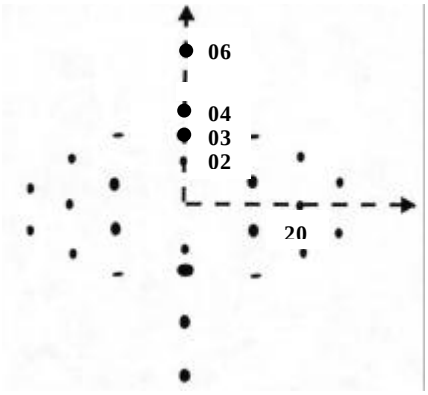
Figure 5.6 *Structure and crystal packing of **X**.*



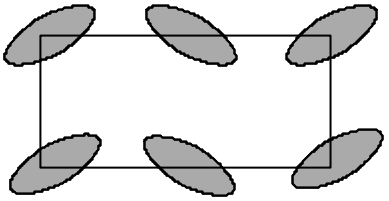
(a)



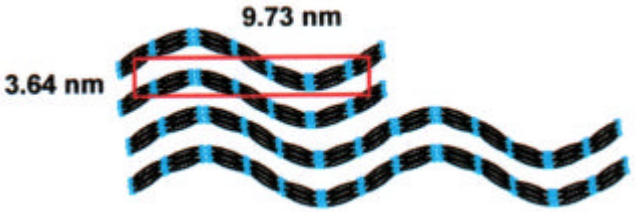
(b)

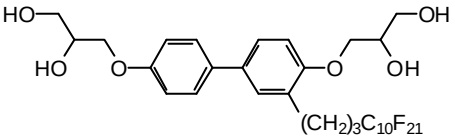


(c)



(d)





(e)

Figure 5.7 (*a) Texture of the columnar mesophase of* ***53-F*** $_{10}$ *at 180 °C i.e. at the transition from the isotropic liquid state to the* Col_r *phase (the black regions are residues of the isotropic phase; (b) X-ray pattern of the rectangular columnar mesophase (p2mg) of* ***53-F*** $_{10}$ *with a lattice parameter: a = 3.6 nm, b = 9.7 nm at 150 °C; (c) sketch of the X-ray differaction pattern; (d) scheme of 2D p2mg lattice; (e)wavy deformed layers forming the* Col_{rmp} *mesophase of* ***53-F*** $_{10}$.

2D X-ray investigations with aligned samples of compound **53-F$_{10}$** (see Figure 5.7b) showed a diffuse scattering in the wide angle region indicating the liquid like disorder within this phase, confirming the presence of a true liquid crystalline phase. The reflexes in the small angle region can be indexed on the basis of a non-centered rectangular phase with the lattice parameter a = 3.6 nm and b = 9.7 nm. In contrast to the Col$_r$-phases of **53-F$_3$** (*c*2*mm*) and **53-F$_4$** (*p*2*gg*) the lattice parameter a and b are quite different from each other. The parameter a is between one and two molecular lengths, whereas b is very large, between four and five molecular lengths. About 17 molecules are arranged in average side by side in the cross section of each unit cell (see Table 5.2). The volume of the lipophilic lateral chains amounts about of 58 % of the total volume. The X-ray diffraction pattern can be assigned to a *p*2*mg* two dimentional lattice. (There is no odd numbered no reflex, but the 03 reflex is present, see Figure 5.7c). Such a *p*2*mg* lattice can be realized if the calamitic cores of the molecule **53-F$_{10}$** are arranged as shown in Figure 5.7d. However, in order to realize a lattice parameter b = 9.7 nm, more molecules must be arranged along the b-axis. In the model shown in Figure 5.7e, the rigid cores form wavy deformed layers, held together by the end-to-end hydrogen bonding between the molecules. The semifluorinated chains are segregated from the rigid cores into separate layers. The 2D-lattice results from the positional correlation between adjacent layers. The number of 17 molecules in the cross-section of the unit cell can be realized if *ca* 3 biphenyl cores are arranged in the cross section of the polar (aromatic + hydrogen bonding) wavy layers.

Compound **53-F$_{6/12}$**, in which the perfluorinated segment is decouped from the aromatic core by a dodecylene spacer has a typical columnar texture, which is different from the other compounds **53-F**. However, its precise structure needs further investigation.

In summary, by attachment of a lateral semifluorinated chain to a bolaamphiphilic rigid core and by its successive elongation, a sequence of different columnar mesophases was observed: Col$_r$ (*c*2*mm*), Col$_r$ (*p*2*gg*), Col$_h$ (*p*6*mm*) and Col$_r$ (*p*2*mg*). The first three columnar phases represent cylinder structures. Their formation is explained as a consequence of the segregation of the lipophilic lateral chains with formation of infinite columns. The rigid aromatic units built up cylinder shells around these columns, held together by the hydrogen bonding networks between the diol groups, which act as glue. The relative volume required by the semifluorinated lipophilic chains with respect to the length of the rigid segments determines the precise shape of the cylinders and hence determines the type of the columnar mesophases. The sequence of their occurrence in dependence on the chain length is the same as found for the hydrocarbon analogues **53-H$_5$ – 53-H$_{12}$**, however the chain length necessary for the occurrence of each columnar phase type is reduced. This should be mainly due to the lager volume of the semifluorinated chains in comparison to the alkyl chains. Indeed, the volume fraction of the lateral chains, required for the formation of different types of columnar phases is identical for the bolaamphiphiles with fluorinated and nonfluorinated (Table 5.2)

lateral chains: Col_r (*c*2*mm*) - f_R = 0.32-0.41; Col_r (*p*2*gg*) - f_R = 0.42-0.46; Col_h (*p*6*mm*) - f_R = 0.52-0.58. The Col_r (*p*2*mg*) mesophase of the homologue with the longest semifluorinated chain (f_R > 0.58) is distinct from the columnar phases of the shorter homologues. Here, the lipophilic parts are too large to allow their organization in distinct columns. Instead the lipophilic regions are fused to form infinite layers, separating the wavy deformed layers of the bolaamphiphilic cores. Again, the bolaamphiphilic cores are held together by the hydrogen bonding networks between the diol groups.

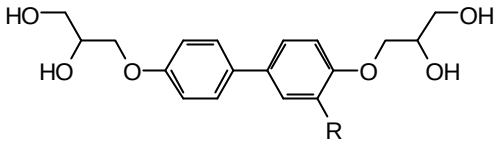
It should be pointed out that these modulated smectic phases (Sm~) are quite distinct from the modulated[79] and non-modulated smectic phases of the classic rod-like mesogens, as the rigid aromatic cores are arranged parallel to the (wavy deformed) layers instead of perpendicular (SmA, SmA~) or tilted (SmC, SmC~) .

Table 5.2 *Molecular lengths (L, distances between the head groups in the most extended conformation, CPK-models), phase types, lattice parameter (a, b), calculated volumes of the unit cells assuming a height of 0.45 nm (V_{cell}), molecular volumina (V_{mol}), calculated using volume increments,[77] molecular masses (M) and the number of the molecules in each 0.45 nm thick sections of the unit cells of the columnar mesophases [n_1 was calculated from the molar volumina; n_2 was caculated according to formula $n_2 = V_{cell}\,(N_A/M)\rho$, whereby ρ (g cm^{-3}) is the density,[80] N_A = Avogadro constant; n_{av} is the average value of n_1 and n_2]; and f_R - volume fractions of the lipophilic lateral chains) of the investigated bolaamphiphiles.*

Comp.	*L* *(nm)*	*Phase type*	*a* *(nm)*	*b* *(nm)*	V_{cell} (nm^3)	V_{mol} (nm^3)	*M* (g mol^{-1})	ρ (g cm^{-3})	n_1	n_2	n_{av}	f_R
53-H$_6$	2.1	Col$_r$ *c2mm*	3.43	3.22	4.97	0.497	419	1	10.4	7.1	8.8	0.32
53-H$_9$	2.1	Col$_r$ *c2mm*	3.21	3.43	4.95	0.553	461	1	8	6.5	7.7	0.42
53-H$_{10}$	2.1	Col$_r$ *P2gg*	5.5	6.2	15.35	0.578	326	1	26.5	28.3	27.4	0.44
53-H$_{11}$	2.1	Col$_r$ *P2gg*	5.4	5.8	14.09	0.603	489	1	23.4	17.3	20.4	0.46
53-H$_{12}$	2.1	Col$_r$ *P2gg*	5.33	6.17	14.80	0.628	503	1	23.6	17.7	20.7	0.48
53-H$_{12}$	2.1	Col$_h$	3.36		4.40	0.628	503	1	7.00	5.3	6.2	0.48
53-H$_{14}$	2.1	Col$_h$	3.59		5.02	0.677	531	1	7.4	5.7	6.6	0.52
53-H$_{18}$	2.1	Col$_h$	3.66		5.22	0.777	587	1	6.7	5.4	6.1	0.58
71-H$_{11}$	1.7	Col$_h$	2.94		3.37	0.513	415	1	6.6	4.9	5.8	0.54
53-F$_3$	2.1	Col$_r$ *c2mm*	3.3	3.4	5.05	0.520	554	1.16	9.71	6.36	8.03	0.38
53-F$_4$	2.1	Col$_r$ *p2gg*	5.9	5.4	14.34	0.557	594	1.19	25.8	17.4	21.6	0.42
53t-F$_4$	2.1	Col$_t$	2.1	2.1	1.98	0.557	594	1.19	3.6	2.4	3.0	0.42
53-F$_6$	2.1	Col$_h$	3.47		4.69	0.630	694	1.25	7.44	5.06	6.25	0.48
53t-F$_6$	2.1	Col$_h$	3.48		4.72	0.630	694	1.25	7.49	5.09	6.29	0.48
53-F$_7$	2.1	Col$_h$	3.5		4.77	0.667	744	1.35	7.16	5.20	6.18	0.52
53-F$_8$	2.1	Col$_h$	3.6		5.05	0.703	794	1.30	7.18	4.96	6.07	0.54
53t-F$_8$	2.1	Col$_h$	3.47		4.69	0.703	794	1.30	6.64	4.59	5.61	0.54
53-F$_{10}$	2.1	Col$_r$	3.64	9.73	15.94	0.776	894	1.33	20.5	14.3	17.4	0.58
53-F$_{4/0}$	2.1					0.482	552	1.23				0.33
53-F$_{8/0}$	2.1	Col$_r$				0.629	752	1.33				0.49

5.3.2 Bolaamphiphiles with completely fluorinated lateral chains

Table 5.3 *Transition temperatures, associated enthalpy values (lower lines, in italics) and volume fractions of the lipophilic lateral chains of compounds* ***53-F$_{4/0}$*** *and* ***53-F$_{8/0}$***.

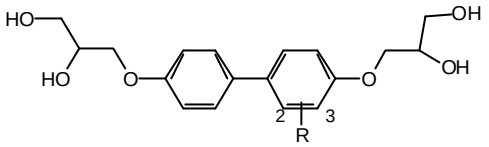


Comp.	R	Phase transitions (T / °C) *ΔH/KJ mol^{-1}*	f_R
53-F$_{4/0}$	C_4F_9	Cr 113 (SmA 81) Iso *34.6*	0.33
53-F$_{8/0}$	C_8F_{17}	Cr 97 Col$_h$ 153 Iso *13.2 7.7*	0.49

All compounds reported up to now had semifluorinated lateral chains, i.e. the perfluorinated segment is decoupled from the aromatic core by a propylene spacer. The two compounds **53-F$_{4/0}$** and **53-F$_{8/0}$**, in which the perfluorinated chains are directly connected with the aromatic units are shown in Table 5.3. Compound **53-F$_{4/0}$** with a short lateral perfluorinated chain (C_4F_9), exhibits a monotropic smectic A mesophase. Compound **53-F$_{8/0}$** with a perfluorooctyl chain exhibits a columnar phase, its stability is between those of the semifluorinated compounds **53-F$_4$** (lateral chain with seven-C atoms) and **53-F$_6$** (lateral chain with nine-C atoms). So it seems that the semifluorinated chains and the perfluorinated chain have the same influence on the stability of the mesophase. Also the melting point of compound **53-F$_{4/0}$** and **53-F$_{8/0}$** are surprising low, if one takes into account that in calamitic mesogens with terminal attached perfluoroalkyl chains, without alkylene spacer, the melting points are extremely high, so that sometimes no liquid crystalline phase can be found.[81] The texture of compound **53-F$_{8/0}$** is identical with those of the hexagonal columnar phases of compounds **53-F$_6$**, **53-F$_7$** and **53-F$_8$**. Miscibility studies indicate a complete and uninterrupt miscibility for the mesophases of these compounds. Therefore the columnar phase of compound **53-F$_{8/0}$** should also be a hexagonal one. This is in full accordance with the prediction based on the volume fraction of the C_8F_7 chains. Hence, it seems that there is no special effect of the hydrocarbon/fluorocarbon incompatibility on the mesomorphic properties of the bolaamphiphiles with semifluorinated lateral chains. Probably, the hydrocarbon segment is too short to induce an additional segregation[82] or this segregation has no significant influence on the mesophase properties.

5.3.3 Influence of the position of the lateral semifluorinated chains

Table 5.4 *The influence of the position of the lateral chain on the mesophase type, the transition temperatures and the lattice parameter of the columnar phases.*



Comp.	R	Phase transitions (T/°C) ΔH/KJ mol^{-1}	Lattice parameter (nm)
53-H$_{11}$	3-$C_{11}H_{23}$	Cr 84 Col_{rp} 116 Iso	a = 5.4, b = 5.8, α = β = 90
53′-H$_{11}$	2-$C_{11}H_{23}$	Cr 64 Col_{rp} 76 Iso	a = 5.4, b = 5.4, α = β = 90
53-F$_4$	3-$(CH_2)_3C_4F_9$	Cr 47 Col_{rp} 135 Iso *8.8* *9.2*	a = 5.9, b = 5.4, a = β = 90
53′-F$_4$	2-$(CH_2)_3C_4F_9$	Cr 96 Col_t 99 Iso *8.1* *7.1*	a = b = 2.1
53-F$_6$	3-$(CH_2)_3C_6F_{13}$	Cr 47.1 Col_h 171 Iso *10.4* *14.4*	a_{hex} = 3.47
53′-F$_6$	2-$(CH_2)_3C_6F_{13}$	Cr < 20 Col_h 134 Iso 8.7	a_{hex} = 3.48
53-F$_8$	3-$(CH_2)_3C_8F_{17}$	Cr 70 Col_h 188 Iso *6.7* *15.7*	a_{hex} = 3.6
53′-F$_8$	2-$(CH_2)_3C_8F_{17}$	Cr < 20 Col_h 161 Iso *7.6*	a_{hex} = 3.47

By shifting the lateral chains along the aromatic unit to the position near the center, the mesophases are destabilized. This is in accordance with the results obtained with amphiphilic[83] and non-amphiphilic liquid crystals[84] and could be due to the change of the conformation of the biphenyl unit (dihedral angle between the planes of the adjacent benzene rings) and to a stronger disturbance of the parallel alignment of the rigid cores by substituents in a central position. The position of the alkyl chain has obviously no significant influence on the mesophase structure. For example, compounds **53-H$_{11}$** and **53′-H$_{11}$** with undecyl chains have non-centred rectangular columnar mesophases with a *p2gg*-lattice.[61] Compounds **53-F$_6$** and **53′-F$_6$** as well as **53-F$_8$** and **53′-F$_8$** with semifluorinated chains show similar textures, characterized by large homeotropic regions with small spherulitic domains, which are typical for hexagonal columnar phases. X-ray studies additional proved the hexagonal columnar structures of these mesophases (see Table 5.4).

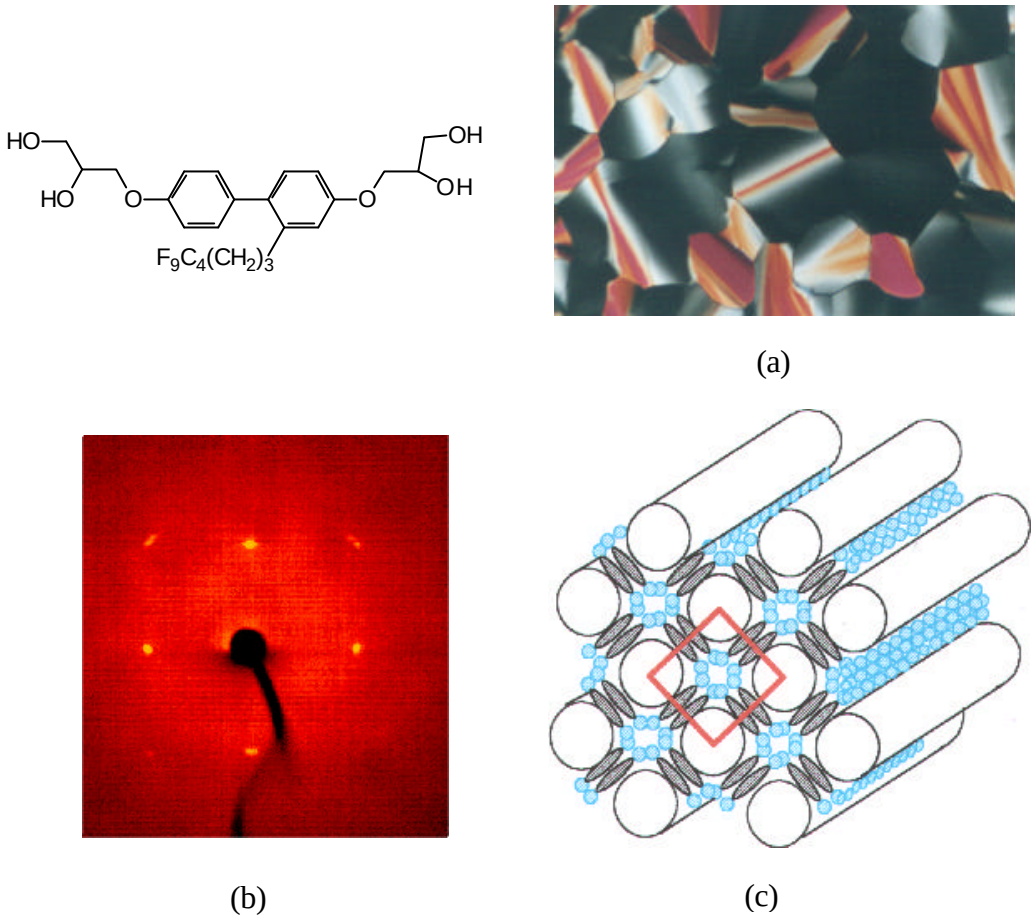


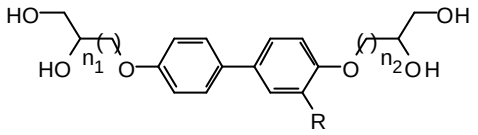
Figure 5.8 *(a) Texture of the columnar phase of* ***53¢-F4*** *at 99 °C; (b) 2D X-ray diffraction pattern of* ***53¢-F4*** *at 99 °C; (c) model of the* Col_t *phase of* ***53¢-F4****.*

However, for compounds **53-F4** and **53¢-F4**, the mesophase types are different. At first, we noticed that compound **53¢-F4** shows a spherulitic texture with homeotropically aligned areas (Figure 5.8), which is quite different from that of compound **53-F4** (see Figure 5.4). It is optically uniaxial in contrast to the rectangular columnar phase of compound **53-F4**. Its two-dimensional X-ray diffraction pattern (shown in Figure 5.8b) indicates a tetragonal columnar mesophase, which is in full accordance with the optical uniaxiality of this mesophase (square lattice of the space group *p*4*mm*). The lattice parameter can be calculated to a = 2.1 nm. The model shown in Figure 5.8d is in good agreement with the experimentally determined lattice parameter. The parameter a corresponds to the molecular length and four molecules are arranged in the cross-section of the unit cell. The arrangement of the molecules in this model is quite similar to that in the *c*2*mm* phase of the shorter homologue **53-F3**, only the columns formed by the semifluorinated chains have a circular instead of an elliptical shape. In average four bolaamphiphilic cores form the cylinder walls around the circular lipophilic columns of the semifluorinated chains. The Col_t-phase of **53¢-F4** can be regarded as intermediate stage at

the transition from the *c*2*mm* lattice (**53-F$_3$**) to the *p*2*gg* lattice (**53-F$_4$**). Hence, the mesophase structure is only slightly changed by changing the position of the lateral $(CH_2)_3C_4F_9$ chain. This behavior is completely different from the observations made with polycatenar compounds, for which a shifting of one alkyl chains from a peripheral to a central position at the rigid core leads to the complete loss of columnar and cubic mesophases and leads to nematic phases without positional long-range order. [85]

5.3.4 Influence of the length of the bolaamphiphilic core

Table 5.5 *Transition temperatures, associated enthalpy values (lower lines, in italics) and lattice parameter of the bolaamphiphiles* ***53^{n_1,n_2}-F*** *incorporating spacer units (n_1, n_2) of different length.*



Comp.	n_1	n_2	R	Phase transitions (T / °C) *ΔH/KJ mol^{-1}*	Lattice parameter (nm)
53^{1,4}-F$_6$	1	4	$(CH_2)_3C_6F_{13}$	Cr 94 Col$_h$ 144 Iso *7.0 5.9*	
53^{1,9}-F$_6$	1	9	$(CH_2)_3C_6F_{13}$	Cr 71 Col$_t$ 117 Iso *41.7 3.2*	a_t = 2.88
53^{4,4}-F$_6$	4	4	$(CH_2)_3C_6F_{13}$	Cr 52 Col 102 Iso *19.0 4.4*	a_t = 3.00
53^{4,1}-F$_8$	4	1	$(CH_2)_3C_8F_{17}$	Cr76 Col$_h$ 138 Iso *22.1 6.4*	a_{hex} = 4.0
53^{1,4}-F$_8$	1	4	$(CH_2)_3C_8F_{17}$	Cr 83 Col$_h$ 161 Iso *21.6 7.7*	a_{hex} = 4.09
53^{1,9}-F$_8$	1	9	$(CH_2)_3C_8F_{17}$	Cr 97 Col$_t$ 135 Iso *29.2 5.2*	

In the next step, we have elongated the bolaamphiphilic core by introduction of alkyl spacers of different lengths between the rigid core and one of the diol head groups. It has been shown with the related hydrocarbon derivatives, that enlargement of a lipophilic spacer between the rigid core and one of the head group, facilitates the formation of smectic phases. This was explained by the larger space available for the accommodation of the lateral alkyl chains and the compatibility between the lipophilic spacers and lipophilic lateral chains. In the case of the compounds **53-F**, with semifluorinated lateral chains, the columnar mesophases remain (Table 5.5), but the mesophase stability decreased with the elongation of the spacers. This indicates, that the disturbing influence of the fluorinated

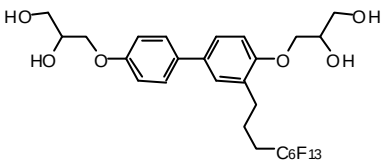
chains on the layer structure is larger than that of the alkyl chain, due to their larger volume and probably also due to their incompatibility with the spacer units. The columnar phases of compounds **53^{1,4}-F$_6$**, **53^{4,1}-F$_8$** and **53^{1,4}-F$_8$** incorporating one butylene spacer have textures with spherulitic domains and large homeotropic regions, similar to those of compound **53-F$_7$** (see Figure 5.5). By X-ray diffraction, the columnar mesophases of compound **53^{4,1}-F$_8$** and **53^{1,4}-F$_8$** were confirmed as hexagonal columnar mesophases. Because compound **53^{1,4}-F$_6$** shows an identical texture and miscibility studies indicated a complete and uninterrupted miscibility with the columnar phase of compounds of **53^{1,4}-F$_6$**, **53^{4,1}-F$_8$** and **53^{1,4}-F$_8$**, we assume, that **53^{1,4}-F$_6$** has a hexagonal columnar mesophase too.

Compounds **53^{1,9}-F$_6$** and **53^{1,9}-F$_8$**, which have a longer nonamethylene spacer have similar textures. X-ray investigations however, indicate the presence of a tetragonal columnar mesophases with lattice parameter corresponding to the molecular lengths. (see Table 5.5 and Table 5.6). The molecular arrangement of the moleculers **53^{1,9}-F$_6$** and **53^{1,9}-F$_8$** in these Col_t-phases should be the same as discussed for **53^{4,4}-F$_4$** (see figure 5.8c). Its occurrence can be explained by the larger space available between the elongated bolaamphiphilic cores. Therefore the lateral chains [$(CH_2)_3C_6F_{13}$, $(CH_2)_3C_8F_{17}$] do not require the organization of six bolaamphiphilic cores arround the lipophilic regions (cylinder model). Instead, four bolaamphiphilic cores are sufficient. It is however remarkable that the tetragonal lattice is often found for the fluorinated compounds instead of the Col_r (*c*2*mm*) lattice, usually observed for bolaamphiphiles with lateral hydrocarbon chains of medium chain length. Compound **53^{4,4}-F$_6$** with two C_4 spacers shows a rectangular columnar mesophase according to its texture, whereas the two-dimensional X-ray diffraction pattern is typical for a square lattice (a_t = 3.0 nm). Hence, the effect of elongation of the bolaamphiphilic backbone is reverse to the effect of elongation of the lateral lipophilic chains.

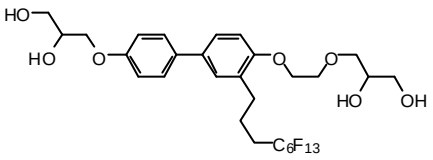
Table 5.6 *Molecular lengths (L), phase types, lattice parameter (a, b), calculated volumes of the unit cells with a height of 0.45 um (V_{cell}), molecular volumina (V_{mol}), molecular masses (M) and the number of molecules in each 0.45 nm thick unit cell (n_1, n_2, n_{av}) of the columnar mesophases and the volume fractions of the lipophilic lateral chains (f_R) of the investigated bolaamphiphiles.*

Comp.	*L* (nm)	*Phase type*	*a* (nm)	*b* (nm)	V_{cell} (nm^3)	V_{mol} (nm^3)	*M* ($g\ mol^{-1}$)	ρ ($g\ cm^{-3}$)	n_1	n_2	n_{av}	f_R
53-^{1,4}F$_6$	2.5	Col_h				0.704	736	1.22				0.43
53-^{1,9}F$_6$	3.2	Col_t	2.88		3.73	0.828	806	1.19	4.4	3.3	3.9	0.37
53-^{4,4}F$_6$	3.1	Col_r	3.00		4.05	0.779	778	1.20	5.3	3.76	4.9	0.39
53-^{4,1}F$_8$	2.5	Col_h	4.0		6.23	0.777	836	1.27	7.9	5.7	6.8	0.49
53-^{1,4}F$_8$	2.5	Col_h	4.1		6.54	0.777	836	1.27	8.3	5.9	7.1	0.49
53-^{1,9}F$_8$	3.2	Col_t				0.902	906	1.23				0.42

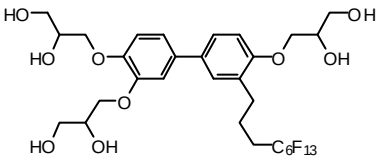
5.3.5 Bolaamphiles with larger head group



53-F$_6$ Cr 47 Col_h 171 Iso



53F.15 Cr <20 Col_h 132 Iso



53F.16 Cr 72 Col_h 106 Iso

Compound **53F.15**, in which one of the terminal diol units is replaced by a 5,6-dihydroxyhexyloxy unit, has a reduced mesophase stability compared with compound **53-F$_6$** with two 2,3-dihydroxypropoxy units and the same chain length. This observation is in accordance with the results obtained for bolaamphiphiles without a lateral chain.[86] The flexible oxyethylene chains usually decrease the mesophase stability.

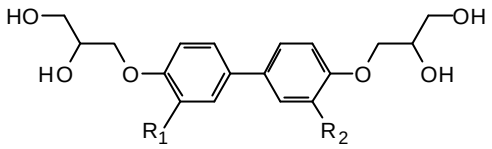
In compound **53F.16**, an additional diol group is introduced in 3-position. This compound shows a drastic mesophase destabilization compared with **53-F$_6$**. Although stronger attractive forces are provided by the additional hydrogen bonding between the molecules, the disturbance caused by the steric effect of the additional diol group which disturbs the parallel organization of the rigid cores seems to be larger, so that the mesophase stability is decreased.

The textures of the mesophases of both compounds are identical with that of compound **53-F$_6$**. Therefore, a hexagonal columnar structure is assumed for these mesophases. It seems that enlarging the polar head group has no influence on the mesophase type. Only a significant mesophase destabilization was found.

5.3.6 Biphenyl tetraols with two lateral chains

The previous investigations have shown that bolaamphiphiles with the very long semifluorinated lateral chains can form modulated layer structures. Probably other smectic phases can be obtained by further enlargement of the volume of the semifluorinated chains. For this purpose bolaamphiphiles with two lateral chains have been synthesized

Table 5.7 *Transition temperatures of biphenyl tetraol derivatives with two lateral chains.*



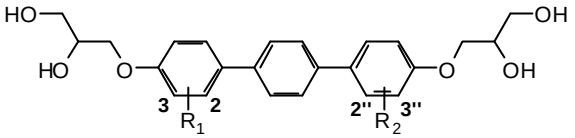
Comp.	R_1	R_2	Phase transitions (T / °C)
54-H$_{9,9}$	C_9H_{19}	C_9H_{19}	Cr 123 Iso
54-H$_{1,18}$	$C_{18}H_{37}$	CH_3	Cr 79 Col 106 Iso
54-H$_1$F$_6$	$(CH_2)_3C_6F_{13}$	CH_3	Cr 97 Col 134 Iso
54-H$_6$F$_6$	$(CH_2)_3C_6F_{13}$	C_6H_{13}	Cr 115 (108 Col) Iso
54-H$_{12}$F$_6$	$(CH_2)_3C_6F_{13}$	$C_{12}F_{25}$	Cr 134 Iso
54-F$_{6,6}$	$(CH_2)_3C_6F_{13}$	$(CH_2)_3C_6F_{13}$	Cr 147 Iso
54-F$_{7,7}$	$(CH_2)_3(CF_2)_4CF(CF_3)_2$	$(CH_2)_3(CF_2)_4CF(CF_3)_2$	Cr 143 Iso

Table 5.7 summarizes the properties of the synthesized compounds. Compounds **54-H$_{1,18}$** and **54-H$_1$F$_6$**, in which the additional lateral substituent is a methyl group exhibit columnar mesophases which have textures identical with that of the hexagonal columnar phase of compound **53-F$_6$**. Because of the complete miscibility with the corresponding compounds **53-H$_{18}$** and **53-F$_6$** without the CH_3-groups respectively, they should be hexagonal columnar phases. This shows that the additional methyl group has no influence on the mesophase type, but the clearing temperatures are significantly reduced. Elongation of the lateral chain further reduces the mesophase stability. The n-hexylsubstituted compound **54-H$_6$F$_6$** has only a monotropic columnar phase. Also the compounds **54-F$_{6,6}$** and **54-F$_{7,7}$** with two semifluorinated chains are only crystalline solids. It shows that bolaamphiphilic biphenyl derivatives with two long lateral chains are nonmesogenic (compounds **54-H$_{9,9}$**,[76] **54-H$_6$F$_6$**, **54-H$_{12}$F$_6$**, **54-F$_{6,6}$** and **54-F$_{7,7}$**), owing to the destabilization of the mesophase by the two lateral chains and to the strong crystallization tendency of these compounds.

5.3.7 Bolaamphiphilic terphenyl derivatives

Because our efforts to change the mesophase structure with two-chain biphenyl tetraols failed, we turn our attention to bolaamphiphilic tertraols incorporating a p-terphenyl rigid core, for which higher mesophase stabilities could be expected.

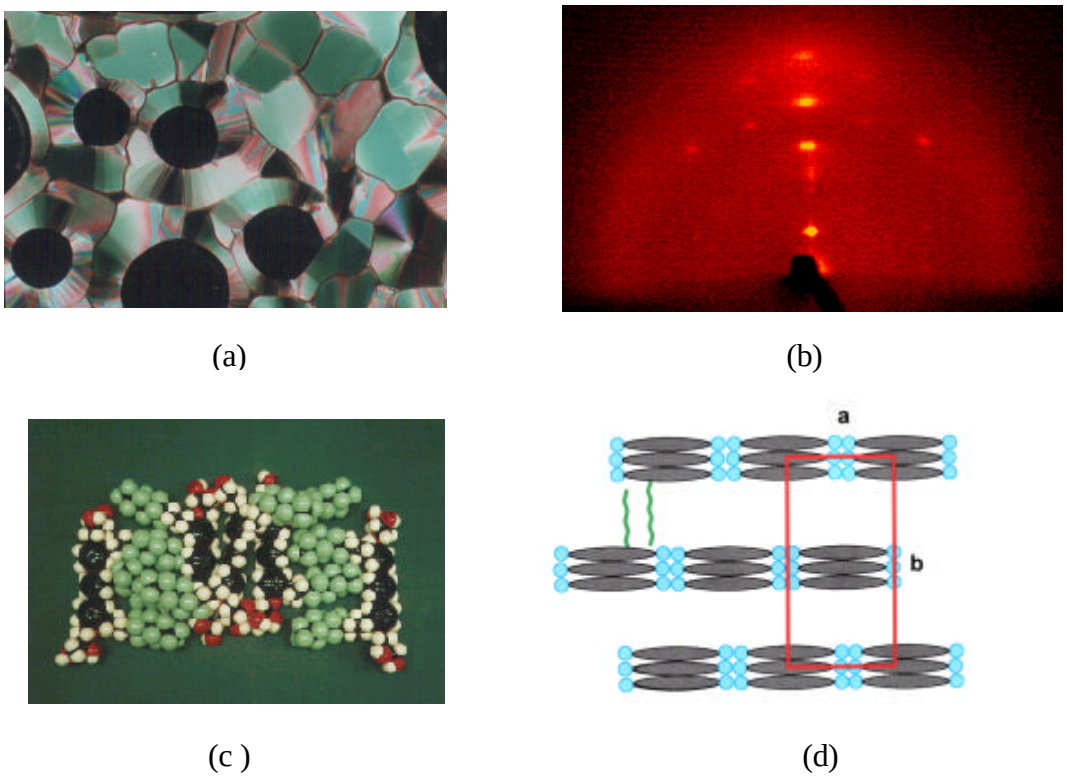
Table 5.8 *Transition temperatures, associated enthalpy values (lower lines, in italics) and lattice parameter of the mesophases of the bolaamphiphilic terphenyl derivatives and volume fractions of the lateral chains*



Comp.	R_1	R_2	Phase transitions (T / °C) ΔH/KJ mol^{-1}	Lattice parameter (nm)	f_R
58-H$_{9,9}$	3-C_9H_{19}	3′′-C_9H_{19}	Cr 133 Iso		0.55
58-F$_{4,4}$	3-$(CH_2)_3$ C_4F_9	3′′-$(CH_2)_3$ C_4F_9	Cr 158 Col (L) 165 Iso *19.1 12.4*		0.62
58-F$_{6,6}$	3-$(CH_2)_3$ C_6F_{13}	3′′-$(CH_2)_3$ C_6F_{13}	Cr 169 Col (L) 185 Iso *31.0 18.0*	a = 1.98, b = 5.1	0.62
58-F$_{6,6}$	2-$(CH_2)_3$ C_6F_{13}	2′′-$(CH_2)_3$ C_6F_{13}	Cr_1 122 Cr_2 142 Cub 160 Iso *31.2 4.15 2.2*		0.59
58-F$_{8,8}$	3-$(CH_2)_3$ C_8F_{17}	3′′-$(CH_2)_3$ C_8F_{17}	Cr 133 Col (L) 185 Smb 197 Iso *27.3 8.5*		0.67
58-F$_{10,10}$	3-$(CH_2)_3$ $C_{10}F_{21}$	3′′-$(CH_2)_3$ $C_{10}F_{21}$	Cr 195 Smb 205 Iso *28.9 5.1*		0.71
58-H$_9$F$_6$	3-C_9H_{19}	3′′-$(CH_2)_3$ C_6F_{13}	Cr 144 Col (L) 150 Iso *17.2 8.2*		0.59

The properties of these compounds are shown in Table 5.8. Compound **58-H$_{9,9}$**[93] with two lateral alkylchains is only a crystalline solid. The related perfluorinated compounds display mesogenic properties. Both compounds: **58-F$_{4,4}$** and **58-F$_{6,6}$** have enantiotropic mesophases. The mesophase of compound **58-F$_{6,6}$** was investigated in more detail. Its mesophase usually shows a mosaic texture (Figure 5.9a), but also spherulitic textures could be obtained. These textural features point to the presence of a columnar mesophase. Preliminary X-ray studies with a non-oriented samples however suggest a layer structure. Therefore this mesophase is tentatively assigned as Col (L)-phase. Also the diffraction pattern of aligned samples show in most cases four to five equidistant reflections in the meridian, pointing to a well defined layer structure (d = 2.59 nm). Remarkably, the 02-reflex is of very low intensity whereas the 03 and 04-reflection are of high intensity. This point to an additional periodicity with d = 0.5 × 2.59 = 1.3 nm). Remarkably, in the layer structure shown in Figure 5.9c, the

aromatic layers and the lipophilic layers have the same thickness of *ca* 1.3 nm, which would explain the extinction of the 02-reflex. However, sometimes, another diffraction pattern can be obtained (Figure 5.9b). Again a sequence of equidistant reflexes is found, but in the middle and wide angle region, distinct out of meridian reflections can be found, which can be indexed on the basis of a two–dimensional lattice with the parameter a = 1.98 nm and b = 5.1 nm. Strangely, however all out of the meridian reflexes in the low angle region are missing. The length of this molecule and the lateral chain in their most extended conformation amount to 2.4 nm and 1.3 nm, respectively. A reasonable model for this mesophase is hard to conceive. In any case the presence of a strong layer reflection with several higher order indicates the presence of a well defined layer structure. The high volume fraction of the lateral chains suggest the occurrence of a layer structure, in which the lipophilic chains are segregated from the rigid cores. However, in contrast to the conventional smectic phases, the aromatic cores should be aligned parallel to the layer planes, as shown in Figure 5.9c, d. Related layer structures have recently been suggested for the anthraquinones $\mathbf{AQ_n}$ and the anthracene derivative $\mathbf{A_n}$ shown in Figure 5.10.[87] Also the SmA phase of the triptycene derivative (**T**) has some similarities with such a structure.[88]



(a) (b)

(c) (d)

Figure 5.9 *(a) Texture of the mesophase of compound **58-F**$_{6,6}$ at 180 °C; (b) diffraction pattern of the columnar mesophase of **58-F**$_{6,6}$ at 177 °C; (c) CPK model showing a possible layer-like arrangement of the molecules **58-F**$_{6,6}$; (d) model of the Col$_r$ mesophase of **58-F**$_{6,6}$.*

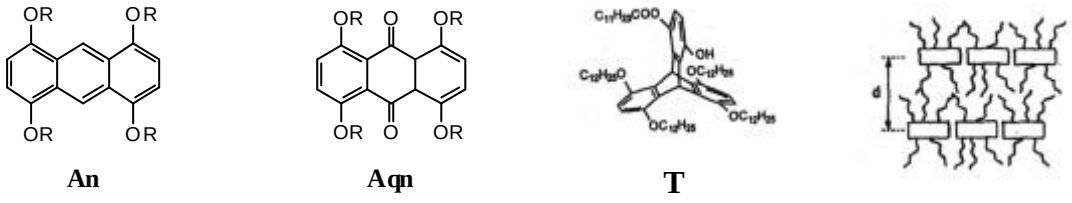


Figure 5.10 *Model of the Smectic phase of compounds anthracene* $\boldsymbol{A_n}$*, anthraquinone* $\boldsymbol{AQ_n}$*, and triptycene derivative* ***T****.*

On the other hand, the optical texture and the out of the meridian reflections suggest the presence of a two-dimensional lattice.

There are at least three possible ways to combine a layer structure with a two-dimensional lattice: One possibility is, that the 2D-lattice occurs perpendicular to the layers as shown with compound **53-F$_{10}$** as a result of a wavy deformation of the layers. However, this would lead to significantly larger lattice parameter.

Secondly, as shown in Figure 5.11a, it can be the result of a correlation between the layers. Here a periodicity is present within the layers and the adjacent layers are positionally and orientationally correlated with each other. In the case of compounds **58-F$_{4,4}$** and **58-F$_{6,6}$** such a periodicity could be provided by the segregation of the H-bonding networks from the aromatic cores within the layers of the bolaamphiphilic cores. The parameter a = 1.98 nm could correspond to the distance between the columns of H-bonding networks within the layers, if the molecules are randomly or uniformly titled within the layers. The parameter b = 5.1 nm is in good agreement with twice the layer distance (d = 2.59 nm) in an arrangement as shown in Figure 5.11a, in which the lateral chains are largely intercalated and in average 3 aromatic cores are arranged in the cross-section of the polar sublayers. Such columnar phases would represent laminated SmA (random tilt) or SmC (uniform tilt) phases, in which adjacent 2D-smectic layers have a positional and orientational correlation, i.e. arrangements of 2D smectic layers, which are separated by the fluid layers of the lateral chains (L_{Sm}).

A third possibility is shown in Figure 5.11c. Here, the 2D-lattice occurs within the aromatic layers. Such a mesophase could be regarded as a laminated modulated smectic phase (2D SmA~ - layers separated by the fluid layers of the lateral chains, $L_{Sm\sim}$). However, in this case the correlation between the layers would lead to a three dimensionally ordered mesophase. On the other hand it cannot be assumed that the 2D-lattice within the layers could be detected by X-ray diffraction if adjacent layers are non-correlated.

Another possible way to combine columnar and lamellar organization is shown in Figure 5.11b. Here, adjacent 2D-smectic layer have only an orientational correlation. This

organization is related to lamellar mesophases (Col_L)[4,5] and the sliding columnar mesophases of DAN-lipid complexes.[89]

The homologues **58-F$_{8,8}$** and **58-F$_{10,10}$** show quite a different novel mesophase. In the case of compound **58-F$_{8,8}$**, a mesophase with a schlieren texture is found. It cannot be homeotropically aligned and hence indicates an optically biaxial mesophase. In other regions a fan-like texture as typical for the smectic A phases could be detected. These textural features point to an optically biaxial smectic phase (Smb). In most optically biaxial smectic phases, the molecules are uniformly titled with respect to the layer plane (SmC), but also optically biaxial SmA-phase have recently been reported.[90] However, in contrast to SmC phases, which exhibit only four brush disclinations, in the smectic mesophases of **58-F$_{8,8}$** and **58-F$_{10,10}$** two brush disclination can be exclusively found. Therefore, this mesophase should be different from conventional SmC phases i.e. there should be no polar direction within the layers. If the models of the mesophase of **58-F$_{4,4}$** and **58-F$_{6,6}$** should be correct, then a laminated nematic structure (L_N) is conceivable for this mesophase, i.e. the calamitic parts of the moleculers are aligned in average parallel to the layer planes and parallel to each other in segregated sheet of the bolaamphiphilic cores, separated by the sublayers of the fluid lateral chains (see Figure 5.11 d).

Compound **58-F$_{8,8}$** shows this biaxial smectic phase only as a high temperature phase. At 185 °C a transition to another mesophase takes place. At this transition the fans get broken and the textural features of the low temperature phases are similar to those of the mesophases of compounds **58-F$_{4,4}$** and **58-F$_{6,6}$** with short lateral chains

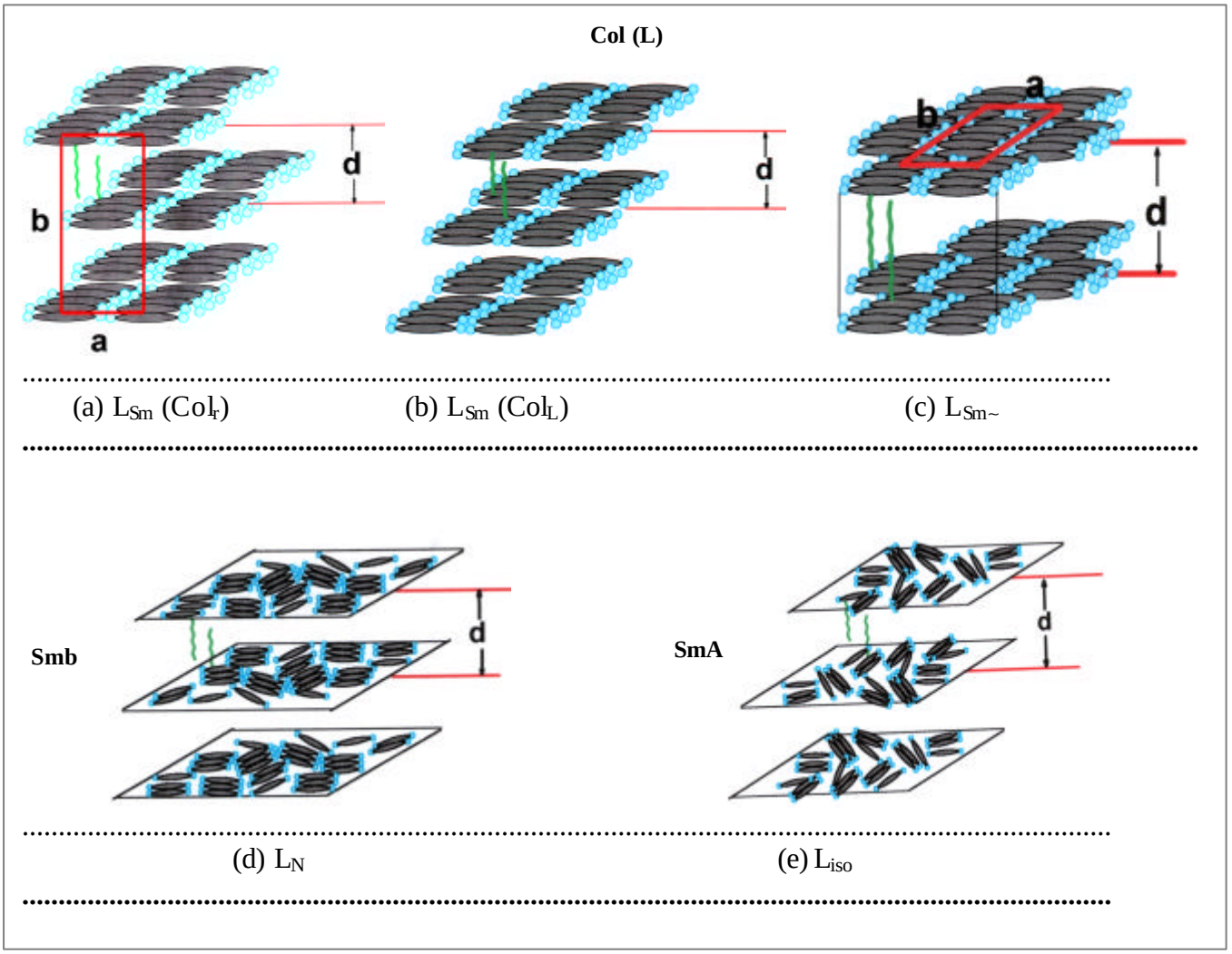


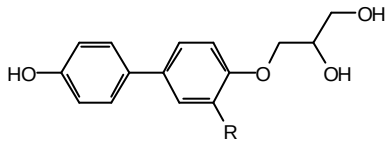
Figure 5.11 *Models of the mesophases of compounds* ***58-F*** $_{4,4}$, ***58-F*** $_{6,6}$, ***58-F*** $_{8,8}$ *and* ***58-F*** $_{10,10}$. *Possible structures of the Col (L) phases are shown in Figures a-c. (a) Laminated SmA-phase (SmC phases are also possible), in which adjacent layers have a positional and orientational correlation [*L_{SmA} *(correlated) =* Col_r*]; (b) laminated SmA-phase, in which adjacent layers have only an orientational correlation (sliding laminated SmA-phase or lamellar columnar phase); (c) laminated modulated smectic phase (2D SmA~ - layers separated by the fluid layers of the lateral chains); (d) proposed structure of the biaxial smectic phase (Smb): laminated nematic structure (*L_N*); (e) alternating arrangement of isotropic 2D-layers in the high temperature SmA phase of compounds* **71-F** $_{10}$ and **71-F** $_{12}$ *(*L_{iso} *= SmA =* L_α*).*

If the two semifluorinated chains in compound **58-F$_{6,6}$** are moved to the more central 2 and 2″-positions at the rigid core (compound **58¢-F$_{6,6}$**), the mesophase type changes. Polarizing microscopy indicates a highly viscous optically completely isotropic mesophase, as typical for cubic mesophase. However, in X-ray studies only one reflection can be found (*d* = 3.0 nm). Therefore a more detailed analysis of this cubic mesophase was not possible.

The terphenyl derivative **58-H$_9$F$_6$** with two different lateral chains, one hydrocarbon chain, the other one a semifluorinated chain shows essentially the same texture as **58-F$_{4,4}$** and **58-F$_{6,6}$**. The X-ray diffraction pattern is characterized by three equidistant reflexes in the small angle region. Hence, the structure of mesophase of **58-H$_9$F$_6$** should be related to those of **58-F$_{4,4}$** and **58-F$_{6,6}$**. A hint on the segregation of the fluorinated and nonfluorinated chains into separated sublayers was not found.

5.3.8 Bolaamphiphilic triols

Table 5.9 *Transition temperatures and associated enthalpy values (lower lines, in italics) of the bolaamphiphilic triols and the lattice parameter of their mesophases (d or a_{hex}) and volume fractions of the lateral chains.*



Comp.	R	Phase transition (*T* / °C) *DH/KJ mol*$^{-1}$	Lattice parameter (nm)	f_R
71-H$_9$	C_9H_{19}	Cr 126 (Col_h 85) Iso		0.50
71-H$_{11}$	$C_{11}H_{23}$	Cr 109 (Co_h102) Iso	a_{hex} = 2.9	*0.55*
71-H$_{14}$	$C_{14}H_{29}$	Cr 115 Iso		
71-F$_6$	$(CH_2)_3C_6F_{13}$	Cr 99 Col_h 125 Iso *26.6 11.5*	a_{hex} = 2.94	0.60
71-F$_8$	$(CH_2)_3C_8F_{17}$	Cr 118 Col (L) 139 Iso *1.2 8.4*	*d* = 3.0	*0.62*
71-F$_{10}$	$(CH_2)_3C_{10}F_{21}$	Cr 135 Col (L) 151 Smb 154 SmA 156 Iso *30.5 2.4 0.1 2.1*	*d* = 3.3	*0.66*
71-F$_{12}$	$(CH_2)_3C_{12}F_{25}$	Cr 154 (Smb 142) SmA 188 Iso *40.0 17.7 1.8*		*0.69*

In the next step we asked if the same sequence of the mesophases, as shown by the terphenyl derivatives **58-F**, could also be obtained if the volume fraction of the lipophilic

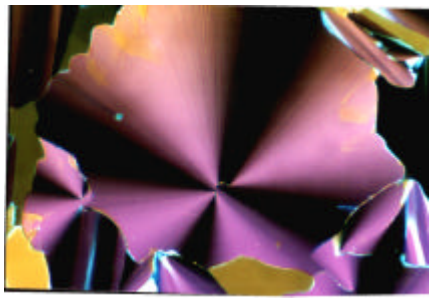
chains is not enhanced by increasing the number of chains, but the space, available for the chains is reduced by reducing the size of the bolaamphiphilic core.

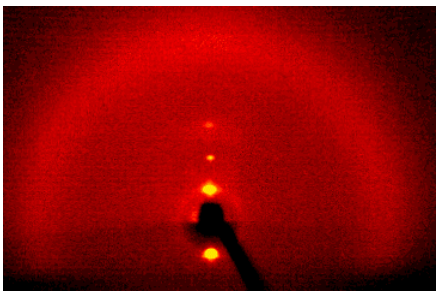
For this purpose the bolaamphiphilic triols **71** have been synthesized (see Table 5.9). In such molecules, one terminal end is replaced by a hydroxy group, the other terminal end is a diol group. In such a way, the length of the bolaamphiphilic core composed of the aromatic rigid units and the terminal polar group is reduced with respect to the volume of the lipophilic region.

For the hydrocarbon derivatives with lateral nonyl and undecyl groups, hexagonal columnar phases were observed[61], and on further elongation of the lateral alkyl chains, the mesogenity is lost (**71-H$_{14}$**). Again, the perfluorinated derivatives show more stable mesophases and they are significantly stabilized on elongation of the lateral semifluorinated chain. Compound **71-F$_6$** shows a hexagonal columnar mesophase with a_{hex} = 2.94 nm. However, compound **71-F$_8$** that has a two CF_2 units larger lateral group shows the same principal mesophase as the terphenyl derivatives **58-F$_{4,4}$** and **58-F$_{6,6}$** with two lateral semifluorinated chains. A spherulitic texture and mosaic-like textures (Figure 5.12a) as typical for columnar mesophases were found by polarizing microscopy, but its X-ray pattern shows only a well defined layer structure, with a layer periodicity of d = 3.0 nm (Figure 5.12b). These observation are reminiscent of the terphenyl compound **58-F$_{6,6}$** with the difference that no 2D-lattice is found and the 02-reflex has a higher intensity than the 03-reflex.

Compound **71-F$_{10}$** shows three distinct mesophases. On cooling from the isotropic liquid state, at first the typical texture of a conventional SmA phase, characterized by the typical fan-texture and homeotropically aligned optical isotropic regions is found. At 154 °C the homeotropic regions become birefringent. The texture of this mesophase is identical with that of the higher temperature mesophase of the terphenyl derivative **58-F$_{8,8}$** [Smb]. On further cooling, an additional phase transition occurs, the phase sequence seems to be the same as that of the terphenyl derivatives **58-F$_{8,8}$** with the difference that an additional SmA phase occurs above the optically biaxial smectic phase. X-ray studies indicate a well defined layer structure in the temperature range of all phases (d = 3.3 nm), but no changes of the X-ray pattern could be observed at the phase transitions. Compound **71-F$_{12}$** exhibits exclusively the biaxial smectic and the SmA phase.

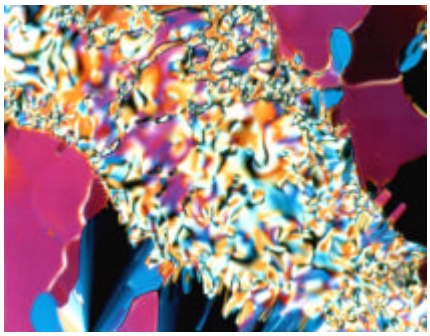
Interestingly, the biaxial smectic phase also occurs in a broad concentration region in a binary system of the terphenyl-derivative **58-F$_{6,6}$** and the biphenyl triol **71-F$_8$**.





(a) (b)

Figure 5.12 *(a) Texture of the mesophase of **71-F$_8$**; (b) 2D X-ray diffraction pattern of **71-F$_8$** at 138 °C.*



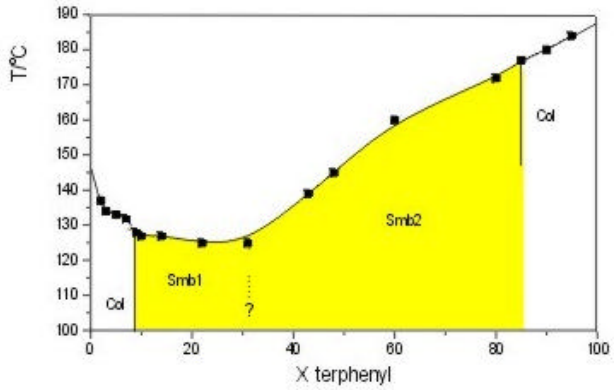
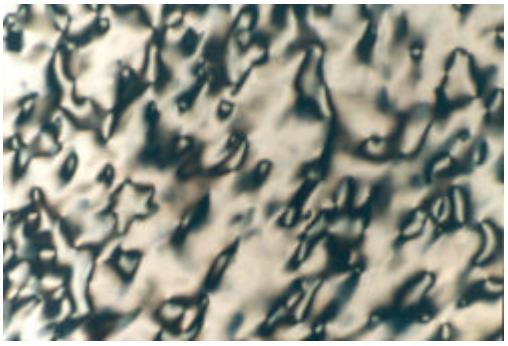


Figure 5.13 *Contact region (comp. **71-F$_8$** at the left hand side and comp. **58-F$_{6,6}$** at the right side) and the binary phase diagram of the binary system of **71-F$_8$** and **58-F$_{6,6}$**.*



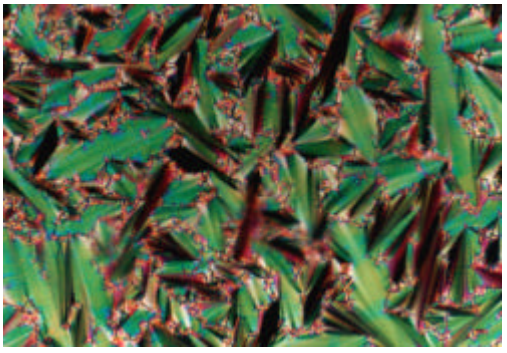


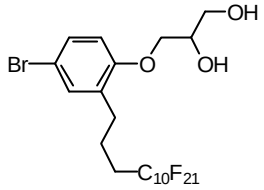
Figure 5.14 *(a) Schlieren texture (Smb$_1$) and (b) fan-like texture (Smb$_2$) found for the biaxial smectic phases in the binary system of **58-F$_{6,6}$** + **71-F$_8$**.*

The detailed phase diagram of the system **58-F$_{6,6}$** + **71-F$_8$** is shown in Figure 5.13. In a concentration region between $X_{\mathbf{58\text{-}F6,6}}$ = 0.08 and $X_{\mathbf{58\text{-}F6,6}}$ = 0.32, the biaxial smectic phase occurs exclusively with a schlieren texture (Smb_1) (Figure 5.14a). The X-pattren of this induced biaxial smectic phase shows a layer structure with d = 3.0 nm. In the region between $X_{\mathbf{58\text{-}F6,6}}$ = 0.32 and $X_{\mathbf{58\text{-}F6,6}}$ = 0.85 only a fan-like texture was observed (Figure 5.14b). Due to the rapid crystallization in this concentration region, no X-ray studies could be carried out. It is therefore not clear, if these are two different biaxial smectic phases in the different concentration regions or not.

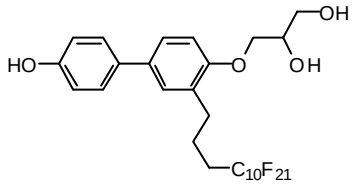
Nevertheless, all these investigations are in accordance with the models for these mesophases explained above. The lipophilic regions formed by the semifluorinated chains are so large that they can fuse with formation of layers, separating the sublayers of the aromatic rigid cores and hydrogen bonding networks. The aromatic cores should be aligned parallel to the layer planes. It seems, that the low temperature mesophases of the pure bolaamphiphiles **58** and **71** with long chains comprise an additional 2D-lattice. A possible explanation could be that at low temperature, the hydrogen bonds between the hydroxy groups form extended cylinders between the aromatic cores (the segregation of aromatic cores and polar regions remains). The aromatic rigid cores form ribbons, which are organized in layers (the layer can be regarded as 2D smectic phases). A two dimensional lattice could result if adjacent layers are positionally correlated. The resulting structure corresponds to a rectangular columnar structure and therefore, the typical texture of Col_r-phase can be observed under the polarizing microscope. However, it might be difficult for X-ray studies to find this 2D-lattice, if the correlation between the layers is only of short range order. At higher temperature, the hydrogen bonding in the layers can be partly destroyed, and the positional order of the aromatic cores in the layer is lost. Only the orientational order in the layer remains (L_N-phase). This more disordered structure could obviously also be achieved if bolaamphiphiles with a different length of the bolaamphiphilic cores are mixed (see figure 5.13b). Such molecules with a different length should prefer a 2D nematic organiztaion instead of a 2D smectic organization. If the bolaamphiphilic cores are rather short and / or the stability of the hydrogen bonding networks is reduced (compounds **71-F$_{10}$** and **71-F$_{12}$**), increasing the temperature could lead to a complete loss of the orientational order of the aromatic cores in the layers. The aromatic cores become disordered within the layers, but still arranged parallel to the layer planes. Hence, a sequence of two isotropic layers remains and the texture turns to that of the conventional SmA phase (L_{iso}, L_α phase).

Though an unambiguous confirmation of the suggested mesophase structures cannot be given with the obtained experiment results, the proposed model of the Smb phase is additional confirmed by investigation of the free-standing films of compound **71-F$_{10}$**. They umambiguously confirm the presence of a layer structure and that the optical axis (i.e. the biphenyl cores) are parallel to the layers planes.[91] Additionally, the dependence of the

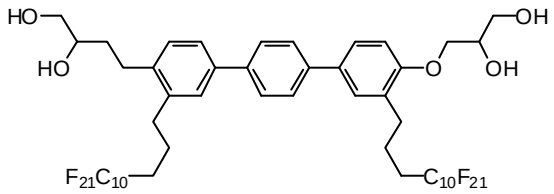
mesomorphic properties on the length of the rigid cores and in dependence on the length of the lateral chains can be successfully explained with the proposed models. Comparison of compounds **47.3**, **71-F$_{10}$** and **58-F$_{10,10}$** shows that elongation of the aromatic rigid core gives rise to an orientational order within the aromatic layers, leading to a transition from the conventional SmA-phase (comp. **47.3**) to a biaxial smectic phases (L_N). At lower temperature a transition of the 2D-nematic order within the aromatic layers to a 2D-smectic structure should give rise to mesophases characterized by well defined layer structures, but textures typical for columnar phases (Figure 5.15).



47.3
Cr 77 SmA 100 Iso.



71-F$_{10}$
Cr 135 Col (L) 151 Smb (L_N) 154 SmA 156 Iso



58-F$_{10,10}$
Cr 195 Smb (L_N) 205 Iso

Figure 5.15 *Elongation of the aromatic rigid core gives rise to an orientational order within the aromatic layers, leading to a transition from the conventional SmA-phase to a biaxial smectic phase (L_N) and 2D-smectic structure [Col (L)].*

5.4 Conclusions

In summary, it was found, that by introduction of partially and totally fluorinated lateral chains in lateral positions of rigid bolaamphiphiles, a wide variety of novel and quite different mesophases can be obtained. Their formation is caused by the segregation of the lateral chains from the bolaamphiphilic cores. In the first step this leads to a frustration of the smectic

monolayer structure formed by the bolaamphiphiles without lateral chains. Biphenyl derivatives with one fluorinated lateral chain, form broad region of quite different columnar liquid-crystalline phases and they have significantly increased mesophase stabilities in comparison to the corresponding hydrocarbon analogues. The formation of these columnar phases is explained as follows: the lipophilic lateral chains segregate with formation of columns. The rigid aromatic units build up cylinder shells around these columns, held together by the hydrogen bonding network between the diol groups. The relative space required by the lipophilic chains with respect to the size of the rigid segments determines the precise shapes of the cylinders and hence, the type of the columnar mesophases. The sequence of their occurrence in dependence on the chain length is Col_r (*c*2*mm*), Col_r (*p*2*gg*), Col_t (*p*4*mm*), Col_h (*p*6*mm*), Col_r *(p*2*mg)*, the same as found for the related hydrocarbon analogues. However, a new Col_r *(p*2*mg)* phase which represents an arrangement of wavy deformed layers is obtained for compound **53-F_{10}** with the longest semifluorinated chain and the chain length required to form each columnar type is reduced due to the larger volume of the semifluorinated chains.

The mesophase type seems to be largely independent on the position of the lateral chain. In the case of the fluorinated compounds, tetragonal columnar mesophase often occurs instead of the Col_r-phases.

Bolaamphiphiles with additional spacers between the rigid cores and the polar groups have reduced mesophase stabilities. The effect of elongation of this spacer is contrary to the effect of elongation of the lateral chains, i.e. on elongation of the spacer, hexagonal columnar phases are replaced by rectangular or tetragonal mesophases.

Enlarging the head group reduce the mesophase stability.

Non-conventional smectic phases in which the calamitic units are organized parallel to the layer planes are suggested for the bolaamphiphilic terphenyl derivative with two lateral chains and the bolaamphiphilic triols with long chains.

Three different phase structures, laminated smectic phases (L_{Sm}), laminated nematic phases (L_N) and an array of isotropic layers (L_{iso}) are suggested for these phases. Additionally, a cubic mesophase was found for one of the terphenyl derivatives. To understand its formation, further investigations are necessary.

Thus starting with the nonsubstituted bolaamphiphile **53-H_0** and ending up with compound **58-$F_{10,10}$**, a transition between two orthogonal sets of layer structures occurs, with columnar phase as intermediate phases at the transition between these two layer structures (Figure 5.16).

All the experimental results indicate, that the fluorophobic effect caused by the fluorinated chains can be used in combination with other incompatibilities to increase the micro-segregation of incompatible molecular parts into different regions and can stabilize the mesophase. There are three distinct effects of the fluorinated chains in these system: i) The fluorinated segments stabilize the mesophases due to the increased incompatibility with both aromatic and polar molecular parts; ii) simultaneously, they reduce the melting points in many cases and thus enlarge the mesomorphic regions; iii) the larger space required by the fluorinated chains increases the size of the segregated lipophilic regions and therefore, modifies the phase structure and leads to novel mesophases. A segregation of the fluorinated and the hydrogenated parts of the lateral chains was not observed in the reported compounds.

Although the self-organisation of this class of mesogenic block-molecules is unique among low molecular weight materials, there is a close relationship to the behavior of the recently reported ABC heteroarm star terpolymers,[92] which can form morphologies quite similar to the Col_r, Col_t and Col_h-phase of the bolaamphiphiles with lateral chains, but on a significantly larger length-scale.

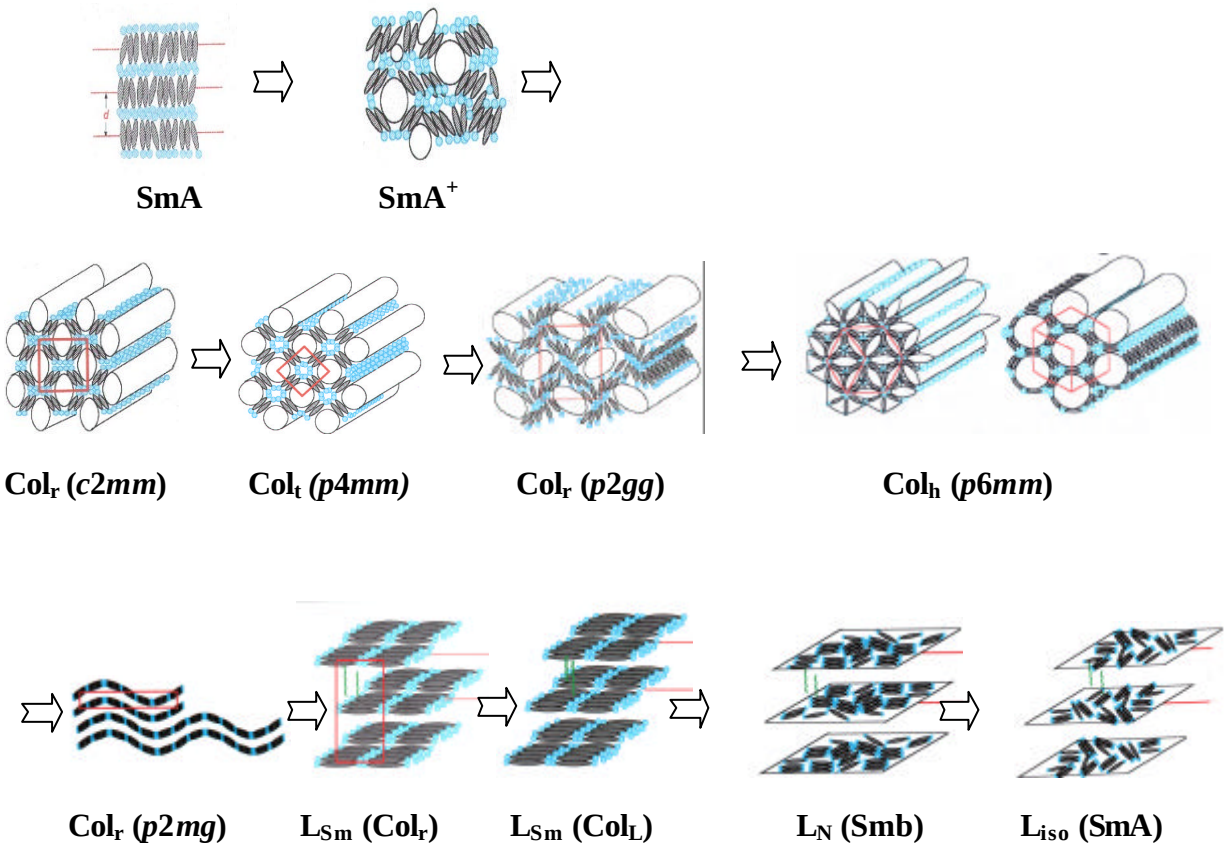
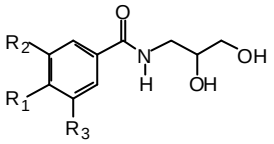


Figure 5.16 *Transition between two orthogonal sets of layers structure with columnar phases as intermediate phases.*

6 Summary

In this work we have synthesized four different classes of nonconventional liquid cystals with perfluorinated chains and investigated their thermotropic liquid crystalline properties. The palladium catalyzed addition of perfluoralkyliodides to alkenes and palladium catalyzed cross coupling reaction were the key steps of the syntheses.

A: Replacement of the alkyl chains in polyhydroxy amphiphiles by semiperfluorinated chains leads to a significant mesophase stabilization and a lowing of the melting points. This is essencially the result of the enlargement of the intramolecular polarity contrast. By adjusting the number and length of the lipophilic chains, smectic A, hexagonal columnar and micellar cubic mesophases were obtained. The value of the interface curvature between hydrophilic regions and lipophilic regions was recognized as the key factor determining the morphology of the polymolecular aggregates forming the mesophase.

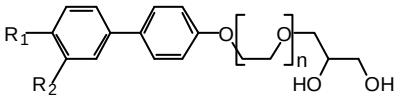


7-1F$_{6/4}$: $R_1 = (CH_2)_4C_6F_{13}$, $R_2 = R_3 = H$: Cr 79 SmA 223 Iso
7-2F$_{6/4}$: $R_1 = R_2 = (CH_2)_4C_6F_{13}$, $R_3 = H$: Cr 86 Cub_{I2} 208 Iso
7-3F$_{6/4}$: $R_1 = R_2 = R_3 = (CH_2)_4C_6F_{13}$: Cr 59 Cub_{I2} 188 Iso
7-3F$_{7/4}$: $R_1 = R_2 = R_3 = (CH_2)_4(CF_2)_4CF(CF_3)_2$: Cr < 20 Cub_{I2} 193 Iso

Because of the larger cross sectional area of the perfluorinated segments in comparison to alkyl chains, only two semifluorinated chains are sufficient to obtain the micellar cubic mesophase (Cub_{I2}). All Cub_{I2} have the *Pm*3*n* lattice. The two chain compounds **7-F$_{4/6}$** and **7-F$_{6/4}$** are the first double chain amphiphiles which form a micellar cubic phase and simultaneously they are the first semifluorinated amphiphiles with an inverse thermotropic cubic phase.

