Star Polymers and Dendrimers
Based on Highly Functional Resorcin- and Pyrogallolarenes

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The present work was carried out under the supervision of Doz. Dr. W. D. Habicher at the Department of Chemistry, University of Technology Dresden from September 2002 to July 2006.
To my parents & Aaliyah
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Introduction and objective of the work

Various polymerization techniques have been used to synthesize a wide variety of macromolecules including linear and cyclic homopolymers, linear copolymers, and functional polymers such as macromonomers. These macromolecules are well-defined with predetermined molar masses, a specific molar mass distributions, and low compositional heterogeneity. Well-defined polymers with low degrees of compositional heterogeneity can provide the information and insights necessary to understand and predict polymer structure-property relationship. Besides the commonly used linear polymers, branched polymers of different structure attracted an increasing interest, because branching in polymers is a useful structural variable that can be used advantageously to modify the processing characteristics and properties of polymers, giving rise to novel and advanced materials with improved attributes.

A branched polymer\textsuperscript{1,2} is comprised of molecules with more than one backbone chain; that is, it is a non-linear polymer, and it is characterized by the presence of branch points (junction points: atoms or a small group from which more than two long chains emanate). Branched polymers exhibit more than two chain end groups. Star-branched polymers (or star polymers) are the simplest case of branched species, where all chains of a given macromolecule are connected to a single nodulus referred to as the core. In contrast, dendrimers are highly branched,
three-dimensional macromolecules with a branch point at each monomer unit; they have structural features analogous to the structure of trees. Dendrimers\(^3\),\(^4\) have exact, monodisperse structures built layerwise in generations around a core moiety. Besides these two branched polymeric architectures, a wide variety of other branched polymer morphologies exist, e.g. statistically branched polymers, comb-shaped polymers or polymer brushes (Figure 1).

Branched macromolecules are more compact than linear homologous ones, because of their higher segment densities. The chain segment density distribution for star-branched polymers is highest at the core and decreases as the distance from the core increases. In contrast, for dendritic polymers the chain segment density increases as the distance from the core increases. In fact it is calculated that a maximum number of dendrimer generations can be formed (starburst dense-packed generation), beyond which only defect structures can be generated.\(^5\) The increased segment density results in a decreased tendency for these macromolecules to interpenetrate in solution as well as in bulk. In order to investigate this influence of structure (number of branches, length of branches) on macromolecular properties, well-defined star-shaped macromolecules and dendrimers, respectively, are required.

To perceive such star polymers and dendrimers with a low degree of compositional heterogeneity, a precise core of known structure and functionality is a prerequisite, from which the arms of a star-branched polymer or the dendrons (tree-like subunits of a dendrimer) emanate. Calix[4]resorcin- and calix[4]pyrogallolarenes\(^6\),\(^7\),\(^8\) fulfill these requirements. They are cyclic tetramers derived from the acid-catalyzed cyclocondensation of either resorcinol or pyrogallol with aliphatic or aromatic aldehydes. They exhibit a precise and high number of reactive phenolic hydroxyl groups, whereas the functionality \(f\) can be easily tuned (\(f = 8-20\)) depending on the aldehyde and phenol derivative used for the cyclotetramerization. Calix[4]resorcin- and calix[4]pyrogallolarenes can be prepared in reasonable high yields, in hundred gram scale via a simple, one-step procedure without the need of templates or high dilution techniques. It’s their easily tunable high functionality and possibility to easily modify the functional groups, which makes them attractive as cores for either star polymers or dendrimers. In the case of dendrimers a high number of functional end-groups can be achieved at rather low generations due to the high functionality of the core molecules.

Many intriguing properties of star polymers and dendrimers have been proposed and some of them have been disclosed recently. The supposed properties of star polymers and dendrimers are related to their well-defined, three-dimensional architecture and their high number of functional end groups. In the case of dendrimers, these features indicate possibilities for a densely packed surface with cavities present in the interior and allow simple modification
methods leading to the utilization of dendritic macromolecules in catalysis, encapsulation, nanotechnology, polymer technology (polymer additives), and biomedical application (e.g. controlled drug release systems).

Star polymers attracted the interest of scientists and industry due to their different properties compared to linear analogues, for example lower solution and melt viscosity, thus evidencing an enhanced ability to flow and enhanced processing characteristics. The recently discovered controlled radical polymerization techniques have made possible their directed preparation, whereupon the tolerance of the radical process towards different functional groups present in the monomers used, offers the feasibility to prepared novel polymeric materials with completely new properties.

The objective of this work was to synthesize star polymers and dendrimers under employment of modern polymerization techniques and adequate reactions, using easily accessible calix[4]resorcin- and calix[4]pyrogallolarenes as highly functional cores.

**More precisely the objective of this work can be portrayed under the following points:**


The following theoretical part will give an overview about general synthetical routes toward star polymers (core-first and arm-first approach) and dendrimers (divergent and convergent approach). The synthesis of calix[4]resorcin- and calix[4]pyrogallolarenes will be encompassed in a bit more detailed way, as well as, atom transfer radical polymerization as method of choice from controlled radical polymerization techniques.
Theoretical part


In 1872 Adolf von Bayer\textsuperscript{9} reported, in a general study on the synthesis of phenol (1) based dyes, that the addition of sulfuric acid to a mixture of benzaldehyde and resorcinol (2) gave a red colored product, which turned violet in alkaline solution. When the mixture was heated under reflux, a crystalline product was formed in addition to the resin obtained normally. Earlier attempts of structural investigation of the crystalline product of the condensation of resorcinol (2) with benzaldehyde failed due to improper analytical techniques for molecular weight determination and led to conflicting statements about the structure of the obtained product. Thus an alkylidene-diphenol structure 3 has been suggested by Michael\textsuperscript{10} who first established the correct elementary composition of the very sparingly soluble, high melting, crystalline product (C\textsubscript{13}H\textsubscript{10}O\textsubscript{2})\textsubscript{n} by elemental analysis (Figure 2). Niederl and Vogel\textsuperscript{11} in 1940 were reinterpreting the structures of the product from the acid-catalyzed reaction of resorcinol (2) and aldehydes (except formaldehyde) and from molecular weight determinations they concluded that the ratio between aldehyde and resorcinol (2) in the product should be 4:4. They proposed the cyclic tetrameric structure 4 (R\textsubscript{1} = aliphatic, R\textsubscript{2} = H). This assignment was approved in 1968 by Erdtman and coworkers through X-ray crystallography.\textsuperscript{12}

\begin{center}
\includegraphics[width=\textwidth]{structure.png}
\end{center}

Figure 2. Alkylidene-diphenol structure 3 proposed by Michael. General structure of a resorcinarene 4.

The official IUPAC-name for compound 4 (R\textsubscript{1} = aliphatic, R\textsubscript{2} = H) is 2,8,14,20-tetraalkylpentacyclo[19.3.1.1\textsuperscript{3,7}.1\textsuperscript{9,13}.1\textsuperscript{15,19}]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,-21,23-dodecaene-4,6,10,12,16,18,22,24-octol. Different trivial names for these compounds
appeared in literature. They were classified as calixarenes by calling them calix[4]resorcinarenes\(^6\), calix[4]resorcarenes\(^7\) or resorcinol-derived calix[4]arenes\(^8,6\), but also other names like Högberg compounds\(^13\), or simply octols\(^14,15\) were introduced. The term calixarene carries a degree of ambiguity. As originally conceived it applied to the phenol-derived cyclic oligomers and included the endo hydroxyl groups, whereas in comparison calix[4]resorcinarenes and calix[4]pyrogallolarenes \(^4\) can be designated as exo-calix[4]-arenes.\(^16\) To accommodate a systematic nomenclature, however, the calixarene descriptor is now taken to designate only the basic macrocyclic framework and the hydroxyls or other substituents are designated as appendages. Also the name resorcinarenes\(^17\) was suggested and will be used throughout this thesis, i.e. pyrogallolarenes for pyrogallol-derived \([1_d]\) methaclophanes.

1.1. Synthesis of resorcin- and pyrogallolarenes

Resorcinarenes and pyrogallolarenes \(^4\) can be prepared in reasonable high yields via a simple, one-step procedure without the need of templates or high dilution techniques. Most cases involve the acid-catalyzed condensation reaction between resorcinol \((2, R_1 = H)\) or pyrogallol \((5, R_1 = OH)\) and an aliphatic or aromatic aldehyde (\textbf{Figure 3}).\(^{13,14}\)

![Figure 3](image-url)\textbf{Figure 3.} Acid-catalyzed cyclocondensation of resorcinol \((2, R_1 = H)\) or pyrogallol \((5, R_1 = OH)\) with aldehydes \((R_2 = \text{aliphatic, aromatic, heterocyclic, etc.})\).

The syntheses are generally carried out with unsubstituted resorcinol \((2, 1,3\text{-dihydroxybenzene})\), but in certain cases, for example in the reaction with formaldehyde, the use of 2-alkyl resorcinol or pyrogallol \((5, 1,2,3\text{-trihydroxybenzene})\) yields isolable amounts of tetrameric product.\(^{18,19,20,21}\)
For each particular aldehyde, however, the optimization of the conditions must be sought. A wide variety of aldehydes\textsuperscript{22} have been employed for the single-step synthesis including:

- simple aliphatic aldehydes,\textsuperscript{15,23,24,25,26,27} from ethanal (6), via hexanal (7) to undeca-nal (8),
- functionalized aliphatic aldehydes such as 5-chloropentanal\textsuperscript{14}, 3,4-dihydro-2Hpyran\textsuperscript{14,28}, 2,3-dihydrofuran\textsuperscript{28} and 2-sulfonatoethanal\textsuperscript{29},
- arylalkyl aldehydes such as phenylethanal\textsuperscript{14},
- unsaturated aliphatic aldehydes such as 9-decenal\textsuperscript{30},
- benzaldehydes\textsuperscript{12,31}, including those with substituents such as alkyl or arylalkyl\textsuperscript{17}, thioalkyl\textsuperscript{13}, OH\textsuperscript{32,33}, NO\textsubscript{2}\textsuperscript{34}, halogen\textsuperscript{14}, CN\textsuperscript{14}, NH\textsubscript{2}\textsuperscript{35}, MeCO\textsuperscript{14}, B(OR)\textsubscript{2}\textsuperscript{36}, crown ether\textsuperscript{37}, and glycosyl\textsuperscript{38},
- α-naphthaldehyde\textsuperscript{39},
- heterocyclic aldehydes\textsuperscript{13} and ferrocenylaldehyde\textsuperscript{40},
- 3,7,12-methylcholanal\textsuperscript{41}.

The few types of aldehydes that fail to give resorcinarenes 4 are those that are highly hindered (e.g. 2,4,6-trimethylbenzaldehyde) or that contain functionality proximate to the aldehyde function (e.g. ClCH\textsubscript{2}CHO)\textsuperscript{14}.

![Lewis acid-promoted cyclotetramerization of 2,4-dimethoxy- and 2,6-dimethoxycinnamic acid esters and amides 9 and 10.](image)

Novel procedures for the high-yield synthesis of resorcinarenes 4 were described, involving the Lewis acid-catalyzed tetramerization of (E)-2,4-dimethoxycinnamic acid esters\textsuperscript{42,43,44} or amides\textsuperscript{45} 9 and (E)-2,6-dimethoxycinnamic acid esters and amides\textsuperscript{46} 10 to yield octamethy-
lated resorcinarenes 11 (Figure 4). The 2,6-dimethoxy isomer 10 rearranges during the course of the reaction.

Also other Lewis acids were successfully applied in the cyclooligomerization towards resorcinarenes 4. The octamethyl ether of methylene bridged resorcinarenes can be obtained in a one-step procedure involving the trifluoroacetic acid–catalyzed reaction of 2,4-dimethoxybenzyl alcohol (12) (Figure 5). Deprotection of the hydroxyl functionalities with BBr₃ affords the free methylene bridged product 13, which is unobtainable by the direct reaction of resorcinol (2) with formaldehyde due to polymerization.⁴⁷

![Figure 5. Lewis acid-promoted cyclotetramerization of 2,4-dimethoxybenzyl alcohol (12).](image)

The use of chlorotrimethylsilane as Lewis acid for the cyclotetramerization of 2,4-diisopropoxybenzyl alcohol followed by deprotection with BCl₃ is just another method to obtain methylene bridged resorcinarenes.⁴⁸

Lewis acid-catalyzed condensation reactions between aldehydes and resorcinol (2) involving Yb(OTf)₃⁴⁹, Sc(OTf)₃⁵⁰, Bi(OTf)₃⁵¹ and SnCl₂⁵² or AlCl₃⁵⁸ have been reported, whereas also the synthesis of higher cyclooligomerization products was successfully achieved. Such calix[n]resorcinarenes with n = 4-7 can also be prepared by the acid-catalyzed cyclocondensation applying very short reaction times.⁵⁴ Using 2-alkylresorcinol and 1,3,5-trioxane, calix[n]resorcinarenes with n = 4-6 were synthesized.⁵⁵,⁵⁶ The solvent-free synthesis of resorcinarenes using p-TsOH as a catalyst has also been reported.⁵⁷,⁵⁸
1.2. Mechanism of formation of resorcin- and pyrogallolarenes under acidic conditions

Weinelt and Schneider$^{34}$ studied the mechanism of the acid-catalyzed condensation reaction between resorcinol (2) and acetaldehyde (6) in MeOH/HCl by following quantitatively the formation of all oligomers and cyclic products over time by $^1$H NMR spectroscopy.

Figure 6. Buildup sequence of oligomers 15, 16, 17 and cyclooligomer 18 for the reaction of resorcinol (2) with acetaldehyde (6).
Formation of cyclotetramer 18 proceeds via sequential coupling of 14 with resorcinol (2) units to form intermediates 15, 16 and 17, or higher oligomers containing more than four monomers.

Under these conditions, the electrophile stems from the rapidly formed dimethyl acetal 14 (Figure 6), and not directly from the aldehyde 6. Higher oligomers were found in concentrations up to 45% at intermediate reaction times, but disappear towards the end of the reaction, since the reaction is reversible under the conditions used. All observed intermediates showed resorcinol and not methoxyethyl units at the terminal positions, which is in accordance with the fast reaction of such species under acidic conditions.59 The dimers 15 and trimers 16 could be isolated, but the tetramers 17 cyclise too fast to accumulate in observable quantities. This fast cyclization is related to their folded rather than linear conformation, through to the ability to form stronger hydrogen-bonds between phenolic hydroxyl groups of adjacent resorcinol units in the folded structure.

1.3. Isomerism and conformational behavior of resorcin- and pyrogallolarenes

Resorcinarenes (or pyrogallolarenes) 4 posses four prochiral centers at the bridging methine carbon and, as a consequence, can exist in four different diastereomeric forms. For the purpose of perceiving the stereochemical relationships between the prochiral centers the macrocyclic ring 4 can be considered as planar with the residue R of the CHR bridge pointing to one or the other side. Assigning one of the prochiral centers as the reference group (r) and then proceeding around the ring in sequential clockwise progression, the residues R of the other prochiral centers can be designated as cis (c) or trans (t) relative to the reference group (r). The reference group (r) is chosen in such a manner, that the number of cis (c) designations maximize (Figure 7). Under consideration of the hydrogen as second substituent at the bridging methine carbon and the individual configuration of the substituents relative to the macrocyclic plane, two different extreme cases can be theoretically observed. All alkyl substituents may be axial to the plane, or, by ring inversion of one or several resorcin units, they may be equatorial. The stereochemistry of resorcinarenes is generally defined as a combination of the three stereochemical elements:

- The relative configuration of the substituents at the methine bridge giving the all-cis (ccc), cis-cis-trans (cct), cis-trans-trans (ctt), and trans-cis-trans (tct) arrangement.
The individual configuration of the substituents at the methine bridges, which, in conformations of the macrocycle with C symmetry, may be either axial or equatorial.

- The conformation of the phenylene units, which can adopt five extreme, symmetrical arrangements, the crown, boat, chair, diamond and saddle conformation (Figure 8).

**Figure 7.** Stereochemical relationship among the four R groups at the methine carbon atoms of resorcin- and pyrogallolarenes 4.

**Figure 8.** Possible conformers of resorcin- and pyrogallolarenes 4.

Combination of these stereochemical elements gives rise to a vast number of possible stereoisomers. In practice however, the product is frequently a single material or, at most, a mixture
of two or three isomers with one predominating. Investigations have shown, that the acid-catalyzed formation of resorcinarenes 4 is reversible and that the major product is:

- the one that is most rapidly formed (the kinetic product – often the isomer (boat, crown) for aliphatic aldehydes, but sometimes the isomer (chair) for aromatic aldehydes, or
- the one that is most stable (the thermodynamic product – generally the ), or
- the one that is least soluble and removed from the reaction by precipitation, or crystallization.

In practice the isomer have always been found to have either the symmetrical crown- or cone-conformation, or the symmetrical boat-conformation. The boat-conformation is interconvertible via a pseudorotation involving the crown-conformation as intermediate (Figure 9).

At room temperature the isomers have been found only in the symmetrical chair-conformation. The isomer assumes a symmetrical diamond-conformation, while the isomer is predicted to assume a symmetrical saddle-conformation. Investigation of the ring-inversion process have shown, that the interconversion of the chair-isomer and of the diamond-isomer into their corresponding crown-conformers is possible.25

Figure 9. Interconversion of boat1 to boat2 conformer via the crown intermediate.
1.4. Chemical modification of resorcin- and pyrogallolarenes

There are three obvious places to modify a resorcinarene (4, \( R_2 = H \)), namely the phenolic hydroxyl groups, the 2-position between the phenolic hydroxyl groups and also a chemical modification of functional groups introduced by the aldehydes during resorcinarene formation is possible (Figure 10). Pyrogallolarenes (4, \( R_2 = \text{OH} \)) can only be modified at two different position, because the 2-position also bears a phenolic hydroxyl function.

When complete functionalization of the macrocyclic core 4 is desired, only reactions with a very high yield are useful e.g. \( O \)-acylation and \( O \)-alkylation. The phenolic hydroxyl groups can be completely acylated and examples of octaesters have been reported\(^{13,19,25,26,27,60}\). Also the regioselective acylation to \( C_{2v} \) symmetrical resorcinarenes with four equivalents of arylsulfonylchloride\(^{62}\) or an aroylchloride\(^{62}\) has been described. The reaction with an excess of diarylchlorophosphate, diphenylchlorophosphane, arylsulfonylchlorides and trimethylchlorosilane furnished octaphosphates\(^{64}\), octaphosphinites\(^{65}\), octasulfonates\(^{66}\) and octatrimethylsilyl\(^{67}\) derivatives of resorcinarenes 4, respectively.

Complete \( O \)-alkylation results in ethers\(^{58,69,70,71,72}\) (Figure 11). In this way, alkylation with an excess of ethyl bromoacetate led to octaethers 19 which were further transformed into the corresponding octaaids 20.\(^{73}\) Such octaaids served as pseudo-stationary phases for the electrokinetic chromatographic separation of amines.\(^{74}\) Aminolysis with chiral amines and aminoalcohols resulted in chiral octaamide derivatives 21.\(^{75}\) Reduction of octaester with LiAlH\(_4\) gave the octol 22 which underwent a Mitsunobu reaction with phthalimide, DEAD and PPh\(_3\), to give an octaphthalimide. Hydrazinolysis of the phthalimido groups resulted in the corresponding octaamine 23.\(^{76}\)
The synthesis of octapropargyl derivatives of tetraethylphenylresorcinarene and reaction with [Co₂(CO)₈] gave octakis[alkyne(dicobalt)] derivatives, the most highly metalated resorcinarenes known till now.⁷⁷,⁷⁸ These examples show that a wide scope of functionalization of the phenolic hydroxyl groups of resorcin- and pyrogallolarenes 4 can be achieved.

**Figure 11.** Modification of resorcinarenes (4) by Williamson etherification and further functionalization.

The synthesis of octapropargyl derivatives 24 of tetraethylphenylresorcinarene and reaction with [Co₂(CO)₈] gave octakis[alkyne(dicobalt)] derivatives, the most highly metalated resorcinarenes known till now.⁷⁷,⁷⁸ These examples show that a wide scope of functionalization of the phenolic hydroxyl groups of resorcin- and pyrogallolarenes 4 can be achieved.

**Figure 12.** Resorcinarenes (4, R₂ = H) modified in 2-position by bromination with NBS and by Mannich reaction with primary and secondary amines.
The presence of two electron-releasing hydroxyl groups on the aromatic rings of resorcinarenes (4, \( R_2 = \text{H} \)) makes them highly activated for electrophilic aromatic substitution reactions like bromination\(^{15,79}\) with N-bromosuccinimide (NBS) to give 25 or diazo coupling with four equivalents of \( p \)-sulfonatebenzenediazonium\(^{80}\). Thiomethylation with formaldehyde and thiols was also possible.\(^{81}\)

Several aminomethylated resorcinarenes 26 have been synthesized by a Mannich reaction with formaldehyde and a secondary amine (Figure 12).\(^{17,82,83}\) When the reaction is carried out with primary amines, the resulting secondary amine 27 reacts intramolecularly with one of the phenolic hydroxyl groups at the ortho-position, and a second equivalent of formaldehyde gives rise to the formation of four 1,3-oxazine rings 28.\(^{82,84,85}\)

The acid-catalyzed cyclocondensation of resorcinol (2) and pyrogallol (5) with aldehydes or their synthons containing hydroxy, alkoxy, aryldiazo, sulfonyl, and \( \text{B(OH)}_2 \)\(^{86}\) groups, halogens, double bonds\(^{87,88}\) and crown ether fragments allow the introduction of additional functional groups into resorcin- and pyrogalolarenes.\(^{14,37,89,90,91,92}\) The functional groups introduced in this way can be further modified, whereas a complete survey of the possible derivatives is beyond the frame of this chapter. The reader may be redirected to comprehensive text books or review articles.\(^{6,7,8,22}\)
2. Star polymers

2.1. Introduction and controlled radical polymerization techniques

Star-shaped polymers have gained increasing interest because of their compact structure and high segment density, their interesting dilute solution properties and because very efficient methods have made possible their preparation and further functionalization of the outer branch ends. The various approaches to access star-shaped polymers, namely ionic polymerization techniques, group transfer polymerization, transition metal catalyzed polymerization, and recently also controlled radial polymerization techniques, mirror the interest in such star-shaped polymeric architectures. Common for all these different approaches is the methodology of a living and controlled polymerization. This concept is the prerequisite for the preparation of well-defined materials with low degrees of compositional heterogeneity. Because termination and chain transfer reactions are theoretically absent and the chain ends may be stable for sufficient time periods, these polymerization techniques have the following useful synthetic attributes for star polymer synthesis:1,2

- One polymer is formed for each initiator molecule, so that the number average molecular weight of polymers or block segments can be predicted from the reaction stoichiometry. A multifunctional initiator with functionality \( f \) can form stars with \( f \) arms.
- If the rate of initiation is rapid or competitive with the rate of propagation, polymers (precursor arms) with narrow molecular weight distribution (\( M_n/M_w < 1.1 \)) are formed.
- When the reaction is quenched or all the monomer has been consumed, the product is a polymer with reactive chain ends that can participate in a variety of postpolymerization reaction:
  a. block copolymerization by addition of a second monomer, and/or
  b. end-linking with multifunctional linking agents to form the corresponding star-branched polymers with uniform arm length.

The products of living and controlled radical polymerizations (CRP) are polymers that retain their active, propagating chain ends when all of the monomer has been consumed. Under appropriate conditions, these polymers exhibit well-defined, predictable number average mo-
molecular weights and narrow molecular weight distributions, i.e., low degree of compositional heterogeneity.

During the past few years a rapid growth in development and understanding of new controlled radical polymerization methods (I, II, and III in Figure 13) was achieved.\(^{93,94}\) All of these methods are based on establishing a rapid equilibration between a minute amount of growing free chain-radicals and a large majority of the dormant species. The dormant chains may be alkyl halides, as in atom transfer radical polymerization (ATRP, II),\(^{95,96}\) thioesters, as in reversible addition fragmentation chain transfer processes (RAFT, III), alkoxyamines, as in nitroxide mediated polymerization (NMP, I),\(^{97}\) and potentially even organometallic species (Figure 13).

![Figure 13. Schematic representation of different CRP methods.](image-url)
Free radicals may be generated by the spontaneous thermal process (NMP, I), via a catalyzed reaction (ATRP, II), or reversibly via the degenerative exchange process with dormant species (RAFT, III). All of the CRP methods, shown in Figure 13, include activation and deactivation steps (with rate constants $k_a$ and $k_d$), although in RAFT the scheme may be formally simplified to just the exchange process with the apparent rate constant $k_{ex}$. Generated free radicals propagate and terminate (with rate constants $k_p$ and $k_t$), as in a conventional free-radical polymerization.

These three main methods, although involving different chemistries, employ the same concept: the persistent radical effect (PRE), an equilibrium between a low concentration of active propagating chains and a large amount of dormant chains, which are unable to propagate or self-terminate. During free-radical polymerization, the ratio of the rate of termination ($R_t$) to the rate of propagation ($R_p$) depends on the concentration of propagating chains ([$P_n•$]):

$$R_t / R_p = k_t[P_n•] / k_p[M]$$

where [M] is the concentration of the monomer. The further the equilibrium is shifted toward dormant species, the greater is the decrease in [$P_n•$], and termination becomes less significant in comparison with propagation. Consequently, in a CRP, termination reactions are minimized but not totally suppressed. CRPs should be carefully distinguished from ideal living polymerizations as defined by Szwarc. Thus, in polymers prepared by CRP, the percentage of living chains capped by a halogen atom (ATRP), an alkoxyamine moiety (NMP), or a dithioester moiety (RAFT) is less than 100%. Moreover, besides bimolecular termination, several side reactions, such as β–hydrogen abstraction and loss of HBr by elimination in ATRP, may affect chain-end functionality during CRP, which additionally reduces the number of living chains.

2.2. Atom transfer radical polymerization (ATRP)

ATRP is, among other CRP methods, the most often applied controlled radical polymerization technique due to its ability to achieve a wide scope of different polymeric architectures. A general mechanism for ATRP is shown in Figure 14. The radical, or active species, are generated through a reversible redox process catalyzed by a transition metal complex ([M$_t^m$-Y/Ligand], where Y may be another ligand or counterion).
which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, R-X.

\[
P_n - X + M_t^{m-Y/Ligand} \xrightarrow{k_a} P_n^* + X-M_t^{m+1-Y/Ligand} \quad \text{Figure 14. General reaction scheme of the atom transfer radical polymerization (ATRP).}
\]

As for all controlled radical polymerization processes, generation of the active radical species occurs with a rate constant of activation \(k_a\), and deactivation to the dormant species with the rate of deactivation \(k_d\). Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a conventional radical polymerization, with a rate constant of propagation \(k_p\). Termination reactions (with rate constant \(k_t\)) also occur in ATRP, mainly through radical coupling and disproportionation and elimination of HBr; however, in a well-controlled ATRP, no more than a few percent (5-10%) of the polymer chains undergo termination during the initial, short, non-stationary stage of the polymerization. Other side reactions may additionally limit the achievable molecular weights. Through termination an excess of oxidized metal complexes \([X-M_t^{m+1-Y/Ligand}]\) as persistent radicals are generated which reduce the stationary concentration of growing, active radicals \(P_n^*\) through deactivation and thereby minimize the contribution of termination. A successful ATRP will have not only a small contribution of terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation.

As a multi-component system, ATRP is composed of the monomer (M), an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand). The following chapter will give a brief introduction into the different system used, whereas the main focus will be based on systems suitable for the polymerization of styrene (29) and its substituted derivatives 30.
Monomers, initiators and transition metals:

Various monomers have been successfully polymerized by using different catalytical active transition-metal complexes for ATRP (Figure 15): (meth)acrylates 32 and 33 by copper, \(^{103,104,105}\) ruthenium, \(^{106,107}\) iron, \(^{108,109,110}\) nickel, \(^{111,112,113}\) palladium \(^{114}\) and rhodium, \(^{115}\) (meth)acrylamides \(^{116}\) and acrylonitrile \(^{117,118,119}\) and other monomers like 4-vinylpyridine (31) and dendronized macromonomers by copper. \(^{120}\) ATRP of styrene (29) and its derivatives 30 has been reported for the different catalytic systems such as copper \(^{121,122,123}\), iron, \(^{124,125}\) ruthenium \(^{126}\) and rhenium \(^{127}\); thus far the copper based system was found to be ideal for this class of monomers.

The reaction may be carried out in bulk or using a solvent, but the stability of the halide end group displays a pronounced solvent dependence as demonstrated by model studies using 1-phenylethyl bromide 35. As a result, nonpolar, nonprotic \(^{128}\) solvents are recommended for styrene ATRP. \(^{129,130,131}\) Better molecular weight control is obtained at lower temperature, presumably due to a lower contribution of the thermal self-initiation. \(^{132,133}\) However, to maintain a sufficient propagation rate, avoid vitrification at high conversion (for polystyrene \(T_g \approx 100 \, ^\circ C\)), and sometimes increase the solubility of the catalysts, higher reaction temperatures (\(T > 100 \, ^\circ C\)) are preferred for styrene ATRP.

Successfully applied initiators for ATRP include 1-phenylethyl halides 35 and benzylic halides 35 and 36 and a variety of other compounds, such as allylic halides, and functional \(\alpha\)-haloesters 38, 39 and 40, \(^{134}\) polyhalogenated alkanes \(^{121,135}\) 34 and arenesulfonyl chlorides \(^{136}\) 37, whereas \(\alpha\)-haloesters 38 to 40 are the most suitable initiators due to fast initiation and easy accessibility by \(O\)-acylation (Figure 16).
The main role of the ligand in ATRP is to solubilize the transition-metal salt in organic media and to adjust the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer. Especially aromatic nitrogen-based ligands, like 2,2’-bipyridine (41), 4,4’-disubstituted 2,2’-bipyridine 42, 1,10-phenanthroline (43), and aliphatic polyamines like PMDETA 44, Me₆-tren 45 and 46 have been used in copper- and iron-mediated ATRP. In contrast to sulfur, oxygen or phosphorus ligands, which have been used for other transition-metals, for copper-mediated ATRP, nitrogen-based ligands are normally utilized due to appropriate electronic effects and favorable binding constants. Catalytic activity of the transition-metal complex greatly depends on the coordination chemistry and on electronic and steric effects of the ligand. Reduced catalytic activity or efficiency is observed when there is excessive steric hindrance around the metal center or the ligand has strongly electron-withdrawing substituents. Activity of N-based ligands decreases with decreasing the number of coordinating sites N4 > N3 > N2 > N1 and with increasing the number of linking C-atoms C2 > C3 > C4. Activity is usually higher for bridged and cyclic systems, than for linear ana-
logues. Examples of some N-based ligands applied in the copper-mediated ATRP are shown in Figure 17.

![Figure 17. Common N-containing ligands used in the atom transfer radical polymerization (ATRP).](image-url)

The determination of the active catalyst structure remains a challenging task. Even in the most thoroughly studied Cu/bpy catalytic system, the exact structure of the active catalyst is not yet completely clear and can be considered as rather complex. Ligands on both the Cu(I) and Cu(II) species are labile in solution, and $^1$H NMR studies indicate that there is fast exchange with the free ligand in solution and the Cu(I) coordinated by bpy. Depending on the used ratio of copper to ligand, different complex structures need to be taken into account, and also the polarity of the utilized solvent plays a significant role during polymerization. A [L$_2$Cu(I)]$^+$ species is suggested to be the active form in polar and aprotic solvents, in contrast to a [L$_2$Cu(I)]$^+$[Cu(I)X]$_2^-$ species in less polar solvents. Perhaps even more complex is the structure of the relevant Cu(II) species. From the X-ray data and EXAFS, it appears that it should have a trigonal bipyramidal cationic structure [X-Cu(II)bpy$_2$]$^+$ (48). However, in nonpolar media, a neutral distorted square planar structure [X$_2$Cu(II)bpy] may be preferred over a pure Cu(II) species. On the other hand, in the presence of Cu(I), it readily converts to [X-Cu(II)bpy$_2$]$^+$ (48) which is accompanied by the anion [X$_2$Cu(I)]$. Thus based on the literature data and ATRP model studies, it seems that the copper species complexed by bpy derivatives and actively involved in the ATRP can be best represented by a tetrahedral [Cu(I)bpy$_2$]$^+$ complex (47) and a trigonal-bipyramidal or distorted square-pyramidal [X-Cu(II)bpy$_2$]$^+$ complex (48) (Figure 18).
2.3. Arm-first and core-first approach towards star polymers

In the arm-first approach, these living polymers are either reacted with a divinyl-compound to form a block co-polymer (Method A)\(^{149}\) which is later crosslinked under appropriate conditions to give a mixture of star-branched polymers with varying and broad molecular weight distribution. Or the living polymer chains are directly reacted with multifunctional linking agents or deactivators (Method B) to form star-branched polymers in which the number of arms corresponds to the functionality \(f\) of the linking agent as shown in Figure 19. \(P^*\) is a living polymer chain obtained by either anionic, cationic or radical polymerization, \(C(Y)_f\) is a multifunctional linking agent or core of functionality \(f\), bearing \(f\) functions Y compatible with X, and \(C(P)_f\) is a star-branched polymer containing \(f\) arms.\(^1,^2\)

The main advantage of these methodologies is, that the arms of the resulting branched polymer are well defined, because the precursor arms can be characterized independently from the star. Due to the well defined arms, the number of arms can be readily determined by measuring the molecular weight of the star. In principle, a wide variety of well-defined, star-branched polymers with different numbers of arms can be prepared using the latter method by varying the functionality \(f\) of the linking agents \(C(Y)_f\). However many of the reported linking reactions are complicated by side reactions and a growing incompleteness in reaction conversion with growing functionality of the core.

\[\text{Figure 18. Illustration of the tetrahedral } [\text{Cu(I)}(\text{bpy})_2]^+ (47) \text{ and the trigonal-bipyramidal } [\text{Cu(II)}(\text{bpy})_2]^+ (48) \text{ species, actively involved in the atom transfer process.}\]
In contrast to the above mentioned methodologies, using the core-first approach, living/controlled polymerization techniques applying a homogeneous, plurifunctional initiator like a core $C(I)_f$ of functionality $f$, can form a star-branched polymer $C(P)_f$ with $f$ arms and a low degree of compositional heterogeneity among the arms if the following conditions prevail (Figure 20):1,2

- All the initiating sites must participate in initiating chain growth (quantitative, efficient initiation). This ensures uniform and predictable arm molecular weights.
- The rate of initiation must be rapid or competitive with respect to the rate of propagation. This is required to obtain a narrow molecular weight distribution.
- All propagating centers must be equally reactive with respect to chain growth (addition of monomer).

**Method A:**

![Diagram of Method A](image)

**Method B:**

![Diagram of Method B](image)

*Figure 19. "Arm-first"-approach towards star-branched polymers.*
Unfortunately, only few plurifunctional initiators satisfy the preceding requirements. The high chain segment density in a growing star-branched molecule exacerbates complications arising from chain end/chain interactions such as aggregation of ionic species, oxidation-reduction reactions of organometallic centers, and bimolecular termination reactions of radicals. As a consequence of these problems, few well-behaved plurifunctional initiating systems are available.

### 2.4. Star polymers based on calix[n]arenes and resorcinarenes – literature overview

The application of controlled polymerization techniques to synthesize star polymers based on calix[n]arenes can be historically traced back to a seminal report of Kennedy et al.\textsuperscript{150} who...
first described the preparation of well-defined star polymers with eight polyisobutylene (PIB) arms emanating from a calix[8]arene core by carbocationic polymerization (Figure 21). The synthesis was achieved with calix[8]arene as initiator and BCl3/TiCl4 in conjunction as coinitiators to induce the controlled and living polymerization of isobutylene (IB). In a later attempt Kennedy et al. used the same initiator for the copolymerization of IB and styrene (S), whereas the living poly-[IB-co-S]-polymer-chains were end-quenched with allyltrimethylsilane to yield star polymers with eight allyl-terminated arms. Hydroboration of the allyl termini afforded telechelic eight-arm star polymers with aliphatic alcohol termini, which were crosslinked by 4,4’-methylene bis(phenyl) diisocyanate and 2,4-tolylenediisocyanate to produce films with potential interest for scratch-resistant and mar-resistant coatings.

By reaction with dichloroacetyl chloride, modified calix[n]arenes (n = 4, 6, 8) as initiators for atom transfer radical polymerization (ATRP) were first described by Sawamoto et al. (Figure 22). The tetra, hexa- and octafunctional initiators were used in the ruthenium-mediated ATRP of methyl methacrylate (MMA) with RuCl2(PPh3)3 and Al(iOPr)3 to give PMMA polymers with narrow molecular weight distribution. Sequential block copolymerization of the living octaarm star polymer with n-butyl methacrylate (BMA) or tert-butyl methacrylate yielded (MMA-co-BMA(t-BMA)-star polymers.

Soon after Sawamoto, Gnanou et al. described the preparation of well-defined octaarm polystyrene stars based on as initiator with CuBr/bpy as atom transfer agent (Figure 22). Using the same catalytic system, Gnanou et al. succeeded in the controlled radical polymerization of styrene (S), tert-butyl acrylate (t-BuA) and methyl methacrylate (MMA) using tetra-, hexa- and octafunctional initiators based on calix[n]arenes (n = 4, 6, 8). The latter were prepared via esterification of the calix[n]arenes with 2-bromo-propionyl bromide and 2-bromo-isobutyryl bromide (53) respectively. Using the derived tetra-, hexa- and octaarm polystyrene star polymers, which still bear reactive benzyl bromide end groups, and substitution with 2-amino-1,3-propanediol, a branching-point was introduced to the end of

Figure 22. ATRP initiators based on calix[n]arenes (n = 4, 6, 8) used by Sawamoto et al. and Gnanou et al..
each polymer-chain. Esterification of free hydroxyl groups of the branch-points with 2-
bromo-isobutyryl bromide (53) allowed the preparation of octa-, dodeca- and hexadeca PS
macronitiators with two geminal ATRP initiating sites per chain-end, which were again subjected to styrene-ATRP. Iteration of the above mentioned two reactions, allowed the proliferation of polystyrene arms up to the third generation, thus resulting in a branched PS star polymer with dendrimer-like architecture.\textsuperscript{158,159} Gnanou \textit{et al.}\textsuperscript{160} also utilized a octafuctional calix[8]arene bearing eight 2-hydroxyethyl functions as initiator for the anionic polymerization of ethylene oxide yielded eight-arm poly(ethylene oxide) (PEO) stars by using diphenylmethyl potassium (DPMK).

Only little is known about the utilization of resorcin- and pyrogallolarenes in controlled polymerizations processes. Coevally with our investigations\textsuperscript{161}, Tenhu\textsuperscript{162} and coworkers described the synthesis of two ATRP initiators 54 and 55 based on tetraethylresorcinarene and their application in the copper-mediated ATRP of MMA and \textit{tert}-butyl acrylate (\textit{t}-BA) using CuCl/bpy as atom transfer agent (\textbf{Figure 23}). Cleavage of the arms by alkaline saponification and molecular weight determination of the individual arms allowed to calculate the functionality of the resorcinarene derived star polymer. Surprisingly it was found, that only four out of the eight initiating sites participated in the polymerization. Subsequent block copolymerization with MMA to give P(\textit{t}-BA-co-MMA)-star polymers was achieved by utilizing another atom transfer agent consisting of CuCl/PMDETA which proved to be more efficient than the CuCl/bpy system. Investigations of other catalytic systems consisting of CuBr/PMDETA, CuBr/Me\textsubscript{6}-tren and CuCl/HMTETA (HMTETA = 1,1,4,7,10,10-hexamethyltriethylene-tetraamine) in the ATRP of MMA and \textit{t}-BA also led to star polymers with only four instead of eight arms, explained by the authors through steric hindrance of the initiating functions caused by their close proximity when attached to the resorcinarene core.\textsuperscript{163}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure23.png}
\caption{Resorcinarene derived octafuctional initiators 54 and 55 utilized by Tenhu and coworkers.}
\end{figure}
3. Dendrimers

3.1. Introduction, divergent and convergent approach

In sharp contrast to the classical approach and the practice of polymer chemists, researchers working on the interface between supramolecular chemistry and biochemistry, on one hand, and polymer synthesis, on the other, have striven during the last 15 years to make truly homostructural and uniform macromolecules. This has led to the emergence of a novel domain of investigation concerned with the synthesis of macromolecules having exactly defined molecular structure for which the size, the shape, the topology and the surface functionalization are unique.

The case of dendrimers illustrates the efforts made to assemble supramolecular structures of nanoscopic scale that are free of any dispersity. The term dendrimer was introduced by Tomalia\textsuperscript{164} to designate three-dimensional layered arrangements of chemical bonds, that arise from the introduction of a branching point at each monomer unit. More precisely, a dendrimer consists of four main components: a central core, arms of identical length, linking branching points that are therefore symmetrically distributed in the dendrimer, and end-standing reactive functions.

Two different approaches, based for both on stepwise reactions and functional group protection strategies have been discovered to match the highly symmetrical and flaw-free nature of dendrimers.

The first approach, known as \textit{divergent synthesis} (Figure 24),\textsuperscript{1,2,3,4,164} implies that the growth of the dendritic structure starts from a plurifunctional molecule and proceeds outwards through successive coupling and activation reactions. This activation step, which could be a deprotection reaction as well, is designed to generate two or more branching sites at the free terminus of the last introduced monomer unit. Iteration of the very same coupling and activation/deprotection reactions progressively gives rise to the dendritic structure.

The first publication of the divergent mode of synthesis of arborescent molecules can be historically traced back to an article by Vögtle\textsuperscript{165} in 1978, who first defined the concept of a cascade process by proliferating amine functions upon starting from benzylamine and repeating a sequence of two reactions: the Michael addition of acrylonitrile and the reduction of nitriles to amines. Vögtle had to stop at an rather early stage while attempting to synthesize his polyamine dendrimers because of a lack of selectivity of the Michael reaction.
Figure 24. Divergent approach towards dendrimers. Model scheme for a core with functionality $f=4$ for a concise representation.
Soon after Vögtle disclosed his cascade process, Denkewalter\textsuperscript{166} ventured on this area and described the synthesis of dendritic polylysine, using standard peptide chemistry and a coupling/deprotection strategy. Repetition of the coupling/deprotection processes allowed Denkewalter to isolate polylysine dendrimers of high generations, although it seems that the products obtained were somewhat contaminated with unwanted species. Several years after these first attempts to make arborescent structures, Tomalia revisited the chemistry used by Vögtle, giving particular attention to both the purification of the products obtained and the selectivity of each reaction carried out. The first report for the concept of so-called Starburst dendrimers was presented by Tomalia\textsuperscript{167} in 1985. Tomalia actually started with ammonia as the central core and used its three sites to attach three ester-terminated branches via Michael addition of methacrylate. He then carried on with the amidation of these esters using a large excess of ethylene diamine that he carefully removed to isolate the first generation polyamidoamine. He routinely repeated the same two reactions and the purification step to obtain polyamidoamines of a higher generation.\textsuperscript{168,169}

Coevally Newkome\textsuperscript{170} reported the synthesis of carbon based dendritic molecules called arborols, a term he coined to feature the tree-like structure and the presence of alcohol functions at the terminal positions.

The second approach, the **convergent synthesis** (Figure 25),\textsuperscript{1,2,3,4} is based on the initial synthesis of tree-like structures – so called dendrons (subunits of dendrimers) – containing a specific function. These tree-like structures are themselves obtained by coupling a molecule containing a particular reactive group with the branching sites of a molecule containing another nonreactive function so that the resulting dendritic structure will carry this remaining nonreactive moiety. Upon activation of the latter, the preceding coupling reaction using the same branching molecule can be repeated, yielding dendritic fragments of a higher generation. The way the latter are built entails an inward growth that actually begins at the chain ends. Upon coupling the dendrons prepared in this way with a core molecule bearing appropriate functions, the dendrimer is completed in its build up sequence.

With the convergent method, the formation of each generation involves the same number of coupling reactions at the branching sites, whereas in divergent synthesis there is an ever-increasing number of reactions as the dendrimer grows. Convergent synthesis therefore offers a better chance to control the purity and integrity of the dendrimer prepared.
Figure 25. Convergent approach towards dendrimers. Model scheme for a core of functionality $f = 4$ for a concise representation.
Because each dendron is the result of a coupling reaction between two dendritic fragments of a smaller generation, the separation of the expected material is straightforward owing to the fact, that the latter is bound to exhibit much larger molar mass than that of the precursor. In divergent synthesis the purification step is much more delicate, because incompletely reacted and exhaustively reacted materials involves only small molar mass differences. The formation of a given generation is indeed the result of the reaction between the dendrimer of the previous generation and a large number of small molecules. But the convergent method also has its weakness. Steric hindrance affects the convergent synthesis more than the divergent method for the same reasons as those invoked for the ease of purification.

Only in the early 1990s did the first account of the synthesis of dendrimers by convergent growth appear in the literature. Fréchet\textsuperscript{171} and Neenan and Miller\textsuperscript{172}, who are the actual pioneers of this method of synthesis, disclosed almost concomitantly that starburst dendrimers could be generated via the convergent route.

Nowadays synthetic routes for a wide variety of dendrimers consisting of different building blocks have been described using either the divergent method (polypropyleneimine\textsuperscript{165} (PPI), polyamidoamine\textsuperscript{164} (PAMAM), carbon-based dendrimers\textsuperscript{170}, polylsiloxane\textsuperscript{173,174,175,176} dendrimers and phosphorous\textsuperscript{177} dendrimers) or the convergent method (polyarylether\textsuperscript{171}, polyarylester\textsuperscript{178,179}, arylamide\textsuperscript{180,181,182} dendrimers and polyphenylene\textsuperscript{183,184,185} dendrimers) whereupon the above mentioned building blocks are only some examples of the dendrimer pool and the exponential growth of the number of publications concerning dendrimers mirrors the high interest in such materials. Especially their potential use as drug delivery systems and the recent development of self-immolative\textsuperscript{186} dendrimers with a trigger that initiates the fragmentation of the dendrimer molecule into its building blocks gained interest during the last years.\textsuperscript{187,188,189}

For further information on the synthesis of dendrimers, their analytical investigation, physical properties and unique features based upon self-assembly and host-guest interactions, and their application in catalysis\textsuperscript{190}, in diagnostics and in drug delivery\textsuperscript{191}, the reader may be redirected at this stage to comprehensive text books\textsuperscript{3,4} and recent reviews.\textsuperscript{164,177,192,193,194,195,196,197,198}
3.2. “Click”-chemistry as methodology for the divergent and convergent synthesis of dendrimers

There is a need to discover cost-effective methodologies towards dendrimer synthesis to allow large scale access to these structurally interesting polymer architectures. To date “click” chemistry and, in particular, copper-mediated (3+2) cycloadditions, offer an opportunity to realize this goal. The rediscovering of the so called “click-chemistry” introduced by Sharpless\textsuperscript{199} et al. as attempt to emulate the efficiency of biological chemistry with the specific aim of producing macromolecules by covalently binding smaller subunits via heteroatom linkages, offers new synthetic routes towards novel polymeric and dendritic structures.