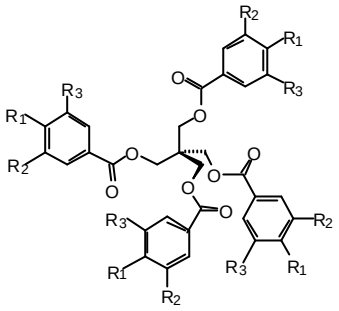
The Cub_{V2} phase can be induced in binary mixtures of single chain with double chain amphiphiles and of single chain with triple chain amphiphiles. It occurs only in a certain temperature range above a distinct temperature. At lower temperature, a direct transition between the SmA phase and the Col_h phase can be observed. This leads to a reentrant behavior of the SmA phases and Col_h phases in certain concentration ranges.

B: Amphiphilic biphenyl derivatives with one or two semifluorinated terminal chains, form smectic and different columnar mesophases. Compared with the corresponding hydrocarbon anaologues the introduction of perfluorinated chains does not cause a significant change of the mesophase behavior.



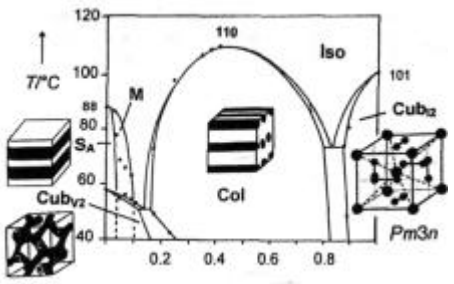
16-1F$_{6/4}$: $R_1 = (CH_2)_4C_6F_{13}$, $R_2 = H$: Cr 147 $Colx_1$ 152 $Colx_2$ SmC 158 SmA 219 Iso
16-1F$_{6/10}$: $R_1 = (CH_2)_{10}C_6F_{13}$, $R_2 = H$: Cr 149 ($Colx_1$ 148) $Colx_2$ 168 SmA 203 Iso
16-2F$_{6/4}$: $R_1 = R_2 = (CH_2)_4C_6F_{13}$: Cr < 20 Col 145 Iso

C: All types of mesophases (smectic, columnar, bicontinuous cubic, and micellar cubic) were realized with semifluorinated pentaerythritol tetrabezonates.



27-1F$_{6/4}$: $R_2 = R_3 = H$, $R_2 = (CH_2)_4C_6F_{13}$: Cr 59 SmA 88 Iso
27-2F$_{6/4}$: $R_1 = R_2 = (CH_2)_4C_6F_{13}$, $R_3 = H$: Cr 88 Cub_{h2} 131 Iso
27-3F$_{6/4}$: $R_1 = R_2 = R_3 = (CH_2)_4C_6F_{13}$: Cr 36 Cub_{I2} 210 Iso

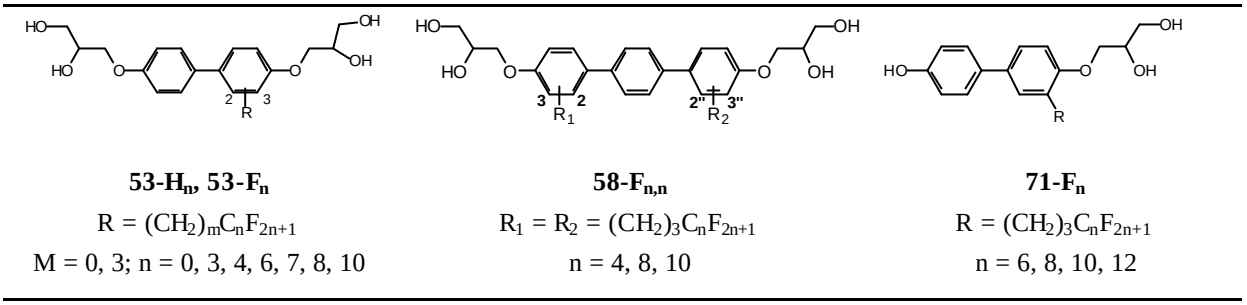
This is the same phase sequence as found in lyotropic systems and for the thermotropic phase sequence of the polyhydroxy amphiphiles in dependence on the number of the lipophilic chains. The increased mesophase stability of all fluorinated compounds in comparison to the related alkyl compounds arises largely from the increased intramolecular polarity contrast on replacing the alkyl chains by semifluoroalkyl chains, which favors micro-segregation. The larger cross-section area of the fluorinated alkyl chains should be responsible for the transition from a columnar to a micellar cubic phase upon replacing the alkyl chains of **27-3H** by semifluorinated chains. These novel compounds can be regarded as low molecular weight block molecules, they represent an interesting borderline case between low molecular weight amphiphiles (surfactants, lipids) and block copolymers.



27-1F$_{6/4}$ **27-3F$_{6/4}$**

D: By introduction of partially and totally fluorinated lateral chains in lateral positions of rigid bolaamphiphiles, a wide variety of the novel and quite different mesophases were obtained. Their formation is caused by the segregation of the lateral chains from the bolaamphiphilic cores, which in the first step leads to a frustration of the smectic monolayer structure formed by the parent bolaamphiphiles without lateral chains. Biphenyl derivatives with one fluorinated lateral chain form broad region of quite different columnar liquid-crystalline phases and they have significantly increased mesophase stabilities in comparison to the corresponding hydrocarbon analogues. The formation of these columnar phases is explained as follows: the lipophilic lateral chains segregate with formation of columns. The rigid aromatic units build up cylinder shells around these columns, held together by the hydrogen bonding network between the diol groups. The relative space required by the lipophilic chains with respect to the size of rigid segments determines the precise shapes of the cylinders and hence, the type of the columnar mesophases. The sequence of their occurrence in dependence on the chain length is Col_r (*c*2*mm*), Col_r (*p*2*gg*), Col_t (*p*4*mm*), Col_h (*p*6*mm*), Col_r (*p*2*mg*). The Col_r (*c*2*mm*), Col_r (*p*2*gg*) and Col_h (*p*6*mm*) phases are the same as found for the hydrocarbon analogues. However, the chain length required to form each columnar type is reduced due to the larger volume of the semifluorinated chains. A

new Col_r-phase with a *p*2*mg* lattice is obtained for compound **53-F$_{10}$** with the longest semifluorinated chain. This columnar phase is built up by wavy deformed layers (Figure 15.6).



53-H$_n$, 53-F$_n$	**58-F$_{n,n}$**	**71-F$_n$**
R = $(CH_2)_mC_nF_{2n+1}$	$R_1 = R_2 = (CH_2)_3C_nF_{2n+1}$	R = $(CH_2)_3C_nF_{2n+1}$
M = 0, 3; n = 0, 3, 4, 6, 7, 8, 10	n = 4, 8, 10	n = 6, 8, 10, 12

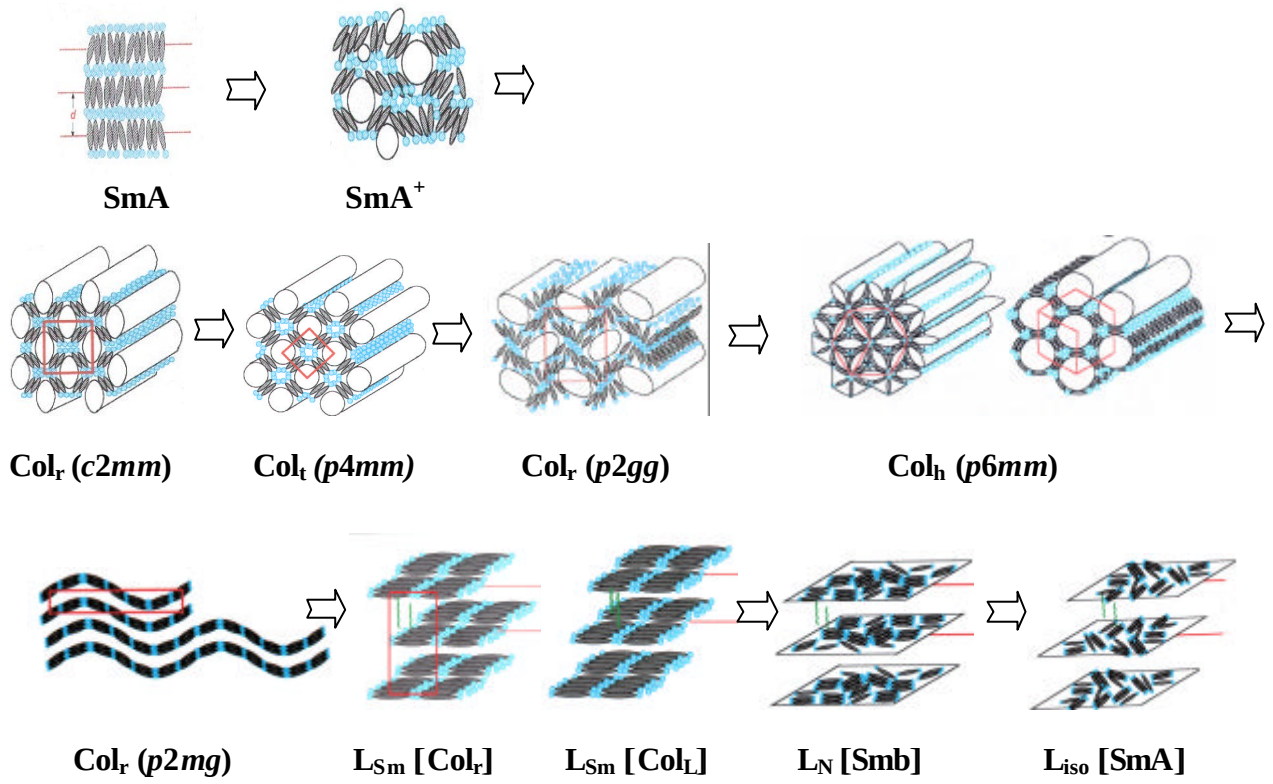


Figure 5.16 *Transition between two orthogonal sets of layers structure with columnar phases as intermediate phases.*

The mesophase type seems to be largely independent on the position of the lateral chain. In the case of the fluorinated compounds, tetragonal columnar mesophases often occur instead of the Col_r-phases with *c*2*mm* and *p*2*gg* lattice.

Bolaamphiphiles with additional alkyl spacers between the rigid core and the polar head groups have reduced mesophase stabilities. The effect of their elongation is contrary to the effect of elongation of the lateral chains, i.e. on elongation of the spacer, hexagonal columnar phases are replaced by rectangular or tetragonal mesophases.

Enlarging the head group size reduce the mesophase stability.

Non-conventional smectic phases in which the calamitic units are organized parallel to the layer planes are suggested for bolaamphiphilic terphenyl derivatives with two lateral chains and bolaamphiphilic triols with one long chain.

Three different phase structures, laminated smectic phases (L_{Sm}), a laminated nematic phases (L_N) and an array of isotropic layers (L_{iso}, SmA) are suggested for these phases. Additionally, a cubic mesophase was found for one of the terphenyl derivatives. To understand its formation, further investigations are necessary.

Thus starting with the nonsubstituted bolaamphiphile **53-H_0** and ending up with compound **58-$F_{10,10}$**, a transition between two orthogonal sets of layer structures occurs, with columnar phases as intermediate phases at the transition between these two layer structures (Figure 5.16).

All the experimental results indicate, that the fluorophobic effect caused by the fluorinated chains can be used in combination with other incompatibilities to increase the micro-segregation of incompatible parts into different regions and can stabilize the mesophase. There are three distinct effects of the fluorinated chains in these systems: i) The fluorinated segments stabilize the mesophases due to the increased incompatibility with both aromatic and polar molecular parts; ii) simultaneously, they reduce the melting points in many cases and thus enlarge the mesomorphic regions; iii) the larger space required by the fluorinated chains increases the size of the segregated lipophilic regions and therefore, modifies the phase structure and leads to novel mesophases. A segregation of the fluorinated and the hydrogenated parts of the lateral chains was observed in only one case.

Although the self-organisation of this class of mesogenic block-molecules is unique among low molecular weight materials, there is a close relationship to the behavior of the recently reported ABC heteroarm star terpolymers, which can form morphologies quite similar to the Col_r, Col_t and Col_h-phase of the bolaamphiphiles with lateral chains, but on a significantly larger length-scale.

The competitive combination of rigidity and micro segregation is a successful principle. In the future, using this principle, new supramolecular structure could be realized, which can be compared with the complex morphology of multiblock-copolymers. The increased incompatibility of perfluorinated segments with other molecular parts is an essential advantage compared to related hydrocarbon compounds. Additionally, it is possible to use the volume effect of perfluorinated chains to control the space filling of the micro-segregated region.

7 References

1. Reviews: (a) H. Stegemeyer, *Topic in Physical Chemistry*, Vol 3, *Liquid Crystals*, Steinkopf Darmstadt, Springer, New York, **1994**; (b) G. W. Gray, J. W. Goodby, *Smectic Liquid Crystals*, Leonard Hill, Glasgow, London, **1984.**
2. (a) D. Demus, J. W. Goodby, G. W. Gray, H. W. Spiess, V. Vill (Hg.); *Handbook of Liquid Crystal*, Wiley-VCH, Weinheim, **1998**.
3. (a) S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, *Pranama*, **1977**, 9, 471; (b) S. Chandrsekhar, *Liq. Crys.*, **1993**, 14, 3; (c) W. Kreuder, H. Ringsdorf, O.-H. Schönherr, J. H. Wendorff, *Angew. Chem*., **1987**, 99, 1300; (d) C. P. Lillya, R. Thaku, *Mol. Cryst. Liq. Cryst*., **1989**, 170, 179; (e) H. Bengs, O. Karthaus, H. Ringsdorf, C. Baehr, M. Ebert, J. H. Wendorff, *Liq. Cryst*., **1991**, 10, 161; (f) K. Ohta, A. Ishhii, H. Muroki, I. Yamamoto, K. Matsuzaki, *Mol. Cryst. Liq. Cryst*., **1985**, 116, 229; (g) C. Piechocki, J. Simon, *Chem. Commun*., **1985**, 259; (h) B. Kohne, K. Praefcke, *Chimia*., **1987**, 41, 196.
4. (a) P. Davidson, A. M. Levelut, H. Strzelecka, V. Gionis, *J. Phys. Lett.*, **1983**, 44, 823; (b) D. Haristory, S. Mery, B. Heinrich, L. Mager, J. F. Nicoud, D. Guillon, *Liq. Cryst*., **2000**, 27, 321; (c) A. C. Ribeiro, A. F. Martins, A. M. Giroud-Godquin, *Mol. Cryst. Liq.Cryst. Lett.*, **1988**, 5, 133; (e) A. M. Levelut, M. Ghedini, R. Bartolino, F. P. Nicoletta, F. Rustichelli, *J. Phys. (Paris)*, **1989**, 50, 113.
5. (a) G. Lattermann, S. Schmidt, R. Kleppinger, J. –H. Wendorff, *Adv. Mater*., **1992**, 4, 30; (b) Y. Shimizu, H. Monobe, S. Mima, T. Higanhiyama, T. Fuchita, T. Sugino, *Res. Soc. Symp. Proc.*, **1999**, 559, 221; (c) G. S. Attard, R. H. Templer, *J. Mater. Chem.*, **1993**, 3, 207; (d) R. Ziessel, L. Douce, A. El- ghayoury, A. Harriman, A. Skoulios, *Angew. Chem. Int. Ed. Engl.*, **2000,** 39, 1489.
6. (a) C. Tschierske, *Progr. Polym. Sci.*, **1996**, 21, 775; (b) M. Paleos, *Mol. Cryst. Liq. Cryst*., **1994**, 243, 159.
7. C. Tschierske, *J. Mater. Chem*., **1998**, 8, 1485.
8. J. N. Israelachvili, D. J. Mitchell, B. W. Ninham, *J. Chem. Soc., Faraday Trans. 2*, **1976,** 72, 1525.
9. K. Borisch, S. Diele, P. Göring, M. H. Kresse, C. Tschierske, *J. Mater. Chem*., **1998**, 8, 529.
10. (a) V. Luzzati, A. P. Spengt, *Nature (London)*, **1967**, 215, 701; (b) J. M. Seddon, R. H. Templer, *Phil. Trans. R. Soc. London.*, **1993**, A 344, 377; (c) G. J. T. Tiddy, *Phys. Rep*., **1980**, 57, 1.
11. (a) M. Clerc, *J. Phys. II Fr.*, **1996**, 6, 961; (b) P. Sakya, J. M. Seddon, R. H. Templer, R. J. Mirkin, G. J. Tiddy, *Langmuir*, **1997**, 13, 3706; (c) A. Gulik, H. Delacroix, G. Kirschner, V. Luzzati, *J. Phys. II Fr.*, **1995**, 5, 445.

12. J. M. Seddon, N. Zeb, R. H. Templer, R. N. McElhaney, D. A. Mannock, *Langmuir*, **1996**, 12, 5250.
13. J.-H. Fuhrhop, D. Fritsh, *J. Am. Chem. Soc*., **1986**, 19, 130.
14. Columnar mesophases have been found for bolaamphiphiles, in which the head group are connected with each other by flexible alkyl chains. The self-organization of these compounds is related to those found for conventional amphiphiles: (a) A. Gulik, V. Luzzati, M. De Rose, A. Gambacorta, *J. Mol. Biol.*, **1985**, 182, 131; (b) H. Gutman, A. Loewenstein,. Z. Luz, R. Poupko, H. Zimmermann, *Liq. Cryst*., **1991**, 9, 607; (c) R. Auzély-Velty, T. Benvegnu, D. Plusquellec, G. Mackenzie, J. A. Haley, J. W. Goodby, *Angew. Chem., Int. Ed.*, **1998**, 37, 251.
15. Reviews: (a) A. E. Skoulios, in *Developments in Block Copolymers*, ed. I. Goodman, Elsevie, *App. Sci. Pub.*, London, **1982**, vol 1, P 81; (b) A. Skoulios, in *Advance in Liquid Crystals*, ed. G. H. Brown, Academic Press, New York, **1975**, p 169; (c) A. Skoulios, D. Guillon, *Mol. Cryst. Liq. Cryst*., **1988**, 165, 317; (d) F. S. Bates, G. H. Fredrickson, *Annu. Rev. Phys. Chem*., **1990**, 41, 525; (e) S. Förstner, *Ber. Bunsenges. Phys. Chem*., **1997**, 101, 1671.
16. I. W. Hamley, K. A. Koppi, J. H. Rosedale, F. S. Bates, K. Almdal, K. Mortensen, *Macromolecules*, **1993**, 26, 5959.
17. D. A. Hajduk, P. E. Harper, S. M. Gruner, C. C. Honeker, G. Kim, E. L. Thomas, L. J. Fetters, *Macromoleculers*, **1994**, 27, 4063.
18. (a) L. Leibler, *Macromolecules*, **1980**, 13, 1602; (b) Block Copolymers: *Science and Technology*, ed. D. J. Meier, IMM Press/Hardwood Academic, New York, **1983**; (c) D. J. Meier, *J. Polym. Sci., C*, **1969**, 26, 81.
19. (a) M. Lee, N. –K. Oh, W. –C. Zin, *Chem. Commun*., **1996**, 1787; (b) M. Lee, N. –K. Oh, H. K. Lee W. –C. Zin, *Macromolecules*, **1996**., 29, 5567.
20. Review: (a) H. Fischer, S. Poser, *Acta Polymerica*, **1996**, 47, 413; (b) E. Chiellini, G. Galli, S. Angelino, M. Laus, *Trends Polym. Sci.*, **1994**, 2, 244; (c) M. Walther, H. Finkelmann, *Prog. Polym. Sci*., **1996**, 21, 951.
21. Y. Hendrikx, A. M. Levelut, *Mol. Cryst. Liq. Cryst*., **1988**, 165, 233.
22. (a) O. Albrecht, W. Cumming, W. Kreuder, A. Laschewsky, H. Ringsdorf, *Colloid Polym. Sci.*, **1986**, 264, 659; (b) M. F. Daniel, O. C. Lettington, S. M. Small, *Mol. Cryst. Liq. Cryst.*, **1983**, 96, 373; (c) S. Fuller, J. Hopwood, A. Rahman, N. Shinde, G. J. Tiddy, G. S. Attard, O. Howell, S. Sproston, *Liq. Cryst.*, **1992**, 12, 521; (d) G. Decher, H. Ringsdorf, *Liq. Cryst*., **1993**, 13, 57; (e) M. C. Everaars, A. T. M. Marcelis, E. J. R. Sudhölter, *Thin Solid Films*, **1994**, 242, 78; (f) D. Joachimi, C. Tschierske, , A. Öhlmann, W. Retting, *J. Mater. Chem.*, **1994**, 4, 1021; (e) M. Woolley, R. H. Tredgold, P. Hodge, *Langmuir*, **1995**, 11, 683.
23. A. Laschewsky, *Adv. Mater*., **1989**, 392; (b) N. C. Maliszewskyj, P. A. Heiny, J. K. Blasie, J. P. McCauley, A. B. Smith, III. *J. Phys., II* **1992,** 75; (c) J. Reiche, R. Dietel,

D. Janietz, H. Lemmetyinen, L. Brehmer, *Thin Solid Films*, **1992**, 226, 265; (d) , D. Janietz, D. Hofmann, J. Reiche, *Thin Solid Films*, **1994**, 244, 794.

24. B. Neumann, C. Sauer, S. Diele, C. Tschierske, *J. Mater, Chem.*, **1996**, 6(7), 1087.
25. M. Kölbel, T. Beyersdorff, I. Sletvold, C. Tschierske, J. Kain, S. Diele, *Angew. Chem*., **1999**, 111, 1146.
26. (a) F. Hildebrandt, J. A. Schröter, C. Tschierske, R. Festag, M. Wittenberg, J. H. Wendorff, *Adv. Mater*., 1997, 9, 564; (b) J. A. Schröter, C. Tschierske, M. Wittenberg, J. H. Wendorff, *Angew. Chem.*, **1997**, 109, 1160; (c) R. Plehnert, J. A. Schröter, C. Tschierske, *J. Mater. Chem.*, **1998**, 8, 2611; (d) J. A. Schröter, C. Tschierske, M. Wittenberg, J. H. Wendorff, *J. Am. Chem. Soc.*, **1998**, 120, 10669.
27. C. Auschra, R. Stadler, *Macromolecules*, **1993**, 26, 2171.
28. (a) T. Inoi, *Organofluorine Chemistry*: *Principles and Commercial Appl.*, **1994**, 263.
29. C. M. Koen, K. Nakagawa, Y. Ishii, F. Funada, M. Matsuura, K. Awane, *Mol. Cryst. Liq. Cyst. Lett.*, **1989**, 6, 185.
30. (a) V. V. Titov, T. I. Zverkova, E. I. Kovshev, Y. N. Fialkov, S.V. Shelazhenko, L. M. Yagupolski, *Mol. Cryst. Liq. Cryst*., **1978**, 47, 1; (b) S. Misaki, S. Takamatsu, M. SuefuJi, T. Mitote, M. Matsumura, *Mol. Cryst. Liq. Cryst*., **1981**, 66, 123; (c) A. V. Ivashcherko, E. Kovshev, V. T. Lazareva, E. K. Prudnikova, V. V. Titov, T. I. Zverkova, M. I. Barnik, L. M. Yagupolski, *Mol. Cryst. Liq. Cyst*., **1981**, 67, 235.
31. C. Viney, T. P. Russell, L. E. Depero , R. J. Twieg, *Mol. Cryst. Liq. Cryst*., **1989,** 168, 63.
32. P. Marczuk, P. Lang, M. Möller, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **2000**, 163, 103.
33. (a) T. Doi, S. Takenaka, S. Kusabayashi, *Mol. Cryst. Liq. Cryst.*, **1991**, 204, 9; (b) G. Johansson, V. Percec, G. Ungar, K. Smith, *Chem. Mater.*, **1997**, 9, 164.
34. Review: (a) H. T. Nguyen, C. Destrade, J. Malthete, *Adv. Mater*., **1997**, 9, 375; (b) J. Malthete, H. T. Nguyen, C. Destrade, *Liq. Cryst.*, **1993,** 13, 171.
35. (a) H. T. Nguyen, G. Sigaud, M. F. Achard, F. Hardouin, R. J. Twieg, K. Betterton, *Liq. Cryst*., **1991**, 10, 389; (b) T. Doi, Y. Sakurai, A. Tamatani, S. Takenaka, S. Kusabashi, Y. Nishihata, H. Terauchi, *J. Mater. Chem*., **1991**, 1, 169; (c) S. Pensec, F.-G. Tournilhac, P. Bassoul, *J. Phys. II Fr.*, **1996**, 6, 1597; (d) S. V. Arehart, C. Pugh, *J. Am. Chem. Soc.*, **1997**, 119, 3027.
36. (a) U. Dahn, C. Erdelen, H. Ringsdorf, R. Festag, J. H. Wendorff, P. A. Heiney, N. C. Maliszewskyj, *Liq. Cryst*., **1995**, 19, 759; (b) H. Bengs, F. Closs, F. Frey, D. Funhoff, H. Ringsdorf, K. Siemensmeyer, *Liq. Cryst.*, **1993**, 15, 565.
37. (a) V. Percec, D. Schluter, Y. K. Kwon, J. Blackwell, M. Möller, P. J. Slangen, *Macromolecules*, **1995,** 28, 8807; (b) G. Johansson, V. Percec, G. Ungar, J. Zhou, *ibid.*, **1996**, 29, 646; (c) V. Percec, G. Johansson, G. Ungar, J. Zhou, *J. Am. Chem. Soc.*, **1996**, 118, 9855.

38. (a) T. A. Lobko, B. I. Ostrovskii, A. I. Pavluchenko, S. N. Sulianov, *Liq. Cryst*., **1993**, 15, 361; (b) B. I. Ostrovskii, *Liq. Cryst*., **1993**, 14, 131; (c) E. Dietzmann, W. Weissflog, S. Markscheffel, A. Jakli, D. Lose, S. Diele, *Ferroelectrics*, **1996**, 180, 341; (d) H. -T. Nguyen, C. Destrade, J. Malthete, *Adv. Mater*., **1997**, 9, 375.
39. B. E. Smart, in *Organofluorine Chemistry Principles and Commercial Applications*, ed. R. E. Banks, B. E. Smart, J. C. Tatlow, Plentum Press, New York, **1994**, p 57.
40. C. W. Bunnn, E. R. Howens, *Nature (London)*, **1954**, 174, 549.
41. J. H. Hildebrand, B. B. Fischer, H. A. Benesi, *J. Am. Chem. Soc*., 1950, 72, 4348.
42. M. P. Turberg, J. E. Brady, *J. Am. Chem. Soc*., **1998**, 110, 7797.
43. (a) S. Diele, D. Lose, H. Kruth, G. Pelzl, F. Guittard, A. Cambon, *Liq. Cryst*., **1996**, 21, 603; (b) S. Pensec, F.-G. Tournilhac, P. Bassoul, *J. Phys. II Fr*., **1996**, 6, 1597.
44. S. Pensec, F. -G. Tournilhac, *J. Chem. Soc. Chem. Commun*., **1997**, 441.
45. (a) T. P. Rieker, E. P. Janulis, *Phys. Rev., E.* **1995**, 52, 2688; (b) T. A. Lobko, B. I. Ostrovskii, A. I. Pavluchenko, S. N. Sulianov, *Liq. Cryst*. **1993**, 15, 361; (c) B. I. Ostrovskii, *Liq. Cryst*., **1993**, 14, 131.
46. G. Knochenhauer, J. Reiche, L. Brehmer, T. Barberka, M. Wolley, R. Tredgold, P. Hodge, *J. Chem. Soc. Chem. Commun*., **1995**, 1619.
47. D. J. Mitchell, G. J. T. Tiddy, L. Waring, T. Bistock, M. P. McDonald, *J. Chem. Soc., Faraday Trans.* 1, **1983**, 79, 975.
48. (a) K. Borisch, C. Tschierske, P. Göring, S. Diele, *J. Chem. Soc. Chem. Commun.*, **1998**, 2711; (b) K. Borisch, S. Diele, P. Göring, H. Müller, C. Tschierske, *Liq. Cryst.*, **1997**, 22, 427; (c) K. Borisch, S. Diele, P. Göring, H. Kresse, C. Tschierske, *Angew. Chem*., **1997**, 109, 2188; *Angew. Chem. Int. Ed. Engl.*, **1997**, 36, 2087.
49. K. Borisch, C. Tschierske, P. Göring, S. Diele, H. Kresse, *Langmuir*, **2000,** 16, 6701.
50. (a) V. S. K. Balagurusamy, G. Ungar, V. Percec, G. Johansson, *J. Am. Chem. Soc*., **1997**, 119, 1539; (b) S. D. Hudson, H.-T. Jung, V. Percec, W.-D. Cho, G. Johansson, G. Ungar, V. S. K. Balagurusamy, *Science*, **1997**, *278*, 449; (c) V. Percec, C.-H. Ahn, W.-D. Cho, A. M. Jamieson, J. Kim, T. Leman, M. Schmidt, M. Gerle, M. Möller, S. A. Prokhorova, S. S. Sheiko, S. Z. D. Cheng, A. Zhang, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc*., **1998**, 120, 8619.
51. (a). Q. -Y Chen, Z. Y. Yang, C. –X. Zhao, Z. M. Qiu, *J. Chem. Soc., Perkin Trans 1*, **1988**, 563; (b) G. J. Johanssson, V. Percec, G. Ungar, J. P. Zhau, *Macromolecules*, **1996**, 29, 646.
52. .X. H. Cheng, A. Pegenau, C. Tschierske, P. Göring, S. Diele, *28. Freiburger Arbeitstagung Flüssigkristalle, Freiburg* **1999**, Poster contributions 8. (b) Recently G. Lattermann etc. have also reported that benzoates of oligo(ethyleneamides) with semifluorinated chain form cubic mesophases (*6th European Conference on Liquid Crystals* **2001**, Oral communications 1.
53. K. Borisch, *Dissertation*, Martin-Luther Universität Halle-Wittenberg, **1999**.

54. This Cub_{V2} phase was confirmed by miscibility experiment: in the contact region between the Cub_{I2}-phase of **7-2F$_{4/6}$** and Cub-phase of **9- 2F$_{4/6}$**, a columnar mesophase is observed, indicating that the cubic-phase of **9-2F$_{4/6}$** should be a Cub_{V2}-phase.
55. (a)N. Lindner, M. Kölbel, C. Sauer, S. Diele, J. Jokiranta, C. Tschierske, *J. Phys. Chem., B*, **1998**, 102, 5261; (b) C. Sauer, S. Diele N. Lindner C. Tschierske, *Liq. Cryst*., **1968**, 25, 109; (c) M. Kölbel, J. Jokiranta, C. Tschierske, unpubliched result.
56. L. Hough, J. K. N. Jones, M. S. Magson, *J. Chem. Soc.*, **1952**, 1525.
57. (a) A. Pegenau, P. Göring, C. Tschierske, *J. Chem. Soc., Chem. Commun*., **1996**, 2563; (b) A. Pegnau, P. Göring, S. Diele, C. Tschierske, *SPIE*, **1998**, 3319, 70; (c) A. Pegenau, T. Hegmann, C. Tschierske, S. Diele, *Chem. Eur. J*., **1999**, 5, 1643.
58. O. Mitsunobu, *Synthesis*, **1981**, 1
59. (a) C. Tschierske, H. Zaschke, *J. prakt. Chem.*, **1989**, 331, 365. (b) A. Pegenau, *Dissertation*, Martin-Luther-Universität Halle Wittenberg, **1999**.
60. (a) J. Charvolin, J. F. Sadoc, *J. Phys. (Paris),* **1988**, 49, 521; (b) K. Fontell, K. K. Fox, E. Hansson, *Mol. Cryst. Liq. Cryst. Lett.,* **1985**, 1, 9; (c) R. Vargas, P. Mariani, A. Gulik, V. Luzzati, *J. Mol. Biol.*, **1992**, 225, 137; (d) H. Delacroix, T. Gulik-Krzywicki, P. Mariani, V. Luzzati, *J. Mol. Biol.*, **1993**, 229, 526.
61. M. Kölbel, T. Beyersdorff, X. H. Cheng, C. Tschierske, J. Kain, S. Diele, *J. Am. Chem. Soc*., in press..
62. G. Majetch, R. Hicks, S. Reister, *J. Org. Chem*., **1997**, 62, 4321.
63. Autorenkollektive, *Organikum*,VEB Deutscher Verlag der Wissenschaften Berlin, **1988**.
64. M. C. Carreno, J. G. Ruano, G. Sanz, M. A. Toledo, A. Urbano, *J. Org. Chem*., **1995**, 60, 5328.
65. (a) V.C. R. McLoughlin, J. Thrower, *Tetrahedron*, **1969**, 25, 5921; (b) G. Pozz, M. Cavazzini, F. Cinato, F. Montanari, S. Quici, *Eur. J. Chem.*, **1999**, 1953.
66. J. Duan, L. H. Zhang, W. R. Dolbier, Jr., *Synlett*., **1999**, 8, 1245.
67. (a) Y. Yamoto, S. Hatsuya, J. Yamada, *J. Org. Chem.*, **1990**, 55, 3119; (b) T. Hegmann, *Diplomarbeit*, Martin-Luther-Universität Halle-Wittenberg, **1997**.
68. J. Krug, *Diplomarbeit*, Martin-Luther-Universität Halle-Wittenberg, **1993**.
69. M. Kitamura, M. Isobe, Y. Ichikawa, T. Goto, *J. Am. Chem. Soc.*, **1984**, 106, 3252.
70. V. Van Rheenen, D. Y. Cha, W. M. Hartley, *Org. Synth.*, **1979**, 58, 43.
71. M. Hird, G. W. Gray, K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **1991**, 206, 187.
72. N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.*, **1981**, 11, 513.
73. (a) M. Demuynck, P. De Clercq, M. Vandewalle, *J. Org. Chem*., **1979**, 44, 4863; (b) P. A. Grieco, M. Nishizawa, T. Oguri, S. D. Burke, N. Marinovic, *J. Am. Chem. Soc*., **1977**, 99, 5773.
74. J. P. Wolfe, R. A. Singer, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc*., **1999**, 121, 9550.

75. (a) B. Neumann, C. Sauer, S. Diele, C. Tschierske, *J. Mater. Chem.*, **1996**, 6, 1087; (b) N. Linder, M. Kölbel, C. Sauer, S. Diele, J. Jokiranta, C. Tschierske, *J. Phys. Chem. B*, **1998**, 102, 5261.
76. M. Kölbel, *Dissertation*, Martin-Luther-Universität Halle-Wittenberg, **1998**.
77. A. Immrizi, B. Perini, *Acta Crystallogr. Sect., A*, **1977**, 33, 216.
78. C. K. Lee, J. C. C. Chen, K. M. Lee, C. W. Liu, I. J. B. Lin, *Chem. Mater*., **1999**, 11, 1237.
79. F. Hardouin, A. M. Levelut, M. F. Achard, G. Sigaud, *J. Chim. Phys*., **1983**, 80, 53.
80. The density of the perfluoralkyl groups was assumed to correspond to the density of perfluorohexane (ρ = 1.682 g cm^{-3}). The density of the other groups was assumed to be 1.0 g cm^{-3}.The density was calculated as the average value of the density of perfluoalkyl group and the hydrocarbon segment according to their volume fractions.
81. M. -A. Guillevic, D. W.Bruce, *Liq. Cryst*, **2000**, 27, 153-156.
82. S. Pensec, F.-G. Tournilhac, P. Bassoul, C. Durliat, *J. Phys. Chem.*, **1998**, 102, 52.
83. M. Kölbel, T. Beyersdorff, C. Tschierske, S. Diele, J. Kain, *Chem. Eur. J.*, **2000**, 6, 3821.
84. (a) G. W. Gray, M. Hird, K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **1991**, 195, 221; (b) M. Hird, K. J. Toyne P. Hindmarrsh, J. C. Jones, V. Minter, *Mol. Cryst. Liq. Cryst*., **1995**, 206, 227; (c) J. Andersch, C. Tschierscke, S. Diele, D. Lose, *J. Mater. Chem*., **1996**, 6, 1297.
85. (a) W. Weissflog, In *Handbook of Liquid Crystals*; D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess, V. Vill, ed. Wiley-VCH: Weinheim, **1998**; Vol 2B, p 835. (b) H.-T, Nguyen, C. Destrade; J, Malthete, In *Handbook of Liquid Crystals*, D. Demus, J. W. Goodby, G. W. Gray, G. W. Gray, H.-W. Spiess, V. Vill, ed. Wiley-VCH: Weinheim, **1998**,Vol 2B, p 866.
86. F. Hentrich, C. Tschierske, S. Diele, C. Sauer, *J. Mater. Chem.*, **1994**, 4, 1547.
87. S. Norvez, F.-G. Tournilhac, P. Bassoul, *CCMM 2000*, **2000**, Poster contributions 15, 16.
88. S. Norvez, J. Simon, *Liq. Cryst*., **1993**, 14, 1389.
89. (a) J. Rädler, I. Koltover, T. Salditt, C. R. Safinya, *Science*, **1997**, 275, 810; (b) E. Sackmann, *Science*, **1996**, 271, 43; (c) H. E. Warriner, S. H. J. Idziak, N. L. Slack, P. Davidson, C. R. Safinya, *Science*, **1996**, 271, 969.
90. (a) T. Hegmann, J. Kain, S. Diele, G. Pelzl, C. Tschierske, *Angew. Chem*. **2001**, in press.
91. N. A. Clark, Personal communication.
92. H. Hückstädt, A. Göpfert, V. Abetz, *Macromol. Chem. Phys.*, **2000**, 201, 296.
93. T. Beyersdorff, , *Diplomarbeit*, Martin-Luther-Universität Halle-Wittenberg, **2000**.

8 *Supplement*

Experiments

8.1 General

The confirmation of the structures of the intermediates and products was obtained by ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectroscopy (Varian Unity 500, Varian Gemini 200 spectrometer). Mass spectra were recorded on an AMD 402 mass spectrometer (70 ev). Microanalysis were performed using a Leco CHNS-932 elemental analyzer. Owing to the hygroscopic properties of some compounds moisture was absorbed during sample preparation and therefore correct combustion analyses were not obtained for some compounds. Transition temperatures were measured using a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon optiphot-2 polarizing microscope and were confirmed using differential scanning calorimeter (perkin-Elmer DSC-7, heating and cooling rate: 10K min^{-1}). The accuracy of the transition temperatures is about ± 0.5K. All phase transitions, except those of cubic and crystalline phases, were completely reversible. If not otherwise stated the transition enthalpies of enantiotropic phases were obtained from the first heating scan, those of monotropic phases from the second heating scan. The accuracy of the enthalpy values is about ± 0.2 kJ mol^{-1}. X-Ray diffraction patterns were obtained on a Guinier diffractometer (Huber) operating with a Cu-Kα_1 beam. The refraction patterns were recorded with a film camera.

Phase diagram were established by the penetration experiments and by investigation of binary mixtures. These mixtures were investigated by optical polarizing microscopy between crossed polarizes.

Purification and drying of the solvents was performed according to the methods described in the literature[63] The water content was determined using Karl-Fisher-Titration (Mitsubishi Moisturemeter MCI Model CA-02). The purity of all compounds was checked by thin-layer chromatography (Silica Gel F_{254}, Merck). Silica Gel 60 was used for column chromatography. For the preparative centrifugal thin-layer chromatography: a Chromatotron from Harrison Research Europe (Muttenz) was used.

8.2 Material

Commercial available substances:

Allylphenol (Fluka)	Allylbromide (Merck)
1-Aminoethanol (Merck)	2-Aminopropane-1,3-diol (Aldrich)
1-Aminopropane-2,3-diol (Merck)	Benzylbromide (Merck)
Boron tribromide (Aldrich)	*N*-Bromosuccinimide (NBS, Merck)
3-Bromophenol (Lancaster)	1-Bromo-4-iodobenzene (Avocado)
4-Bromobenzene (Merck)	n-Butyllithium (Aldrich)
3-Buten-1-ol (Fluka)	*N*-Cyclohexyl-*N*¢-(morpholinoethyl) carbodiimide methyl-p-toluenesulfonated (CMC, Fluka)
9-Decen-1-ol (Fluka)	2,2-Dimethoxypropane (Merk)
Dimethylaminopyridine (DMAP, Merck)	Ethyl 4-hydroxybenzoate (Aldrich)
Ethyl 3,4-dihydroxybenzoate (Aldrich)	Ethyl 3,4,5-trihydroxybenzoate (Fluka)
5-Hexen-1-ol (Fluka)	1-Iodoperfluorobutane (Aldrich)
1-Iodoperfluoroisoheptane (FC)	1-Iodoperfluorodecane (AlBCR)
1- Iodoperfluoropropane (ABCR)	1-Iodoperfluorohexane (Merk)
1-Iodoperfluorooctane (ABCR)	*N*-Methylmorpholine *N*-oxide (NMMNO, 60% aqoues solution Aldrich)
Osmiumtetroxide (Berlin Chemie)	Palladium, 10% on carbon (Merck)
Pentaerythritol (Merck)	PPTS (Aldrich)
Trifluoro acetic acid (Merck)	Undec-10-enylbromide (Lancaster)

The following substances are available in our laboratary:

Tetrakis (triphenylphosphine)palladium (0) [$Pd(PPh_3)_4$]

4-Benzyloxybenzeneboronic acid[76]

1-Toluenesulfonyloxy-3-oxa-5-hexene[55,74]

11-Bromoundecyl-1,2-diol[68]

4-(4′-Bromophenyloxymethyl)-2,2-dimethyl-1,3-dioxolane[93]

4-[4-(4-Bromophenyloxy)-2-oxa-butyl]-2,2-dimethyl-1,3-dioxolane **14** [55]

4-(4-Bromobutyl)-2,2-dimethyl-1,3-dioxolane **44**[67]

2,2-Bis (3,4-didecyloxybenzyloxymethyl)-1,3-propanediol[59b]

4-methoxybenzene boronic acid

2,2-Dimethyl-4-{4'-[(2,2-dimethyl-1,3-dioxolan-4-yl) methoxy]-3'-methyl-3-octadecyl biphenyl-4-yloxymethyl}-1,3-dioxolane.

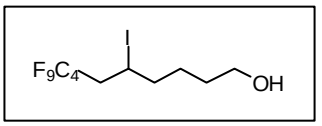
3,4,5-Tris(1H,1H,2H,2H,3H,3H,4H,4H-perfluoroctyl-1-oxy)benzoic acid **6.4**

8.3 Synthesis of amphiphilic diols

8.3.1 Synthesis of the semifluorinated iodoalkanols 2

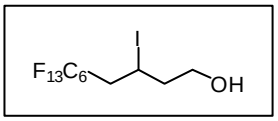
Addition of pefluoroalkyliodides to w-alkenols - general procedure 8.3.1: The appropriate ù-unsaturated alcohol (107 mmol), the appropriate 1-iodoperfluoroalkane (110 mmol) and dry hexane (80 mL) were put into a three necked flask. The flask was placed in an ultra sonic bath under an argon atmosphere for 30 min. Then the mixture was cooled to –78 °C and the flask was evacuated, back-filled with argon and warmed up to room temperature. This procedure was repeated for three times. The mixture was cooled to 0 °C, $Pd(PPh_3)_4$ (5.6 g, 4.0 mol %) was added. The heterogeneous orange reaction mixture was allowed to reach room temperature while stirring. The reaction was completed after 36 h. The mixture was filtered through silica gel and the residue was washed thoroughly with diethyl ether. The solvent was removed in *vacuo*, and the residue was used without further purification.

1H,1H,2H,2H,3H,3H,4H,4H,5H,6H,6H-Perfluoro-5-iododecan-1-ol 2.1



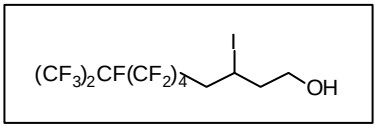
Prepared according to the general procedure **8.3.1** from 5-hexen-1-ol (10.7 g, 107 mmol), 1-iodoperfluorobutane (38.0 g, 110 mmol) and $Pd(PPh_3)_4$ (5.6 g, 4.0 mol %) in hexane (80 mL).
Yield: 48.1 g (100 %); yellow oil; $C_{10}H_{12}OF_9I$ (446).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 4.29 (m, 1 H, CHI), 3.61 (m, 2 H, HOC**H**$_2$), 2.82 (m, 2 H, CF_2CH_2), 2.25 (s, 1 H, OH), 1.80 (m, 2 H, CH_2), 1.50 (m, 4 H, 2 CH_2).

1H,1H,2H,2H,3H,4H,4H-Perfluoro-3-iododecan-1-ol 2.2



Prepared according to the general procedure **8.3.1** from 3-buten-1-ol (7.72 g, 107 mmol), $Pd(PPh_3)_4$ (5.6 g, 4.0 mol %) and 1-iodoperfluorohexane (49.05 g, 110 mmol) in hexane (80 mL).
Yield: 55.4 g (100 %); yellow oil; $C_{10}H_8OF_{13}I$ (518).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 4.50 (m, 1 H, CHI), 3.82 (m, 2 H, HOC**H**$_2$), 2.92 (m, 2 H, $C_4F_9CH_2$), 2.02 (m, 2 H, $HOCH_2CH_2$).

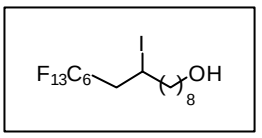
1H,1H,2H,2H,3H,4H,4H-Perfluoro-3-iodoisoundecan-1-ol 2.3



Prepared according to the general procedure **8.3.1** from 3-buten-1-ol (3.86 g, 53.5 mmol), 1-iodoperfluoroisoheptane (27.28 g, 55 mmol) and $Pd(PPh_3)_4$ (2.8 g, 4.0 mol %) in hexane (50 mL).
Yield: 27.1 g (89.3 %); yellow oil; $C_{11}H_8OF_{15}I$ (568).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 4.49 (m, 1 H, CHI) 3.79 (m, 2 H, HOC**H**$_2$), 2.89 (m, 2 H, CF_2CH_2), 2.28 (s, 1 H, OH), 2.01 (m, 2 H, $HOCH_2C$**H**$_2$).

1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H,8H,8H,9H,10H,10H-Perfluoro-9-iodohexadecan-1-ol 2.4



Prepared according to the general procedure **8.3.1** from 9-decen-1-ol (16.7 g, 107 mmol), 1-iodoperfluorohexane (49.05 g, 110 mmol) and $Pd(PPh_3)_4$ (5.6 g, 4.0 mol %) in hexane (50 mL).

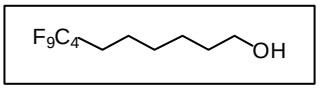
Yield: 64.6 g (100 %); yellow oil; $C_{16}H_{20}OF_{13}I$ (602).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 4.32 (m, 1 H, CHI), 3.62 (m, 2 H, HOC**H**$_2$), 2.85 (m, 2 H, CF_2C**H**$_2$), 1.85-1.26 (m, 14 H, 7 CH_2).

8.3.2 Synthesis of the semifluorinated alkanols 3

Reduction of the semifluorinated iodoalkanols - general procedure 8.3.2: To a slurry of $LiAlH_4$ (81.8 mmol) in dry Et_2O (100 mL), the appropriate semifluorinated iodoalkanols **2** (98.4 mmol) dissolved in dry diethyl ether (100 mL) was added dropwise to maintain the solution at reflux. The mixture was refluxed for further 2 h, and cooled to RT. Afterwards, water was added dropwise until all the unreacted $LiAlH_4$ was decomposed. Then 50 % aqueous H_2SO_4 was carefully added to dissolve the solid. The organic layer was separated and the aqueous layer was extracted with Et_2O (3×150 mL), the organic layers were combined and washed with 10 % aqueous $Na_2S_2O_3$ till the aqueous layer remained colorless. After being washed further with H_2O (2×100 mL) and brine (2×100 mL) and dried over Na_2SO_4, the solvent was removed in *vacuo*, the oily residue was distilled in *vacuo*.

1H,1H,2H,2H3H,3H,4H,4H,5H,5H6H,6H-Perfluorodecan-1-ol 3.1

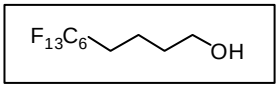


Prepared according to the general procedure **8.3.2** from **2.1** (48.1 g, 107.8 mmol) with $LiAlH_4$ (4.5 g, 118.7 mmol) in diethyl ether (300 mL).

Yield: 23.2 g (67.1 %); yellow oil; bp: 98 °C / 6 mbar; $C_{10}H_{13}OF_9$ (320).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 3.64 (t, ^3J(H, H) 6.25, 2 H, CH_2OH), 1.89-2.16 (m, 2 H, $CH_2C_6F_{13}$), 1.34-1.62 (m, 8 H, 4 CH_2).

1H,1H,2H,2H,3H,3H,4H,4H-Perfluorodecan-1-ol 3.2



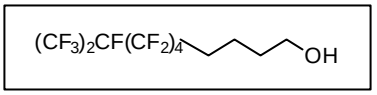
Prepared according to the general procedure **8.3.2** from **2.2** (51.3 g, 98.4 mmol) with $LiAlH_4$ (3.1 g, 81.8 mmol) in dry diethyl ether (200 mL).

Yield: 33.6 g (87.1 %); yellow oil; bp: 80 °C / 9 mbar; $C_{10}H_9OF_{13}$ (392).

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ =3.67 (t, ^3J(H, H) 6.01, 2 H, CH_2OH), 2.09 (m, 2 H, $CH_2C_6F_{13}$), 1.74-1.60 (m, 4 H, 2 CH_2).

1H,1H,2H,2H,3H,3H,4H,4H-Perfluoroisoundecan-1-ol 3.3

Prepared according to the general procedure **8.3.2** from **2.3** (27.1 g, 47.8 mmol) with $LiAlH_4$ (2.0 g, 52.8 mmol) in dry diethyl ether (160 mL).

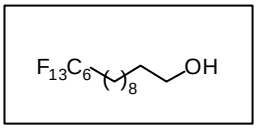


Yield: 37.4 g (73.1 %); yellow oil; bp: 80 °C / 0.12 mbar; $C_{11}H_9OF_{15}$ (442).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ =3.62 (t, ^3J(H, H) 5.9, 2 H, C**H**$_2$OH), 2.55 (br s, 1 H, OH), 2.24 (m, 2 H, CH_2CF_2), 1.77-1.51 (m, 4 H, 2 CH_2).

1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H,8H,8H,9H,9H,10H,10H-Perfluorohexadecan-1-ol 3.4

Prepared according to the general procedure **8.3.2** from **2.4** (64.6 g, 107 mmol) with $LiAlH_4$ (4.5 g, 118.7 mmol) in diethyl ether (300 mL).The rough product was used without further purification.



Yield: 37.4 g (73.1 %); colorless solid; mp: 32 °C; $C_{16}H_{23}OF_{13}$ (478).

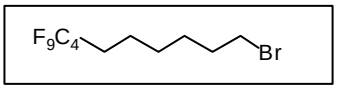
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 3.62 (t, ^3J(H, H) 6.5, 2 H, C**H**$_2$OH), 2.16 (m, 2 H, $CH_2C_6F_{13}$), 1.29-1.58 (m, 16 H, 8 CH_2).

8.3.3 Synthesis of the semifluorinated 1-bromoalkanes 4

Bromonation of the semifluorinated alkanols - general procedure 8.3.3: A mixture of **3** (61 mmol), 98 % H_2SO_4 (6 mL), 48 % aqueous HBr (28 mL, 168 mmol), and tetra-n-butylammoniumhydrogensulfate (1 g) was heated to 100 °C while stirring. After 12 hour, the reaction was complete. The mixture was cooled to room temperature and extracted with Et_2O (3×100 mL). The combined organic layers were washed with H_2O (3×50 mL), dried over Na_2SO_4, and the solvent was removed in *vacuo*, the residue was distilled in *vacuo* yielding the product.

1-Bromo-1H,1H,2H,2H3H,3H,4H,4H,5H,5H,6H,6H-perfluorodecane 4.1

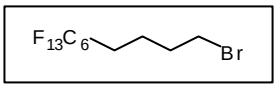
Prepared according to the general procedure **8.3.3** from **3.1** (23.2 g, 72.4 mmol), 98 % H_2SO_4 (7.5 mL) and 48 % aqueous HBr (46 mL, 276 mmol), tetra-n-butylammoniumhydrogensulfate (1 g).



Yield: 24.3 g (87.7 %); yellow oil; bp: 90 °C / 6 mbar; $C_{10}H_{12}F_9Br$ (383).

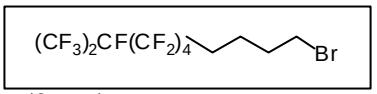
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 3.39 (t, ^3J(H, H) 6.64, 2 H, CH_2Br), 1.39-2.17 (m, 10 H, 5 CH_2).

1-Bromo-1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecane 4.2



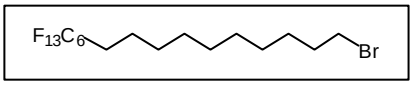
Prepared according to the general procedure **8.3.3** from **3.2** (31.3 g, 79.8 mmol), 98 % H_2SO_4 (7.5 mL) and 48 % aqueous HBr (20 mL, 120 mmol), tetra-n-butylammoniumhydrogensulfate (1 g).
Yield: 21.4 g (59.0 %); yellow oil; bp: 93 °C / 9 mbar; $C_{10}H_8F_{13}Br$ (455).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 3.41 (t, ^3J(H, H) 6.3, 2 H, CH_2Br), 1.752-2.22 (m, 6 H, 3 CH_2).

1-Bromo-1H,1H,2H,2H,3H,3H,4H,4H-perfluoroisoundecane 4.3



Prepared according to the general procedure **8.3.3** from **3.3** (8.7 g, 19.7 mmol), 98 % H_2SO_4 (1.8 mL) and 48 % aqueous HBr (25 mL, 150 mmol), tetra-n-butylammoniumhydrogensulfate (0.5 g).
Yield: 7.1 g (71.7 %); yellow oil; bp: 90 °C / 0.45 mbar; $C_{11}H_8F_{15}Br$ (505).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 3.41 (t, 2 H, ^3J(H, H) 6.3, CH_2Br), 2.22-1.68 (m, 6 H, 3 CH_2).

1-Bromo-1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H,8H,8H,9H,9H,10H,10H,-perfluorohexadecane 4.4

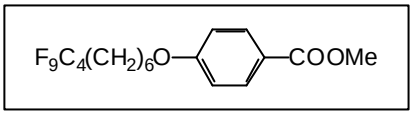


Prepared according to the general procedure **8.3.3** from **3.4** (37.0 g, 78.6 mmol), 98 % H_2SO_4 (3.5 mL) and 48 % aqueous HBr (10 mL, 60 mmol), tetra-n-butylammoniumhydrogensulfate (0.5 g).
Yield: 24.3 g (57.3 %); yellow oil; bp: 138 °C / 0.21 mbar; $C_{16}H_{20}F_{13}Br$ (539).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 3.41 (t, ^3J(H, H) 6.8, 2 H, CH_2Br), 1.76-2.15 (m, 4 H, 2 CH_2), 1.61-1.29 (m, 14 H, 7 CH_2).

8.3.4 Synthesis of the semifluorinated alkoxybenzoates 5, 24 and 26

Etherification of hydroxybenzoates - general procedure 8.3.4: To a mixture of K_2CO_3 (3 mmol for 1 mmol each hydroxygroup), the appropriate hydroxybenzoate (1 mmol) in dry DMF (100 mL), the appropriate semifluorinated 1-bromoalkanes **4** (1.1 mmol for each hydroxygroup) was added under an argon atmosphere. The mixture was heated to 65 °C and stirred for 2 h. After the reaction was complete (TLC), the mixture was cooled to RT, poured into ice water (200 mL) and acidified with 10 % HCl to pH = 4-5. The mixture was extracted with Et_2O (3×100 mL). The combined extracts were washed with H_2O (2×50 mL), dried over Na_2SO_4, then the solvent was removed in *vacuo*. The residue was purified by chromatography or recrystallization.

Methyl 4-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-perfluorodecyl-1-oxy) benzoate 5.1.1

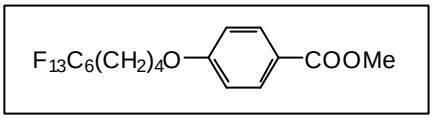


Prepared according to the general procedure **8.3.4** from **4.1** (5 g, 13.5 mmol), methyl 4-hydroxybenzoate (1.83 g, 12 mmol) and K_2CO_3 (5.0 g, 36 mmol) in dry DMF (60 mL). Purification by recrystallization from petroleum ether

Yield: 2.0 g (37.0 %); colorless solid; mp: 31 °C; $C_{18}H_{19}F_9O_3$ (454).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.94 (dd, ^3J(H, H) 8.9, ^4J(H, H) 2.0, 2 H, Ar-H), 6.98 (d, ^3J(H, H) 8.9, 2 H, Ar-H), 4.02 (t, ^3J(H, H) 6.3, 2 H, OCH_2), 3.86 (s, 3 H, OCH_3), 2.05 (m, 2 H, $C_4F_9CH_2$), 1.92 (m, 2 H, CH_2), 1.41-1.83 (m, 6 H, 3 CH_2).

Methy 4-(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoate 5.2.1

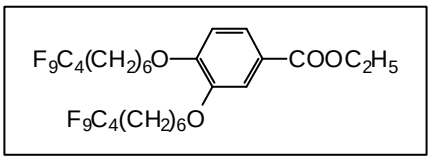


Prepared according to the general procedure **8.3.4** from **4.2** (4 g, 8.8 mmol), methyl 4-hydroxybenzoate (1.1 g, 7.3 mmol) and K_2CO_3 (2.9 g, 21 mmol) in dry DMF (60 mL). Purification by recrystallization from petroleum ether.

Yield: 3.6 g (93.4 %); mp: 51 °C-55 °C; $C_{18}H_{15}F_{13}O_3$ (526).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 8.25 (dd, ^3J(H, H) 8.9, ^4J(H, H) 2.15, 2 H, Ar-H), 7.20 (dd, ^3J(H, H) 8.9, ^4J(H, H) 2.15, 2 H, Ar-H), 4.40 (t, ^3J(H, H) 5.7, 2 H, O**C**$\mathbf{H}_2$$CH_2$), 4.20 (s, 3 H, OCH_3), 2.40 (m, 2 H, C_6F_{13}**C**$\mathbf{H}_2$), 2.20 (m, 4 H, **C**$\mathbf{H}_2$**C**$\mathbf{H}_2$).

Ethyl 3,4-bis(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-perfluorodecyl-1-oxy) benzoate 5.1.2

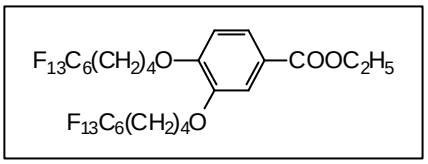


Prepared according to the general procedure **8.3.4** from **4.1** (5 g, 13.05 mmol), ethyl 3,4-dihydroxybenzoate (1.1 g, 6.04 mmol) and K_2CO_3 (5.0 g, 36 mmol) in dry DMF (60 mL). Purification by recrystallization from petroleum ether.

Yield: 3.0 g (63.6 %); colorless solid; mp: 31 °C; $C_{29}H_{32}F_{18}O_4$ (786).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.65 (dd, ^3J(H, H) 8.4 Hz, ^4J(H, H) 2.0, 1 H, Ar-H), 7.23 (s, 1 H, Ar-H), 6.86 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 4.38 (q, ^3J(H, H) 7.2, 2 H, O**C**$\mathbf{H}_2$$CH_3$), 4.06 (t, 4 H, 2 OCH_2), 2.15 –1.44 (m, 20 H, 2C_4F_9**C**$\mathbf{H}_2$**C**$\mathbf{H}_2$**C**$\mathbf{H}_2$**C**$\mathbf{H}_2$**C**$\mathbf{H}_2$), 1.39 (t, ^3J(H, H) 7.2, 3 H, CH_3).

Ethyl 3,4-bis(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoate 5.2.2

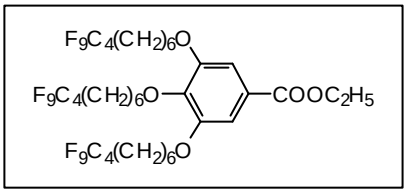


Prepared according to the general procedure **8.3.4** from **4.2** (5.2 g, 11.3 mmol), ethyl 3,4-dihydroxybenzoate (0.95 g, 5 mmol) and K_2CO_3 (4.1 g, 30 mmol) in dry DMF (30 mL). Purification by recrystallization from petroleum ether.

Yield: 2.3 g (49.1 %); colorless crystals; mp: 49 °C; $C_{27}H_{24}F_{26}O_4$ (930).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.62 (dd, ^3J(H, H) 8.4, ^4J(H, H) 2.0, 1 H, Ar-H), 7.45 (d, ^4J(H, H) 2.0, 1 H, Ar-H), 6.82 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 4.25 (q, ^3J(H, H) 7.2, 2 H, OCH_2CH_3), 4.00 (t, ^3J(H, H) 5.7, 4 H, 2 OCH_2), 2.00 (m, 4 H, 2 $C_6F_{13}CH_2$), 1.90 (m, 8 H, 2 CH_2CH_2), 1.30 (t, ^3J(H, H) 7.2, 3 H, CH_2CH_3).

Ethyl 3,4,5-tris(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-perfluorodecyl-1-oxy)benzoate 5.1.3

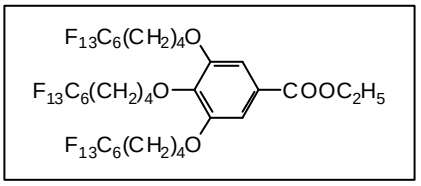


Prepared according to the general procedure **8.3.4** from **4.1** (5.2 g, 13.1 mmol), ethyl 3,4,5-trihydroxybenzoate (0.79 g, 4 mmol) and K_2CO_3 (5.0 g, 36 mmol) in dry DMF (30 mL). Purification by recrystallization from petroleum ether.

Yield: 3.8 g (86.0 %); colorless crystals; mp: 37 °C; $C_{39}H_{44}F_{27}O_5$ (1105).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.24 (s, 2 H, Ar-H), 4.39 (q, ^3J(H, H) 7.2, 2 H, OCH_2CH_3), 3.96 (m, 6 H, 3 OCH_2), 2.15 (m, 6 H, 3 $C_4F_9CH_2$), 1.52-1.91 (m, 24 H, 3 $CH_2CH_2CH_2CH_2$), 1.33 (t, ^3J(H, H) 7.2, 3 H, CH_2CH_3).

Ethyl 3,4,5-tris(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoate 5.2.3

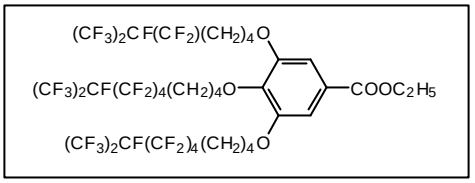


Prepared according to the general procedure **8.3.4** from **4.2** (4.3 g, 9.4 mmol), ethyl 3,4,5-trihydroxybenzoate (0.50 g, 2.8 mmol) and K_2CO_3 (3.9 g, 28.0 mmol) in dry DMF (60 mL). Purification by recrystallization from petroleum ether.

Yield: 2.1 g (56.7 %); yellow crystals; mp: 50 °C; $C_{39}H_{31}F_{39}O_5$ (1320).

^{1}H-NMR (200 MHz, $CDCl_3$; *J*/Hz): δ = 7.25 (s, 2 H, Ar-H), 4.36 (q, ^3J(H, H) 7.2, 2 H, OCH_2CH_3), 4.05 (m, 6 H, 3 OCH_2), 2.14 (m, 6 H, 3 $C_6F_{13}CH_2$), 1.51-1.87 (m, 12 H, 3 CH_2CH_2), 1.37 (t, ^3J(H, H) 7.2, 3 H, CH_2CH_3).

Ethyl 3,4,5-tris(1H,1H,2H,2H,3H,3H,4H,4H perfluoroisoundecyl-1-oxy)benzoate 5.3



Prepared according to the general procedure **8.3.4** from **4.3** (6.2 g, 12.3 mmol), ethyl 3,4,5-trihydroxybenzoate (0.67 g, 3.4 mmol) and K_2CO_3 (4.7 g, 34.1 mmol) in dry DMF (60 mL). Purification by preparative centrifugal thin layer chromatography (eluent: petroleum ether→chloroform).

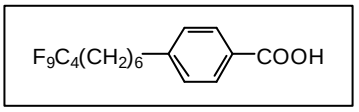
Yield: 3.5 g (70.0 %); yellow oil; $C_{42}H_{31}F_{45}O_5$ (1470).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.24 (2 s, 2 H, Ar-H), 4.36 (q, ^3J(H, H) 7.2, 2 H, OC**H**$_2$CH$_3$), 4.05 (m, 6 H, 3 OC**H**$_2$), 1.62-2.12 (m, 18 H, 9 CH_2), 1.33 (t, ^3J(H, H) 7.2, 3 H, CH_2C**H**$_3$).

8.3.5 Synthesis of the semifluorinated alkoxybenzonic acids 6

Saponification of the benzoates - general procedure 8.3.5: A mixture of the appropriate semifluorinated alkoxybenzoate (1.6 mmol), 95 % EtOH (10 mL), and 10 N aqueous KOH (1 mL) was heated to reflux. After 2 h, the hydrolysis was complete (TLC). The mixture was concentrated with a rotatory evaporator, and diethyl ether (100 mL) was added to dissolve the reside. This solution was acidified with concentrated HCl to pH = 4, additional diethyl ether (100 mL) was added untill all precipiate was dissolved. The organic layer was separated, the aqueous layer was extracted three times with diethyl ether, the combined organic extracts were washed twice with H_2O, and dried over Na_2SO_4, diethyl ether was removed in *vacuo* to yield a colorless waxy solid. Purification of the product was done by recrystallization from ethanol.

4-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-Perfluorodecyl-1-oxy)benzoic acid 6.1.1

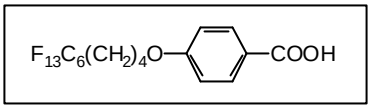


Prepared according to the general procedure **8.3.5** from **5.1.1** (2 g, 4.4 mmol), 95 % EtOH (50 mL), and 10 N aqueous KOH (5 mL).

Yield: 0.63 g (32.5 %); transition temperatures (°C): Cr 150 SmA 169 Iso; $C_{17}H_{17}F_9O_3$ (440).

^{1} H-NMR (200 MHz; DMSO-D_6, *J*/Hz): δ = 12.52 (s, 1 H, COOH), 7.88 (d, ^3J(H, H) 8.4, 2 H, Ar-H), 6.96 (d, ^3J(H; H) 8.6, 2 H, Ar-H), 4.06 (t, ^3J(H, H) 6.5, 2 H, $ArOCH_2$), 2.18-2.34 (m, 2 H, CH_2), 1.72 (m, 2 H, CH_2), 1.45-1.69 (m, 6 H, 3 CH_2).

4-(1H,1H,2H,2H,3H,3H,4H,4H-Perfluorodecyl-1-oxy)benzoic acid 6.2.1

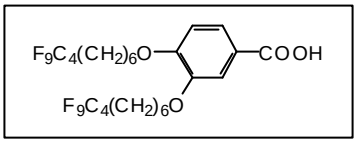


Prepared according to the general procedure **8.3.5** from **5.2.1** (3.6 g, 6.84 mmol), 95 % EtOH (70 mL), and 10 N aqueous KOH (7 mL).

Yield: 2.1 g (60.0 %); transition temperatures (°C): Cr 165 SmA 185 Iso; $C_{17}H_{13}F_{13}O_3$ (512).

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 7.87 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 7.00 (m, ^3J(H, H) 8.8, 2 H, Ar-H), 4.10 (t, ^3J(H, H) 6.3, 2 H, $ArOCH_2$), 2.30 (m, 2 H, $C_6F_{13}CH_2$), 1.84-1.69 (m, 4 H, 2.20 (m, 4 H, 2 CH_2).

3,4-Bis(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-perfluorodecyl-1-oxy)benzoic acid 6.1.2

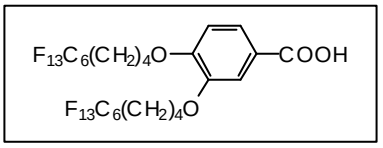


Prepared according to the general procedure **8.3.5** from **5.1.2** (2.85 g, 3.62 mmol), 95 % EtOH (45 mL), and 10 N aqueous KOH (4.5 mL).

Yield: 2.0 g (73.0 %); transiton temperatures (°C): Cr 58 Col 131 Iso; $C_{27}H_{28}F_{18}O_4$ (758).

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 12.59 (s, 1 H, COOH), 7.54 (dd, ^3J(H, H) 8.4, ^4J(H, H) 2.0, 1 H, Ar-H), 7.04 (d, 1 H, ^3J(H, H) 8.4, Ar-H), 4.05 (m, 4 H, $ArOCH_2$), 2.28 (m, 4 H, 2 CH_2), 1.72 (m, 4 H, 2 CH_2), 1.62-1.46 (m, 12 H, 6 CH_2).

3,4-Bis(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoic acid 6.2.2

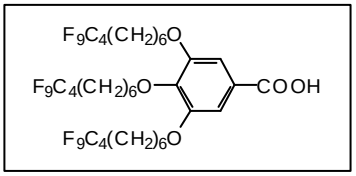


Prepared according to the general procedure **8.3.5** from **5.2.2** (2.26 g, 2.4 mmol), 95 % EtOH (30 mL), 10 N aqueous KOH (3 mL).

Yield: 2.0 g (73.0 %); transition temperatures (°C); Cr 82 Col 116 Iso; $C_{27}H_{20}F_{26}O_4$ (902).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.68 (dd, ^3J(H, H) 8.6, ^4J(H, H) 1.9, 1 H, Ar-H), 7.58 (d, ^4J(H, H) 1.9, 1 H, Ar-H), 6.85 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 4.10 (m, 4 H, 2 CH_2O), 1.00-2.20 (m, 12 H, 6 CH_2).

3,4,5-Tris(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-perfluorodecyl-1-oxy)benzoic acid 6.1.3

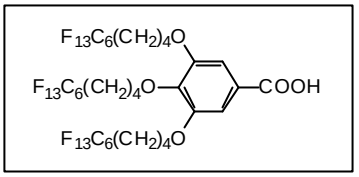


Prepared according to the general procedure **8.3.5** from **5.1.3** (3.6 g, 3.3 mmol), 95 % EtOH (45 mL), 10 N aqueous KOH (4.5 mL).

Yield: 1.8 g (50.7 %); mp: 43 °C; $C_{37}H_{40}F_{27}O_5$ (1077).

^{1}H-NMR (200 MHz; $CDCl_3$, *J*/Hz): δ = 7.30 (s, 1 H, Ar-H), 7.24 (s, 1 H, Ar-H), 4.05 (t, ^3J (H, H) 6.3, 6 H, 3 CH_2O), 2.09-2.01 (m, 6 H, 3 $CH_2C_4F_9$), 1.76-1.48 (m, 24 H, 12 CH_2).

3,4,5-Tris(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoic acid <u>6.2.3</u>

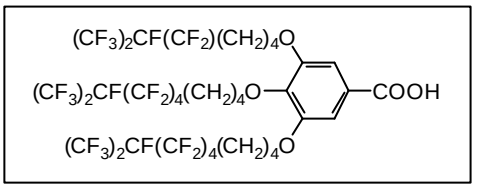


Prepared according to the general procedure **8.3.5** from **<u>5.2.3</u>** (2.9 g, 2.2 mmol), 95 % EtOH (38 mL), 10 N aqueous KOH (3.5 mL).