A wide range of reactions were surveyed and the (3+2) cycloaddition of azides 56 with alkynes 57, developed by Huisgen and co-workers, to afford triazoles 58 proved to be the most effective “click”-reaction (Figure 26). Applications of this reaction now include drug discovery\textsuperscript{200} and selective molecular recognition directed coupling reactions\textsuperscript{201}. Unfortunately, minimal control of regiochemistry in the (3+2) cycloaddition of azides 56 with alkynes 57 arises as a consequence of the orbital symmetry and the cycloaddition leads to the production of two regioisomers of 58 via syn and anti approaches. However, the anti-regioisomer of 58 as the sole product can be obtained by employing a copper-mediated cycloaddition reaction.\textsuperscript{202,203} The mechanism of this copper-mediated “click”-reaction is shown in Figure 27.

Hawker and Wooley\textsuperscript{204,205} et al. used Huisgen’s (3+2) cycloaddition approach to afford dendritic architectures via a divergent-growth methodology. Dehaen\textsuperscript{206} et al. have applied a convergent-growth methodology to afford polyaromatic ether triazole dendrimers. In a similar approach Lee and Kim\textsuperscript{207} produced convergently grown dendrimers via a copper-mediated “click”-reaction. Hawker, Voit, Fréchet and Sharpless\textsuperscript{208} et. al. utilized the efficiency of copper-mediated “click” (3+2) cycloaddition reactions to produce polyaromatic triazole dendrimers in high yield by microwave irradiation with minimal purification required. Stoichiometric quantities of AB\textsubscript{2}-type monomers and dendrons were used in these efficient

\textbullet\textsuperscript{202}203
cycloadditions, thus eradicating the need of numerous column chromatography purifications after each coupling stage.

**Figure 27.** Copper-mediated (3+2) cycloaddition of azides 56 to alkynes 57 to afford the *anti*-isomer 58.

### 3.3. Dendrimers based on calix[n]arenes and resorcinarenes – literature overview

The use of calix[4]arenes and resorcinarenes 4 (R₂ = H) as core molecules in the synthesis of dendrimers has attracted the interest of several groups recently, whereas especially the ease of synthesis of such macrocyclic cores is one of the main advantages of calix[4]arenes and resorcinarenes 4 (R₂ = H) compared to other macrocyclic systems. Resorcinarenes and pyrogallolarenes 4 (R₂ = H, OH) in contrast to normal calix[4]arenes offer the possibility to easily tune the initial number of functions located at the core molecule, whereas the size of the core does not change significantly compared with calix[n]arenes (n = 4, 5...). Theoretically resorcin- and pyrogallolarene cores 4 (R₂ = H, OH) bearing 8, 12, 16 and 20 functionalities can be...
synthesized in a single step reaction depending upon the functionalized aldehyde which is utilized in the acid-catalyzed cyclocondensation.

A calix[4]arene platform was used as a core to which photochromic dyes and carbohydrate dendrons were attached. Also peptide-based dendrons and polyamide dendrons emanating from a calix[4]arene core were reported. Also calix[5]arenes were used. Examples of using calix[4]arenes as building blocks instead as core molecule were undertaken as well. However, the repetitive branching strategy for the preparation of higher dendritic generations was not clearly visible and had not been demonstrated until a seminal report by Rissanen and co-workers based on multiple amide bond formation between appropriately functionalized calix[4]arene amines and calix[4]arene acid chlorides. A second generation calix[4]-dendrimer with a tren core was reported several years later by Vicens applying the divergent and convergent approach, whereas Huang et al. succeeded in the convergent preparation of dendrons based on calix[4]crowns.

The use of resorcinarenes 4 (R2 = H) as core molecules for the construction of dendrimers was reported by Ueda and co-workers to obtain photoresist and negative photoresist working dendrimers by divergently grown arylether dendrons. The same approach was used by Asai et al. with two resorcinarenes 4 (R2 = H) bearing 12 and 16 reactive phenolic hydroxyl groups. The size and shape of such resorcinarene based dendrimers was investigated by Verhaert by means of small angle X-ray scattering (SAXS). Only Rissanen and co-workers used a convergent approach towards arylether dendrimers by attaching the convergently grown dendrons not to the phenolic hydroxyl groups, but to the 2-position between them via a Mannich reaction between the amine functionalized dendrons and three different unfunctionalized rccc-C-alkylresorcinarenes 4 (R2 = H).
Results and Discussion

4. Synthesis of resorcin- and pyrogallolarenes

4.1. Synthesis of C-alkylresorcinarennes and C-alkylpyrogallolarenes

According to well known procedures, C-alkylresorcinarennes 59 and 60 and C-alkylpyrogallolarenes 61 to 63 were synthesized starting from acetaldehyde (6), n-hexanal (7) and n-dodecanal (8) by the HCl-catalyzed cyclocondensation with resorcinol (2) and pyrogallol (5) respectively (Figure 28).

It’s well known that long alkyl chains as substituents at the bridging methine carbon can positively influence the solubility of these compounds in aprotic and unpolar solvents. Especially long tails like a pentyl- or undecyl-chain enhance the solubility in less polar solvents, e.g. chloroform, where resorcin- and pyrogallolarenes 4 are normally insoluble. This enhanced solubility was envisaged by using hexanal (7) and dodecanal (8) as carbonyl-component in order to prevent heterogeneous reaction conditions during the subsequent modification by substitution. All C-alkylresorcin- and -pyrogallolarenes 59 to 63 were synthesized in moderate yields in multigramm scale starting with 250 mmol resorcinol (2) and pyrogallol (5) respectively. According to 2-dimensional NMR investigations they were formed as recc-isomers (all-cis, all axial) in their crown-conformation. This conformation is stabilized by

\[
\begin{align*}
\text{Resorcinarennes} & : R_1 = H, R_2 = C_5H_{11} & \text{yield} & 83 \% \\
& : R_1 = H, R_2 = C_{11}H_{23} & \text{isomer} & \text{recc} \\
\text{Pyrogallolarenes} & : R_1 = OH, R_2 = C_1H_{3} & \text{yield} & 53 \% \\
& : R_1 = OH, R_2 = C_5H_{11} & \text{isomer} & \text{recc} \\
& : R_1 = OH, R_2 = C_{11}H_{23} & \text{isomer} & \text{recc}
\end{align*}
\]

Figure 28. Synthesis and achieved yields of C-alkylresorcin- and C-alkylpyrogallolarenes 59 to 63.
intramolecular hydrogen-bonding between adjacent resorcin and pyrogallol units, respectively. The structure of the C-alkylresorcin- and -pyrogallolarenes 60 and 63 bearing undecyl substituents at the bridging methine carbon was further confirmed by single crystal X-ray diffraction.

4.2. Synthesis of C-arylresorcinarenes and C-arylpyrogallolarenes

The use of 4-hydroxybenzaldehyde (64) as carbonyl component instead, lead to mixtures of the \( rccc \) (all-\( cis \), all axial) and the \( rctt \)-isomers (\( cis-trans-trans \), all axial) of C-arylresorcin- and –pyrogallolarenes 65 and 66, respectively (Figure 29). Even long reaction times of approximately 2 weeks did not afford a single isomeric product as shown by Högberg\(^{27,31} \). In the cases when resorcinol (2) was applied in the reaction, a 4:5 mixture of \( rctt:recc \)-isomers was obtained, whereas in the case of pyrogallol (5), a 10:1 mixture (\( rctt:recc \)) could be isolated. In both cases both isomers could be fully verified by 2-dimensional NMR and their spectra could be completely correlated and discriminated using nuclear Overhauser enhancement spectroscopy (NOESY and ROESY). Also differences of the integrals as a consequence of the different ratios of the isomers aided the structure determination. In the case of the C-arylresorcinarene 65 also the crystal structure of the \( rctt \)-isomer could be redetermined, whereas no evidence can be given, if either crystals of the \( recc \)-isomer were also present or if the \( rctt \)-isomer crystallized as the sole isomer from the solution in the NMR tube.

\[
\begin{array}{c}
\text{Resorcinarenes} \\
65: R_1 = H, R_2 = p-C_6H_4OH \\
yield \quad \text{isomer} \\
88 \% \quad recc + rctt (4:5)
\end{array}
\]

\[
\begin{array}{c}
\text{Pyrogallolarenes} \\
66: R_1 = OH, R_2 = p-C_6H_4OH \\
yield \quad \text{isomer} \\
86 \% \quad recc + rctt (1:10)
\end{array}
\]

Figure 29. Synthesis and achieved yields of C-arylresorcin- and C-arylpyrogallolarenes 65 and 66.
4.3. Synthesis of 2-hydroxyethyl-prefunctionalized C-arylresorcinarenes

When 2,2'-(1,3-phenylenebis(oxy))diethanol (67) was used instead of resorcinol (2) in the cyclooligomerization with 4-hydroxybenzaldehyde (64), a resorcinarene core 68 bearing eight 2-hydroxyethyl substituents and four phenolic hydroxyl groups could be synthesized (Figure 30).

![Chemical structure](image)

Figure 30. Synthesis and achieved yield of a 2-hydroxyethyl-functionalized C-arylresorcinarene 68.

Also in this case a 5:1 mixture of the rett- and rcce-isomers was obtained, with the rett-isomer as the major component. The different reactivity of both, aliphatic and phenolic hydroxyl groups, offers an easy access towards a regioselective functionalization of the resorcinarene core by, e.g. Williamson etherification. The use of a weak base such as K$_2$CO$_3$ will lead to selective substitution of the phenolic hydroxyl groups at the periphery of 68, whereas the aliphatic hydroxyl groups will stay unchanged. Such resorcinarenes might show enhanced complexation ability, whereas with this compound, the phenolic hydroxyl groups can be further functionalized to enhance the solubility of such supramolecular aggregates, or to achieve completely new materials, which might show improved properties in catalysis.
4.4. Structural peculiarities of resorcin- and pyrogallolarenes in solution

Hydrogen-bonding is an important noncovalent interaction, which has been extensively used to construct supramolecular systems. In recent years, this interaction has been utilized for the preparation of hydrogen-bonded molecular capsules through self-assembly processes.

Among those hydrogen-bound capsules, calixarene-based molecular capsules have attracted considerable interest. It was the seminal paper by the Atwood group in 1997 that probed and launched the research of large-cavity hydrogen-bound molecular capsules based on calixarene scaffold. The resorcin- and pyrogallolarene macrocycles form capsules both in solid state and even in C₆D₆ or CDCl₃ solutions. In the latter solvent Avram and Cohen deduced a hexameric assembly using DOSY NMR. Unlike related resorcinarene capsules, capsules formed by pyrogallolarenes (4, R₂ = OH) do not require water for assembly.

This fact was observed when preparing the NMR sample of 63 using CDCl₃ and brief heating. The obtained spectra revealed the phenolic protons of 63 as three downfield resonances (4a, 4a’ and 5a in Figure 32), indicating three distinct chemical environments for these hydroxyls. The remaining resonances are typical for the pyrogallolarene 63. Upon addition of DMSO-d₆ to the CDCl₃ solution the ¹H NMR spectra changed and only two signal for the phenolic protons can be observed. The same sensitivity for the aggregation mode was found in the ¹³C NMR spectra of 63. In pure CDCl₃ six signals can be observed, indicating that all aromatic

Figure 31. Schematic drawing of formation of a hexameric pyrogallolarene capsule through hydrogen-bond driven self assembly of 63.
carbons in the phenyl ring are not chemically equivalent. Indeed upon addition of DMSO-$d_6$, the monomeric form of 63 prevails, presenting only four signals in the aromatic region.

Figure 32. $^1$H NMR of the hexameric pyrogallolarene capsule, upper part shows the zoomed aromatic region.
4.5. Structural peculiarities of resorcin- and pyrogallolarenes in solid state

By single crystal X-ray diffraction (SXD), the redetermination of the crystal structure of the rctt-isomer of 65 was achieved (Figure 33). The crystals were obtained directly from the NMR tubes. As already shown by Shivayuk et al. the C-arylresorcinarene 65 can be considered as a quasi-completely solvated molecule in the crystalline state.

**Figure 33.** Schematic drawing of structure of the rctt-isomer of 65.

**Figure 34.** Packing diagram of 65 in solid state, representing the quasi-solution of 65 molecules in the crystal lattice by DMSO solvent molecules. Hydrogen-bonds are shown as red dashed lines.
The distances between neighboring resorcinol rings and of the cis-oriented phenolic moieties are too long to allow intramolecular hydrogen-bonding and therefore twelve intermolecular hydrogen-bonds pointing in all directions are formed to twelve DMSO molecules (Figure 34). Six additional DMSO molecules fill voids in the lattice. In conclusion, the molecule 65 is almost entirely surrounded by solvent in the crystal and can be considered as “completely solvated”, since hydrogen-bonding gives by far the highest contribution to the solvation enthalpy. It can be considered that the crystal structure is formed by molecules of 65 and their first and most ordered solvation shell.

The crystals suitable for X-ray diffraction of 60 and 63 were also obtained directly from solutions in the NMR sample-tubes, but only from mixtures of DMSO/CDCl₃ (Figure 35). The crystallization of a hexameric capsule, which was observed in solution in pure CDCl₃ for the pyrogallolarene 63 was unsuccessful. Both crystal structures of these long-tailed resorcin- and pyrogallololarenes 60 and 63 were already determined by several groups, but these structures were obtained from polar solvents like DMF, DMA, dioxane or ethanol, whereas no structure in combination with CDCl₃/DMSO can be found in Crystallographic Structure Database.

Both compounds 60 and 63 adopt a crown-conformation in the crystal with very similar geometry parameters. The arrangement of the molecules in the crystal is also similar, with the long alkyl chains lying nearly parallel to the c axis and with crown-to-crown interactions being mediated through van der Waal forces and hydrogen-bonding involving solvate molecules (DMSO in both cases). The C₁₁ alkyl chains on both molecules 60 and 63 are flexible and

![Figure 35](image)
orientate themselves in a way to optimize inter-chain contacts (C···C non-bonded distance > 3.6 Å). One striking feature common to both crystal structures is the interdigitation of the long alkyl chains which lie nearly parallel to the c axis of the unit cell. These chains are interdigitated to an extent of nine C atoms for the resorcinarene 60 and eight C atoms for the pyrogallolarene 63, respectively. This phenomenon of interdigitation is presumably a response to the favorable packing forces and it also imposes the crown conformation, besides hydrogen-bonding, as opposed to other arrangements.

C-undecylresorcinarene 60 crystallized with one host molecule, four DMSO molecules and one molecule of CDCl₃ in the asymmetric unit. The aromatic rings of the resorcinarene moiety are arranged in a crown-conformation with their hydroxyl groups in close proximity (Figure 36). The crown-conformation is stabilized by four intramolecular hydrogen-bonds between adjacent resorcin units with donor···acceptor distances between 2.756(3) Å and 2.812(3) Å.

The resorcinarene molecules 60 are packed in a crown-to-crown fashion with alternating hydrophilic and hydrophobic layers. Among the solvent molecules, the chloroform is located in the hydrophobic region, whereas the four DMSO molecules are located in the hydrophilic region. One of these DMSO molecules is located inside the cavity of the resorcinarene-crown and undergoes weak CH···π interaction with one of the methyl groups and the resorcin units. The same DMSO molecule undergoes hydrogen-bonding to another resorcinarene moiety which is related by an inversion center with the first one, resulting in the layered packing of
the crystals. The other three DMSO molecules fill voids in the hydrophilic part of the crystal lattice and stabilize the crystal structure by intermolecular hydrogen-bonds with resorcinarene moieties with donor···acceptor distances between 2.584(4) Å and 2.621(3) Å, which can be considered as fairly strong. 

The crystals of C-undecylpyrogallolarene 63 crystallized with one host molecule, five DMSO molecules, one molecule of EtOH and one molecule of chloroform in the asymmetric unit. The aromatic rings of the pyrogallolarene moiety are also arranged in a crown conformation with their hydroxyl groups in close proximity (Figure 37). The crown conformation is stabilized by five intramolecular hydrogen-bonds between adjacent pyrogallol units with donor···acceptor distances between 2.764(6) Å and 2.798(6) Å. Additional short contacts between hydroxyl groups in 2-position of the pyrogallol units are observed.

![Figure 37. Left: ORTEP-plot: top-view inside the cavity of 63, alkyl chains and H bound to C-atoms omitted for clarity; Right: Packing diagram of 63, hydrogen atoms omitted for clarity.](image-url)

The DMSO molecules are situated similar in the crystal lattice as for the resorcinarene 60, with one of the DMSO molecules inside the cavity of the pyrogallolarene 63 and four outside, stabilizing the crystal lattice by intermolecular hydrogen-bonding. The EtOH molecule is located at the outer rim of the hydrophilic crown and fills void in the lattice, but does not undergo hydrogen-bonding with one of the pyrogallol moieties or the DMSO solvent. Due to the absence of such hydrogen-bonding the EtOH is highly disordered. Two adjacent pyrogal-
lolarene molecules of one layer are connected by two bifurcated hydrogen-bound DMSO molecules which occupy void between the two pyrogallolarene moieties. Here the additional hydroxyl groups of the pyrogallolarene positively influences the stability of the crystal lattice by additional contribution to the hydrogen-bond network between solvent and pyrogallolarene molecules 63.

5. Chemical modification of resorcin- and pyrogallolarenes

5.1. Modification of resorcin- and pyrogallolarenes by O-alkylation with methyl bromoacetate

According to general etherification procedures, the resorcin- and pyrogallolarenes 59 to 63, 65 and 66 were O-alkylated by Williamson etherification with methyl bromoacetate (69) (Figure 38). Excellent yields could be achieved for C-arylresorcin- and C-
Results and discussion

arylpyrogallolarenes 72 and 76 within one day of reaction time. The C-alkylresorcin- and C-alkylpyrogallolarenes 70, 71 and 73 to 75 were also obtained in very high yields in the etherification reaction, but their purification by crystallization from MeOH was found to be more time consuming, due to the large excess of methyl bromoacetate (69) used and an enhanced solubility of these compounds in MeOH. It was observed, that all seven alkylated resorcin- and pyrogallolarenes 70 to 76 incorporate unreacted methyl bromoacetate (69), and a separation could only be achieved by subjecting the crude products to Kugel-Rohr distillation at pressures around $p = 10^{-4}$ mbar. Only by this procedure solid products were obtained, whereas direct attempts to precipitate or crystallize the crude products failed and led to all nuances of slime and tar, mainly consisting of methyl bromoacetate (69).

By 2D-NMR correlation, the conformation of octa-, dodeca- and hexadecamethyl acetates 70 to 76 could be assigned. All C-alkylresorcin- and C-alkylpyrogallolarenes 70, 71 and 73 to 75 were found to be in an interconverting boat-conformation in solution. The boat-conformation is favored in this case, because no intramolecular hydrogen-bonding between adjacent resorcin or pyrogallol units is possible, which stabilizes the crown-conformation. Due to the fast interconversion compared to the NMR time scale only the crown-conformer is observed, which is the intermediate between the two interconverting boat-conformations.

![Figure 39. Single crystal of dodecamethyl acetate substituted pyrogallolarene 74.](image)

The C-arylresorcinarene 72 was obtained as a mixture of its $rcce$ and $rcct$-isomers. The $rcce$-isomer was found to be in a fixed boat-conformation at room temperature and no interconversion of the two possible boat-conformers could be observed. The $rcce$-isomer of the C-arylpyrogallolarene 76 could not be isolated due to the very low content in the mixture. The
Results and discussion

*rctt*-isomers of 72 and 76 respectively, were found to be in the classical chair-conformation normally observed for *rctt*-isomers of resorcin- and pyrogallolarenes. By slow evaporation of the methanolic solutions of the methyl acetate functionalized resorcin- and pyrogallolarenes 70 to 76 crystals of the compounds were grown and subjected to single crystal X-ray diffraction. Especially compound 74 showed a very good crystallization behavior and a single crystal of approximately a = b = c = 0.8 cm could be grown over a period of two month from the methanol solution (Figure 39).

*Figure 40.* Representation of the boat-conformers for crystal structures of C-alkylresorcinarene 70 and C-arylresorcinarene 72.

*Figure 40* shows the crystal structures of the octafunctional C-alkylresorcinarene 70 and the dodecafunctional C-arylresorcinarenes 72. This time only crystals of the *rcce*-isomer of the C-arylresorcinarene 72 were obtained, in contrast to the crystal structure of the unsubstituted 65,
where the $rctt$-isomer crystallized. As can be seen both $rccc$-isomers of 70 and 72 crystallized in the boat-conformation with the aliphatic and aromatic residues on the bridging methine carbon pointing into one direction.

The same conformation was obtained in solid state for two dodecafunctional C-alkylpyrogallolarenes 73 and 74 (Figure 41).

Figure 41. Representation of the boat-conformer for crystal structures of C-alkylpyrogallolarene 73 and C-arylpyrogallolarene 74.
5.2. Modification by reduction of methyl acetates of resorcin- and pyrogallolarenes with LiAlH₄

The methyl acetate functionalized resorcin- and pyrogallolarenes 70 to 76 were further modified by reduction with LiAlH₄. The reduction of these plurifunctional macrocycles 70 to 76 was found to be difficult, due to large amounts of precipitate which formed in the course of the reaction. By MALDI-TOF-MS it was found, that a complete reduction could be achieved within 24 h of reaction time followed by 2 h of refluxing. The obtained crude products were very well soluble in water. A separation from the inorganic salts and the aqueous phase, after quenching, by liquid/liquid extraction could only be achieved for the resorcinarene 77 bearing a lipophilic C₁₁ chain at the bridging methine carbon (Figure 42). For all other resorcin and pyrogallolarenes no liquid/liquid extraction with different organic solvents was possible. Even the pyrogallolarene with C₁₁ chain bearing hydroxyethyl substituents could not be isolated. The products remained in the aqueous phase and were discarded.

The isolated octa-hydroxyethyl functionalized resorcinarene 77 can be further used as a core bearing a precise number of initiating sites for the anionic polymerization of oxiranes using diphenylmethyl potassium (DPMK), or it might be an useful complexing and extracting agent.

Figure 42. Synthesis of octa-2-hydroxyethyl-C-alkylresorcinarene 77.
5.3. Modification by reductive dimethylation of methyl acetates of resorcinarenes with the Grignard-reagent MeMgBr

![Chemical structure of octamethyl acetate functionalized resorcinarene 71 and its reaction with MeMgBr to form resorcinarene 78.]

Figure 43. Synthesis and achieved yield for the Grignard reaction of 71 with MeMgBr.

The octamethyl acetate functionalized resorcinarene 71 was subjected to a Grignard reaction using methylmagnesium bromide (Figure 43). Very fast conversion was indicated by MALDI-TOF-MS analysis of the reaction mixture. After only 2 h complete conversion was reached. Like derivative 77, this resorcinarene 78 bearing eight tertiary hydroxyl groups, might be a useful initiator in the synthesis of star-shaped polyoxirane polymers via an anionic polymerization route.

5.4. Modification by \(\text{O-alkylation}\) of resorcin- and pyrogallolarenes with \(N\)-bromopropylphthalimide

Six of the resorcin- and pyrogallolarenes 59, 60, 62, 63, 65 and 66 were subjected to Williamson etherification with \(N\)-bromopropylphthalimide (79) and \(\text{K}_2\text{CO}_3\) as the base (Figure 44). Additionally 18-crown-6 (18-C-6) was added for a better solubility of \(\text{K}_2\text{CO}_3\) in the organic media and to enhance the strength of the base. Even under these conditions very long reaction times were needed for complete substitution. The C-alkylresorcinarenes 80, 81 and C-alkylpyrogallolarenes 83 and 84 were obtained as pure products in moderate yields after extensive column chromatography.
In the case of C-arylresorcinarene 82 and C-arylpyrogallolarene 85 only mixtures of the completely substituted with incompletely substituted byproducts could be obtained, as indicated by MALDI-TOF-MS. A chromatographic separation of the fully substituted products failed due to very similar elution properties. In both cases mixtures of at least three compounds were achieved after several chromatographic steps.

\[
\text{Resorcinarenes} \\
80 : R_3 = H, R_4 = C_5H_{11} \\
81 : R_3 = H, R_4 = C_{11}H_{23} \\
82 : R_3 = H, R_4 = p-C_6H_4O(CH_2)_3Nphth \\
\text{Pyrogallolarenes} \\
83 : R_3 = O(CH_2)_3Nphth, R_4 = C_5H_{11} \\
84 : R_3 = O(CH_2)_3Nphth, R_4 = C_{11}H_{23} \\
85 : R_3 = O(CH_2)_3Nphth, R_4 = p-C_6H_4O(CH_2)_3Nphth \\
\]

\text{yield} \quad \text{isomer} \\
62\% \quad \text{rccc} \\
70\% \quad \text{rccc} \\
59\% \quad \text{rccc} + \text{recc} \text{ (crude)} \\
82\% \quad \text{rccc} \\
86\% \quad \text{rccc} \\
75\% \quad \text{rccc} + \text{recc} \text{ (crude)} \\

\text{Figure 44. Synthesis and achieved yields for the O-alkylation or resorcin- and pyrogallolarenes with N-bromopropylphthalimide (79).}
5.5. Modification by $O$-alkylation of resorcin- and pyrogallolarenes with propargyl bromide

The two resorcin- and pyrogallolarenes 59 and 62 bearing a C$_5$ chain at the bridging methine carbon were used in the $O$-alkylation with propargyl bromide (86) (Figure 45). Both propargyl-functionalized compounds 87 and 88 could be isolated in excellent yields and were found to be in the crown-conformation in solution by NMR, whereas also in this case it has to be considered that both compounds are in an interconverting boat-conformation. The octapropargyl functionalized resorcinarene 87 crystallized from an acetonitrile solution upon steady evaporation at room temperature. Compound 87 crystallized in the triclinic crystal system with unit cell dimension of a = 12.819(1) Å, b = 13.775(1) Å, c = 19.735(2) Å, $\alpha$ = 81.40(1)$^\circ$, $\beta$ = 88.73(1)$^\circ$, and $\gamma$ = 64.08(1)$^\circ$ in the space group P1bar. Like the unsubstituted derivatives, compound 87 packs in a layered manner, with an interdigitation of the alkyl chains to an extend of two carbon atoms and hydrophilic interactions between the crown parts of the molecules. No, by means of X-ray diffraction, detectable amounts of solvent are incorporated in the crystal lattice, whereas during sample preparation the crystals of 87 were found to be very unstable when removed from the mother liquor. This indicated, that a certain amount of solvent is incorporated in the lattice, but more or less statistically. No high residual electron density could be revealed after refinement. Figure 46 illustrates the boat-conformation and the packing diagram of compound 87.
The use of the macrocyclic core 68, bearing phenolic, as well as aliphatic hydroxy groups, in the O-alkylation with propargylbromide (86) led to a tetrapropargyl-functionalized resorcinnarene 89 which still bears free aliphatic hydroxyl groups for further substitution reactions (Figure 47). Full etherification of all phenolic hydroxyl groups of 68 could be achieved within one day of reaction time, but the presence of eight free aliphatic hydroxyl groups exacerbated the purification of this compound due to an improved solubility in protic and polar...
solvents. Also a kind of aggregation or micellation of 89 was observed in water which was not further investigated.

**Figure 47.** Synthesis of tetrapropargyl-C-arylresorcinarene 89 with eight 2-hydroxyethyl-functions.
6. Star polymers based on resorcin- and pyrogallolarene cores

6.1. Synthesis of plurifunctional ATRP initiators with mono-, di-, tri-, octa-, dodeca- and hexadeca-α-bromoester moieties

6.1.1. Synthesis of mono-, di- and trifunctional initiators based on phenol, oligophenols, resorcinol and pyrogallol

Prior to the synthesis of ATRP initiators based on resorcinarenes and pyrogallolarenes, three suitable trial-initiators 90, 91 and 92 (tertiary α–bromoesters) based on phenol (1), resorcinol (2) and pyrogallol (5) were synthesized in high yields according to general esterification procedures. Full esterification was achieved within one hour by using a twofold excess of 2-bromo-isobutyryl bromide (53) in the presence of pyridine (py) as the base (Figure 48). Even when three adjacent hydroxyl groups are present like in 1,2,3-trihydroxybenzene (pyrogallol, 5), full functionalization with the sterically demanding α–bromoesters could be realized within one hour.

The structure of the initiator 92 derived from pyrogallol (5) was further determined by means of single crystal X-ray diffraction (SXD). Compound 92 crystallized without solvent molecules in the centrosymmetric space group P21/c (No. 14) with four molecules per unit cell of the dimension a = 12.738(2) Å, b = 14.360(1) Å, c = 12.361(1) Å and β = 109.410(1)°. The
three adjacent $\alpha$–bromoester substituents connected to the phenyl ring orientate themselves in a way to avoid intramolecular contacts with the same direction of all bromides with respect to the phenyl ring. The crystal lattice is stabilized by weak intermolecular CH···Br interaction of the $\alpha$–methyl groups and bromines of the median $\alpha$–bromoester of two molecules of 92 related by their inversion centre. Additional weak CH···O interactions between $\alpha$–methyl groups and carbonyl oxygen enhance the stability of the crystal lattice (Figure 49).

Two additional initiators based on oligophenols 95 and 96 were synthesized under the same conditions (Figure 50). The trifunctional initiator 95 could only be isolated in 7 % yield from a mixture with its difunctional derivative. A TLC analysis evidenced a rough 1:1 mixture of both compounds after one hour reaction time, but no suitable eluent mixture was found for a chromatographic separation due to very close elution properties. Only a small fraction of the pure trifunctional initiator 95 could be obtained, which was enough to perform the later polymerizations. The disubstituted derivative could not be isolated in the necessary purity to perform subsequent polymerization reactions but by 2D-NMR correlation of the mixture, it was found, that only the external phenolic hydroxyl groups were substituted under the conditions used. To explain the high content of the difunctionalized initiator, it has been speculated that the median free hydroxyl group undergoes hydrogen-bonding to one of the two proximate ester groups, resulting in a circumvention of further acylation.
When the ortho-tert-butyl substituted oligophenol 94 was subjected to the substitution reaction only the monosubstituted product 96 was formed under the conditions used. It was expected to provide further information about the influence of free hydroxyl groups in the atom transfer radical polymerization process.

The structure of the monofunctional initiator 96 derived from 2,2'-[(2-hydroxy-5-methyl-1,3-phenylene)bis(methylene)]bis(4,6-di-tert-butylphenol) (94) was further determined by means of single crystal X-ray diffraction (SXD).

Compound 96 crystallized in the centrosymmetric space group C2/c (No. 15) with the cell dimensions of \( a = 34.757(1) \) Å, \( b = 11.699(1) \) Å, \( c = 20.320(1) \) Å and \( \beta = 108.13(1)^\circ \) with eight molecules per unit cell. One of the di-tert-butyl-phenol groups of 96 is disordered into two positions related by a 180° rotation axis through the methylene bridge and the aromatic para-carbon. The crystal lattice is stabilized by intramolecular and intermolecular hydrogen-bonds between free OH groups and the carbonyl oxygen of the \( \alpha \)-bromoester with donor-acceptor distances between 2.843(5) Å and 3.066(4) Å (Figure 51).
6.1.2. Synthesis of octa-, dodeca- and hexadecafunctional initiators based on resorcin- and pyrogallolarenes

**Figure 51.** Left: intramolecular hydrogen-bonding of 96; right: intra- and intermolecular hydrogen-bonds of 96. Dashed lines represent disordered parts.

**Figure 52.** Synthesis and achieved yields for octa-, dodeca- and hexadecafunctional ATRP-initiators 97 to 102 based on resorcin- and pyrogallolarenes.
The envisaged tertiary octa-, dodeca- and hexadeca α-bromoesters 97 to 102, of the resorcin- and pyrogallolarenes 59, 60, 62, 63, 65 and 66, respectively, were prepared by slow addition of a fourfold excess of 2-bromo-isobutyryl bromide (53) to the macrocyclic core in the presence of pyridine as a base. Fast esterification was observed by following the course of the reaction with MALDI-TOF-MS. After a period of 1 h, only peaks for the fully substituted products 97 to 102 could be observed using either 4-nitroaniline (4-NA) or 1,8,9-trihydroxyanthracene (Dithranol) as matrix. Both matrices were found to be suitable for the matrix assisted laser desorption/ionization process.

A better ionization could be observed by using 4-NA for the complete substituted products, while with Dithranol the ionization of the partially substituted products was favored. Due to that, Dithranol was used to estimate the completion of the reaction. Solid reaction products were only received by removing the excess of 2-bromo-isobutyryl bromide (53) under high vacuum and precipitation from methanol.
In high resolution MALDI-TOF-MS experiments the expected [M+Na]$^+$ and [M+K]$^+$ were observed. The presence of eight bromine atoms attached to the macrocyclic core of the initiator 97 could be clearly evidenced by comparing the measured and the calculated isotopic distribution pattern (Figure 53 and Figure 54). Good agreement for the observed and calculated isotopic distribution patterns could be also found for 99 and 102 bearing 12, or 16 bromines respectively.

The structure and conformation of the α-bromoesters of all six resorcin- and pyrogallolarenes 97 to 102 has been determined by means of 2D-NMR (COSY, HSQC, HMBC, NOESY and ROESY) and temperature dependent NMR measurements due to a lack of good crystallographic data. Since the conformation of the initiator determines the general structure of the polymer derived from it, conformational information is important.

The α-bromoesters 97, 98, 100 and 101, bearing aliphatic chains as residue on the bridging methine carbon are fixed in the $C_{2v}$ boat-conformation at room temperature. A conformational change from one boat-conformation to the other is slow compared to the NMR timescale and could only be observed for the resorcinarenes 97 and 98 at temperatures above 100 °C in solution with 1,1,2,2-tetrachloroethane-$d_2$ (TCl). Temperature dependent NMR experiments of the substituted pyrogallolarenes 100 and 101 did not show coalescence for the proton signals, which indicates an even bigger constrain caused by the larger number of bulky substituents.

The pyrogallolarenes 100 and 101 were found to be fixed in one of their boat-conformations and do not undergo any conformational change in the observed temperature range. The free activation enthalpy for the conformational change of the resorcinarene 97 from boat1 to boat2 ($\Delta G_c = 19.9\pm4$ kcal/mol) could be calculated from the determined coalescence temperatures $T_c$ for the protons H4b/H4b* and H5/H5* ($T_c = 406.2K$) using the coalescence point approximation.251

The ROESY measurements for the resorcinarene initiator 97 showed a negative crosspeak for the in-plane H5 protons and the out-of-plane H5* protons, which seems to be the indicator of a conformational change between boat1 and boat2 which can only take place for the rcce-isomer. But coevally an unusual positive crosspeak for H3/H3* was observed (Figure 55). The assignment of the in-plane protons H3 and the out-of-plane protons H3* was achieved by comparing the volume integrals for the crosspeak of H6/3 and H6/3* (see Figure 56). The proximity of the out-of-plane standing proton H3* to the proton H6 of the axial chain R4 is responsible for a higher volume integral, while the distance between the in-plane proton H3 and H6 is slightly bigger. Additionally a change of sign for H3/3* was observed for all resorcin- and pyrogallolarenes bearing aliphatic chains on the bridging carbon by changing the
deuterated solvent. In chloroform-$d_1$ the H3/3* crosspeak is always positive whereas the value becomes negative in 1,1,2,2-tetrachloroethane-$d_2$ (TCl).

These experimental data show that the conformational reorientation from boat$_1$ to boat$_2$ is faster in TCl than in chloroform. The C-arylresorcinarene 99 and the C-arylpyrogallolarene 102 always show a positive crosspeak for H3/3*. The sequence of the appearance of the H3 and H3* signals is vice versa compared with the calixarenes bearing aliphatic chains. Additionally, the proton signals of the aromatic side groups on the bridging carbon always show negative crosspeaks due to a hindered rotation of the more sterically demanding aromatic substituents for both isomers (rcce and rctt) in the case of 99 and the rctt isomer for 102. The proton signals for the terminal CH$_3$ groups of the tertiary bromide, substituted to the in-plane laying phenolic subunits, are also shifted to high field due to an increased steric constrain.
6.2. Atom transfer radical polymerization of styrene in bulk using mono-, di-, tri-, octa-, dodeca- and hexadecafunctional initiators

6.2.1. General considerations

The mono-, di- and tri-, octa-, dodeca- and hexadecafunctional initiators 90 to 92, and 95 to 102 synthesized via esterification of the corresponding phenols and resorcin- and pyrogallolarenes with 2-bromo-isobutyryl bromide (53) were applied in the atom transfer radical polymerization (ATRP) of styrene (29). Styrene (29) has been chosen due to the fact, that it is one of the simplest and most widely used monomers in radical polymerization reactions in industrial and even in laboratory scale, with a very good availability of a variety of analytical data.

Two different transition metal catalysts were used as atom transfer agent, the well known and often used CuBr/bpy system and a system consisting of CuBr/tbbpy (tbbpy = 2,2’-di-tert-butyl-4,4’-bipyridine), which revealed better solubility in styrene when applied in bulk polymerizations.

The polymerizations were prepared in such a manner, that regardless on the initiator used, the number of initiating sites n[I] was always chosen to be equal n[I] = 0.10 mmol in the reaction mixture with a varying content of monomer [M] between [I]:[M] = 1:100 to 1:1000 compared to the amount of initiator [I]. A 1:3 ratio of CuBr to bpy (or tbbpy) was chosen according to procedures published in recent literature with an equal amount of CuBr moieties per initiating α–bromoester sites, giving raise to the total consistency of the polymerization mixture with [I]:[CuBr]:[ligand]:[M] = 1:1:3:100-1000 with n[I] = 0.10 mmol. With increasing functionality f of the core, while maintaining the concentration of initiating sites in the vessel equal, the effective concentration of the initiator decreases with respect to the monomer content, because with increasing functionality f of the core, more α–bromoester sites are located on a single molecule, lowering the effective amount of initiator molecules to 1/2, 1/3, 1/8, 1/12 and 1/16 of n[I] = 0.10 mmol for di-, tri-, octa-, dodeca- and hexadecafunctional initiators 90 to 92 and 95 to 102 respectively. If the concentration of the core would have been kept equal to [I]: [M] = 1:100 to 1:1000 in comparison to monomer, the concentration of the catalytic system had to be adjusted for each reaction mixture resulting in different concentrations for each polymerization reaction.

All polymerization vessels were prepared in the same manner by weighting the appropriate amounts of initiator, CuBr, ligand (either bpy or tbbpy) and monomer into a dry Schlenk-tube.
The tubes were then degassed by several freeze-thaw-cycles and stirred until complete dissolution of the catalyst was achieved. The polymerization reactions were carried out at 120 °C for exact 4 hours and stopped by placing the tubes in an ice-bath. The general reaction scheme for the ATRP of styrene (29) using the monofunctional initiator 90 is shown in Figure 57, representing the reversible activation and deactivation step and the chain propagation by addition of monomer 29.

**Figure 57.** Scheme of styrene-ATRP representing the initiation by monofunctional 90 and the reversible activation/deactivation steps during monomer (29) addition.
6.2.2. ATRP of styrene with mono- di- and trifunctional initiators based on phenol, oligophenols, resorcinol and pyrogallol

The mono-, di- and trifunctional initiators 90 to 92, 95 and 96 were subjected to initiate the bulk polymerization of styrene (29) (Figure 58). All polymerization reactions using the above mentioned initiators were carried out with either CuBr/bpy or CuBr/tbppy as the atom transfer agent. In order to adjust and improve the reaction conditions for the later used octa-, dodeca- and hexadecafunctional initiators 97 to 102, some trial polymerizations were carried out with the initiators 90 to 92, 95 and 96 bearing one, two and three initiating sites respectively. A ratio of initiator:CuBr:bpy:monomer with [I]:[CuBr]:[ligand]:[M] = 1:1:3:500 was used in all polymerization reactions with n[I] = 0.10 mmol. The exact amounts are given in the practical part. All polymers were investigated by means of size exclusion chromatography in combination with a refractive index detector (SEC-RI) and matrix assisted LASER desorption/ionization – time of flight – mass spectrometry (MALDI-TOF-MS). The values for $M_n$, $M_w$ and PDI of the different mono-, di- and triarm star polymers are given combined in a table at the end of this chapter for better comparison.

![Figure 58. Mono-, di- and trifunctional initiators 90 to 92, 95 and 96 used in the bulk polymerization of styrene (29), applying either CuBr/bpy or CuBr/tbppy as atom transfer agent.](image)

The two monofunctional initiators 90 and 96 prepared from phenol (1) and 2,2’-[(2-hydroxy-5-methyl-1,3-phenylene)bis(methylene)]bis(4,6-di-tert-butylphenol) (94) respectively, yielded
linear polystyrene (PS) macromolecules with a narrow molecular weight distribution. The CuBr/bpy system was found to be less soluble in styrene when used in bulk polymerizations. Due to that a catalytical system consisting of CuBr/tbbpy was also investigated, which showed an enhanced solubility in unpolar media like styrene (29).

![SEC-RI plots for linear PS polymers derived from monofunctional initiators 90 and 96.](image)

**Figure 59.** SEC-RI plots for linear PS polymers derived from monofunctional initiators 90 and 96.

But a dropout in the propagation rate was observed when using tbbpy as ligand for complex formation. SEC-plots of the linear PS polymers revealed monomodal peaks indicating a good control over molecular weight and molecular weight distribution (Figure 59). No influence of the free phenolic hydroxyl groups in the polymerization reaction was found when initiator 96 was used. Also when the difunctional initiator 91 and the trifunctional initiators 92 and 95 were applied in the bulk polymerization of styrene (29) under the above mentioned conditions, good control over the molecular weight distribution could be achieved (Figure 60). The same lower propagation rate was found for all polymerization reactions when using the 4,4’-di-tert-butyl substituted bpy ligand. The trifunctional initiator 92 derived from pyrogallol (5) also yielded PS star polymers with a low polydispersity, whereas the trifunctional initiator 95 derived from oligophenol 93 revealed a trimodal molecular weight distribution (Figure 61). Possible impurities by CHCl₃ solvent, which was used for purification by column chromatography are expected to be the reason for this uncontrolled polymerization behavior.
Results and discussion

Figure 60. SEC-RI plot of linear PS polymers derived from difunctional initiator 91.

Figure 61. SEC-RI plot of PS triarm-star polymers derived from trifunctional initiators 92 and 95.
In order to prove this fact, the initiator was further dried in high vacuum at elevated temperature. The subsequent polymerization, using 95 and the 'bbpy ligand, finally showed a monomodal molecular weight distribution in the SEC-plot but not the expected lower propagation rate. The results of the SEC-RI and MALDI-TOF-MS analysis of the different obtained mono-, di- and triarm star polymers is presented in (Table 1).

Table 1. Results of molecular weight determination by means of SEC-RI and MALDI-TOF-MS for mono-, di- and triarm-PS stars derived from mono-, di- and trifunctional initiators 90 to 92, 95 and 96 based on phenol (1), oligophenols (93, 94), resorcinol (2) and pyrogallol (5).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Ligand</th>
<th>(M_n) g/mol</th>
<th>(M_w) g/mol</th>
<th>PDI</th>
<th>(M_n) g/mol</th>
<th>(M_w) g/mol</th>
<th>PDI</th>
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<td>12250</td>
<td>1.34</td>
<td>7500</td>
<td>9100</td>
<td>1.21</td>
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<tr>
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<td>5300</td>
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<tr>
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<td>bpy</td>
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<td>13760</td>
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<td>7900</td>
<td>10000</td>
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<td>'bbpy'</td>
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<td>4600</td>
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<td>1.11</td>
</tr>
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<td>91-Br2</td>
<td>bpy</td>
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<td>19300</td>
<td>1.20</td>
<td>20100</td>
<td>22500</td>
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<td>16100</td>
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<td>31900</td>
<td>34400</td>
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<td>'bbpy'</td>
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<td>10140</td>
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<td>8400</td>
<td>9100</td>
<td>1.08</td>
</tr>
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<td>39270</td>
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<td>32000</td>
<td>34200</td>
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<tr>
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<td>30130</td>
<td>1.21</td>
<td>34600</td>
<td>36300</td>
<td>1.05</td>
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</tbody>
</table>

MALDI-TOF-MS for the linear PS polymers obtained from 90 and 96 as initiators, compared with the SEC-RI results indicate a good agreement of both methods, even when the obtained molecular weight in MALDI-TOF-MS analysis is slightly smaller than the value obtained by SEC-RI (entries 1 to 4). With increasing number of arms a growing mismatch between both analytical methods is observed, which can be traced back to the smaller hydrodynamic volume of star-shaped polymers when compared with linear analogues of the same molar mass, even when only one or two additional arms are attached to the appropriate cores (entries 5 to 10). A more detailed description of this behavior will be given in the chapter where the results for octa-, dodeca- and hexadecaarm star polymers are compared and discussed. SEC-RI as analytical method for molecular weight determination can be used to obtain relative values for molecular weight and molecular weight distribution but not absolute values. For structural similar polymers it should be possible to compare values measured by this method, whereas
due to an universal calibration with linear polymer standards, an increasing error in estimation of the molecular weight of star polymers need to be taken into account. As the name indicates, SEC (size exclusion chromatography) in combination with a RI-detector (refractive index) is a method, where differences in the hydrodynamic volume of the different macromolecular species in the mixture are the factors which influence the retention time of the different species on the separating column. The smaller the macromolecule, the longer will be the dwell period of the macromolecule on the column due to an increased interpenetration into the porous packing material. This results in an under-estimation of the molecular weights of star polymers compared to linear macromolecules of the same molecular weight, when determined by SEC-RI, as a result of the smaller hydrodynamic radius of such star-shaped polymers. Independent from this fact, SEC-RI can be consulted to measure relative alterations of the molecular weight in dependence of the reaction conditions used for the polymerization experiment.

6.2.3. ATRP of styrene with octa-, dodeca- and hexadecafucntional initiators based on resorcin- and pyrogallolarenes

As shown in Figure 62 for resorcinarene 97 for example, all six synthesized plurifunctional initiators 97 to 102 based on resorcin- and pyrogallolarenes were used in the atom transfer
radical polymerization of styrene (29) with both, the Cu/bpy and the CuBr/tbbpy catalytic systems. The obtained polystyrene macromolecules were investigated by means of SEC-RI, MALDI-TOF-MS and additionally by SEC-MALLS (multi angle laser light scattering) which gives more reliable results in molecular weight determination than the SEC-RI technique. MALDI-TOF-MS allows the investigation of the species of single-star polymers, but cannot be used to investigate species like double-star polymers which are a result of bimolecular termination reaction during the polymerization reaction. In MALDI-TOF-MS analysis of polymeric materials very often dimerization and trimerization are observed as a result of the laser desorption/ionization-process. Also intermolecular interlinking of star polymers with long arms has to be taken into account during the sample preparation. Figure 63 shows a MALDI-TOF-MS spectra of a commercially available linear polystyrene standard of rather low molecular weight ( \( M_n = 24000 \) g/mol, PDI = 1.02). Even in this case dimers, trimers and tetramers can be observed. This means that it is not possible to distinguish between covalently bound dimers and trimers formed by intermolecular termination through star-star coupling, and the dimers and trimers formed through the desorption/ionization process.