Yield: 1.5 g (52.8 %); transition temperatures (°C): Cr 47 Col 80 Iso; $C_{37}H_{27}F_{39}O_5$ (1293).

^{1}H-NMR(200 MHz; $CDCl_3$, *J*/Hz): δ = 7.31 (s, 2 H, Ar-H), 4.06 (t, ^3J(H, H) 6.05, 6 H, 3 CH_2O), 1.88-1.22 (m, 12 H, 3 CH_2CH_2).

3,4,5-Tris(1H,1H,2H,2H,3H,3H,4H,4H-perfluoroisoundecyl-1-oxy)benzoic acid <u>6.3</u>



Prepared according to the general procedure **8.3.5** from **<u>5.3</u>** (3.4 g, 2.3 mmol), 95 % EtOH (40 mL), 10 N aqueous KOH (4 mL).

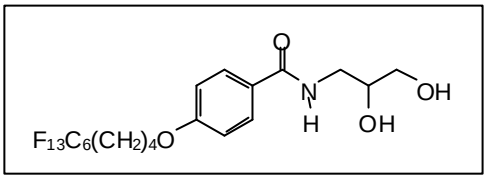
Yield: 2.3 g (68.3 %); transition temperatures (°C): Cr 56 Col 79 Iso; $C_{40}H_{27}F_{45}O_5$ (1442).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.32 (s, 2 H, 2 Ar-H), 4.06 (m, 6 H, 3 CH_2O), 1.94-2.21 (m, 6 H, 3 CH_2), 1.65-1.93 (m, 12 H, 6 CH_2).

8.3.6 Synthesis of the 1-benzoylaminopropane-2,3-diols 7, benzoylaminopropane-1,3-diol 8-2F and benzoylaminoethan-2-ol 9-2F

Aminolysis of acid chlorides - general procedure 8.3.6: The appropriately substituted benzoic acid (1.5 mmol) and thionyl chloride (10 mL) were heated to reflux for 3 h. The excess thionyl chloride was distilled off and the residue was dissolved in dry CH_2Cl_2. The appropriate amino alcohol (15 mmol) was dissolved in dry DMF (30 mL) under an argon atmosphere and DMAP (10 mg) was added. To this solution the benzoyl chloride, dissolved in dry CH_2Cl_2 (5 mL) was added while stirring at 80 °C. The resulting mixture was heated at this temperature for 4 h and was stirred for additional 24 h at room temperature. Afterwards the solvent was removed in *vacuo* and the residue was purified by recrystallization or by preparative centrifugal thin layer chromatography on a Chromototron.

1-[4-(1H,1H,2H,2H,3H,3H,4H,4H-Perfluorodecyl-1-oxy)benzoylamino] propane-2,3-diol 7-1F$_{6/4}$



Synthesized according to the general procedure **8.3.6** from **6.1.1** (1 g, 1.9 mmol), thionyl chloride (10 mL) and 1-aminopropane-2,3-diol (1.73 g, 19 mmol). The residue was purified twice by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10:1), and recrystallized from $CHCl_3$.

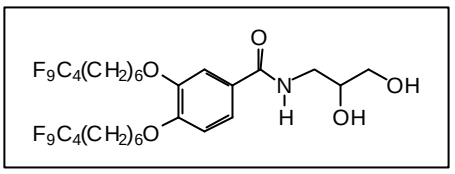
Yield: 260 mg (23.4 %); transition temperatures (°C): Cr 79 SmA 223 Iso; $C_{20}H_{20}F_{13}O_4N$ (585). Anal. Calcd.: C, 41.0, H, 3.42, N, 2.39; Found: C, 40.96, H, 4.04, N, 2.44.

^{1}H-NMR (400 MHz; acetone-D_6; *J*/Hz): δ = 7.91 (d, ^3J(H, H) 5.9, ^4J(H, H) 2.2, 2 H, Ar-H), 7.75 (br.t, 1 H, NH), 7.03 (d, ^3J(H, H) 6.9, ^4J(H, H) 2.1, 2 H, Ar-H), 4.16 (m, 2 H, OCH_2), 3.52 (m, 5 H, C**H**$_2$NH, C**H**$_2$OH, C**H**OH), 2.82 (m, 2 H, C**H**$_2C_6F_{13}$), 2.07 (m, 2 H, OCH_2C**H**$_2$), 1.84 (m, 2 H, C**H**$_2CH_2C_6F_{13}$).

^{13}C-NMR (100 MHz; acetone-D_6; *J*/Hz): δ = 162.8 (CO), 130.1, 127.9, 115.1 (Ar-C), 72.3 (CHOH), 68.3 (OCH_2), 64.5 (CH_2OH), 43.7 (CH_2NH), 31.3, 31.1, 30.8 (t, ^2J(C, F) 22.3, CH_2), 17.8 (CH_2).

^{19}F-NMR (200 MHz; acetone-D_6; *J*/Hz): δ = -82.17 (overlapped t, 3 F, CF_3), -114.99 (t, 2 F, CH_2CF_2), -122.66 (s, 2 F, $CF_3(CF_2)_3$C**F**$_2$), -123.65 (s, 2 F, $CF_3(CF_2)_2$C**F**$_2$), -124.26 (s, 2 F, CF_3CF_2C**F**$_2$), -126.95 (s, 2 F, CF_3C**F**$_2$).

1-[3,4-Bis(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-perfluorodecyl-1-oxy)benzoylamino]propane-2,3-diol 7-2F$_{4/6}$



Synthesized according to the general procedure **8.3.6** from **6.1.2** (1 g, 1.32 mmol), thionyl chloride (10 ml) and 1-aminopropane-2,3-diol (0.9 g, 10 mmol). Purified twice by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10:1), and recrystallization from $CHCl_3$.

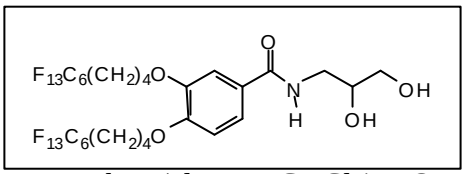
Yield: 210 mg (19.2 %); transition temperatures (°C): Cr 67 Cub_{I2} 162 Iso; $C_{30}H_{35}F_{18}O_5N$ (831); Anal. Calcd.: C, 43.32, H, 4.21, N, 1.68; Found: C, 43.13, H, 4.34, N, 1.62.

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.36 (m, ^3J(H, H) 8.4, 2 H, Ar-H), 7.21 (br s, 1 H, NH), 6.77 (d, ^3J(H, H) 8. 4.1 H, Ar-H), 4.20 (br s, 1 H, OH), 3.95 (m, 2 CH_2O), 3.85 (t, *J*(H, H) 5.07, 1 H, OH), 3.42-3.56 (m, 5 H, NC**H**$_2$, C**H**$_2$OH, C**H**OH), 1.93-2.11 (m, 4 H, 2 $CH_2C_6F_{13}$), 1.89-1.92 (m, 16 H, 8 CH_2).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 168.8 (CO), 112.2, 112.7, 120.1, 126.0, 148.8, 152.2 (Ar-C), 71.2 (CHOH), 68.7, 69.0 (OCH_2), 63.8 CH_2OH), 43.7 (CH_2NH), 31.1, 30.6, 30.2 (t, ^2J(C, F) 22.4, CH_2), 20.0, 25.7, 28.8, 29.1, 29.0 (CH_2), 14.8 (CH_3).

^{19}F-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = -82.92 (overlapped t, 6 F, CF_3), -116.41 (t, 4 F, 2 CH_2CF_2), -126.26 (s, 4 F, 2 CF_3CF_2C**F**$_2$), -127.8 (m, 4 F, CF_3C**F**$_2$).

1-[3,4-Bis(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoyl amino]propane-2,3-diol 7-2F$_{6/4}$



Synthesized according to the general procedure **8.3.6** from **6.2.2** (1 g, 1.11 mmol), thionyl chloride (10 mL) and 1-aminopropane-2,3-diol (1.3 g, 15 mmol). Purified by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10:0.5), and then recrystallized twice from CH_3OH.

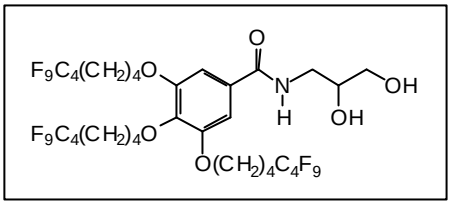
Yield: 235 mg (22.0 %); transition temperatures (°C): Cr 86 Cub_{I2} 208 Iso; $C_{30}H_{27}O_5F_{26}N$ (975). Anal. Calcd.: C, 36.92, H, 2.77, N, 1.44; Found: C, 36.86, H, 3.08, N, 1.41.

^{1}H-NMR (200 MHz; $(CD_3)_2CO$; *J*/Hz): δ = 7.81 (br s, 1 H, NH), 7.55 (dd, ^3J(H, H) 10.0, ^4J(H, H) 1.95, 2 H, Ar-H), 7.04 (d, ^3J(H, H) 8.4, 1 H, Ar-H), 4.10-4.17 (m, 4 H, 2 CH_2O), 3.76 (d, ^3J(H, H) 4.9, 1 H, OH), 3.60 (t, ^3J(H, H) 4.9, 1 H, OH), 3.43-3.54 (m, 5 H, NC**H**$_2$, C**H**$_2$OH, C**H**OH), 2.25-2.48 (m, 4 H, 2 C**H**$_2C_4F_9$), 1.80-2.07 (m, 8 H, 2 CH_2CH_2).

^{13}C-NMR (100 MHz; $(CD_3)_2CO$; *J*/Hz): δ = 168.8 (CO), 113.6, 114.0, 121.8, 128.3, 149.8, 153.0 (ArC), 72.4 (CHOH), 69.2, 69.4 (OCH_2), 64.6 (CH_2OH), 43.9 (CH_2NH), 30.9, 31.1, 31.4 (t, ^2J(C, F) 22.4, CH_2CF_2), 29.2, 18.0 (CH_2).

^{19}F-NMR (200 MHz; $(CD_3)_2CO$; *J*/Hz): δ = -78.24 (overlapped t, 6 F, 2 CF_3), -111.12, -111.27, -111.34 (t, 4 F, 2 CH_2CF_2), -118.94 (s, 4 F, 2 $CF_3(CF_2)_3C$**F**$_2$), -119.9 (m, 4 F, 2 $CF_3(CF_2)_2C$**F**$_2$), -120.4 (m, 4 F, 2 CF_3CF_2C**F**$_2$), -123.23 (m, 4 F, 2 CF_3C**F**$_2$).

1-[3,4,5-Tris(1H,1H,2H,2H,3H,3H,4H,4H-perfluorooctyl-1-oxy) benzoylamino]propane-2,3-diol 7-3F$_{4/4}$



Synthesized according to the general procedure **8.3.6** from benzoic acid **6.4** (1 g, 1.01 mmol), thionyl chloride (10 mL) and 1-aminopropane-2,3-diol (0.9 g, 9.9 mmol). Purified by twice preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10:0.5), then recrystallization firstly from $CHCl_3$, and secondly from CH_3OH.

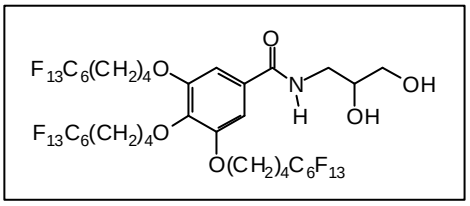
Yield: 221 mg (21.0%); transition temperatures (°C): Cr 49 Cub_{I2} 154 Iso; $C_{34}H_{34}O_6F_{27}N$ (1065). Anal. Calcd.: C, 38.31, H, 3.19, N, 1.31; Found: C, 38.07, H, 3.50, N, 1.35.

^{1}H-NMR (200 MHz; acetone-D_6; *J*/Hz): δ = 7.87 (br s, 1H, NH), 7.27 (s, 2 H, Ar-H), 4.16 (m, ^3J(H, H) 5 7, 6 H, 3 C**H**$_2$O), 4.03 (d, ^3J(H, H) 5.3, 1 H, OH), 3.91 (t, ^3J(H, H) 6.3, 1 H, OH), 3.42-3.55 (m, 5 H, NC**H**$_2$, C**H**$_2$OH, C**H**OH), 2.06-2.48 (m, 6 H, 3 C**H**$_2$C$_4$F$_9$), 1.80-2.01 (m, 24 H, 12 CH_2).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 168.8 (CO), 107.2, 119.9, 130.9, 142.1, 154.2 (Ar-C), 73.7 (CHOH), 69.7, 72.1 (OCH_2), 64.7 (CH_2OH), 43.7 (CH_2NH), 30.6, 31.4, 31.6 (t, ^2J(C,F) 22.4, CH_2), 18.1, 29.7 (CH_2).

^{19}F-NMR (200 MHz, $CDCl_3$, *J*/Hz): δ = -82.75 (overlapped t, 9 F, 3 C**F$_3$**), -116.34 (t, 6 F, 3 CH_2C**F$_2$**), -126.13 (s, 6 F, 3 CF_3CF_2C**F$_2$**), -127.74 (m, 6 F, 3 CF_3**CF$_2$**).

1-[3,4,5-Tris(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoylamino] propane-2,3-diol 7-3F$_{6/4}$



Synthesized according to the general procedure **8.3.6** from benzoic acid **6.2.3** (1 g, 0.77 mmol), thionyl chloride (10 mL) and 1-aminopropane-2,3-diol (0.69 g, 7.6 mmol). Purified by twice preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10:0.5), then recrystallization from $CHCl_3$/CH_3OH 10:2.

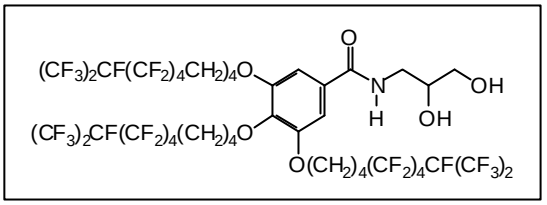
Yield: 231 mg (22.0 %); transition temperatures (°C): Cr 59 Cub_{I2} 188 Iso; $C_{40}H_{34}O_6F_{39}N$ (1365). Anal. Calcd.: C, 35.16, H, 2.49, N, 1.02; Found: C, 35.10, H, 2.90, N, 1.00.

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 6.97 (s, 2 H, Ar-H), 6.52 (br.t, 1 H, NH), 4.04 (m, 6 H, 3 OCH_2), 3.64 (m, 5 H, C**H**$_2$NH, C**H**$_2$OH, C**H**OH), 3.90 (m, 1 H, OH), 2.94 (m, 1 H, OH), 2.15 (m, 6 H, 3 OCH_2C**H**$_2$), 1.85 (m, 12 H, 3 (C**H**$_2$)$_2$C$_6$F$_{13}$).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 168.7 (CO), 153.9, 141.9, 130.9, 107.3 (Ar-C), 73.3 (CHOH), 72.4, 69.4 (OCH_2), 64.8 (CH_2OH), 44.1 (CH_2NH), 31.24 (t, ^2J(C, F) 22.0, CH_2), 18.1 (CH_2).

^{19}F-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = -82.36 (overlapped t, 9 F, 3 CF_3), -115.14 (t, 6 F, 3 CH_2CF_2), -122.76 (s, 6 F, 3 CF_3 $(CF_2)_3C\mathbf{F_2}$), -123.74 (s, 6 F, 3 CF_3 $(CF_2)_2C\mathbf{F}_2$), -124.24 (s, 6 F, 3 $CF_3CF_2C\mathbf{F}_2$), -127.08 (s, 6 F, 3 $CF_3C\mathbf{F}_2$).

1-[3,4,5-Tris(1H,1H,2H,2H,3H,3H,4H,4H-perfluoroisoundecyl-1-oxy) benzoylamino]propane-2,3-diol 7-3F$_{7/4}$



Synthesized according to the general procedure **8.3.6** from benzoic acid **6.3** (1 g, 0.69 mmol), thionyl chloride (10 mL) and 1-aminopropane-2,3-diol (0.63 g, 6.9 mmol). Purified by twice preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10:0.5).

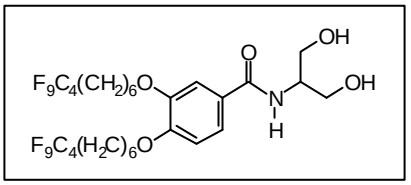
Yield: 131 mg (12.5 %); transition temperatures (°C): Cr < 20 Cub_{I2} 193 Iso; $C_{43}H_{34}O_6F_{45}N$ (1515). Anal. Calcd.: C, 34.06, H, 2.24, N, 0.92; Found: C, 33.81, H, 2.83, N, 0.90.

^{1}H-NMR (200 MHz; $CDCl_3$+$ClCF_2CFCl_2$; *J*/Hz): δ = 7.03 (s, 2 H, Ar-H), 6.57 (br t, 1 H, NH), 4.07 (m, 6 H, 3 CH_2O), 3.87 (m, 2 H, 2 OH), 3.59-3.67 (m, 5 H, $NC\mathbf{H}_2C\mathbf{H}OHC\mathbf{H}_2OH$), 2.15 (m, 6 H, 3 CH_2CF_2), 1.87-1.92 (m, 12 H, 3 $C\mathbf{H}_2C\mathbf{H}_2$).

^{13}C-NMR (100 MHz; $CDCl_3$+$ClCF_2CFCl_2$; *J*/Hz): δ = 169.1 (CO), 153.35, 129.46, 120.0, 106.3 (ArC), 72.9 (CHOH), 71.4 (CH_2OAr), 68.9 ($2CH_2OAr$), 64.0 (CH_2OH), 43.0 (CH_2N), 31.0 ($\mathbf{C}H_2CF_2$), 29.8, 28.9 (CH_2), 17.4 (CH_2).

^{19}F-NMR (188 MHz; $CDCl_3$+$ClCF_2CFCl_2$; *J*/Hz): δ = -83.58 (m, 18 F, 6 CF_3), -116.45 (m, 6 F, 3 CH_2CF_2), -116.96 (m, 6 F, 3 $CH_2CF_2C\mathbf{F}_2$), -122.61 (m, 6 F, 3 $CH_2CF_2CF_2C\mathbf{F}_2$), -124.92 (m, 6 F, 3 $CF_3CFC\mathbf{F}_2$), -188.04 (m, 3 F, 3 $CF_3C\mathbf{F}$).

2-[3,4-Bis(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-perfluorodecyl-1oxy) benzoylamino]propane-1,3-diol 8-2F$_{4/6}$



Synthesized according to the general procedure **8.3.6** from benzoic acid **6.1.2** (0.72 g, 0.92 mmol), thionyl chloride (10 mL) and 2-aminopropane-1,3-diol (0.84 g, 9.25 mmol). Purified by twice preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10:1).

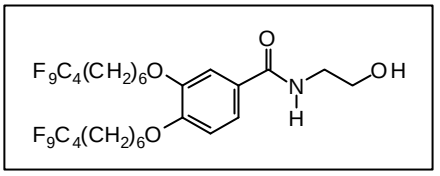
Yield: 231 mg (30.0 %); transition temperatures (°C): Cr 71 Col_h 177 Iso; $C_{30}H_{35}O_5F_{18}N$ (831). Anal. Calad.: C, 43.32, H, 4.21, N, 1.68; Found: C, 42.83, H, 3.89, N, 1.55.

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.40 (br s, 1 H, NH), 7.31 (dd, ^4J(H, H) 1.95, ^3J(H, H) 8.4, 2 H, Ar-H), 6.82 (d, ^3J(H, H) 8.4, 1 H, Ar-H), 4.16-3.82 (m, 9 H, $HOC\mathbf{H}_2C\mathbf{H}C\mathbf{H}_2OH$, 2 CH_2O), 3.50 (br s, 1 H, OH), 2.65 (br s, 1 H, OH), 1.48-2.14 (m, 20 H, 2 $(CH_2)_5$).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 168.0 (CO), 112.4, 113.0, 120.0, 126.7, 149.1, 152.8 (Ar-H), 69.0, 68.8 (CH_2OAr), 63.7 (CH_2OH), 52.8 (CHNH), 30.6 (CH_2CF_2), 20.0, 25.6, 28.7, 28.8, 28.9 (CH_2).

^{19}F-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = -82.72 (overlapped t, 6 F, 2 CF_3), -116.32 (t, 4 F, 2 CH_2CF_2), -126.15 (s, 4 F, 2 $CF_3CF_2C\mathbf{F}_2$), -127.74 (s, 4 F, 2 $CF_3C\mathbf{F}_2$).

2-[3,4-Bis(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-perfluorodecyl-1-oxy) benzoylamino]ethan-2-ol <u>9-2F$_{4/6}$</u>



Synthesized according to the general procedure **8.3.6** from **<u>6.1.2</u>** (1.4 g, 1.85 mmol), thionyl chloride (10 mL) and 2-amino ethanol (0.56 g, 9.25 mmol). Purified by twice preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH: 10:0.5).

Yield: 211 mg (14 .3 %); transition temperatures (°C): Cr 71 Cub_{V2} 112 Iso; $C_{29}H_{33}F_{18}O_4N$ (801). Anal. Calad.: C, 43.44, H, 4.12, N, 1.75; Found: C, 43.30, H, 4.01, N, 1.62.

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.39 (d, ^4J(H, H) 2.15, 1H, Ar-H), 7.26 (dd, ^4J(H, H) 1.95, ^3J(H, H) 8.4, 1 H, Ar-H), 6.81 (d, ^3J(H, H) 8.4, 1 H, Ar-H), 6.56 (br t, 1 H, NH), 4.03 (m, 4 H, OCH_2), 3.81 (m, 2 H, CH_2), 3.60 (m, 2 H, CH_2NH), 2.73 (br s, 1 H, OH), 2.10 (m, 4 H, 2 $CH_2C_4F_9$), 1.86 (m, 4 H, 2 $C\mathbf{H}_2CH_2OH$), 1.40-1.65 (m, 16 H, 2 $CH_2CH_2CH_2CH_2$).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 168.4 (C=O), 112.4, 113.0, 119.8, 126.9, 149.1, 152.1 (Ar-H), 68.8, 69.0 (CH_2OAr), 62.6 (CH_2OH), 42.9 (CH_2NH), 30.6 (t, $\mathbf{C}H_2CF_2$), 25.6, 28.7, 28.8, 28.9(CH_2).

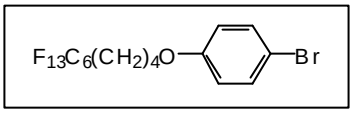
^{19}F-NMR (188 MHz; $CDCl_3$; *J*/Hz): δ = -82.72 (overlapped t, 6 F, 2 CF_3), -116.32 (t, 4 F, 2 CH_2CF_2), -126.15 (s, 4 F, 2 $CF_3CF_2C\mathbf{F}_2$), -127.74 (s, 4 F, 2 $CF_3C\mathbf{F}_2$).

8.4 Synthesis of amphiphilic biphenyl derivatives 13 and 16

8.4.1 Synthesis of the semifluorinated single and double chain bromo benzenenes 11 and 19

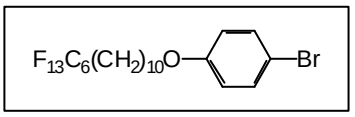
Etherification of 4-bromophenols - general procedure 8.4.1.1: The appropriate alkylbromide (6.6 mmol) was added to a mixture of the appropriate 4-bromophenol (6 mmol) and K_2CO_3 (12 mmol) in dry CH_3CN (20 mL) under an argon atmosphere. The mixture was refluxed for 2 h (TLC). The solvent was evaporated in *vacuo*. Water (50 mL) and diethyl ether (50 mL) were added to the residue. The layers were separated, and the aqueous layer was extracted with Et_2O (3×75 mL), and the combined organic layers were washed with H_2O (3×50 mL) and dried over Na_2SO_4. Finally the solvent was evaporated in *vacuo*. Purification of the product was done by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$) or recrystallization from petroleum ether.

4-(1H,1H,2H,2H,3H,3H,4H,4H-Perfluorodecyl-1-oxy)bromobenzene 11Fa



Prepared according to the general procedure **8.4.1.1** from **4.2** (5.0 g, 11.0 mmol), 4-bromophenol (2.85 g, 16.5 mmol) and K_2CO_3 (2.0 g, 14.5 mmol) in dry CH_3CN (35 mL). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).
Yield: 4.83 g (72.9 %); colorless solid; mp: 29 °C; $C_{16}H_{12}OF_{13}Br$ (547).
^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 7.37 (m, 2 H, Ar-H), 6.78 (m, 2 H, Ar-H), 3.94 (t, *J*(H, H) 5.66, 1 H, CH_2Ar), 2.08-2.21 (m, 2 H, C**H**$_2CF_2$), 1.87-1.77 (m, 4 H, CF_2CH_2C**H**$_2C$**H**$_2$).

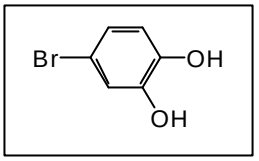
4-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H,8H,8H,9H,9H,10H,10H-Perfluorohexadecyl-1-oxy)bromobenzene 11Fb



Prepared according to the general procedure **8.4.1.1** from **4.4** (5.0 g, 9.28 mmol), 4-bromophenol (2.4 g, 14.5 mmol), K_2CO_3 (2.0 g, 14.5 mmol) and KI (0.5 g) in dry CH_3CN (35 mL). Purification by recrystallization from petroleum ether.
Yield: 3.2 g (54.61 %); colorless solid; mp: 44 °C; $C_{22}H_{24}OF_{13}Br$ (631).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.36 (d, 2 H, ^{3}*J*(H, H) 9.0, Ar-H), 6.73 (d, ^{3}*J*(H, H) 6.7, 2 H, Ar-H), 3.89 (t, 2 H, ^{3}*J*(H, H) 6.6, OCH_2), 1.30-2.17 (m, 18 H, 9 CH_2).

3,4-Bis(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyloxy)bromobenzene 19

*4-Bromo-1,2-dihydroxybenzene **18***

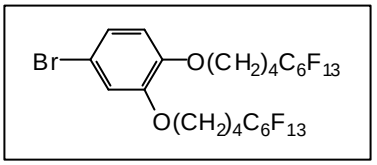


A mixture of 4-bromoveratrole (20 g, 92.1 mmol) and BBr_3 (25 mL) in dry CH_2Cl_2 (250 mL) was refluxed for 4 h, and stirred for 20 h at RT. Water (30 mL) was added carefully, the solvent was distilled off and the residue was dissolved in diethyl ether (100 mL). The solution was washed with saturated $NaHCO_3$ solution (2×30 mL), dried over Na_2SO_4 and the solvent was distilled off. Purification of the product was done by fractional distillation .

Yield: 9.1 g (52.3 %); colorless waxy solid; bp: 120 °C / 0.21 mbar; $C_6H_5BrO_2$ (189).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.12-6.69 (m, 3 H, Ar-H), 5.83 (m, 2 H, OH).

*3,4-Bis(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyloxy)bromobenzene **19***



Prepared according to the general procedure **8.4.1.1** from **4.2** (7.72 g, 16.96 mmol), **18** (1.46 g, 7.71mmol), K_2CO_3 (2.0 g, 14.5 mmol) and KI (0.5 g) in dry CH_3CN (35 mL). Purification by preparative centrifugal thin layer chromatography (eluent: petroleum ether).

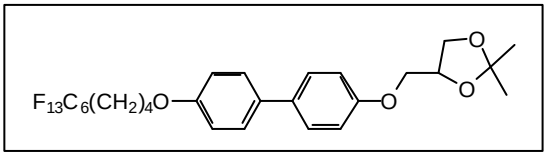
Yield: 4.7 g (65.0 %); colorless solid; mp: 38 °C; $C_{26}H_{19}O_2F_{26}Br$ (937).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 6.73-7.27 (m, 3 H, Ar-H), 4.03 (m, 4 H, 2 CH_2), 1.84-2.26 (m, 12 H, 3 CH_2CH_2).

8.4.2 Synthesis of the biphenyl 2,2-dimethyl-1,3-dioxolane derivatives 12, 15, 20 and 22

Pd^0-catalyzed cross coupling reaction (I) - general procedure 8.4.2: A mixture of the appropriately substituted bromobenzene (7.41 mmol), benzeneboronic acid (8.89 mmol), $Pd(PPh_3)_4$ (0.25 g), ethyleneglycoldimethylether (45 mL), and saturated $NaHCO_3$ solution (35 mL) was refluxed for 6 h under an argon atmosphere. After staying over night at RT, the precipitate was filtered, and dissolved in chloroform (50 mL). The solution was dried over Na_2SO_4, filtered through silica gel and the silica gel was washed thoroughly with chloroform (100 mL), the solvent was evaporated and the product was purified as described below.

4-[4'-(1H,1H,2H,2H,3H,3H,4H,4H-Perfluorodecyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolane 12Fa

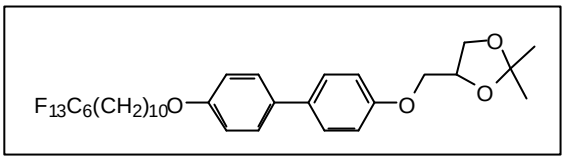


Prepared according to the general procedure **8.4.2** from **11Fa** (2.1 g, 3.84 mmol), **49b.1** (1.16 g, 4.6 mmol), glyme (40 mL), saturated

$NaHCO_3$ solution (30 mL), $Pd(PPh_3)_4$ (0.1 g). Purification by recrystallization from $CHCl_3$.
Yield: 0.9 g (35.9 %); yellow oil; $C_{28}H_{27}O_4F_{13}$ (674).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.43 (m, 4 H, Ar-H), 6.94 (m, 4 H, Ar-H), 54.51-3.86 (m, 7 H, OCH_2, OCH_2OCHCH_2O), 1.80-2.25 (m, 4 H, $CF_2C\mathbf{H}_2C\mathbf{H}_2$), 1.45, 1.39 (2 s, 6 H, 2 CH_3).

4-[4'-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H,8H,8H,9H,9H,10H,10H-Perfluorohexadecyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolane 12Fb

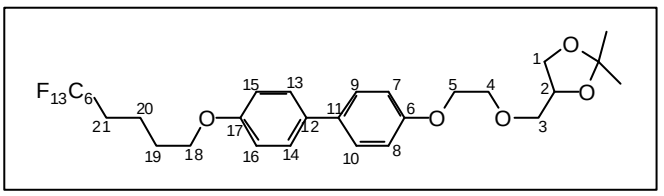


Prepared according to the general procedure **8.4.2** from **11Fb** (1.0 g, 1.58 mmol), **49b.1** (0.48 g, 1.90 mmol), glyme (20 mL), saturated $NaHCO_3$ solution (15 mL), $Pd(PPh_3)_4$ (0.1 g). Purification by recrystallization from $CHCl_3$.
Yield: 0.9 g (75 %); transition temperatures (° C): Cr 104 SmA 134 Iso; $C_{34}H_{39}O_4F_{13}$ (758).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.46 (m, 4 H, Ar-H), 6.94 (m, 4 H, Ar-H), 4.48-3.89 (m, 7 H, 2 ArOC$\mathbf{H}_2$, C$\mathbf{H}$C$\mathbf{H}_2$O), 1.60-2.25 (m, 18 H, 9 CH_2), 1.39, 1.46 (2 s, 6 H, 2 CH_3).

^{19}F-NMR (188 MHz; $CDCl_3$; *J*/Hz): δ = -82.34 (overlapped t, 3 F, CF_3), -115.85 (m, 2 F, $CH_2C\mathbf{F}_2$), -123.52 (m, 2 F, $CH_2CF_2C\mathbf{F}_2$), -124.48 (s, 2 F, $CF_3CF_2CF_2C\mathbf{F}_2$), -125.16 (s, 2 F, $C\mathbf{F}_2CF_2CF_3$), -127.72 (m, 2 F, $CF_3C\mathbf{F}_2$).

4-{4-[4'-(1H,1H,2H,2H,3H,3H,4H,4H-Perfluorodecyloxy)biphenyl-4-yloxy]-2-oxabutyl}-2,2-dimethyl-1,3-dioxolane 15Fa



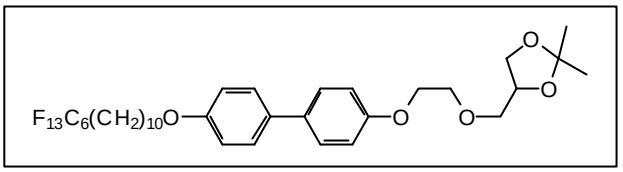
Prepared according to the general procedure **8.4.2** from 4-[4-(4-bromophenyloxy)-2-oxa-butyl]-2,2-dimethyl-1,3-dioxolane **14** (1.16 g, 3.5mmol), **49a.2** (1.66 g, 3.24 mmol), glyme (30 mL), saturated $NaHCO_3$ solution (20 mL), $Pd(PPh_3)_4$ (0.1 g). Purification by recrystallization from ethyl acetate/methanol 10:2.
Yield: 1.25 g (53.6 %); transition temperatures (°C): Cr 101 SmA 121 Iso; $C_{30}H_{31}O_5F_{13}$ (718). Anal. Calcd.: C, 50.14, H, 4.32; Found: C, 50.06, H, 4.76.

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.46 (m, 4 H, Ar-H), 6.93 (m, 4 H, Ar-H), 4.33-3.56 (m, 11 H, ArOC$\mathbf{H}_2$C$\mathbf{H}_2$OC$\mathbf{H}_2$C$\mathbf{H}$C$\mathbf{H}_2$, ArOC$\mathbf{H}_2$), 2.23-2.02 (m, 2 H, C$\mathbf{H}_2$$CF_2$), 1.92-1.78 (m, 4 H, CH_2CH_2), 1.35, 1.42 (2 s, 6 H, 2 CH_3)

^{13}C-NMR (100 MHz; DMSO-D_6, *J*/Hz): δ = 158.12 (C_6), 158.07 (C_7), 133.74 (C_{11}), 133.83(C_{12}), 127.85 (C_9, C_{10}), 127.80 (C_{13}, C_{14}), 115.02 (C_7, C_8), 114.83 (C_{15}, C_{16}), 109.53 (tert-C), 79.76(C_5), 72.50 (C_{18}), 70.13 (C_4), 67.52 (C_2), 67.27 (C_3), 66.76 (C_1), 30.85 (C_{21}), 28.65 (C_{19}), 26.67 (CH_3), 25.29 (CH_3), 15.1 (C_{20}).

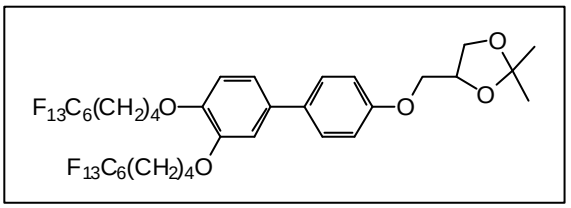
^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -82.34 (overlapped t, 3 F, CF_3), -115.97 (m, 2 F, CH_2CF_2), -123.52 (s, 2 F, $CH_2CF_2C\mathbf{F}_2$), -124.50 (s, 2 F, $CF_3CF_2CF_2C\mathbf{F}_2$), -125.16 (s, 2 F, $C\mathbf{F}_2CF_2CF_3$), -127.74 (m, 2 F, $CF_3C\mathbf{F}_2$).

4-{4-[4′-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H,8H,8H,9H,9H,10H,10H-Perfluorohexadecyloxy)biphenyl-4-yloxy]-2-oxabutyl}-2,2-dimethyl-1,3-dioxolane 15Fb



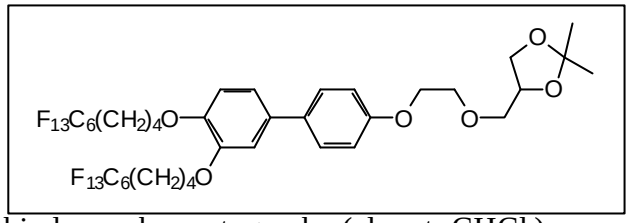
Prepared according to the general procedure **8.4.2** from 4[4-(4′-bromophenyl-4-oxy)-2-oxa-butyl]-2,2-dimethyl-1,3-dioxolane **14** (0.66 g, 2.0 mmol), **49a.3** (1.1 g, 1.85 mmol), glyme (20 mL), saturated $NaHCO_3$ solution (12 mL), $Pd(PPh_3)_4$ (0.1 g). Purification by recrystallization from ethyl acetate/methanol 10:2.
Yield: 0.90 g (60.4 %); transition temperatures (°C): Cr 95 SmA 105 Iso; $C_{36}H_{43}O_5F_{13}$ (806).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.42-7.51 (m, 4 H, Ar-H), 6.96-6.89 (m, 4 H, Ar-H), 4.36-3.47 (m, 9 H, CH_2OAr, $OC\mathbf{H}_2C\mathbf{H}_2OC\mathbf{H}_2C\mathbf{H}C\mathbf{H}_2O$), 2.15-1.41 (m, 18 H, 9 CH_2), 1.35, 1.31 (2 s, 6 H, 2 CH_3).

4-[3′,4′-Bis(1H,1H,2H,2H,3H,3H,4H,4H,-perfluorodecyloxy)biphenyl-4-yloxymethyl]-2,2-dimethyl-1,3-dioxolane 20Fa



Prepared according to the general procedure **8.4.2** from **19** (1.5 g, 1.60 mmol), **49b.1** (0.48 g, 1.90 mmol), glyme (20 mL), saturated $NaHCO_3$ solution (15 mL), $Pd(PPh_3)_4$ (0.1 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).
Yield: 1.2 g (70.6 %); transition temperatures (°C): Cr < 20 Col 65 Iso; $C_{38}H_{34}O_5F_{26}$ (1064).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.47 (m, 2 H, Ar-H), 7.08 (m, 1 H, Ar-H), 6.94 (m, 4 H, Ar-H), 4.48 (m, 1 H), 4.18-3.65 (m, 9 H, 2 $C\mathbf{H}_2O$, $OC\mathbf{H}_2C\mathbf{H}C\mathbf{H}_2O$), 2.23-1.82 (m, 12 H, 6 CH_2), 1.46, 1.40 (2 s, 6 H, 2 CH_3).

4-{4-[3′,4′-Bis(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyloxy)biphenyl-4-yloxy]-2-oxabutyl}-2,2-dimethyl-1,3-dioxolane 22Fa



Prepared according to the general procedure **8.4.2** from **19** (1.0 g, 1.07 mmol), **49b.2** (0.3 g, 1.07 mmol), glyme (20 mL), saturated $NaHCO_3$ solution (12 mL), $Pd(PPh_3)_4$ (0.1 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

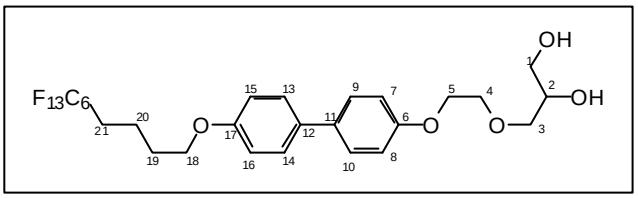
Yield: 1.33 g (59.1 %); mp: 60 °C; $C_{40}H_{38}O_6F_{26}$ (1180).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7 .49 (m, 2 H, Ar-H), 7.28 (m, 1 H, Ar-H), 7.05 (m, 1 H, Ar-H), 6.84 (m, 3 H, Ar-H), 4.31-3.54 (m, 11 H, OC**H**$_2$C**H**$_2$OC**H**CH_2O, 2 OC**H**$_2$), 2.22-1.60 (m, 12 H, 6 CH_2), 1.42, 1.35 (2 s, 6 H, 2 CH_3).

8.4.3 Synthesis of the amphiphilic biphenyl derivatives 13 and 16

Hydrolysis of isopropylidene acetals - general procedure 8.4.3: A mixture of the appropriate 2,2-dimethyl-1,3-dioxolane derivative (1.04 g, 1.27 mmol) and 10% HCl (1 mL) in EtOH (20 mL) was refluxed for 3 h (TLC). The solvent was evaporated in *vacuo*, the residue was dissolved in ethyl acetate (100 mL), the solution was washed with saturated $NaHCO_3$ (2×30 mL), H_2O (2×30 mL) and brine (2×30 mL). The organic layer was dried over $NaSO_4$, and the solvent was evaporated in *vacuo*. The products were purified by recrystallization.

6-[4'-(1H,1H,2H,2H,3H,3H,4H,4H-Perfluorodecyloxy)biphenyl-4-yloxy]4-oxahexane-1,2-diol 16-1F$_{6/4}$



Prepared according to the general procedure **8.4.3** from **15Fa** (1.2 g, 1.67 mmol), 10 % HCl (1 mL), EtOH (40 mL). Purification by recrystallization from EtOH.

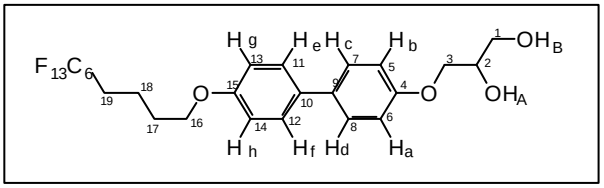
Yield: 332 mg (29.4 %); transition temperatures (°C): Cr 147 Col_{X1} 152 Col_{X2} SmC 158 SmA 219 Iso; $C_{27}H_{27}O_5F_{13}$ (678). Anal. Calcd.: C, 47.79, H, 3.98; Found: C, 47.94, H, 4.15.

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 7.50 (d, ^3J(H, H) 8.6, 4 H, Ar-H), 6.97 (m, 4 H, Ar-H), 4.64 (d, 1 H, ^3J(H, H) 5.1, sec.OH), 4.48 (t, 1 H, ^3J(H, H) 5.5, prim. OH), 4.11 (t, ^3J(H, H) 4.3, 2 H, $ArOCH_2$), 4.05 (t, 2 H, ^3J(H, H) 6.1, $ArOCH_2$), 3.74 (t, ^3J(H, H) 4.7, 2 H, $ArOCH_2C\mathbf{H}_2O$), 3.57 (m, 1 H, C**H**OH), 3.47-3.26 (m, 4 H, $HOC\mathbf{H}_2$, CH_2O), 2.35 (m, 2 H, $C\mathbf{H}_2CF_2$), 1.85 (m, 2 H, CH_2), 1.70 (m, 2 H, CH_2).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 157.8 (C_6, C_{17}), 132.5 (C_{11}, C_{12}), 127.3 (C_9, C_{10}, C_{13}, C_{14}), 115.0 (C_7, C_8), 114.9 (C_{15}, C_{16}), 72.8 (C_5), 70.6 (C_{18}), 69.2 (C_4), 67.3 (C_2), 67.0 (C_3), 63.1 (C_1), 30.9 (C_{21}), 27.7 (C_{19}), 16.6 (C_{20}).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.07 (overlapped t, 3 F, CF_3), -110.27 (m, 2 F, CH_2CF_2), -118.61(s, 2 F, $CH_2CF_2C\mathbf{F}_2$), -119.54 (s, 2 F, CF_3CF_2 $CF_2C\mathbf{F}_2$), -119.30 (s, 2 F, $C\mathbf{F}_2CF_2CF_3$), -122.63 (m, 2 F, $CF_3C\mathbf{F}_2$).

3-[4'-(1H,1H,2H,2H,3H,3H,4H,4H-Perfluorodecyloxy)biphenyl-4-yloxy]propane-1,2-diol 13-1F$_{6/4}$



Prepared according to the general procedure **8.4.3** from **12Fa** (850 mg, 1.26 mmol), 10 % HCl (1 mL), EtOH (20 mL). Purification by recrystallization from $CHCl_3$.

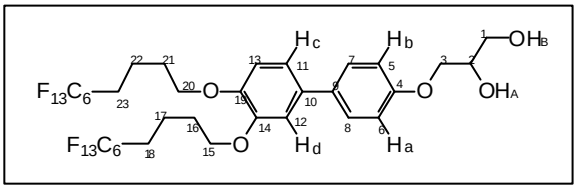
Yield: 137 mg (17.1 %); transition temperatures (°C): Cr 175 SmA 242 Iso; $C_{25}H_{23}O_4F_{13}$ (634). Anal. Calacd.: C, 47.32, H, 3.63; Found: C, 47.22, H, 3.79.

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.50 (d, 4 H, ^3J(H, H) 8.0, H_c, H_d, H_e, H_f), 6.97 (m, 4 H, H_a, H_b, H_g, H_h), 4.94 (d, 1 H, ^3J(H, H) 5.3, OH_A), 4.65 (t, 1 H, ^3J(H, H) 5.7, OH_B), 4.05-3.99 (m, 5 H, C**H**OH, C**H**$_2$O, C**H**$_2$OH), 3.44 (t, 2 H, ^3J(H, H) 5.7, OCH_2), 2.26-2.40 (m, 2 H, CF_2C**H**$_2$), 1.66-1.87 (m, 4 H, C**H**$_2$C**H**$_2CH_2C$**F**$_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 158.1 (C_4), 157.8 (C_{15}), 132.4 (C_9, C_{10}), 127.3 (C_7, C_8), 127.3 (C_{11}, C_{12}), 115.0 (C_5, C_6), 114.9 (C_{13}, C_{14}), 70.0 (C_3), 69.7 (C_{16}), 67.0 (C_2), 62.7 (C_1), 38.9 (C_{19}), 27.7 (C_{17}), 16.6(C_{18}).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.09 (overlapped t, 3 F, CF_3), -110.27 (m, 2 F, CH_2CF_2), -118.61 (s, 2 F, CH_2CF_2C**F**$_2$), -119.54 (s, 2 F, CF_3 CF_2CF_2C**F**$_2$), -119.93 (s, 2 F, C**F**$_2CF_2CF_3$), -122.63 (m, 2 F, CF_3CF_2).

3-[3',4'-Bis(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyloxy)biphenyl-4-yloxy] propane-1,2-diol <u>13-2F$_{6/4}$</u>



Prepared according to the general procedure **8.4.3** from **<u>20Fa</u>** (1.0 g, 0.94 mmol), 10 % HCl (1 mL), EtOH (40 mL). Purification by recrystallization from EtOH.

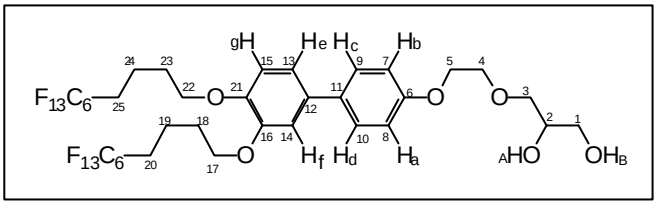
Yield: 132 mg (13.7 %); transition temperatures (^{o} C): Cr 87 Col 137 Iso; $C_{35}H_{30}O_5F_{26}$ (1025).

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.47 (m, 2 H, Ar-H), 7.08 (m, 1 H, Ar-H), 6.96-6.85 (m, 4H, Ar-H), 4.13 (m, 5 H, OC**H**$_2$C**H**OHC**H**$_2$OH), 3.87-3.64 (m, 4 H, $2CH_2O$), 2.15 (m, 4 H, $2CF_2C$**H**$_2$), 1.94 (m, 4 H, 2 C**H**$_2CH_2CF_2$), 1.55 (m, 4 H, 2 CH_2).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 157.9 (C_4), 152.6 (C_{19}), 145.8 (C_{14}), 136.2 (C_9), 134.5 (C_{10}), 130.7 (C_8), 128.1 (C_{12}), 124.2 (C_7), 122.9 (C_{11}), 119.7 (C_5), 114.9 (C_{13}), 114.2 (C_6), 72.0 (C_3), 70.3 (C_{20}), 69.2 (C_{15}), 68.0 (C_2), 63.7 (C_1), 30.6 (C_{18}, C_{23}), 29.5 (C_{16}), 28.8 (C_{21}), 17.3 (C_{22}), 17.0 (C_6).

^{19}F-NMR (188 MHz; $CDCl_3$; *J*/Hz): δ = -77.95 (overlapped t, 3 F, CF_3), -110.97 (m, 2 F, CH_2CF_2), -119.06 (s, 2 F, CH_2CF_2C**F**$_2$), -120.16 (s, 2 F, $CF_3CF_2CF_2C$**F**$_2$), -120.26 (s, 2 F, C**F**$_2CF_2CF_3$), -123.27 (m, 2 F, CF_3C**F**$_2$).

6-[3',4'-Bis(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyloxy)biphenyl-4-yloxy]4-oxahexane-1,2-diol 16-2F$_{6/4}$



Prepared according to the general procedure **8.4.3** from **22Fa** (1.33 g, 1.20 mmol), 10 % HCl (1 mL), EtOH (50mL). Purification by recrystallization from ethyl acetate/hexane 3:5.

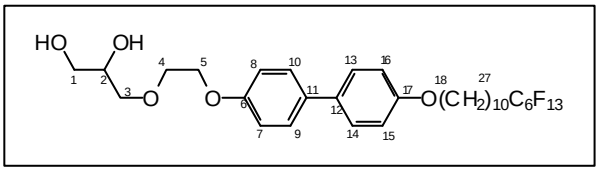
Yield: 147 mg (11.4 %); transition temperatures (°C): Cr < 20 Col 145 Iso; $C_{37}H_{34}O_6F_{26}$ (1069).

^{1}H-NMR (400 MHz; DMSO-D$_6$; *J*/Hz): δ = 7.29 (m, 2 H, Ar-H), 6.68-6.98 (m, 5 H, Ar-H), 4.64 (m, 1H, OH_A), 4.47 (m, 1 H, OH_B), 3.97-3.26 (m, 13 H, ArOC**H**$_2$C**H**$_2$OC**H**$_2$C**H**C**H**$_2$OH, 2 OC**H**$_2$), 2.07 (m, 4 H, 2 CH_2CF_2), 1.60 (m, 8 H, 2 C**H**$_2$C**H**$_2$$CH_2CF_2$).

^{13}C-NMR (100 MHz; DMSO-D$_6$; *J*/Hz): δ = 157.8 (C_{21}), 152.2 (C_6), 148.8 (C_{16}), 147.8 (C_{11}), 145.0 (C_{12}), 135.0 (C_{14}), 130.2 (C_{13}), 130.0 (C_9), 127.3 (C_{10}), 124.0 (C_{15}), 114.7 (C_7), 113.9 (C_8), 72.8 ($C_{22,}$ C_{17}), 70.56 (C_5), 69.2 (C_4), 68.0 (C_2), 67.2 (C_3), 63.1 (C_1), 29.5 (C_{20}, C_{25}), 28.7 (C_{19}, C_{24}), 16.50 (C_{23}, C_{18}).

^{19}F-NMR (188 MHz; DMSO-D$_6$): δ = -79.48 (overlapped t, 6 F, 2 CF_3), -111.67 (m, 4 F, 2 CH_2CF_2), -119.68 (s, 4 F, 2 CH_2CF_2C**F**$_2$), -120.80 (s, 4 F, 2 $CF_3CF_2CF_2C$**F**$_2$), -121.15 (s, 4 F, 2 C**F**$_2CF_2CF_3$), -124.30 (m, 4 F, 2 CF_3CF_2).

6-[4'-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H,8H,8H,9H,9H,10H,10H-Perfluorohexadecyloxy)biphenyl-4-yloxy]4-oxahexane-1,2-diol 16-1F$_{6/10}$



Prepared according to the general procedure **7.4.3** from **15Fb** (0.56 g, 0.69 mmol), 10 % HCl (1 mL), EtOH (40 mL). Purification of the product was done by recrystallization from EtOH.

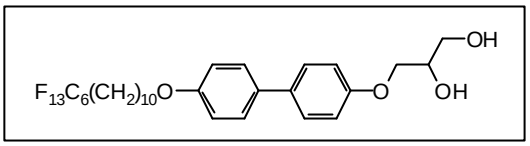
Yield: 151 mg (28.5 %); transition temperatures (°C): Cr 149 ($Colx_1$ 148) $Colx_2$ 168 SmA 203 Iso; $C_{33}H_{39}O_5F_{13}$ (762).

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.46 (m, 4 H, Ar-H), 6.96 (m, 4 H, Ar-H), 4.15 (t, ^{3}*J*(H, H 4.69, 2 H, ArOC**H**$_2$$CH_2$O), 3.97 (t, ^{3}*J*(H, H) 6.64, 2 H, ArOC**H**$_2$), 3.88 (m, 3 H, $ArOCH_2$C**H**$_2$O, CH); 3.65 (m, 4 H, OC**H**$_2$CHOHC**H**$_2$OH), 2.65 (br s, 2 OH), 2.06 (m, 4 H, 2 CH_2), 1.80 (m, 2 H, CH_2), 1.24-1.61 (m, 12 H, 6 CH_2).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 158.6 (C_6), 157.9 (C_{17}), 134.3 (C_{11}), 133.4 (C_{12}), 127.9 (C_9, C_{10}), 127.8 (C_{13}, C_{14}), 115.1(C_7, C_8), 115.0 (C_{15}, C_{16}), 73.2 (C_5), 70.6 (C_{18}), 70.23 (C_4), 68.2 (C_2), 67.6 (C_3), 64.1 (C_1), 30.9 (C_{27}), 29.6, 29.4, 29.3, 29.2, 29.0, 26.0, 20.1, 17.0 (C_{19}-C_{26}).

^{19}F-NMR (188 MHz; $CDCl_3$; *J*/Hz): δ = -82.47 (overlapped t, 3 F, CF_3), -115.71 (m, 2 F, CH_2CF_2), -123.45 (m, 2 F, $CH_2CF_2C\mathbf{F}_2$), -124.40 (s, 2 F, $CF_3CF_2CF_2C\mathbf{F}_2$), -125.08 (s, 2 F, $C\mathbf{F}_2CF_2CF_3$), -127.64 (m, 2 F, $CF_3C\mathbf{F}_2$).

3-[4'-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H,8H,8H,9H,9H,10H,10H-Perfluorohexadecyloxy)biphenyl-4-yloxy]propane-1,2-diol 13-1F$_{6/10}$



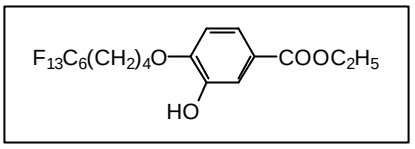
Prepared according to the general procedure **7.4.3** from **12Fb** (0.8 g, 1.06 mmol), 10 % HCl (1 mL), EtOH (40 mL). Purification of the product by recrystallization from EtOH.

Yield: 231mg (30.4 %); transition temperatures (°C): Cr 168 SmA 225 Iso; $C_{31}H_{35}O_4F_{13}$ (718).

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.44 (m, 4 H, Ar-H), 6.94 (m, 4 H, Ar-H), 4.08-3.77 (m, 7 H, ArOC$\mathbf{H}_2$C$\mathbf{H}$OHC$\mathbf{H_2}$OH, ArOC$\mathbf{H}_2$), 2.51 (br s, 2 OH), 2.01 (m, 4 H, 2 CH_2), 1.79 (m, 2 H, CH_2), 1.19-1.78 (m, 12 H, 6 CH_2).

8.5 Synthesis of the semifluorinated pentaerythritol benzoates 27, 28 and 29

8.5.1 Ethyl 3-hydroxy-4-(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoate 24

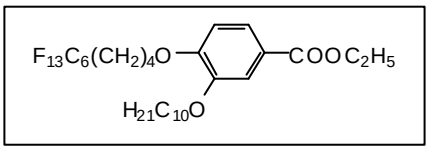


Under an argon atmosphere, a solution of ethyl 3,4-dihydroxybenzoate (1.37 g, 7.5 mmol), dry triphenylphosphine (5.9 g, 22.5 mmol), and **3.2** (8.82 g, 22.5 mmol) in dry THF (80 mL) was cooled to 0-5 °C. DEAD (3.54 mL, 22.5 mmol) was added dropwise through a spectrum during 30 min. The mixture was allowed to reach RT and was stirred for two days at RT. The solvent was evaporated, H_2O was added to the oily residue, the precipitated was filtered, and washed with water.

Yield: 1.5 g (36.0 %); gray solid; mp: 118 °C; $C_{19}H_{17}F_{13}O_4$ (556).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.60 (m, 2 H, Ar-H), 6.8 (m, 1 H, Ar-H), 4.30 (q, ^3J(H, H) 7.2, 2 H, OC**H**$_2$CH$_3$), 4.13 (t, ^3J(H, H) 6.3, 2 H, OC**H**$_2$CH$_2$), 2.20 (m, 2 H, C_6F_{13}C**H**$_2$), 1.90 (m, 4 H, 2 CH$_2$), 1.38 (t, 3 H, CH$_2$**CH$_3$**).

Ethyl 3-decyloxy-4-(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoate 25

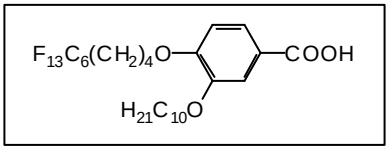


Prepared according to the general procedure **8.3.4** from **24** (1.0 g, 1.8 mmol), 1-bomodecane (0.44 g, 2 mmol), and K_2CO_3 (0.5 g, 3.6 mmol) in dry DMF (20 mL). Purification by recrystallization from petroleum ether.

Yield: 0.7 g (56.0 %); colorless solid; mp: 49 °C; $C_{29}H_{37}F_{13}O_4$ (697).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.62 (dd, ^3J(H, H) 8.4, ^4J(H, H) 1.9, 1 H, Ar-H), 7.45 (d, ^4J(H, H) 1.9, 1 H, Ar-H), 6.82 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 4.25 (q, ^3J(H, H) 7.2, 2 H, OC**H**$_2$CH$_3$), 4.00 (m, 4 H, OC**H**$_2$(CH$_2$)$_3$C$_6$F$_{13}$, OC**H**$_2$(CH$_2$)$_8$CH$_3$), 2.20 (m, 2 H, C_6F_{13}CH$_2$), 1.90 (m, 6 H, C**H**$_2$C**H**$_2$CH$_2$C$_6$F$_{13}$, OCH$_2$C**H**$_2$C$_8$H$_{17}$), 1.40 (t, ^3J(H, H) 7.2, 3 H, C**H**$_3$CH$_2$OCO), 1.20 (m, 14 H, OCH$_2$CH$_2$(C**H**$_2$)$_7$CH$_3$), 0.9 (t, 3 H, O(CH$_2$)$_9$C**H**$_3$).

3-Decyloxy-4-(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoic acid 26



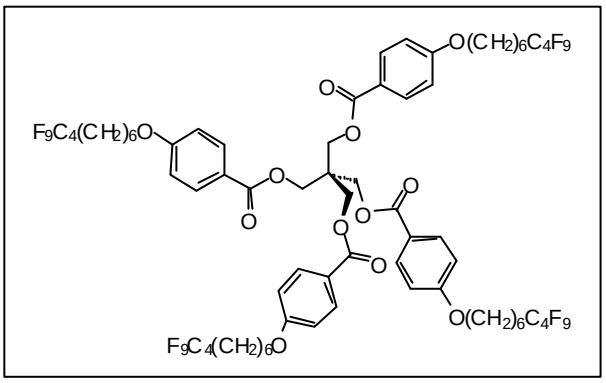
Prepared according to the general procedure **8.3.5** from **25** (0.7 g, 1.00 mmol), 95 % EtOH (10 mL), 10 N aqueous KOH (1 mL). The purification of the product was done by recrystallization from ethanol.

Yield: 0.60 g (89.8 %); colorless solid; mp: 91-92 °C; $C_{27}H_{33}F_{13}O_4$ (668).

^{1}H-NMR (200 MHz, DMSO-D_6, *J*/Hz): δ = 7.50 (dd, ^{3}*J*(H, H) 8.4, ^{4}*J*(H, H) 1.8, 1 H, Ar-H), 7.45 (d, ^{4}*J*(H, H) 1.8, 2 H, 2 Ar-H), 4.10 (m, 2 H, OC**H**$_2$(CH_2)$_3$$C_6F_{13}$), 3.90 (t, ^{3}*J*(H, H) 6.1, 2 H, OC**H**$_2$(CH_2)$_8$$CH_3$), 2.25 (m, 2 H, C_6F_{13}C**H**$_2$), 1.70 (m, 6 H, C**H**$_2$C**H**$_2$$CH_2C_6F_{13}$, OCH_2C**H**$_2$$C_8H_{17}$), 1.25 (m, 14 H, OCH_2CH_2(C**H**$_2$)$_7$$CH_3$), 0.8 (t, ^{3}*J*(H, H) 6.5, 3 H, O(CH_2)$_9$C**H**$_3$).

Esterification - general procedure 8.5.1: A suspension of the appropriate polyhydroxy compound [pentaerythritol or 2,2-bis(3,4-didecyloxybenzyloxymethyl)-1,3-propanediol][49b] was stirred at 20 °C in an 1:1 mixture of dry CH_2Cl_2 and Freon 113 (7 mL for each OH-group and each mmol polyhydroxy compound). 1–2 Equivalents of the appropriately substituted benzoic acid, 1-2.4 equivalents of CMC per OH-group and a catalytic amount of DMAP (20 mg) were added, the mixture was stirred for 72 h at 20 °C and afterwards washed once with water. The aqueous phase was extracted with CH_2Cl_2 (20 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed in *vacuo*. The crude product was purified by preparative centrifugal thin layer chromatrography (Chromatotron, Harrison Research, eluent: $CHCl_3$).

1,3-Bis[4-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-perfluorodecyl-1-oxy) benzoyloxy]-2,2-bis[4-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-perfluorodecyl-1-oxy)benzoyloxylmethyl]propane <u>27-1F$_{4/6}$</u>



Synthesized according to the general procedure **8.5.1** from pentaerythritol (20 mg, 0.15 mmol), **<u>6.1.1</u>** (0.27 g, 0.6 mmol), CMC (0.7 mmol, 0.3 g), and DMAP (20 mg) in a 1:1 mixture of dry CH_2Cl_2 and Freon 113 (20 mL).

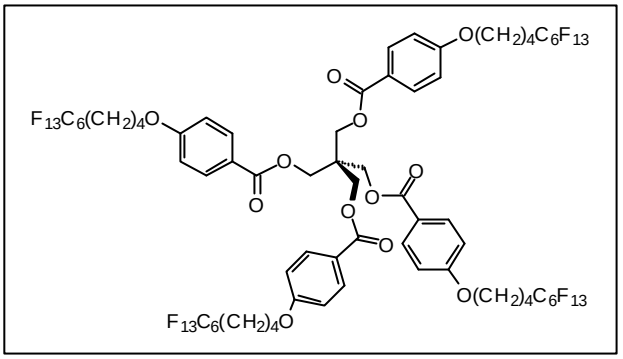
Yield: 101 mg (36.9 %); transition temperatures (°C): Cr < 20 Cub_{V2} 49 Iso; $C_{73}H_{72}F_{36}O_{12}$ (1825). Anal. Calcd.: C, 48.03, H, 3.95; Found: C, 48.16, H, 3.97.

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.94 (d, ^{3}*J*(H, H) 8.8, 8 H, Ar-H), 6.86 (d, ^{3}*J*(H, H) 8.9, 8 H, Ar-H), 4.62 (s, 8 H, 4 C**H**$_2$C), 3.98 (t, ^{3}*J*(H, H) 6.3, 8 H, 4 OCH_2), 2.19-1.83 (m, 8 H, 4 OCH_2C**H**$_2$), 1.77-1.80 (m, 8 H, 4 C**H**$_2$$C_6F_{13}$), 1.73-1.24 (m, 24 H, 4 $CH_2CH_2CH_2$).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 166.0 (C=O), 163.3, 131.8, 121.8, 118.3 (Ar-C), 67.9 (**C**H_2OC=O), 63.3 (CH_2OH), 43.0 (quart C), 30.9, 30.7, 30.4 (t, ^{2}*J*(C, F) 22.8, CF_2**C**H_2), 25.6, 25.0 (CH_2), 20.0 (CH_2).

^{19}F-NMR (188 MHz, $CDCl_3$ *J*/Hz): δ = -82.7 (overlapped t, 12 F, 4 CF_3), -116.2 (t, 8 F, 4 CH_2CF_2), -126.1 (s, 8 F, 4 CF_3CF_2C**F**$_2$), -127.7 (m, 8 F, 4 CF_3C**F**$_2$).

1,3-Bis[4-(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyloxy)benzoyl-1-oxy]-2,2-bis[4-(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoyloxymethyl]propane
27-1F$_{6/4}$



Synthesized according to the general procedure **8.5.1** from pentaerythritol (20 mg, 0.15 mmol), **6.2.1** (0.3 g, 0.6 mmol), CMC (0.3 g, 0.7 mmol), and DMAP (20 mg) in a 1:1 mixture of dry CH_2Cl_2 and Freon 113 (20 mL).

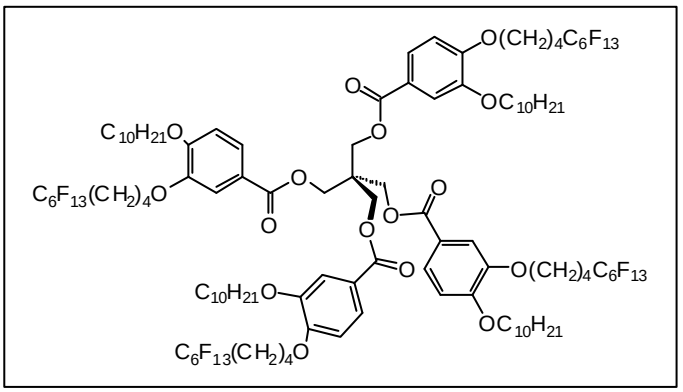
Yield: 100 mg (31.5 %); transition temperatures (°C): Cr 59 SmA 88 Iso; $C_{73}H_{56}F_{52}O_{12}$ (2113). Anal. Calcd.:C, 41.46, H, 2.65; Found: C, 41.79, H, 2.94.

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.94 (d, ^3J(H, H) 9.0, 8 H, Ar-H), 6.86 (d, ^3J(H, H) 9.0, 8 H, Ar-H), 4.62 (s, 8 H, 4 CH_2C), 4.04 (t, ^3J(H, H) 6.3, 8 H, 4 CH_2), 2.24 (m, 8 H, 4 CH_2), 1.85 (m, 16 H, 4 CH_2CH_2).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 166.9 (C=O), 164.0, 132.9, 123.07, 115.24 (Ar-C), 68.39 (**C**H_2OC=O), 64.41 (CH_2OH), 43.99 (quart C), 31.79 (t, ^2J(C, F) 22.4, CF_2CH_2), 29.46 (**C**$H_2CH_2CF_2$), 18.14 (CH_2).

^{19}F-NMR (188 MHz; $CDCl_3$; *J*/Hz): δ = -82.38 (overlapped t, 12 F, 4 CF_3), -116.08 (t, 8 F, 4 CH_2CF_2), -123.52 (s, 8 F, 4 $CF_3(CF_2)_3C\mathbf{F}_2$), -124.48 (s, 8 F, 4 $CF_3(CF_2)_2C\mathbf{F}_2$), -125.14 (s, 8 F, 4 $CF_3CF_2C\mathbf{F}_2$), -127.72 (s, 8 F, 4 $CF_3C\mathbf{F}_2$).

1,3-Bis(3-decyloxy-4-1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyloxybenzoyl-1-oxy)-2,2-bis(3-decyloxy-4-1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxybenzoyloxymethyl)propane 28



Synthesized according to the general procedure **8.5.1** from pentaerythritol (17.5 mg, 0.13 mmol), **26** (0.9 g, 1.34 mmol), CMC (0.6 g, 1.4 mmol), and DMAP (20 mg) in a 1:1 mixture of dry CH_2Cl_2 and Freon 113 (20 mL).

Yield: 251 mg (70.6 %); transition temperatures (°C): Cr < 20 Col_h 108 Iso; $C_{113}H_{136}F_{52}O_{16}$ (2738). Anal. Calcd.:C, 49.52, H, 4.98; Found: C, 49.76, H, 5.03.

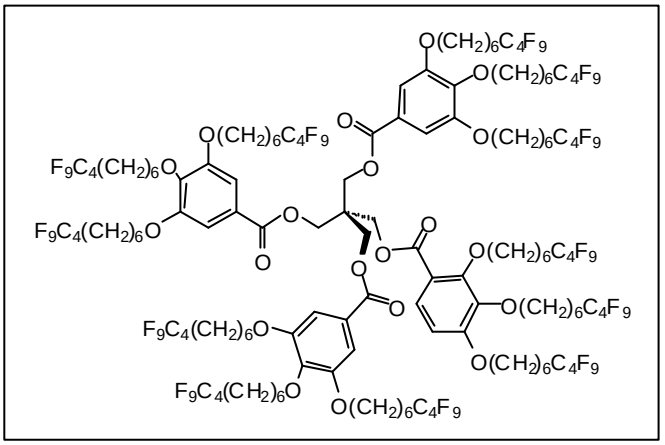
^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.57 (dd, ^{3}J(H, H) 8.4, ^{4}J(H, H) 2.0, 4 H, Ar-H), 7.47 (d, ^{4}J(H, H) 1.8, 4 H, Ar-H), 6.78 (d, ^{3}J(H, H) 8.6, 4 H, Ar-H), 4.61 (s, 8 H, 4 CCH_2), 4.06 (t, ^{3}J(H, H) 5.7, 8 H, 4 $OC\mathbf{H}_2CH_2$), 3.98 (t, ^{3}J(H, H) 6.4, 8 H, 4 $OC\mathbf{H}_2CH_2$), 2.12-2.22 (m, 8 H, 4 $OCH_2C\mathbf{H}_2$), 1.90-1.93 (m, 8 H, 4 $OCH_2C\mathbf{H}_2$), 1.74-1.84 (m, 16 H, 4 $(C\mathbf{H}_2)_2C_6F_{13}$), 1.24-1.55 (m, 56 H, 4 $(C\mathbf{H}_2)_7CH_3$), 0.90 (t, ^{3}J(H, H) 6.4, 12 H, 4 CH_3).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 167.0 (CO), 154.2, 150.0, 124.6, 123.2, 115.2, 113.2 (Ar-C), 69.3, 70.2 ($ArOCH_2$), 64.3 (CH_2OH), 43.5 (quart C), 31.6 (t, ^{2}J(C, F) 22.4, 30.5, 30.3, 30,2, 30.1, 29.5, 26.9, 23.5, 18.2 (CH_2), 14.8 (CH_3).

^{19}F-NMR (188 MHz; $CDCl_3$; *J*/Hz): δ = -82.40 (overlapped t, 12 F, 4 CF_3), -115.93, -116.00, -116.08 (t, 8 F, 4 CH_2CF_2), -123.54 (s, 8 F, 4 $CF_3(CF_2)_3C\mathbf{F}_2$), -124.50 (s, 8 F, 4 $CF_3(CF_2)_2C\mathbf{F}_2$), -125.04 (s, 8 F, 4 $CF_3CF_2C\mathbf{F}_2$), -127.76 (s, 8 F, 4 $CF_3C\mathbf{F}_2$).

1,3-Bis[3,4,5-tris(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-perfluorodecyl-1-oxy) benzoyl-1-oxy]-2,2-bis[3,4,5-tris(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H-perfluorodecyl-1-oxy)benzoyloxymethyl]propane <u>27-3F$_{4/6}$</u>

Synthesized according to the general procedure **8.5.1** from pentaerythritol (20 mg, 0.15 mmol), **<u>6.1.3</u>** (0.65 g, 0.6 mmol), CMC (0.3 g, 0.7 mmol), and DMAP (20 mg) in a 1:1 mixture of dry CH_2Cl_2 and Freon 113 (20 mL).



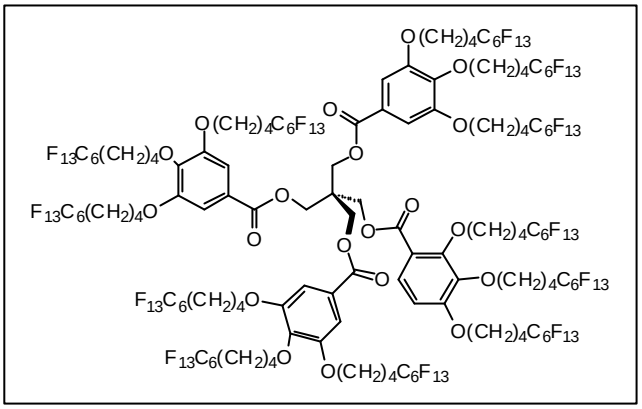
Yield: 165.1mg (25.2 %); transition temperatures (°C): Cr < 20 Cub_{I2} 73 Iso; $C_{153}H_{160}F_{108}O_{20}$ (4371). Anal. Calcd.: C, 42.03, H, 3.66; Found: C, 42.18, H, 3.64.

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.24 (s, 8 H, Ar-H); 4.58 (s, 8 H, 4 CCH_2), 3.97 (t, ^{3}J(H, H) 6.45, 24 H, 12 OCH_2), 2.07-1.79 (m, 24 H, 12 $OCH_2C\mathbf{H}_2$), 1.65-1.36 (m, 96 H, 12 $(C\mathbf{H}_2)_4C_4F_9$).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 166.9, 154.0, 144.0, 125.1, 109.3 (Ar-H), 69.9, 74.2 ($\mathbf{C}H_2OOC$), 64.1, 61.9 (OCH_2), 44.3 (quart C), 32.6 (t, ^{2}J(C, F) 22.4), 31.35, 30.94, 30.57, 29.97, 29.80, 29.70, 26.69, 26.65, 20.96, 15.18 (CH_2).

^{19}F-NMR (188 MHz; $CDCl_3$; *J*/Hz): δ = -82.92 (overlapped t, 36 F, 12 CF_3), -116.39 (t, 24 F, 12 $CH_2C\mathbf{F}_2$), -126.63 (s, 24 F, 12 $CF_3CF_2C\mathbf{F}_2$), -127.86 (m, 24 F, 12 $CF_3C\mathbf{F}_2$).

1,3-Bis[3,4,5-tris(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoyloxy]-2,2-bis[3,4,5-tris(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoyloxy methyl]propane 27-3F$_{6/4}$



Synthesized according to the general procedure **8.5.1** from pentaerythritol (20 mg, 0.15 mmol), **6.2.3** (0.77 g, 0.6 mmol), CMC (0.3 g, 0.7 mmol), and DMAP (20 mg).

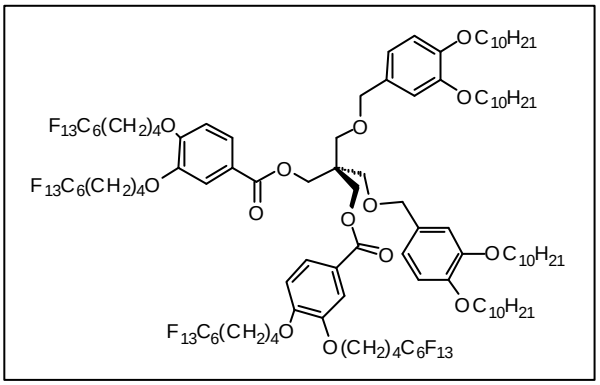
Yield: 212 mg (27.0 %); transition temperatures (^{o}C): Cr 36 Cub$_{I2}$.101 Iso; $C_{153}H_{112}F_{156}O_{20}$ (5234). Anal. Calcd.: C, 35.08, H, 2.14; Found: C, 34.88, H, 2.27.

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.26 (s, 8 H, Ar-H), 4.64 (s, 8 H, CCH_2), 3.99 (t, ^{3}J(H, H) 5.1, 24 H, 12 OCH_2), 2.17 (m, 24 H, 12 OCH_2CH_2), 1.85 (m, 48 H, 12 $(CH_2)_2C_6F_{13}$).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 166.7 (C=O), 153.8, 143.6, 125.4, 109.1 (Ar-C), 69.4, 73.7 (CH_2OOC), 65.0 (OCH_2), 44.0 (quart C), 31.7 (t, ^{2}J(C, F) 22.4), 30.57, 29.64, 18.12 (CH_2).

^{19}F-NMR (188 MHz, $CDCl_3$): δ = -82.72 (overlapped t, 36 F, 12 CF_3), -116.34 (t, 24 F, 12 CH_2CF_2), -123.78 (s, 24 F, 12 $CF_3(CF_2)_3CF_2$), -124.48 (s, 24 F, 12 $CF_3(CF_2)_2CF_2$), -125.14 (s, 24 F, 12 $CF_3CF_2CF_2$), -127.72 (s, 24 F, 12 CF_3CF_2).

1,3-Bis[3,4-bis(1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecyl-1-oxy)benzoyloxy]-2,2-bis[3,4-didecyl-1-oxybenzyloxymethyl]propane 29



Synthesized according to the general procedure **8.5.1** from 2,2-bis(3,4-didecyloxybenzyloxymethyl)-1,3-propanediol (0.173 mg, 0.185 mmol), **6.2.2** (0.5 g, 0.55 mmol), CMC (0.19 g, 0.44 mmol), and DMAP (20 mg).

Yield: 128 mg (25.6 %); transition temperatures (°C): Cr 19 Col$_{ob}$ 31 Col$_h$ 63 Iso.

$C_{113}H_{140}O_{14}F_{52}$ (2710). Anal. Calad.: C, 50.0, H, 5.17; Found: C, 49.85, H, 5.24.

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.45 (m, ^{3}J(H, H) 8.2, ^{4}J(H, H) 2.0, 4 H, Ar-H), 6.78 (m, ^{3}J(H, H) 6.8, ^{3}J(H, H) 8.2, 8 H, Ar-H), 4.45 (s, 4 H, 2 COOC**H**$_2$), 4.39 (s, 4 H, 2 OC**H**$_2$Ar), 4.05 (t, ^{3}J(H, H) 5.5, 8 H, 4 OC**H**$_2$CH$_2$), 3.98 (t, ^{3}J(H, H) 5.8, 8 H, 4 OC**H**$_2$CH$_2$), 3.89 (t, ^{3}J(H, H) 6.8, 8 H, 4 OC**H**$_2$CH$_2$), 3.59 (s, 4 H, 2 CCH$_2$), 2.15 (m, 8 H, 4 C**H**$_2$C$_6$F$_{13}$), 1.89 (m, 16 H, 4 C**H**$_2$C**H**$_2$CH$_2$C$_6$F$_{13}$), 1.75 (m, 8 H, 4 OCH$_2$C**H**$_2$), 1.42 (m, 8 H, 4 C**H**$_2$CH$_2$C$_6$F$_{13}$), 1.25 (m, 56 H, 4 (C**H**$_2$)$_7$CH$_3$), 0.87 (t, ^{3}J(H, H) 5.1, 12 H, 4 CH$_3$).

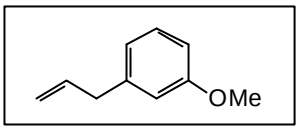
^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 167.1 (C=O), 153.9, 150.4, 149.9, 149.4, 132.0, 124.8, 123.8, 121.2, 115.2, 114.9, 114.7, 113.0 (Ar-C), 74.5 (C**H**$_2$OOC), 69.2, 69.4, 70.0, 70.2, 70.4 (OCH$_2$), 65.0 (**C**H$_2$ - quart C), 45.2 (quart C), 32.8, 30.4, 27.0, 23.5, 18.2 (CH$_2$), 14.9 (CH$_3$).

^{19}F-NMR (188 MHz, $CDCl_3$): δ = -82.57 (overlapped t, 8 F, CF$_3$), -116.14, -116.22, -116.30 (t, 8 F, CH$_2$CF$_2$), -123.68 (s, 8 F, CF$_3$ (CF$_2$)$_3$C**F**$_2$), -124.61 (s, 8 F, CF$_3$ (CF$_2$)$_2$C**F**$_2$), -125.18 (s, 8 F, CF$_3$CF$_2$C**F**$_2$),-127.88 (s, 8 F, CF$_3$CF$_2$).

8.6 Synthesis of bolaamphiphiles

8.6.1 Synthesis of the 2-alkenylanisoles 34, 38 and the 2-perfluoralklyanisoles 42

3-(Prop-2-en-1-yl)anisole 34

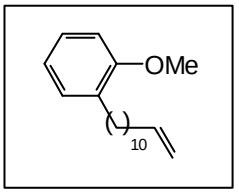


Magnesium turnings (14.4 g, 0.6 mol) were covered by dry diethyl ether (80 mL) and bromoanisole (9.3 g, 0.05 mmol, 1 % g) was added. After the reaction has started, the remaining bromoanisole (84.1 g, 0.45 mol) dissolved in dry diethyl ether (120 mL) was added dropwise, maintaining the Grignard solution to reflux. Stirring was continued under reflux for 2 h, and then the mixture was cooled to RT and transferred to an additional flask under an argon atmosphere, the flask was cooled to 0 °C, allylbromide (61.5 g, 0.5 mol) dissolved in dry diethyl ether (100 mL) was added dropwise, maintaining the temperature of the solution below 5 °C. Stirring of the mixture was continued for additional 3 h at 0 °C, and then overnight at RT. The reaction mixture was quenched with crushed ice (50 g), and 6 N HCl was added until the precipitate was dissolved. The diethyl ether layer was separated and the aqueous layer was extracted with diethyl ether (3×100 mL). Fractional distillation of the combined diethyl ether extracts, at first at ambient pressure and then under *vacuo* yielded the product.

Yield: 35.5 g (48.0 %); yellow oil; bp: 88 °C / 12 mbar; $C_{10}H_{12}O$ (148).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.24 (m, 1 H, Ar-H), 6.82 (m, 2 H, Ar-H), 6.03 (m, 1 H, CH=), 5.15 (m, 2 H, CH_2=), 3.80 (s, 3 H, CH_3), 3.38 (m, 2 H, $ArCH_2$).

2-(Dodec-11-en-1-yl)anisole 38



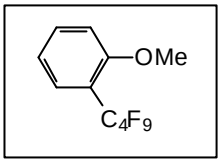
Prepared according to the procedure described for **34** from undec-10-enylbromide (42.0 g, 0.18 mol), magnesium turnings (5.2 g, 0.22 mol) and 2-methoxybenzylchloride (28.0 g, 0.18 mol) in dry diethyl ether (180 mL).

Yield: 29.4 g (59.6 %); yellow oil; bp: 165 °C / 0.079 mbar; $C_{19}H_{30}O$ (274).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.22 (m, 2 H, Ar-H), 6.87 (m, 2 H, Ar-H), 5.89 (m, 1 H, CH=), 5.06 (m, 2 H, CH_2=), 3.84 (s, 3 H, CH_3), 2.64 (t, ^3J(H, H) 7.42, 2 H, $ArCH_2$), 2.09 (m, 2 H, **CH**$_2$CH=), 1.63(m, 2 H, CH_2), 1.30 (m, 14 H, 7 CH_2).

Preparation of activated Cu powder: $CuSO_4 \cdot 5H_2O$ (1 mol) was dissolved in boiling water (100 mL), cooled to RT and zinc powder (1.1 mol) was added portionwise while stirring. The solvent turned to be colorless. Stirring was continued for 5 min, the precipitated copper was filtered and washed with water, 5 % HCl (50 mL), and acetone (75 mL) and dried in *vacuo* at 130 °C for 4 h.

2-Perfluoropropylanisole <u>42.1</u>

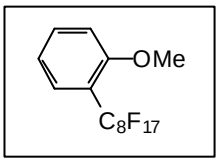


A mixture of 2-iodoanisole (17.5 g, 75 mmol), activated Cu powder (18.4 g, 296 mmol) [prepared from $CuSO_4 \cdot 5H_2O$ (67.4 g, 270 mmol), and zinc powder (23.2 g, 289 mmol)] and dry DMF (50 mL) was heated to 125 °C while stirring. 1-Iodoperfluoropropane (13.1 g, 38 mmol) was added dropwise directly into the solution. Stirring was continued at this temperature for further 7 h. Then the mixture was cooled to RT, H_2O (120 mL) and diethyl ether (30 mL) were added. The solid was filtered off and washed thoroughly with diethyl ether. The organic phase was separated and the aqueous layer was extracted with diethyl ether (3×150 mL), the diethyl ether extracts were combined with the organic phase and washed with H_2O (2×100 mL), brine (2×100 mL) and dried over Na_2SO_4. Afterwards, the diethyl ether was distilled off and the residue was distilled in *vacuo* to yield the product.

Yield: 8.04 g (71.1 %); yellow oil; bp: 45 °C / 0.071 mbar; $C_{11}H_7OF_9$ (326).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.51 (m, 2 H, Ar-H), 7.03 (m, 2 H, Ar-H), 3.85 (s, 3 H, OCH_3).

2-Perfluorooctylanisole <u>42.2</u>



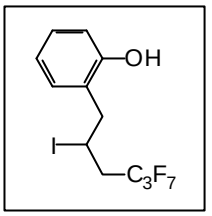
Prepared according to the procedure described for **<u>42.1</u>** from 2-iodoaniso1e (5 g, 6.4 mmol), activated Cu powder (2.16 g, 34.2 mmol) [prepared from $CuSO_4 \cdot 5H_2O$ (8.0 g, 32 mmol) and zinc powder (2.7 g, 42 mmol)], dry DMF (10 mL), and 1-iodoperfluorooctane (3.9 g, 7.0 mmol). Purification of the product was done by preparative centrifugal thin layer chromatography (eluent: petroleum ether).

Yield: 1.7 g (50.0 %); yellow oil; $C_{15}H_7OF_{17}$ (526).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.52 (m, 2 H, Ar-H), 7.03 (m, 2 H, Ar-H), 3.84 (s, 3 H, OCH_3).

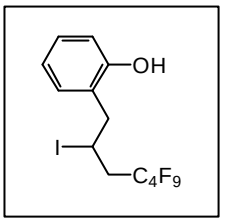
8.6.2 Synthesis of the semifluorinated 2-(2-iodoalkyl)phenols 30 and the 3-(2- iodoalkyl)anisoles: 35 and 39

2-(1H,1H,2H,3H,3H-Perfluoro-2-iodohexyl)phenol 30.1



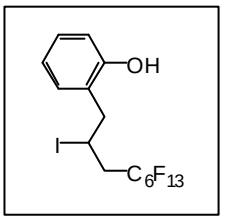
Prepared according to the general procedure **8.3.1** from allylphenol (7.6 g, 56.3 mmol), $Pd(PPh_3)_4$ (2.8 g, 4.0 mol %) and 1-iodoperfluoropropane (25 g, 84.5 mmol) in dry hexane (40 mL).
Yield: 23.4 g (67.6 %); yellow oil; $C_{12}H_{10}OIF_7$ (430).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.16-6.75 (m, 4 H, Ar-H), 5.40 (s, 1 H, OH), 4.69 (m, 1H, CHI), 3.26 (m, 2 H, CH_2Ar), 2.88 (m, 2 H, C**H**$_2CF_2$).

2-(1H,1H,2H,3H,3H-Perfluoro-2-iodoheptyl)phenol 30.2



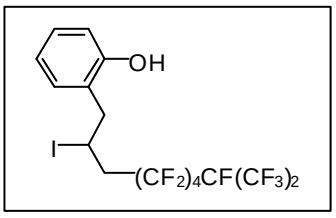
Prepared according to the general procedure **8.3.1** from allylphenol (8.0 g, 59.6 mmol), $Pd(PPh_3)_4$ (2.8 g, 4.0 mol %) and 1-iodoperfluorobutane (22.1 g, 64 mmol) in dry hexane (40 mL).
Yield: 28.6 g (100 %); yellow oil; $C_{13}H_{10}OIF_9$ (480).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.00 (m, 4 H, Ar-H), 5.60 (s, 1 H, OH), 4.70 (m, 1 H, CHI), 3.20 (m, 2 H, CH_2Ar), 2.80 (m, 2 H, CH_2CF_2).

2-(1H,1H,2H,3H,3H-Perfluoro-2-iodononyl)phenol 30.3



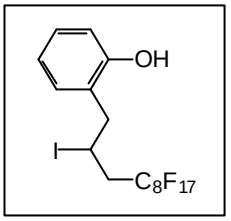
Prepared according to general procedure **8.3.1** from allylphenol (8.0 g, 59.6 mmol), $Pd(PPh_3)_4$ (2.8 g, 4.0 mol %) and 1-iodoperfluorohexane (28.5 g, 64 mmol) in dry hexane (40 mL).
Yield: 37.9 g (100 %); yellow oil; $C_{15}H_{10}OIF_{13}$ (580).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.00 (m, 4 H, Ar-H), 5.00 (s, 1 H, OH), 4.70 (m, 1 H, CHI), 3.30 (m, 2 H, CH_2Ar), 2.80 (m, 2 H, CH_2CF_2).

2-(1H,1H,2H,3H,3H-Perfluoro-2-iodoisodecyl)phenol 30.4



Prepared according to general procedure **8.3.1** from allylphenol (6 g, 44.7 mmol), $Pd(PPh_3)_4$ (1.4 g, 4.0 mol %) and 1-iodoperfluoroisoheptane (23.9 g, 48.1 mmol) in dry hexane (30 mL).
Yield: 28.2 g (100 %); yellow oil; $C_{16}H_{10}OIF_{15}$ (630).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.00 (m, 4 H, Ar-H), 5.00 (s, 1 H, OH), 4.70 (m, 1 H, CHI), 3.30 (m, 2 H, CH_2Ar), 2.80 (m, 2 H, CH_2CF_2).

2-(1H,1H,2H,3H,3H-Perfluoro-2-iodoundecyl)phenol <u>30.5</u>

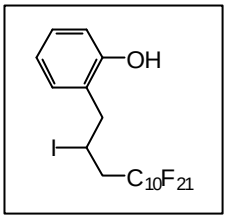


Prepared according to general procedure **8.3.1** from allylphenol (8 g, 59.6 mmol), $Pd(PPh_3)_4$ (2.8 g, 4.0 mol %) and 1-iodoperfluorooctane (34.9 g, 64 mmol) in dry hexane (40 mL).

Yield: 40.26g (99.3%); yellow oil; $C_{17}H_{10}OIF_{17}$ (680).

^{1}H-NMR (200 MHz, $CDCl_3$; *J*/Hz): δ = 7.00 (m, 4 H, Ar-H), 5.1 (s, 1 H, OH), 4.70 (m, 1 H, CHI), 3.30 (m, 2 H, CH_2Ar), 2.80(m, 2 H, CH_2CF_2).

2-(1H,1H,2H,3H,3H-Perfluoro-2-iodotridecyl)phenol <u>30.6</u>

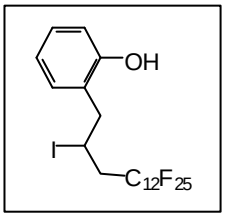


Prepared according to general procedure **8.3.1** from allylphenol (4 g, 29.8 mmol), $Pd(PPh_3)_4$ (1.4 g, 4.0 mol %) and 1-iodoperfluorodecane (20.6 g, 32 mmol) in dry hexane (20 mL).

Yield: 28.6 g (100 %); yellow oil; $C_{19}H_{10}OIF_{21}$ (780).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.00 (m, 4 H, Ar-H), 4.90 (s, 1 H, OH), 4.70 (m, 1 H, CHI), 3.30 (m, 2 H, $CH_2C\mathbf{H}_2CF_2$), 2.80 (m, 2 H, CH_2Ar).

2-(1H,1H,2H,3H,3H-Perfluoro-2-iodopentadecyl)phenol <u>30.7</u>

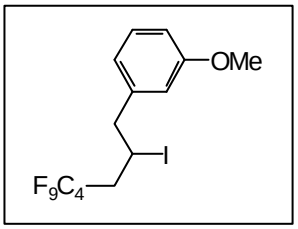


Prepared according to general procedure **8.3.1** from allylphenol (2.2 g, 16.3 mmol), $Pd(PPh_3)_4$ (0.7 g, 4.0 mol %) and 1-iodoperfluorododecane (12.2 g, 16.3 mmol) in dry hexane (20 mL).

Yield: 7.2 g (50.0 %); yellow waxy solid; $C_{21}H_{10}OIF_{25}$ (880).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.18 (m, 4 H, Ar-H), 4.89 (s, 1 H, OH), 4.69 (m, 1 H, CHI), 3.33 (m, 2 H, $CH_2C\mathbf{H}_2CF_2$), 2.95 (m, 2 H, CH_2Ar).

3-(1H,1H,2H,3H,3H-Perfluoro-2-iodoheptyl)anisole <u>35.1</u>

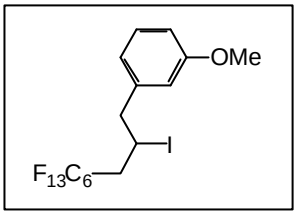


Prepared according to general procedure **8.3.1** from **<u>34</u>** (4 g, 27.0 mmol), $Pd(PPh_3)_4$ (1.2 g) and 1-iodoperfluorobutane (10.3 g, 29.7 mmol) in dry hexane (40 mL).

Yield: 13.3 g (100 %); yellow oil; $C_{14}H_{12}OIF_9$ (494).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.22 (m, 1 H, Ar-H), 6.80 (m, 3 H, Ar-H), 4.48 (m, 1 H, CHI), 3.81 (s, 3 H, CH_3), 3.23 (t, ^3J(H, H) 6.1, 2 H, $ArCH_2$), 2.77-3.12 (m, 2 H, CH_2).

3-(1H,1H,2H,3H,3H-Perfluoro-2-iodononyl)anisole 35.2

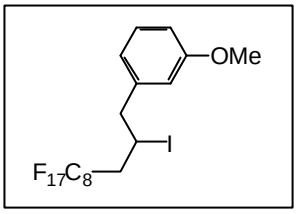


Prepared according to general procedure **8.3.1** from **34** (10 g, 67.6 mmol), $Pd(PPh_3)_4$ (3 g) and 1-iodoperfluorohexane (33.1 g, 74.3 mmol) in dry hexane (60 mL).

Yield: 36.4 g (100 %); yellow oil; $C_{16}H_{12}OIF_{13}$ (594).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.28 (m, 1 H, Ar-H), 6.86 (m, 3 H, Ar-H), 4.49 (m, 1 H, CHI), 3.84 (s, 3 H, CH_3), 3.25 (m, 2 H, $ArCH_2$), 2.98 (m, 4 H, CH_2).

3-(1H,1H,2H,3H,3H-Perfluoro-2-iodoundecyl)anisole 35.3

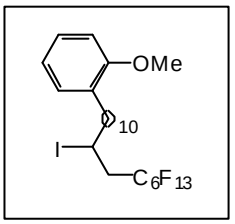


Prepared according to the general procedure **8.3.1** from **34** (4 g, 27.0 mmol), $Pd(PPh_3)_4$ (1.2 g) and 1-iodoperfluorooctane (16.2 g, 29.7 mmol) in dry hexane (40 mL).

Yield: 18.75 g (100 %); yellow oil; $C_{16}H_{12}OIF_{13}$ (594).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.24 (m, 1 H, Ar-H), 6.84 (m, 3 H, Ar-H), 4.45 (m, 1 H, CHI), 3.80 (s, 3 H, CH_3), 3.21 (t, 2 H, ^3J (H, H) 6.4, $ArCH_2$), 2.85 (m, 2 H, CH_2).

2-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H,8H,8H,9H, 9H,10H,10H,11H,12H,12H-perfluoro-11-iodooctadecyl)anisole 39



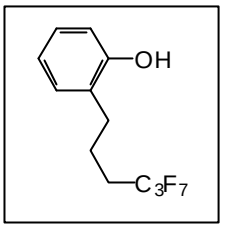
Prepared according to general procedure **8.3.1** from **38** (5.5 g, 20 mmol), $Pd(PPh_3)_4$ (1 g), and 1-iodoperfluorohexane (10.7 g, 24 mmol) in dry hexane (60 mL).

Yield: 12.3 g (85.4 %); yellow oil; $C_{25}H_{30}OIF_{13}$ (720).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.19 (m, 2 H, Ar-H), 6.89 (m, 2 H, Ar-H), 4.37 (m, 1 H, CHI), 3.84 (s, 3 H, CH_3), 2.64 (t, ^3J(H, H) 7.6, 2 H, $ArCH_2$), 1.84 (m, 2 H, CH_2), 1.63 (m, 2 H, CH_2), 1.33 (m, 16 H, 8 CH_2).

8.6.3 Synthesis of the semifluorinated alkylphenols and alkylanisoles: 31, 36 and 40

2-(1H,1H,2H,2H,3H,3H-Perfluorohexyl)phenol 31.1

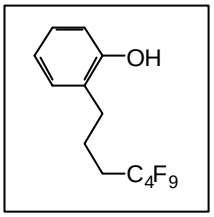


Prepared according to the general procedure **8.3.2** from **30.1** (23.3 g, 54.3 mmol) and $LiAlH_4$ (2 g) in dry diethyl ether (50 mL). Distillation yielded the pure product.

Yield: 15.6 g (74.2 %); yellow oil; bp: 87 °C / 0.35-0.29 mbar; $C_{12}H_{11}OIF_7$ (304).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.16 (m, 2 H, Ar-H), 6.91 (m, 1 H, Ar-H), 6.72 (d, ^3J (H, H) 7.69, 1 H, Ar-H), 4.87 (s, 1 H, OH), 2.77 (t, ^3J(H, H) 7.32, 2 H, C**H**$_2$Ar), 1.89-2.23 (m, 4 H, $CF_2C\mathbf{H}_2C\mathbf{H}_2$).

2-(1H,1H,2H,2H,3H,3H-Perfluoroheptyl)phenol 31.2

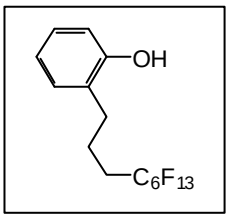


Prepared according to the general procedure **8.3.2** from **30.2** (28.6 g, 59.6 mmol) and $LiAlH_4$ (2 g) in dry diethyl ether (100 mL). Distillation yielded the pure product.

Yield: 15.6 g (74.2 %); yellow oil; bp: 85 °C / 0.5 mbar; $C_{13}H_{11}OIF_9$ (354).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.16-7.11 (m, 2 H, Ar-H), 6.91-6.95 (m, 1 H, Ar-H), 6.81 (d, ^3J(H, H) 7.8, 1 H, Ar-H), 4.88 (s, 1 H, OH), 2.75 (t, ^3J(H, H) 7.42, 2 H, C**H**$_2$Ar), 1.93-2.24 (m, 4 H, $CF_2C\mathbf{H}_2C\mathbf{H}_2$).

2-(1H,1H,2H,2H,3H,3H-Perfluorononyl)phenol 31.3

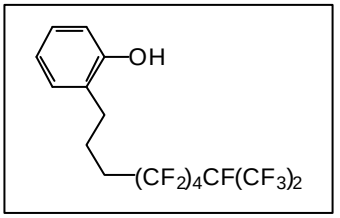


Prepared according to the general procedure **8.3.2** from **30.3** (37.9 g, 65.3 mmol) and $LiAlH_4$ (2.04 g) in dry diethyl ether (80 mL). Distillation yielded the pure product.

Yield: 21.2 g (78.3 %); colorless waxy solid; bp: 115 °C / 0.31 mbar (mp: 43-45 °C); $C_{13}H_{11}OIF_9$ (354).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.11 (m, 2 H, Ar-H), 6.89 (m, 1 H, Ar-H), 6.73 (m, 1 H, Ar-H), 4.69 (s, 1 H, OH), 2.72 (t, ^3J(H, H)7.6, 2 H, C**H**$_2$Ar), 1.93-2.19 (m, 4 H, $CF_2C\mathbf{H}_2C\mathbf{H}_2$).

2-(1H,1H,2H,2H,3H,3H-Perfluoroisodecyl)phenol 31.4



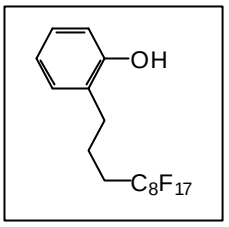
Prepared according to the general procedure **8.3.2** from **30.4** (28.2 g, 44.7 mmol) and $LiAlH_4$ (1.5 g) in dry diethyl ether (80 mL). Distillation yielded the pure product.

Yield: 24.7 g (75.6 %); colorless waxy solid; bp: 115 °C / 0.19

mbar; $C_{16}H_{11}OIF_{15}$ (504).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.18 (m, 2 H, Ar-H), 6.94 (m, 1 H, Ar-H), 6.75 (d, 1 H, ^3J(H, H) 8.2, Ar-H), 4.85 (s, 1 H, OH), 2.73 (t, ^3J(H, H) 7.1, 2 H, CH_2Ar), 1.87-2.25 (m, 4 H, $CH_2CH_2C_8F_{17}$).

2-(1H,1H,2H,2H,3H,3H-Perfluoroundecyl)phenol <u>31.5</u>



Prepared according to the general procedure **8.3.2** from **<u>30.5</u>** (40.3 g, 59.2 mmol) and $LiAlH_4$ (1.8 g) in dry diethyl ether (100 mL). Column chromatography (eluent: $CHCl_3$) yielded the pure product.

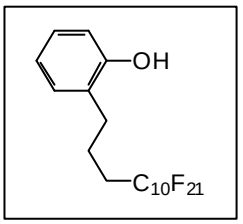
Yield: 21.7 g (66.4 %); colorless waxy solid; mp: 68 °C; $C_{17}H_{11}OIF_{17}$ (554).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.48 (m, 2 H, Ar-H), 6.92 (m, 1 H, Ar-H), 6.88 (d, 1 H, ^3J(H, H) 8.4, Ar-H), 4.68 (s, 1 H, OH), 2.72(t, ^3J(H, H) 7.4, 2 H, CH_2Ar), 1.99 (m, 4 H, CH_2CH_2 C_8F_{17}).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 153.6, 132.5, 127.7, 121.1, 115.3, 115.2 (Ar-H), 31.0 (CH_2CF_2), 29.2 (CH_2), 20.2 (CH_2).

^{19}F-NMR (188 MHz; $CDCl_3$; *J*/Hz): δ = -82.3 (overlapped t, 3 F, C**F**$_3$), -115.7 (m, 2 F, CH_2C**F**$_2$), -123.43 (m, 6 F, $CH_2CF_2(C$**F**$_2)_3$), -124.28 (m, 2 F, $CF_3(CF_2)_2C$**F**$_2$), -125.02 (m, 2 F, CF_3CF_2C**F**$_2$), -127.66 (m, 2 F, CF_3C**F**$_2$).

2-(1H,1H,2H,2H,3H,3H-Perfluorotridecyl)phenol <u>31.6</u>

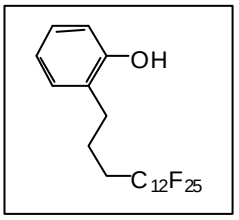


Prepared according to the general procedure **8.3.2** from **<u>30.6</u>** (23.2 g, 29.7 mmol) and $LiAlH_4$ (1 g) in dry diethyl ether (50 mL). Column chromatography (eluent: $CHCl_3$) yielded the pure product.

Yield: 10.0 g (51.5 %); colouless waxy solid; mp: 83 °C; $C_{19}H_{11}OF_{21}$ (654).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.24 (m, 2 H, Ar-H), 6.87 (m, 1 H, Ar-H), 6.74 (d, 1H, ^3J(H, H) 8.0, Ar-H), 4.70 (s, 1 H, OH), 2.70 (t, ^3J(H, H) 7.23, 2 H, CH_2Ar), 1.88-2.31(m, 4 H, $CH_2CH_2C_{10}F_{21}$).

2-(1H,1H,2H,2H,3H,3H-Perfluoropentadecyl)phenol <u>31.7</u>

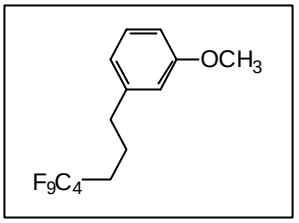


Prepared according to the general procedure **8.3.2** from **<u>30.7</u>** (7.2 g, 8.2 mmol) and $LiAlH_4$ (0.3 g) in dry diethyl ether (20 mL). The product was purified by recrystallization twice from $CHCl_3$.

Yield: 3.9 g (63.5 %); colorless waxy solid; mp: 110 °C; $C_{21}H_{11}OF_{25}$ (754).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.12 (m, 2 H, Ar-H), 6.87 (m, 1 H, Ar-H), 6.69 (d, 1H, ^3J(H, H) 8.0, Ar-H), 2.70 (t, ^3J(H, H) 7.69, 2 H, CH_2Ar), 1.89-2.24 (m, 4 H, $C\mathbf{H}_2C\mathbf{H}_2C_{12}F_{25}$).

3-(1H,1H,2H,2H,3H,3H-Perfluoroheptyl)anisole <u>36.1</u>

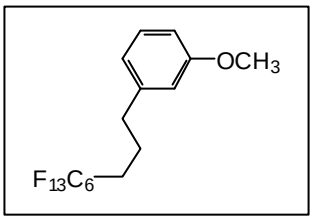


Prepared according to the general procedure **8.3.2** from **<u>35.1</u>** (21.6 g, 43.7 mmol) and $LiAlH_4$ (2.3 g) in dry diethyl ether (80 mL). Distillation yielded the pure product.

Yield: 6.0 g (60.4 %); yellow oil; bp: 125 °C / 11 mbar; $C_{14}H_{13}OF_9$ (368).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.31 (m, 1 H, Ar-H), 6.84 (m, 3 H, Ar-H), 3.85 (s, 3 H, CH_3), 2.73 (t, 2 H, ^3J(H, H) 7.0, $ArCH_2$), 2.27-1.92 (m, 4 H, 2 CH_2).

3-(1H,1H,2H,2H,3H,3H-Perfluorononyl)anisole <u>36.2</u>

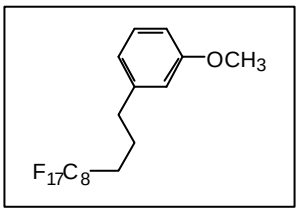


Prepared according to the general procedure **8.3.2** from **<u>35.2</u>** (36.4 g, 61.3 mmol) and $LiAlH_4$ (2.5 g) in dry diethyl ether (80 mL). Distillation yielded the pure product.

Yield: 13.7 g (47.7 %); yellow oil; bp: 84 °C / 0.18 mbar; $C_{16}H_{13}OF_{13}$ (468).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.29 (m, 1 H, Ar-H), 6.79 (m, 3 H, Ar-H), 3.79 (m, 3 H, CH_3), 2.67 (t, ^3J(H, H) 7.6, 2 H, $ArC\mathbf{H}_2$), 2.16-1.91 (m, 4 H, CH_2).

3-(1H,1H,2H,2H,3H,3H-Perfluoroundecyl)anisole <u>36.3</u>

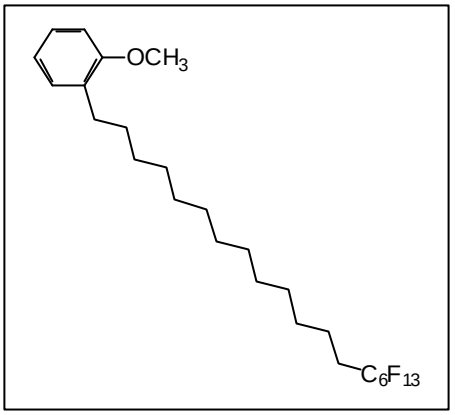


Prepared according to the general procedure **8.3.2** from **<u>35.3</u>** (18.7 g, 27.0 mmol) and $LiAlH_4$ (1.1 g) in dry diethyl ether (40 mL). Distillation yielded the pure product.

Yield: 7.0 g (45.6 %); yellow waxy solid; bp: 115 °C / 0.087 mbar; $C_{18}H_{13}OF_{17}$ (568).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.24 (m, 1 H, Ar-H), 6.79 (m, 3 H, Ar-H), 3.82 (s, 3 H, CH_3), 2.70 (t, 2 H, ^3J(H, H) 7.4, $ArCH_2$), 2.17-1.93 (m, 4 H, 2 CH_2).

2-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H,8H,9H,9H,10H,10H,11H, 11H,12H,12H-Perflurorooctadecyl)anisole 40



Prepared according to the general procedure **8.3.2** from **39** (12.3 g, 17.1mmol) and $LiAlH_4$ (1 g) in dry diethyl ether (40 mL). Column chromatography (eluent: $CHCl_3$) yielded the pure product.

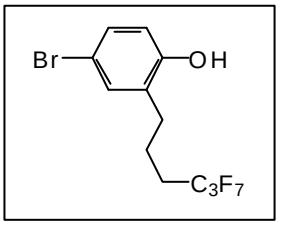
Yield: 7.16 g (70.2 %); colorless waxy solid; $C_{25}H_{31}OF_{13}$ (594).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.26 (m, 2 H, Ar-H), 6.92 (m, 2 H, Ar-H), 3.85 (s, 3 H, CH_3), 2.62 (t, 2 H, ^3J(H, H) 7.23, $ArCH_2$), 2.09 (m, 2 H, CH_2), 1.64 (m, 2 H, CH_2), 1.49 (m, 18 H, 9 CH_2).

8.6.4 Synthesis of the 4-bromophenols 32 and 4-bromoanisoles 33, 37, 41 and 43

Bromination of substituted phenols - general procedure 8.6.4.1: A mixture of the appropriate semifluoroalklyphenol (36.2 mmol), acetic acid (99 mL) and 33 % HBr in acetic acid (50 mL) was cooled in an ice bath to –5 °C. Then DMSO (50 mL) was added dropwise. The mixture was stirred at 5-10 °C for 30 min, then saturated aqueous $NaHCO_3$ solution (100 mL) was added to quench the reaction. The mixture was extracted with diethyl ether (3×100 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution until pH = 6-7. Then the solution was washed with H_2O (3×75 mL), brine (3×75 mL), dried over Na_2SO_4 and the solvent was evaporated.

4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluorohexyl)phenol 32.1

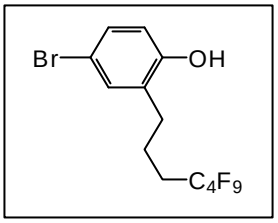


Prepared according to the general procedure **8.6.4.1** from **31.1** (11 g, 36.2 mmol), acetic acid (99 mL) and 33 % HBr in acetic acid (50mL), DMSO (50 mL). Column chromatography yielded pure product (eluent: $CHCl_3$/CH_3OH 10:1).

Yield: 11.59 g (83.6 %); yellow oil; $C_{12}H_{10}OBrF_7$ (383).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.19 (m, 2 H, Ar-H), 6.57 (d, 1 H, ^3J(H, H) 8.4, Ar-H), 5.31 (br s, 1 H, OH), 2.61 (t, ^3J(H, H) 7.3, 2 H, C**H**$_2$Ar), 2.22-1.83 (m, 4 H, $CF_2C\mathbf{H}_2C\mathbf{H}_2$).

4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluoroheptyl)phenol 32.2

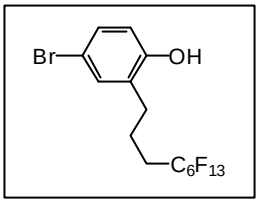


Prepared according to the general procedure **8.6.4.1** from **31.2** (15.7 g, 44.2 mmol), acetic acid (100 mL), 33 % HBr in acetic acid (60 mL), DMSO (60 mL). Column chromatrography yielded pure product (eluent: $CHCl_3/CH_3OH$ 10:1).

Yield: 12.3 g (64.1 %); yellow oil; $C_{13}H_{10}OBrF_9$ (433).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.21-7.15 (m, 2 H, Ar-H), 6.63 (d, ^3J(H, H) 8.4, 1 H, Ar-H), 5.27 (br s, 1 H, OH), 2.63 (t, ^3J(H, H) 7.6, 2 H, C**H**$_2$Ar), 2.03-2.15 (m, 2 H, $CF_2C\mathbf{H}_2$), 1.94-1.86 (m, 2 H, $CF_2CH_2C\mathbf{H}_2$).

4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluorononyl)phenol 32.3

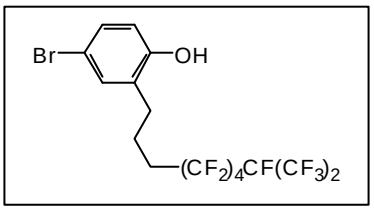


Prepared according to the general procedure **8.6.4.1** from **31.3** (22 g, 48.5 mmol), acetic acid (133 mL), 33 % HBr in acetic acid (66 mL), DMSO (66 mL). Distillation yielded the pure product.

Yield: 22.3 g (86.1 %); bp: 140 °C / 0.31 mbar; yellow oil; $C_{15}H_{10}OBrF_{13}$ (533).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.23 (d, ^4J(H, H) 2.4, 1 H, Ar-H), 7.18 (dd, ^3J(H, H) 8.4, ^4J(H, H) 2.4, 1 H, Ar-H), 6.64 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 5.00 (s, 1 H, OH), 2.70 (t, ^3J(H, H) 7.4, 2 H, CH_2Ar), 2.00 (m, 4 H, $CH_2CH_2CF_2$).

4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluoroisodecyl)phenol 32.4

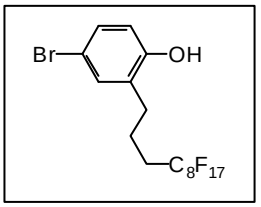


Prepared according to the general procedure **8.6.4.1** from **31.4** (11.5 g, 22.8 mmol), acetic acid (50 mL), 33 % HBr in acetic acid (30 mL), DMSO (30 mL). Column chromatography (eluent: $CHCl_3/CH_3OH$ 10:2) yielded the pure product.

Yield: 10.4 g (78.3 %); yellow oil; $C_{16}H_{10}OBrF_{15}$ (583).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.16-7.24 (m, 2 H, Ar-H), 6.63 (d, 1 H, ^3J(H, H) 8.4, Ar-H), 5.37 (br s, 1 H, OH), 2.66 (t, ^3J(H, H) 7.61, 2 H, C**H**$_2$Ar), 2.03-2.16 (m, 2 H, $CF_2C\mathbf{H}_2$), 1.94-1.86 (m, 2 H, $CF_2CH_2C\mathbf{H}_2$).

4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)phenol 32.5



Prepared according to the general procedure **8.6.4.1** from **31.5** (21.56 g, 38.97 mmol), acetic acid (52 mL), 33 % HBr in acetic acid (26 mL), DMSO (26 mL). Column chromatography ($CHCl_3/CH_3OH$ 10: 2) yielded the pure product.

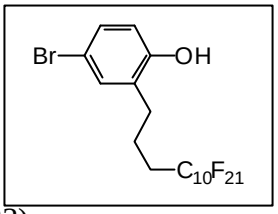
Yield: 20.2 g (81.9 %); yellow solid; mp: 61 °C; $C_{17}H_{10}OBrF_{17}$ (633).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.24 (s, 1 H, Ar-H), 7.22 (dd, ^3J(H, H) 8.4, ^4J(H, H) 2.3, 1 H, Ar-H), 6.62 (d, ^3J(H, H) 8.4, 1 H, Ar-H), 4.80 (s, 1 H, OH), 2.66 (t, ^3J(H, H) 7.6, 2 H, C**H**$_2$Ar), 2.16 (m, 2 H, C**H**$_2$CF$_2$), 1.93 (m, 4 H, 2 C**H**$_2$).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 152.7, 133.1, 130.4, 129.63, 117.0, 114.0 (Ar-C), 30.4 (t, CH_2CF_2), 29.2 (CH_2), 20.2 (CH_2).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -82.3 (overlapped t, 3 F, CF_3), -115.7 (m, 2 F, CH_2CF_2), -123.43 (m, 6 F, $CH_2CF_2(CF_2)_3$), -124.28 (m, 2 F, $CF_3(CF_2)_2CF_2$), -125.0 (m, 2 F, $CF_3CF_2CF_2$), -127.7 (m, 2 F, CF_3CF_2).

4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluorotridecyl)phenol 32.6

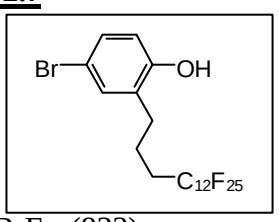


Prepared according to the general procedure **8.6.4.1** from **31.6** (10 g, 15.27 mmol), acetic acid (35 mL), 33 % HBr in acetic acid (21 mL), DMSO (21 mL). Column chromatography ($CHCl_3$/CH_3OH 10:2) yielded the pure product.

Yield: 7.1 g (59.5 %); colorless solid; mp: 90 °C; $C_{19}H_{10}OBrF_{21}$ (733).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.22 (d, ^3J(H, H) 2.54, 1 H, Ar-H), 7.19 (dd, ^3J(H, H) 8.4, ^3J(H, H) 2.54, 2 H, Ar-H), 4.79 (s, 1 H, OH), 2.66 (t, ^3J(H, H) 7.6, 2 H, C**H**$_2$Ar), 1.87-2.16 (m, 4 H, CF_2C**H**$_2$C**H**$_2$)

4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluoropentadecyl)phenol 32.7



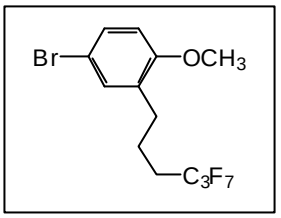
Prepared according to the general procedure **8.6.4.1** from **31.7** (3.9 g, 5.17 mmol), acetic acid (5 mL), 33 % HBr in acetic acid (10 mL), DMSO (5 mL). The product was purified by twice recrystallization from hexane.

Yield: 3.82 g (88.6 %); colorless waxy solid; mp: 115 °C; $C_{21}H_{10}OBrF_{25}$ (833).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.21 (d, ^3J(H, H) 2.56, 1 H, Ar-H), 6.64 (dd, ^3J(H, H) 8.06, ^3J(H, H) 2.54, 2 H, Ar-H), 5.15 (br s, 1 H, OH), 2.66 (t, ^3J(H, H) 7.7, 2 H, C**H**$_2$Ar), 1.84-2.23 (m, 4 H,CF_2C**H**$_2$C**H**$_2$)

Etherification of semifluoroalkylsubstituted phenols - general procedure 8.6.4.2: MeI (45.4 mmol, 1.5eq) was added to a mixture of the appropriate 4-bromo-2-semifluoroalkylphenol (30.3 mmol) and K_2CO_3 (90.8 mmol) in dry CH_3CN (50 mL), while stirring under an argon atmosphere. The mixture was refluxed for 2 h (TLC). The CH_3CN was distilled off. Water (100 mL) and diethyl ether (100 mL) were added to the residue. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2×70 mL) and the combined extracts were washed with H_2O (2×50 mL), dried over Na_2SO_4, and finally the diethyl ether was distilled off. The crude product was further purified by column chromatography.

4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluorohexyl)anisole 33.1

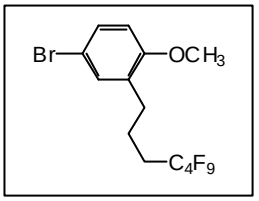


Prepared according to the general procedure **8.6.4.2** from **32.1** (11.6 g, 30.3 mmol), MeI (6.4 g, 45.4 mmol, 1.5 eq) and K_2CO_3 (12.5 g, 90.8 mmol) in dry CH_3CN (50 mL). Purification by column chromatography (eluent: petroleum ether).

Yield: 8.8 g (73.3 %); yellow oil; $C_{13}H_{12}OBrF_7$ (397).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.22-7.33 (m, 2 H, Ar-H), 6.69 (d, 1 H, ^3J(H, H) 8.4, Ar-H), 3.79 (s, 3 H, CH_3), 2.66 (t, ^3J(H, H) 7.3, 2 H, CH_2Ar), 2.13-1.83 (m, 4 H, 2 CH_2).

4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluoroheptyl)anisole 33.2

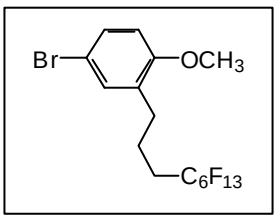


Prepared according to the general procedure **8.6.4.2** from **32.2** (4 g, 9.2 mmol), MeI (2.0 g, 13.9 mmol, 1.5 eq) and K_2CO_3 (3.8 g, 27.6 mmol) in dry CH_3CN (30 mL). Purification by preparative centrifugal thin layer chromatography (eluent: petroleum ether).

Yield: 2.7 g (65.4 %); yellow oil; $C_{14}H_{12}OBrF_9$ (447).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.25-7.33 (m, 2 H, Ar-H), 6.70 (d, 1H, ^3J(H, H) 8.4, Ar-H), 3.80 (s, 3 H, CH_3), 2.42 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 1.86-2.25 (m, 4 H, $CF_2C\mathbf{H}_2C\mathbf{H}_2$).

4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluorononyl)anisole 33.3

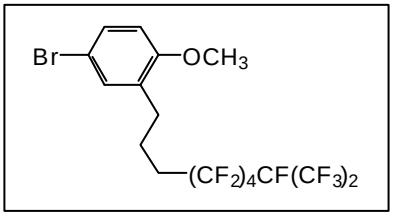


Prepared according to the general procedure **8.6.4.2** from **32.3** (4 g, 7.5 mmol), MeI (1.6 g, 11.3 mmol) and K_2CO_3 (5.0 g, 36.2 mmol) in dry CH_3CN (30 mL). Purification by preparative centrifugal thin layer chromatography (eluent: petroleum ether).

Yield: 3.8 g (93.2 %); yellow oil; $C_{16}H_{12}OBrF_{13}$ (547).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.30 (m, 2 H, Ar-H), 6.73 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 3.78 (s, 3 H, OCH_3), 2.64 (t, ^3J(H, H) 7.4, 2 H, CH_2Ar), 1.86-2.21 (m, 4 H, $CH_2CH_2CF_2$).

4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluoroisodecyl)anisole 33.4

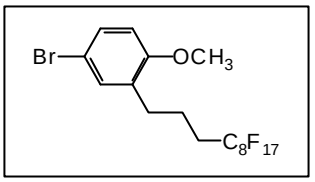


Prepared according to the general procedure **8.6.4.2** from **32.4** (4.0 g, 6.9 mmol), MeI (1.5 g, 10.3 mmol) and K_2CO_3 (5.0 g, 36.2 mmol) in dry CH_3CN (20 mL). Purification by preparative centrifugal thin layer chromatography (eluent: petroleum ether).

Yield: 3.1 g (75.1 %); yellow oil; $C_{17}H_{12}OBrF_{15}$ (597).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.22-7.32 (m, 2 H, Ar-H), 6.74 (d, 1 H, ^3J(H, H) 8.6, Ar-H), 3.79 (s, 3 H, CH_3), 2.65 (t, ^3J(H, H) 7.62, 2 H, C**H**$_2$Ar), 1.79-2.22 (m, 4 H, CF_2C**H**$_2C$**H**$_2$).

4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)anisole 33.5

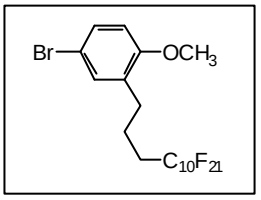


Prepared according to the general procedure **8.6.4.2** from **32.5** (7.2 g, 11.4 mmol), MeI (2.4 g, 17.1 mmol) and K_2CO_3 (5.0 g, 36.2 mmol) in dry CH_3CN (40 mL). Purification by preparative centrifugal thin layer chromatography (eluent: petroleum ether).

Yield: 6.1 g (83.0 %); yellow oil; $C_{18}H_{12}OBrF_{17}$ (647).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.30 (dd, ^3J(H, H) 8.6, *J*(H, H) 2.5, 1 H, Ar-H), 7.22 (d, *J*(H, H) 2.4, 1 H, Ar-H), 6.72 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 3.78 (s, 3 H, CH_3), 2.64 (t, ^3J(H, H) 7.61, 2 H, $ArCH_2$), 2.14-1.89 (m, 4 H, CH_2).

4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluorotridecyl)anisole 33.6



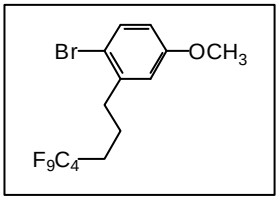
Prepared according to the general procedure **8.6.4.2** from **32.6** (4.0 g, 5.5 mmol), MeI (1.2 g, 8.2 mmol) and K_2CO_3 (3.0 g, 21.7 mmol) in dry CH_3CN (40 mL). Purification by preparative centrifugal thin layer chromatography (eluent: petroleum ether).

Yield: 3.6 g (87.5 %); colorless solid; mp: 52 °C; $C_{20}H_{12}OBrF_{21}$ (747).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.29 (dd, ^3J(H, H) 8.8, *J*(H, H) 2.35, 1 H, Ar-H), 7.21 (d, *J*(H, H) 2.34, 1 H, Ar-H), 6.72 (d, ^3J(H, H) 8.8, 1 H, Ar-H), 3.78 (s, 3 H, CH_3), 2.64 (t, ^3J(H, H) 7.42, 2 H, Ar**CH$_2$**), 2.15-1.84 (m, 4 H, CH_2).

Bromination of semifluoroalkylsubstituted anisoles - general procedure 8.6.4.3: A mixture of the appropriate semifluoroalkyl anisole (25.1 mmol), NBS (27.6 mmol, 1.1 eq) in dry CH_3CN (80 mL) was stirring for 8 h at RT. Afterwards the solvent was distilled off at a rotatory evaporator. Carbon tetrachloride was added to the residue. The solid (succinimide) was filleted off and washed with carbon tetrachloride thoroughly.

4-Bromo-3-(1H,1H,2H,2H,3H,3H-perfluoroheptyl)anisole 37.1

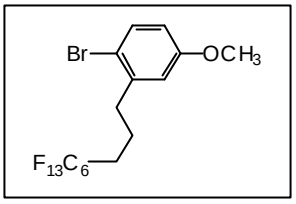


Prepared according to the general procedure **8.6.4.3** from **36.1** (9.3 g, 25.1 mmol), NBS (4.9 g, 27.6 mmol), dry CH_3CN (80 mL). *Vacuo* distillation yielded the product.

Yield: 8.9 g (79.3 %); Yellow oil; bp: 120 °C / 0.035 mbar; $C_{14}H_{12}OBrF_9$ (447).

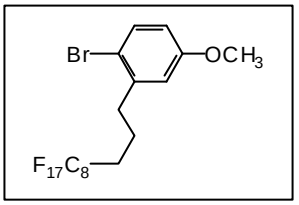
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.44 (d, ^3J(H, H) 8.8, 1 H, Ar-H), 6.77 (d, ^4J(H, H) 2.9, 1 H, Ar-H), 6.67 (dd, ^3J(H, H) 8.8, ^4J(H, H) 2.9, 1 H, Ar-H), 3.77 (s, 3 H, CH_3), 2.79 (t, ^3J(H, H) 7.6, 2 H, $ArCH_2$), 2.29-1.87 (m, 4 H, 2 CH_2).

4-Bromo-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)anisole <u>37.2</u>



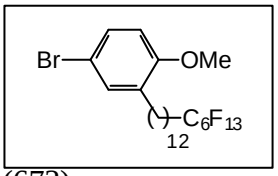
Prepared according to the general procedure **8.6.4.3** from **<u>36.2</u>** (10.2 g, 21.8 mmol), NBS (4.3 g, 24.0 mmol, 1.1eq), CH_3CN (80 mL). The crude product was used for the next step.
Yield: 9.2 g (82.1 %); yellow oil; $C_{16}H_{12}OBrF_{13}$ (547).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.43 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 6.58 (d, ^3J(H, H) 2.9, 1 H, Ar-H), 5.67 (dd, ^4J(H, H) 3.12, ^3J(H, H) 8.8, 1 H, Ar-H), 3.77 (s, 3 H, CH_3), 2.77 (t, ^3J(H, H) 7.43, $ArCH_2$), 2.18-1.93 (m, 4 H, CH_2).

4-Bromo-3-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)anisole <u>37.3</u>



Prepared according to the general procedure **8.6.4.3** from **<u>36.3</u>** (16.9 g, 29.8 mmol), NBS (5.8 g, 32.8 mmol, 1.1 eq), CH_3CN (120 mL). The crude product was used for the next step.
Yield: 17.0 g (88.1 %); yellow solid; $C_{18}H_{12}OBrF_{13}$ (647).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.43 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 6.74 (d, ^4J(H, H) 2.9, 1 H, Ar-H), 6.64 (dd, ^3J(H, H) 8.8, ^4J(H, H) 2.9, 1 H, Ar-H), 3.76 (s, 3 H, CH_3), 2.77 (t, 2 H, ^3J(H, H) 7.62, $ArCH_2$), 2.27-1.85 (m, 4 H, 2 CH_2).

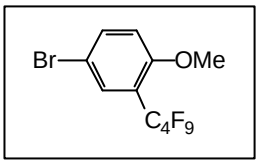
4-Bromo-2-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H7H,7H,8H,8H,9H,9H, 10H,10H,11H,11H,12H,12H-perfluorooctadecyl)anisole <u>41</u>



Prepared according to the general procedure **8.6.4.3** from **<u>40</u>** (7.2 g, 12.0 mmol), NBS (2.4 g, 13.2 mmol, 1.1 eq), CH_3CN (60 mL). Recrystallisation from ethanol yielded the pure product.
Yield: 2.4g (29.6 %); yellow waxy solid; mp: 100 °C; $C_{25}H_{30}OBrF_{13}$ (673).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.10 (m, 1 H, Ar-H), 6.86 (m, 1 H, Ar-H), 6.71 (m, 1 H, Ar-H), 3.78 (s, 3 H, CH_3), 2.59 (m, 2 H, $ArCH_2$), 2.08 (m, 2 H, CH_2), 1.58-1.27 (m, 20 H, 10 CH_2).

Bromination of perfluoroalkylsubstituted anisoles - general procedure 8.6.4.4: A appropriate perfluoroalkylsubstituted anisole (21.9 mmol) dissolved in CF_3COOH (20 mL) was cooled with ice bath. NBS (32.8 mmol, 1.5 eq) was added portionwise with stirring. Stirring was continued for 30 min at 0 °C. Then the mixture was poured into ice water. The phases were separated, the aqueous phase was extracted with methylene chloride (3×50 mL). The combined organic phases were washed with brine and dried over $CaCl_2$.

4-Bromo-2-perfluoropropylanisole 43.1

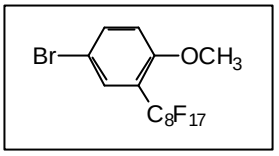


Prepared according to the general procedure **8.6.4.4** from **42.1** (7.1 g, 21.9 mmol) and NBS (5.8 g, 32.8 mmol, 1.5 eq) in CF_3COOH (20 mL). Purification was done by fractional distillation.

Yield: 5.8 g (65.2 %); yellow oil; bp: 117 °C / 12 mbar; $C_{11}H_6OBrF_9$ (405).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.03 (m, 2 H, Ar-H), 6.84 (m, 1 H, Ar-H), 3.82 (s, 3 H, CH_3).

4-Bromo-2-perfluorooctylanisole 43.2



Prepared according to the general procedure **8.6.4.4** from **42.2** (1.3 g, 3 mmol) and NBS (0.7 g, 4.1 mmol, 1.4 eq) in CF_3COOH (13 mL). The crude product was used without further purification.

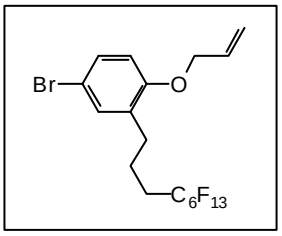
Yield: 1.3 g (72.1 %); yellow oil; $C_{15}H_6OBrF_{17}$ (605).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.58 (m, 2 H, Ar-H), 6.87 (m, 1 H, Ar-H), 3.81 (s, 3 H, CH_3).

8.6.5 Synthesis of the 1-allyloxy-4-bromo-2-semifluoralkylbenzenes 45 and 6-[4-bromo-2-(1H,1H,2H,2H,3H,3H-perfluorononyl)phenyloxy]-4-oxahexene 62

Etherification - general procedure 8.6.5: The appropriated alk(en)yl bromide (6.7 mmol for each OH-group) was added under an argon atmosphere to a mixture of the appropriate phenol (5.63 mmol) and K_2CO_3 (14.5 mmol) in dry CH_3CN (20 mL). The mixture was refluxed for 2 h (TLC). CH_3CN was evaporated in *vacuo*. Water (100 mL) and diethyl ether (100 mL) were added to the residue. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3×100 mL). The combined extracts were washed with H_2O (3×75 mL), dried over Na_2SO_4 and the solvent were evaporated in *vacuo*. Purification of the product was done by chromatography.

1-Allyloxy-4-bromo-2-(1H,1H,2H,2H,3H,3H-perfluorononyl)benzene 45.1



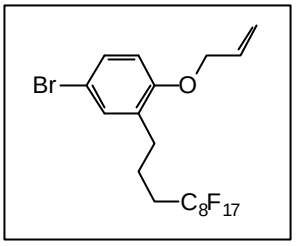
Prepared according to the general procedure **8.6.5** from **32.3** (3.0 g, 5.63 mmol), allylbromide (0.817 g, 6.75 mmol) and K_2CO_3 (2.0 g,14.5 mmol) in dry CH_3CN (20 mL). Purification by preparative centrifugal thin layer chromatography (eluent: petroleum ether).

Yield: 3.0 g (92.9 %); yellow oil; $C_{18}H_{14}F_{13}BrO$ (573).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.29-7.22 (dd, ^4J(H, H) 2.5, ^3J(H, H) 5.86, 2 H, Ar-H), 6.68 (d, 1 H, ^3J(H, H) 8.4, 1 H, Ar-H), 6.11-5.92 (m, 1 H, CH=), 5.24-5.43 (m, 2 H,

CH_2=), 4.49 (m, 2 H, OCH_2), 2.67 (t, ^3J(H, H) 7.42, 2 H, CH_2Ar), 1.82-2.27 (m, 4 H, CH_2 CH_2).

1-Allyloxy-4-bromo-2-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)benzene 45.2

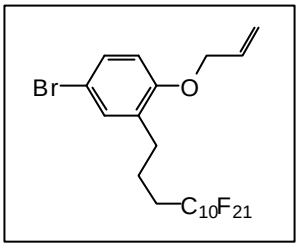


Prepared according to the general procedure **8.6.5** from **32.5** (10 g, 15.8 mmol), allylbromide (2.3 g, 19.0 mmol) and K_2CO_3 (4.0 g, 29.0 mmol) in dry CH_3CN (60 mL). Purification by column chromatography (eluent: $CHCl_3$).

Yield: 8.19 g (79.8 %); yellow oil; $C_{20}H_{14}F_{17}BrO$ (673).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.26 (m, 2 H, Ar-H), 6.75 (d, ^3J(H, H) 8.2, 1 H, Ar-H), 6.13-5.45 (m, 1 H, CH=), 5.45-5.27 (m, 2 H, CH_2=), 4.54 (m, 2 H, CH_2O), 2.75 (t, 2 H, ^3J(H, H) 7.2, C**H**$_2$Ar), 2.18-1.88 (m, 4 H, 2 C**H**$_2$).

1-Allyloxy-4-bromo-2-(1H,1H,2H,2H,3H,3H-perfluorotridecyl)benzene 45.3

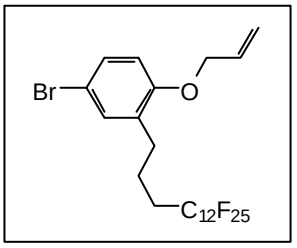


Prepared according to the general procedure **8.6.5** from **32.6** (21.0 g, 28.6 mmol), allylbromide (5.2 g, 42.9 mmol) and K_2CO_3 (20 g, 149.2 mmol) in dry CH_3CN (100 mL). Purification by chromatography (eluent: $CHCl_3$).

Yield: 21.0g (95.0 %); colorless waxy solid; mp: 39 °C, $C_{20}H_{14}F_{21}BrO$ (873).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.26 (m, 2 H, Ar-H), 6.73 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 6.03 (m, 1 H, CH=), 5.41-5.27 (m, 2 H, CH_2=), 4.53 (m, 2 H, CH_2O), 2.69 (t, 2 H, ^3J(H, H) 7.6, C**H**$_2$Ar), 2.08-1.93 (m, 4 H, 2 C**H**$_2$).

1-Allyloxy-4-bromo-2-(1H,1H,2H,2H,3H,3H-perfluoropentadecyl)benzene 45.8

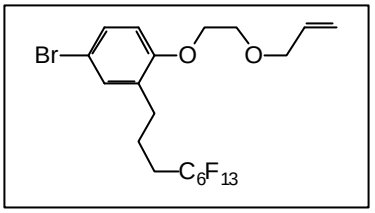


Prepared according to the general procedure **8.6.5** from **32.7** (3.76 g, 4.51 mmol), allylbromide (0.5 g, 4.3 mmol) and K_2CO_3 (2 g, 1.5 mmol) in dry CH_3CN (30 mL). Purification by chromatography (eluent: $CHCl_3$).

Yield: 3.2 g (81.2 %); colorless waxy solid; mp: 84 °C; $C_{24}H_{14}F_{25}BrO$ (873).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.23 (m, 2 H, Ar-H), 6.72 (d, ^3J(H, H) 8.3, 1 H, Ar-H), 6.10 (m, 1 H, CH=), 5.41-5.24 (m, 2 H, CH_2=), 4.49 (m, 2 H, CH_2O), 2.71 (t, 2 H, ^3J(H, H) 7.3, C**H**$_2$Ar), 2.21-1.81 (m, 4 H, 2 C**H**$_2$).

6-[4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluorononyl)phenyloxy]-4-oxahexene 62



Prepared according to the general procedure **8.6.5** from **32.3** (3.0 g, 5.63 mmol), 1-toluenesulfonyloxy-3-oxa-5-hexene (1.73 g, 6.76 mmol) and K_2CO_3 1.0 g (7.24 mmol) in dry CH_3CN (30 mL). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

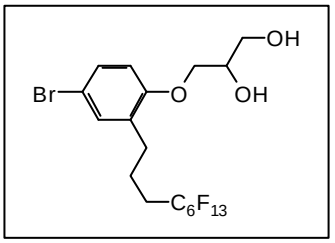
Yield: 2.8 g (82.5 %); yellow oil; $C_{20}H_{18}O_2F_{13}Br$ (617).

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.21-7.35 (m, ^3J(H, H) 8.4, 2 H, Ar-H), 6.73 (d , ^3J(H, H) 8.6, 1 H, Ar-H), 5.99-5.83 (m, 1H, CH=), 5.15-5.33 (m, 2 H, CH_2=), 4.11-4.03 (m, 4 H, OC**H**$_2$C**H**$_2$O), 3.75 (m, 2 H, CH_2), 2.66 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.29-1.67 (m, 4 H, C**H**$_2$C**H**$_2$$CF_2$).

8.6.6 Synthesis of the 3-[4-bromo-2-(semifluoroalkyl)phenyloxy]propane-1,2-diols 47

Dihydroxylation - general procedure 8.6.6: The appropriate 1-allyloxy-4-bromo-2-semifluoroalkylbenzene (1.4 mmol), and NMMNO (1.2 mL, 7.1 mmol of 60 % solution in water) were dissolved in acetone (20 mL). Osmium tetroxide (1.25ml of a 0.004 M solution in *tert*-butanol) was added, and the solution was stirred 2 h at RT. Afterwards, saturated aqueous Na_2SO_3 solution (5 mL) was added and the mixture was stirred for 30 min at RT. The mixture was filtered over a silica bed. The residue was carefully washed twice with acetone (50 mL), and the solvent was evaporated in *vacuo*. The residue was dissolved in ethyl acetate (100 mL). The solution was washed with 10 % aqueous H_2SO_4 (30 ml), satuated $NaHCO_3$ solution (30 mL) and H_2O (30 mL). The organic layer was dried over $NaSO_4$, and the solvent was evaporated in *vacuo*. Purification was done by recrystallization.

3-[4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluorononyl)phenyloxy]propane-1,2-diol 47.1

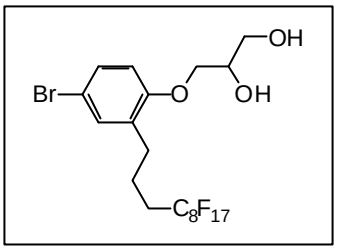


Prepared according to the general procedure **8.6.6** from **45.1** (3.0 g, 5.23 mmol), NMMNO (2.5 mL, 60 % solution in water) and osmiumtetroxide (2.5 mL, 0.004 M) in acetone (25 mL). Purification by recrystallization from hexane.

Yield: 2.1 g (65.6 %); colorless solid; mp: 56 °C; $C_{18}H_{16}F_{13}BrO_3$ (607).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.30 (m, 2 H, Ar-H), 6.75 (d, 1 H, ^3J(H, H) 8.6, Ar-H), 4.02 (m, 3 H, $ArOCH_2CH$), 3.76 (m, 2 H, CH_2OH), 2.65 (t, ^3J(H, H) 7.4, 2 H, $CH_2C_6F_{13}$), 2.22-1.83 (m, 4 H, CH_2CH_2).

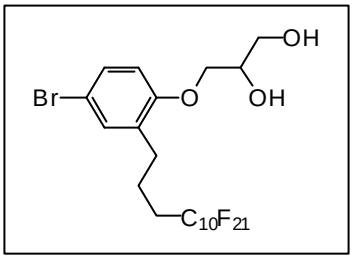
3-[4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)phenyloxy]propane-1,2-diol 47.2



Prepared according to the general procedure **8.6.6** from **45.2** (3.0 g, 12.5 mmol), N-methylmorpholine-N-oxide (3 mL, 60 % solution in water) and osmiumtetroxide (1.7 mL, 0.004 M) in acetone (50 mL). Purification by crystallization from hexane.
Yield: 2.1 g (65.6 %); colorless solid; mp: 48 °C-50 °C; $C_{20}H_{16}O_3F_{17}Br$ (707).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.30 (m, 2 H, Ar-H), 6.75 (d, 1 H, ^3J(H, H) 8.6, Ar-H), 4.02 (m, 3 H, $ArOCH_2CH$), 3.76 (m, 2 H, CH_2OH), 2.65 (t, ^3J(H, H) 7.4, 2 H, CH_2Ar), 2.22-1.83 (m, 4 H, 2 C**H**$_2$).

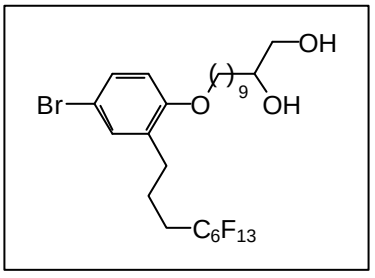
3-(4-Bromo-2-1H,1H,2H,2H,3H,3H-perfluorotridecylphenyloxy)propane-1,2-diol 47.3



Prepared according to the general procedure **8.6.6** from **45.3** (20.8 g, 27.4 mmol), N-methylmorpholine-N-oxide (3 mL, 60 % solution in water) and osmiumtetroxide (3 mL 0.004 M) in acetone (50 mL). Purification by recrystallization from hexane.
Yield: 14.1 (63.7 %); transition temperatures (°C): Cr 77 SmA 100 Iso.