![Figure 63](image_url)

**Figure 63.** MALDI-TOF-MS spectra of a commercially available linear PS standard, showing dimers, trimers and higher oligomers through oligomerization during the desorption/ionization-process.
Nevertheless, by MALDI-TOF-MS, it is possible to analyze the fraction of single-star polymers in the presence of the coupled byproducts in order to calculate $M_n$ and the polydispersity index.

In all the polymerization reactions carried out, the occurrence of low molecular weight byproducts was observed. These byproducts are formed from chloroform as initiator, which was used in the chromatographic purification of the initiators 97 to 102 prior to their use in polymerization reactions. NMR spectra always showed a peak, significant to chloroform, which indicates an incorporation of the solvent in the dry material. It was found that up to 4 weight% chloroform can be found in the products dried at room temperature and high vacuum. Compared to the molar masses of the macrocyclic initiators 97 to 102, this is equal with up to 40 mol% of chloroform in comparison to the initiators 97 to 102. The content of this solvent could be reduced by proper drying of the compounds at elevated temperatures ($T = 150 \, ^\circ C$) under high vacuum. Prior to the exhaustive drying, thermogravimetrical analysis of the initiators 97 to 102 has been used to determine, whether the substances are stable under the temperature regime used for drying, or if elimination of HBr occurs. It was found, that the octa-, dodeca- and hexadecafunctional initiators 97 to 102 are up stable to $T = 225 \, ^\circ C$, before loss of HBr through elimination and further decomposition occurs. Figure 64 shows the TGA-plot for the dodecafunctional initiator 100 which is exemplary for all the initiators.

**Figure 64.** TGA-plot of dodecafunctional initiator 100, illustrating the loss of residual chloroform solvent and further decomposition at $T > 225 \, ^\circ C$. 
Bulk ATRP of styrene using [I]:[M] = 1:100 and CuBr/tbbpy as atom transfer agent

When subjecting all six octa-, dodeca- and hexadecafunctional initiators 97 to 102 to the bulk polymerization of styrene (29) with a low [I]:[M] ratio (1:100), massive intermolecular star-star coupling was observed. The high polymerization conversion under these conditions led to an increased viscosity of the reaction mixtures during the course of the polymerization reaction and a proper mixing by stirring was not longer given.

Even with the SEC-RI technique the coupling products could be observed in high quantities. In all SEC-plots a bimodal peak was observed with a shoulder at lower elution times (higher molecular weight region) which indicated the presence of these coupled byproducts (Figure 65 and Table 2). SEC-MALLS measurements also indicated that not only double-star polymers are formed, but also trimers, tetramers and even higher coupling products. A comparison between results obtained by SEC-MALLS and MALDI-TOF-MS (Table 3) suggests, that in some case (entry 16, 18 and 19) the pure single-star polymer was only a minor fraction left in the polymerization mixture, whereas the major fraction consisted of intermolecular coupled star polymers. Due to the compositional heterogeneity of the polymers obtained, broad molecular weight distributions were observed.
Table 2. Results of molecular weight determination by means of NMR, SEC-RI for octa-, dodeca- and hexadecaarm PS-stars derived from octa-, dodeca- and hexadecafunctional initiators 97 to 102 with [I]:[M] = 1:100 and CuBr/tbbpy.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Ligand</th>
<th>$^1$H_polymer integral</th>
<th>Conv. %</th>
<th>$M_n$(theo.) g/mol</th>
<th>$M_n$ g/mol</th>
<th>$M_w$ g/mol</th>
<th>PDI</th>
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<tr>
<td>12</td>
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Table 3. Results of molecular weight determination by means of SEC-MALLS and MALDI-TOF-MS for octa-, dodeca- and hexadecaarm PS-stars derived from octa-, dodeca- and hexadecafunctional initiators 97 to 102 with [I]:[M] = 1:100 and CuBr/tbbpy.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Ligand</th>
<th>$M_n$ g/mol</th>
<th>$M_w$ g/mol</th>
<th>PDI</th>
<th>$M_n$ g/mol</th>
<th>$M_w$ g/mol</th>
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<td>72700</td>
<td>1.04</td>
</tr>
<tr>
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</table>

If one considers that the growing arms in octa-, dodeca- and hexadecaarm stars have the same probability of recombination as that of linear chains of similar concentration, the fraction that should be affected by termination should be 8, 12 and 16 times higher the value for linear species. As described by Gnanou and coworkers, another fact which has to be taken into account is the influence of the peculiar shape of the star polymers on the occurrence of these side reactions. Stars are generally pictured as spherical objects whose density increases towards the central core and whose arm tips are restricted in their motion to a region that corresponds to their external corona. A star-containing medium can thus be portrayed, above the
critical overlap concentration $C^*$ (with $C^* = 3M_w/4\pi R_g^3 N_a$ where $M_w$ is the absolute mass average molar mass of the star obtained by light scattering and $R_g$ is the radius of gyration of a linear polystyrene polymer exhibiting the same hydrodynamic volume as that of the star), as a collection of overlapping spheres whose respective arms are forced to remain in a close vicinity, resulting in a higher tendency of intermolecular star-star coupling.\textsuperscript{156}

**Bulk ATRP of styrene using [I]:[M] = 1:500 and CuBr/$\text{bbpy}$ as atom transfer agent**

By using higher [I]:[M] ratios (1:500) and restricting the conversion of the polymerization reaction to values below 20\%, it was possible to omit star-star coupling to a great extend, but not completely. The occurrence of coupled stars could be best followed with the SEC-MALLS technique, which is capable to reveal also traces of coupled byproducts. The SEC-RI technique in this case has a too low limit of detection and due to that the results shown in Figure 66 and Table 4 indicate a very low compositional heterogeneity.

By comparing the results obtained by SEC-RI, SEC-MALLS and MALDI-TOF-MS (Table 5 and Figure 67) one can clearly see, that the synthesis of star polymers with a low polydispersity is possible even at a [I]:[M] ration of 1:500. But these results also indicate that the dilu-
tion factor is not sufficient enough to omit star-star coupling and higher [I]:[M] ratios need to be applied.

Good control over molecular weight and molecular weight distribution was found to be no longer given with CuBr/bbpy as the catalytic system. The complete table of all the polymerizations undertaken with the six plurifunctional initiators 97 to 102 (practical part: Table 17) with this atom transfer agent and a ratio of [I]:[M] = 1:500 shows varying results to a great extent for the molecular weights obtained under these conditions, indicating a loss of control. Also the conversions reached under the same conditions vary for experiments undertaken with the same initiator.

Table 4. Results of molecular weight determination by means of NMR, SEC-RI for octa-, dodeca- and hexadecaarm PS-stars derived from octa-, dodeca- and hexadecafunctional initiators 97 to 102 with [I]:[M] = 1:500 and CuBr/bbpy.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Ligand</th>
<th>( ^1H_{\text{polymer integral}} )</th>
<th>Conv. %</th>
<th>( M_n(\text{theo.}) ) g/mol</th>
<th>( M_n ) g/mol</th>
<th>( M_w ) g/mol</th>
<th>PDI</th>
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</tbody>
</table>

Table 5. Results of molecular weight determination by means of SEC-MALLS and MALDI-TOF-MS for octa-, dodeca- and hexadecaarm PS-stars derived from octa-, dodeca- and hexadecafunctional initiators 97 to 102 with [I]:[M] = 1:500 and CuBr/bbpy.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Ligand</th>
<th>( M_n ) g/mol</th>
<th>( M_w ) g/mol</th>
<th>PDI</th>
<th>( M_n ) g/mol</th>
<th>( M_w ) g/mol</th>
<th>PDI</th>
</tr>
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<tbody>
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<td>SEC-MALLS</td>
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<tr>
<td>35</td>
<td>97-Br(_8)</td>
<td>(^t)bbpy</td>
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<td>26200</td>
<td>28100</td>
<td>1.07</td>
</tr>
<tr>
<td>37</td>
<td>98-Br(_8)</td>
<td>(^t)bbpy</td>
<td>36100</td>
<td>36600</td>
<td>1.01</td>
<td>33700</td>
<td>35700</td>
<td>1.06</td>
</tr>
<tr>
<td>43</td>
<td>99-Br(_{12})</td>
<td>(^t)bbpy</td>
<td>54600</td>
<td>138800</td>
<td>2.54</td>
<td>30500</td>
<td>32800</td>
<td>1.08</td>
</tr>
<tr>
<td>47</td>
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<td>(^t)bbpy</td>
<td>50600</td>
<td>51100</td>
<td>1.01</td>
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<td>55900</td>
<td>1.10</td>
</tr>
<tr>
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<td>101-Br(_{12})</td>
<td>(^t)bbpy</td>
<td>50700</td>
<td>197700</td>
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<td>20000</td>
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</tr>
<tr>
<td>50</td>
<td>102-Br(_{16})</td>
<td>(^t)bbpy</td>
<td>182400</td>
<td>731500</td>
<td>4.01</td>
<td>54900</td>
<td>58200</td>
<td>1.06</td>
</tr>
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</table>
Nevertheless, even when coupled stars are present in the product and control over propagation was lost, MALDI-TOF-MS of the polymers obtained, indicate that the single-star polymers are of rather low compositional heterogeneity as indicated by PDI values between PDI = 1.06-1.10.

![MALDI-TOF-MS spectra of octaarm-PS-star polymer derived from initiator 97 (entry 35).](image)

**Figure 67.** MALDI-TOF-MS spectra of octaarm-PS-star polymer derived from initiator 97 (entry 35).

**Bulk ATRP of styrene using [I]:[M] = 1:500 and CuBr/bpy as atom transfer agent**

In order to overcome the loss of molecular weight control, the usually used catalytic system CuBr/bpy was utilized in polymerization reactions with all six initiators 97 to 102 based on resorcin- and pyrogallololarenes. Better control and reproducibility over molecular weight and molecular weight distribution was achieved with this atom transfer agent, even when the system is somewhat heterogeneous due to the less solubility of the Cu(bpy)$_2$Br complex in pure styrene. At room temperature large amounts of the catalytic species are present as precipitate in the reaction vessel, whereas as soon as the vessel is heated to 120 °C the precipitate dissolves and the reaction mixture becomes homogeneous.
The CuBr/bpy system revealed a much higher propagation rate than the CuBr/tbbpy system. An explanation of this observation is difficult, due to the fact that more experiments need to be undertaken with different bipyridine ligands to compare the reactivity of the formed complexes towards ATRP of styrene (29) with the different resorcin- and pyrogallolarene based initiators 97 to 102. As explained in the literature, ligands bearing electron withdrawing substituents should have a decreased efficiency in ATRP, than unsubstituted ones, or ligands bearing electron-donating substituents.95 The observations made, indicate a behavior vise versa to the statements in literature. Also steric effects can not explain the decreased efficiency of the di-tert-butyl substituted ligand. If one considers a square-pyramidal or trigonal-bipyramidal structure of the oxidized catalytic Cu(II)-species, then the tert-butyl substituents should point away from the corners of the square-pyramid or the trigonal-bipyramid resulting in no steric interaction or strain of the substituents and due to that no steric shielding of the copper-center and no distortion of the complex-structure.147

Good agreement for the analytical results for both, SEC-MALLS and MALDI-TOF-MS were found for octa- and dodecaarm star polymers (Table 7), whereas a higher deviation for the results obtained by normal SEC-RI measurements (Table 6 and Figure 68) compared with SEC-MALLS was observed for all star-polymers based on octa-, dodeca-, and hexadecafunctional initiators 97 to 102.

Figure 68. SEC-RI plots of octa- dodeca- and hexadeca-PS-star polymers derived from 97, 99 and 102, applying a 1:500 ratio of [I]:[M] and CuBr/bpy as atom transfer agent.
Results and discussion

Table 6. Results of molecular weight determination by means of NMR, SEC-RI for octa-, dodeca- and hexadecaarm PS-stars derived from octa-, dodeca- and hexadecafunctional initiators 97 to 102 with [I]:[M] = 1:500 and CuBr/bpy.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Ligand</th>
<th>(^1H_{polymer}) integral</th>
<th>Conv. %</th>
<th>(M_n) (theo.) g/mol</th>
<th>(M_n) g/mol</th>
<th>(M_w) g/mol</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>97-Br(_8)</td>
<td>bpy</td>
<td>0.96</td>
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<td>103000</td>
<td>69000</td>
<td>74200</td>
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</tr>
<tr>
<td>55</td>
<td>98-Br(_8)</td>
<td>bpy</td>
<td>1.16</td>
<td>28</td>
<td>118000</td>
<td>72400</td>
<td>78500</td>
<td>1.09</td>
</tr>
<tr>
<td>60</td>
<td>99-Br(_{12})</td>
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<tr>
<td>64</td>
<td>100-Br(_{12})</td>
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<td>1.09</td>
</tr>
<tr>
<td>65</td>
<td>101-Br(_{12})</td>
<td>bpy</td>
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<td>18</td>
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<td>63700</td>
<td>70000</td>
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</tr>
<tr>
<td>67</td>
<td>102-Br(_{16})</td>
<td>bpy</td>
<td>0.59</td>
<td>16</td>
<td>140000</td>
<td>66900</td>
<td>71900</td>
<td>1.07</td>
</tr>
</tbody>
</table>

This deviation can be traced back to the volume of such star-polymers, which is, according to scaling theories, models and experiments, much smaller than the volume of linear polymers of the same molecular weight.\(^1\) The deviation will become more significantly the higher the molecular weight of the individual arms and the higher the functionality \(f\) of the core is. SEC-RI therefore gave nearly the same molecular weights for the different octa-, dodeca-, and hexadecaarm star-polymers as shown in Table 6, because the only property which influences the retention time of the polymer in size exclusion chromatography is their size and shape and the only value which is detectable is the concentration by refractive index measurements. In a good solvent for polystyrene, like CHCl\(_3\) or THF, the individual arms can be considered as still coiled, but the size of the coils is maximized. The hydrodynamic volume and shape of

Table 7. Results of molecular weight determination by means of SEC-MALLS and MALDI-TOF-MS for octa-, dodeca- and hexadecaarm PS-stars derived from octa-, dodeca- and hexadecafunctional initiators 97 to 102 with [I]:[M] = 1:500 and CuBr/bpy.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Ligand</th>
<th>(M_n) g/mol</th>
<th>(M_w) g/mol</th>
<th>PDI</th>
<th>(M_n) g/mol</th>
<th>(M_w) g/mol</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
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<td>53</td>
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<td>bpy</td>
<td>97200</td>
<td>101200</td>
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<td>bpy</td>
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<td>1.05</td>
</tr>
<tr>
<td>65</td>
<td>101-Br(_{12})</td>
<td>bpy</td>
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<td>107800</td>
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</tr>
<tr>
<td>67</td>
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<td>281700</td>
<td>1.57</td>
<td>122400</td>
<td>129200</td>
<td>1.07</td>
</tr>
</tbody>
</table>
such star-polymers therefore depends rather on the length of the individual arms than of the number of arms attached to the core (for cores with low functionality $f = 8-16$), resulting in comparable volumes for octa-, dodeca-, and hexadecaarm star polymers, even when the segment density increases with increasing functionality $f$ (Figure 69). Therefore only by the MALLS-technique, which is based upon the interference of scattered light caused by multiple scattering centers in the macromolecule and correlation of this scattered light with the size, shape and radius of gyration of the macromolecules, it is possible to obtain the real values for the molecular weight.

![Figure 69. Schematic drawing of the hydrodynamic volumes of octa- and dodecaarm-star polymers.](image)

The presence of coupled star polymers as indicated by SEC-MALLS for the pyrogallolarene based star polymers derived from 100, 101 and 102 can be explained by the higher presumption of dodeca- and hexadecaarm star polymers to undergo star-star coupling, even when the concentration of the individual polymer-“particles” is less than that for the octaarm star polymers in the reaction medium.
6.2.4. Cleavage of the polystyrene arms from the resorcin- and pyrogallolarene cores by alkaline saponification

The cleavage of the ester linkages of the individual arms attached to the resorcin- and pyrogallolarene cores of the synthesized star polymers under alkaline conditions afforded the free polymeric arms (Figure 70), which were further investigated by means of SEC-RI, which this time gave reliable results for the molecular weight due to the calibration with linear PS standards. From in this way obtained molecular weights of the arms (\(M_n(\text{arm})\)), the functionality of the star-polymers (\(f_{\text{star}}\)) was calculated in order to determine whether all tert-\(\alpha\)-bromoesters of the initiators 97 to 102 participated in the initiation of a polymer chain, or if some of the initiating sites stayed unchanged (Table 8). Significant results can only be obtained by this calculation, when nearly no star-star coupled byproducts are present and when the compositional heterogeneity of the single-star polymers is rather low (PDI \(\leq 1.1\)). Otherwise the error of such a calculation will become too large to obtain reliable results. Table 8 shows the results obtained from equation \(f_{\text{star}} = (M_n(\text{star})M_{\text{init}})/M_n(\text{arm})\) (with \(M_{\text{init}}\) = the molecular weight of the initiator) for the functionality of the star-polymers, whereas the calculation has been done for both, the molecular weight obtained by SEC-MALLS and MALDI-TOF-MS.

**Figure 70.** Cleavage of the PS-arms by alkaline saponification of the ester-linkages giving resorcinarene core 59 and individual arms of the star polymers shown for a octaarm star polymer derived from 97 as example.
Table 8. Results of molecular weight determination of the individual arms by means of SEC-RI after arm-cleavage of octa-, dodeca- and hexadecaarm PS stars by alkaline saponification of the ester-linkages.

<table>
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<tr>
<th>Entry</th>
<th>M_n(star) g/mol</th>
<th>M_n(star) g/mol</th>
<th>M_n(arm) g/mol</th>
<th>M_w(arm) g/mol</th>
<th>PDI</th>
<th>f_core</th>
<th>SEC-RI</th>
<th>MALDI-TOF-MS</th>
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<th>MALDI</th>
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<td>23.3 15.9</td>
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</tr>
</tbody>
</table>

Due to the fact, that SEC-MALLS measurements give an overview over the whole content of star-species (single-, double-, triple-stars) in the sample, an overestimation of the functionality
$f_{\text{star}}$ can be observed for samples consisting of such coupled byproducts. Due to that, it seems to be better to calculate the functionality of the core from results obtained by MALDI-TOF-MS for the single stars and SEC-RI for the individual arms, because if the concentration of coupled stars is rather low compared to the content of single-star polymers, the longer arms, which are a result of intermolecular coupling, are most probably not detected by SEC-RI, due to the low content in the mixture after cleavage.

In contrast to the results obtained by Tenhu$^{162,163}$ and co-workers, it was found, that all tert-$\alpha$-bromoesters attached to resorcin- and pyrogallololarenes 97 to 102 participate in the initiation of a polymer chain as shown in Table 8. Even for the dodeca- and hexadecaarm star polymers derived from dodeca- and hexadecafunctional initiators 99 to 102 the functionality of the star polymers are close to the theoretical values of $f_{\text{star}} = 12$ for dodecafunctional and $f_{\text{star}} = 16$ for hexadecafunctional derivatives. Especially for polymerization reactions carried out with the CuBr/bpy system good agreement for theoretical and experimental functionality was found.
7. Dendrimers based on resorcin- and pyrogallolarene cores

7.1. Synthesis of benzyl end-capped AB$_2$-monomers and dendrons suitable for the convergent approach via Williamson etherification and “click”-reaction

According to the procedure published by Sharpless et al.$^{208}$ and Gutsche et al.$^{252}$ the synthesis of the AB$_2$-monomers was performed starting from commercially available 3,5-dihydroxybenzoic acid (103, DHB). Compound 103 was first transformed to the corresponding methyl ester 104 according to well known procedures (Figure 71).$^{256}$

![Figure 71. Synthesis and achieved yield for the esterification of DHB (103).](image1)

Subsequent $O$-alkylation via Williamson etherification with an excess of 3-bromoprop-1-yn (86) afforded the bis-propargyl derivative 105 in quantitative yield (Figure 72). On this stage the synthesis of polyaryl ether dendrons according to procedures by Fréchet and co-workers was also performed, but a functionalization with propargylbromide (86) followed by a (3+2) cycloaddition for the generation growth reaction offers the possibility to introduce a triazole spacer group which increases molecular flexibility and gives rise to less sterically hindered dendrons on higher generations. They should be more easily linked to resorcin- or pyrogallolarene cores 87 and 88 due to the high functionality ($f = 8, 12$) of these macrocyclic sys-
tems, than sterically more crowded polyaryl ether dendrons, where only a methylene bridge acts as spacer between the different generations and as linker between the core and the attached dendron.

Crystallization from MeOH provided crystals of 105, which were suitable for single crystal X-ray diffraction in order to determine the crystal structure of 105, which was unknown so far (Figure 73). Compound 105 crystallized in the space group Pca2₁ of the orthorhombic crystal system with unit cell dimensions of \(a = 21.402(2)\) Å, \(b = 3.914(1)\) Å, \(c = 14.476(1)\) Å, and \(\alpha = \beta = \gamma = 90^\circ\). The crystal lattice is held together by weak CH···O interactions with donor···acceptor distances between 3.2319(2) and 3.391(2) Å. No solvent molecules (MeOH) are incorporated into the crystal lattice of 105 and a calculation by PLATON revealed that there is no residual solvent accessible void.

Figure 73. Left: Crystal structure of 105; right: packing-diagram of 105, illustrating the weak intermolecular CH···O interactions.

Reduction of methyl 3,5-bis(prop-2-yn-1-yloxy)benzoate 105 with LiAlH₄ afforded the bis-propargyl functionalized benzyl alcohol 106 in moderate yield (Figure 74). Upon crystallization from a EtOH/n-pentane mixture, the up to now unknown crystal structure of [3,5-bis(prop-2-yn-1-yloxy)phenyl]methanol 106 could be determined.
Results and discussion

This compound 106 crystallized in the space group P2₁/n in the monoclinic crystal system with the unit cell dimensions of \(a = 15.559(2) \text{ Å}, b = 4.485(1) \text{ Å}, c = 17.104(3) \text{ Å}, \) and \(\beta = 104.54(1)^\circ\). Intermolecular hydrogen-bonding between terminal hydroxyl functions with donor···acceptor distances of 2.717(1) Å stabilizes the crystal lattice of 106 by formation of infinite hydrogen-bound chains parallel to the b axis of the unit cell (Figure 75).

The focal benzylic alcohol functionality of 106 was then treated with SOCl₂ in the presence of pyridine as a base to yield the bis-propargyl functionalized benzylic chloride 107. 1-(chloromethyl)-3,5-bis(prop-2-yn-1-yloxy)benzene (107) can be considered as a AB₂-type monomer, whereas the chloromethyl functionality represents a reactive function for a generation growth by Williamson etherification or, the nonreactive focal point, which can be transformed into an azide functionality in the activation step, prior to the next generation step via (3+2) cycloaddition of azides to alkynes (Figure 76).