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.27 (dd, ^3J(H, H) 8.8, *J*(H, H) 2.2, 1 H, Ar-H), 7.02 (d, 1 H, ^3J(H, H) 8.7, Ar-H), 6.90 (d, 1 H, ^3J(H, H) 8.8, Ar-H), 4.88 (d, ^3J(H, H) 4.8, 1 H, OH), 4.60 (t, ^3J(H, H) 5.5, 1 H, OH), 4.01-3.75 (m, 3 H, $ArOCH_2CH$), 3.46 (m, 2 H, C**H**$_2$OH), 2.64 (t, ^3J(H, H) 7.3, 2 H, CH_2Ar), 2.25-1.74 (m, 4 H, CH_2CH_2).

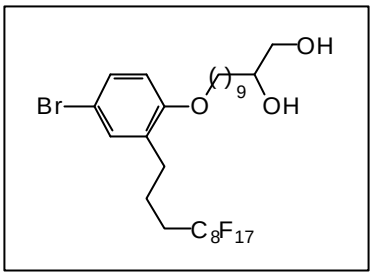
11-(4-Bromo-2-1H,1H,2H,2H,3H,3H-perfluorononylphenyloxy)undecane-1,2-diol 47.4



Prepared according to the general procedure **8.6.5** from **32.3** (2.5 g, 4.7 mmol), 11-bromo-undecyl-1,2-diol (1.2 g, 4.7 mmol) and K_2CO_3 (2.0 g, 14.5 mmol) in dry CH_3CN (40 mL). Purification by recrystallization from ethanol.
Yield: 1.4 g (52.2 %); colorless solid; mp: 35 °C; $C_{26}H_{32}O_3F_{13}Br$ (719).

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 7.34 (m, 2 H, Ar-H), 6.97 (d, 1 H, Ar-H), 4.38 (t, ^3J(H, H) 5.7, 1 H, OH), 4.25 (d, ^3J(H, H) 4.68, 1 H, OH), 3.94 (m, 2 H, ArOC**H**$_2$), 3.30 (m, 3 H, CH_2O, CHOH), 2.60 (t, ^3J(H, H) 7.8, 2 H, C**H**$_2$Ar), 2.20 (m, 2 H, ArC**H**$_2$), 1.75 (m, 4 H, 2 CH_2), 1.35 (m, 14 H, 7 CH_2).

11-(4-Bromo-2-1H,1H,2H,2H,3H,3H-perfluoroundecylphenyloxy)-undecane-1,2-diol 47.5

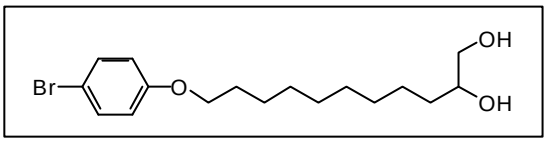


Prepared according to the general procedure **8.6.5** from **32.4** (2.0 g, 3.2 mmol), 11-bromoundecane-1,2-diol (0.8 g, 3.2 mmol), K_2CO_3 (2.0 g, 14.5 mmol) and KI (1 g) in dry CH_3CN (40 mL). Purification by recrystallization from ethanol.

Yield: 1.3 g (51.9 %); colorless solid. mp: 69 °C; $C_{29}H_{32}F_{17}O_3Br$ (831).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.30 (m, 2 H, Ar-H), 6.73 (d, ^3J(H, H) 8.6, Ar-H), 3.96 (t, ^3J(H, H) 6.25, 2 H, CH_2OAr), 3.68 (m, 2 H, CH_2OH), 3.47 (m, 1 H, CHOH), 2.66 (t, ^3J(H, H) 7.23, 2 H, C**H**$_2CF_2$), 2.23-1.49 (m, 10 C**H**$_2$, 20 H).

11-(4-Bromophenyl-4-oxy)undecane-1,2-diol 47.6

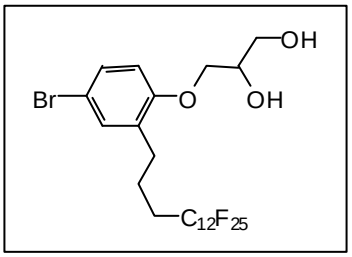


Prepared according to the general procedure **8.6.5** from 4-bromophenol (6.5 g, 37.3 mmol), 11-bromoundecan-1,2-diol (8 g, 29.8 mmol), K_2CO_3 (12 g, 86.9 mmol), KI (0.4 g), and CH_3CN (60 mL).

Yield: 9 g (84.1 %); colorless solid; mp: 68 - 70 °C; $C_{17}H_{27}O_3Br$ (359).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.36 (d, 2 H, ^3J(H, H) 9.0, Ar-H), 6.77 (d, 2 H, ^3J(H, H) 9.0, Ar-H), 3.89 (t, ^3J(H, H) 6.4, 2 H, CH_2OAr), 3.64 (m, 2 H, CH_2OH), 3.45 (m, 1 H, C**H**OH), 1.78 (m, 2 H, CH_2), 1.29-1.54 (m, 14 H, 8 CH_2).

3-(4-Bromo-2-1H,1H,2H,2H,3H,3H-perfluoropentadecylphenyloxy)propane-1,2-diol



47.8 Prepared according to the general procedure **8.6.5** from **45.8** (3.0 g, 3.4 mmol), N-methylmorpholine-N-oxide (3 mL, 60 % solution in water) and osmiumtetroxide (1 mL, 0.004 M) in acetone (50 mL). Purification by recrystallization from hexane.

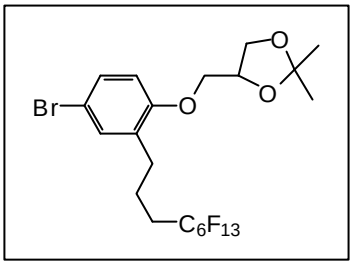
Yield:2.0 (64.1 %); colorless solid; mp: 112 °C, $C_{24}H_{16}O_3F_{25}Br$ (907).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.27 (m, 2 H, Ar-H), 6.75 (d, 1 H, ^3J(H, H) 8.4, Ar-H), 4.09-3.21 (m, 5 H, ArOC**H**$_2$C**H**C**H**$_2$OH), 2.66 (t, ^3J(H, H) 7.7, 2 H, CH_2Ar), 2.19-1.87 (m, 4 H, CH_2CH_2).

8.6.7 Synthesis of the 4-{w-[4-bromo-2-(semifluoroalkyl)phenoxy]alkyl}-2,2-dimethyl-1,3-dioxolanes 48

Protection of 1,2-diol groups - general procedure 8.6.7: A mixture of the appropriate ω-(4-bromo-2-semifluoroalkylphenyloxy)alkane-1,2-diol (5.11 mmol), PPTS (200 mg) and 2,2-dimethoxypropane (50 mL) was stirred at RT for 24 h (TLC). The solvent was distilled off, the residue was dissolved in diethyl ether (100 mL) and washed with saturated aqueous $NaHCO_3$ (2×35 mL), H_2O (2×35 mL), brine (2×35 mL), and dried over Na_2SO_4. The solvent was distilled off at a rotatory evaporator and the product was purified by column chromatography (eluent: $CHCl_3$).

4-[4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluorononyl)phenyloxymethyl]-2,2-dimethyl-1,3-dioxolane 48.1

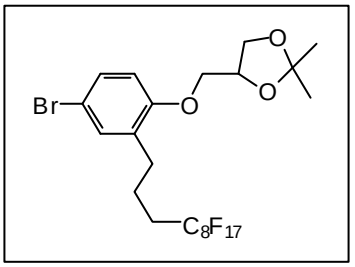


Prepared according to the general procedure **8.6.7** from **47.1** (3.1 g, 5.11 mmol), PPTS (200 mg) and 2,2-dimethoxypropane (50 mL).

Yield: 3.1 g (92.4 %); yellow oil; $C_{21}H_{30}OBrF_{13}$ (647).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.30 (dd, ^4J(H, H) 2.5, ^3J(H, H) 8.6, 1H, Ar-H), 7.2 (d, ^4J(H, H) 2.3, 1 H, Ar-H), 6.70 (d, 1 H, ^3J(H, H) 8.6, Ar-H), 4.00 (m, 5 H, OCH_2CHCH_2O), 2.72 (t, ^3J(H, H) 7.43, 2 H, $CH_2C_6F_{13}$), 1.99 (m, 4 H, CH_2CH_2Ar), 1.40 (2 s, 6 H, 2 CH_3).

4-[4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)phenyloxymethyl]-2,2-dimethyl-1,3-dioxolane 48.2

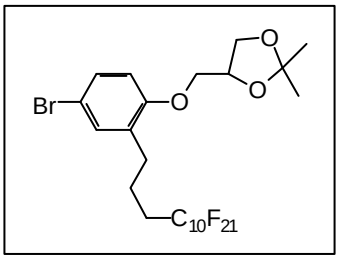


Prepared according to the general procedure **8.6.7** from **47.2** (6.6 g, 9.3 mmol), PPTS (200 mg) and 2,2-dimethoxypropane (80 mL).

Yield: 5.52 g (79.5 %); colorless solid; mp: 36 °C; $C_{23}H_{20}O_3F_{17}Br$ (747).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.24 (m, 2 H, Ar-H), 6.73 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 4.46-3.84 (m, 5 H, $ArOCH_2CHCH_2O$), 2.69 (t, ^3J(H, H) 7.2, 2 H, C**H**$_2$Ar), 2.21-1.79 (m, 4 H, 2 CH_2), 1.42, 1.37 (2 s, 6 H, 2 CH_3).

4-[4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluorotridecyl)phenyloxymethyl]-2,2-dimethyl-1,3-dioxolane 48.3



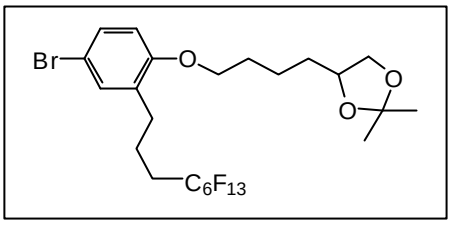
Prepared according to the general procedure **8.6.7** from **47.3** (1.57 g, 1.94 mmol), PPTS (20 mg) and 2,2-dimethoxypropane (15 mL).

Yield: 0.7 g (45.7 %); colorless solid; mp: 58 °C; $C_{25}H_{20}O_3BrF_{21}$ (847).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.29 (m, 2 H, Ar-H), 6.73 (d, ^3J 7.42, 1 H, Ar-H), 4.49

-3.84 (m, 5 H, $ArOCH_2CHCH_2O$), 2.65 (t, 2H, ^3J(H, H) 7.32, CH_2Ar), 2.17-1.87 (m, 4 H, 2 CH_2), 1.42, 1.37 (2 s, 6 H, 2 CH_3).

4-{4-[4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluorononyl)phenyloxy]butyl}-2,2-dimethyl-1,3-dioxolane 48.4

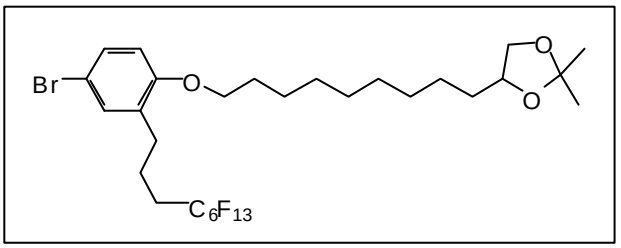


Prepared according to the general procedure **8.6.5** from **32.3** (2.1 g, 4.0 mmol), 4-(4-bromobutyl)-2,2-dimethyl-1,3-dioxolane **44** (1 g, 4.2 mmol), K_2CO_3 (5.5 g, 39.9 mmol), CH_3CN (10 mL).

Yield: 2.3 g (81.7 %); yellow waxy solid; $C_{24}H_{26}O_3BrF_{13}$(689).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.27 (m, 2 H, Ar-H), 6.65 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 4.00 (m, 4 H, $ArOC\mathbf{H}_2$, $OC\mathbf{H}_2$), 3.49 (t, ^3J(H, H) 7.3, 1 H, CHO), 2.68 (t, ^3J(H, H) 7.4, 2 H, CH_2Ar), 2.20 (m, 2 H, $C\mathbf{H}_2$), 1.90-1.45 (m, 6 H, $3C\mathbf{H}_2$), 1.38, 1.33 (2 s, 6 H, 2 CH_3).

4-{9-[4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluorononyl)phenyloxy]nonyl}-2,2-dimethyl-1,3-dioxolane 48.5

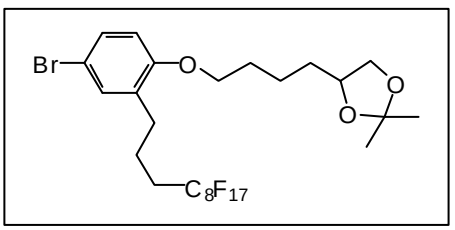


Prepared according to the general procedure **8.6.7** from **47.4** **(**1.4 g, 1.95 mmol), PPTS (20 mg) and 2,2-dimethoxypropane (10 mL).

Yield: 1.46 g (98.6 %); yellow waxy solid; $C_{29}H_{36}O_3BrF_{13}$(759).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.27 (m, 2 H, Ar-H), 6.65 (d, 1 H, ^3J(H, H) 8.4, Ar-H), 4.02 (m, 4 H, $ArOC\mathbf{H}_2$, $OC\mathbf{H}_2$), 3.47 (t, 1 H, ^3J(H, H) 7.3, CHO), 2.68 (t, ^3J(H, H) 7.4, 2 H, CH_2Ar), 2.17 (m, 2 H, $C\mathbf{H}_2$), 1.80 (m, 4 H, 2 $C\mathbf{H}_2$), 1.40 (m, 14 H, 7 $C\mathbf{H}_2$), 1.38, 1.33 (2 s, 2 CH_3).

4-{4-[4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)phenyloxy]butyl}-2,2-dimethyl-1,3-dioxolane 48.6



Prepared according to the general procedure **8.6.5** from **32.5** (3.8 g, 5.8 mmol), 4-(4-bromobutyl)-2,2-dimethyl-1,3-dioxolane **44** (1.4 g, 5.91 mmol), K_2CO_3 (7 g, 50.7 mmol), KI (1 g) and CH_3CN (35 mL).

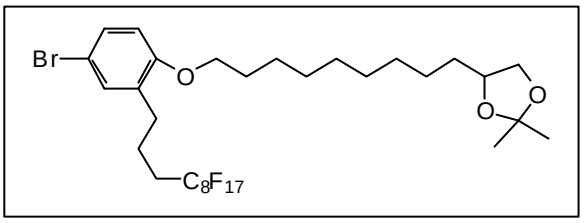
Yield: 1.5 g (32.0 %); colorless solid; mp: 68 °C-70 °C; $C_{26}H_{26}F_{17}O_3Br$ (789).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.30 (m, 2 H, Ar-H), 6.72 (d, ^{3}J(H, H) 8.6, Ar-H), 4.17-3.83 (m, 4 H, $ArOCH_2$, CH_2O), 3.55 (t, ^{3}J(H, H) 7.0, 1 H, CHO), 2.67 (t, ^{3}J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.27-1.48 (m, 4 H, 2 C**H**$_2$), 1.41, 1.35 (2 S, 2 CH_3), 1.20-1.40 (m, 6 H, 2 CH_2).

^{13}C-NMR (100 MHz; $CDCl_3$; *J*/Hz): δ = 157.1, 133.7, 132.6, 131.3, 113.8, 113.6, 109.8 (Ar-C), 76.8 (CH_2OAr), 70.3 (CHO), 68.8 (CH_2O), 34.2 (CH_2Ar), 31.5, 30.6, 27.7 (CH_2), 26.4, 23.4 (CH_3).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz) δ = -82.53 (overlapped t, 3 F, CF_3), -115.77 (m, 2 F, CH_2CF_2), -123.52 (m, 6 F, $CH_2CF_2(CF_2)_3$), -124.38 (m, 2 F, $CF_3(CF_2)_2CF_2$), -125.04 (m, 2 F, $CF_3CF_2CF_2$), -127.80 (m, 2 F, CF_3CF_2).

4-{9-[4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)phenyloxy]nonyl}-2,2-dimethyl-1,3-dioxolane <u>48.7</u>

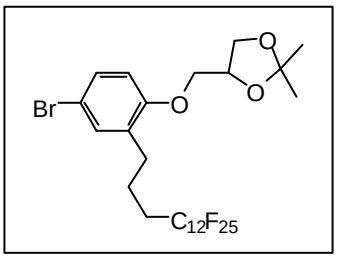


Prepared according to the general procedure **8.6.7** from **<u>47.5</u>** (1.35 g, 1.65 mmol), PPTS (40 mg) and 2,2-dimethoxypropane (15 mL).

Yield: 1.0 g (73.2 %); yellow oil; $C_{31}H_{36}O_3BrF_{17}$ (859).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.28 (m, 2 H, Ar-H), 6.73 (d, ^{3}J(H. H) 8.6, 1 H, Ar-H), 4.08 (m, 4 H, ArOC**H**$_2$CH, C**H**$_2$O), 3.50 (m, 1H, CHOH), 2.17 (m, 2 H, C**H**$_2$Ar), 1.87 (m, 2 H, CH_2), 1.2-1.41 (m. 16 H, 8 CH_2), 1.42, 1.35 (2s, 2 CH_3, 6 H).

4-[4-Bromo-2-(1H,1H,2H,2H,3H,3H-perfluoropentadecyl)phenyloxymethyl]-2,2-dimethyl-1,3-dioxolane <u>48.8</u>



Prepared according to the general procedure **8.6.7** from **<u>47.8</u>** (1.80 g, 1.98 mmol), PPTS (10 mg) and 2,2-dimethoxypropane (15 mL).

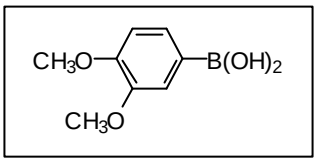
Yield: 0.8 g (45.3 %); colorless solid; mp: 72 °C; $C_{27}H_{20}O_3BrF_{25}$ (947).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.28 (m, 2 H, Ar-H), 6.72 (d, ^{3}J 8.6, 1 H, Ar-H), 4.46-3.86 (m, 5 H, ArOC**H**$_2$C**H**C**H**$_2$O), 2.65(t, 2H, ^{3}J(H, H) 7.50, CH_2Ar), 2.15-1.83 (m, 4 H, 2CH_2), 1.42, 1.37(2 s, 6 H, 2 CH_3).

8.6.8 Synthesis of the boronic acids 49a, 73 and 49b

Synthesis of boronic acids - genaral procedure 8.6.8: The appropriate bromobenzene derivative (46.1 mmol) was dissolved in dry THF (100 mL) and cooled to –78 °C. BuLi (64.5 mmol, 40 mL of a 1.6 M in hexane) was added dropwise at that temperature. Afterwards the solution was stirred at –100 °C for 15 min. Then trimethyl borate (16 mL, 143 mmol) was added dropwise at -78 °C. Afterwards, the solution was stirred over night at room temperature. The mixture was cooled to 0 °C in an ice bath and 10 % HCl (115 mL) was added carefully with stirring. Stirring was continued at 0 °C for 1 h, then diethyl ether (150 mL) was added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3×30 mL). The combined extracts were washed with H_2O (2×100 mL) and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by recrystallization.

3,4-Dimethoxybenzeneboronic acid 49a.1

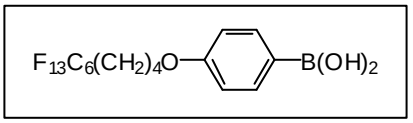


Prepared according to the general procedure **8.6.8** from 4-bromoveratrole **17** (10.0 g, 46.1 mmol), BuLi (40.3 mL, 64.5 mmol, 1.6 M in hexane), dry THF (100 ml), trimethyl borate (16 mL, 143.2 mmol), and 10 % HCl (115 mL). Purification by recrystallization from ethyl acetate/petroleum ether 0.5:10.

Yield: 3.9 g (46.1 %); colorless solid; mp: 242 °C; $C_8H_{11}O_4B$ (182).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.86 (dd, ^3J(H, H) 8.0, *J*(H, H) 1.0, 1 H, Ar-H), 7.67 (d, *J*(H, H) 1.0, 1 H, Ar-H), 7.02 (d, ^3J(H, H) 7.0, 1 H, Ar-H), 4.00, 3.96 (2 s, 6 H, 2 CH_3).

4-(1H,1H,2H,2H,3H,3H,4H,4H-Perfluorodecyloxy)benzeneboronic acid 49a.2

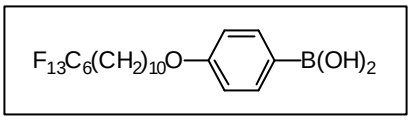


Prepared according to the general precedure **8.6.8** from **11Fa** (3.2 g, 5.85 mmol), BuLi (5.1 mL, 8.16 mmol, 1.6 M in hexane), dry THF (20 mL), trimethyl borate (1.9 mL, 17.55 mmol), 10 % HCl (15 mL). Purification by recrystallization from ethyl acetate/hexane 1:10.

Yield: 1.7 g (56.9 %); colorless solid; mp: 118 °C; $C_{16}H_{14}O_3BF_{13}$ (512)

^{1}H-NMR (200 MHz; acetone-D_6; *J*/Hz): δ =7.83 (d, ^3J(H, H) 8.6, 2 H, Ar-H), 6.90 (m, 2 H, Ar-H), 4.09(t, ^3J(H, H) 6.05, 2 H, OCH_2), 2.49-2.22 (m, 2 H, $\mathbf{CH_2}CF_2$), 2.06-1.78 (m, 4 H, CH_2CH_2).

4-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H,8H,8H,9H,9H,10H,10H-Perfluorohexadecyloxy)benzeneboronic acid 49a.3

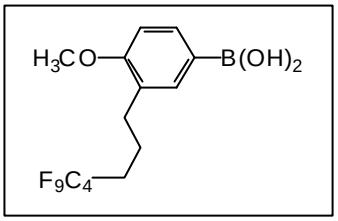


Prepared according to the general precedure **8.6.8** from **11Fb** (2.5 g, 4.0 mmol), BuLi (3.6 mL, 5.7 mmol, 1.6 M in hexane), dry THF (20 mL), trimethyl borate (1.4 mL, 12.5 mmol), and 10 % HCl (15 mL). Purification by recrystallization from toluene.

Yield: 1.3 g (55.1 %); colorless solid; mp: 95 °C; $C_{22}H_{26}O_3F_{13}B$ (596).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 8.15 (d, ^3J(H, H) 8.4, 1H, Ar-H), 7.76 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 6.92 (d, ^3J(H, H) 8.4, 2 H, Ar-H), 4.03 (t, ^3J(H, H) 6.06, 2 H, OCH_2), 1.24-2.31 (m, 18 H, 9 CH_2).

4-Methoxy-3-(1H,1H,2H,2H,3H,3H-perfluoroheptyl)benzeneboronic acid 49a.4

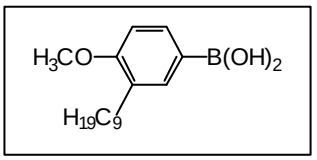


Prepared according to the general precedure **8.6.8** from **33.2** (5 g, 11.2 mmol), BuLi (9.8 ml, 15.7 mmol, 1.6 M in hexane), dry THF (50 mL), trimethyl borate (4 mL, 40.1 mmol), and 10 % HCl (28 mL). Purification by recrystallization from ethyl acetate /hexane 1:10.

Yield: 3.2 g (69.4 %); colorless solid; mp: 81 °C; $C_{14}H_{14}O_3BF_9$ (412).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.44 (m, 2 H, Ar-H), 6.89 (m, 1 H, Ar-H), 5.70 (br s, 2 H, 2OH), 3.86 (s, 3 H, CH_3), 2.80 (t, 2 H, ^3J(H, H) 7.2, $ArCH_2$), 2.37-1.82 (m, 4 H, 2 CH_2).

4-Methoxy-3-nonylbenzeneboronic acid 73

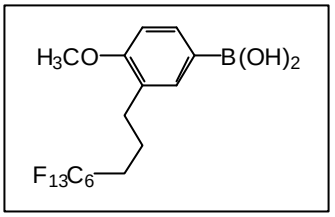


Prepared according to the general precedure **8.6.8** from 4-methoxy-3-nonylbromobenzene (7 g, 22.4 mmol), BuLi (21 mL, 33.6 mmol, 1.6 M in hexane),), dry THF (50 mL), trimethyl borate (7.6 mL, 76.1 mmol), 10 % HCl (30 mL). Purification by recrystallization from hexane.

Yield: 3.6 g (57.8 %); colorless waxy solid; $C_{16}H_{27}O_3B$ (278).

^{1}H-NMR (200 MHz; acetone-D_6; *J*/Hz): δ = 7.66 (m, 1 H, Ar-H), 6.86 (m, 2 H, Ar-H), 5.70 (br s, 2 H, 2 OH), 3.83 (s, 3 H, CH_3), 2.59 (t, 2 H, ^3J(H, H) 7.3, $ArCH_2$), 1.56 (m, 2 H, CH_2), 1.28 (m, 12 H, 6 CH_2), 0.87 (t, 3 H, CH_3).

4-Methoxy-2-(1H,1H,2H,2H,3H,3H-perfluorononyl)benzeneboronic acid 49a.5

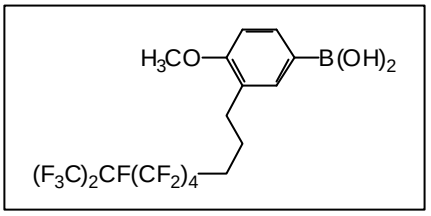


Prepared according to the general precedure **8.6.8** from **33.3** (7.0 g, 12.8 mmol), BuLi (11.2 mL, 17.92 mmol, 1.6 M in hexane), dry THF (50 mL), trimethyl borate (4.48 mL, 430.1 mmol), 10 % HCl (32 mL). Purification by recrystallization from ethyl acetate/hexane 1:10.

Yield: 4.16 g (63.5 %); colorless solid; mp: 97 °C; $C_{16}H_{14}O_3BF_{13}$ (512).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.44 (m, 2 H, Ar-H), 6.89 (m, 1 H, Ar-H), 5.70 (br s, 2 H, 2 OH), 3.86 (s, 3 H, CH_3), 2.80 (t, ^3J(H, H) 7.2, 2 H, $ArCH_2$), 2.37-1.82 (m, 4 H, 2 CH_2).

4-Methoxy-2-(1H,1H,2H,2H,3H,3H-perfluoroisodecyl)benzeneboronic acid 49a.6

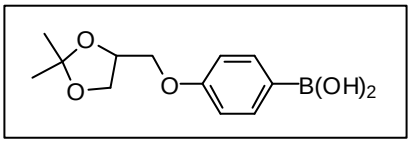


Prepared according to the general precedure **8.6.8** from **33.4** (3.0 g, 5.0 mmol), BuLi (4.4 mL, 7.0 mmol, 1.6 M in hexane), dry THF (20 mL), trimethyl borate (1.8 mL, 15.9 mmol), and 10 % HCl (16 mL). Purification by recrystallization from ethyl acetate/hexane 1:10.

Yield: 2.0 g (71.3 %); colorless solid; mp: 101 °C; $C_{17}H_{14}O_3BF_{15}$ (562).

^{1}H-NMR (200 MHz; acetone-D_6; *J*/Hz): δ = 7.67 (m, 2 H, Ar-H), 6.92 (m, 1 H, Ar-H), 3.86 (s, 3 H, CH_3), 2.80 (t, 2 H, *J*(H, H) 7.42, $ArCH_2$), 2.37-1.82 (m, 4 H, 2 CH_2).

4-(2,2-Dimethyl-1,3-dioxolan-4-ylmethoxy)benzeneboronic acid 49b.1

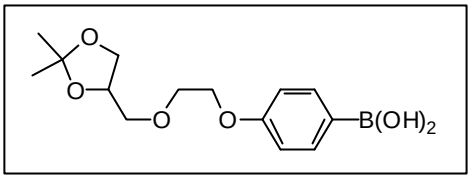


4-(4-bromophenyloxymethyl)-2,2-dimethyl-1,3-dioxolane (10.9 g, 40 mmol) was dissolved in dry THF (100 ml) under an argon atmosphere, and cooled to –100 °C. Then BuLi (35 mL, 56 mmol, 1.6 M in hexane) was added dropwise. During the addition, the temperature remained below –90 °C. Stirring was continued at –100 °C for 15 min, then trimethyl borate (14 mL, 123.3 mmol) was added dropwise at –90 °C. After stirring over night at RT, the mixture was cooled in an ice bath and phosphate buffer pH = 5 (200 mL) was carefully added with stirring at 0 °C. Stirring was continued at that temperature for 1 h, diethyl ether (150 mL) was addedm and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3×30 mL). The combined exacts were washed with H_2O (2×100 mL) and dried over Na_2SO_4. The solvent was distilled off in vacuum, and n-pentane was added to the residue. The precipitate was filtered and washed with n-pentane. The product was purified by recrystallization from toluoene

Yield: 5.6 g (55.9 %); colorless solid; mp: 85 °C.

^{1}H-NMR (400 MHz; acetone-D_6; *J*/Hz): δ = 7.83 (d, ^{3}*J*(H, H) 8.4, 2 H, Ar-H), 7.02 (m, 2 H, Ar-H), 4.47 (m, 1 H, $CH_2C\mathbf{H}$), 4.18-3.85(m, 4 H, ArOC$\mathbf{H_2}$CHOC$\mathbf{H_2}$), 1.32, 1.37 (2 s, 2 CH_3).

4-[4-(2,2-Dimethyl-1,3-dioxolan-4-yl)-3-oxabutoxy]benzeneboronic acid 49b.2

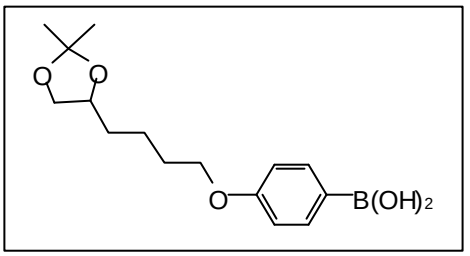


Prepared according to the procedure described for **49b.1** from 4-[4-(4-bromophenoxy)-2-oxabutyl]-2,2-dimethyl-1,3-dioxolane **14** (6.3 g, 20 mmol), BuLi (17 mL, 28 mmol, 1.6 M in hexane), dry THF (50 mL), trimethyl borate (7 mL, 61.5 mmol), phosphate buffer pH=5 (100 mL). The crude product was used without further purification for the next step.

Yield: 1.5 g (46.2 %); colorless waxy solid; $C_{14}H_{21}O_6B$ (296).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.83 (d, ^{3}*J*(H, H) 8.8, 2 H, Ar-H), 6.93(d, ^{3}*J*(H, H) 8.6, 2 H, Ar-H), 4.25-3.49 (m, 9 H, $CH_2CH_2OCH_2CHCH_2O$), 2.84(s, 3 H, CH_3), 1.26, 1.32 (2 s, 6 H, 2 CH_3).

4-[4-(2,2-Dimethyl-1,3-dioxolan-4-yl)butoxy]benzeneboronic acid 49b.3

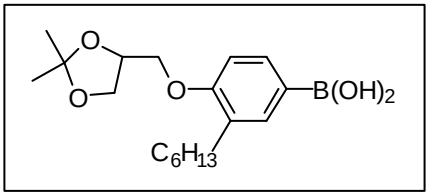


Prepared according to the procedure described for **49b.1** from 4-[4-(4-bromophenyloxy)butyl]-2,2-dimethyl-1,3-dioxolane (6.3 g, 20 mmol), BuLi (17 mL, 28 mmol, 1.6 M in hexane), dry THF (50 mL), trimethyl borate (7 mL, 61.5 mmol), phosphate buffer pH=5 (100 mL). The crude product was used without further purification for the next step.

Yield: 2.5 g (42.5 %); colorless waxy solid; $C_{15}H_{33}O_5B$ (294).

^{1}H-NMR (200 MHz; $CDCl_3$, *J*/Hz): 7.80 (d, 2 H, ^{3}*J*(H, H) 8.6, Ar-H)), 6.89 (m, 2 H, Ar-H), 4.20-3.99 (m, 4 H, ArOC$\mathbf{H}_2$, C$\mathbf{H}_2$OH), 3.50 (m, 1 H, CHOH), 1.84 (m, 2 H, CH_2), 1.62 (m, 4 H, 2 CH_2), 1.31, 1.26 (2 s, 2 CH_3).

4-(2,2-Dimethyl-1,3-dioxolan-4-ylmethoxy)-3-hexylbenzeneboronic acid 49b.4



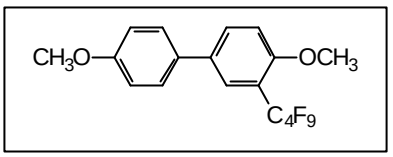
Prepared according to the procedure described for **49b.1** from 4-(4-bromo-2-hexylphenyloxymethyl)-2,2-dimethyl-1,3-dioxolane (3.3 g, 8.9 mmol), BuLi (7.8 mL, 12.4 mmol, 1.6 M in hexane), dry THF (50 mL), trimethyl borate (3.1 mL, 27.7 mmol), phosphate buffer pH=5 (50 mL). The crude product was used without further purification for the next step.

Yield: 1.5 g (49.0 %); colorless crystals; mp: 110 °C; $C_{18}H_{29}O_5B$ (337).

^{1}H-NMR (400 MHz; acetone-D_6; *J*/Hz): δ = 7.69 (m, 2 H, Ar-H), 6.93 (m, 1 H, Ar-H), 4.48 (m, 1 H, CH_2**CH**), 4.18-3.85 (m, 4 H, ArO**CH_2**, O**CH_2**), 2.59 (t, 2 H, ^{3}J (H, H) 7.42, CH_2), 1.58 (m, 2 H, CH_2), 1.33 (2 s, 2 CH_3), 1.28 (m, 6 H, 3 CH_2), 0.87 (t, ^{3}J (H, H) 7.0, CH_3).

8.6.9 Synthesis of the 4,4‴-dimethoxybiphenyl derivatives 50, the 4,4‴‴-dimethoxyterphenyl derivatives 55, 75, 76 and the 4-bromo-3‴-nonyl-4‴-methoxybiphenyl 75

4,4‴-Dimethoxy-3-perfluorobutylbiphenyl 50.1

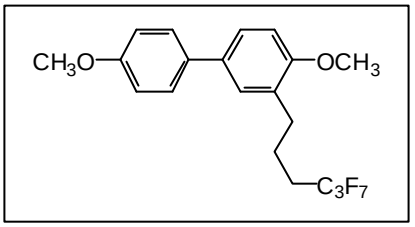


Prepared according to the general procedure **8.4.2** from **43.1** (3 g, 7.4 mmol), 4-methoxybenzeneboronic acid (1.3 g, 8.9 mmol), $Pd(PPh_3)_4$ (0.2 g), glyme (45 mL), and saturated $NaHCO_3$ solution (35 mL). Purification by recrystallization from methanol/ethyl acetate 1:5.

Yield: 1.2 g (43.6 %); colorless solid; mp: 58 °C; $C_{18}H_{13}O_2F_9$ (387).

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.67 (m, 2 H, Ar-H), 7.47 (m, 2 H, Ar-H), 6.98 (m, 3 H, Ar-H), 3.88, 3.87 (2 s, 6 H, 2 CH_3).

4,4‴-Dimethoxy-3-(1H,1H,2H,2H,3H,3H-perfluorohexyl)biphenyl 50.2

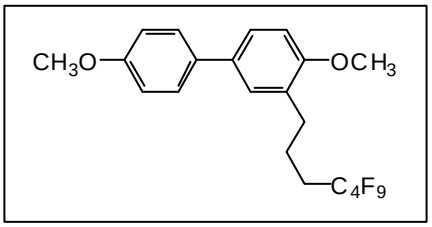


Prepared according to the general procedure **8.4.2** from **33.1** (3 g, 7.5 mmol), 4-methoxybenzeneboronic acid (1.4 g, 9.1 mmol), glyme (45 mL), saturated $NaHCO_3$ solution (35 mL) and $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 2.7 g (48.1 %); yellow waxy solid, $C_{20}H_{19}O_2F_7$ (424).

^{1}H-NMR (200 MHz; *J*/Hz): δ = 7.57 (m, 2 H, Ar-H), 7.31 (m, 2 H, Ar-H), 6.98 (m, 3 H, Ar-H), 3.85 (s, 6 H, 2 CH_3O), 2.75 (t, ^3J(H, H) 7.6, 2 H, C**H**$_2$Ar), 1.93-2.14 (m, 4 H, C**H**$_2$C**H**$_2$$CF_2$).

4,4‴-Dimethoxy-3-(1H,1H,2H,2H,3H,3H-perfluoroheptyl)biphenyl 50.3

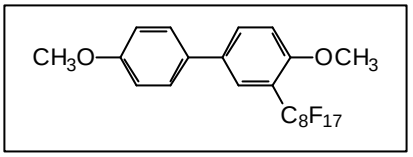


Prepared according to the general procedure **8.4.2** from **33.2** (2.7g, 6.0 mmol), 4-methoxybenzeneboronic acid (1.1 g, 7.2 mmol), glyme (45 mL), saturated $NaHCO_3$ solution (35 mL), $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 2.7 g (48.1 %); yellow waxy solid; $C_{21}H_{19}O_2F_{13}$ (474).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ= 7.45 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 7.36 (m, 2 H, Ar-H), 6.92 (m, 3 H, Ar-H), 3.84 (s, 6 H, 2 CH_3O), 2.74 (t, ^3J(H, H) 7.2, 2 H, CH_2Ar), 1.86-2.26 (m, 4 H, C**H**$_2$C**H**$_2$$CF_2$).

4,4'-Dimethoxy-3-perfluorooctylbiphenyl 50.4

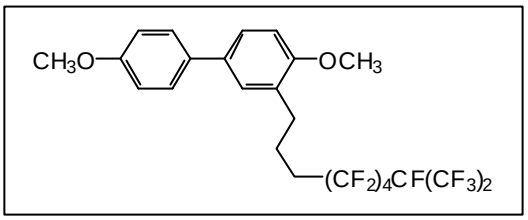


Prepared according to the general procedure **8.4.2** from **43.2** (1.9 g, 3.1 mmol), 4-methoxybenzeneboronic acid (0.6 g, 3.8 mmol), glyme (35 mL), saturated $NaHCO_3$ solution (20 mL), and $Pd(PPh_3)_4$ (0.1 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 1.2 g (59.1 %); yellow solid; mp: 82 °C; $C_{22}H_{13}O_2F_{17}$ (632).

^{1}H-NMR (200 MHz; *J*/Hz): δ = 7.64 (m, 2 H, Ar-H), 7.43 (m, 2 H, Ar-H), 6.98 (m, 3 H, Ar-H), 3.88, 3.83 (2 s, 6 H, 2 CH_3).

4,4'-Dimethoxy-3-(1H,1H,2H,2H,3H,3H-perfluoroisodecyl)biphenyl 50.5

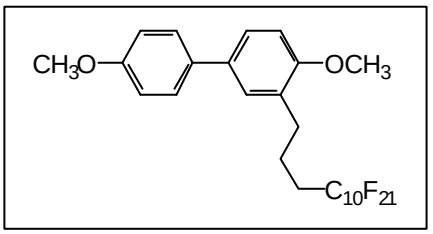


Prepared according to the general procedure **8.4.2** from **33.4** (3.1 g, 5.2 mmol), 4-methoxybenzeneboronic acid (0.9 g, 6.2 mmol), glyme (45 mL), saturated $NaHCO_3$ solution (35 mL), $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 2.7 g (48.1 %); yellow waxy solid; $C_{21}H_{19}O_2F_{13}$ (474).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.46 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 7.29 (m, 1 H, Ar-H), 6.92 (m, 3 H, Ar-H), 3.84 (s, 6 H, 2 CH_3O), 2.73 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 1.84-2.25 (m, 4 H, C**H**$_2$C**H**$_2$$CF_2$).

4,4'-Dimethoxy-3-(1H,1H,2H,2H,3H,3H-perfluorotridecyl)biphenyl 50.6

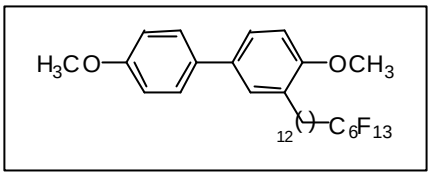


Prepared according to the general procedure **8.4.2** from **33.6** (3.6 g, 4.8 mmol), 4-methoxybenzeneboronic acid (0.9 g, 5.7 mmol), glyme (45 mL), saturated $NaHCO_3$ solution (35 mL), and $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 1.2 g (32.7 %); yellow waxy solid; $C_{27}H_{19}O_2F_{21}$(774).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.46 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 7.24 (m, 2 H, Ar-H), 6.88 (m, 3 H, Ar-H), 3.84 (s, 6 H, 2 CH_3O), 2.71 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 1.96-2.11 (m, 4 H, C**H**$_2$C**H**$_2$$CF_2$).

4,4'-Dimethoxy-3-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H,8H,8H, 9H,9H,10H,10H,11H,11H,12H,12H-perfluorooctadecyl)biphenyl 50.7

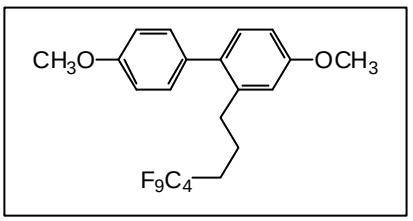


Prepared according to the general procedure **8.4.2** from **41** (2.3 g, 3.4 mmol), 4-methoxybenzeneboronic acid (0.5 g, 3.4 mmol), glyme (35 mL), saturated $NaHCO_3$ solution (25 mL), and $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 310 mg (13.0 %); colorless solid; mp: 40 °C; $C_{32}H_{37}O_2F_{13}$ (700).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.53 (d, ^3J(H, H) 8.8, 2 H, Ar-H), .38 (m, 2 H, Ar-H), 6.85-7.01 (m, 3 H, Ar-H), 3.86, 3.85 (2 s, 6 H, 2 CH_3), 2.68 (t, ^3J(H, H) 7.4, 2 H, CH_2), 2.26-1.94 (m, 4 H, 2 CH_2), 1.66-1.55 (18 H, 9 CH_2).

4,4'-Dimethoxy-2-(1H,1H,2H,2H,3H,3H-perfluoroheptyl)biphenyl 50.8

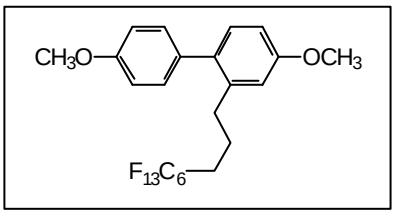


Prepared according to the general procedure **8.4.2** from **37.1** (3 g, 6.7 mmol), 4-methoxybenzeneboronic acid (1.2 g, 8.0 mmol), glyme (40 mL), saturated $NaHCO_3$ solution (35 mL) and $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 1.74 g (86.3%); yellow oil; $C_{21}H_{19}O_2F_9$ (474).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.22 (m, 3 H, Ar-H), 6.99 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 6.86 (m, 2 H, Ar-H), 3.87, 3.86(2 s, 6 H, 2 CH_3), 2.71 (t, ^3J(H, H) 7.6, 2 H, CH_2), 2.01-1.77 (m, 4 H, 2 CH_2).

4,4'-Dimethoxy-2-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl 50.9

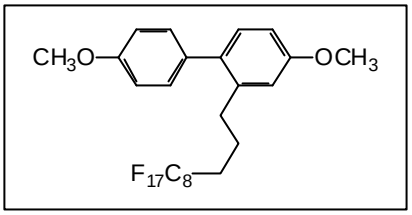


Prepared according to the general procedure **8.4.2** from **37.2** (3 g, 5.5 mmol), 4-methoxybenzeneboronic acid (1 g, 6.6 mmol), glyme (45 mL), saturated $NaHCO_3$ solution (35 mL), and $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 1.5 g (48.1%); colorless solid; mp: 97 °C; $C_{23}H_{19}O_2F_{13}$ (574).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.18 (m, 3 H, Ar-H), 6.94 (m, 2 H, Ar-H), 6.81 (m, 2 H, Ar-H), 3.84 (2 s, 6 H, 2 CH_3), 2.66 (t, ^3J(H, H) 7.6, 2 H, $ArCH_2$), 1.93-1.56 (m, 4 H, CH_2).

4,4'-Dimethoxy-2-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)biphenyl 50.10

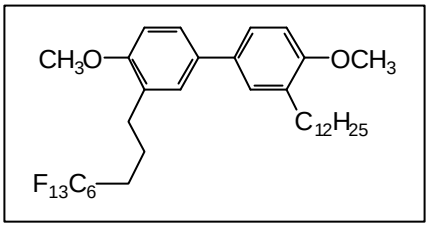


Prepared according to the general procedure **8.4.2** from **37.3** (2.4 g, 3.7 mmol), 4-methoxybenzeneboronic acid (0.7 g, 4.5 mmol), glyme (35 mL), saturated $NaHCO_3$ solution (25 mL), and $Pd(PPh_3)_4$ (0.1 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 2.1 g (83.7 %); colorless solid; mp: 45°C; $C_{23}H_{19}O_2F_{17}$ (674).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.17 (m, 3 H, Ar-H), 6.91 (m, 2 H, Ar-H), 6.79 (m, 2 H, Ar-H), 3.87, 3.82 (2 s, 6 H, 2 CH_3), 2.64 (t, ^3J(H, H) 7.6, 2 H, CH_2), 1.94-1.69 (m, 4 H, 2 CH_2).

4,4'-Dimethoxy-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)-3'-dodecylbiphenyl 50.12

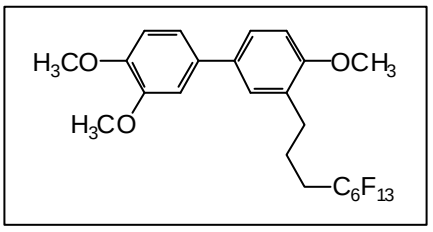


Prepared according to the general procedure **8.4.2** from 4-methoxyl-3-dodecylbromobenzene (0.3 g, 1.0 mmol), **49a.5** (0.5 g, 1.0 mmol), glyme (45 mL), saturated $NaHCO_3$ solution (35 mL), $Pd(PPh_3)_4$ (0.1 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 0.4 g (65.7 %); yellow solid; mp: 30 °C; $C_{35}H_{43}O_2F_{13}$ (743).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.42 (m, 4 H, Ar-H), 6.89 (m, 2 H, Ar-H), 3.86, 3.85 (2 s, 6 H, 2 CH_3), 2.77-2.53 (m, 4 H, 2 CH_2Ar), 2.16-1.93 (m, 4 H, 2 CH_2), 1.61 (m, 2 H, CH_2), 1.26 (m, 12 H, 6 CH_2), 0.88 (t, ^3J(H, H) 7.0, 3 H, CH_3).

3',4',4-Trimethoxy-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl 65

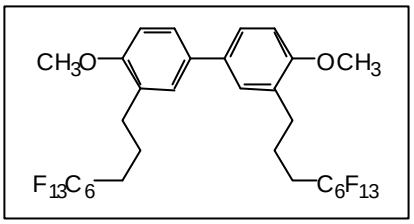


Prepared according to the general procedure **8.4.2** from **33.3** (3.3 g, 6.0 mmol), **49a.1** (1.3 g, 7.1 mmol), glyme (90 mL), saturated $NaHCO_3$ solution (70 mL), $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 2.6 g (72.5 %); yellow solid; mp: 70 °C; $C_{24}H_{21}O_3F_{13}$ (604).

^{1}H-NMR (200 MHz; $CDCl_3$;*J*/Hz): δ = 7.41.(dd, ^3J(H, H) 8.4, ^4J(H, H) 2.8, 1 H, Ar-H), 7.31 (d, ^4J(H. H) 2.5, 1 H, Ar-H), 7.06 (m, 2 H, Ar-H), 6.94 (dd, ^3J(H, H) 8.2, *J*(H, H) 2.7, 2 H, Ar-H), 3.95, 3.92, 3.87 (3 s, 3 CH_3), 2.77 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 1.90-2.28 (m, 4 H,CF_2C**H**$_2C$**H**$_2$).

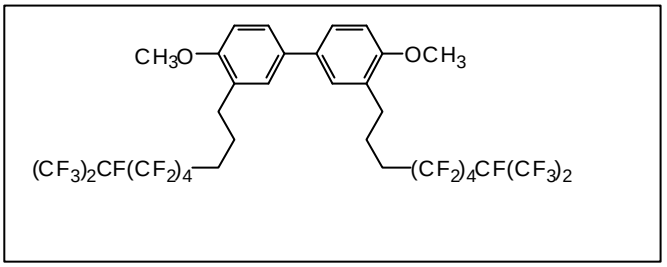
4,4'-Dimethoxy-3,3'-bis(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl 50.11



Prepared according to the general procedure **8.4.2** from **33.3** (2 g, 3.7 mmol), **49a.5** (2.0 g, 4.0 mmol), glyme (35 mL), saturated $NaHCO_3$ solution (25 mL), $Pd(PPh_3)_4$ (0.1 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).
Yield: 1.2 g (78.9 %); yellow waxy solid; $C_{32}H_{24}OF_{26}$ (934).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.37 (dd, ^3J(H, H) 8.6, ^4J(H, H) 2.3, 2 H, Ar-H), 7.27 (m, 2 H, Ar-H), 6.91 (m, 2 H, Ar-H), 3.84 (s, 6 H, 2 CH_3O), 2.74 (t, ^3J(H, H) 7.4, 4 H, 2 C**H**$_2$Ar), 1.96-2.18 (m, 8 H, 2 C**H**$_2$C**H**$_2$CF$_2$).

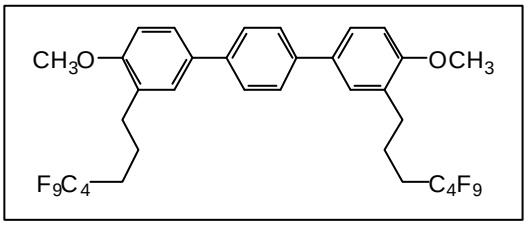
4,4'-Dimethoxy-3,3'-bis(1H,1H,2H,2H,3H,3H-perfluoroisodecyl)biphenyl 50.13



Prepared according to the general procedure **8.4.2** from **33.4** (2.1 g, 3.6 mmol), **49a.6** (2.0 g, 3.6 mmol), glyme (45 mL), saturated $NaHCO_3$ solution (35 mL), $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).
Yield: 1.2 g (32.7 %); yellow waxy solid; $C_{27}H_{19}O_2F_{21}$(774).

^{1}H-NMR (200 MHz; $CDCl_3$ *J*/Hz): δ = 7.46 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 7.24 (m, 2 H, Ar-H), 6.88 (m, 2 H, Ar-H), 3.84 (s, 6 H, 2 CH_3O), 2.71 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 1.96-2.11 (m, 4 H, C**H**$_2$C**H**$_2$CF$_2$).

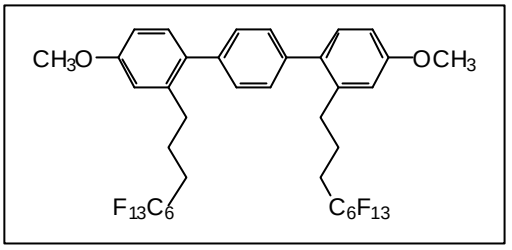
4,4''-Dimethoxy-3,3''-bis(1H,1H,2H,2H,3H,3H-perfluoroheptyl)-p-terphenyl 55.1



Prepared according to the general procedure **8.4.2** from **33.3** (3.0 g, 6.7 mmol), benzene-1,4-diboronic acid (0.5 g, 3.1 mmol), glyme (40 mL), saturated $NaHCO_3$ solution (25 mL), and $Pd(PPh_3)_4$ (0.3 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10:1).
Yield: 0.5 g (19.8 %); yellow solid; mp: 154 °C; $C_{34}H_{28}O_2F_{18}$ (811).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.46 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 7.24 (m, 2 H, Ar-H), 6.88 (m, 3 H, Ar-H), 3.84 (s, 6 H, 2 CH_3O), 2.71 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 1.96-2.11 (m, 4 H, C**H**$_2$C**H**$_2$CF$_2$).

4,4¢¢-Dimethoxy-2,2¢¢-bis(1H,1H,2H,2H,3H,3H-perfluorononyl)-p-terphenyl 55.2



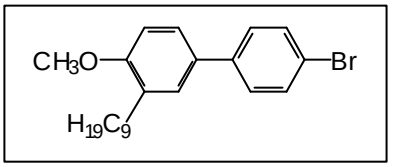
Prepared according to the general procedure **8.4.2** from **37.2** (3.0 g, 5.5 mmol), benzene-1,4-diboronic acid (0.4 g, 2.4 mmol), glyme (40 mL), saturated $NaHCO_3$ solution (25 mL), and $Pd(PPh_3)_4$ (0.3 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 2.2 g (92.2 %); yellow waxy solid;. $C_{38}H_{28}O_2F_{26}$ (1011).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.46 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 7.24 (m, 2 H, Ar-H), 6.88 (m, 3 H, Ar-H), 3.84 (s, 6 H, 2 CH_3O), 2.71 (t, ^3J(H, H) 7.43, 2 H, C**H**$_2$Ar), 1.96-2.11 (m, 4 H, C**H**$_2$C**H**$_2$CF$_2$).

4,4¢¢-Dimethoxy-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)-3¢¢-nonly terphenyl 76

*4-Bromo-3¢-nonyl-4¢-methoxybiphenyl **75***

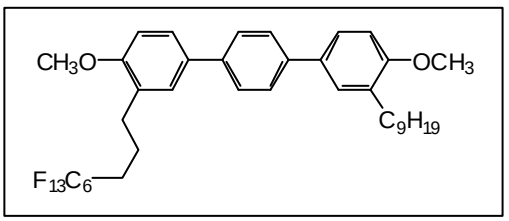


Prepared according to the general procedure **8.4.2** from 1-bromo-4-iodobenzene (2.9 g, 10.3 mmol), boronic acid **74** (2.9 g, 10.3 mmol), glyme (70 mL), saturated $NaHCO_3$ solution (60 mL), and $Pd(PPh_3)_4$ (0.2 g). The reaction was carried out at 40 °C. Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 2.5 g (62.3 %); yellow oil; $C_{22}H_{29}OBr$ (389).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.53 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 7.44-7.24 (m, 4 H, Ar-H), 6.92 (m, 1 H, Ar-H), 3.86 (s, 3 H, CH_3O), 2.67 (t, ^3J(H, H) 7.3, 2 H, CH_2Ar), 1.63 (m, 2 H, CH_2), 1.29 (m, 12 H, 6 CH_2), 0.90 (t, ^3J(H, H) 6.6, 3 H, CH_3).

*4,4¢¢-Dimethoxy-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)-3¢¢-nonly terphenyl **76***



Prepared according to the general procedure **8.4.2** from **75** (2.4 g, 6.2 mmol), boronic acid **49a.5** (3.16 g, 6.2 mmol), glyme (45 mL), saturated $NaHCO_3$ solution (35 mL) and $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$), followed by recrystallization from ethyl acetate/methanol: 10:1.

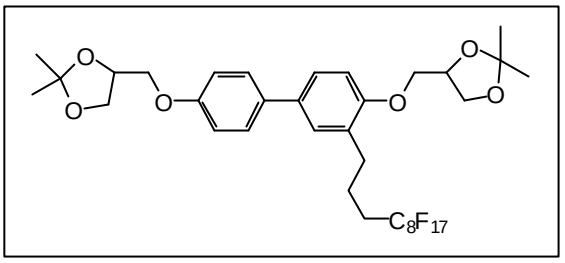
Yield: 2.24 g (39.6 %); colorless solid; mp: 167 °C; $C_{38}H_{41}O_2F_{13}$ (777).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.59 (m, 4 H, Ar-H), 7.48-7.34 (m, 4 H, Ar-H), 6.92 (m, 2 H, Ar-H), 3.86 (s, 6 H, 2 CH_3O), 2.76 (t, ^3J(H, H) 7.6, 2 H, C**H**$_2$Ar), 2.65 (t, ^3J(H, H)

7.6, 2 H, C**H**$_2$Ar), 2.19-1-91 (m, 4 H, 2 CH_2), 1.65 (m, 2 H, CH_2), 1.26 (m, 12 H, 6 CH_2), 0.86 (t, ^3J(H, H) 7.0, 3 H, CH_3).

8.6.10 Synthesis of the acetonides 59, 60 and 63

2,2-Dimethyl-4-{4'-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]-3-(1H,1H, 2H,2H,3H,3H-perfluoroundecyl)biphenyl-4-yloxymethyl}-1,3-dioxolane 59.1

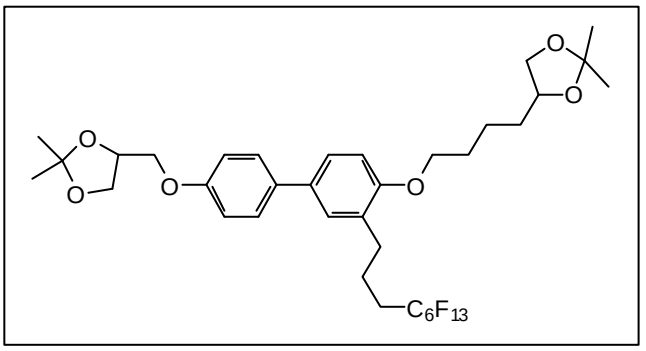


Prepared according to the general procedure **8.4.2** from **48.2** (2.0 g, 2.7 mmol), **49b.1** (0.7 g, 2.7 mmol), glyme (40 mL), saturated $NaHCO_3$ solution (35 mL) and $Pd(PPh_3)_4$ (0.1 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 1.71 g (72.6 %); colorless solid; mp: 88-90 °C; $C_{35}H_{35}O_6F_{17}$ (875).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ =7.45 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 7.36 (m, 2 H, Ar-H), 6.90 (m, 3 H, Ar-H), 4.48 (m, 1 H, CHO), 4.20-3.86 (m, 9 H, 2 $ArOCH_2$, 2 OCH_2, CHO), 2.77 (t, ^3J(H, H) 7.6, 2 H, CH_2Ar), 1.92-2.152 (m, 4 H, CF_2C**H**$_2C$**H**$_2$), 1.52, 1.46, 1.45, 1.39 (4 s, 4 CH_3).

2,2-Dimethyl-4-(4-{4'-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]-3-(1H,1H, 2H,2H,3H,3H-perfluorononyl)biphenyl-4-yloxy}buyl)-1,3-dioxolane 59.2



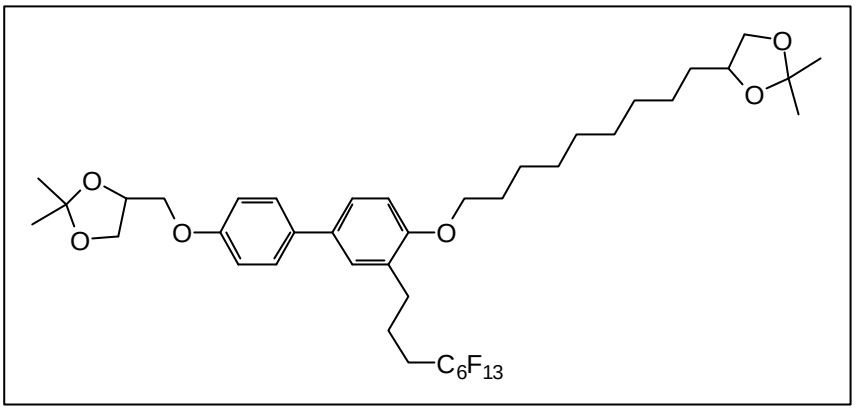
Prepared according to the general procedure **8.4.2** from **48.4** (2.3 g, 3.3 mmol), **49b.1** (0.9 g, 3.5 mmol), glyme (45 mL), saturated $NaHCO_3$ solution (35 mL), $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 1.4 g (51.8 %); colorless solid; mp: 58 °C; $C_{36}H_{41}O_6F_{13}$ (817).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.46 (d, ^3J(H, H) 7.8, 2 H, Ar-H), 7.28 (m, 2 H, Ar-H), 6.97 (m, 3 H, Ar-H), 4.45 (m, 1 H, C**H**OH), 4.20-3.82 (m, 9 H, 2 $ArOCH_2$, 2 CH_2O, CHO), 2.67 (t, ^3J(H, H) 7.2, 2 H, CH_2Ar), 2.67 (t, ^3J(H, H) 7.2, 2 H, CH_2Ar), 2.20-1.40 (m, 10 H, 5 C**H**$_2$), 1.39, 1.34, 1.52, 1.54 (12 H, 4 CH_3).

2,2-Dimethyl-4-(9-{4'-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyloxy]-3-(1H,1H,2H, 2H,3H,3H-perfluorononyl)biphenyl-4-yloxy}nonyl)-1,3-dioxolane 59.3

Prepared according to the general procedure **8.4.2** from **48.5** (2.0 g, 2.9 mmol), **49b.1** (0.8 g, 3.2 mmol), glyme (45 mL), saturated $NaHCO_3$ solution (35 mL), $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

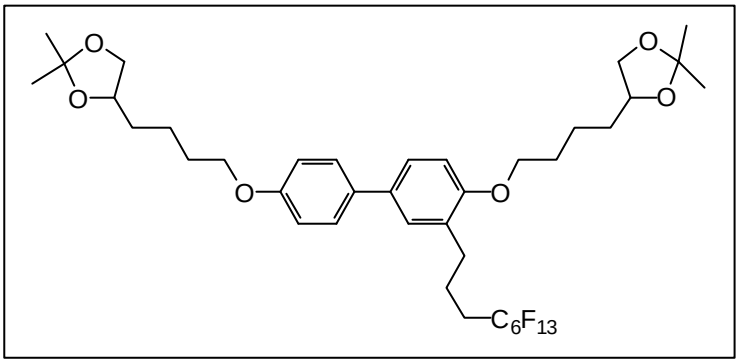


Yield: 0.6 g (25 %); colorless solid; mp: 79 °C; $C_{41}H_{51}O_6F_{13}$ (886).

^{1}H-NMR (200 MHz; *J*/Hz): δ = 7.61-7.23 (m, 4 H, Ar-H), 7.01-6.83 (m, 2 H, Ar-H), 4.45(m, 1 H, CHOH), 4.20-3.82(m, 9 H, 2 ArOC**H**$_2$, 2 OC**H**$_2$, OC**H**), 2.67 (t, ^3J(H, H) 7.2, 2 H, CH_2Ar), 2.20 (m, 2 H, CF_2C**H**$_2$), 1.90 (m, 4 H, 4 CH_2), 1.40 (m, 14 H, 7 CH_2), 1.39, 1.34, 1.48, 1.54 (4 s, 12 H, 4 CH_3).

2,2-Dimethyl-4-(4-{4'-[4-(2,2-dimethyl-1,3-dioxolan-4-yl)butyloxy]-3-(1H,1H,2H,2H, 3H,3H-perfluorononyl)biphenyl-4-yloxy}butyl)-1,3-dioxolane 59.4

Prepared according to the general procedure **8.4.2** from **48.4** (2.1 g, 3.1 mmol), **49b.3** (0.9 g, 3.1 mmol), glyme(45 mL), saturated $NaHCO_3$ solution (35 mL) and $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).



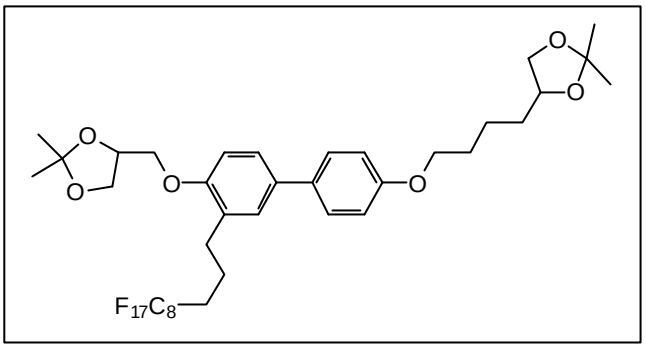
Yield: 1.3 g (48.3 %); yellow waxy solid; $C_{39}H_{47}O_6F_{13}$ (859).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.2-7.4 (m, 4 H, Ar-H), 6.80-7.00(m, 3 H, Ar-H), 4.20-3.95 (m, 8 H, 2 ArOCH_2, 2 CH_2O), 3.50 (m, 2 H, 2 CHO), 2.74 (t, ^3J(H, H) 7.6, 2 H, C**H**$_2$Ar), 2.14 (m, 2 H, C**H**$_2$$CF_2$), 1.34-1.98 (m, 14 H, 7 CH_2), 1.41, 1.40, 1.35, 1.34 (4 s, 12 H, 4 CH_3).

2,2-Dimethyl-4-(4-{4'-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]-3'-(1H,1H,2H,2H, 3H,3H-perfluoroundecyl)biphenyl-4-yloxy}butyl)-1,3-dioxolane 59.5

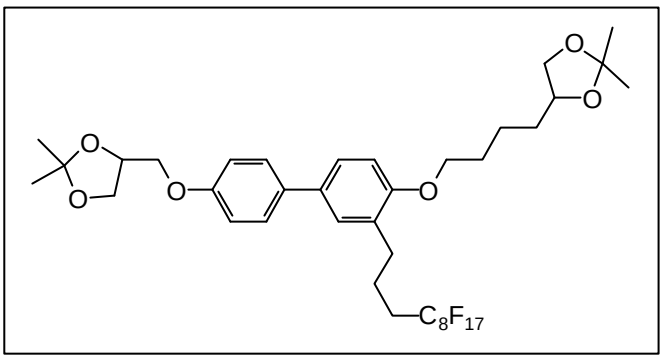
Prepared according to the general procedure **8.4.2** from **48.2** (1.0 g, 1.3 mmol), **49b.3** (0.4 g, 1.3 mmol), glyme (40 mL), saturated $NaHCO_3$ solution (35 mL), and $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 1.1 g (91.7 %); colorless solid; mp: 88-90 °C; $C_{38}H_{41}O_6F_{17}$ (916). ^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.60-7.20 (m, 4 H, Ar-H), 6.89 (m, 3 H, Ar-H), 4.48 (m, 1H, C**H**O), 4.20-3.80 (m, 9 H, 2 ArOC**H**$_2$, 2 OC**H**$_2$), 3.51 (m, 1 H, C**H**O), 2.71 (t, ^{3}*J*(H, H) 7.0, 2 H, CH_2Ar), 2.26 (m, 2 H, CF_2CH_2), 1.83-1.21 (m, 8 H, 4 CH_2).



2,2-Dimethyl-4-(4-{4'-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]-3-(1H,1H,2H,2H, 3H,3H-perfluoroundecyl)biphenyl-4-yloxy}butyl)-1,3-dioxolane 59.6

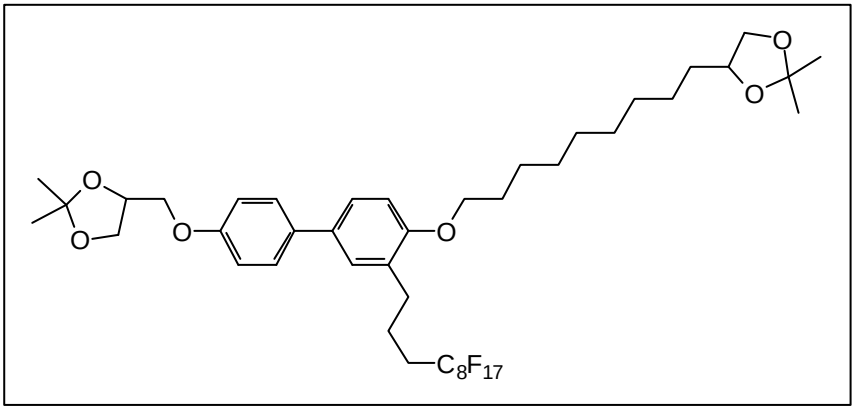
Prepared according to the general procedure **8.4.2** from **48.6** (1.5 g, 1.8 mmol), **49b.1** (0.5 g, 1.8 mmol), glyme (25 mL), saturated $NaHCO_3$ solution (20 mL), $Pd(PPh_3)_4$ (0.1 g). The product was purified by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).



Yield: 1.0 g (59.2 %); colorless solid; mp: 88-90 °C; $C_{38}H_{41}O_6F_{17}$(917). ^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.55 (m, 4 H, Ar-H), 6.88 (m, 3 H, Ar-H), 4.55 (m, 1 H, C**H**O), 4.08 (m, 8 H, 2 ArOC**H**$_2$, 2 OC**H**$_2$), 3.50 (m, 1 H, C**H**O), 2.73 (t, ^{3}*J*(H, H) 7.0, 2 H, C**H**$_2$Ar), 2.07 (m, 2 H, CF_2C**H**$_2$), 1.87 (m, 2 H, C**H**$_2$$CH_2CF_2$), 1.82-1.41 (m, 6 H, 3 CH_2), 1.53, 1.46, 1.39, 1.33 (4 s, 12 H, 4 CH_3).

2,2-Dimethyl-4-(9-{4'-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]-3-(1H,1H,2H, 2H,3H,3H- perfluoroundecyl)biphenyl-4-yloxy}nonyl)-1,3-dioxolane 59.7

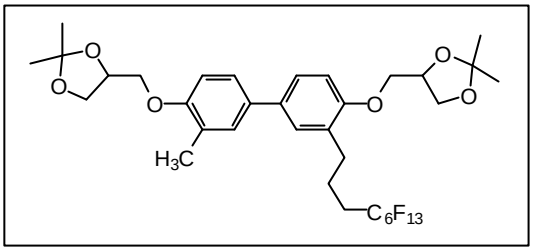
Prepared according to the general procedure **8.4.2** from **48.7** (1.6 g, 1.9 mmol), **49b.1** (0.5 g, 1.9 mmol), glyme (40 mL), saturated $NaHCO_3$ solution (20 mL), $Pd(PPh_3)_4$ (0.1 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).



Yield: 0.67 g (35.8 %); yellow solid; mp: 45 °C; $C_{43}H_{51}O_6F_{17}$(987).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.55 (m, 4 H, Ar-H), 6.99 (m, 3 H, Ar-H), 4.55 (m, 1 H, CH), 4.21-3.85 (m, 8 H, 2 $ArOCH_2$, 2 OCH_2), 3.47 (m, 1 H, OC**H**), 2.68 (t, ^3J(H, H) 7.0, 2 H, CH_2Ar), 2.30 (m, 2 H, $CF_2C\mathbf{H}_2$), 2.22 (m, 2 H, CH_2), 1.42-1.23 (m, 16 H, 8 CH_2), 1.25, 1.30, 1.39, 1.46 (4 s, 4 CH_3).

2,2-Dimethyl-4-{4'-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]-3'-methyl-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4-yloxymethyl}-1,3-dioxolane 59.8

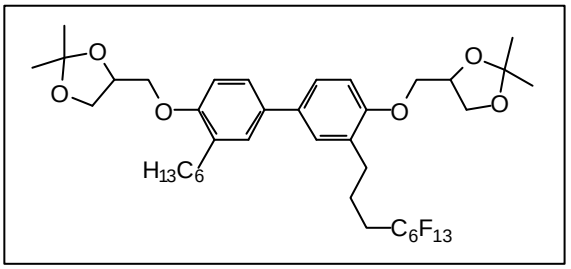


Prepared according to the general procedure **8.4.2** from **48.1** (0.9 g, 1.4 mmol), 4-(2,2-dimethyl-1,3-dioxolan-4-ylmethyoxy)-2-methylphenylboronic acid (0.4 g, 1.5mmol), glyme (30 mL), saturated $NaHCO_3$ solution (25 mL), and $Pd(PPh_3)_4$ (0.1 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 0.71 g (65.7 %); colorless solid; mp: 70 °C; $C_{38}H_{41}O_6F_{17}$(917).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.39 (m, 4 H, Ar-H), 6.90 (m, 2 H, Ar-H), 4.55 (m, 2 H, 2 CHO), 4.22-3.94 (m, 8 H, 2 $ArOCH_2$, 2 OCH_2), 2.78 (t, ^3J(H, H) 7.4, 2 H, CH_2Ar), 2.64 (m, 2 H, CH_2Ar), 2.31 (s, 3 H, CH_3), 2.22-1.94 (m, 4 H, 2 CH_2), 1.50, 1.49, 1.44, 1.43 (4 s, 12 H, 4 CH_3).

2,2-Dimethyl-4-{4'-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]-3'-hexyl-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4-yloxymethyl}-1,3-dioxolane 59.9

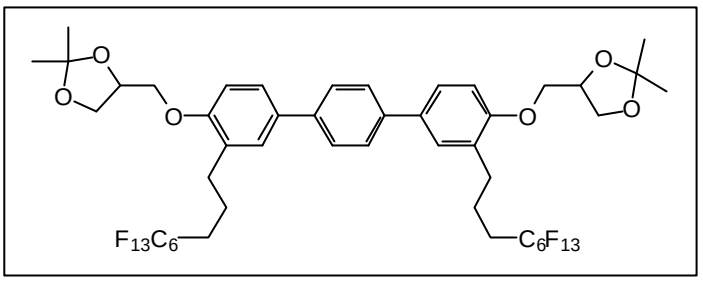


Prepared according to the general procedure **8.4.2** from **48.1** (0.9 g, 1.4 mmol), **49b.4** (0.5 g, 1.5 mmol), glyme (30 mL), saturated $NaHCO_3$ solution (25 mL), and $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 0.6 g (47.5 %); colorless solid; mp: 79 °C; $C_{39}H_{47}O_6F_{13}$(859).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.33 (m, 4 H, Ar-H), 6.87 (m, 2 H, Ar-H), 4.48 (m, 2 H, 2 CHOH), 4.18-3.90 (m, 8 H, 2 $ArOCH_2$, 2 OCH_2), 2.74 (t, ^3J(H, H) 7.6, 2 H, C**H**$_2$Ar), 2.64 (m, 2 H, CH_2Ar), 2.20 (m, 4 H, $2CH_2$), 2.04 (m, 2 H, CH_2), 1.39, 1.40, 1.44, 1.45 (4 s, 12 H, 4 CH_3), 1.28 (m, 6 H, 3 CH_2), 0.87 (t, 3 H, ^3J(H, H) 7.0, CH_3).

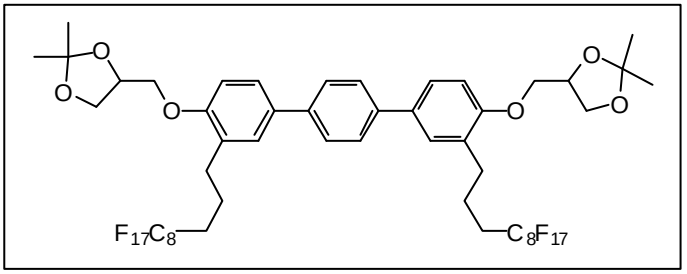
4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis(1H,1H,2H,2H, 3H,3H-perfluorononyl)-p-terphenyl 60.1



Prepared according to the general procedure **8.4.2** from **48.1** (3.1 g, 4.7 mmol), benzene-1,4-diboronic acid (0.4 g, 2.2 mmol), glyme (40 mL), saturated aqueous $NaHCO_3$ solution (35 mL), and $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).
Yield: 1.8 g (91.7%); colorless solid; mp: 97 °C; $C_{48}H_{44}O_6F_{26}$ (1210).
^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.58 (m, 4 H, Ar-H), 7.39 (m, 4 H, Ar-H), 6.94 (d, 2 H, ^{3}*J*(H, H) 8.4, Ar-H), 4.46 (m, 2 H, 2 C**H**OH), 3.89-4.20 (m, 8 H, 2 $ArOCH_2$, 2 CH_2O), 2.76 (t, ^{3}*J*(H, H) 7.6, 2 H, C**H**$_2$Ar), 2.17-1.94 (m, 8 H, 2 C**H**$_2$C**H**$_2$$CF_2$), 1.39-1.45 (4 s, 12 H, 4 CH_3).

Pd°-Catalyzed cross coupling (II) – general procedure 8.6.10: Under an argon atmosphere, $Pd(OAc)_2$ (0.896 mg, 0.004 mmol), 2-(di-*ter*-butylphosphino)biphenyl (2.4 mg, 0.008 mmol), KF (125 mg, 2.15 mmol) and benzene-1,4-diboronic acid (40 mg, 0.24 mmol) were dissolved in dry THF (5 mL). **48** (0.72 mmol) was added. After stirring for 36 h at room temperature, diethyl ether (50 ml) was added, the solution was washed with 10% aqueous NaOH solution (2×15 ml), the organic phase was seperated, the aqueous layer was extracted with diethyl ether (3×50 ml), the diethy ether extracts were combined with organic phase and washed with water (2×25 ml), brine (2×25 ml) and dried over Na_2SO_4. Afterwards, the diethyl ether was distilled off and the residue was purified by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

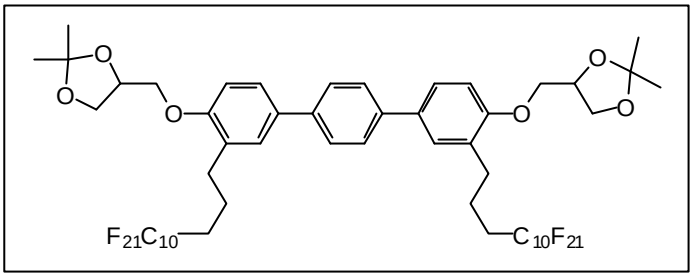
4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis(1H,1H,2H,2H, 3H,3H-perfluoroundecyl)-p-terphenyl 60.2



Prepared according to the general procedure **8.6.10** from **48.2** (538 mg, 0.72 mmol), $Pd(OAc)_2$ (0.90 mg, 0.004 mmol), 2-(di-*ter*-butylphosphine)biphenyl (2.4 mg, 0.008 mmol), KF (125 mg, 2.15 mmol) and benzene-1,4-diboronic acid (40 mg, 0.24 mmol) in 5 ml dry THF.
Yield: 135 mg (39.8 %); colorless solid; mp: 125 °C; $C_{52}H_{44}O_6F_{34}$ (1410).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.58 (m, 4 H, Ar-H), 7.39 (m, 4 H, Ar-H), 6.94 (d, 2 H, ^{3}*J*(H, H) 8.5, Ar-H), 4.49 (m, 2 H, 2 C**H**OH), 3.90-4.21 (m, 8 H, 2 $ArOCH_2$, 2 CH_2O), 2.77 (t, ^{3}*J*(H, H) 7.3, 2 H, C**H**$_2$Ar), 2.18-1.95 (m, 8 H, 2 C**H**$_2$C**H**$_2$$CF_2$), 1.40, 1.46 (2 s, 12 H, 4 CH_3).

4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis-(1H,1H,2H,2H, 3H,3H-perflurotridecyl)-p- terphenyl <u>60.3</u>

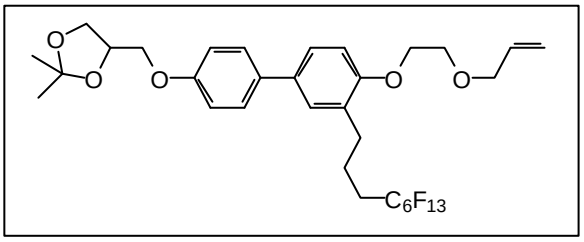


Prepared according to the general procedure **8.6.10** from **<u>48.3</u>** (609.8 mg, 0.72 mmol), $Pd(OAc)_2$ (0.896 mg, 0.004 mmol), 2-(di-*ter*-butylphosphine)biphenyl (2.4 mg, 0.008 mmol), KF (125 mg, 2.15 mmol) and benzene-1,4-diboronic acid (40 mg, 0.24 mmol) in 5 ml dry THF.

Yield: 62 mg (16.1 %); colorless solid; mp: 147 °C; $C_{56}H_{44}O_6F_{42}$ (1610).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.58 (m, 4 H, Ar-H), 7.39 (m, 4 H, Ar-H), 6.94 (d, 2 H, ^{3}*J*(H, H) 8.4, Ar-H), 4.46 (m, 2 H, 2 C**H**OH), 3.89-4.20 (m, 8 H, 2 $ArOCH_2$, 2 CH_2O), 2.76 (t, ^{3}*J*(H, H) 7.6, 2 H, C**H**$_2$Ar), 2.17-1.94 (m, 8 H, 2 C**H**$_2$C**H**$_2$$CF_2$), 1.39-1.45 (4 s, 12 H, 4 CH_3).

6-[4'-(2,2-Dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4-yloxy]-4-oxahexene <u>63</u>



Prepared according to the general procedure **8.4.2** from **<u>62</u>** (2.8 g, 4.5 mmol), **<u>49b.1</u>** (1.3 g, 5.3 mmol), glyme (80 mL), saturated $NaHCO_3$ solution (60 mL), and $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10: 0.5).

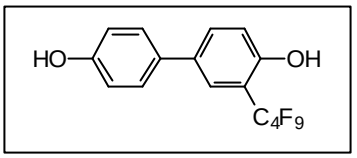
Yield: 2.6 g (72.5 %); yellow oil; $C_{32}H_{33}O_5F_{13}$ (744).

^{1}H-NMR (200 MHz; $CDCl_3$ *J*/Hz): δ = 7.44 (m, 2 H, Ar-H), 7.34 (m, 2 H, Ar-H), 6.94 (m, 3 H, Ar-H), 5.96-5.89(m, 1 H, CH=), 5.15-5.32(m, 2 H, CH_2=), 4.49 (m, 1 H, OCH), 4.19-3.80 (m, 10 H, 5 CH_2O), 2.60 (t, ^{3}*J*(H, H) 7.80, 2 H, C**H**$_2$Ar), 1.81-2.10 (m, 4 H, CF_2C**H**$_2$C**H**$_2$).

8.6.11 Synthesis of the divalent phenols 51, 56, 66 and 77

Cleavage of methyl ethers - general procedure 8.6.11: Appropriate methyl ether (4.7 mmol) was dissolved in CH_2Cl_2 (45 mL), BBr_3 (0.49 mL, 5.17 mmol) was added and the solution was reflex for 4 h. After stirring for 20 h at room temperature, water (30 mL) was carefully added, the solvent was distilled off, the residue was dissolved in diethyl ether (100 mL) and washed with saturated $NaHCO_3$ solution (2×30 mL), and dried over Na_2SO_4, the solvent was distilled off in *vacuo*. The product was purified by recrystallization or chromatrography.

3-Perfluorobutylbiphenyl-4,4′-diol 51.1

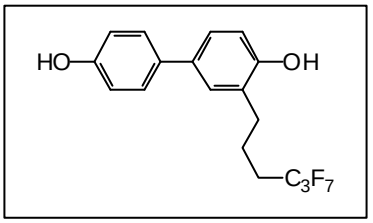


Prepared according to general procedure **8.6.11** from **50.1** (1.8 g, 4.7 mmol), BBr_3 (0.5 mL, 5.2 mmol) and CH_2Cl_2 (45 mL). Purification by recrystallization from $CHCl_3$/MeOH 5:2.

Yield: 0.8 g (44.2 %); colorless solid; mp: 155 °C; $C_{16}H_9O_2F_9$ (404).

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 10.43, 9.50 (2 s, 2 H, 2 OH), 7.67 (dd, ^3J(H, H) 8.6, ^4J(H, H) 2.0, 1 H, Ar-H), 7.49 (m, 1 H, Ar-H), 7.39 (d, ^3J(H, H) 8.6, 2 H, Ar-H), 7.08 (dd, ^3J (H, H) 8.6, ^4J(H, H) 3.52, 1 H, Ar-H), 6.81 (d, ^3J(H, H) 8.6, 2 H, Ar-H).

3-(1H,1H,2H,2H,3H,3H-Perfluorohexyl)biphenyl-4,4′-diol 51.2

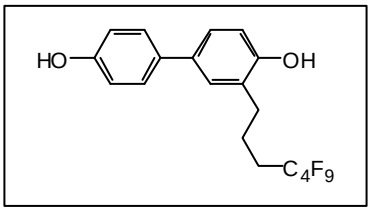


Prepared according to general procedure **8.6.11** from **50.2** (1.5 g, 3.6 mmol), BBr_3 (0.6 mL, 6.6 mmol), CH_2Cl_2 (35 mL). Purification by recrystallization from $CHCl_3$.

Yield: 600 mg (42.0 %);colorless solid; mp: 126 °C; $C_{18}H_{15}O_2F_7$ (396).

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 9.36 (br s, 2 H, 2 OH), 7.36 (d, ^3J(H, H) 8.5, 2 H, Ar-H), 7.27 (d, ^4J(H, H) 2.4, 1 H, Ar-H), 7.20 (dd, ^3J(H, H) 8.2, ^4J(H, H) 2.3, 1 H, Ar-H) , 6.79 (m, 3 H, Ar-H), 2.66 (t, ^3J(H, H) 7.4, 2 H, CH_2Ar), 2.20 (m, 2 H, $CH_2C\mathbf{H}_2CF_2$), 1.83 (m, 2 H, $C\mathbf{H}_2CH_2CF_2$).

3-(1H,1H,2H,2H,3H,3H-Perfluoroheptyl)biphenyl-4,4′-diol 51.3



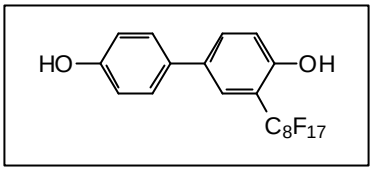
Prepared according to general procedure **8.6.11** from **50.3** (2.7 g, 6.0 mmol), BBr_3 (0.6 mL, 6.6 mmol), CH_2Cl_2 (35 mL). Purification by recrystallization from $CHCl_3$.

Yield: 1.7 g (64.2 %); colorless solid; mp: 120 °C; $C_{19}H_{15}O_2F_9$ (446).

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 9.34 (br s, 2 H, 2 OH), 7.35 (d, ^3J(H, H) 8.6, 2 H, Ar-H), 7.27 (d, ^3J(H, H) 2.3, 1 H, Ar-H), 7.20 (dd, ^3J (H, H) 8.6, ^4J(H, H) 2.3, 1 H, Ar-H), 6.79 (m, 3 H, Ar-H), 2.66 (t, ^3J(H, H) 7.7, 2 H, C**H**$_2$Ar), 2.18-2.32 (m, 2 H, CH_2C**H**$_2$$CF_2$), 1.79-1.87 (m, 2 H, C**H**$_2$$CH_2CF_2$).

3-Perfluorooctylbiphenyl-4,4′-diol <u>51.4</u>

Prepared according to general procedure **8.6.11** from **<u>50.4</u>** (1.1 g, 1.8 mmol), BBr_3 (0.2 mL, 2.0 mmol), CH_2Cl_2 (20 mL). Purification by recrystallization from $CHCl_3$/MeOH 5:2.

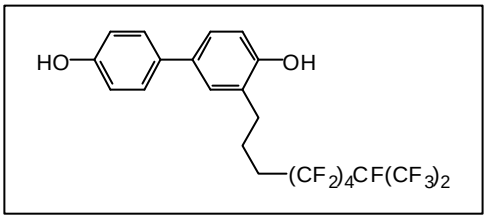


Yield: 0.5 g (43.1 %); colorless solid; mp: 180 °C; $C_{20}H_9O_2F_{17}$ (604).

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 10.5 (s, 1 H, OH), 9.54 (s, 1 H, OH), 7.68 (dd, ^3J(H, H) 8.4, ^4J(H, H) 3.52, 1 H, Ar-H), 7.53 (m, 1 H, Ar-H), 7.41 (d, ^3J(H, H) 8.6, 2 H, Ar-H), 7.07 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 6.87(d, ^3J(H, H) 8.8, 2 H, Ar-H).

3-(1H,1H,2H,2H,3H,3H-Perfluoroisodecyl)biphenyl-4,4′-diol <u>51.5</u>

Prepared according to general procedure **8.6.11** from **<u>50.5</u>** (2.8 g, 4.4 mmol), BBr_3 (0.5 mL, 4.9 mmol), CH_2Cl_2 (35 mL). Purification by recrystallization from $CHCl_3$.

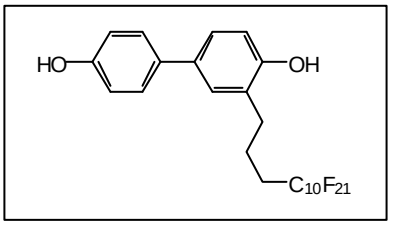


Yield: 2.1 g (79.2 %); colorless solid; mp: 135 °C; $C_{22}H_{15}O_2F_{15}$ (596).

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 9.35 (br s, 2 H, 2 OH), 7.36 (d, ^3J(H, H) 8.6, 2 H, Ar-H), 7.27 (d, ^4J(H, H) 2.34, 1 H, Ar-H), 7.22 (dd, ^3J(H, H) 8.22, ^4J(H, H) 2.34, 1 H, Ar-H), 6.79 (m, 3 H, Ar-H), 2.66 (t, ^3J(H, H) 7.61, 2 H, C**H**$_2$Ar), 2.19-2.26 (m, 2 H, CH_2C**H**$_2$$CF_2$), 1.81-1.87 (m, 2 H, C**H**$_2$$CH_2CF_2$).

3-(1H,1H,2H,2H,3H,3H-Perfluorotridecyl)biphenyl-4,4′-diol <u>51.6</u>

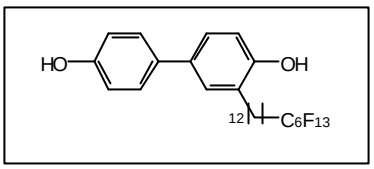
Prepared according to general procedure **8.6.11** from **<u>50.6</u>** (1.0 g 1.3 mmol), BBr_3 (0.1 mL, 1.4 mmol), CH_2Cl_2 (20 mL). Purification by recrystallization from $CHCl_3$.



Yield: 0.7 g (73.9 %); colorless solid; mp: 150 °C; $C_{25}H_{15}O_2F_{21}$ (746).

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 9.33 (br s, 2 H, 2 OH), 7.33 (d, ^3J(H, H) 8.6, 2 H, Ar-H), 7.27 (m, 1 H, Ar-H), 7.20 (m, 1 H, Ar-H), 6.80 (m, 3 H, Ar-H), 2.65 (t, ^3J(H, H)7.7, 2 H, C**H**$_2$Ar), 2.21 (m, 2 H, CH_2C**H**$_2$$CF_2$), 1.92 (m, 2 H, C**H**$_2$$CH_2CF_2$).

3-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H,8H,8H,9H,9H,10H,10H, 11H,11H,12H,12H-Perfluorooctadecyl)biphenyl-4,4′-diol 51.7

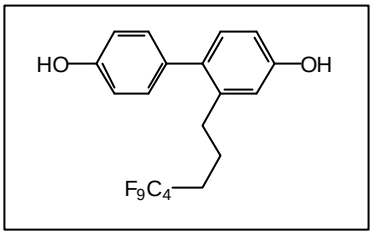


Prepared according to general procedure **8.6.11** from **50.7** (1.1 g, 1.6 mmol), BBr_3 (0.2 mL, 1.8 mmol), CH_2Cl_2 (40 mL). Purification by recrystallization from $CHCl_3$.

Yield: 0.8 g (72.7 %); colorless solid; mp: 108 °C; $C_{30}H_{33}O_2F_{13}$ (672).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.40 (m, 2 H, Ar-H), 7.26 (m, 2 H, Ar-H), 6.80 (m, 3 H, Ar-H), 2.62 (t, ^3J(H, H) 7.2, 2 H, C**H**$_2$Ar), 2.00 (m, 2 H, C**H**$_2$CF$_2$), 1.58 (m, 4 H, 2 CH_2), 1.20 (m, 16 H, 8 CH_2).

2-(1H,1H,2H,2H,3H,3H-Perfluoroheptyl)biphenyl-4,4′-diol 51.8

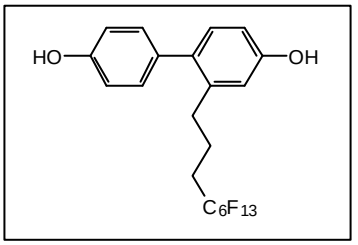


Prepared according to general procedure **8.6.11** from **50.8** (2.7 g, 5.8 mmol), BBr_3 (0.6 mL, 6.4 mmol), CH_2Cl_2 (35 mL). Purification by recrystallization from $CHCl_3$/MeOH 5:2.

Yield: 0.8 g (44.2 %); colorless solid; mp: 105 °C; $C_{19}H_{15}O_2F_9$(446).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.22 (m, 3 H, Ar-H), 6.99 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 6.86 (m, 2 H, Ar-H), 3.87, 3.86 (2 s, 6 H, 2 CH_3), 2.71 (t, ^3J(H, H) 7.6, 2 H, CH_2), 2.01-1.77 (m, 4 H, 2 CH_2).

2-(1H,1H,2H,2H,3H,3H-Perfluorononyl)biphenyl-4,4′-diol 51.9

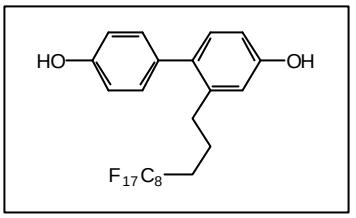


Prepared according to general procedure **8.6.11** from **50.9** (1.5 g, 2.6 mmol), BBr_3 (0.3 mL, 2.9 mmol), CH_2Cl_2 (25 mL). The product was purified by recrystallization from $CHCl_3$/MeOH 5:2.

Yield: 0.8 g (44.2 %); yellow oil, $C_{21}H_{15}O_2F_{13}$ (546).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.16-7.00 (m, 3 H, Ar-H), 6.87-6.81 (m, 2 H, Ar-H), 6.72-6.67 (m, 2 H, Ar-H), 4.75 (br s, 2 H, 2 OH), 2.64 (t, ^3J(H, H) 7.6, 2 H, $ArCH_2$), 2.08-1.24 (m, 4 H, 2 CH_2).

2-(1H,1H,2H,2H,3H,3H-Perfluoroundecyl)biphenyl-4,4'-diol 51.10

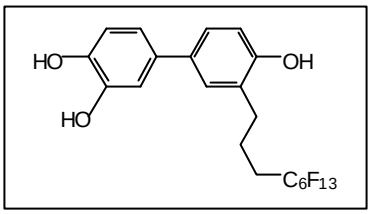


Prepared according to general procedure **8.6.11** from **50.10** (2.0 g, 3.0 mmol), BBr_3 (0.3 mL, 3.3 mmol), CH_2Cl_2 (25 mL). Purification by recrystallization from $CHCl_3$/MeOH 5:2.

Yield: 1.8 g (94.3 %); colourless solid; mp: 215 °C; $C_{23}H_{15}O_2F_{17}$ (646).

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 9.34, 9.28 (2 s, 2 OH), 7.02-6.59 (m, 7 H, Ar-H), 2.57(t, ^3J(H, H) 7.81, 2 H, CH_2), 2.20-1.45 (m, 4 H, 2 CH_2)

3'-(1H,1H,2H,2H,3H,3H-Perfluorononyl)biphenyl-3,4,4'-triol 66

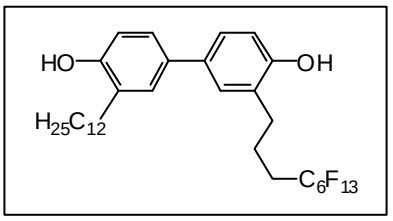


Prepared according to general procedure **8.6.11** from **65** (2.6 g, 4.4 mmol), BBr_3 (0.1 g, 0.6 mmol), CH_2Cl_2 (40 mL). Purification by recrystallization from $CHCl_3$.

Yield: 1.9 g (77.6 %); colorless solid; mp: 165 °C; $C_{21}H_{15}O_3F_{13}$ (562).

^{1}H-NMR (200 MHz;DMSO-D_6, *J*/Hz): δ = 9.32 (s, 1 H, OH), 9.54 (br s, 2 H, 2 OH), 7.22 (d, ^4J(H, H) 2.3, 1 H, Ar-H), 7.17 (dd, ^3J(H, H) 8.2, ^4J(H, H) 2.3, 1 H, Ar-H), 6.92(d, ^4J(H, H) 2.2, 1 H, Ar-H), 6.81 (d, ^3J(H, H) 8.4, 2 H, Ar-H), 6.74 (d, ^3J(H, H) 8.2, 1 H, Ar-H), 2.66 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.32-2.23 (m, 2 H, CF_2C**H**$_2$), 1.86-1.80 (m, 2 H, C**H**$_2CH_2CF_2$).

3-Dodecyl-3'-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4,4'-diol 51.12

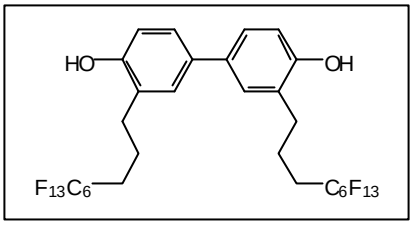


Prepared according to general procedure **8.6.11** from **50.12** (0.4 g, 0.6 mmol), BBr_3 (0.1 mL, 1.6 mmol), CH_2Cl_2 (20 mL). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 0.2 g (44.4 %); colorless solid; mp: 89 °C; $C_{21}H_{39}O_2F_{13}$ (570).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.25 (m, 4 H, Ar-H), 6.80 (m, 2 H, Ar-H), 4.71, 4.67 (2 s, 2 H, 2 OH), 2.79 (t, ^3J(H, H) 7.42, 2 H, C**H**$_2$Ar), 2.62 (t, 2 H, ^3J(H, H) 7.6, C**H**$_2$Ar), 2.21 (m, 2 H, C**H**$_2$), 1.95 (m, 2 H, CH_2), 1.65 (m, 2 H, CH_2), 1.25 (m, 18 H, 9 CH_2), 0.87 (t, ^3J(H, H) 7.0, 3 H, CH_3).

3,3'-Bis(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4,4'-diol 51.11

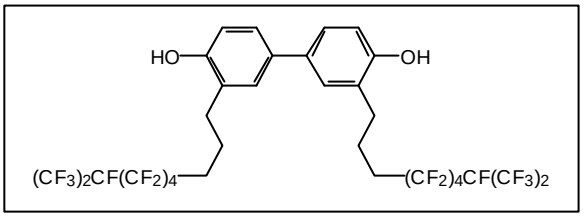


Prepared according to general procedure **8.6.11** from **50.11** (2.7 g, 2.9 mmol), BBr_3 (0.6 mL, 6.4 mmol), CH_2Cl_2 (50 mL). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 0.8 g (74.0 %); yellow solid; mp: 107 °C; $C_{30}H_{20}O_2F_{26}$ (906).

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 7.40 (m, 2 H, Ar-H), 7.26 (m, 2 H, Ar-H), 6.80 (m, 3 H, Ar-H), 6.12 (br s, 2 H, 2 OH), 2.62 (t, ^3J(H, H) 7.2, 2 H, CH_2), 2.03 (m, 2 H, CH_2), 1.58 (m, 4 H, 2 CH_2), 1.21 (m, 16 H, 8 CH_2).

3,3'-Bis(1H,1H,2H,2H,3H,3H-perfluoroisodecyl)biphenyl-4,4'-diol 51.13

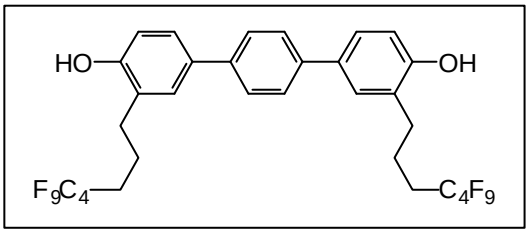


Prepared according to general procedure **8.6.11** from **50.12** (2.2 g, 2.2 mmol), BBr_3 (0.5 mL, 4.8 mmol), CH_2Cl_2 (50 mL). Purification by recrystallization from hexane.

Yield: 1.3 g (59.9 %); yellow solid; mp: 89 °C; $C_{32}H_{20}O_2F_{30}$ (570).

^{1}H-NMR (200 MHz; $CDCl_3$ *J*/Hz): δ = 7.25 (m, 4 H, Ar-H), 6.77 (m 2 H, Ar-H), 4.69 (br s, 2 H, 2 OH), 2.75 (t, ^3J(H, H) 7.23, 4 H, 2 CH_2), 2.19-1.93 (m, 8 H, 4 CH_2).

3,3''-Bis(1H,1H,2H,2H,3H,3H-perfluoroheptyl)-p-terphenyl-4,4''-diol 56.1

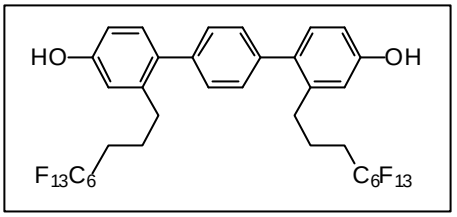


Prepared according to general procedure **8.6.11** from **55.1** (0.5 g, 0.6 mmol), BBr_3 (0.1 mL, 1.4 mmol), CH_2Cl_2 (20 mL). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$).

Yield: 0.2 g (41.7 %); yellow solid; mp: 107 °C; $C_{32}H_{22}O_2F_{18}$(782).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.62 (m, 4 H, Ar-H), 7.34 (m, 4 H, Ar-H), 6.82 (d, ^3J(H, H) 8.9, 2 H, Ar-H), 4.80 (br. s, 2 H, 2 OH), 2.81 (t, ^3J(H, H) 7.4, 4 H, 2 $ArCH_2$), 1.94-2.29 (m, 8 H, 2 CH_2CH_2).

2,2‴-Bis(1H,1H,2H,2H,3H,3H-perfluorononyl)-p-terphenyl-4,4‴-diol 56.2

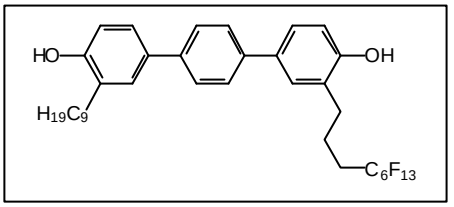


Prepared according to general procedure **8.6.11** from **55.2** (2.2 g, 2.2 mmol), BBr_3 (0.5 mL, 4.9 mmol), CH_2Cl_2 (30 mL). Purification by recrystallization from $CHCl_3$/MeOH 5:2.

Yield: 0.8 g (38.5 %); yellow solid; mp: 175 °C; $C_{36}H_{24}O_2F_{26}$ (982).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.25 (m, 4 H, Ar-H), 6.99 (m, 2 H, Ar-H), 6.67-6.73 (m, 4 H, Ar-H), 2.64 (t, ^3J(H, H) 8.2, 4 H, 2 Ar**CH_2**), 2.67-1.97 (m, 4 H, 2 CH_2), 1.58 (m, 4 H, 2 CH_2).

3-Nonly-3‴-(1H,1H,2H,2H,3H,3H-perfluorononyl)terphenyl-4,4‴-diol 77



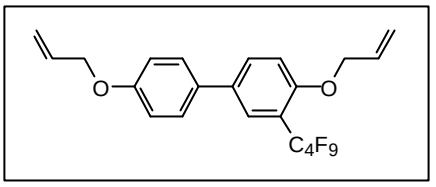
Prepared according to general procedure **8.6.11** from **76** (1.7 g, 2.2 mmol), BBr_3 (0.5 mL, 5.4 mmol), CH_2Cl_2 (40 mL). Purification by recrystallization from hexane/ethyl acetate 20:1.

Yield: 1.3 g (79.3 %); colorless solid; mp: 149 °C; $C_{36}H_{37}O_2F_{13}$ (749).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.55 (m, 4 H, Ar-H), 7.36 (m, 4 H, Ar-H), 6.84 (m, 2 H, Ar-H), 4.73, 4.79 (2 s, 2 H, 2 OH), 2.77 (t, ^3J(H, H) 7.6, 2 H, $ArCH_2$), 2.65 (t, ^3J(H, H) 7.6, 2 H, $ArCH_2$), 2.20-1-97 (m, 4 H, 2 CH_2), 1.65 (m, 2 H, CH_2), 1.26 (m, 12 H, 6CH_2), 0.86 (t, ^3J(H, H) 7.0, 3 H, CH_3).

8.6.12 Synthesis of the allyl ethers 52, 57, 67, 72 and 78

4,4'-Diallyloxy-3-perfluorobutylbiphenyl 52.1

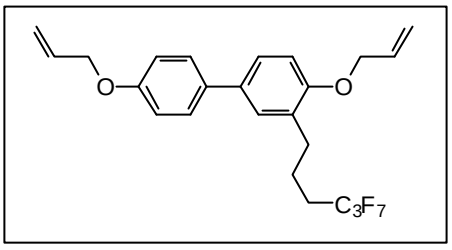


Prepared according to general procedure **8.6.5** from **51.1** (0.8 g, 2.0 mmol), allylbromide (0.4 mL, 4.9 mmol), K_2CO_3 (0.4 g, 3.0 mmol), and dry CH_3CN (30 mL). Purified by preparative centrifugal thin layer chromatography (eluent: petroleum ether).

Yield: 0.7 g (73.5 %); yellow solid; mp: 48 °C; $C_{22}H_{17}O_2F_9$ (484).

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.66 (m , 2 H, Ar-H), 7.42 (m, 2 H, Ar-H), 6.99 (m, 3 H, Ar-H), 6.11 (m, 2 H, 2 CH=), 5.49-5.25 (m, 4 H, 2 CH_2=), 4.59 (m, 4 H, 2 CH_2).

4,4'-Diallyloxy-2-(1H,1H,2H,2H,3H,3H-perfluorohexyl)biphenyl 52.2



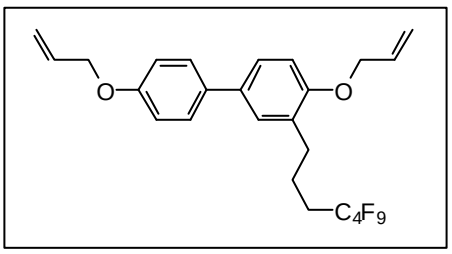
Prepared according to general procedure **8.6.5** from **51.2** (500 mg, 1.3 mmol), allylbromide (0.4 mL, 4.6 mmol), K_2CO_3 (0.4 g, 2.9 mmol), and dry CH_3CN (50 mL). Crude product was used for the next step.

Yield: 420 mg (73.4 %); yellow solid; mp: 75 °C;

$C_{24}H_{23}O_2F_7$ (476).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.46 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 7.36 (m, 2 H, Ar-H), 6.85 (m, 3 H, Ar-H), 5.96-6.16 (m, 2 H, 2 C**H**=CH_2), 5.26-5.46 (m, 4 H, 2 CH=C**H$_2$**), 4.57 (2 s, 4 H, 2 CH_2O), 2.77 (t, ^3J(H, H) 7.3, 2 H, C**H**$_2$Ar), 2.24-1.87 (m, 4 H, C**H$_2$**C**H**$_2$$CF_2$).

4,4'-Diallyloxy-3-(1H,1H,2H,2H,3H,3H-perfluoroheptyl)biphenyl 52.3



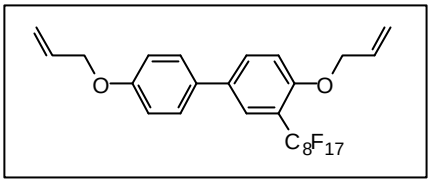
Prepared according to general procedure **8.6.5** from **51.3** (1.7 g, 3.8 mmol), allylbromide (0.8 mL, 9.2 mmol), K_2CO_3 (0.8 g, 5.7 mmol), and dry CH_3CN (50 mL). Crude product was used for the next step.

Yield: 1.9 g (92.6 %); yellow solid; mp: 70 °C;

$C_{25}H_{23}O_2F_9$ (526).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.24-7.52 (m, 4 H, Ar-H), 6.85-6.99 (m, 3 H, Ar-H), 5.96-6.16 (m, 2 H, 2 C**H**=CH_2), 5.25-5.47 (m, 4 H, 2 CH=**CH$_2$**), 4.57 (2 s, 4 H, 2 CH_2O), 2.77 (t, ^3J(H, H) 7.2, 2 H, C**H**$_2$Ar), 2.25-1.87 (m, 4 H, C**H$_2$**C**H**$_2$$CF_2$).

4,4'-Diallyloxy-3-perfluorooctylbiphenyl 52.4

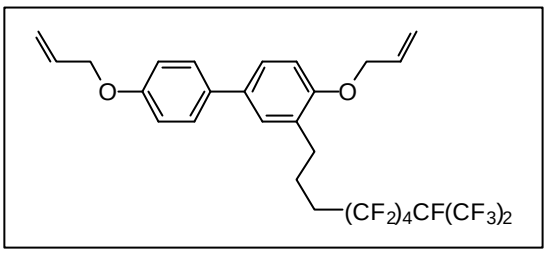


Prepared according to general procedure **8.6.5** from **51.4** (0.5 g, 0.8 mmol), allylbromide (0.2 mL, 1.9 mmol), K_2CO_3 (0.2 g, 1.2 mmol), and dry CH_3CN (20 mL). Crude product was used for the next step.

Yield: 0.7 g (73.5 %); yellow solid; mp: 81 °C; $C_{26}H_{17}O_2F_{17}$ (684).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.64 (m, 2 H, Ar-H), 7.45 (m, 2 H, Ar-H), 7.02 (m, 3 H, Ar-H), 6.03 (m, 2 H, 2 CH=), 5.47-5.27 (m, 4 H, 2 CH_2=), 4.80 (m, 4 H, 2 CH_2).

4,4'-Diallyloxy-3-(1H,1H,2H,2H,3H,3H-perfluoroisodecyl)biphenyl 52.5

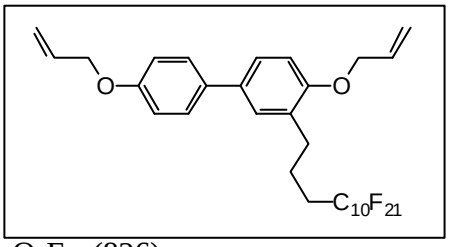


Prepared according to general procedure **8.6.5** from **51.5** (2.0 g, 3.4 mmol), allylbromide (0.7 mL, 8.1 mmol), K_2CO_3 (0.7 g, 5.0 mmol), and dry CH_3CN (50 mL). Crude product was used for the next step.

Yield: 1.9 g (92.5 %); yellow solid; mp: 85 °C; $C_{28}H_{23}O_2F_9$ (676).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.24-7.52 (m, 4 H, Ar-H), 6.85-6.97 (m, 3 H, Ar-H), 5.96-6.16 (m, 2 H, 2 C**H**=CH_2), 5.24-5.46 (m, 4 H, 2 CH=**CH_2**), 4.57 (2 s, 4 H, 2 CH_2O), 2.77 (t, ^3J (H, H) 7.0, 2 H, C**H**$_2$Ar), 2.25-1.90 (m, 4 H, C**H**$_2$C**H**$_2$$CF_2$).

4,4'-Diallyloxy-3-(1H,1H,2H,2H,3H,3H-perfluorotridecyl)biphenyl 52.6



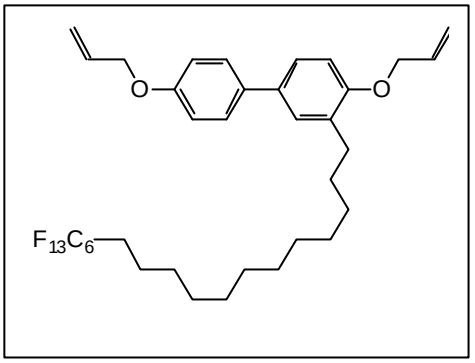
Prepared according to general procedure **8.6.5** from **51.6** (0.7 g, 1.0 mmol), allylbromide (0.2 mL, 2.3 mmol), K_2CO_3 (0.2 g, 1.4 mmol), and dry CH_3CN (50 mL). Crude product was used for the next step.

Yield: 1.9 g (92.5 %); yellow solid; mp: 116 °C; $C_{31}H_{23}O_2F_{21}$ (826).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.24-7.46 (m, 4 H, Ar-H), 6.86-6.97 (m, 3 H, Ar-H), 6.00-6.11 (m, 2 H, 2 C**H**=CH_2), 5.25-5.44 (m, 4 H, 2 CH=**CH_2**), 4.55 (m, 4 H, 2 CH_2O), 2.77 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.15-1.90 (m, 4 H, C**H**$_2$C**H**$_2$$CF_2$).

4,4'-Diallyloxy-3-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H,7H,7H, 8H,8H,9H,9H,10H,10H,11H,11H,12H,12H -perfluorooctadecyl)biphenyl 52.7

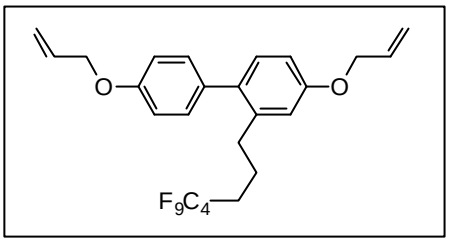
Prepared according to general procedure **8.6.5** from **51.7** (1.1 g, 1.6 mmol), allylbromide (0.4 mL, 4.5 mmol), K_2CO_3 (0.2 g, 1.4 mmol), and dry CH_3CN (50 mL). Crude product was used for the next step.



Yield: 1.1 g (100 %); colorless solid; mp: 68 °C; $C_{36}H_{41}O_2F_{21}$ (753).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.47 (d, ^{3}*J*(H, H) 2 H, Ar-H), 7.27 (m, 2 H, Ar-H), 6.82-6.96 (m, 3 H, Ar-H), 6.16-5.97 (m, 2 H, 2 C**H**=CH_2), 5.23-5.47 (m, 4 H, 2 CH=**CH_2**), 4.56 (m, 4 H, 2 CH_2O), 2.70 (t, ^{3}*J*(H, H) 7.0, 2 H, C**H**$_2$Ar), 2.15-1.89 (m, 4 H, C**H**$_2$C**H**$_2$$CF_2$), 1.61 (m, 4 H, 2 CH_2), 1.26 (m, 16 H, 8 CH_2).

4,4'-Diallyloxy-2-(1H,1H,2H,2H,3H,3H-perfluoroheptyl)biphenyl <u>52.8</u>

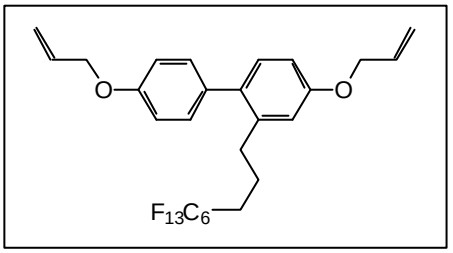


Prepared according to general procedure **8.6.5** from **<u>51.8</u>** (2.0 g, 4.5 mmol), allylbromide (0.9 mL, 10.9 mmol), K_2CO_3 (0.9 g, 6.8 mmol), and dry CH_3CN (20 mL). Crude product was used for the next step.

Yield: 2.4 g (100 %); yellow oil; $C_{25}H_{23}O_2F_9$ (526).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.19 (m, 3 H, Ar-H), 6.98 (m, 2 H, Ar-H), 6.79 (m, 2 H., Ar-H), 6.16 (m, 2 H, 2CH=), 5.49 (m, 4 H, 2 CH_2=), 4.57 (m, 4 H, 2 OCH_2), 2.71 (t, ^{3}*J*(H, H) 7.6, 2 H, CH_2), 2.01-1.67 (m, 4 H, 2 CH_2).

4,4'-Diallyloxy-2-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl <u>52.9</u>

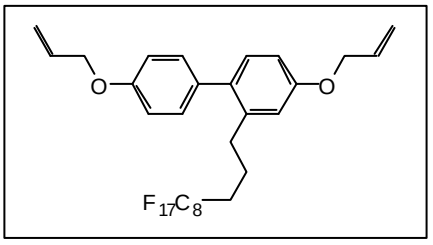


Prepared according to general procedure **8.6.5** from **<u>51.9</u>** (1.1 g, 2.0 mmol), allylbromide (0.5 mL, 6.1 mmol), K_2CO_3 (0.7 g, 5.1 mmol), and dry CH_3CN (20 mL). Crude product was used for the next step.

Yield: 1.3 g (100 %); yellow oil; $C_{27}H_{23}O_2F_{13}$ (626).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.24-7.09 (m, 3 H, Ar-H), 6.96-6.63 (m, 4 H, Ar-H), 6.10 (m, 2 H, 2 CH=), 5.26-5.48 (m, 4 H, 2 CH_2=), 4.58 (m, 4 H, 2 CH_2O), 2.65 (t, ^{3}*J*(H, H) 7.2, 2 H, Ar**CH_2**), 2.04-1.64 (m, 4 H, 2 CH_2).

4,4'-Diallyloxy-2-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)biphenyl <u>52.10</u>



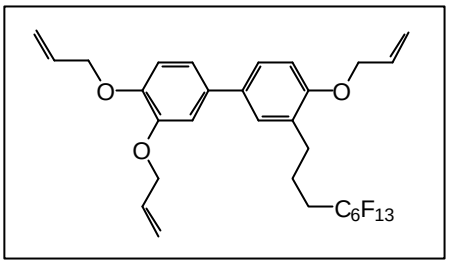
Prepared according to general procedure **8.6.5** from **<u>51.9</u>** (1.8 g, 2.8 mmol), allylbromide (0.6 mL, 6.7 mmol), K_2CO_3 (0.6 g, 4.2 mmol), and dry CH_3CN (50 mL). Crude product was used for the next step.

Yield: 1.9 g (92.6 %); yellow oil; $C_{29}H_{23}O_2F_{17}$ (726).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.17 (m, 3 H, Ar-H), 6.96 (m, 2 H, Ar-H), 6.79 (m, 2 H., Ar-H), 6.14 (m, 2 H, 2 CH=), 5.47-5.28 (m, 4 H, $2CH_2$=), 4.58 (m, 4 H, 2 OCH_2), 2.67 (t, ^3J(H, H) 7.8, 2 H, CH_2), 2.11-1.70 (m, 4 H, 2 CH_2).

3,4,4'-Triallyloxy-3'-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl 67

Prepared according to general procedure **8.6.5** from **66** (1.9 g, 3.4mmol), allylbromide (1.1 mL, 12.2 mmol), K_2CO_3 (0.7 g, 5.0 mmol), and dry CH_3CN (30 mL). Purification by preparative centrifugal thin layer chromatography (eluent: petroleum ether).

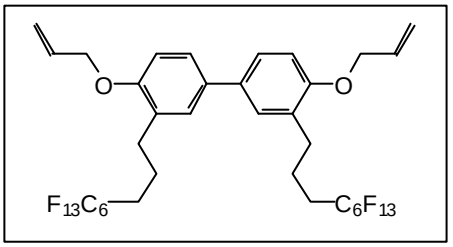


Yield: 1.7 g (73.3 %); yellow solid; mp: 58 °C; $C_{30}H_{27}O_3F_{13}$ (682).

^{1}H-NMR (400 MHz; $CDCl_3$; *J*/Hz): δ = 7.34 (dd, ^3J(H, H) 8.4, ^4J(H, H) 2.3, 1 H, Ar-H), 7.27 (dd, ^3J(H, H) 8.6, ^4J(H, H) 2.2, 1 H, Ar-H), 7.07 (m, 2 H, Ar-H), 7.03 (d, ^4J(H, H) 2.2, 1 H, Ar-H), 6.90 (d, ^3J(H, H) 8.6, 1 H, Ar-H), 6.85 (d, ^3J(H, H) 8.4, 1 H, Ar-H), 6.15 (m, 3 H, 3 CH=), 5.47-5.24 (m, 6 H, 3 CH_2=), 4.57 (m, 6 H, 3 CH_2), 2.77 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.25-1.82 (m, 4 H, **CH$_2$CH$_2$**CF_2).

4,4'-Diallyloxy-3,3'-di(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl 52.11

Prepared according to general procedure **8.6.5** from **51.11** (1.9 g, 2.1 mmol), allylbromide (0.7 mL, 7.7 mmol), K_2CO_3 (0.3 g, 1.9 mmol), and dry CH_3CN (50 mL). Crude product was used for the next step.

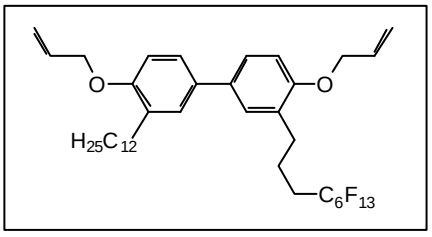


Yield: 2.1 g (100 %); yellow solid; mp: 48 °C; $C_{36}H_{28}O_2F_{26}$ (987).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.35 (dd, ^3J (H, H) 8.4, *J*(H, H) 2.3, 2 H, Ar-H), 7.27 (m, 4 H, Ar-H), 6.85 (d, ^3J(H, H) 8.4, 2 H, Ar-H), 5.96-6.15 (m, 2 H., 2 CH=), 5.24-5.45 (m, 4 H, 2 CH_2=), 4.55 (m, 4 H, 2 OCH_2), 2.74 (t, ^3J(H, H) 7.4, 4 H, 2 CH_2), 2.26-1.88 (m, 8 H, 4 CH_2).

4,4'-Diallyloxy-3-dodecyl-3'-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl 52.12

Prepared according to general procedure **8.6.5** from **77** (0.2 g, 0.5 mmol), allylbromide (0.1 mL, 1.2 mmol), K_2CO_3 (0.1 g, 0.7 mmol), and dry CH_3CN (50 mL). Crude product was used for the next step.

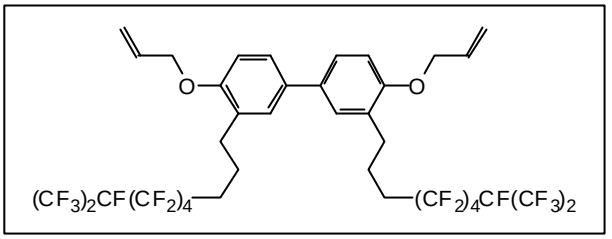


Yield: 160 mg (50.3 %); yellow solid; mp: 62 °C; $C_{27}H_{47}O_2F_{13}$(650).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.34 (dd, ^3J(H, H) 8.4, *J*(H, H) 2.4, 2 H, Ar-H), 7.29 (m, 2 H, Ar-H), ,6.88 (m, 2 H, Ar-H), 6.1 (m, 2 H, 2 CH=), 5.45-5.24 (m, 4 H, $2CH_2$=), 4.57 (m, 4 H, OCH_2), 2.79 (t, ^3J(H, H) 7.43, 2 H, C**H**$_2$Ar), 2.66 (t, 2 H, ^3J(H, H) 7.6, C**H**$_2$Ar), 2.14 (m, 2 H, C**H**$_2$), 1.99 (m, 2 H, CH_2), 1.61 (m, 2 H, CH_2), 1.24 (m, 18 H, 9 CH_2), 0.86 (t, ^3J(H, H) 7.0, 3 H, C**H**$_3$).

4,4'-Diallyloxy-3,3'-di(1H,1H,2H,2H,3H,3H-perfluoroisodecyl)biphenyl 52.13

Prepared according to general procedure **8.6.5** from **51.13** (1.3 g, 1.3 mmol), allylbromide (0.3 mL, 3.9 mmol), K_2CO_3 (0.3 g, 1.9 mmol), and dry CH_3CN (50 mL). Crude product was used for the next step.

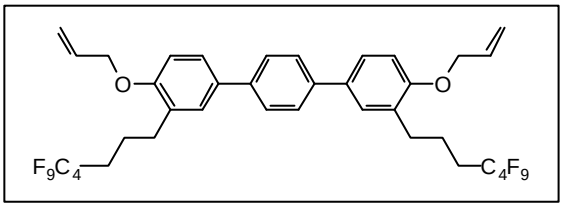


Yield: 1.3 g (100 %); yellow solid; mp: 64 °C; $C_{38}H_{28}O_2F_{30}$(1086).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.34 (dd, ^3J(H, H) 8.4, ^4J(H, H) 2.3, 2 H, Ar-H), 7.29 (m, 4 H, Ar-H), 6.86 (d, ^3J(H, H) 8.6, 2 H, Ar-H), 6.09 (m, 2 H., 2 CH=), 5.28-5.44 (m, 4 H, 2 CH_2=), 4.57 (m, 4 H, 2 OCH_2), 2.71 (t, ^3J(H, H) 7.4, 4 H, 2 CH_2), 2.13-1.72 (m, 8 H, 4 CH_2).

4,4''-Diallyloxy-3,3''-di(1H,1H,2H,2H,3H,3H-perfluoroheptyl)terphenyl 57.1

Prepared according to general procedure **8.6.5** from **56.1** (0.2 g, 0.3 mmol), allylbromide (0.05 mL, 0.6 mmol), K_2CO_3 (0.1 g, 0.7 mmol), and dry CH_3CN (50 mL). Crude product was used for the next step.

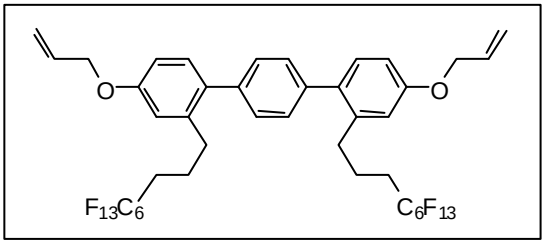


Yield: 0.3 g (100 %); mp: 140 °C; $C_{38}H_{23}O_2F_{18}$ (862).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.63 (m, 4 H, Ar-H), 7.45 (m, 4 H, Ar-H), 6.92 (d, ^3J(H, H) 8.4, 2 H, Ar-H), 6.08 (m, 2 H, 2 CH=), 5.27-5.44 (m, 4 H, 2 CH_2=), 4.59 (m, 4 H, 2 CH_2O), 2.79 (t, ^3J(H, H) 7.4, 4 H, 2 $ArCH_2$), 1.93-2.18 (m, 8 H, 2 CH_2CH_2).

4,4''-Diallyloxy-2,2''-di(1H,1H,2H,2H,3H,3H-perfluorononyl)terphenyl 57.2

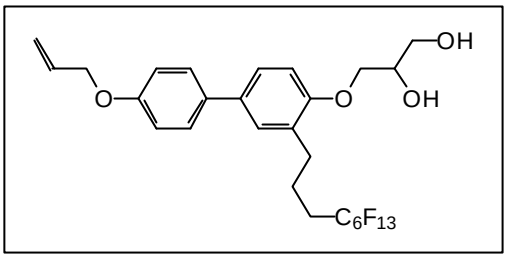
Prepared according to general procedure **8.6.5** from **56.2** (0.8 g, 0.9 mmol), allylbromide (0.2 mL, 2.0 mmol), K_2CO_3 (0.2 g, 1.3 mmol), and dry CH_3CN (50 mL). Crude product was used for the next step.



Yield: 0.7 g (92.5 %); yellow solid; mp: 87 °C; $C_{42}H_{32}O_2F_{26}$ (1062).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.31-7.15 (m, 6 H, Ar-H), 6.81 (m, 4 H, Ar-H), 6.17-5.98 (m, 2 H, 2 CH=), 5.26-5.47 (m, 4 H, 2 CH_2=), 4.55 (m, 4 H, 2 CH_2O), 2.65 (t, ^3J(H, H) 7.23, 4 H, 2 $ArCH_2$), 1.98-1.72 (m, 8 H, 2 CH_2CH_2).

3-[4'-Allyloxy-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4-yloxy]-propane-1,2-diol 72

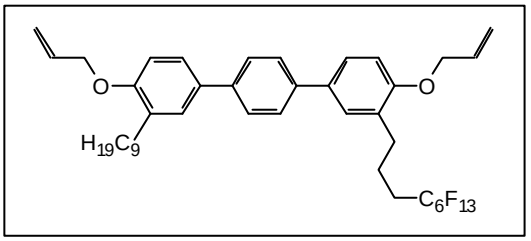


Prepared according to general procedure **8.6.5** from **71F.1** (0.3 g, 0.5 mmol), allylbromide (0.06 mL, 0.7 mmol), K_2CO_3 (0.1 g, 0.7 mmol), and dry CH_3CN (25 mL). Crude product was used for the next step.

Yield: 0.3 g (100 %); mp: 90 °C; $C_{27}H_{25}O_4F_{13}$ (660).

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 7.53 (d, ^3J (H, H) 8.8, 2 H, Ar-H), 7.40 (m, 2 H, Ar-H), 7.00 (m, 3 H, Ar-H), 6.15 (m, 1 H, CH=), 5.43 (dd, ^3J(H, H)17.9, ^4J (H, H) 2.0, 1 H, trans, C**H**$_2$=CH), 5.28 (dd, ^3J(H, H)10.6, ^4J(H, H) 1.4, 1 H, cis, C**H**$_2$=CH), 4.90 (br s, 1 H, sec OH), 4.66 (m, 3 H, prim OH, CH_2=CH-C**H**$_2$), 4.05-3.77 (m, 3 H, $ArOCH_2CH$), 3.49 (m, 2 H, CH_2OH), 2.83 (t, ^3J(H, H) 7.23, 2 H, $ArCH_2$), 2.35 (m, 2 H, CH_2CF_2), 1.88 (CH_2).

4,4''-Diallyloxy-3-nonyl-3''-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl 78



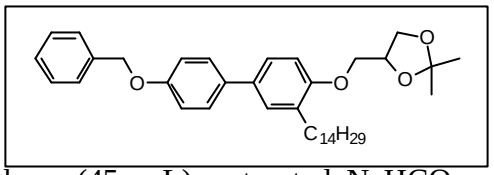
Prepared according to general procedure **8.6.5** from **77** (1.3 g, 1.7 mmol), allylbromide (0.3 mL, 3.7 mmol), K_2CO_3 (0.1 g, 0.7 mmol), and dry CH_3CN (50 mL). Crude product was used for the next step.

Yield: 1.5 g (72.7 %); mp: 139 °C; $C_{42}H_{45}O_2F_{13}$ (829).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.61 (m, 4 H, Ar-H), 7.45 (m, 4 H, Ar-H), 6.92 (d, ^3J(H, H) 8.6, 2 H, Ar-H), 6.09 (m, 2 H, 2 CH=), 5.26-5.47 (m, 4 H, 2 CH_2=), 4.59 (m, 4 H, 2 CH_2O), 2.81 (t, ^3J(H, H) 7.4, 2 H, $ArCH_2$), 2.69 (t, ^3J(H, H) 7.6, 2 H, $ArCH_2$), 2.19-1.95 (m, 4 H, 2 CH_2), 1.64 (m, 2 H, CH_2), 1.37-1.26 (m, 12 H, 6 CH_2), 0.86 (t, ^3J(H, H) 7.0, 3 H, CH_3).

8.6.13 Synthesis of the 4-(4′-benzyloxybiphenyl-4-yloxymethyl)-2,2-dimethyl-1,3-dioxolanes 69

4-(4′-Benzyloxy-3-tetradecylbiphenyl-4-yloxymethyl)-2,2-dimethyl-1,3-dioxolane 69H.3

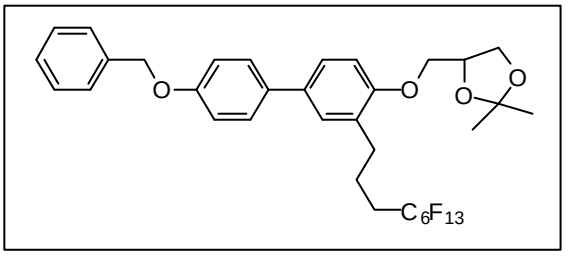


Prepared according to the general procedure **8.4.2** from 4-(4-bromo-3-tetradecylphenyloxylmethyl) -2,2-dimethyl-1,3-dioxolane (2 g, 4.1 mmol), 4-benzyloxybenzeneboronic acid (1.3 g, 8.9 mmol), glyme (45 mL), saturated $NaHCO_3$ solution (35 mL), $Pd(PPh_3)_4$ (0.2 g). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3/CH_3OH$ 10:1).

Yield: 650 mg (26.9 %); colorless solid; mp: 45 °C; $C_{39}H_{54}O_4$(586).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.43 (m, 9 H, Ar-H), 7.02 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 6.88 (d, ^3J(H, H) 8.4, 1 H, Ar-H), 5.10 (s, 2 H, BENZYL CH_2), 4.50 (m, 1 H, Sec CH), 4.19 (m, 1 H, ArOC**H$_a$**H$_b$), 4.11 (m, 1 H, ArOCH$_a$**H$_b$**),3.99 (m, 2 H, CH(O)C**H**$_2$), 2.70(t, *J*(H, H) 7.03, 2 H, C**H**$_2$Ar), 2.30-1.80 (m, 24 H, 12 C**H**$_2$), 1.5 (2 s, 6 H, 2 CH_3), 0.86 (t, ^3J(H, H) 7.03, 3 H, CH_3).

4-[4′-Benzyloxy-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4-yloxymethyl] -2,2-dimethyl-1,3-dioxolane 69F.1

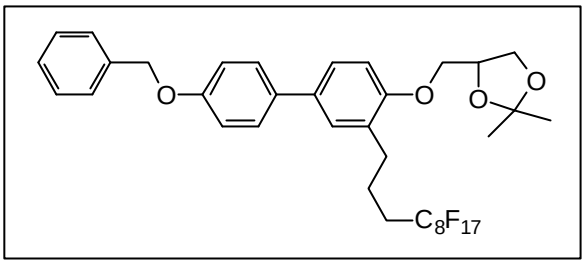


Prepared according to the general procedure **8.4.2** from **48.1** (1.2 g, 1.5 mmol), 4-benzyloxybenzeneboronic acid (0.4 g, 1.3 mmol), glyme (10 mL), saturated aqueous $NaHCO_3$ solution (6 mL), $Pd(PPh_3)_4$ (0.04 g). Purification by re crystallization from ethyl acetate/methanol 1:1.

Yield: 1.2 g (43.5 %); colorless solid; mp: 89 °C; $C_{34}H_{31}O_4F_{13}$ (750).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.43 (m, 9 H, Ar-H), 7.02(d, ^3J(H, H) 8.8, 2 H, Ar-H), 6.88 (d, ^3J(H, H) 8.4, 1 H, Ar-H), 5.10 (s, 2 H, BENZYL CH_2), 4.50 (m, 1 H, Sec CH), 4.19 (m, 1 H, ArOC**H$_a$**H$_b$), 4.11 (m, 1 H, ArOCH$_a$**H$_b$**), 3.99 (m, 2 H, CH(O)C**H**$_2$), 2.70 (t, ^3J(H, H) 7.03, 2 H, CH_2Ar), 2.30-1.80 (m, 4 H, 2 CH_2), 1.5 (2 s, 6 H, 2 CH_3).

4-[4'-Benzyloxy-3-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)biphenyl-4-yloxy methyl]-2,2-dimethyl-1,3-dioxolane 69F.2

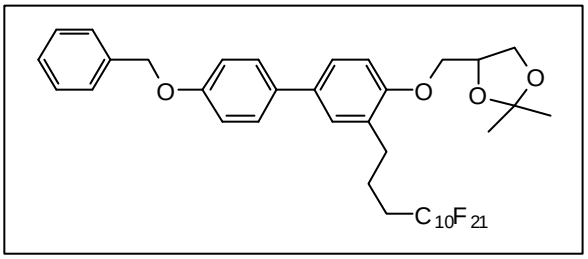


Prepared according to the general procedure **8.4.2** from **48.2** (4 g, 5.4 mmol), 4-benzyloxybenzeneboronic acid (1.2 g, 5.4 mmol), glyme (75 mL), saturated aqueous $NaHCO_3$ solution (65 mL), $Pd(PPh_3)_4$ (0.2 g). Purification by recrystallization from ethyl acetate/hexane 1:1.

Yield: 2.8 g (61.4 %); colorless solid; mp: 115 °C; $C_{36}H_{31}O_4F_{17}$ (850).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.43 (m, 9 H, Ar-H), 7.01(d, ^3J(H,H) 8.8, 2 H, Ar-H), 6.86 (d, ^3J(H,H) 8.4, 2 H, Ar-H), 5.10 (s, 2 H; BENZYL CH_2), 4.40 (m, 1 H, Sec CH), 4.20-3.80 (m, 4 H, ArOC**H**$_2$, CH(O)C**H**$_2$), 2.77 (t, ^3J(H,H) 7.42, 2 H, C**H**$_2$Ar), 2.16-1.92 (m, 4 H, 2 C**H**$_2$), 1.45, 1.24 (2 s, 6 H, 2 CH_3).

4-[4'-Benzyloxy-3-(1H,1H,2H,2H,3H,3H-perfluorotridecyl)biphenyl-4-yloxy methyl]-2,2-dimethyl-1,3-dioxolane 69F.3

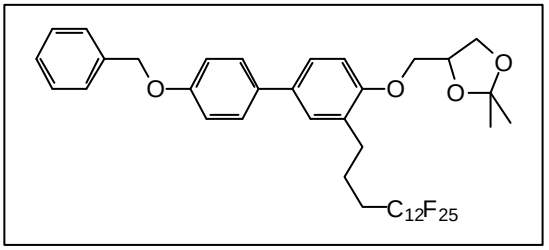


Prepared according to the general procedure **8.4.2** from **48.3** (3 g, 3.5 mmol), 4-benzyloxybenzeneboronic acid (0.8 g, 3.5 mmol), glyme (75 mL), saturated aqueous $NaHCO_3$ solution (65 mL), $Pd(PPh_3)_4$ (0.2 g). Purification by recrystallization from ethyl acetae/methanol 2:1.

Yield: 2.5 g (61.4 %); colorless solid; mp: 129 °C; $C_{38}H_{31}O_4F_{21}$ (950).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.46-7.25 (m, 9 H, Ar-H), 7.02 (m, 2 H, Ar-H), 6.89 (d, ^3J(H,H) 8.4, 1 H, Ar-H), 5.09 (s, 2 H, BENZYL CH_2), 4.50-4.44 (m, 1 H, Sec CH), 4.18 (m, 1 H, ArOC**H**$_a$H$_b$), 4.11 (m, 1 H, ArOCH$_a$**H**$_b$), 3.99-3.90 (m, 2 H, CH(O)C**H**$_2$), 2.74 (t, ^3J(H,H) 7.4, 2 H, C**H**$_2$Ar), 2.17-1.93 (m, 4 H, 2 C**H**$_2$), 1.44 (2 s, 6 H, 2 CH_3).

4-[4'-Benzyloxy-3-(1H,1H,2H,2H,3H,3H-perfluoropentadecyl)biphenyl-4-yloxy methyl]-2,2-dimethyl-1,3-dioxolane 69F.4



Prepared according to the general procedure **8.4.2** from **48.8** (0.8 g, 0.9 mmol), 4-benzyloxybenzeneboronic acid (0.2 g, 1.0 mmol), glyme (35 mL), saturated $NaHCO_3$ solution (25 mL), $Pd(PPh_3)_4$ (0.2 g). Purification

by preparative centrifugal thin layer chromatography (eluent: $CHCl_3/CH_3OH$ 10:0.5), folowed by recrystallization from ethyl acetate/methanol: 5:3.

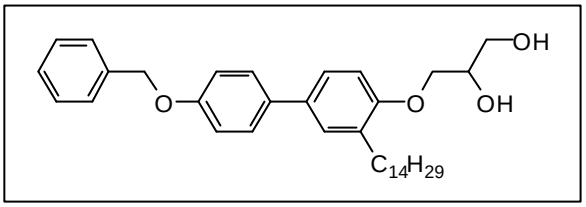
Yield: 0.5g (59.8 %); colorless solid; mp: 137 °C; $C_{40}H_{31}O_4F_{25}$ (1050).

^{1}H-NMR (200 MHz; $CDCl_3$ *J*/Hz): δ = 7.47-7.24 (m, 9 H, Ar-H), 7.02 (d, ^3J(H,H) 8.8, 2 H, Ar-H), 6.89 (d, ^3J(H,H) 8.4, 1 H, Ar-H), 5.09 (s, 2 H, BENZYL CH_2), 4.71-3.88 (m, 5 H, ArOC**H**$_2$C**H**O, C**H**$_2$O), 2.73 (t, ^3J(H,H) 7.3, 2 H, C**H**$_2$Ar), 2.15-1.92 (m, 4 H, 2 C**H**$_2$), 1.47, 1.39 (2 s, 6 H, 2 CH_3).

8.6.14 Synthesis of the 3-(4'-benzyloxybiphenyl-4-yloxy)propane-1,2-diols 70

3-(4'-Benzyloxy-3-tetradecylbiphenyl-4-yloxy)propane-1,2-diol 70H.3

Prepared according to the general procedure **8.4.3** from **69H.3** (550 mg, 0.9 mmol), and 10 % HCl (1 mL) in EtOH (50 mL). Purification by recrystallization from $CHCl_3$/MeOH 10:0.5.



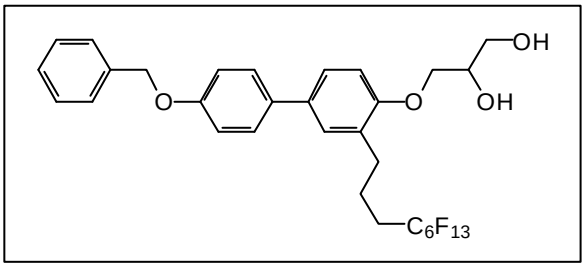
Yield: 330 mg (64.4 %); mp: 84 °C; $C_{36}H_{50}O_4$ (546).

^{1}H-NMR (200 MHz; $CDCl_3$ *J*/Hz): δ = 7.46 (m, 9 H, Ar-H), 7.02 (d, ^3J(H, H) 8.8, 2 H, Ar-H), 6.88 (d, ^3J(H, H) 9.2, 2 H, Ar-H), 5.09 (s, 2 H, $ArCH_2O$), 4.14-3.79 (m, 5 H, ArOC**H**$_2$C**H**O, C**H**$_2$O), 2.75 (t, ^3J(H, H) 7.8, 2 H, C**H**$_2$Ar), 1.61 (m, 2 H, CH_2), 1.28 (m, 22H, 11CH_2), 0.86 (t, ^3J(H, H) 6.8, 3 H, CH_3).

3-[4'-Benzyloxy-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4-yloxy) propane-1,2-diol 70F.1

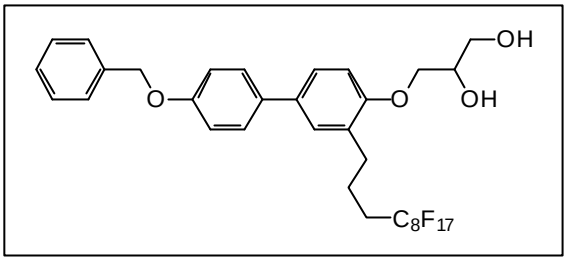
Prepared according to the general procedure **8.4.3** from **69F.1** (500 mg, 0.7 mmol), 10% HCl (1 mL), EtOH (50 mL). Purification by recrystallization from EtOH.