Figure 74. Synthesis and achieved yield in the reduction of 105 with LiAlH₄ to afford benzyl alcohol 106.

Figure 75. Left: Crystal structure of 106; right: illustration of the infinite hydrogen-bound chain formed by focal benzylic alcohol moieties of 106.
In order to prevent the propyne functions of the AB₂-monomer on the periphery from taking part in further reactions, compound 107 was end-capped with benzyl azide (109) via copper-mediated (3+2) cyclocondensation. Benzyl azide (109) was easily prepared by treatment of benzyl bromide (108) with a 0.5 mol NaN₃ solution in DMSO (Figure 77).²⁵³ In contrast to the published synthesis, a reaction temperature of 80 °C was used instead of room temperature to drive the conversion of the reaction to quantitative yield. At room temperature only incomplete conversion was observed.

![Figure 76](image_url)

**Figure 76.** Achieved yield in the treatment of 106 with thionyl chloride to afford benzyl chloride 107.

Two different methodologies were applied in the copper-mediated (3+2) cycloaddition between bis-propargyl derivative 107 and benzyl azide (109). A aqueous system consisting of CuSO₄/Na-ascorbate and THF/H₂O as solvent and a non-aqueous, microwave-assisted (3+2) cycloaddition at 140 °C nominal temperature with Cu(PPh₃)₃Br (110) as catalytical active species in a non-aqueous THF solution.²⁰⁸ Compound 110 was prepared according to published procedures.²⁵⁷ Both methodologies were found to be suitable for the (3+2) cycloaddition of 107 with benzyl azide (109). A 10 % excess of benzyl azide (109) was used in both cases to drive the reaction to completion (Figure 78).
Results and discussion

The aqueous system afforded the end-capped dendron 111 in 85 % yield, due to the instability of the benzylic chloride group under the conditions used. The only side-product observed under these conditions was the benzyl alcohol. Flash-chromatographic separation followed by precipitation afforded the pure G1-dendron 111 in multigramm scale.

In comparison, the microwave-assisted (MW) (3+2) cycloaddition of 107 with 109 afforded the pure G1-dendron 111 in quantitative yield after only 10 minutes of reaction time. The only drawback of this methodology are the small achievable amounts of product due to a limitation of the reactants to approx. 100 mg per reaction vessel.

Figure 78. Synthesis and achieved yield for the aqueous (a) and non-aqueous (b) copper-mediated (3+2) cycloaddition of 107 with benzyl azide (109)

The aqueous system afforded the end-capped dendron 111 in 85 % yield, due to the instability of the benzylic chloride group under the conditions used. The only side-product observed under these conditions was the benzyl alcohol. Flash-chromatographic separation followed by precipitation afforded the pure G1-dendron 111 in multigramm scale.

In comparison, the microwave-assisted (MW) (3+2) cycloaddition of 107 with 109 afforded the pure G1-dendron 111 in quantitative yield after only 10 minutes of reaction time. The only drawback of this methodology are the small achievable amounts of product due to a limitation of the reactants to approx. 100 mg per reaction vessel.

Figure 79. Achieved yield in the treatment of G1-dendron 111 with NaN₃ to afford azide functionalized G1-dendron 112.
Compound 111 represents a pseudo-G1-dendron suitable for a core-coupling reaction via Williamson etherification. Upon substitution of the benzyl chloride 111 with NaN₃, a similar G1-dendron 112 was prepared (Figure 79), suitable for the (3+2) cycloaddition with propargyl functionalized cores 87 and 88. The resulting 1,2,3-triazole in this case acts as a spacer group between the different generations and should offer a higher flexibility of the dendrimer resulting in a less sterical constrain when coupled with resorcin- and pyrogallolarene core molecules 87 and 88, bearing eight or twelve proximate propyne functions.

![Image](image_url)

**Figure 80.** Abortive synthesis of G2-dendron 113 via copper-mediated (3+2) cycloaddition of 112 and AB₂-monomer 107.

Repetition of the microwave-assisted (3+2) cycloaddition of stoichiometric amounts of 112 with the AB₂-monomer 107 afforded the crude G2-dendron 113 together with impurities of the mono-addition product. When performing flash-chromatographic purification an unusual heavy warming was observed during the elution process. The sole product which could be obtained revealed, according to MALDI-TOF-MS, a mass of m/z = 1955.863 (Bruker Biflex IV), e.g. m/z = 1960 (Kratos Compact II) instead of m/z = 1248 for 113 (Figure 80). No proposition can be made about the product obtained. Calculation of the molar masses of possible side-products or inclusion compounds with the catalyst 110 did not lead to the measured...
mass. Even in the original publication no analytical data is given for the G2-dendron 113, whereas in the publication the synthesis is mentioned and described as prosperous done.  

Repetition of the reaction under aqueous conditions using CuSO₄/Na-ascorbate afforded the G2-dendron with a benzylic alcohol function at the focal point as the sole product after 72 h of reaction time. Subsequent bromination by Mukaiyama redox-condensation with CBr₄ and PPh₃ did not lead to the G2-bromide. Instead absolutely no conversion could be detected by following the course of the reaction with MALDI-TOF-MS.

In order to overcome the difficulties in the synthesis of a G2-dendron, the G1-dendron 111 was subjected to a generation growth step using ordinary 5-(hydroxymethyl)benzene-1,3-diol (114) in a Williamson etherification (Figure 81). The G2-dendron 115 with a benzylic hydroxy function was obtained in 63 % yield after 24 h of reaction time and several purification steps by flash-chromatography.

![Figure 81. Synthesis of G2-dendron 115 via Williamson etherification of 114 with G1-dendron 111.](image)

Surprisingly also in this case a further activation to the benzyl bromide functionalized G2-dendron 116 could not be successfully achieved under standard Mukaiyama redox-condensation conditions (Figure 82). The attempts to synthesize a G2-dendron were stopped at this stage due to the difficulties which arose from the halogenation reaction.
Figure 82. Abortive synthesis of bromide 116 via Mukaiyama redox-condensation of G2-dendron 115.
7.2. Synthesis of styrene end-capped AB$_2$-monomers and dendrons suitable for the convergent approach via Williamson etherification

Another G1-Frédchet-type dendron (polyaryl ether-type) was prepared by subsequent O-alkylation of 104 with 1-(chloromethyl)-4-vinylbenzene (117) via Williamson etherification to afford the bis-(4-vinylbenzyl) derivative 118 in 61 % yield after one week of reaction time. In order to prevent polymerization during the long period, care has been taken when degassing the mixture and the reaction was carried out at room temperature. Also a spattle of BHT (Ionol) was added (Figure 83).

![Chemical structure of 104, 117, and 118](image)

Figure 83. Synthesis and achieved yield in the Williamson etherification of DHB (104) with 4-vinylbenzyl chloride (117) to afford methyl 3,5-bis[(4-vinylbenzyl)oxy]benzoate (118).

Reduction of methyl 3,5-bis[(4-vinylbenzyl)oxy]benzoate (118) with LiAlH$_4$ afforded the bis-(4-vinylbenzyl) functionalized benzyl alcohol 119. Careful cooling of the reaction mixture during the addition of LiAlH$_4$ and during quenching with EtOAc and H$_2$O prevented the material from unwanted side reactions and 119 could be obtained in 75 % yield (Figure 84).

![Chemical structure of 118 and 119](image)

Figure 84. Synthesis and achieved yield in the reduction of 118 with LiAlH$_4$ to afford benzyl alcohol 119.
Bromination of compound \textbf{119} with CBr\textsubscript{4} and PPh\textsubscript{3} for 4 h afforded the benzyl bromide \textbf{120} in only 13 \% yield. \textbf{120} can be considered as a pseudo-G1-dendron bearing two styrene functions (\textbf{Figure 85}).

It was expected that, upon coupling with a resorcin- or pyrogallolarene core 4 and subsequent radical generation using Mn(OAc)\textsubscript{3} followed by trapping with nitroxyl radicals under conditions recently investigated in our group,\textsuperscript{254} a dendritic alkoxyamine-initiator could be obtained, which can be used in nitroxide-mediated radical polymerization (NMP).

\textbf{Figure 85.} Synthesis and achieved yield of bromide \textbf{120} via Mukaiyama redox-condensation of G2-dendron \textbf{119}.
7.3. Core-coupling of convergent grown dendrons with resorcin- and pyrogallolarene cores via “click”-reaction

In order to prove the efficiency of the copper-mediated (3+2) cycloaddition of azides 56 with alkynes 57, a trial reaction was carried out with octapropargyl-functionalized resorcinarene 87 and an excess of benzyl azide (109) (Figure 86). The aqueous system consisting of CuSO₄/Na-ascorbate in THF/H₂O was used to estimate the efficiency of the reaction. 24 h of reaction time at room temperature afforded the octa-4-methylene(1-benzyl-1H-1,2,3-triazole)resorcinarene 121 in nearly quantitative yield. No column chromatography was needed in the work-up process, because the excess benzyl azide (109) could be easily removed under high vacuum by Kugel-Rohr distillation.

Extensive washing with brine and H₂O afforded the pure product, which was subjected to several crystallization experiments. Only bad crystals could be obtained from solutions of 121 in toluene, THF, chloroform and MeOH. Finally a solution of compound 121 in acetonitrile afforded crystals suitable for single crystal X-ray diffraction. 121 crystallized as boat-
The results and discussion section of a scientific paper describes the structure of a compound, 

\[
\text{a = 17.697(1) Å, b = 18.688(1) Å, c = 20.975(1) Å and } \alpha = 81.45(1)^\circ, \beta = 86.85(1)^\circ, \gamma = 61.95(1)^\circ.
\]

One disordered molecule MeOH was revealed from the electron density map. The solvent stems from the initial crystallization experiments with MeOH and is a vestige which remained incorporated in the material upon evaporating the MeOH solution of \(\text{121}\). The eight methylene-1-benzyl-1\(H\)-1,2,3-triazole moieties are oriented in a way to optimize interatomic contacts, by wrapping around the core. The resorcinarene core of \(\text{121}\) is more or less completely surrounded by these moieties, of which three are disordered into two positions. The resorcinarene moieties of \(\text{121}\) themselves are packed in a layered fashion, with interdigitating C\(_5\) chains to an extend of four carbon atoms per chain. Voids which result from this interdigitation are partially filled by the disordered 1-benzyl-1\(H\)-1,2,3-triazole moieties (Figure 87).

---

**Figure 87.** Top: Illustration of the boat-conformer adopted by \(\text{121}\) in solid state; bottom: packing-diagram of \(\text{121}\), representing the interdigitation of the alkyl-chains of \(\text{121}\).
Also the azide functionalized G1-dendron 112 was reacted with the octapropyneresorcinarene 87 under both conditions, the aqueous one and the non-aqueous one (Figure 88). Under aqueous conditions, complete addition of the G1-dendron 112 could be achieved within 24 h of reaction time using an 10 % excess of the dendron 112. Complications arose during the purification of the obtained reaction mixture. It seems that the unreacted G1-dendron 112 is somehow incorporated in the dendrimer 122, or that intermolecular interaction between the dendrimer 122 and the dendron 112 are stronger than the interaction of 112 with the silicagel, which was used for flash-chromatographical purification. TLC indicated well separated spots for both substances 112 and 122, but the same mixture as applied on top of the chromatography-column was sustained back after elution. Several eluent-mixtures were tried, but with none of them good separation could be achieved. Fivefold repetition of flash-chromatography using a 10:1 mixture of CHCl3/MeOH finally afforded around 60 % of nearly pure G1-dendrimer 122.

Much faster conversion was observed when subjecting stoichiometric amounts of 112 and 122 to microwave irradiation using Cu(PPh3)3Br (110) as catalyst. Within only 10 minutes the dendrimer 122 was formed in nearly quantitative yield. MALDI-TOF-MS indicated the presence of minor traces of incompletely reacted dendrimers. Again flash-chromatography was performed in order to yield the pure and fully functionalized dendrimer 122 (Figure 88). This time the pure material could be obtained in 98 % yield.

The latter procedure was also used in the synthesis of G1-dendrimer 123 based on the dodecapropynepyrogallolarene 88. Stoichiometric amounts of G1-dendron 112 and pyrogallolarene 88 were reacted under microwave irradiation (Figure 89). Incomplete conversion was indicated by MALDI-TOF-MS, so that a 10 % excess of the G1-dendron 112 was added and the mixture was again subjected to microwave irradiation. MALDI-TOF-MS analysis after another 10 minutes of reaction time showed that, despite of the formation of the fully functionalized dendrimer 123, incompletely dendrimers were still present, mainly the nona-, deca-, and undecafunctionalized pyrogallolarene dendrimers. It is speculated that the eight propyne functions similarly present in the resorcinarene 87 are first functionalized via (3+2) cycloaddition to yield the octafunctionalized dendrimer followed by the remaining four propyne groups of 88. Their close proximity to the two adjacentlly attached dendrons per pyrogallol unit and caused by that, the catchier accessibility of these reactive function by the azide functionalized G1-dendron 112 and the catalyst Cu(PPh3)3Br (110) exacerbates further attachment of dendrons to the core. Such dendrimers consisting of triazole building-blocks
might prove to be good ligands for copper or silver, yielding highly active catalysts, which can be removed during workup under appropriate conditions by simple precipitation.

Figure 88. Synthesis and achieved yields of resorcinarene-dendrimer 122 via „click“-reaction.
Results and discussion

Figure 89. Synthesis and achieved yields of pyrogallol-dendrimer 123 via „click“-reaction.
**Figure 90.** MALDI-TOF-MS spectrum of 123, showing the impurities of incompletely functionalized derivatives of 123.
7.4. Core-coupling of convergent grown dendrons with resorcin- and pyrogallolarenes via Williamson etherification

Neither the Williamson etherification of the G1-dendron 120 with the resorcinarene 59 and the pyrogallolarene 62, nor the Williamson etherification with simple 1-(chloromethyl)-4-vinylbenzene (117) afforded a completely substituted product, even after 2 weeks reaction time (Figure 91). This result can be traced back to complications which arise from the thermal instability of the 4-vinylbenzene functions of 117 and 120. The reactions were only carried out at room temperature to prevent autopolymerization of 117 and 120 which can take place at elevated temperatures. Even the addition of 18-crown-6 and NaI did not drive the reaction towards completion. In the case, when 1-(chloromethyl)-4-vinylbenzene (117) was used, a maximum substitution of only six out of eight phenolic hydroxyl groups was observed for the resorcinarene 59 and 62 as indicated by MALDI-TOF-MS. When the sterically more demanding G1-dendron 120 was used, only a maximally fourfold substitution of 59 and 62 was observed. None of the reaction mixtures were subjected to work up, due to the impossibility to separate such mixtures consisting of more or less partially substituted resorcinarenes by simple precipitation or crystallization. Column chromatography in both cases proved to be not efficient.

![Diagram](image)

**Figure 91.** Abortive convergent synthesis of G1-dendrimers based on resorcin- and pyrogallolarenes 59, 62 via Williamson etherification with 117, or 120.

\[
\begin{align*}
R = H & \quad 59 \\
R = OH & \quad 62
\end{align*}
\]

K₂CO₃, CH₃CN, NaI, 18-C-6, BHT, r.t., 2 weeks

only mixtures of incompletely substituted dendrimers
The same problem in reaction conversion was observed for the benzyltriazole functionalized G1-dendron 111 (Figure 92), even when in this case a reaction temperature of 90 °C was used only a sixfold substitution for 59 and sevenfold substitution of 62 was observed by MALDI-TOF-MS.

R = H 59
R = OH 62

\[ \text{only mixtures of incompletely substituted dendrimers} \]

**Figure 92.** Abortive convergent synthesis of G1-dendrimers based on resorcin- and pyrogallolarenes 59, 62 via Williamson etherification with 111.

Combination of these observations indicate, that a convergent access towards dendrimers via Williamson etherification of dendronized benzylhalides 111 and 120 with resorcin- or pyrogallolarenes 59 and 62 is not favorable. Mainly steric reasons and caused through this, protective shielding of the phenolic hydroxyl groups are preventing a complete functionalization of the resorcinarene cores and in particular the functionalization of pyrogallolarenes. There is a need for a long spacer group between the core and the dendritic shell due to the high functionality of the core (\( f = 8 \) for 59 and \( f = 12 \) for 62). The fact that no literature is available for convergent polyaryl ether dendrimers based on resorcin- and pyrogallolarenes via functionalization of the phenolic hydroxyl groups through Williamson etherification fortify this hypothesis. The only way to synthesize polyaryl ether dendrimers based on resorcin- and pyrogallolarenes seems to be the divergent route as shown by the groups of Asai and Ueda.\(^{220,221,222,223,224}\)
Practical Part

8. Materials and analytical techniques

Materials and solvents:
All materials were purchased either from Merck®, Acros®, FLUKA®, SIGMA-ALDRICH® or Riedel de Häen® and used without any further purification. Solvents and pyridine were purified and dried by standard procedures (THF over Na, CH₂Cl₂ over CaH₂, MeOH over Mg) and further dried using molecular sieve 4 Å.

Nomenclature:
IUPAC conform names for small molecules were generated using ACD-Labs 8.0 software. For resorcin- and pyrogallolarenes rules according to multiplicative IUPAC nomenclature were applied. Atom numbering for NMR correlation and SXD are different from IUPAC nomenclature and also numbering for NMR and SXD in comparison differs.

Thin layer chromatography (TLC):
Analytical thin-layer chromatography was performed on commercial Merck® plates coated with silica gel 60 F₂₅₄ (0.25 mm thick) or on pre-coated plastic sheets from MACHERY-NAGEL® with either 0.20 mm silica gel (POLYGRAM® SIL G/UV₂₅₄) or 0.20 mm aluminum oxide (POLYGRAM® ALOX N/UV₂₅₄). For detection either UV light with a wavelength of \( \lambda = 254 \) nm or one of the following colorizing agents were used by dipping the plate into the colorizing agent followed by heating with a hot air pistol:

- colorizing agent based on anisaldehyde:  
  23.00 ml anisaldehyde  
  8.75 ml glacial acetic acid  
  31.30 ml conc. H₂SO₄  
  845.00 ml ethanol

- colorizing agent based on KMnO₄:  
  3.00 g KMnO₄  
  20.00 g K₂CO₃  
  5.00 ml 5%-KOH  
  300.00 ml H₂O
Practical part

- colorizing agent based on Ce(IV):  
  10.00 g Ce(SO₄)₂  
  25.00 g H₃Mo₁₂O₄₀P  
  80.00 ml conc. H₂SO₄  
  1000.00 ml H₂O

Flash-chromatography:
Preparative flash-chromatography was performed using Merck© silica gel 60 (0.040-0.063 mm) and glass columns with diameters of 10-100 mm. Used eluents can be found in the syn- 
thetical procedures whereas in general a gradient from unpolar to polar mixtures of solvents 
was utilized. The elution process was accelerated by applying pressures of 1.5 bar to the 
equipment.

Nuclear magnetic resonance (NMR) techniques:
Nuclear magnetic resonance (NMR) spectroscopy was performed either on a Bruker© AC-300 
(300.1 MHz) equipped with a variable temperature controller, or a Bruker© DRX 500 (500.1 
MHz), using deuterated acetone-₆₆, chloroform-₁ (CHCl₃), dimethyl sufoxide-₆₆ (DMSO) or 
₁,₁,₂,₂-tetrachloroethane-₂ (TCI) as solvent and the internal solvent peak as reference. Struc-
tural information was taken from 2-dimensional ¹H/¹H-COSY, ¹H/¹³C-HSQC, ¹H/¹³C-HMBC, 
ROESY and NOESY (DRX 500) experiments and temperature dependent NMR measure-
ments (AC-300). Signal multiplicity was abbreviated as follows: s (singlet), d (duplet), t (trip-
let), q (quartet), m (multiplet), br. (broad signal).

Matrix-assisted-LASER-desorption-ionization MS (MALDI-TOF-MS):
Mass spectra were obtained either on a Fujitsu/Siemens© Kratos MALDI Kompakt II or a 
Bruker© Biflex IV using 1,₈,₉-trihydroxyanthracene (Dithranol) or 4-nitroanilin (4-NA) as 
matrix. For polymeric materials silver bistri fluoride (Ag(OTf)₂) was added to favor ionization by 
cation attachment.

Electron spray ionization MS (ESI-MS) and liquid-chromatography-MS (LC-MS):
Mass spectra were obtained on a Bruker© Esquire MS with an ion trap detector in combina-
tion with an Agilent/HP 1100 HPLC-device.
**Gas-chromatography MS (GC-MS):**
Mass spectroscopy in combination with gas chromatography was performed on a AGILENT Technologies© 6890N Network gas chromatography system equipped with a AGILENT Technologies© 5973 mass selective detector. A DB 35ms column (l = 30 m, d = 0.25 mm, 0.25 μm thick film of (35%-phenyl)-methylpolysiloxane) was used for separation and a flow of 1.0 ml/min inert He gas was applied.

**Elemental analysis (EA):**
The determination of C, H and N contents was performed either on Elemental Analyzers Model EA 1108 (CARLO ERBA INSTRUMENTS©) or Model EURO EA 3000 (HEKATECH©).

**Single crystal X-ray diffraction (SXD):**
Diffraction experiments were performed on a Kappa-CCD diffractometer (Bruker AXS©) with four-circle geometry using fine focused sealed tubes with Mo- (λ = 0.71073 Å) or Cu-irradiation (λ = 1.54184 Å). A Cryo 700 cooling system from Oxford Cryosystems© was used for measurements at -75 °C by applying a stream of cold N₂ to the goniometer head in order to prevent decomposition of the crystal by loss of solvent during the experiment. The following software was used for structure solution and refinement:

**Size exclusion chromatography with refractive index detector (SEC-RI):**
Size exclusion chromatography in combination with a refractive index detector was performed with chloroform/0.1 vol.% Et₃N as eluent and 1.0 ml/min flow rate delivered by a Jasco© 880 pump. For separation Styragel-columns (d = 60 mm, l = 300 mm, 1x 10⁴ + 1x 10⁵ + 1x 10⁶ Å) were used. Calibration was done with linear PS standards or PMMA standards in some cases. A Waters© RI-detector Model 2410 was used for detection.
Size exclusion chromatography with multi angle LASER light scattering detector (SEC-MALLS):

The molar masses and the dispersities of obtained products were also determined by GPC using Polymer Standard Service (PSS) columns SDV 1x10^5 + 1x10^3 + 2x10^2 Å with a differential refractive index detector Dn-1000 RI (WGE Dr. Bures) and a multiangle light scattering detector DAWN EOS of Wyatt Technologies© (LASER-wavelength: 690 nm). Measurements were performed in THF as solvent at 35 ºC with a nominal flow rate of 1 ml/min. Results were evaluated using the ASTRA software from Wyatt Technologies© and WINGPC software from PSS.

Microwave irradiation (MW):

Reaction under microwave irradiation were performed in sealed 10.0 ml vessels in a CEM© Discover reactor. THF was used as solvent and a power of 250 W was applied to reach a nominal temperature of 140 ºC.
Practical part

9. Synthesis of resorcin- and pyrogallolarenes


250.00 mmol of resorcinol (2) (e. g. pyrogallol (5)) were weighted into a 1000 ml three necked round bottom flask connected with a 250 ml dropping funnel. 500 ml of ethanol were added and the mixture was cooled to 0 °C. Under further cooling with ice and vigorous stirring, first 250.0 mmol of the aldehyde 6, 7, 8 or 64 and then 500.0 mmol concentrated HCl were added drop wise to the mixture over a period of 1 h. The ice bath was removed and the flask was flushed with argon for 10 min to prevent oxidation. After connecting an argon-balloon, the mixture was heated to 70 °C under stirring for 2-14 days. In the course of the reaction large amounts of precipitate formed. After cooling to 0 °C the precipitate was filtered and washed several times with cold ethanol and recrystallized several times from ethanol.
9.1.1. Synthesis of 2,8,14,20-tetrapentylpentacyclo[19.3.1.1.3.7.1.15.19]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,6,10,12,16,18,22,24-octol (59)

27.53 g (250.00 mmol) resorcinol (2), 25.04 g (250.00 mmol) hexanal (7) and 49.31 ml (500.00 mmol) conc. HCl were reacted as described in the general procedure GP I. The course of the reaction was followed by MALDI-TOF-MS and after 3 days the mixture was cooled to room temperature. The precipitate was filtered, washed with 250 ml ethanol and suspended in another 500 ml of ethanol. The suspension was refluxed for 10 minutes, cooled to 0°C with an ice bath, filtered and washed with 100 ml ethanol. The procedure was repeated until only colorless filtrate was observed. 40.02 g (83.3 % yield, m.p.: > 365 °C) pure 59 as its rccc-isomer were obtained as a slightly yellow powder.

\[\text{rccc-isomer in cone conformation}\]

$\delta$ (ppm) = 7.13 (s, 4 H, H5), 6.19 (s, 4 H, H3), 4.14 (t, $\Delta(J,H,H)=7.8$ Hz, 4 H, H1), 2.12 (dt, $\Delta(J,H,H)=7.7$, 7.8 Hz, 8 H, H6), 1.36-1.15 (m, 24 H, H7-H9), 0.84 (t, $\Delta(J,H,H)=7.2$ Hz, 12 H, H10).

\[\text{rccc-isomer in cone conformation}\]

$\delta$ (ppm) = 151.29 (s, C4i), 123.66 (s, C2i), 123.14 (s, C5), 102.76 (s, C3), 32.88 (s, C6), 32.81 (s, C1), 31.39 (s, C8), 27.37 (s, C7), 22.24 (s, C9), 13.78 (s, C10).

MALDI-TOF-MS (4-NA): calcd. for C_{48}H_{64}O_{8}: $m/z = 768.460$ [M]+; found: $m/z = 792$ [M+Na]+, 809 [M+K]+.

EA: calcd. for C_{48}H_{64}O_{8}: C 74.97 %, H 8.39 %; found: C 75.04 %, H 8.41 %.
9.1.2. Synthesis of 2,8,14,20-tetraundecylnpentacyclo[19.3.1.3.7.1.15.19]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,6,10,12,16,18,22,24-octol (60)

27.53 g (250.00 mmol) resorcinol (2), 46.08 g (250.00 mmol) dodecanal (8) and 49.31 ml (500.00 mmol) conc. HCl were reacted as described in the general procedure GP I. The course of the reaction was followed by MALDI-TOF-MS and after 4 days the mixture was cooled to room temperature. The precipitate was filtered, washed with 250 ml ethanol and suspended in another 500 ml of ethanol. The suspension was refluxed for 10 minutes, cooled to 0 °C with an ice bath, filtered and washed with 100 ml ethanol. The procedure was repeated until only colorless filtrate was observed. 54.24 g (78.5 % yield, m.p.: 297-299 °C) pure 60 as its rccc-isomer were obtained as a slightly yellow powder.

\( ^1 \text{H NMR} \) (500.1 MHz, CDCl\(_3\) + DMSO, r.t.): \textit{rccc-isomer in cone conformation:}

\[ \delta \text{ (ppm)} = 6.95 \text{ (s, 4 H, H5)}, 6.13 \text{ (s, 4 H, H3)}, 4.07 \text{ (t, } J(H,H)=7.8 \text{ Hz, 4 H, H1)}, 2.00 \text{ (dt, } J(H,H)=7.6, 7.5 \text{ Hz, 8 H, H6)}, 1.22 \text{ (s, 8 H, H15)}, 1.14 \text{ (m, 64 H, H7-14)}, 0.73 \text{ (t, } J(H,H)=7.0 \text{ Hz, 12 H, H16}).

\( ^{13} \text{C NMR} \) (125.7 MHz, CDCl\(_3\) + DMSO, r.t.): \textit{rccc-isomer in cone conformation:}

\[ \delta \text{ (ppm)} = 151.38 \text{ (s, C4i)}, 123.92 \text{ (s, C2i)}, 122.87 \text{ (s, C5)}, 103.16 \text{ (s, C3)}, 33.15 \text{ (s, C6)}, 33.01 \text{ (s, C1)}, 31.58 \text{ (s, C14)}, 29.47-29.04 \text{ (6s, C8-C13)}, 27.82 \text{ (s, C7)}, 22.34 \text{ (s, C15)}, 13.81 \text{ (s, C16)}.\]

\textbf{MALDI-TOF-MS (4-NA):} calcd. for C\(_{72}\)H\(_{112}\)O\(_8\): \( m/z = 1104.836 [M]^+ \); found: \( m/z = 1129 [M+Na]^+, 1145 [M+K]^+ \).

\textbf{EA:} calcd. for C\(_{72}\)H\(_{112}\)O\(_8\): C 78.21 %, H 10.21 %; found: 78.18 C %, H 10.15 %.

\textbf{SXD:}

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C(<em>{81})H(</em>{137})Cl(<em>3)O(</em>{12})S(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moiety formula</td>
<td>C(<em>{72})H(</em>{112})O(_8) . 4(C(_2)H(_6)OS) . CHCl(_3)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1537.50</td>
</tr>
</tbody>
</table>
Temperature 198(2) K
Wavelength 0.71073 Å
Crystal system Triclinic
Space group P1\textbar\ (No. 2)
Unit cell dimensions 
\begin{align*}
a &= 11.797(2) \text{ Å} & \alpha &= 80.80(3)^\circ. \\
b &= 13.358(2) \text{ Å} & \beta &= 87.77(3)^\circ. \\
c &= 27.976(6) \text{ Å} & \gamma &= 84.96(3)^\circ.
\end{align*}
Volume 4333.7(14) Å³
Z 2
Density (calculated) 1.178 Mg/m³
Absorption coefficient 0.257 mm⁻¹
F(000) 1668
Crystal size 0.41 x 0.38 x 0.23 mm³
Theta range for data collection 3.07 to 25.40°.
Index ranges -14<=h<=14, -16<=k<=15, -33<=l<=33
Reflections collected 82184
Independent reflections 15864 [R(int) = 0.0326]
Completeness to theta = 25.40° 99.4 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.9433 and 0.9019
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 11578 / 30 / 947
Goodness-of-fit on F² 1.033
Final R indices [I>2σ(I)] R₁ = 0.0614, wR₂ = 0.1489
R indices (all data) R₁ = 0.0890, wR₂ = 0.1638
Largest diff. peak and hole 1.370 and -0.791 eÅ⁻³
Practical part

Table 9. Hydrogen-bonds for 60 [Å and °].

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(4)-H(4A)...O(24)</td>
<td>0.84</td>
<td>2.00</td>
<td>2.812(3)</td>
<td>161.4</td>
</tr>
<tr>
<td>O(10)-H(10A)...O(6)</td>
<td>0.84</td>
<td>1.95</td>
<td>2.776(3)</td>
<td>168.7</td>
</tr>
<tr>
<td>O(12)-H(12A)...O(16)</td>
<td>0.84</td>
<td>1.94</td>
<td>2.779(3)</td>
<td>172.5</td>
</tr>
<tr>
<td>O(22)-H(22A)...O(18)</td>
<td>0.84</td>
<td>1.92</td>
<td>2.756(3)</td>
<td>173.2</td>
</tr>
<tr>
<td>O(6)-H(6A)...O(30X)#1</td>
<td>0.84</td>
<td>1.76</td>
<td>2.584(4)</td>
<td>165.3</td>
</tr>
<tr>
<td>O(24)-H(24A)...O(40X)#1</td>
<td>0.84</td>
<td>1.85</td>
<td>2.687(16)</td>
<td>172.7</td>
</tr>
<tr>
<td>O(16)-H(16A)...O(50)#2</td>
<td>0.84</td>
<td>1.78</td>
<td>2.621(3)</td>
<td>177.9</td>
</tr>
<tr>
<td>O(18)-H(18A)...O(60X)#2</td>
<td>0.84</td>
<td>1.76</td>
<td>2.599(3)</td>
<td>176.2</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+2,-z+1  #2 -x+1,-y+1,-z+1

Figure 94. ORTEP-plot of the asymmetric unit of 60 with 50 % probability level. Hydrogen atoms omitted for clarity.
Figure 95. Packing diagram of 60 showing the intra- and intermolecular hydrogen-bonds. View along a-axis of unit cell (b: red, c: green).

Figure 96. Packing diagram of 60 in CPK style.
9.1.3. Synthesis of 2,8,14,20-tetrakis(4-hydroxyphenyl)pentacyclo[19.3.1.1^3,7.1^9,13.1^15,19]-octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,6,10,12,16,18,-22,24-octol (65)

27.53 g (250.00 mmol) resorcinol (2), 30.53 g (250.00 mmol) 4-hydroxybenzaldehyde (64) and 49.31 ml (500.00 mmol) conc. HCl were reacted as described in the general procedure GP I. The course of the reaction was followed by MALDI-TOF-MS and after 10 days the mixture was cooled to room temperature. The precipitate was filtered, washed with 250 ml ethanol and suspended in another 500 ml of ethanol. The suspension was refluxed for 10 minutes, cooled to room temperature, filtered and washed with 100 ml ethanol. The procedure was repeated until only colorless filtrate was observed. 46.88 g (87.5 % yield, m.p.: > 365 °C) pure 65 as a mixture of its rccc- and rctt-isomers were obtained as a slightly violet powder.

$^1$H NMR (500.1 MHz, DMSO, r.t.): *rctt*-isomer in chair conformation: $\delta$ (ppm) = 8.67 (s, 4 H, OH), 8.40 (s, 4 H, OH), 8.36 (s, 4 H, OH), 6.44 (d, $^3J(H,H)$=8.5 Hz, 8 H, H7), 8.34 (d, $^3J(H,H)$=8.5 Hz, 8 H, H8), 6.32 (s, 2 H, H3*), 6.30 (s, 2 H, H5*), 6.11 (s, 2 H, H5), 5.94 (s, 2 H, H3), 5.44 (s, 4 H, H1).

*rccc*-isomer in cone conformation: $\delta$ (ppm) = 8.83 (s, 4 H, OH), 8.43 (s, 8 H, OH), 6.63 (d, $^3J(H,H)$=8.5 Hz, 8 H, H7), 6.50 (s, 4 H, H3/3*), 6.47 (d, $^3J(H,H)$=8.5 Hz, 8 H, H8), 6.08 (s, 4 H, H5/5*), 5.52 (s, 4 H, H1).

$^{13}$C NMR (125.7 MHz, DMSO, r.t.): *rctt*-isomer in chair conformation: $\delta$ (ppm) = 154.27 (s, C9i), 152.58 (s, C4i), 152.25 (s, C4i*), 134.44 (s, C6i), 131.54 (s, C3*), 129.80 (s, C7), 128.48 (s, C3), 121.87 (s, C2i), 120.80 (s, C2i*), 114.00 (s, C8), 101.73 (s, C5*), 101.56 (s, C5), 41.20 (s, C1).

*rccc*-isomer in cone conformation: $\delta$ (ppm) = 154.43 (s, C9i), 152.31 (s, C4i/4i*), 135.96 (s, C6i), 130.50 (br. s, C3/3*), 129.55 (s, C7), 120.97 (s, C2i/2i*), 113.82 (s, C8), 102.04 (s, C5/5*), 40.52 (s, C1).

MALDI-TOF-MS (4-NA): calcd. for C_{52}H_{40}O_{12}: $m/z$ = 856.252 [M$^+$];
found: $m/z$ = 869 [M+Na$^+$], 897 [M+K$^+$].
EA: calcd. for C$_{52}$H$_{40}$O$_{12}$: C 72.89 %, H 4.71 %; found: C 72.95 %, H 4.78 %.

SXD:

Empirical formula  
Moiety formula  
Formula weight  
Temperature  
Wavelength  
Crystal system  
Space group  
Unit cell dimensions  
Volume  
Z  
Density (calculated)  
Absorption coefficient  
F(000)  
Crystal size  
Theta range for data collection  
Index ranges  
Reflections collected  
Independent reflections  
Completeness to theta = 26.40°  
Absorption correction  
Max. and min. transmission  
Refinement method  
Data / restraints / parameters  
Goodness-of-fit on F$^2$  
Final R indices [I>2σ(I)]  
R indices (all data)  
Largest diff. peak and hole
Table 10. Hydrogen-bonds for 65 [Å and °].

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(6)-H(6A)...O(90X)</td>
<td>0.84</td>
<td>1.74</td>
<td>2.58(3)</td>
<td>173.8</td>
</tr>
<tr>
<td>O(6)-H(6A)...S(90X)</td>
<td>0.84</td>
<td>2.62</td>
<td>3.339(4)</td>
<td>144.5</td>
</tr>
<tr>
<td>O(8)-H(8A)...O(40)</td>
<td>0.84</td>
<td>1.93</td>
<td>2.774(5)</td>
<td>178.4</td>
</tr>
<tr>
<td>O(8)-H(8A)...S(40)</td>
<td>0.84</td>
<td>2.95</td>
<td>3.721(3)</td>
<td>153.5</td>
</tr>
<tr>
<td>O(2)-H(2A)...O(60)#2</td>
<td>0.84</td>
<td>1.82</td>
<td>2.653(4)</td>
<td>169.8</td>
</tr>
<tr>
<td>O(2)-H(2A)...S(60)#2</td>
<td>0.84</td>
<td>2.85</td>
<td>3.609(3)</td>
<td>150.3</td>
</tr>
<tr>
<td>O(12)-H(12B)...O(50)#2</td>
<td>0.84</td>
<td>1.82</td>
<td>2.658(4)</td>
<td>178.7</td>
</tr>
<tr>
<td>O(17)-H(17A)...O(70Y)#1</td>
<td>0.84</td>
<td>1.64</td>
<td>2.409(15)</td>
<td>151.7</td>
</tr>
<tr>
<td>O(17)-H(17A)...S(70Y)#1</td>
<td>0.84</td>
<td>2.83</td>
<td>3.651(9)</td>
<td>164.5</td>
</tr>
<tr>
<td>O(23)-H(23A)...O(95X)#3</td>
<td>0.84</td>
<td>1.97</td>
<td>2.80(6)</td>
<td>169.6</td>
</tr>
<tr>
<td>O(23)-H(23A)...S(95X)#3</td>
<td>0.84</td>
<td>2.95</td>
<td>3.648(6)</td>
<td>142.4</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1
#2 -x+1,-y+1,-z+1
#3 x-1,y,z+1

Figure 97. ORTEP-plot of the asymmetric unit of 65 with 50 % probability level. Hydrogen atoms omitted for clarity.
Figure 98. Packing diagram of 65 showing the intermolecular hydrogen bonds. View along b-axis of unit cell (a: gray, c: green).

Figure 99. Packing diagram of 65 in CPK style.

100.00 g (504.50 mmol) 2,2’-[1,3-phenylenebis(oxy)]diethanol (67), 61.61 g (504.50 mmol) 4-hydroxybenzaldehyde (64) and 98.62 ml (1009.00 mmol) conc. HCl were reacted as described in the general procedure GP I. The course of the reaction was followed by MALDI-TOF-MS and after 2 days the mixture was cooled to room temperature.

The precipitate was filtered, washed with 250 ml ethanol and suspended in another 500 ml of ethanol. The suspension was refluxed for 10 minutes, cooled to 0 °C, filtered and washed with 100 ml ethanol. The procedure was repeated until only colorless filtrate was observed. 72.80 g (47.7 % yield, m.p.: > 300 °C decomp.) pure 68 as a mixture of its rcce- and rctt-isomers were obtained as a slightly violet powder.

1H NMR (500.1 MHz, DMSO, r.t.): rctt-isomer in chair conformation: δ (ppm) = 8.81 (br. s, 4 H, OH9a), 6.61 (s, 2 H, H5*), 6.46 (d, J(H,H)=8.8 Hz, 10 H, H5 and H7), 6.38 (d, J(H,H)=8.5 Hz, 8 H, H8), 6.14 (s, 2 H, H3), 6.05 (s, 2 H, H3*), 5.55 (s, 4 H, H1), 5.00-4.11 (br. s, 8 H, OH11 and OH11*), 4.00 (m, 4 H, H10a*), 3.89 (m, 4 H, H10a), 3.76 (m, 4 H, H10b), 3.55 (m, 12 H, H10b* and H11), 3.29 (m, 8 H, H11*).

rcce-isomer: too low concentration for NMR correlation.

13C NMR (125.7 MHz, DMSO, r.t.): rctt-isomer in chair conformation: δ (ppm) = 155.03 (s, C4i*), 154.91 (s, C9i), 154.33 (s, C4i), 132.61 (s, C6i), 130.54 (s, C3*), 130.03 (s, C7), 127.33 (s, C2i), 126.46 (s, C3), 124.22 (s, C2i*), 114.21 (s, C8), 99.82 (s, C5), 98.54 (s, C5*), 70.79 (s, C10), 70.02 (s, C10*), 59.90 (s, C11), 59.72 (s, C11*), 41.95 (s, C1).

rcce-isomer: too low concentration for NMR correlation.


EA: calcd. for C_{68}H_{72}O_{20}: C 67.54 %, H 6.00 %; found: C 67.64 %, H 6.02 %.
9.1.5. Synthesis of 2,8,14,20-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,5,6,10,11,12,16,17,18,-22,23,24-dodecol (61)

31.53 g (250.00 mmol) pyrogallol (5), 11.01 g (250.00 mmol) acetaldehyde (6) and 49.31 ml (500.00 mmol) conc. HCl were reacted as described in the general procedure GP I. The course of the reaction was followed by MALDI-TOF-MS and after 2 days the mixture was cooled to room temperature. The precipitate was filtered, washed with 250 ml ethanol and suspended in another 500 ml of ethanol. The suspension was refluxed for 10 minutes, cooled to 0 °C with an ice bath, filtered and washed with 100 ml ethanol. The procedure was repeated until only colorless filtrate was observed. 21.14 g (53.1 % yield, m.p.: > 160 °C decomp.) pure 61 as its rccc-isomer were obtained as a white powder.

$^1$H NMR (500.1 MHz, DMSO, r.t.): rccc-isomer in cone conformation: $\delta$ (ppm) = 8.21 (br. s, 8 H, OH), 7.98 (br. s, 4 H, OH), 6.72 (s, 4 H, H3), 4.47 (q, $^3J(H,H)$=6.9 Hz, 4 H, H1), 1.50 (d, $^3J(H,H)$=7.2 Hz, 12 H, H6).

$^{13}$C NMR (125.7 MHz, DMSO, r.t.): rccc-isomer in cone conformation: $\delta$ (ppm) = 140.21 (s, C4i), 132.50 (s, C5i), 124.90 (s, C2i), 114.37 (s, C3), 28.88 (s, C1), 21.02 (s, C6).

MALDI-TOF-MS (4-NA): calcd. for C$_{32}$H$_{32}$O$_{12}$: $m/z = 608.189$ [M]$^+$;

EA: calcd. for C$_{32}$H$_{32}$O$_{12}$: C 63.15 %, H 5.30 %; found: 63.27 C %, H 5.38 %.

31.53 g (250.00 mmol) pyrogallol (5), 25.04 g (250.00 mmol) n-hexanal (7) and 49.31 ml (500.00 mmol) conc. HCl were reacted as described in the general procedure GP I. The course of the reaction was followed by MALDI-TOF-MS and after 2 days the mixture was cooled to room temperature. The precipitate was filtered, washed with 250 ml ethanol and suspended in another 500 ml of ethanol. The suspension was refluxed for 10 minutes, cooled to 0 °C with an ice bath, filtered and washed with 100 ml ethanol. The procedure was repeated until only colorless filtrate was observed. 44.05 g (84.6 % yield, m.p.: 315 °C decomp.) pure 62 as its rccc-isomer were obtained as a white powder.

$^1$H NMR (500.1 MHz, CDCl$_3$ + DMSO, r.t.): rccc-isomer in cone conformation:
\[\delta \text{ (ppm) = 8.62 (br. s, 8 H, OH), 8.00 (br. s, 4 H, OH), 6.75 (s, 4 H, H3), 4.18 (t, }^3J(H,H)=7.8 \text{ Hz, 4 H, H1), 2.11 (dt, }^3J(H,H)=7.7, 7.5 \text{ Hz, 8 H, H6), 1.35-1.17 (m, 24 H, H7-9), 0.85 (t, }^3J(H,H)=7.2, 12 \text{ H, H10).} \]

$^{13}$C NMR (125.7 MHz, CDCl$_3$ + DMSO, r.t.): rccc-isomer in cone conformation:
\[\delta \text{ (ppm) = 139.49 (s, C4i), 132.74 (s, C5i), 124.41 (s, C2i), 112.75 (s, C3), 33.74 (s, C6), 32.89 (s, C1), 31.50 (s, C8), 27.58 (s, C7), 22.35 (s, C9), 13.95 (s, C10).} \]

MALDI-TOF-MS (4-NA): calcd. for C$_{48}$H$_{64}$O$_{12}$: m/z = 832.440 [M]$^+$

EA: calcd. for C$_{48}$H$_{64}$O$_{12}$: C 69.21 %, H 7.74 %; found: C 69.23 %, H 7.69 %.
9.1.7. Synthesis of 2,8,14,20-tetraundecylpentacyclo[19.3.1.1\(^3\)7.1\(^{13}\)15.19]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,5,6,10,11,12,16,17,18,-22,23,24-dodecol (63)

31.53 g (250.00 mmol) pyrogallol (5), 46.08 g (250.00 mmol) \(n\)-dodecanal (8) and 49.31 ml (500.00 mmol) conc. HCl were reacted as described in the general procedure GP I. The course of the reaction was followed by MALDI-TOF-MS and after 5 days the mixture was cooled to room temperature. The precipitate was filtered, washed with 250 ml ethanol and suspended in another 500 ml of ethanol. The suspension was refluxed for 10 minutes, cooled to 0 °C with an ice bath, filtered and washed with 100 ml ethanol. The procedure was repeated until only colorless filtrate was observed. 66.83 g (91.4 % yield, m.p.: 285-288 decomp.) pure 63 as its \(rrcc\)-isomer were obtained as a white powder.

\(^1\)H NMR (500.1 MHz, CDCl\(_3\), r.t.): \(rrcc\)-isomer in cone conformation as hexameric capsule around a CHCl\(_3\) cluster: \(\delta\) (ppm) = 8.77 (s, 4 H, OH5a), 7.46 (s, 4 H, OH4a*), 6.87 (s, 4 H, OH4a), 6.82 (s, 4 H, H3), 4.36 (t, \(^3J(H,H)\)=7.4 Hz, 4 H, H1), 2.30-2.10 (br. m, 8 H, H6), 1.41 (br. s, 8 H, H8), 1.37-1.19 (br. m, 64 H, H7 and H9-15), 0.87 (t, \(^3J(H,H)\)=6.8 Hz, 12 H, H16).

\(^{13}\)C NMR (125.7 MHz, CDCl\(_3\), r.t.): \(rrcc\)-isomer in cone conformation as hexameric capsule around a CHCl\(_3\) cluster: \(\delta\) (ppm) = 138.47 (s, C4i*), 137.32 (s, C4i), 131.35 (s, C5i), 125.37 (s, C2i), 124.05 (s, C2i*), 113.76 (s, C3), 34.07 (s, C1), 33.14 (s, C6), 31.96 (s, C14), 29.91 (s, C8), 29.81-29.43 (m, C9-13), 28.26 (s, C7), 22.71 (s, C15), 14.12 (s, C16).