Yield: 290 mg (47.7 %); mp: 120 °C; $C_{31}H_{27}O_4F_{13}$ (710).



^{1}H-NMR (200 MHz; $CDCl_3$ *J*/Hz): δ = 7.46 (m, 9 H, ArH), 7.03(d, ^3J(H,H) 8.8, 2 H, ArH), 6.88 (d, ^3J(H,H) 8.4, 1 H, ArH), 5.09 (s, 2 H, $ArCH_2OAr$), 4.09-3.60 (m, 5 H, ArOC**H**$_2$C**H**O, C**H**$_2$O), 2.70 (t, ^3J(H,H) 7.0, 2 H, C**H**$_2$Ar), 2.30-1.80 (m, 4 H, 2 C**H**$_2$).

3-[4'-Benzyloxy-3-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)biphenyl-4-yloxy) propane-1,2-diol 70F.2

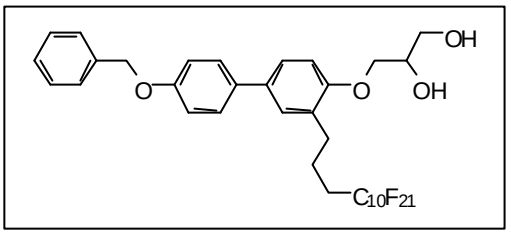


Prepared according to the general procedure **8.4.3** from **69F.2** (2.2 g, 2.6 mmol), 10 % HCl (1 mL), EtOH (50 mL). Purification by recrystallization from EtOH

Yield: 1.7 mg (81.9 %); mp: 134 °C; $C_{43}H_{27}O_4F_{17}$ (810).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.43 (m, 9 H, Ar-H), 7.03(d, ^3J(H,H) 8.8, 2 H, Ar-H), 6.88 (d, ^3J(H,H) 8.4, 1 H, Ar-H), 5.09 (s, 2 H, $ArCH_2O$), 4.09-3.60 (m, 5 H, ArOC**H**$_2$C**H**O, C**H**$_2$O), 2.75 (t, ^3J(H,H) 7.0, 2 H, C**H**$_2$Ar), 2.30-1.80 (m, 4 H, 2 C**H**$_2$).

3-[4'-Benzyloxy-3-(1H,1H,2H,2H,3H,3H-perfluorotridecyl)biphenyl-4-yloxy) propane-1,2-diol 70F.3

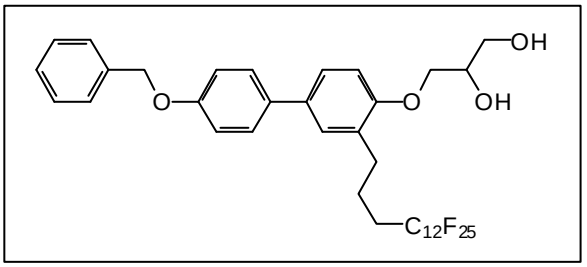


Prepared according to the general procedure **8.4.3** from **69F.3** (2.5 g, 2.6 mmol), 10 % HCl (1 mL), EtOH (50 mL). Purification by recrystallization from EtOH

Yield: 2.1 g (90.2 %); mp: 145 °C; $C_{35}H_{27}O_4F_{21}$ (910).

^{1}H-NMR (200 MHz; $CDCl_3$; *J*/Hz): δ = 7.46-7.29 (m, 9 H, Ar-H), 7.04 (d, *J*(H,H) 7.8, 2 H, Ar-H), 6.88 (d, ^3J(H,H) 8.06, 2 H, Ar-H), 5.09 (s, 2 H, $ArCH_2O$), 4.16-3.74 (m, 5 H, ArOC**H**$_2$C**H**O, C**H**$_2$O), 2.75 (t, ^3J(H,H) 7.3, 2 H, C**H**$_2$Ar), 2.30-1.87 (m, 4 H, 2 C**H**$_2$).

3-[4'-Benzyloxy-3-(1H,1H,2H,2H,3H,3H-perfluoropentadecyl)biphenyl-4-yloxy) propane-1,2-diol 70F.4



Prepared according to the general procedure **8.4.3** from **69F.4** (0.5 g, 0.5 mmol), 10 % HCl (1 mL), EtOH (50 mL). Purification by recrystallization from EtOH.

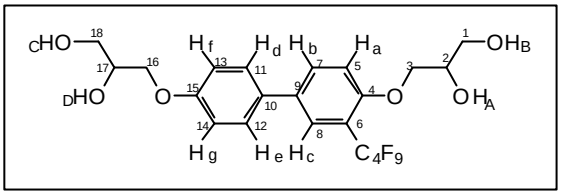
Yield: 311 mg (77.5 %); mp: 151 °C; $C_{37}H_{27}O_4F_{25}$ (1010).

^{1}H-NMR (200 MHz; $CDCl_3$ *J*/Hz): δ = 7.47-7.24 (m, 9 H, Ar-H), 7.03 (d, ^3J(H,H) 8.2, 2 H, Ar-H), 6.88 (d, ^3J(H,H) 8.2, 2 H, Ar-H), 5.09 (s, 2 H, $ArCH_2O$), 4.09-3.71 (m, 5 H, ArOC**H**$_2$C**H**O, C**H**$_2$O), 2.74 (t, ^3J(H,H) 7.3, 2 H, C**H**$_2$Ar), 2.09-1.93 (m, 4 H, 2 C**H**$_2$).

8.6.15 Synthesis of the bolaamphiphiles 53-F and 58-F

8.6.15.1 Synthesis of the bolaamphiphiles with one lateral chains 53-F

3-[4'-(2,3-Dihydroxypropyloxy)-3-perfluorobutylbiphenyl-4-yloxy]propane-1,2-diol 53F$_{4/0}$



Prepared according to the general procedure **8.6.6** from **52.1** (0.7 g, 1.44 mmol), NMMNO (1.2 mL, 7.1 mmol of 60 % solution in water), and osmium tetroxide (1.2 mL, 0.004 M solution in *tert*-butanol) in acetone (20 mL). Purification by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.

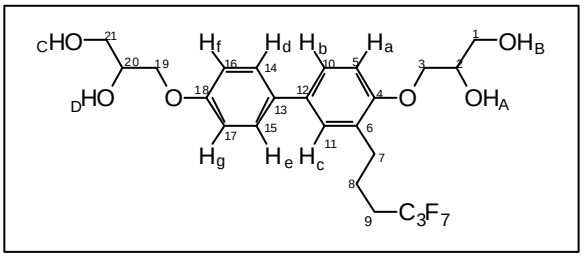
Yield: 200 mg (25.1 %); transition temperatures (°C): Cr 113 (SmA 81) Iso; $C_{22}H_{21}O_6F_9$ (552). Anal. Calcd. C, 47.83, H, 3.80; Found: C, 47.67, H, 4.08.

^{1}H-NMR (400 MHz; DMSO-D$_6$; *J*/Hz): δ = 7.88 (dd, ^3J(H, H) 8.6, ^4J(H, H) 2.3, 1 H, H$_b$), 7.64 (d, ^4J(H, H) 2.3, 1 H, H$_c$), 7.57 (dd, ^3J(H, H) 6.8, ^{4}J(H, H) 1.95, 2 H, H$_d$ H$_e$), 7.35 (d, ^3J(H, H) 8.9, 1H, H$_a$), 7.02 (dd, ^3J(H, H) 8.8, ^4J(H, H) 1.95, 2 H, H$_g$ H$_f$), 4.96 (d, ^3J(H, H) 5.08, 1 H, OH$_A$), 4.90 (d, ^3J(H, H) 4.88, 1 H, OH$_D$), 4.67 (m, 2 H, OH$_B$, OH$_C$), 4.09-3.60 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.51-3.40 (m, 4 H, 2 C**H**$_2$OH).

^{13}C-NMR (100 MHz; DMSO-D$_6$): δ = 158.7 (C$_4$), 156.7 (C$_{15}$), 132.5 (C$_9$, C$_{10}$), 132.2 (C$_8$), 130.8 (C$_7$), 127.6 (C$_{12,}$ C$_{11}$), 126.1 (C$_6$), 115.2 (C$_{14}$, C$_{13}$), 114.9 (C$_5$), 70.3 (C$_3$), 70.0 (C$_{16}$), 69.9 (C$_2$), 69.8 (C$_{17}$), 62.7 (C$_1$), 62.5 (C$_{18}$).

^{19}F-NMR (188 MHz; DMSO-D$_6$; *J*/Hz): δ = -77.19 (m, ^2J(C, F) 10.1, 3 F, CF$_3$), -103.55 (m, 2 F, CH$_2$CF$_2$), -118.08 (s, 2 F, CH$_2$CF$_2$C**F**$_2$), -122.38 (m, 2 F, CF$_3$C**F**$_2$).

3-[4'-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluorohexyl)biphenyl -4-yloxy]propane-1,2-diol 53-F$_3$



Prepared according to the general procedure **8.6.6** from **52.2** (420 g, 0.9 mmol), NMMNO (1.0 mL, 5.7 mmol of 60 % solution in water) and osmiumtetroxide (1 mL, 0.004 M solution in *tert*-butanol) in acetone (10 mL). Purification by recrystallization from ethyl acetate/hexane 1:1

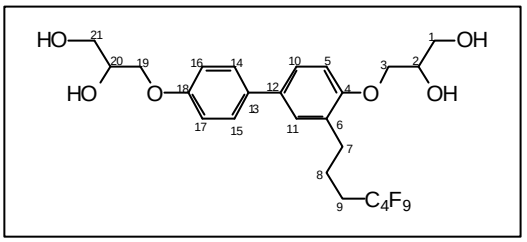
Yield: 102 mg (21.3 %); transition temperatures (°C): Cr 97 Col$_{rc}$ 119 Iso; $C_{24}H_{27}O_6F_7$ (554). Anal. Calcd. C, 52.94, H, 4.96; Found: C, 52.65, H, 5.24; MS (70 ev) *m/z* (%): 544 (M^+, 100).

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.52 (d, ^{3}J(H, H) 8.8, 2 H, H_d, H_e), 7.42 (m, 2 H, H_c, H_b), 6.99 (m, 3 H, H_a, H_f, H_g), 4.94 (d, ^{3}J(H, H) 5.1, 1 H, OH_A), 4.90 (d, ^{3}J(H, H) 5.20, 1 H, OH_D), 4.65 (m, 2 H, OH_B, OH_C), 4.03-3.76 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.49 (m, 4 H, 2 C**H**$_2$OH), 2.74 (t, ^{3}J(H, H) 7.6, 2 H, C**H**$_2$Ar), 2.22 (m, 2 H, CF_2C**H**$_2$), 1.85 (m, 2 H, C**H**$_2$$CH_2CF_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 158.1 (C_4), 156.0 (C_{18}), 132.5 (C_{12}), 132.2 (C_{13}), 129.5 (C_{10}), 127.9 (C_{11}), 127.3 (C_{14}, C_{15}), 125.3 (C_6), 115.0 (C_{16}, C_{17}), 112.2 (C_5), 70.1, 70.0 (C_3, C_{19}), 69.7 (C_2, C_{20}), 62.8, 62.7 (C_1, C_{21}), 29.6 (t, ^{2}J(C, F) 22.8, C_9), 28.9 (C_7), 20.1 (C_8).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -80.62 (overlapped t, 3 F, ^{2}J(C, F) 9.15, CF_3), -114.35 (m, 2 F, CH_2CF_2), -127.56 (m, 2 F, CF_2CF_3).

3-[4'-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluoroheptyl) biphenyl-4-yloxy]propane-1,2-diol <u>53-F$_4$</u>



Prepared according to the general procedure **8.6.6** from **<u>52.3</u>** (1.6 g, 3.0 mmol), NMMNO (1.2 mL, 7.2 mmol of 60 % solution in water) and osmiumtetroxide (1 mL, 0.004 M solution in *tert*-butanol) in acetone (40 mL). Purification by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.

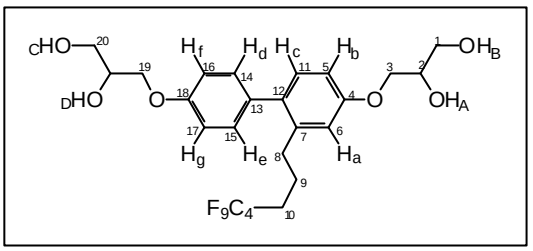
Yield: 202 mg (11.3 %); transition temperatures (°C): Cr 47 Col_{rp} 135 Iso; $C_{25}H_{27}O_6F_9$ (594). Anal. Calcd. C, 50.51, H, 4.54; Found: C, 50.51, H, 4.58.

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.50 (d, ^{3}J(H, H) 8.9, 2 H, H_d, H_e), 7.41 (m, 2 H, H_c, H_b), 6.98 (m, 3 H, H_a, H_f, H_g), 4.93 (d, ^{3}J(H, H) 5.3, 1 H, OH_A), 4.89 (d, ^{3}J(H, H) 5.1, 1 H, OH_D), 4.65 (m, 2 H, OH_B, OH_C), 4.03-3.77 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.45 (m, 4 H, 2 C**H**$_2$OH), 2.74 (t, ^{3}J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.26 (m, 2 H, CF_2C**H**$_2$), 1.86 (m, 2 H, C**H**$_2$$CH_2CF_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 158.1 (C_4), 155.9 (C_{18}), 132.5 (C_{12}), 132.2 (C_{13}), 129.5 (C_{10}), 127.8 (C_{11}), 127.3 (C_{14}, C_{15}), 125.2 (C_6), 114.9 (C_{16}, C_{17}), 112.2 (C_5), 70.5 (C_3, C_{19}), 70.0, 69.7(C_2, C_{20}), 62.7 (C_1, C_{21}), 29.7 (C_9), 28.9(C_7), 20.1 (C_8).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.37 (overlapped t, 3 F, ^{2}J(C, F) 10.1, CF_3), -110.28 (m, 2 F, CH_2CF_2), -120.84 (s, 2 F, CH_2CF_2C**F**$_2$), -122.65 (s, 2 F, C**F**$_2$$CF_3$).

3-[4'-(2,3-Dihydroxypropyloxy)-2-(1H,1H,2H,2H,3H,3H-perfluoroheptyl) biphenyl-4-yloxy]propane-1,2-diol 53'-F_4



Prepared according to the general procedure **8.6.6** from **52.8** (3.0 g, 5.6 mmol), NMMNO (2.5 mL, 14.37 mmol, 60 % solution in water) and osmiumtetroxide (2 ml, 0.004 M solution in *tert*-butanol) in acetone (10 mL). Purification by recrystallization from $CHCl_3/MeNO_2$ 5:3.

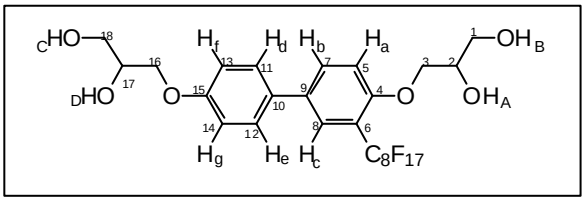
Yield: 212 mg (6.4 %); transition temperatures (°C): Cr 96 Col_t 99 Iso; $C_{25}H_{27}O_6F_9$ (594); Anal. Calcd.: C, 50.50, H, 4.55; Found: C, 50.33, H, 5.01.

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.15 (d, ^3J(H, H) 8.6, 2 H, H_d, H_e), 7.03 (d, ^3J(H, H) 8.4, 1 H, H_c), 6.96 (d, ^3J(H, H) 8.6, 2 H, H_f, H_g), 6.89 (d, *J*(H, H) 2.5, 1 H, H_a), 6.81 (dd, ^3J(H, H) 8.4, ^4J(H, H) 2.5, 1 H, H_b), 4.93 (t, ^4J(H, H) 5.1, 2 H, OH_A, OH_D), 4.66 (m, 2 H, OH_B, OH_C), 4.03-3.77 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.46 (m, 4 H, 2 C**H**$_2$OH), 2.66 (t, ^3J(H, H) 7.6, 2 H, C**H**$_2$Ar), 2.06 (m, 2 H, CF_2C**H**$_2$), 1.64 (m, 2 H, C**H**$_2$$CH_2CF_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 158.2 (C_4), 157.8 (C_{18}), 139.7 (C_7), 133.7 (C_{12}), 133.3 (C_{13}), 131.2 (C_{11}), 130.2 (C_{14}, C_{15}), 115.3 (C_6), 114.3 ($C_{16,}$ C_{17}), 112.4 (C_5), 70.0 (C_3, C_{19}), 69.6 (C_2, C_{20}), 62.7 (C_1, C_{21}), 31.6 (C_8), 29.3 (C_{10}), 21.0 (C_9).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.50 (overlapped t, ^2J(C, F) 10.1, 3 F, $CF_{3,}$), -110.37 (m, 2 F, CH_2C**F**$_2$), -120.94 (m, 2 F, CH_2CF_2C**F**$_2$), -122.61 (m, 2 F, CF_3C**F**$_2$).

3-[4'-(2,3-Dihydroxypropyloxy)-3-perfluorooctylbiphenyl-4-yloxy]propane-1,2-diol 53-$F_{8/0}$



Prepared according to the general procedure **8.6.6** from **52.4** (0.54 g, 0.79 mmol) , NMMNO (1 mL, 5.75 mmol of 60 % solution in water) and osmiumtetroxide (1 mL, 0.004 M solution in *tert*-butanol) in acetone (10 mL). Purification by recrystallization from $CHCl_3/MeNO_2$ 5:3.

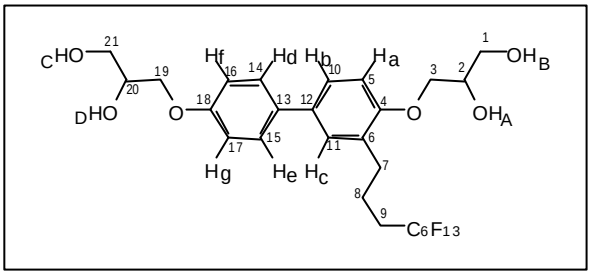
Yield: 319 mg (53.7 %); transition temperatures (°C): Cr 97 Col_h 153 Iso; $C_{26}H_{21}O_6F_{17}$ (752); Anal. Calcd.: C, 41.49, H, 2.79; Found: C, 40.90, H, 3.39.

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.87 (dd, ^3J(H, H) 8.8, ^4J(H, H) 2.15, 1 H, H_b), 7.62 (d, ^3J(H, H) 8.8, 1 H, H_c), 7.55 (dd, ^3J(H, H) 8.8, ^4J(H, H) 1.95, 2 H, H_d, H_e), 7.33 (d, ^3J(H, H) 8.8, 1H, H_a), 7.00 (d, ^3J(H, H) 8.9, 2 H, H_f, H_g), 4.95 (d, ^3J 5.07, 1 H, OH_A), 4.88 (d, ^3J(H, H) 4.9, 1 H, OH_D), 4.60 (m, 2 H, OH_B, OH_C), 4.08-3.61 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.49-3.28 (m, 4 H, 2 C**H**$_2$OH).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 160.1 (C_4), 158.0 (C_{15}), 133.9 (C_{10}), 133.6 (C_9), 132.3 (C_7, C_8), 129.2 (C_{11}, C_{12}), 126.5 (C_6), 116.6 (C_{13}, C_{14}), 116.3 (C_5), 71.7 (C_3), 71.4 (C_{16}), 71.3 (C_2), 71.2 (C_{17}), 64.1 (C_1), 63.9 (C_{18}).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.11 (overlapped t, 3 F, ^2J(C, F) 10.1, CF_3), -103.38 (m, 2 F, $CH_2\mathbf{CF_2}$), -117.23 (m, 2 F, $CH_2CF_2\mathbf{CF_2}$), -118.38 (m, 6 F, $CH_2(CF_2)_2(C\mathbf{F_2})_3$, -119.33 (m, 2 F, $CF_3CF_2\mathbf{CF_2}$), -122.61 (m, 2 F, $\mathbf{CF_2}CF_3$).

3-[4'-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluorononyl) biphenyl-4-yloxy]propane-1,2-diol 53-F_6



Prepared according to the general procedure described for **8.6.6** from **72** (0.4 g, 0.6 mmol), NMMNO (1.25 ml, 60 % solvent in water) and osmiumtetroxide (1 ml, 0.004 M solution in *tert*-butanol) in acetone (40 mL). Purification by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.

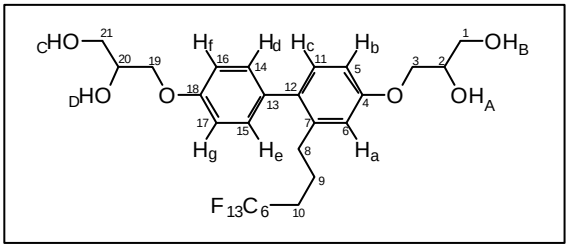
Yield: 187 mg (46.5 %); transition temperatures (°C): Cr 47 Col_h 171 Iso; $C_{27}H_{27}O_6F_{13}$ (694). Anal. Calcd.: C, 46.68, H, 3.98; Found: C, 46.97, H, 3.90.

^{1}H-NMR(200 MHz, DMSO-D_6, *J*/Hz): δ = 7.56 (d, ^3J(H, H) 8.8, 2 H, H_d, H_e), 7.45 (m, 2 H, H_c, H_b), 7.04 (m, 3 H, H_a, H_f, H_g), 4.96 (d, ^3J(H, H) 4.9, 1 H, OH_A), 4.92 (d, 1 H, OH_D), 4.06 (m, 2 H, OH_B, OH_C), 4.02-3.81 (m, 6 H, 2 ArOC$\mathbf{H}_2$C$\mathbf{H}$OH), 3.52 (m, 4 H, C$\mathbf{H}_2$OH, C$\mathbf{H}_2$OH), 2.75 (t, ^3J(H, H) 7.0, 2 H, C$\mathbf{H}_2$Ar), 2.35 (m, 2 H, $CF_2C\mathbf{H}_2$), 1.90 (m, 2 H, C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz; DMSO-D_6 *J*/Hz): δ = 158.0 (C_4), 155.9 (C_{18}), 132.5 (C_{12}), 132.2 (C_{13}), 129.5 (C_{11}), 127.8 (C_{10}), 127.3 (C_{14}, C_{15}), 125.2 (C_6), 114.9 (C_{16}, C_{17}), 112.2 (C_5), 70.0 (C_3, C_{19}), 70.0, 69.7 (C_2, C_{20}), 62.7 (C_1, C_{21}), 29.6 (t, ^2J(C, F) 22.8, C_9), 28.80 (C_7), 20.13 (C_8).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.11 (overlapped t, 3 F, CF_3), -109.96 (m, 2 F, $CH_2\mathbf{CF_2}$), -118.59 (s, 2 F, $CH_2CF_2\mathbf{CF_2}$),-119.50 (s, 2 F, $CF_3CF_2CF_2\mathbf{CF_2}$), -119.87 (s, 2 F, $\mathbf{CF_2}CF_2CF_3$), -122.61 (s, 2 F, $CF_3\mathbf{CF_2}$).

3-[4'-(2,3-Dihydroxypropyloxy)-2-(1H,1H,2H,2H,3H,3H-perfluorononyl) biphenyl-4-yloxy]propane-1,2-diol 53'-F_6



Prepared according to the general procedure described for **8.6.6** from **52.9** (1.34 g, 2.14 mmol), NMMNO (2.5 mL, 14.37 mmol of 60 % solution in water) and osmiumtetroxide (2 ml, 0.004 M solution in *tert*-butanol) in acetone

(40 mL). Purification by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.

Yield: 201 mg (14.3 %); transition temperatures (°C): Cr <20 Col_h 134 Iso; $C_{27}H_{27}O_6F_{13}$ (694). Anal. Calcd.: C, 46.68, H, 3.89; Found: C, 46.12, H, 4.46.

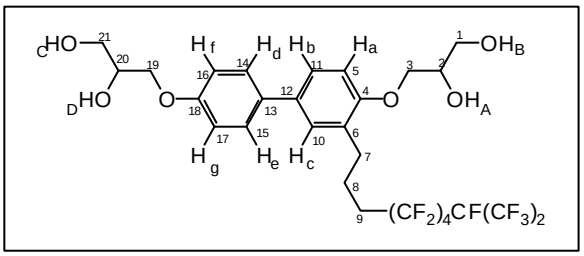
^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.13 (d, ^3J(H, H) 8.8, 2 H, H_d, H_e), 7.05 (d, ^3J(H, H) 8.9, 1 H, H_c), 6.96 (d, ^3J(H, H) 8.8, 2 H, H_f, H_g), 6.80 (m, 2 H, H_a, H_b), 4.92 (t, ^3J(H, H) 4.9, 2 H, OH_A, OH_D), 4.63 (t, ^3J(H, H) 5.5, 2 H, OH_B, OH_C), 4.02-3.79 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.49-3.28 (m, 4 H, 2 C**H**$_2$OH), 2.64 (t, ^3J(H, H) 7.6, 2 H, Ar**CH$_2$**), 2.05 (m, 2 H, C**H**$_2$CF$_2$), 1.63 (m, 2 H, C**H**$_2$CH$_2$CF$_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 162.3 (C_4), 162.0 (C_{18}), 143.9 (C_7), 137.9 (C_{12}), 137.4 (C_{13}), 135.4 (C_{11}), 134.4 (C_{14}, C_{15}), 119.5 (C_6), 118.5 (C_{16}, C_{17}), 116.5 (C_5), 74.2 (C_3, C_{19}), 73.8 (C_2, C_{20}), 66.9 (C_1, C_{21}), 35.8 (C_8), 33.6 (C_{10}), 25.1 (C_9).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.15 (overlapped t, ^2J (C, F) 10.1, 3 F, CF_3), -110.00 (m, 2 F, CH_2CF_2), -118.65 (m, 2 F, CH_2CF_2**CF$_2$**), -119.58 (s, 2 F, $CF_3CF_2CF_2$**CF$_2$**), -119.97 (s, 2 F, **CF$_2$**CF_2CF_3), -122.65 (m, 2 F, CF_3**CF$_2$**).

3-[4'-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluoroisodecyl)biphenyl-4-yloxy]propane-1,2-diol <u>53-F$_7$</u>

Prepared according to the general procedure **8.6.6** from **<u>52.5</u>** (2.1 g, 3.11 mmol), NMMNO (1.25 mL, 7.18 mmol of 60 % solution in water) and osmiumtetroxide (1 mL, 0.004 M solution in *tert*-butanol) in acetone (40 mL). Purification by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.



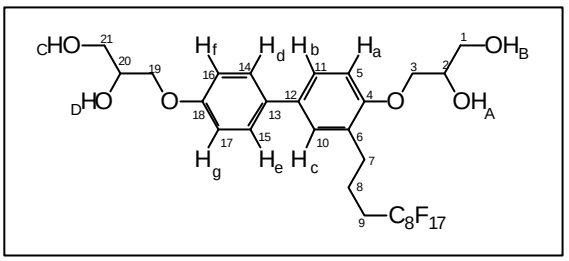
Yield: 402 mg (17.4 %); transition temperatures (°C): Cr 45 Col_h 179 Iso; $C_{28}H_{27}O_6F_{15}$(744); Anal. Calcd.: C,45.16, H, 3.63; Found: C, 45.15, H, 3.71.

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.50 (d, ^3J(H, H) 8.8, 2 H, H_d, H_e), 7.40 (m, 2 H, H_c, H_b), 6.96 (m, 3 H, H_a, H_f, H_g), 4.92 (d, ^3J(H, H) 5.1, 1 H, OH_A), 4.89 (d, ^3J(H, H) 5.3, 1 H, OH_D), 4.63 (m, 2 H, OH_B, OH_C), 4.03-3.76 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.49 (m, 4 H, 2 C**H**$_2$OH), 2.73 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.48 (m, 2 H, CF_2C**H**$_2$), 1.84 (m, 2 H, C**H**$_2$CH$_2$CF$_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ =158.0 (C_4), 155.9 (C_{18}), 132.5 (C_{12}), 132.2 (C_{13}), 129.5 (C_{10}), 127.8 (C_{11}), 127.3 (C_{14}, C_{15}), 125.2 (C_6), 114.9 (C_{16}, C_{17}), 112.1 (C_5), 70.0 (C_3, C_{19}), 70.0, 69.7 (C_2, C_{20}), 62.7 (C_1, C_{21}), 29.6 (C_9), 28.9(C_7), 20.1 (C_8).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -68.25 (m, 6 F, 2 CF_3), -110.04 (m, 2 F, CH_2CF_2), -111.91 (s, 2 F, CH_2CF_2**CF$_2$**), -117.52 (s, 2 F, $CH_2(CF_2)_2$**CF$_2$**), -119.44 (s, 2 F, $CH_2(CF_2)_3$**CF$_2$**), -182.60 (s, 1 F, **CF**$(CF_3)_2$).

3-[4'-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluoroundecyl) biphenyl-4-yloxy]propane-1,2-diol 53-F_8



Prepared according to the general procedure **8.4.3** from **59.1** (1.7 g, 1.94 mmol), 10 % HCl (2 mL), EtOH (70 mL). Purification by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.

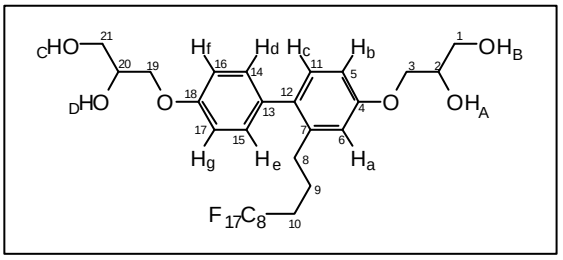
Yield: 435 mg (28.2 %); transition temperatures (°C): Cr 70 Col_h 188 Iso; $C_{29}H_{27}O_6F_{17}$ (794). Anal. Calcd.: C, 43.83, H, 3.40; Found: C, 43.49, H, 3.68.

^{1}H-NMR (400MHz; DMSO-D_6; *J*/Hz): δ = 7.52 (d, ^3J(H, H) 8.8, 2 H, H_d, H_e), 7.40 (m, 2 H, H_c, H_b), 6.96 (m, 3H, H_a, H_f, H_g), 4.94 (d, ^3J(H, H) 5.1, 1 H, OH_A), 4.89 (d, ^3J(H, H) 5.3, 1 H, OH_D), 4.65 (m, OH_B, OH_C), 4.03-3.83 (m, 4 H, 2 ArOC**H**$_2$), 3.70 (m, 2 H, 2 C**H**OH), 3.43 (m, 4 H, 2 C**H**$_2$OH), 2.75 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.20 (m, 2 H, CF_2C**H**$_2$), 1.85 (m, 2 H, C**H**$_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 158.1 (C_4), 155.9 (C_{18}), 132.5 (C_{12}), 132.2 (C_{13}), 129.5 (C_{10}), 127.8 (C_{11}), 127.3 (C_{14}, C_{15}), 125.2 (C_6), 114.9 (C_{16}, C_{17}), 112.2 (C_5), 70.1 (C_3), 70.0 (C_{19}), 69.7 (C_2, C_{20}), 62.74 (C_1, C_{21}), 29.6 (C_7), 28.9 (C_8), 20.1 (C_9).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.04 (overlapped t, ^2J(C, F) 10.1, 3 F, CF_3), -109.91 (m, 2 F, CH_2CF_2), -118.49 (m, 6 F, (C**F**$_2$)$_3$$CF_2CH_2$), -119.33 (m, 2 F, $CF_3(CF_2)_2$C**F**$_2$), -119.85 (m, 2 F, C**F**$_2CF_2CF_3$), -122.59 (m, 2 F, CF_3C**F**$_2$).

3-[4'-(2,3-Dihydroxypropyloxy)-2-(1H,1H,2H,2H,3H,3H-perfluoroundecyl) biphenyl-4-yloxy]propane-1,2-diol 53'-F_8



Prepared according to the general procedure **8.6.6.** from **52.10** (1.88 g, 2.59 mmol), NMMNO (1.25 mL, 7.18 mmol of 60 % solution in water) and osmiumtetroxide (1mL, 0.004 M solution in *tert*-butanol) in acetone (10 mL). Purification by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.

Yield: 202 mg (9.8 %); transition temperatures (°C): Cr < 20 Col_h 161 Iso; $C_{29}H_{27}O_6F_{17}$ (794). Anal. Calcd.: C,43.83, H, 3.40; Found: C, 43.40, H, 3.84.

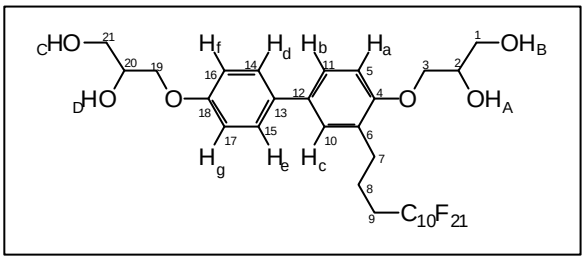
^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.13 (d, ^3J(H, H) 8.6, 2 H, H_d, H_e), 7.05 (d, ^3J(H, H) 8.4, 1 H, H_c), 6.96 (d, ^3J(H, H) 8.8, 2 H, H_f, H_g), 6.88 (d, ^4J(H, H) 2.5, 1H, H_a), 6.80 (dd, ^3J(H, H) 8.4, ^4J(H, H) 2.5, 1 H, H_b), 4.92 (t, ^3J(H, H) 5.08, 1 H, OH_A, OH_D), 4.64 (t, ^3J(H, H) 5.1, 2 H, OH_B, OH_C), 4.03-3.76(m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.46 (m, 4 H, 2

C**H**$_2$OH), 2.61 (t, ^3J(H, H) 7.6, 2 H, C**H**$_2$Ar), 2.11-1.97 (m, 2 H,CF_2C**H**$_2$), 1.67-1.59 (m, 2 H, C**H**$_2CH_2CF_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 158.1 (C_4), 157.8 (C_{18}), 139.7 (C_7), 133.7 (C_{12}), 133.3 (C_{13}), 131.2 (C_{11}), 130.2 (C_{14}, C_{15}), 115.3 (C_6), 114.3 (C_{16}, C_{17}), 112.3 (C_5), 70.0 (C_3, C_{19}), 69.6 (C_2, C_{20}), 62.8 (C_1, C_{21}), 31.6 (C_8), 29.4 (C_{10}), 20.96 (C_9).

^{19}F-NMR NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.11 (overlapped t, CF_3, 3F, ^2J(C, F) 10.1, CF_3), -110.12 (m, 2 F, CH_2C**F**$_2$), -118.57 (m, 6 F, $CH_2(CF_2)_2C$**F**$_2$), -119.39 (m, 2 F, $CH_2(CF_2)_3C$**F**$_2$), -119.95 (m, 2 F, CF_3CF_2**CF**$_2$), -122.66 (m, 2 F, **CF**$_2CF_3$).

3-[4'-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluorotridecyl) biphenyl-4-yloxy]propane-1,2-diol 53-F$_{10}$



Prepared according to the general procedure **8.6.6** from **52.6** (0.8 g, 0.9 mmol), NMMNO (1 mL, 5.7 mmol of 60 % solution in water) and osmiumtetroxide (1 mL, 0.004 M solution in *tert*-butanol) in acetone (10 mL). Purification by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.

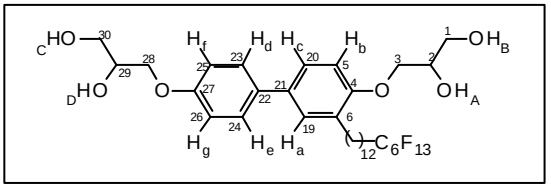
Yield: 304 mg (36.2 %); transition temperatures (°C): Cr 57 Col_r 180 Iso; $C_{31}H_{27}O_6F_{21}$ (894). Anal. Calcd.: C, 41.61, H, 3.02; Found: C, 41.45, H, 3.65.

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.53 (d, ^3J(H, H) 8.6, 2 H, H_d, H_e), 7.37 (m, 2 H, H_c, H_b), 6.94 (m, 3 H, H_a, H_f, H_g), 4.93 (d, ^3J(H, H) 5.1, 1 H, OH_A), 4.85 (d, ^3J(H, H) 5.1, 1 H, OH_D), 4.59 (m, 2 H, OH_B, OH_C), 4.20-3.75 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.46 (m, 4 H, 2 C**H**$_2$OH), 2.67 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.18 (m, 2 H, CF_2C**H**$_2$), 1.81 (m, 2 H, C**H**$_2CH_2CF_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 158.0 (C_4), 155.9 (C_{18}), 132.5 (C_{12}), 132.2 (C_{13}), 129.8 (C_{10}), 127.7 (C_{11}), 127.2 (C_{14}, C_{15}), 125.2 (C_6), 114.9 (C_{16}, C_{17}), 112.1 (C_5), 70.0 (C_3, C_{19}), 69.7 (C_2, C_{20}), 62.7 (C_1, C_{21}), 29.6 (C_9), 28.9 (C_7), 20.1 (C_8).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -78.30 (overlapped t, ^2J(C, F) 10.1, 3 F, CF_3), -110.72 (m, 2 F, CH_2CF_2), -119.09 (s, 10 F, $CH_2CF_2(CF_2)_5$), -120.10 (s, 2 F, $CF_3CF_2CF_2CF_2$), -120.34 (s, 2 F, $CF_2CF_2CF_3$), -123.56 (m, 2 F, CF_3CF_2).

3-[4'-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H,4H,4H,5H,5H,6H,6H 7H,7H,8H,8H,9H,9H,10H,10H,11H,11H,12H,12H-perfluorooctadecyl) biphenyl-4-yloxy]propane-1,2-diol 53-F$_{6/12}$



Prepared according to the general procedure **8.6.6** from **52.7** (340 g, 0.45 mmol), NMMNO (1 mL, 5.17 mmol of 60 %

solution in water) and osmiumtetroxide (1 mL, 0.004 M solution in *tert*-butanol) in acetone (25 mL). Purification by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.

Yield: 150 mg (37.3 %); transition temperatures (°C): Cr < 20 Col 150 Iso; $C_{36}H_{45}O_6F_{13}$(820). Anal. Calad.: C, 52.70, H, 5.49; Found: C, 52.19, H, 5.97.

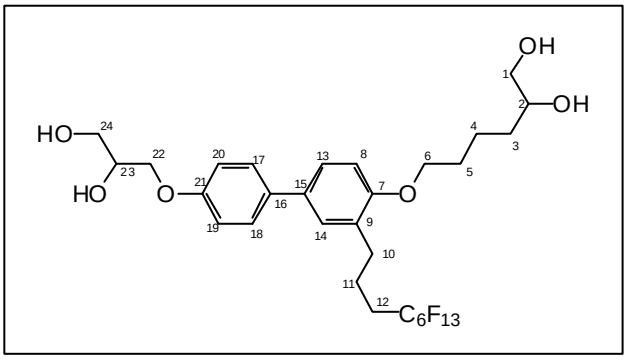
^{1}H-NMR (400 MHz; DMSO-D_6, *J*/Hz): δ = 7.50 (d, ^3J(H, H) 8.8, 2 H, H_d, H_e), 7.36 (d, ^4J(H, H) 2.3, 1 H, H_a), 7.32 (dd, ^3J(H, H) 6.6, ^4J(H, H) 2.3, 1 H, H_c), 6.97 (m, 3 H, H_b, H_f, H_g), 4.95 (d, ^3J(H, H) 5.1, 1 H, OH_A), 4.88 (d, ^3J(H, H) 5.1, 1 H, OH_B), 4.62 (m, 2 H, OH_C, OH_D), 4.20-3.77 (m, 6 H, 2 ArOC**H**$_2$, 2 CHOH), 3.47 (m, 4 H, 2 C**H**$_2$OH), 2.58 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.18 (m, 2 H,CF_2C**H**$_2$), 1.48 (m, 2 H, C**H**$_2$$CH_2CF_2$), 1.28 (m, 18 H, 9 CH_2).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 158.0 (C_4), 155.9 (C_{27}), 132.7 (C_{21}), 132.1 (C_{22}), 131.1 (C_{19}), 127.6 (C_{20}), 127.3 (C_{23}, C_{24}), 124.6 (C_6), 114.9 (C_{25}, C_{26}), 112.0 (C_5), 70.1 (C_3), 70.0 (C_{28}), 69.7 (C_2), 69.6 (C_{29}), 62.9 (C_1), 62.8 (C_{30}), 29.8, 29.4, 29.0, 28.9, 28.8, 28.7, 28.5, 28.1, 19.6 (CH_2).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.09 (overlapped t, ^2J(C, F) 10.1, 3 F, CF_3), -110.12 (m, 2 F, CH_2CF_2), -118.59 (s, 2 F, $CF_3CF_2CF_2C$**F**$_2$), -119.52 (m, 2 F, C**F**$_2CF_2CF_3$), -122.61 (m, 2 F, CF_3C**F**$_2$).

8.6.15.2 Synthesis of bolaamphiphilic biphenyl derivatives with spacer units

6-[4'-(2,3-dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4-yloxy]hexane-1,2-diol <u>53^{1,4}-F$_6$</u>



Prepared according to the general procedure **8.4.3** from **<u>59.2</u>** (1.0 g, 1.3 mmol), 10 % HCl (1 mL), EtOH (20 mL). Purification by recrystallization from n-hexan/ethyl acetate 10:4 (30 mL).

Yield: 143 mg (15.3 %); transition temperatures (°C): Cr 94 Col_h 144 Iso; $C_{30}H_{33}O_6F_{13}$ (736).

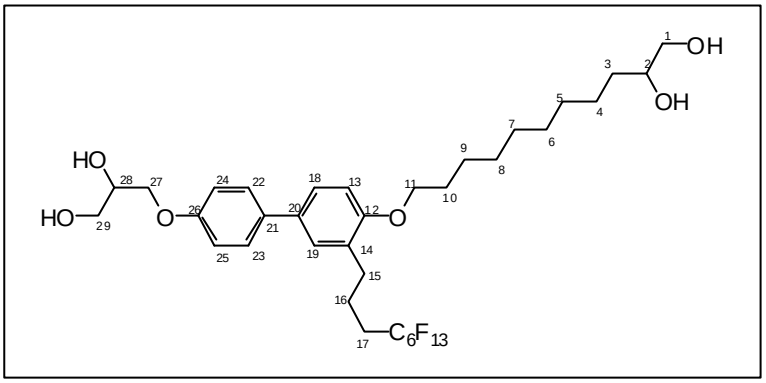
^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 7.51 (d, ^3J(H, H) 8.4, 2 H, H_d, H_e), 7.48 (m, 2 H, H_c, H_b), 6.98 (m, 3 H, H_a, H_f, H_g), 4.94 (s, 1 H, OH_A), 4.66 (s, 1 H, OH_D), 4.35 (m, 2 H, OH_B, OH_C), 4.02 (m, 6 H, ArOC**H**$_2$C**H**OH, ArOC**H**$_2$$CH_2$ C**H**OH), 3.27 (m, 4 H, C**H**$_2$OH, C**H**$_2$OH), 2.71 (t, ^3J(H, H) 7.03, 2 H, C**H**$_2$Ar), 2.26 (m, 2 H, CF_2C**H**$_2$), 1.83-1.21 (m, 10 H, 5 C**H**$_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 159.5 (C_7), 157.3 (C_{21}), 134.0 (C_{15}), 133.5 (C_{16}), 130.8 (C_{14}), 129.3 (C_{17}), 128.7 (C_{18}), 126.7 (C_9), 116.4 (C_{19}, C_{20}), 113.5 (C_8), 72.5

(C_{22}), 71.4 (C_6), 71.2 (C_{23}), 69.1 (C_{24}), 67.4 (C_1), 64.2 (C_2), 34.4 (CH_2), 31.0 (C_{12}), 23.1 (CH_2), 21.6(CH_2).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.17 (overlapped t, ^2J(C, F) 10.1, 3 F, CF_3), -109.92 (m, 2 F, $CH_2\mathbf{C}\mathbf{F_2}$), -118.67 (s, 2 F, $CH_2CF_2\mathbf{C}\mathbf{F_2}$), -119.60 (s, 2 F, $CF_3CF_2CF_2\mathbf{C}\mathbf{F_2}$), -119.97 (s, 2 F, $\mathbf{C}\mathbf{F_2}CF_2CF_3$), -122.71 (m, 2 F, $CF_3\mathbf{C}\mathbf{F_2}$).

11-[4'-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluorononyl) biphenyl-4-yloxy]undecane-1,2-diol 53^{1,9}-F$_6$



Prepared according to the general procedure **8.4.3** from **59.3** (1.1 g, 1.2 mmol), 10 % HCl (2 mL), EtOH (40 mL). Purification by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.

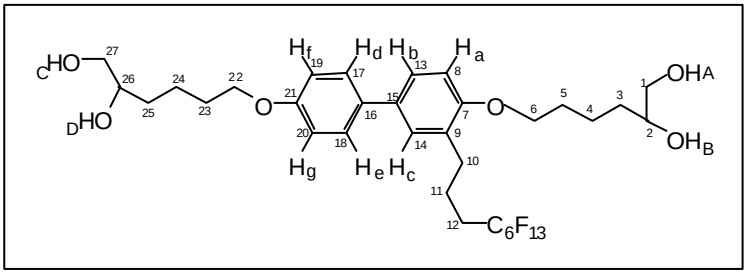
Yield: 141 mg (13.8 %); transition temperatures (°C): Cr 71 Col_t 117 Iso; $C_{35}H_{43}O_6F_{13}$ (806). Anal. Calad.: C, 52.11, H, 5.33; Found: C, 51.88, H, 5.99.

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.60 (d, ^3J(H, H) 8.0, 2 H, H_d, H_e), 7.40 (m, 2 H, H_c, H_b), 6.98 (m, 3H, H_a, H_f, H_g), 4.96 (d, ^3J(H, H) 4.1, 1 H, OH_C), 4.66 (t, ^3J(H, H) 4.9, 1 H, OH_D), 4.35 (m, 2 H, OH_A, OH_D), 4.38 (t, ^3J(H, H) 5.3, 1 H, H_B), 4.27(d, ^3J(H, H) 4.7, 1 H, H_C), 3.99 (m, 5 H, ArOC$\mathbf{H}_2$C$\mathbf{H}$OH, ArOC$\mathbf{H}_2$CH$_2$), 3.46 (m, 3 H, C$\mathbf{H}_2$OH, C$\mathbf{H}$OH), 3.21 (m, 2 H, C$\mathbf{H}_2$OH), 2.72 (t, ^3J(H, H) 7.0, 2 H, C$\mathbf{H}_2$Ar), 2.22 (m, 2 H,CF$_2$C$\mathbf{H}_2$), 1.85 (m, 2 H, C$\mathbf{H}_2$), 1.69 (m, 2 H, C$\mathbf{H}_2$), 1.24-1.42 (m, 14 H, 7 C$\mathbf{H}_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 158.1 (C_{12}), 155.9 (C_{26}), 132.5 (C_{21}), 132.1 (C_{20}), 129.3 (C_{19}), 127.9 (C_{22}), 127.3 (C_{23}), 125.3 (C_{14}), 114.9 (C_{24}, C_{25}), 112.0 (C_{13}), 71.1 (C_{27}), 70.0 (C_{11}), 69.7 (C_{28}), 67.5 (C_{29}), 66.0 (C_1), 62.8 (C_2), 33.3 (CH_2), 29.7 (t, C_{17}), 25.63 (CH_2), 25.1 (CH_2), 20.3 (C_{16}).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.25 (overlapped t, ^2J(C, F) 10.1, 3 F, CF_3), -110.0 (m, 2 F, CH_2CF_2), -118.7 (s, 2 F, $CH_2CF_2CF_2$), -119.6 (s, 2 F, $CF_3(CF_2)_2C\mathbf{F}_2$), -120.0 (m, 2 F, $C\mathbf{F}_2CF_2CF_3$), -122.7 (m, 2 F, $CF_3C\mathbf{F}_2$).

6-[4'-(5,6-Dihydroxyhexyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4-yloxy]hexane-1,2-diol 53^{4,4}-F$_6$



Prepared according to the general procedure **8.4.3** from **59.4** (1.3 g, 1.5 mmol), 10 % HCl (2 mL), EtOH (40 mL).

Purification by recrystallization from $CHCl_3/MeNO_2$ 5:3.

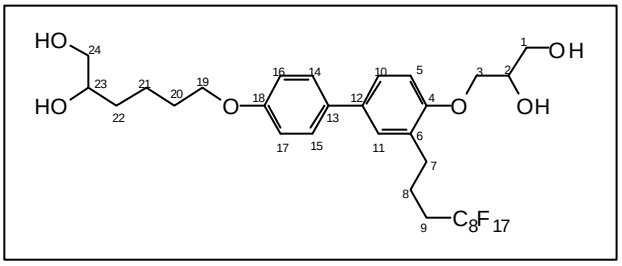
Yield: 137 mg (11.8 %); transition temperatures (°C): Cr 52 Col_r 102 Iso; $C_{33}H_{39}O_6F_{13}$ (778). Anal. Calad.: C, 50.90, H, 5.01; Found: C, 50.54, H, 5.15.

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.50 (d, ^3J(H, H) 8.8, 2 H, H_d, H_e), 7.38 (m, 2 H, H_c, H_b), 6.96 (m, 3 H, H_a, H_f, H_g), 4.45-4.35 (m, 4 H, 4 OH), 3.96 (m, 4 H, 2 ArOC**H**$_2$), 3.41 (m, 2 H, 2 CHOH), 3.25 (m, 4 H, C**H**$_2$OH), 2.70 (t, ^3J(H, H) 7.23, 2 H, C**H**$_2$Ar), 2.22 (m, 2 H,CF_2C**H**$_2$), 1.83-1.24 (m, 16 H, 6 C**H**$_2$).

^{13}C-NMR (100 MHz; DMSO-D_6): δ = 158.0 (C_7), 155.9 (C_{21}), 132.5 (C_{16}), 132.2 (C_{15}), 129.3 (C_{13}), 127.9 (C_{14}), 127.3 (C_{17}, C_{18}), 125.3 (C_9), 114.9 (C_{19}, C_{20}), 112.1 (C_8), 71.1 (C_6), 71.0 (C_{22}), 67.6 (C_2), 67.6 (C_{26}), 66.0 (C_1), 66.0 (C_{27}), 33.1 (C_3), 33.0 (C_{25}), 29.4 (**C**H_2CF_2), 29.1 (C_{10}), 28.9 (C_4, C_{23}), 21.8 (C_{24}), 21.7 (C_5), 20.2 (C_{11}).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.25 (overlapped t, ^2J(C, F) 10.1, 3 F, CF_3), -110.1 (m, 2 F, CH_2CF_2), -118.7 (s, 2 F, CH_2CF_2C**F**$_2$), -119.6 (s, 2 F, $CF_3(CF_2)_2$C**F**$_2$), -120.0 (s, 2 F, C**F**$_2CF_2CF_3$), -122.8 (m, 2 F, CF_3CF_2).

6-[4'-(2,3-Dihydroxypropyloxy)-3'-(1H,1H,2H,2H,3H,3H-perfluoroundecyl) biphenyl-4-yloxy]hexane-1,2-diol 53^{4,1}-F$_8$



Prepared according to the general procedure **8.4.3** from **59.5** (1.0 g, 1.1 mmol), 10 % HCl (1 mL), EtOH (50 mL). Purification by recrystallization from $CHCl_3/MeNO_2$ 5:3.

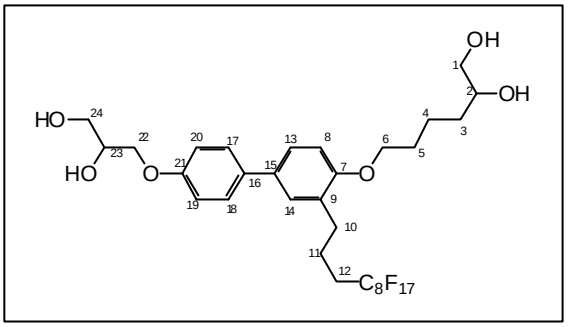
Yield: 176 mg (19.3 %); transition temperatures (°C): Cr 76 Col_h 138 Iso; $C_{32}H_{33}O_6F_{17}$ (836)**;** MS (70ev): m/z (%): 836 (M^+, 96), 720 (82), 646 (100), 199 (52), 85 (39).

^{1}H-NMR (400MHz; DMSO-D_6; *J*/Hz): δ = 7.49 (d, ^3J(H, H) 8.8, 2 H, H_d, H_e), 7.39 (m, 2 H, H_c, H_b), 6.96 (m, 3 H, H_a, H_f, H_g), 4.88 (d, ^3J(H, H) 5.1,1 H, OH_A), 4.62 (t, ^3J(H, H) 5.7,1 H,. OH_D), 4.43 (t, ^3J(H, H) 5.7, 1 H, OH_B), 4.38 (d, ^3J(H, H) 5.7, 1 H, OH_C), 4.06-3.90 (m, 4 H, 2ArOC**H**$_2$), 3.82 (m, 1 H, C**H**OH), 3.48 (m, 2 H, C**H**$_2$OH), 3.41 (m, 1 H, C**H**OH), 3.25 (m, 2 H, C**H**$_2$OH), 2.73 (t, ^3J(H, H) 7.23, 2 H, C**H**$_2$Ar), 2.25 (m, 2 H, CF_2C**H**$_2$), 1.88 (m, 2 H, CH_2), 1.75 (m, 2 H, CH_2), 1.20-1.65 (m, 6 H, 3 C**H**$_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 158.0 (C_4), 155.9 (C_{18}), 132.4 (C_{12}), 133.2 (C_{13}), 129.5 (C_{10}), 127.8 (C_{11}), 127.3 (C_{14}, C_{15}), 125.2 (C_6), 114.9 (C_{16}, C_{17}), 112.2 (C_5), 71.1 (C_3), 70.1 (C_{19}), 69.7 (C_2), 67.6 (C_1), 66.0 (C_{24}), 62.7 (C_{23}), 33.1 (C_7), 29.6 (t, **C**H_2CF_2), 28.9 (C_8), 21.7 (C_{20}), 20.2 (C_{21}).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.07 (overlapped t, ^2J(C, F) 10.1, 3 F, CF_3), -110.00 (m, 2 F, CH_2CF_2), -118.51 (m, 6 F, CH_2CF_2(C**F**$_2$)$_3$), -119.35 (m, 2 F, $CH_2(CF_2)_4$C**F**$_2$), -119.87 (m, 2 F, C**F**$_2CF_2CF_3$), -122.71 (m, 2 F, CF_3C**F**$_2$).

6-[4'-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluoroundecyl) biphenyl-4-yloxy]hexane-1,2-diol 53^{1,4}-F$_8$



Prepared according to the general procedure **8.4.3** from **59.6** (0.9 g, 1.1mmol), 10 % HCl (1 mL), EtOH (50 mL). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH: 10:2), followed by recrystallization from $CHCl_3$.

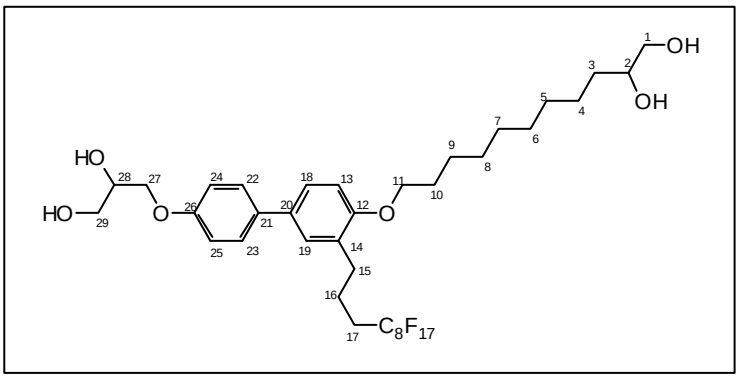
Yield: 178 mg (21.7 %); transition temperatures (°C): Cr 83 Col$_h$ 161 Iso; $C_{32}H_{33}O_6F_{17}$ (836). Anal. Calcd.: C, 45.93, H, 3.95; Found: C, 45.78, H, 4.18.

^{1}H-NMR (400 MHz; DMSO-D$_6$; *J*/Hz): δ = 7.51 (d, ^3J(H, H) 8.8, 2 H, H$_d$, H$_e$), 7.40(m, 2 H, H$_c$, H$_b$), 6.96 (m, 3 H, H$_a$, H$_f$, H$_g$), 4.94 (d, ^3J(H, H) 5.1, 1 H, OH$_A$), 4.64 (t, ^3J(H, H) 5.7, 1 H, OH$_D$), 4.41 (t, ^3J(H, H) 5.7, 1 H, OH$_B$), 4.34 (d, ^3J(H, H) 4.9, 1 H, OH$_C$), 3.77-4.01 (m, 5 H, ArOC**H**$_2$C**H**OH, ArOC**H**$_2$CH$_2$), 3.46 (m, 3 H, C**H**$_2$OH, C**H**OH), 3.29 (m, 2 H, C**H**$_2$OH), 2.73 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.25 (m, 2 H,CF$_2$C**H**$_2$), 1.88 (m, 4 H, 2 C**H**$_2$), 1.45 (m, 4 H, 2 CH$_2$).

^{13}C-NMR (100 MHz; DMSO-D$_6$; *J*/Hz): δ = 158.1 (C$_7$), 155.9 (C$_{21}$), 132.5 (C$_{15}$), 132.1 (C$_{16}$), 129.3 (C$_{13}$), 127.9 (C$_{14}$), 127.3 (C$_{17}$, C$_{18}$), 125.3 (C$_9$), 115.0 (C$_{19,}$ C$_{20}$),112.1 (C$_8$), 71.0 (C$_{22}$), 70.0 (C$_6$), 69.7 (C$_{23}$), 67.6 (C$_{24}$), 65.9 (C$_1$), 62.7 (C$_2$), 32.0 (CH$_2$Ar), 29.1 (**C**H$_2$CF$_2$), 28.9, 21.7, 20.2 (CH$_2$).

^{19}F-NMR (188 MHz; DMSO-D$_6$; *J*/Hz): δ = -77.14 (overlapped t, ^2J(C, F) 10.1, 3 F, CF$_3$), -109.91 (m, 2 F, CH$_2$CF$_2$), -118.49 (m, 6 F, (C**F**$_2$)$_3$CF$_2$CH$_2$), -119.33 (m, 2 F, CF$_3$(CF$_2$)$_2$C**F**$_2$), -119.85 (m, 2 F, C**F**$_2$CF$_2$CF$_3$), -122.59 (m, 2 F, CF$_3$CF$_2$).

3-[4'-(2,3-Dihydroxpropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluoroundecyl) biphenyl-4-yloxy]undecane-1,2-diol 53^{1,9}-F$_8$



Prepared according to the general procedure **8.4.3** from **59.7** (0.7 g, 0.7 mmol), 10 % HCl (1 mL), EtOH (50 mL). The product was purified by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10:2), followed by recrystallization from $CHCl_3$.

Yield: 178 mg (20.9 %); transition temperatures (°C): Cr 97 Col$_t$ 135 Iso; $C_{37}H_{43}O_6F_{17}$ (906); Anal. Calcd. C, 49.00, H, 4.75; Found: C, 49.10, H, 4.50.

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 7.52 (d, ^{3}J(H, H) 8.8, 2 H, H_d, H_e), 7.41 (m, 2 H, H_c, H_b), 6.99 (m, 3 H, H_a, H_f, H_g), 4.94 (d, ^{3}J(H, H) 5.1, 1 H, OH_A), 4.68 (t, ^{3}J(H, H) 5.7, 1 H,. OH_D), 4.36 (t, ^{3}J(H, H) 5.5, 1 H, OH_B), 4.26 (d, ^{3}J(H, H) 4.88, 1 H, OH_C), 3.99 (m, 5 H, ArOC**H**$_2$C**H**OH, ArOC**H**$_2$CH_2), 3.47 (m, 3 H, C**H**$_2$OH, C**H**OH), 3.24 (m, 2 H, C**H**$_2$OH), 2.74 (t, ^{3}J(H, H) 7.6, 2 H, C**H**$_2$Ar), 2.23 (m, 2 H,CF_2C**H**$_2$), 1.71 (m, 4 H, 2 C**H**$_2$), 1.24 (s, br, 14 H, 7 CH_2).

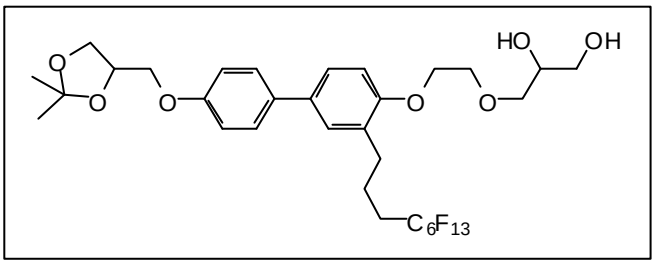
^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 158.1 (C_{12}), 155.9 (C_{26}), 132.5 (C_{21}), 132.1(C_{20}), 129.3 (C_{19}), 128.0 (C_{22}), 127.3 (C_{23}), 125.3 (C_{14}), 114.9 (C_{25}), 113.6 (C_{24}), 112.0 (C_{13}), 71.1 (C_{27}), 70.0 (C_{11}), 69.7 (C_{28}), 67.5 (C_{29}), 66.0 (C_1), 62.8 (C_2), 33.1, 29.2, 29.0, 28.8, 25.1, 20.4 (CH_2).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.11 (overlapped t, 3 F, ^{2}J(C, F) 10.1, CF_3), -109.89 (m, 2 F, CH_2CF_2), -118.53 (m, 6 F, (C**F**$_2$)$_3$$CF_2CH_2$), -119.53 (m, 2 F, $CF_3(CF_2)_2CF_2$), -119.87 (m, 2 F, C**F**$_2$$CF_2CF_3$), -122.61 (m, 2 F, CF_3CF_2).

8.6.15.3 Synthesis of the bolaamphiphiles 53F.15 and 53F.16

6-[4′-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluorononyl) biphenyl-4-yloxy]-4-oxahexane-1,2-diol 53F.15

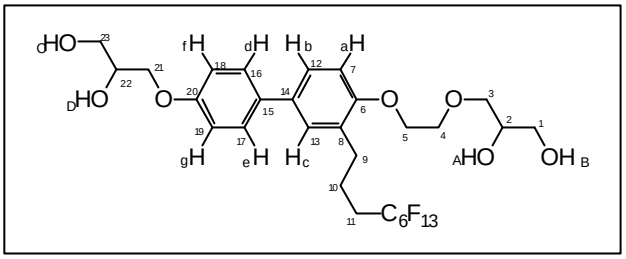
*6-[4′-(2,2-Dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4-yloxy]-4-oxahexane-1,2-diol **64***



Prepared according to the procedure described for **8.6.6** from **63** (2.6 g, 3.5 mmol), NMMNO (2 mL, 60 % solvent in water), and osmiumtetroxide (1 mL, 0.01 M) in acetone (10 mL).
Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10:1).
Yield: 571mg (21.1 %); yellow oil; $C_{32}H_{35}O_7F_{13}$ (779).

^{1}H-NMR (200 MHz; $CDCl_3$ *J*/Hz): δ = 7.43 (dd, ^{4}J(H, H) 2.2, ^{3}J(H, H) 6.8, 2 H, Ar-H), 7.34 (m, 2 H, Ar-H), 6.94 (dd, *J*(H, H) 2.0, ^{3}J(H, H) 6.8, 2 H, Ar-H), 6.87 (d, ^{3}J(H, H) 8.4, 1H, Ar-H), 4.51 (m, 1 H, OCH), 4.18-3.57 (m, 13 H, OC**H**$_2$C**H**O, 5 C**H**$_2$O), 3.29 (m, 1 H, OH), 2.95 (m, 1H, OH), 2.76 (t, ^{3}J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.17-1.94 (m, 4 H, CF_2C**H**$_2$C**H**$_2$).

6-[4¢-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluorononyl) biphenyl-4-yloxy]-4-oxahexane-1,2-diol ***53F.15***



Prepared according to the general procedure **8.4.3** from **64** (568 mg, 0.7 mmol), 10 % HCl (1 mL), EtOH (20 mL). Purification by recrystallization from $CHCl_3$.

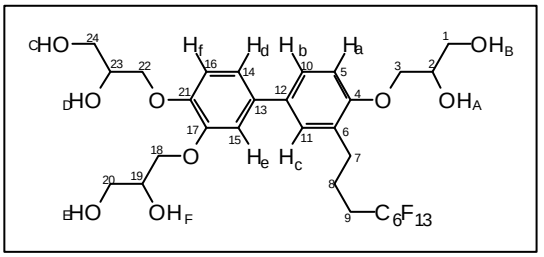
Yield: 157 mg (29.1 %); transition temperatures (° C): Cr < 20 Col_h132 Iso; $C_{29}H_{31}O_7F_{13}$ (738); Anal. Calcd. C, 47.15, H, 4.20; Found: C, 47.24, H, 4.51.

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.52 (dd, ^3J(H, H) 8.8, ^4J(H, H) 2.0, 2 H, H_d, H_e), 7.42 (m, 2 H, H_c, H_b), 6.96 (m, 3 H, H_a, H_f, H_g), 4.92 (d, ^3J(H, H) 5.3, 1 H, OH_A), 4.66 (t, ^3J(H, H) 5.7, 1 H, OH_D), 4.60 (d, ^3J(H, H) 4.9, 1 H, OH_B), 4.43 (t, ^3J(H, H) 5.7, 1 H, OH_C), 4.13-3.74 (m, 7 H, 2ArOC**H**$_2$, C**H**$_2$O, C**H**OH), 3.60-3.25 (m, 7 H, C**H**OH, C**H**$_2$O, 2C**H**$_2$OH), 2.73 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.26 (m, 2 H,CF_2C**H**$_2$), 1.83 (m, 2 H, C**H**$_2$$CH_2CF_2$).

^{13}C-NMR (100 MHz; DMSO-D_6): δ = 158.1 (C_{20}), 155.7 (C_6), 132.4 (C_{14}, C_{15}), 129.6 (C_{12}), 127.9 (C_{13}), 127.2 (C_{16}, C_{17}), 125.2 (C_8), 114.9 (C_{18}, C_{19}), 112.4 (C_7), 72.78 (C_5), 70.57(C_4), 70.0 (C_{21}), 69.7 (C_3), 69.3 (C_{22}), 67.7 (C_2), 63.0 (C_{23}), 62.7 (C_1), 29.5 (C_{11}), 29.0 (C_9), 20.06(C_{10}).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.13 (overlapped t, 3 F, CF_3), -110.00 (m, 2 F, CH_2CF_2), -118.63 (s, 2 F, CH_2CF_2C**F**$_2$), -119.56 (s, 2 F, $CF_3CF_2CF_2$C**F**$_2$), -119.93 (s, 2 F, C**F**$_2CF_2CF_3$), -122.65 (m, 2 F, CF_3C**F**$_2$).

3-[3¢,4¢-Bis(2,3-dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluorononyl) biphenyl-4-yloxy]propane-1,2-diol 53F.16



Prepared according to the general procedure described for **8.6.6** from **67** (1.7 g, 2.5 mmol), NMMNO (0.6 mL, 3.4 mmol of 60 % solution in water) and osmiumtetroxide (1 mL, 0.004 M solution in *tert*-butanol),) in acetone (10 mL). Purification by preparative centrifugal thin layer chromatography ($CHCl_3$/MeOH 10:1), followed by recrystallization from ethyl acetate.

Yield: 800 mg (41.4 %); transition temperatures (°C): Cr 72 Col_h 106 Iso; $C_{30}H_{33}O_9F_{13}$ (786).

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.44 (m, 2 H, Ar-H), 7.19 (d, ^4J(H, H) 2.0, 1 H, Ar-H), 7.10 (dd, ^3J(H, H) 8.2, ^4J(H, H) 2.0, 1 H, Ar-H), 6.98 (m, 2 H, Ar-H), 4.89 (br s, 3 H,

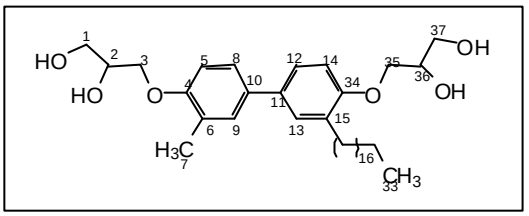
3 OH), 4.63 (br s, 3 H, 3 OH), 4,.07-3.80 (m, 9 H, 3 ArOC**H**$_2$, 3 C**H**OH), 3.46 (m, 6 H, 3 C**H$_2$**OH), 2.72 (t, ^3J(H, H) 7.23, 2 H, C**H**$_2$Ar), 2.32-2.18 (m, 2 H,CF_2C**H**$_2$), 1.89-1.81 (m, 2 H, C**H**$_2$$CH_2CF_2$).

^{13}C-NMR (100 MHz; DMSO-D_6): δ = 156.0 (C_{21}), 149.2 (C_4), 148.1 (C_{17}), 133.4 (C_{13}), 132.3 (C_{12}), 129.5 (C_{14}), 128.0 (C_{15}), 125.4 (C_{10}), 118.9 (C_{11}), 114.8 (C_6), 112.7 (C_{16}), 112.1 (C_5), 70.9 (C_3), 70.1 (C_{22}), 70.2 (C_{18}), 69.7 (C_2), 62.9 ($C_{19,}$ C_{23}), 62.7 ($C_{20,}$ C_{24}), 59.7 (C_1), 29.6 (C_9), 29.0 (C_7), 20.2 (C_8).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz):δ = -77.15 (overlapped t, 3 F, CF_3), -110.06 (m, 2 F, CH_2CF_2), -118.65 (s, 2 F, CH_2CF_2C**F**$_2$), -119.58 (s, 2 F, $CF_3CF_2CF_2C$**F**$_2$), -119.93 (s, 2 F, C**F**$_2CF_2CF_3$), -122.67 (m, 2 F, CF_3C**F**$_2$).

8.6.15.4 Synthesis of the bolaamphiphiles with two lateral chains 54

3-[4'-(2,3-Dihydroxypropyloxy)-3-octadecyl-3'-methylbiphenyl-4-yloxy]propane-1,2-diol 54-H$_{1,18}$



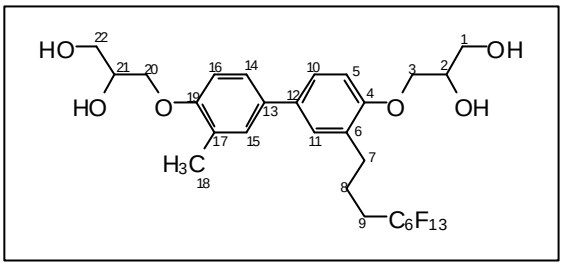
Prepared according to the general procedure **8.4.3** from 2,2-Dimethyl-4-{4'-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]-3'-methyl-3-octadecyl biphenyl-4-yloxymethyl}-1,3-dioxolane (592 mg, 0.87 mmol), 10 % HCl (1 mL), EtOH (50 mL). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10:2), followed by recrystallization from $CHCl_3$/CH_3NO_2 10:1.

Yield: 178 mg (34.0 %); transition temperatures (°C): Cr 79 Col 106 Iso; $C_{37}H_{60}O_6$ (601).

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 7.35 (d, ^3J(H, H) 8.4, 2 H, Ar-H), 7.32 (m, 2 H, Ar-H), 6.94 (dd, *J*(H, H) 8.4, ^4J(H, H) 2.2, 2 H, Ar-H), 4.90 (d, ^3J(H, H) 5.1, 1 H, 1 OH), 4.86 (d, ^3J(H, H) 4.9, 1 H, 1 OH), 4.61 (m, 2 H, 2 OH), 4.02-3.76 (m, 6 H, 2 ArOC**H**$_2$C**H**OH), 3.53 (m, 4 H, C**H**$_2$OH, C**H**$_2$OH), 2.58 (t, ^3J(H, H) 6.8, 2 H, C**H**$_2$Ar), 2.20 (s, 3 H, C**H**$_3$), 1.54 (m, 2 H,CF_2C**H**$_2$), 1.21 (m, 32 H, 16 C**H**$_2$), 0.84 (t, ^3J(H, H) 7.0, 3 H, CH_3).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 156.3 (C_4), 156.0 (C_{34}), 132.5 (C_{10}), 132.4 (C_{11}), 131.2 (C_9), 128.6 (C_{13}), 127.8 (C_8), 126.6 (C_{12}), 124.8 (C_6, C_{15}), 112.2 (C_{14}), 111.9 (C_5), 70.3 (C_3, C_{35}), 69.9 (C_2, C_{36}), 63.0 (C_1, C_{37}), 31.4 (CH_3), 30.0, 29.6, 29.1, 29.0, 28.8, 22.2, 16.2 (CH_2), 14.0 (C_{33}).

3-[4'-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluornonyl)-3'-methylbiphenyl-4-yloxy]propane-1,2-diol 54-H_1F_6



Prepared according to the general procedure **8.4.3** from **59.8** (0.7 g, 0.9 mmol), 10 % HCl (1 mL), EtOH (50 mL). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH: 10:2), followed recrystallization from $CHCl_3$.

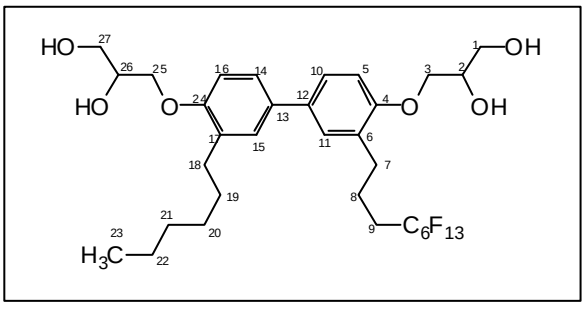
Yield: 435 mg (68.18 %); transition temperatures (°C): Cr 97 Col 134 Iso. $C_{28}H_{29}O_6F_{13}$ (708). Anal. Calcd.: C, 74.00, H, 10.00; Found: C, 74.03, H, 9.93.

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 7.39 (m, 4 H, Ar-H), 6.95 (m, 2 H, Ar-H), 4.89 (br s, 2 OH), 4.61 (br s, 2 H, 2 OH), 4.02-3.78 (m, 6 H, 2 ArOC**H**$_2$C**H**OH), 3.48 (m, 4 H, C**H**$_2$OH, C**H**$_2$OH), 2.73 (t, ^3J(H, H) 7.30, 2 H, C**H**$_2$Ar), 2.20 (s, 3 H, C**H**$_3$), 2.24 (m, 2 H, CF_2C**H**$_2$), 1.85 (m, 2 H, C**H**$_2$).

^{13}C-NMR (100 MHz; DMSO-D_6, *J*/Hz): δ = 156.1 (C_4), 155.8 (C_{19}), 132.4 (C_{12}), 132.1 (C_{13}), 129.4 (C_{11}), 128.4 (C_{15}), 127.8 (C_6), 126.4 (C_{17}), 125.2 (C_{10}), 124.6 (C_{14}), 112.1 (C_5), 111.8 (C_{16}), 70.0 (C_3, C_{20}), 69.7 (C_2, C_{21}), 62.7 (C_1, C_{22}), 29.3 (t, ^2J(C, F) 21.6, C_9), 28.9 (C_7), 20.2 (C_8), 16.0 (C_{18}).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -80.77 (overlapped t, 3 F, CF_3), -113.52 (m, 2 F, CH_2CF_2), -122.07 (s, 2 F, CH_2CF_2C**F**$_2$), -123.00 (s, 2 F, $CF_3CF_2CF_2$C**F**$_2$), -123.39 (s, 2 F, C**F**$_2CF_2CF_3$), -126.07 (s, 2 F, CF_3C**F**$_2$).

3-[4'-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluornonyl)-3'-hexylbiphenyl-4-yloxy]propane-1,2-diol 54-H_6F_6



Prepared according to the general procedure **8.4.3** from **59.9** (0.6 g, 0.7 mmol), 10 % HCl (1 mL), EtOH (50 mL). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10:2), followed by recrystallization from $CHCl_3$.

Yield: 315 mg (58.01 %); transition temperatures (°C): Cr 115 (Col 108) Iso; $C_{33}H_{39}O_6F_{13}$ (778).

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 7.40 (m, 4 H, Ar-H), 6.96 (m, 2 H, Ar-H), 4.89 (t, ^3J(H, H) 5.7, 2 H, 2 OH), 4.63 (m, 2 H, 2 OH), 4.02-3.77 (m, 6 H, 2 ArOC**H**$_2$C**H**OH), 3.49 (m, 4 H, C**H**$_2$OH, C**H**$_2$OH), 2.73 (t, ^3J(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.57 (t, ^3J(H, H) 7.2, 2

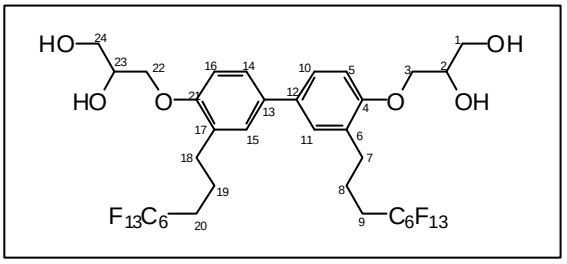
H, C**H**$_2$Ar), 2.28 (m, 2 H, CF_2C**H**$_2$), 1.89 (m, 2 H, C**H**$_2$), 1.55 (m, 2 H, C**H**$_2$),1.28 (m, 6 H, 3 C**H**$_2$), 0.81 (t, 3 H, ^3J(H, H) 7.0, C**H**$_3$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 155.9 (C_4), 155.8 (C_{24}), 132.5 (C_{12}), 132.1 (C_{13}), 131.1 (C_{11}), 129.4 (C_{15}), 127.8 (C_6), 127.6 (C_{17}), 125.2 (C_{10}), 124.6 (C_{14}), 112.1 (C_5), 112.0 (C_{16}), 70.1, 70.1 (C_3, C_{25}), 69.7, 69.6 (C_2, C_{26}), 62.8, 62.7 (C_1, C_{27}), 31.0 (C_{21}), 29.8 (C_{19}), 29.4 (C_9, C_7), 28.8 (C_{18}), 28.6 (C_{20}), 22.0 (C_{21}, C_{22}), 20.1 (C_8), 13.8 (C_{23}).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -80.76 (overlapped t, 3 F, CF_3), -113.56 (m, 2 F, CH_2CF_2), -122.10 (s, 2 F, $CF_2CF_2CH_2$),-123.02 (s, 2 F, C**F**$_2$$CF_2CF_2CF_3$), -123.43 (s, 2F, C**F**$_2$$CF_2CF_3$), -126.12 (s, 2 F, C**F**$_2$$CF_3$).

3-[4‹-(2,3-Dihydroxypropyloxy)-3,3‹-bis(1H,1H,2H,2H,3H,3H-perfluornonyl)biphenyl-4-yloxy]propane-1,2-diol <u>54-F$_{6.6}$</u>

Prepared according to the general procedure **8.6.6** from **<u>52.11</u>** (2.1 g, 2.2 mmol), NMMNO (1 mL, 5.7 mmol of 60 % solution in water) and osmiumtetroxide (1 mL, 0.004 M solution in *tert*-butanol) in acetone (25 mL). Purification by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.



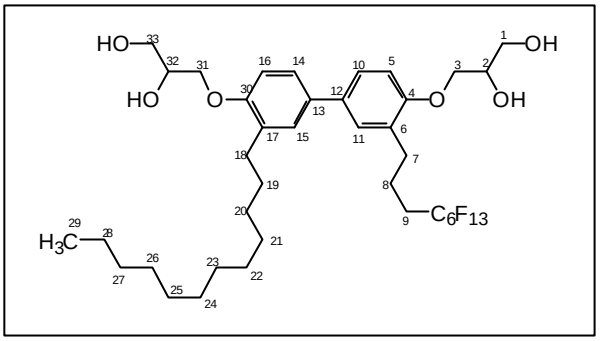
Yield: 1.3 mg (55.4 %); colorless crystals; mp:147 °C; $C_{36}H_{32}O_6F_{26}$ (1054).

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.40 (dd, ^3J(H, H) 8.9, ^4J(H, H) 2.3, 2 H, Ar-H), 7.37(d, ^4J(H, H) 2.14, 2 H, Ar-H), 6.97 (m, 2 H, Ar-H), 4.88 (m, 2 H, 2 OH), 4.62 (m, 2 H, 2 OH), 4.01-3.79 (m, 6 H, 2 ArOC**H**$_2$C**H**OH), 3.47 (m, 4 H, 2 C**H**$_2$OH, C**H**$_2$OH)), 2.71 (t, ^3J(H, H) 7.2, 4 H, 2 C**H**$_2$Ar), 2.23 (t, 4 H, ^3J(H, H) 7.0, 2 C**H**$_2$), 1.84 (m, 4 H, 2 CH_2).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 157.4 (C_4, C_{21}), 137.7 (C_{12}, C_{13}), 130.7 (C_{11}, C_{15}), 129.2 (C_6, C_{17}), 126.7 (C_{10}, C_{14}), 113.6 (C_5, C_{16}), 71.5 (C_3, C_{22}), 71.4 (C_2, C_{23}), 71.1 (C_1, C_{24}), 31.0 (C_9, C_{20}), 30.8 (C_7, C_{18}), 21.3 (C_8, C_{19}).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -81.01 (overlapped t, 6 F, 2 CF_3), -113.65 (m, 4 F, 2 CH_2CF_2), -122.24 (s, 4 F, 2 $CF_2CF_2CH_2$), -123.19 (s, 4 F, 2 C**F**$_2$$CF_2CF_2CF_3$), -123.48 (s, 4 F, 2 C**F**$_2$$CF_2CF_3$), -126.27 (s, 4 F, 2 C**F**$_2$$CF_3$).

3-[4'-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluornonyl)-3'-dodecylbiphenyl-4-yloxy]propane-1,2-diol 54-$H_{12}F_6$



Prepared according to the general procedure **8.6.6** from **52.12** (150 g, 0.2 mmol), NMMNO (1 mL, 5.7 mmol of 60 % solution in water) and osmiumtetroxide (1 mL, 0.004 M solution in *tert*-butanol) in acetone (25 mL). Purification by recrystallization from ethyl acetate/hexane 2:1.

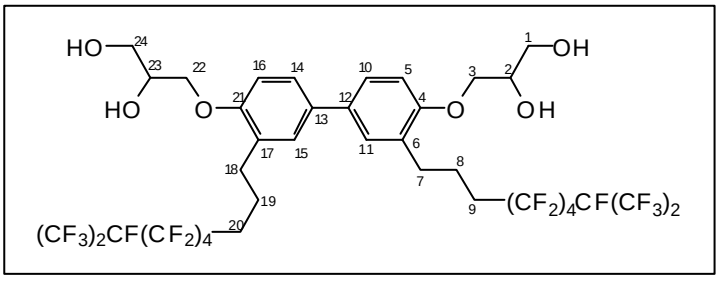
Yield: 902 mg (45.4 %); mp: 134 °C; $C_{39}H_{51}O_6F_{13}$ (862).

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.39 (m, 4 H, Ar-H), 6.98 (m, 2 H, Ar-H), 4.89 (m, 2 H, 2 OH), 4.61 (m, 2 H, 2 OH), 4.02-3.77 (m, 6 H, 2 ArOC**H**$_2$C**H**OH), 3.54 (m, 4 H, 2 C**H**$_2$OH), 2.73 (t, ^{3}*J*(H, H) 7.4, 2 H, C**H**$_2$Ar), 2.58 (t, 2 H, ^{3}*J*(H, H) 7.0, C**H**$_2$Ar), 2.23 (m, 2 H, C**H**$_2$), 1.87 (m, 2 H, CH_2), 1.56 (m, 2 H, CH_2), 1.21 (m, 18 H, 9 CH_2), 0.84 (t, ^{3}*J*(H, H) 6.84, 3 H, C**H**$_3$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 156.1 (C_4, C_{30}), 132.7 (C_{12}), 132.4 (C_{13}), 131.2 (C_{11}), 129.6 (C_{15}), 128.0 (C_6), 127.8 (C_{17}), 125.5 (C_{10}), 124.9 (C_{14}), 112.3 (C_5), 112.2 (C_{16}), 70.3 (C_3), 70.3 (C_{31}), 69.9 (C_2), 69.8 (C_{32}), 63.1 (C_1), 63.0 (C_{33}), 31.4, 29.9, 29.6, 29.1, 29.1, 29.0, 28.8, 22.2, 20.3 (CH_2), 14.0 (CH_3).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -80.83 (overlapped t, 3 F, CF_3), -113.52 (m, 2 F, CH_2CF_2), -122.07 (s, 2 F, CH_2CH_2C**F**$_2$), -122.99 (s, 2 F, $CF_3CF_2CF_2C$**F**$_2$), -123.40 (s, 2 F, C**F**$_2CF_2CF_3$), -126.08 (s, 2 F, CF_3CF_2).

3-[4'-(2,3-Dihydroxypropyloxy)-3,3'-bis(1H,1H,2H,2H,3H,3H-perfluoro isodecyl)biphenyl-4-yloxy]propane-1,2-diol 54-$F_{7.7}$



Prepared according to the general procedure **8.6.6** from **52.13** (2.1 g, 1.9 mmol), NMMNO (1 mL, 5.7 mmol of 60 % solution in water) and osmiumtetroxide (1mL, 0.004 M solution in *tert*-butanol) in acetone (25 mL). Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$/MeOH 10:1), followed by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.

Yield: 983 mg (45.1 %); mp:143 °C; $C_{38}H_{32}O_6F_{30}$ (1154).

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 7.41 (dd, ^{3}*J*(H, H) 8.4, ^{4}*J*(H, H) 2.3, 2 H, Ar-H), 7.37 (d, ^{4}*J*(H, H) 2.35, 2 H, Ar-H), 6.98 (d, ^{3}*J*(H, H) 8.1, 2 H, Ar-H), 4.89 (br s, 2 OH),

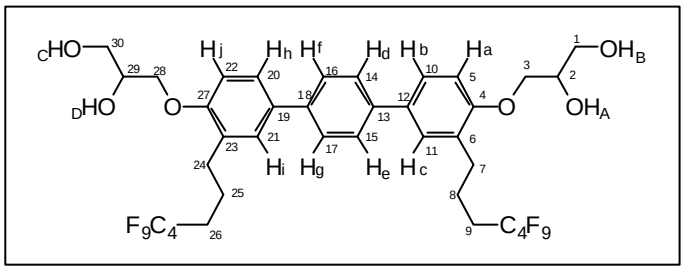
4.61 (br s, 2 H, 2 OH), 4.02-3.78 (m, 6 H, 2 ArOC**H**$_2$C**H**OH), 3.48 (m, 4 H, C**H**$_2$OH, C**H**$_2$OH), 2.75 (t, ^3J(H, H) 7.4, 4 H, 2 C**H**$_2$Ar), 2.20 (m, 4 H, 2 C**H**$_2$), 1.83 (m, 4 H, 2 C**H**$_2$).

^{13}C-NMR (100 MHz; DMSO-D$_6$; *J*/Hz): δ = 157.3 (C_4, C_{21}), 133.7 (C_{12}, C_{13}), 130.6 (C_{11}, C_{15}), 129.1 (C_6, C_{17}), 126.7 (C_{10}, C_{14}), 113.2 (C_5, C_{16}), 71.5 (C_3, C_{22}), 71.1 (C_2, C_{23}), 64.2 (C_1, C_{24}), 30.8 (C_9, C_{20}), 30.0 (C_7, C_{18}), 21.2 (C_8, C_{19}).

^{19}F-NMR (188 MHz; DMSO-D$_6$; *J*/Hz): δ = -68.29 (m, 6 F, 2 CF_3), -110.08 (m, 4 F, 2 CH_2CF_2), -111.93 (s, 4 F, 2 $CH_2CF_2C\mathbf{F}_2$), -117.56 (s, 4 F, 2 $CH_2(CF_2)_2C\mathbf{F}_2$), -119.54 (s, 4 F, 2 $CH_2(CF_2)_3C\mathbf{F}_2$), -182.64 (m, 2 F, 2 C**F**$(CF_3)_2$).

8.6.15.5 Synthesis of the bolaamphiphilic p-terphenyl derivatives 58

3-[4″-(2,3-Dihydroxypropyloxy)-3,3″-bis(1H,1H,2H,2H,3H,3H-perfluoroheptyl)-p-terphenyl-4-yloxy]propane-1,2-diol 58-F$_{4,4}$



Prepared according to general procedure **8.6.6** from **57.1** (0.3 g, 0.4 mmol), NMMNO (1 mL, 5.8 mmol, 60 % solution in water) and osmiumtetroxide (1 mL, 0.004 M solution in *tert*-butanol) in acetone (25 mL). Purification by recrystallization from $CHCl_3$/MeOH 10:0.5.

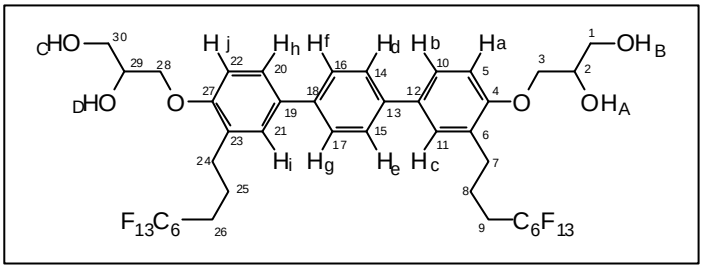
Yield: 101 mg (26.5 %); transition temperatures (°C): Cr 158 Col (L) 165 Iso; $C_{38}H_{36}O_6F_{18}$ (931); Anal. Calcd.: C, 49.03, H, 3.87; Found: C, 48.82, H, 4.26.

^{1}H-NMR (400 MHz; DMSO-D$_6$; *J*/Hz): δ = 7.66 (m, 4 H, H_b, H_c, H_i, H_h), 7.51 (m, 4 H, H_d, H_e, H_f, H_g), 7.03 (d, ^3J(H, H) 8.4, 2 H, H_a, H_j), 4.92 (d, 2 H, OH_A, OH_D), 4.63 (m, 2 H, OH_C, OH_B), 4.05-3.81(m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.48 (m, 4 H, 2 C**H**$_2$OH), 2.78 (t, ^3J (H, H) 7.2, 4 H, 2 C**H**$_2$Ar), 2.31 (m, 4 H, 2 $CF_2C\mathbf{H}_2$), 1.91 (m, 4 H, 2 C**H**$_2CH_2CF_2$).

^{13}C-NMR (100 MHz; DMSO-D$_6$; *J*/Hz): δ = 158.0 (C_4, C_{27}), 139.7 (C_{12}, C_{19}), 133.4 (C_{13}, C_{18}), 131.1 (C_{11}, C_{21}), 129.5 (C_{10}, C_{20}), 128.1 (C_{16}, C_{17}, C_{14}, C_{15}), 127.1 (C_6, C_{23}), 113.7 (C_5, C_{22}), 71.5 (C_3, C_{28}), 71.2 (C_2, C_{29}), 64.2 (C_1, C_{30}). 30.9 (C_9, C_{26}), 30.3 (C_7, C_{24}), 21.5 (C_8, C_{25}).

^{19}F-NMR (188 MHz; DMSO-D$_6$; *J*/Hz): δ = -77.35 (overlapped t, 6 F, 2 CF_3), -110.88 (m, 4 F, 2 CH_2CF_2), -119.04 (s, 4 F, 2 $CH_2CF_2C\mathbf{F}_2$), -119.99 (s, 4 F, 2 $CF_3(CF_2)_2C\mathbf{F}_2$), -120.44 (s, 4 F, 2 $C\mathbf{F}_2CF_2CF_3$), -123.17 (m, 4 F, 2 $CF_3C\mathbf{F}_2$).

3-[4''-(2,3-Dihydroxypropyloxy)-3,3''-bis(1H,1H,2H,2H,3H,3H-perfluorononyl)-p-terphenyl-4-yloxy]propane-1,2-diol 58-$F_{6,6}$



Prepared according to the procedure described for **8.4.3** from **60.1** (0.7 g, 0.6 mmol), 10 % HCl (1 mL), EtOH (50 mL). Purification by recrystallization from $CHCl_3$/MeOH 10:0.5.

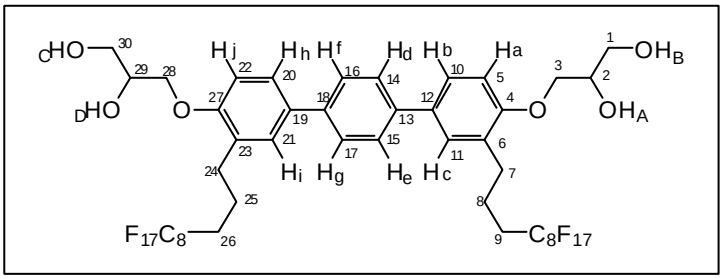
Yield: 357 mg (54.6 %); transition temperatures (°C): Cr 169 Col (L) 185 Iso; $C_{42}H_{36}O_6F_{26}$ (1130); Anal. Calad.: C, 44.60, H, 3.18; Found: C, 44.57, H, 3.41.

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.66 (m, 4 H, H_b, H_c, H_i, H_h), 7.53 (m, 4 H, H_d, H_e H_f, H_g), 7.05 (d, 2 H, ^3J(H, H) 8.4, H_a, H_j), 4.91 (d, 2 H, OH_A, OH_D), 4.64 (m, 2 H, OH_C, OH_B), 4.05-3.91 (m, 4 H, 2 ArOC**H**$_2$), 3.81 (m, 2 H, 2 CHOH), 3.48 (m, 4 H, 2 C**H**$_2$OH), 2.76 (t, ^3J (H, H) 7.6, 4 H, 2 C**H**$_2$Ar), 2.32-2.18 (m, 4 H, 2 CF_2C**H**$_2$), 1.91-1.83 (m, 4 H, 2 C**H**$_2$$CH_2CF_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 156.5 (C_4, C_{27}), 138.3 (C_{12}, C_{19}), 132.5 (C_{13}, C_{18}), 129.6 (C_{11}, C_{21}), 128.1 (C_{10}, C_{20}), 126.6 (C_{16}, C_{17}, C_{14}, C_{15}), 125.6 (C_6, C_{23}), 112.2 (C_5, C_{22}), 70.1 (C_3, C_{28}), 69.7 (C_2, C_{29}), 62.7 (C_1, C_{30}), 29.6 (C_9, C_{26}), 28.9 (C_7, C_{24}), 20.1 (C_8, C_{25}).

^{19}F NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.13 (overlapped t, 6 F, 2 CF_3), -110.00 (m, 4 F, 2 CH_2CF_2), -118.63 (s, 4 F, 2 $CH_2CF_2CF_2$), -119.56 (s, 4 F, 2 $CF_3(CF_2)_2$C**F**$_2$), -119.93 (s, 4 F, 2 $CF_2CF_2CF_3$), -122.70 (m, 4 F, 2 CF_3CF_2).

3-[4''-(2,3-Dihydroxypropyloxy)-3,3''-bis(1H,1H,2H,2H,3H,3H-perfluoroundecyl)-p-terphenyl-4-yloxy]propane-1,2-diol 58-$F_{8,8}$



Prepared according to the procedure described for **8.4.3** from **60.2** (135 mg, 0.09 mmol), 10 % HCl (1 mL), EtOH (50 mL). Purification by recrystallization from $CHCl_3$/MeOH 10:0.5.

Yield: 78 mg (65.1 %); transition temperatures (°C): Cr 133 Col (L) 185 Smb 197 Iso; $C_{46}H_{36}O_6F_{34}$ (1330).

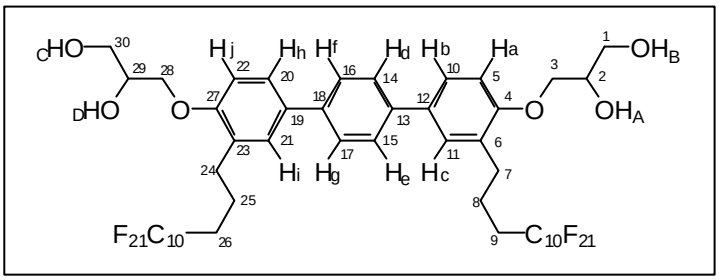
^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.65 (m, 4 H, H_b, H_c, H_i, H_h), 7.50 (m, 4 H, H_d, H_e H_f, H_g), 7.05 (d, 2 H, ^3J(H, H) 8.9, H_a, H_j), 4.91 (d, 2 H, OH_A, OH_D), 4.64 (m, 2 H, OH_C, OH_B), 4.02-3.89 (m, 4 H, 2 ArOC**H**$_2$), 3.81 (m, 2 H, 2 CHOH), 3.48 (m, 4 H, 2 C**H**$_2$OH),

2.76 (t, ^3J (H, H) 7.3, 4 H, 2 C**H**$_2$Ar), 2.32-2.18 (m, 4 H, 2 CF$_2$C**H**$_2$), 1.91-1.83 (m, 4 H, 2 C**H**$_2$CH$_2$CF$_2$).

^{13}C-NMR (100 MHz; DMSO-D$_6$; *J*/Hz): δ = 156.2 (C$_4$, C$_{27}$), 138.1 (C$_{12}$, C$_{19}$), 131.7 (C$_{13}$, C$_{18}$), 129.3 (C$_{11}$, C$_{21}$), 127.8 (C$_{10}$, C$_{20}$), 126.4 (C$_{16}$, C$_{17}$, C$_{14}$, C$_{15}$), 125.4 (C$_6$, C$_{23}$), 112.1 (C$_5$, C$_{22}$), 70.0 (C$_3$, C$_{28}$), 69.7 (C$_2$, C$_{29}$), 62.7 (C$_1$, C$_{30}$), 29.5 (C$_9$, C$_{26}$), 28.7 (C$_7$, C$_{24}$), 20.0 (C$_8$, C$_{25}$).

^{19}F-NMR (188 MHz; DMSO-D$_6$; *J*/Hz): δ = -77.04 (overlapped t, ^2J(C, F) 10.1, 6 F, 2 CF$_3$), -109.91 (m, 4 F, 2 CH$_2$CF$_2$), -118.49 (m, 12 F, 2 (C**F**$_2$)$_3$CF$_2$CH$_2$), -119.33 (m, 4 F, 2 CF$_3$(CF$_2$)$_2$C**F**$_2$), -119.85 (m, 4 F, 2 C**F**$_2$CF$_2$CF$_3$), -122.59 (m, 4 F, 2 CF$_3$C**F**$_2$).

3-[4‴-(2,3-Dihydroxypropyloxy)-3,3‴-bis(1H,1H,2H,2H,3H,3H-perfluorotridecyl)-p-terphenyl-4-yloxy]propane-1,2-diol <u>58-F$_{10, 10}$</u>



Prepared according to the procedure described for **8.4.3** from **<u>60.3</u>** (72 mg, 0.04 mmol), 10 % HCl (1 mL), EtOH (50 mL). Purification by recrystallization from CHCl$_3$/MeOH 10:0.5.

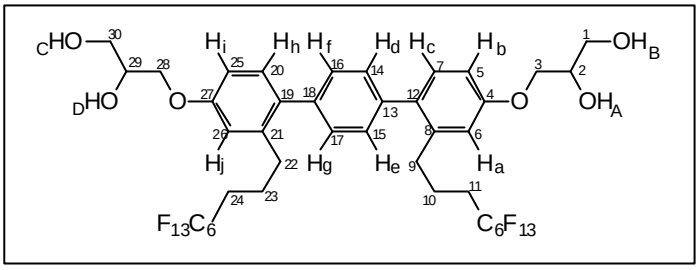
Yield: 51 mg (75.0 %); transition temperatures (°C): Cr 195 Smb 205 Iso; C$_{50}$H$_{36}$O$_6$F$_{42}$ (1530).

^{1}H-NMR (400 MHz; DMSO-D$_6$; *J*/Hz): δ = 7.66 (m, 4 H, H$_b$, H$_c$, H$_i$, H$_h$), 7.53 (m, 4 H, H$_d$, H$_e$ H$_f$, H$_g$), 7.05 (d, 2 H, ^3J(H, H) 8.4, H$_a$, H$_j$), 4.91 (d, 2 H, OH$_A$, OH$_D$), 4.64 (m, 2 H, OH$_C$, OH$_B$), 4.05-3.91 (m, 4 H, 2 ArOC**H**$_2$), 3.81 (m, 2 H, 2 CHOH), 3.48 (m, 4 H, 2 C**H**$_2$OH), 2.76 (t, ^3J (H, H) 7.6, 4 H, 2 C**H**$_2$Ar), 2.32-2.18 (m, 4 H, 2 CF$_2$C**H**$_2$), 1.91-1.83 (m, 4 H, 2 C**H**$_2$CH$_2$ CF$_2$).

^{13}C-NMR (100 MHz; DMSO-D$_6$; *J*/Hz): δ = 156.5 (C$_4$, C$_{27}$), 138.3 (C$_{12}$, C$_{19}$), 132.5 (C$_{13}$, C$_{18}$), 129.6 (C$_{11}$, C$_{21}$), 128.1 (C$_{10}$, C$_{20}$), 126.6 (C$_{16}$, C$_{17}$, C$_{14}$, C$_{15}$), 125.6 (C$_6$, C$_{23}$), 112.2 (C$_5$, C$_{22}$), 70.1 (C$_3$, C$_{28}$), 69.7 (C$_2$, C$_{29}$), 62.7 (C$_1$, C$_{30}$), 29.6 (C$_9$, C$_{26}$), 28.9 (C$_7$, C$_{24}$), 20.1 (C$_8$, C$_{25}$).

^{19}F-NMR (188 MHz; DMSO-D$_6$; *J*/Hz): δ = -78.30 (overlapped t, ^2J(C, F) 10.1, 6 F, 2 CF$_3$), -110.72 (m, 4 F, 2 CH$_2$CF$_2$), -119.09 (s, 20 F, 2 CH$_2$CF$_2$(C**F**$_2$)$_5$), -120.10 (s, 4 F, 2 CF$_3$CF$_2$CF$_2$C**F**$_2$), -120.34 (s, 4 F, 2 C**F**$_2$CF$_2$CF$_3$), -123.56 (m, 4 F, 2 CF$_3$C**F**$_2$).

3-[4‴-(2,3-Dihydroxypropyloxy)-2,2‴-bis(1H,1H,2H,2H,3H,3H-perfluorononyl)-p-terphenyl-4-yloxy]propane-1,2-diol <u>58‴-F$_{6,6}$</u>



Prepared according to the general procedure **8.6.6** from **<u>57.2</u>** (0.7 g, 0.6 mmol), NMMNO (1 mL, 5.7 mmol of 60 % solution in water) and osmiumtetroxide (1 mL, 0.004 M solution in *tert*-butanol) in acetone (25 mL). Purification by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.

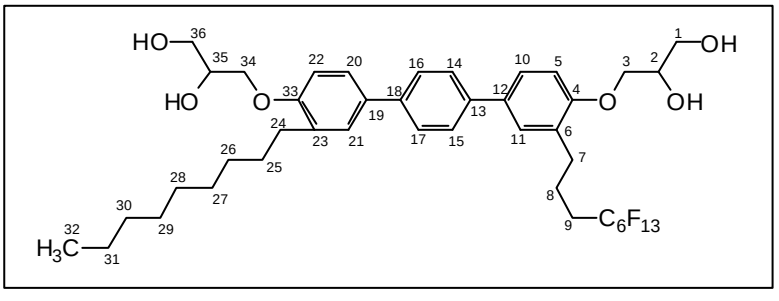
Yield: 231 mg (32.9 %); transition temperatures (°C): Cr_1 122 Cr_2 142 Cub 160 Iso; $C_{42}H_{36}O_6F_{26}$ (1131). Anal. Calcd.: C, 44.60, H, 3.18; Found: C, 43.93, H, 3.67.

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.25 (m, 4 H, H_d, H_e, H_f, H_g), 7.10 (d, ^3J(H, H) 8.4, 2 H, H_c, H_h), 6.89 (m, 2 H, H_b, H_i), 6.83 (dd, ^3J(H, H) 8.4, ^4J(H, H) 2.4, 2 H, H_a, H_j), 4.91 (d, ^3J(H, H) 5.1, 2 H, OH_A, OH_D), 4.64 (t, ^3J(H, H) 5.5, 2 H, OH_B, OH_C), 4.02-3.77 (m, 6 H, 2 ArOC**H**$_2$, 2 C**H**OH), 3.44 (m, 4 H, 2 C**H**$_2$OH), 2.86 (t, ^3J(H, H) 7.6, 4 H, 2 Ar**CH$_2$**), 1.95 (m, 4 H, 2 CH_2), 1.60 (m, 4 H, 2 CH_2).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 158.6 (C_4, C_{27}), 139.8 (C_{12}, C_{19}), 139.7 (C_{13},C_{18}), 133.8 (C_8, C_{21}), 131.2 (C_7, C_{20}), 129.2 (C_{14}, C_{15}, C_{16}, C_{17}), 115.8 (C_5, C_{25}), 112.6 (C_6, C_{26}), 70.2 (C_3, C_{28}), 69.8 (C_2, C_{29}), 63.0 (C_1, C_{30}), 31.9 (C_9, C_{22}), 29.5 (C_{11}, C_{24}), 21.04 (C_{10}, C_{23}).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.77 (overlapped t, 3 F, CF_3), -110.86 (m, 2 F, CH_2CF_2), -119.04 (m, 2 F, CH_2CF_2C**F**$_2$), -119.99 (s, 2 F, $CF_3CF_2CF_2C$**F**$_2$), -120.44 (s, 2 F, C**F**$_2CF_2CF_3$), -123.17 (m, 2 F, CF_3C**F**$_2$).

3-[4‴-(2,3-Dihydroxypropyloxy)-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)-3‴-nonyl-p-terphenyl-4-yloxy]propane-1,2-diol <u>58-H$_9$F$_6$</u>



Prepared according to the general procedure **8.6.6** from **<u>78</u>** (1.5 g, 1.8 mmol), NMMNO (1 mL, 5.7 mmol of 60 % solution in water) and osmiumtetroxid (1mL of a 0.004 M solution in *tert*-butanol) in acetone (25 mL). Purification by preparative centrifugal thin layer chromatography ($CHCl_3$), followed by recrystallization from $CHCl_3$/$MeNO_2$ 5:3.

Yield: 201 mg (12.6 %); transition temperatures (°C): Cr 144 Col (L) 150 Iso; $C_{42}H_{49}O_6F_{13}$ (897).

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 7.65 (m, 4 H, Ar-H), 7.53-7.44 (m, 4 H, Ar-H), 6.99-7.05 (m, 2 H, Ar-H), 4.90 (m, 2 H, OH_A, OH_D), 4.63 (m, 2 H, OH_B, OH_C), 4.05-3.79 (m, 6 H, 2 A rOC**H**$_2$, 2 C**H**OH), 3.49-3.44 (m, 4 H, 2 C**H**$_2$OH), 2.78 (t, ^3J(H, H) 7.6, 2 H, Ar**CH$_2$**), 2.62 (t, ^3J(H, H) 7.6, 2 H, Ar**CH$_2$**), 2.31-2.21 (m, 2 H, CH_2), 1.87 (m, 2 H, CH_2), 1.57 (m, 2 H, CH_2), 1.26 (m, 12 H, 6 CH_2), 0.83 (t, ^3J(H, H) 6.6, 3 H, CH_3).

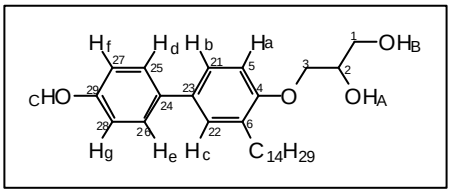
^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 156.5 (C_4, C_{33}), 138.5 (C_{12}), 138.2 (C_{19}), 131.9 (C_{13}), 131.7 (C_{18}), 131.2 (C_{11}), 129.6 (C_{20}), 128.1 (C_{10}), 127.8 (C_{21}), 126.6 (C_{14}, C_{15}, C_{16}, C_{17}), 125.6 (C_6), 125.0 (C_{23}), 112.2 (C_5), 112.1 (C_{22}), 70.1 (C_3), 70.0 (C_{34}), 69.7 (C_2), 69.6(C_{35}), 62.8 (C_1), 62.7 (C_{36}), 31.2 (C_7, C_{24}), 29.5 (C_9), 28.9, 28.8, 28.6, 22.0, 20.1, (CH_2), 13.8 (C_{32}).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -80.71 (overlapped t, 3 F, CF_3), -113.44 (m, 2 F, CH_2CF_2), -122.03 (m, 2 F, CH_2CF_2C**F**$_2$), -122.94 (s, 2 F, $CF_3CF_2CF_2C$**F**$_2$), -123.31 (s, 2 F, C**F**$_2CF_2CF_3$), -126.03 (m, 2 F, CF_3C**F**$_2$).

8.6.15.6 Synthesis of the bolaamphiphilic triol derivatives <u>71</u>

Hydrogenolysis of benzyl groups - general procedure 8.6.15.6: The appropriate 3-(4′-benzyloxybiphenyl-4-yloxy)propane-1,2-diol (1.0 mmol), was dissolved in ethyl acetate (50 mL), palladium on carbon (0.03 g) was added, and the solution was shaken in a hydrogen atmosphere at ambient pressure at RT for 36 h (TLC). The mixture was filtered over a silica bed. The residue was carefully washed twice with ethyl acetate (50 mL), and the solvent was evaporated in vacuum. The product was purified by recrystallization.

3-(4′-Hydroxy-3-tetradecylbiphenyl-4-yloxy)propane-1,2-diol <u>71-H$_{14}$</u>



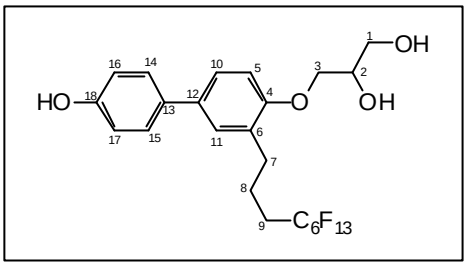
Prepared according to the general procedure **8.6.15.6** from **<u>70H.3</u>** (330 mg, 0.60 mmol), Pd-C (0.01 g). Purification by recrystallization from hexane/ethyl acetate 2:1.

Yield: 106 mg (38.7 %); mp: 115 °C; $C_{29}H_{44}O_4$ (456). Anal. Calcd.: C, 76.3, H, 9.65; Found: C, 76.41, H, 9.67.

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 9.40 (br s, 1H, OH_C), 7.39 (d, 2 H, ^3J(H, H) 8.6, H_d, H_e), 7.35-7.28 (m, 2 H, H_b, H_c), 6.94 (d, 1H, ^3J(H, H) 8.4, H_a), 6.78 (d, ^3J(H, H) 8.6, 2 H, H_f, H_g), 4.86 (br s, 1 H, OH_A), 4.61(br s, 1 H, OH_B), 3.98-3.86 (m, 3 H, ArOC**H**$_2$C**H**OH), 3.48 (m, 2 H, C**H**$_2$OH), 2.56 (t, ^3J(H, H) 7.2, 2 H, C**H**$_2$Ar), 1.54 (m, 2 H, C**H**$_2$), 1.36 (m, 22 H, 11 C**H**$_2$), 0.84 (t, ^3J(H, H) 7.03, 3 H, CH_3).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 156.6 (C_4), 155.7 (C_{29}), 132.5 (C_{23}), 131.2 (C_{24}), 131.0 (C_{22}), 127.5 (C_{21}), 127.3 (C_{25}, C_{26}), 124.4 (C_6), 115.7 (C_{27}, C_{28}), 112.0 (C_5), 70.1 (C_3), 69.6 (C_2), 62.8 (C_1), 31.2, 29.7, 29.4, 29.0, 28.8, 28.6, 22.0 (CH_2), 13.8 (CH_3).

3-[4'-Hydroxy-3-(1H,1H,2H,2H,3H,3H-perfluorononyl)biphenyl-4-yloxy]propane-1,2-diol 71-F_6



Prepared according to the general procedure **8.6.15.6** from **70F.1** (0.70 g, 1.0 mmol), Pd-C (0.03 g). The Purification by recrystallization from $CHCl_3$/MeOH 20:3.

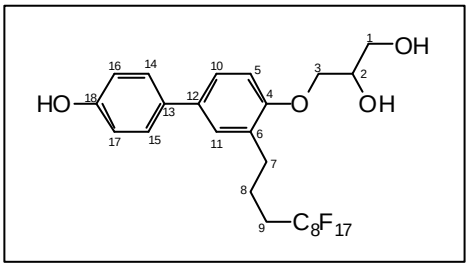
Yield: 290 g (47.7 %); transition temperatures (°C): Cr 99 Col_h 125 Iso; $C_{24}H_{21}O_4F_{13}$ (619). Anal. Calad.: C, 46.45, H, 3.39; Found: C, 46.30, H, 3.92.

^{1}H-NMR (200 MHz; DMSO-D_6; *J*/Hz): δ = 9.38 (s, 1 H, OH_C), 7.42 (d, 2 H, ^3J(H, H) 8.6, H_d, H_e), 7.35-7.28 (m, 2 H, H_c, H_b), 6.94 (d, 1H, ^3J(H, H) 9.2, H_a), 6.81 (d, ^3J(H, H) 8.6, 2 H, H_f, H_g), 4.8 (br s, 1 H, OH_A), 4.6 (br s, 2 H, OH_B), 4.02 (m, 5 H, ArOC**H**$_2$C**H**OH, C**H**$_2$O), 2.71 (t, ^3J(H, H) 7.0, 2 H, C**H**$_2$Ar), 2.26 (m, 2 H,CF_2C**H**$_2$), 1.83-1.21 (m, 2 H, C**H**$_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 152.5 (C_4), 151.5 (C_{18}), 128.5 (C_{13}), 126.8 (C_{12}), 125.7 (C_{10}), 123.5 (C_{11}), 123.2 (C_{14}, C_{15}), 120.9 (C_6), 111.5 (C_{16}, C_{17}), 118.0 (C_5), 65.9 (C_3), 65.5 (C_2), 58.6 (C_1), 25.4 (t, C_9), 24.7 (C_7), 16.0 (C_8).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.15 (overlapped t, 3 F, CF_3), -109.98 (m, 2 F, CH_2CF_2), -118.61 (s, 2 F, CH_2CF_2C**F**$_2$), 119.54 (s, 2 F, $CF_3CF_2CF_2$C**F**$_2$), -119.91 (s, 2 F, C**F**$_2CF_2CF_3$), -122.63 (m, 2 F, CF_3C**F**$_2$).

3-[4'-Hydroxy-3-(1H,1H,2H,2H,3H,3H-perfluoroundecyl)-biphenyl-4-yloxy]propane-1,2-diol 71-F_8



Prepared according to the general procedure **8.6.15.6** from **70F.2** (1.5 g, 1.0 mmol) , Pd-C (0.03 g). Purification by recrystallization from $CHCl_3$/MeOH 20:3.

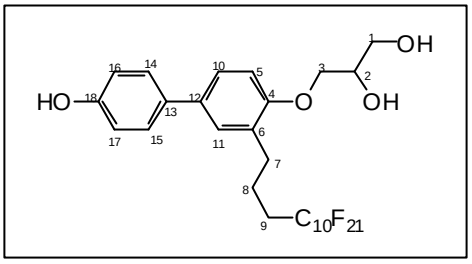
Yield: 1.0 g (77.4 %); transition temperatures (°C): Cr 118 Col (L) 139 Iso; $C_{26}H_{21}O_4F_{17}$ (720). Anal. Calad.: C, 43.40, H, 2.92; Found: C, 43.30, H, 3.26.

^{1}H-NMR (400MHz; DMSO-D_6; *J*/Hz): δ = 9.37 (s, 1 H, OH_C), 7.39 (d, 2 H, ^3J(H, H) 8.6, H_d, H_e), 7.35 (m, 2 H, H_c H_b), 6.97 (d, ^3J(H, H) 8.8, 1 H, H_a), 6.80 (d, ^3J(H, H) 8.6, H_f, H_g), 4.86 (d, *J*(H, H) 5.19, 1 H, OH_A), 4.59 (m, 1 H, OH_B), 4.02-3.78 (m, 3 H, ArC**H**$_2$OC**H**), 3.48 (m, 2 H, C**H**$_2$OH), 2.70 (t, 2 H, ^3J(H, H) 7.5, C**H**$_2$Ar), 2.49 (2 H, C**H**$_2CF_2$), 1.97 (m, 2 H, C**H**$_2CH_2CF_2$).

^{13}C-NMR (100 MHz; DMSO-D_6; *J*/Hz): δ = 156.4 (C_4), 155.5 (C_{18}), 132.5 (C_{13}), 130.8 (C_{12}), 129.2 (C_{11}), 127.5 (C_{10}), 127.1 (C_{14} C_{15}), 124.9 (C_6), 115.5 ($C_{16,}$ C_{17}), 111.99 (C_5), 70.01 (C_3), 69.61 (C_2), 62.71 (C_1), 31.68 (C_9), 28.91 (C_7), 20.18 (C_8).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -77.27 (overlapped t, 3 F, CF_3), -110.14 (m, 2 F, $CH_2C\mathbf{F}_2$), -118.65 (m, 6 F, $CH_2CF_2(C\mathbf{F}_2)_3$), -119.48 (m, 2 F, $CF_3(CF_2)_2C\mathbf{F}_2$), -119.97 (m, 2 F, $C\mathbf{F}_2CF_2CF_3$), -122.77 (m, 2 F, $CF_3C\mathbf{F}_2$).

3-[4'-Hydroxy-3-(1H,1H,2H,2H,3H,3H-perfluorotridecyl)biphenyl-4-yloxy] propane-1,2-diol 71-F_{10}



Prepared according to the general procedure **8.6.15.6** from **70F.3** (2.0 g, 2.2 mmol), Pd-C (0.06 g). Purification by recrystallization from hexane/ethyl acetate 2:3.

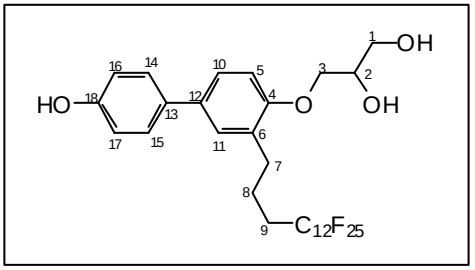
Yield: 1.1 g (62.8 %); transition temperatures (°C): Cr 135 Col (L) 151 Smb 154 SmA 156 Iso; $C_{28}H_{21}O_4F_{21}$ (820). Anal. Calcd.: C, 40.97, H, 2.56; Found: C, 40.83, H, 2.99.

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 9.36 (s, 1 H, OH_C), 7.33 (d, ^3J(H, H) 8.6, 2 H, H_d, H_e), 7.28 (m, 2 H, H_c H_b), 6.91 (d, ^3J(H, H) 8.4, 1 H, H_a), 6.77 (d, ^3J(H, H) 8.6, 2 H, H_f, H_g), 4.84 (br s, 1 H, OH_A), 4.58 (m, 1 H, OH_B), 3.76-3.49 (m, 3 H, $ArCH_2OCH$)), 3.46 (m, 2 H, $C\mathbf{H}_2OH$), 2.60 (t, 2 H, ^3J(H, H) 7.2, $C\mathbf{H}_2Ar$), 2.08 (2 H, $C\mathbf{H}_2CF_2$), 1.75 (m, 2 H, $C\mathbf{H}_2CH_2CF_2$).

^{13}C-NMR (100 MHz; DMSO-D_6, *J*/Hz): δ = 156.6 (C_4), 155.6 (C_{18}), 132.7 (C_{13}), 131.1 (C_{12}), 129.4 (C_{11}), 127.4 (C_{10}), 127.3 (C_{14}, C_{15}), 125.1 (C_6), 115.6 (C_{16}, C_{17}), 112.1 (C_5), 70.0 (C_3), 69.5 (C_2), 62.7 (C_1), 29.8 (C_7), 20.1 (C_8).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -82.46 (overlapped t, 3 F, CF_3), -114.40 (m, 2 F, $CH_2C\mathbf{F}_2$), -122.74 (m, 12 F, $CH_2CF_2(C\mathbf{F}_2)_6$), -123.91 (m, 2 F, $C\mathbf{F}_2CF_2CF_3$), -127.32 (m, 2 F, $C\mathbf{F}_2CF_3$).

3-[4'-Hydroxy-3-(1H,1H,2H,2H,3H,3H-perfluoropentadecyl)biphenyl-4-yloxy] propane-1,2-diol 71-F_{12}



Prepared according to the general procedure **8.6.15.6** from **70F.3** (0.3 g, 0.30 mmol) , Pd-C (0.01 g), Purification by preparative centrifugal thin layer chromatography (eluent: $CHCl_3/CH_3OH$ 10:2), followed by recrystallization from hexane/ethyl acetate 2:3.

Yield: 75 mg (27.6 %); transition temperatures

(°C): Cr 154 [Smb 142] SmA 188 Iso; $C_{30}H_{21}O_4F_{25}$ (920).

^{1}H-NMR (400 MHz; DMSO-D_6; *J*/Hz): δ = 9.32 (s, 1 H, OH_C), 7.25 (d, ^3J(H, H) 8.6, 2 H, H_d, H_e), 7.28 (m, 2 H, H_c H_b), 6.86 (d, ^3J(H, H) 8.6, 1 H, H_a), 6.74 (d, ^3J(H, H) 8.4, 2 H, H_f,

H_g), 4.81 (m,1 H, OH_A), 4.55 (m, 1 H,. OH_B), 3.94-3.75 (m, 3 H, $ArCH_2OCH$)), 3.46 (m, 2 H, C**H**$_2$OH), 2.56 (m, 2 H, C**H**$_2$Ar), 2.02 (2 H, C**H**$_2$$CF_2$), 1.69 (m, 2 H, C**H**$_2$$CH_2CF_2$).

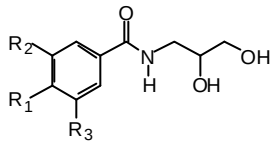
^{13}C-NMR (100 MHz; DMSO-D_6): δ = 156.6 (C_4), 155.5 (C_{18}), 132.7 (C_{13}), 131.0 (C_{12}), 129.4 (C_{11}), 127.2 (C_{10}), 127.1 (C_{14}, C_{15}), 125.0 (C_6), 115.6 (C_{16}, C_{17}), 112.0 (C_5), 70.0 (C_3), 69.4 (C_2), 62.7 (C_1), 29.8 (C_7), 20.0 (C_8).

^{19}F-NMR (188 MHz; DMSO-D_6; *J*/Hz): δ = -83.19 (overlapped t, 3 F, CF_3), -114.76 (m, 2 F, CH_2C**F**$_2$), -123.03 (m, 16 F, $CH_2CF_2(C$**F**$_2)_8$), -124.18 (m, 2 F, C**F**$_2CF_2CF_3$), -127.88 (m, 2 F, C**F**$_2CF_3$).

Zusammenfassung

Im Rahmen dieser Arbeit wurden insgesamt 4 verschiedene Klassen von unkonventionellen Flüssigkristallen mit perfluorierten Ketten synthetisiert. Die Polymorphie der neu synthetisierten Verbindungen wurde polarisationsmikroskopisch, differentialkalorimetrisch und röntgenographisch untersucht. Die Synthese der Verbindungen erfolgte stets über eine palladiumkatalysierte radikalische Addition von Perfluoalkyliodiden an Alkene und palladiumkatalysierte Kreuzkupplungsreaktion zum Aufbau der aromatischen Grundkörper.

A: Bei amphiphilen Benzoylaminopropan-2,3-diolderivaten bewirkt der Austausch von Alkylketten durch semifluorierte Ketten eine signifikante Stabilisierung der Mesophasen und eine Herabsetzung der Schmelzpunkte. Dies sollte im Wesentlichen das Resultat der Vergrößerung des intramolekularen Polaritätskontrastes sein. Bei Vergrößerung der Anzahl der lipophilen Ketten dieser Moleküle wurde ein Übergang von einer smektischen, über hexagulal kolumnare Phasen zu einer mizellar kubischen thermotropen Mesophase beobachtet. Wie bei den analogen Kolhenwasserstoffderivaten bestimmt der Betrag der Krümmung der polar-apolar-Grenzfläche ganz wesentlich den beobachteten Phasentyp.



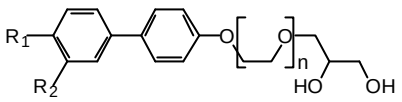
7-1F$_{6/4}$: $R_1 = (CH_2)_4C_6F_{13}$, $R_2 = R_3 = H$: Cr 79 SmA 223 Iso
7-2F$_{6/4}$: $R_1 = R_2 = (CH_2)_4C_6F_{13}$, $R_3 = H$: Cr 86 Cub_{I2} 208 Iso
7-3F$_{6/4}$: $R_1 = R_2 = R_3 = (CH_2)_4C_6F_{13}$: Cr 59 Cub_{I2} 188 Iso
7-3F$_{7/4}$: $R_1 = R_2 = R_3 = (CH_2)_4(CF_2)_4CF(CF_3)_2$: Cr < 20 Cub_{I2} 193 Iso

Auf Grund des größeren Querschnitts der perfluorierten Segmente, reichen bei den fluorierten Verbindungen jedoch bereits zwei semifluorierte Ketten aus, um eine mizellar kubische Phase zu induzieren.

Alle mizellar kubischen Phasen (Cub_{I2}) weisen die Raumgruppe *Pm*3*n* auf. Bei den zweikettigen semifluorierten Verbindungen handelt es sich um die ersten zweikettigen Amphiphile, die diesen Mesophasentyp ausbilden können. Gleichzeitig sind sie die ersten perfluorierten Verbindungen mit thermotropen mizellar kubischen Mesophasen.

Bikontinuierlich kubische Phasen können in binären Mischungen zwischen einkettigen und zwei- oder dreikettigen semifluorierten Verbindungen induziert werden. Ungewöhnlich, und bei den entsprechenden Kohlenwasserstoffenderivaten noch nicht beobachtet, ist der Verlust der induzierten Cub_{V2}-Phase bei Temperaturverringerung, was in bestimmten Konzentrationsbereichen zu den ungewöhnlichen thermotropen Phasensequenzen Col_{h2}–Cub_{V2}-Col_{h2} bzw. SmA-Cub_{V2}-SmA führt (re-entrant einer kolumnaren bzw. smektischen Phase).

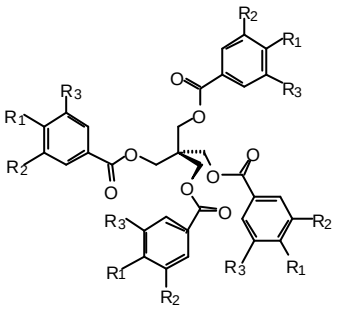
B: Amphiphile Biphenylderivate mit einer oder zwei semifluorierten Ketten bilden verschiedene Schichtstrukturen (SmA, SmC) und verschiedene kolumnare Phasen aus.

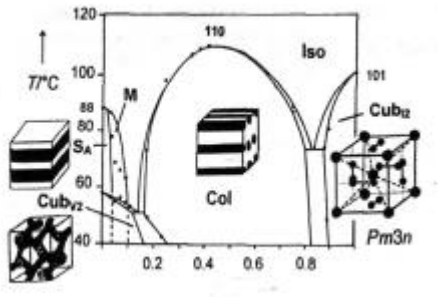


16-1F$_{6/4}$: $R_1 = (CH_2)_4C_6F_{13}$, R_2 = H: Cr 147 $Colx_1$ 152 $Colx_2$ SmC 158 SmA 219 Iso
16-1F$_{6/10}$: $R_1 = (CH_2)_{10}C_6F_{13}$, R_2 = H: Cr 149 ($Colx_1$ 148) $Colx_2$ 168 SmA 203 Iso
16-2F$_{6/4}$: $R_1 = R_2 = (CH_2)_4C_6F_{13}$: Cr < 20 Col 145 Iso

Die Einführung der perfluorierten Segmente in die lipophilen Ketten dieser Biphenylderivate bewirkt zwar eine Veränderung im Detail, zeigt aber keine dramatischen Effekte.

C: Mittels der Pentaerythritoltetrabenzoate mit semifluorierten Ketten ist es uns erstmals gelungen, alle Grundtypen flüssigkristalliner Phasen (smektisch, kolumnar, bikontinuierlich kubisch und mizellar kubisch) ohne die klassischen Konzepte von Rigidität, Formanisotropie und ausgeprägter Amphiphilie zu realisieren. Daß die fluorierten Verbindungen **27-1F→27-3F** generell eine höhere Mesophasenstabilität aufweisen als die verwandten Kohlenwasserstoffe, sollte wiederum hauptsächlich durch den vergrößerten intramolekularen Polaritätskontrast der inkompatiblen Molekülsegmente begründet sein.





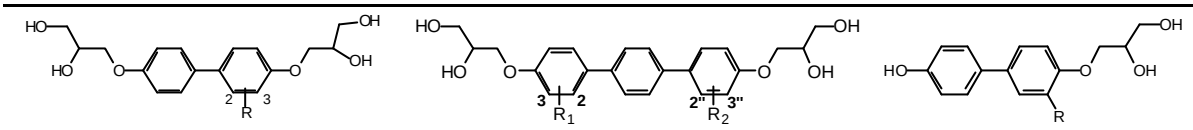
27-1F$_{6/4}$: $R_2 = R_3$ = H, $R_2 = (CH_2)_4C_6F_{13}$: Cr 59 SmA 88 Iso
27-2F$_{6/4}$: $R_1 = R_2 = (CH_2)_4C_6F_{13}$, R_3 = H: Cr 88 Cub_{h2} 131 Iso
27-3F$_{6/4}$: $R_1 = R_2 = R_3 = (CH_2)_4C_6F_{13}$: Cr 36 Cub_{I2} 210 Iso

27-1F$_{6/4}$ **27-3F$_{6/4}$**

Der größere Querschnitt fluorierter Alkylketten sollte für den Übergang von einer kolumnaren zu einer mizellar kubischen Phase bei Ersatz der Alkylketten durch semifluorierte Ketten verantwortlich sein. Diese sternförmigen Blockmoleküle können als niedermolekulare Analoge der entsprechenden Blockcopolymere und „core-shell"-Dendrimere angesehen werden. Sie vermitteln somit einen Übergang zwischen zwei wichtigen, zur Ausbildung geordneter fluider Phasen befähigten Systemen, den Blockcopolymeren und den klassische Amphiphilen.

D: Durch den Einbau von semifluorierten Ketten oder perfluorierten Ketten in die laterale Position rigider Bolaamphiphile wurden ganz unterschiedliche Mesophasen realisiert. Diese Moleküle bestehen aus drei miteinander inkompatiblen Segmenten: den rigiden Biphenyl-

bzw. Terphenyleinheiten, zwei polaren, zur Wasserstoffbrückenbindung befähigten terminalen Gruppen und ein oder zwei semifluorierten Ketten in lateraler Position.



53-H_n, 53-F_n	**58-$F_{n,n}$**	**71-F_n**
R = $(CH_2)_mC_nF_{2n+1}$	$R_1 = R_2 = (CH_2)_3C_nF_{2n+1}$	R = $(CH_2)_3C_nF_{2n+1}$
m = 0, 3; n = 0, 3, 4, 6, 7, 8, 10	n = 4, 8, 10	n = 6, 8, 10, 12

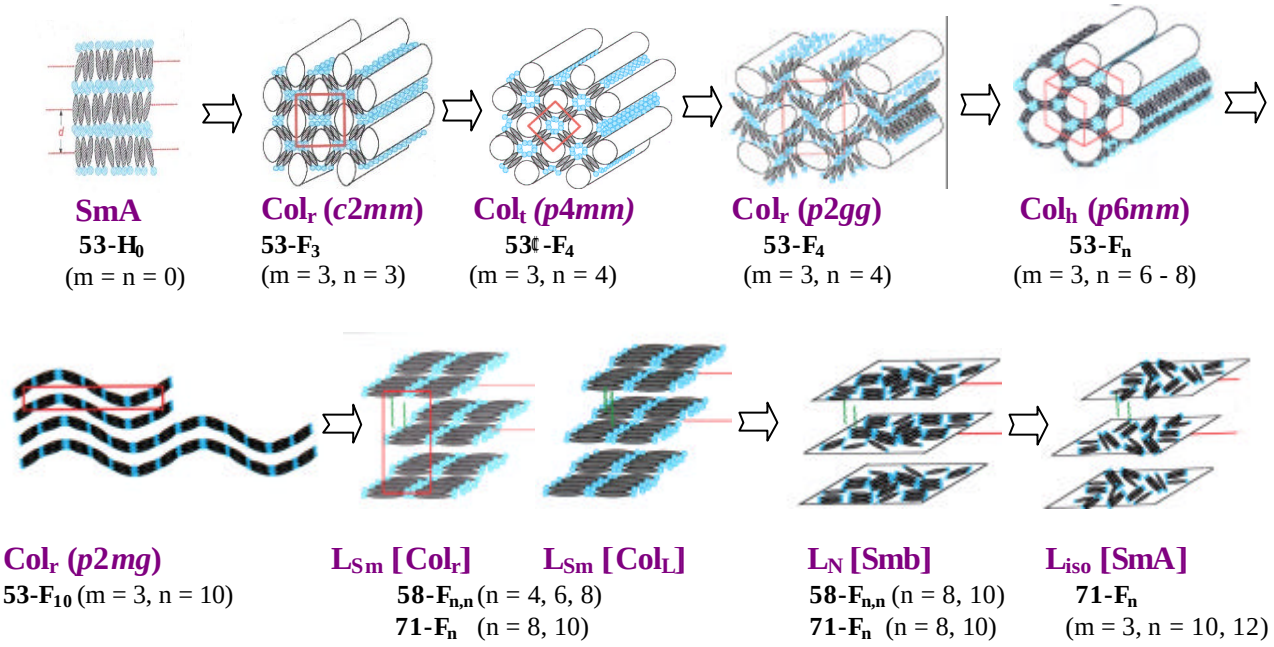


Abb. 5.16 *Mesophasenmorphologien der rigiden Bolaamphiphile mit lateralen semifluorierten Ketten.*

Bolaamphiphile ohne laterale Ketten bilden extrem stabile smektische Phase mit Monolayerstruktur aus. Bolaamphiphile Tetraole des Types **53-F_n** (Biphenylderivate) mit einer semifluorierten lateralen Ketten in Position 3 weisen demgegenüber kolumnare Mesophasen auf. Die Organisation der Moleküle in den kolumnaren Phasen kann wie folgt erklärt werden: Die Separation der lipophilen lateralen Gruppen von den rigiden Biphenyleinheiten und den polaren Diolgruppen führt zur Ausbildung von Regionen, in denen diese lateralen Gruppen konzentriert sind. Diese haben die Gestalt von Zylindern, und werden von den rigiden Biphenyleinheiten umgeben. Die Netzwerke der Wasserstoffbrückenbindungen zwischen den Diolgruppen verknüpfen die Biphenyleinheiten miteinander, so daß diese geschlossene Zylinder um diese lipophilen Regionen ausbilden. Der Raumbedarf der lipophilen Ketten in Bezug auf die Größe der rigiden Segmente legt die exakte Form der Zylinder und folglich die Art der kolumnaren Mesophase fest. Moleküle mit relativ kurzen lateralen Ketten bilden rechtwinklig

kolumnare Phasen (Col_r) mit einen *c*2*mm*-Gitter aus (s. Abb. 15.6). Bei schrittweiser Verlängerung wird diese durch eine Col_r-Phase mit *p2gg*-Gitter und schließlich durch eine hexagonal kolumnare Phase ersetzt. Somit resultiert bei Verlängerung der lateralen Kette die Phasensequenz Col_r (*c*2*mm)* - Col_r(*p*2*gg)* - Col_h*(p6mm)*. Das Tetraol **53-F$_{10}$** mit der längsten semifluorierten Kette weist eine rechtwinklig kolumnare Phase mit einem *p*2*mg*-Gitter auf. Für diese kolumnare Phase wird das Modell einer wellenförmig deformierten Schichtstruktur vorgeschlagen (s. Abb.15.6).

Die Position der lateralen Kette am rigiden Mittelteil hat offenbar wenige Einfluß auf die Art der Mesophase. Nur in einem Fall (**53t-F$_4$**) findet man für eine in 2-Position substituierte Verbindung eine tetragonal kolumnare Phase Col_t *(p4mm)* anstatt der rechtwinklig kolumnaren Phase (*p2gg*) der isomeren 3-substituierten Verbindung.

Die Einführung von lipophilen Spacern zwischen rigidem Kern und einer oder beiden Kopfgruppen führte zu einer Destabilisierung der Mesophasen. Gleichzeitig werden hexagonale Mesophasen durch rechtwinklige oder tetragonale Mesophasen ersetzt, d.h. der Effekt der Verlängerung des Spacers ist entgegengesetzt zu dem Einfluß der Verlängerung der lateralen Kette.

Unkonventionelle Schichtstrukturen, in denen die rigiden calamitischen Einheiten parallel zur Schichtebene angeordnet sind, wurden für die Terphenylderivate **58-F$_{8,8}$** and **58-F$_{10,10}$** mit zwei lateralen Ketten und die Triole **71-F$_{10}$** und **71-F$_{12}$** mit jeweils einer langen lateralen Kette gefunden. Drei verschiedene Typen derartiger Mesophasen wurden in Abhängigkeit von der Länge der lateralen Kette und der Temperatur beobachtet. Bei niedriger Temperatur (kurze Kettenlänge) findet man eine Mesophase mit einer für kolumnare Phasen typischen Textur [Col (L)]. Gefolgt wird diese von einer biaxial smektischen Phase (Smb) und einer uniaxial smektischen Phase (SmA). Für diese drei Mesophasen werden Schichtstrukturen vorgeschlagen, in denen die Schichten der über Wasserstoffbrücken verknüpfen aromatischen Segmente durch die Schichten der fluiden semifluorierten lateralen Ketten separiert sind, wobei die aromatischen Molekülteile parallel zu den Schichtebenen angeordnet sind. Dabei können die aromatischen Segmente in diesen Schichten eine Positions- und/oder Orientierungsfernordnung aufweisen (2D-smektisch), lediglich eine Orientierungsfernordnung besitzen (2D nematisch) oder ungeordnet sein (2D isotrop). (s. Abb.15.6). Die Col (L)-Phasen sollten positions– und/oder orientierungsferngeordnete 3D-Organisationen 2D-smektischer Lamellen darstellen. Die biaxial smektische Phase sollte einer Parallelorganisation 2D-nematischer Schichten und die uniaxial smektische Phase der Organisation 2D-isotroper Schichten entsprechen. Zusätzlich wurde ein kubische Phase für eines der Terphenylderivate gefunden.

Insgesamt führt die sukzessive Vergrößerung des Volumens der lateralen Ketten in Bezug zur Länge der rigiden bolaamphiphilen Segmente zu einem Übergang zwischen zwei

unterschiedlichen Schichtstrukturen, d.h. von konventionellen smektischen Phasen, in denen die rigiden Segmente senkrecht zu den Schichten ausgerichtet sind zu neuen unkonventionellen Schichtstrukturen in denen sie parallel zu den Schichten liegen. Kolumnare Mesophasen und wellenförmig deformierte Schichtstrukturen werden am Übergang zwischen diesen zwei Arten von Schichtstrukturen als intermediäre Phasen gefunden (Abbidung 5.16).

Somit stellen Bolaamphiphile mit lateralen lipophilen Ketten eine neuartige Klasse thermotrop flüssigkristalliner Materialen dar. Die komplexen supramolekularen Strukturen dieser Mesophasen weisen eine Analogie zu den Morphologieen von Stern-Dreiblockcopolymeren auf. Die kompetitive Kombination von Rigidität und Mikrosegregation ist also ein erfolgreiches Konzept, welches bei niedermolekularen Amphiphilen zu neuen und komplexen flüssigkristallinen Phasen führt.

Allgemein kann man sagen, daß semifluorierte Ketten in ganz verschiedene Substanzklassen die Ausbildung von flüssigkristallinen Phasen begünstigen. Diese Mesophasenstabilisierung ist zu einem wesentlichen Teil auf die Erhöhung des intramolekularen Polaritätskontrastes zurückzuführen. Der Mesophasentyp wird ganz wesentlich durch den Raumbedarf der Perfluoralkylketten bestimmt.

Publications

(a) "Design of Liquid-Crystalline Block-Molecules with Non-conventional Mesophase Morphologies: Calamitic Bolaamphiphiles with lateral Alkyl Chains", M. Kölbel, T. Beyersdorff, X. H. Cheng, C. Tschierske, J. Kain, S. Diele, *J. Am. Chem. Soc*., **2001**, in press.

(b) "Molecular Design of Liquid-Crystalline Block molecules : Semifluorinated Pentaerythritol Tetrabenzoates Exhibiting Lamellar, Columnar and Cubic Mesophases", X. H. Cheng, S. Diele, C. Tschierske, *Angew. Chem.*, **2000**, 112, 605.

(c) "Novel rigid bolaamphiphiles with perfluorinated lateral chains", X. H. Cheng, T. Beyersdorff, C. Tschierske, J. Kain, S. Diele, *CCMM (Chemistry and characterization of mesophase material),* **2000**, Poster contributions 17.

(d) "Calamitic bolaamphiphiles with perfluorinated lateral chains", X. H. Cheng, T. Beyersdorff, C. Tschierske, J. Kain, S. Diele, *29th Freiburger arbeitstagung Flüssigkristalle,* **2000**, Poster contributions 3.

(e) "Formation of mesophases based on micro-segregation: columnar liquid-crystalline phase of first generation dendrimers with perfluorinated segments", A. Pegenau, X.H. Cheng, C. Tschierske, P. Göring, S. Diele, *New J. Chem.*, **1999**, 23, 465

(f) "Columnar mesophases of tetrahedral molecules with perfluorinated segments", X. H. Cheng, A. Pegenau, C. Tschierske, P. Göring, S. Diele, *28. Freiburger Arbeitstagung Flüssigkristalle, Freiburg* **1999**, Poster contributions 8.

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Erklärung

Hiermit erkläre ich an Eides statt, dass ich die vorliegende Arbeit selbständig und nur unter Verwendung der angegebenen Hilfsmittel angefertigt habe. Den benuzten Werken wörtlich oder inhaltlich entnommene Stellen sind als solche kenntlich gemacht.
Diese Arbeit wurde bisher an keiner anderen Universität oder Hochschule vorgelegt. Ferner habe ich mich an keiner weiteren Institution um die Erlangung des Doktorgrades beworben.

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