MALDI-TOF-MS (4-NA): calcd. for C\(_{72}\)H\(_{112}\)O\(_{12}\): \(m/z\) = 1168.815 [M]\(^+\);
found: \(m/z\) = 1192 [M+Na]\(^+\), 1210 [M+K]\(^+\).

EA: calcd. for C\(_{72}\)H\(_{112}\)O\(_{12}\): C 73.93 %, H 9.65 %; found: C 74.01 %, H 9.58 %.
SXD:

Empirical formula \( \text{C}_8\text{H}_4\text{O}_1\text{Cl}_3\text{S}_5 \)

Moiety formula \( \text{C}_7\text{H}_{12}\text{O}_{12} \cdot \text{CHCl}_3 \cdot \text{C}_2\text{H}_6\text{O} \cdot 5(\text{C}_2\text{H}_6\text{OS}) \)

Formula weight 1725.69

Temperature 223(2) K

Wavelength 1.54184 Å

Crystal system Triclinic

Space group \( \text{P1bar (No. 2)} \)

Unit cell dimensions

\[
\begin{align*}
\alpha &= 95.07(1)° . \\
\beta &= 92.68(1)° . \\
\gamma &= 102.23(1)° .
\end{align*}
\]

Volume \( 4691.8(6) \text{ Å}^3 \)

\( Z \)

2

Density (calculated) 1.222 Mg/m³

Absorption coefficient 2.420 mm⁻¹

\( F(000) \)

1868

Crystal size \( 0.55 \times 0.10 \times 0.05 \text{ mm}^3 \)

Theta range for data collection 3.11 to 63.20°.

Index ranges \( 0 \leq h \leq 14, -15 \leq k \leq 14, -33 \leq l \leq 31 \)

Reflections collected 12379

Independent reflections 12379 \( [R(\text{int}) = 0.0000] \)

Completeness to theta = 63.20° 81.1 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.8886 and 0.3495

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 12379 / 28 / 1059

Goodness-of-fit on \( F^2 \) 1.296

Final R indices \( [I>2\sigma(I)] \) \( R1 = 0.1183, wR2 = 0.3199 \)

R indices (all data) \( R1 = 0.1599, wR2 = 0.3545 \)

Largest diff. peak and hole 0.795 and -0.596 e.Å⁻³
Table 11. Hydrogen-bonds for 63 [Å and °].

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(4)-H(4A)...O(24)</td>
<td>0.83</td>
<td>1.96</td>
<td>2.769(6)</td>
<td>163.1</td>
</tr>
<tr>
<td>O(5)-H(5A)...O(4)</td>
<td>0.83</td>
<td>2.29</td>
<td>2.723(5)</td>
<td>112.6</td>
</tr>
<tr>
<td>O(6)-H(6A)...O(5)</td>
<td>0.83</td>
<td>2.26</td>
<td>2.700(5)</td>
<td>113.7</td>
</tr>
<tr>
<td>O(10)-H(10A)...O(6)</td>
<td>0.83</td>
<td>1.92</td>
<td>2.745(6)</td>
<td>172.2</td>
</tr>
<tr>
<td>O(11)-H(11A)...O(50)</td>
<td>0.83</td>
<td>2.31</td>
<td>3.137(6)</td>
<td>178.8</td>
</tr>
<tr>
<td>O(11)-H(11A)...S(50)</td>
<td>0.83</td>
<td>2.41</td>
<td>3.106(5)</td>
<td>141.5</td>
</tr>
<tr>
<td>O(11)-H(11A)...O(12)</td>
<td>0.83</td>
<td>2.35</td>
<td>2.760(6)</td>
<td>111.0</td>
</tr>
<tr>
<td>O(12)-H(12A)...O(50)</td>
<td>0.83</td>
<td>1.90</td>
<td>2.677(5)</td>
<td>156.5</td>
</tr>
<tr>
<td>O(12)-H(12A)...S(50)</td>
<td>0.83</td>
<td>3.02</td>
<td>3.840(4)</td>
<td>171.9</td>
</tr>
<tr>
<td>O(16)-H(16A)...O(12)</td>
<td>0.83</td>
<td>1.99</td>
<td>2.798(6)</td>
<td>164.5</td>
</tr>
<tr>
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Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1  #2 x+1,y,z  #3 x,y+1,z  #4 -x+1,-y+1,-z+1
Figure 100. ORTEP-plot of the asymmetric unit of 63 with 50 % probability level. Hydrogen atoms omitted for clarity.

Figure 101. Packing diagram of 63 showing the intermolecular hydrogen bonds. View along a-axis of unit cell (b: red, c: green).
9.1.8. Synthesis of 2,8,14,20-tetrakis(4-hydroxyphenyl)pentacyclo[19.3.1.13,7.19,13.115,19]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,5,6,10,11,12,16,17,18,22,23,24-dodecol (66)

31.53 g (250.00 mmol) pyrogallol (5), 30.53 g (250.00 mmol) 4-hydroxybenzaldehyde (64) and 49.31 ml (500.00 mmol) conc. HCl were reacted as described in the general procedure GP I. The course of the reaction was followed by MALDI-TOF-MS and after 14 days the mixture was cooled to room temperature. The precipitate was filtered, washed with 250 ml ethanol and suspended in another 500 ml of ethanol. The suspension was refluxed for 10 minutes, cooled to room temperature, filtered and washed with 100 ml ethanol. The procedure was repeated until only colorless filtrate was observed. 49.62 g (86.2 % yield, m.p.: > 365 decomp.) pure 66 as a 1:4 mixture of its rccc- and rctt-isomers were obtained as a violet powder.

$^1$H NMR (500.1 MHz, DMSO, r.t.): rctt-isomer in chair conformation: δ (ppm) = 8.68 (s, 4 H, OH), 7.69 (s, 4 H, OH), 7.50 (s, 4 H, OH), 7.33 (s, 4 H, OH), 6.41 (d, $^3$J(H,H)=8.5 Hz, 8 H, H7), 6.32 (d, $^3$J(H,H)=8.5 Hz, 8 H, H8), 5.34 (s, 2 H, H3), 5.57 (s, 4 H, H1), 5.54 (s, 2 H, H3*).

rcce-isomer in cone conformation: δ (ppm) = 8.83 (s, 4 H, OH), 7.78 (s, 4 H, OH), 7.71 (s 4 H, OH), 7.51 (s, 4 H, OH), 6.67 (d, $^3$J(H,H)=8.5 Hz, 8 H, H7), 7.46 (d, $^3$J(H,H)=8.5 Hz, 8 H, H8), 6.22 (s, 4 H, H3), 5.66 (s, 4 H, H1).

$^{13}$C NMR (125.7 MHz, DMSO, r.t.): rctt-isomer in chair conformation: δ (ppm) = 154.40 (s, C9i), 142.20 (s, C4i*), 142.02 (s, C4i), 134.29 (s, C6i), 131.54 (s, C5i*), 131.41 (s, C5i), 129.82 (s, C7), 122.75 (s, C3*), 122.22 (s, C2i), 121.66 (s, C2i*), 119.28 (s, C3), 113.90 (s, C8), 41.73 (s, C1).

rcce-isomer in cone conformation: δ (ppm) = 154.57 (s, C9i), 141.80 (s, C4i), 135.69 (s, C6i), 131.67 (s, C5i), 129.68 (s, C7), 121.88 (s, C2i), 121.21 (s, C3), 114.04 (s, C8), 41.18 (s, C1).

MALDI-TOF-MS (4-NA): calcd. for C$_{52}$H$_{40}$O$_{16}$: m/z = 920.232 [M]$^+$; found: m/z = 954 [M+Na]$^+$, 961 [M+K]$^+$.

EA: calcd. for C$_{52}$H$_{40}$O$_{16}$: C 67.82 %, H 4.38 %; found: C 67.95 %, H 4.46 %.
10. Chemical modification of resorcin- and pyrogallolarenes

10.1. Modification of resorcin- and pyrogallolarenes by $O$-alkylation with methyl bromoacetate

10.1.1. General procedure for the $O$-alkylation of resorcin- and pyrogallolarenes with methyl bromoacetate – GP II

![Diagram of chemical reaction]

**Resorcinarenes**

70: $R_3 = H, R_4 = C_6H_{11}$  
71: $R_3 = H, R_4 = C_{11}H_{23}$  
72: $R_3 = H, R_4 = p-C_6H_4OCH_2COOMe$

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</tr>
<tr>
<td>72</td>
<td>92 %</td>
<td>$rccc + rctt$</td>
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</table>

**Pyrogallolarenes**

73: $R_3 = OCH_2COOMe, R_4 = C_6H_3$

74: $R_3 = OCH_2COOMe, R_4 = C_5H_{11}$

75: $R_3 = OCH_2COOMe, R_4 = C_{11}H_{23}$

76: $R_3 = OCH_2COOMe, R_4 = p-C_6H_4OCH_2COOMe$

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<td>74</td>
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<td>$rccc$</td>
</tr>
<tr>
<td>76</td>
<td>96 %</td>
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*Figure 102. Synthesis and obtained yields of methyl acetate functionalized C-alkyl- and C-arylresorcin- and -pyrogallolarenes.*

15.00 g of resorcin- or 10.00 g pyrogallolarene were weighted into a flame dried 500 ml three necked round bottom flask in an argon counter stream. 2 equivalents of prior dried anhydrous $K_2CO_3$ were added, followed by 300 ml of dry acetonitrile. Under stirring 2 equivalents of methyl bromoacetate (69) per phenolic hydroxyl group were added by syringe. The mixture was further flushed with argon for 10 minutes and afterwards heated to 90 °C for approx. 1 day. The course of the reaction was controlled by MALDI-TOF-MS. The reactions were stopped when only peaks of the fully substituted cores could be observed. The mixture was
then filtrated and the residual solid suspended in chloroform, refluxed for 10 minutes and again screened from the inorganic solids. The procedure was repeated two times more. The combined organic phases were evaporated to dryness and the residue dissolved in chloroform. The solution was washed with brine several times and dried over MgSO₄. After evaporation of the solvent, educts and side products were removed under high vacuum by Kugel-Rohr distillation. The resulting solid has been transferred to a 250 ml round bottom flask and dissolved in the appropriate amount of hot MeOH to yield a saturated solution. The desired octa-, dodeca- and hexadecamethyl acetates of the resorcin- and pyrogallolarenes 70 to 76 respectively were then recrystallized or precipitated several times from MeOH at -30 °C.

10.1.1.1. Synthesis of octamethyl 2,2’,2”,2”’,2””,2”’”,2”’’”,2”’’’”,2”’’’’’’’-[2,8,14,20-tetrapentylpentacyclo[19.3.1.13.7.19.13.15.19]octacosa-1(25),3(28),4,6,9(27),10-12,15(26),16,18,21,23-dodecaene-4,6,10,12,16,18,22,24-octayl]octakis(oxy)]-octaacetate (70)

15.00 g (19.51 mmol) 59, 47.74 g (312.10 mmol) methyl bromoacetate (69) and 43.13 g (312.10 mmol) dry K₂CO₃ were reacted as described in the general procedure GP II. The crude octamethyl acetate was further purified by dissolution in hot MeOH and crystallization at -30 °C. 15.79 g (60.2 % yield, m.p.: 121-123 °C) pure 70 were obtained as its recc-isomer as a colorless solid.

¹H NMR (500.1 MHz, CDCl₃, r.t.): **recc-isomer in cone conformation**: δ (ppm) = 6.60 (s, 4 H, H5/5*), 6.19 (s, 4 H, H3/3*), 4.57 (t, ³J(H,H)=7.4 Hz, 4 H, H1), 4.35-4.21 (m, 16 H, H4a/4a*), 3.74 (m, 24 H, H4c/4c*), 1.83 (m, 8 H, H6), 1.37-1.20 (br. m, 24 H, H7-9), 0.83 (t, ³J(H,H)=6.9 Hz, 12 H, H10).

¹³C NMR (125.7 MHz, CDCl₃, r.t.): **recc-isomer in cone conformation**: δ (ppm) = 169.81 (s, C4b/4b*), 154.44 (s, C4i/4i*), 128.52 (s, C2i/2i*), 126.53 (s, C5/5*), 100.72 (s, C3/3*), 67.14 (s, C4a/4a*), 51.94 (s, C4c/4c*), 35.67 (s, C1), 34.47 (s, C6), 32.10 (s, C8), 27.68 (s, C7), 22.68 (s, C9), 14.16 (s, C10).

MALDI-TOF-MS (4-NA): calcd. for C₇₂H₉₆O₂₄: m/z = 1344.629 [M]+;
found: $m/z = 1368 \ [M+Na]^+$, 1383 $[M+K]^+$.

**EA:** calcd. for $C_{72}H_{96}O_{24}$: C 64.27 %, H 7.19 %; found: 64.34 C %, H 7.25 %.

**SXD:**

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<tr>
<td>R indices (all data)</td>
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Largest diff. peak and hole 0.827 and -0.474 eÅ⁻³

**Figure 103.** ORTEP-plot of the asymmetric unit of 70 with 50 % probability level. Hydrogen atoms omitted for clarity.

**Figure 104.** Packing diagram of 70. View along a-axis of unit cell (b: red, c: green).
10.1.1.2. Synthesis of octamethyl 2',2'',2''',2''''',2'''''',2''''''-[2,8,14,20-tetraundecylpentacyclo[19.3.1.13.7.19.13.115.19]octacosa-1(25),3(28),4,6,9(27),10,-12,15(26),16,18,21,23-dodecaene-4,6,10,12,16,18,22,24-octayl]octakis(oxy)]-octaacetate (71)

15.00 g (13.56 mmol) 60, 33.21 g (217.07 mmol) methyl bromoacetate (69) and 30.00 g (217.07 mmol) dry K₂CO₃ were reacted as described in the general procedure GP II. The crude octamethyl acetate was further purified by dissolution in hot MeOH and crystallization at -30 °C. 19.45 g (85.3 % yield, m.p.: 99-100 °C) pure 71 were obtained as its rcce-isomer as a colorless solid.

¹H NMR (500.1 MHz, CDCl₃, r.t.): rcce-isomer in cone conformation: δ (ppm) = 6.59 (s, 4 H, H5/5*), 6.19 (s, 4 H, H3/3*), 4.56 (t, 3J(H,H)=7.4 Hz, 4 H, H1), 4.35-4.17 (m, 16 H, H4a/4a*), 3.80-3.70 (m, 24 H, H4c/4c*), 1.82 (m, 8 H, H6), 1.28 (br. s, 16 H, H7 and H8), 1.27-1.22 (m, 8 H, H15), 1.20 (s, 48 H, H9-14), 0.84 (t, 3J(H,H)=7.0 Hz, 12 H, H16).

¹³C NMR (125.7 MHz, CDCl₃, r.t.): rcce-isomer in cone conformation: δ (ppm) = 169.79 (s, C4b/4b*), 154.43 (s, C4i/4i*), 128.48 (s, C2i/2i*), 126.53 (s, C5/5*), 100.73 (s, C3/3*), 67.11 (s, C4a/4a*), 51.90 (s, C4c/4c*), 35.69 (s, C1), 34.50 (s, C6), 31.92 (s, C10), 30.00 (s, C8), 29.87-29.38 (s, C9 and C11-C14), 28.07 (s, C7), 22.68 (s, C15), 14.10 (s, C16).


EA: calcd. for C₉₆H₁₄₄O₂₄: C 68.54 %, H 8.63 %; found: C 68.22 %, H 8.93 %.
10.1.1.3. **Synthesis of octamethyl 2,2',2''',2''''',2''''''',2''''''''-[2,8,14,20-tetrakis[4-(2-methoxy-2-oxoethoxy)phenyl]pentacyclo[19.3.1.1^3^7^1^9^1^3.1^1^5^1^9]-octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,6,10,12,16,18,22,24-octayl]octakis(oxy)octaacetate (72)**

15.00 g (17.51 mmol) methyl bromoacetate (69) and 58.07 g (420.14 mmol) dry K$_2$CO$_3$ were reacted as described in the general procedure GP II. The crude dodecamethyl acetate was further purified by dissolution in hot CHCl$_3$ and repeated precipitation from MeOH at -30 °C. 27.57 g (91.5 % yield, m.p.: 155-156 °C and 236-237 °C) pure 72 were obtained as a mixture of its $rccc$- and $rctt$-isomers as a yellow solid.

**$^1$H NMR (500.1 MHz, CDCl$_3$, r.t.):**  
*rccc*-isomer in fixed boat conformation:  
δ (ppm) = 6.70 (d, $^3$J(H,H)=8.5 Hz, 8 H, H7), 6.63 (d, $^3$J(H,H)=8.8 Hz, 8 H, H8), 6.33 (s, 2 H, H5), 6.18 (s, 2 H, H5*), 6.06 (s, 2 H, H3), 5.86 (s, 4 H, H1), 5.82 (s, 2 H, H3*), 4.62 (s, 8 H, H9), 4.38 (s, 2 H, H4a), 4.35 (s, 2 H, H4a), 4.30 (s, 2 H, H4a$_2$), 4.27 (s, 2 H, H4a$_2$), 4.20 (s, 2 H, H4a$_2$), 1.7 (s, 2 H, H4a$_2$), 1.7 (s, 2 H, H4a$_2$), 3.81 (s, 12 H, H9), 3.71 (s, 12 H, H4), 3.67 (s, 12 H, H4).

*rctt*-isomer in chair conformation:  
δ (ppm) = 6.56 (d, $^3$J(H,H)=8.5 Hz, 8 H, H7), 6.52 (d, $^3$J(H,H)=9.1 Hz, 8 H, H8), 6.29 (s, 2 H, H5), 6.27 (s, 2 H, H5*), 6.16 (s, 2 H, H3), 5.86 (s, 4 H, H1), 5.68 (s, 2 H, H3*), 4.56 (s, 8 H, H9), 4.45 (s, 2 H, H4a), 4.41 (s, 2 H, H4a), 4.39 (s, 4 H, H4a$_2$ and H4a$_2$), 4.36 (s, 4 H, H4a$_2$ and H4a$_2$), 4.30 (s, 2 H, H4a$_2$), 4.27 (s, 2 H, H4a$_2$), 3.79 (s, 12 H, H9), 3.72 (s, 12 H, H4), 3.67 (s, 12 H, H4).

**$^{13}$C NMR (125.7 MHz, CDCl$_3$, r.t.):**  
*rccc*-isomer in fixed boat conformation:  
δ (ppm) = 169.68 (s, C9b), 169.64 (s, C4b), 169.53 (s, C4b), 155.82 (s, C9), 154.80 (s, C4i), 154.65 (s, C4i), 135.93 (s, C6i), 132.68 (s, C3*), 129.92 (s, C7), 128.65 (s, C3), 127.36 (s, C2i and C2i*), 113.91 (s, C8), 101.42 (s, C5*), 101.00 (s, C5), 67.30 (s, C4a*), 67.13 (s, C4a), 65.34 (s, C9a), 52.08 (s, C9c), 51.91 (s, C4c), 51.88 (s, C4c*), 42.21 (s, C1).

*rctt*-isomer in chair conformation:  
δ (ppm) = 169.62 (s, C9b), 169.55 (s, C4b), 169.19 (s, C4b), 155.65 (s, C9i), 154.78 (s, C4i), 154.41 (s, C4i), 153.95 (s, C6i), 132.33 (s, C3*), 130.05 (s, C7), 128.88 (s, C3), 127.24 (s, C2i), 126.66 (s, C2i*), 113.70 (s, C8), 100.51 (s,
Practical part

C5), 99.01 (s, C5*), 67.02 (s, C4a), 66.67 (s, C4a*), 65.23 (s, C9a), 52.03 (s, C9c), 51.91 (s, C4c*), 51.88 (s, C4c), 41.99 (s, C1).

**MALDI-TOF-MS** (4-NA):  calcd. for C_{88}H_{88}O_{36}:  m/z = 1720.506 [M]^+;  found:  m/z = 1744 [M+Na]^+ , 1760 [M+K]^+.

**EA**:  calcd. for C_{88}H_{88}O_{36}:  C 61.39 %, H 5.15 %;  found:  C 61.38 %, H 5.34 %.

**SXD**:

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Goodness-of-fit on $F^2$ 1.061
Final R indices [I>2σ(I)] R1 = 0.0853, wR2 = 0.2369
R indices (all data) R1 = 0.1241, wR2 = 0.2612
Largest diff. peak and hole 0.786 and -0.525 e.Å$^{-3}$

Figure 105. ORTEP-plot of the asymmetric unit of 72 with 50 % probability level. Hydrogen atoms omitted for clarity.

Figure 106. Packing diagram of 72.
10.1.1.4. Synthesis of dodecamethyl \(\text{2,2',2''',2''''',2'''',2''''''',2'''''''',2''''''''',2'''''''''',2''''''''''',}[2,8,14,20\text{-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23\text{-dodecaene-4,5,6,-10,11,12,16,17,18,22,23,24-dodecayl:dodekakis(oxy)]dodecaacetate (73)\)

10.00 g (16.43 mmol) \(61\), 60.33 g (394.35 mmol) methyl bromoacetate (69) and 54.50 g (394.35 mmol) dry K\(_2\)CO\(_3\) were reacted as described in the general procedure GP II. The crude dodecamethyl acetate was further purified by dissolution in hot MeOH and crystallization at -30 °C. 18.47 g (76.31 % yield, m.p.: 182-183 °C) pure 73 were obtained as its \textit{rcce-}isomer as colorless solid.

\(^1\)H NMR (500.1 MHz, CDCl\(_3\), r.t.): \textit{rcce-}isomer in cone conformation: \(\delta\) (ppm) = 6.35 (br. s, 4 H, H3/3*), 4.77 (m, 4 H, H1), 4.62 (m, 8 H, H4a), 4.52 (br. s, 8 H, H5a/5a*), 4.17 (m, 8 H, H4a*), 3.72 (s, 12 H, H5c/5c*), 3.70 (s, 24 H, H4c/4c*), 1.46 (d, 12 H, H6).

\(^{13}\)C NMR (125.7 MHz, CDCl\(_3\), r.t.): \textit{rcce-}isomer in cone conformation: \(\delta\) (ppm) = 169.56 (s, C4b/4b*), 169.12 (s, C5b/5b*), 147.53 (s, C4i/4i*), 143.00 (s, C5i/5i*), 135.21 (s, C3/3i*), 120.82 (s, C2i/2i*), 69.94 (s, C5a/5a*), 69.59 (s, C4a/4a*), 51.75 (s, C5c/5c* and C4c/4c*), 32.02 (s, C1), 20.65 (s, C6).

MALDI-TOF-MS (4-NA): calcd. for C\(_{68}\)H\(_{80}\)O\(_{36}\): \(m/z = 1472.443\) [M]\(^+\);
found: \(m/z = 1497\) [M+Na]\(^+\), 1512 [M+K]\(^+\).

EA: calcd. for C\(_{68}\)H\(_{80}\)O\(_{36}\): C 55.43 %, H 5.47 %; found: C 55.44 %, H 5.50 %.

SXD:

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Figure 107. ORTEP-plot of the asymmetric unit of 73 with 50 % probability level. Hydrogen atoms omitted for clarity.

Figure 108. Packing diagram of 73.
10.1.1.5. Synthesis of dodecamethyl \(2,2',2'',2''',2'''',2''''',2''''''',2''''''''',2'''''''''',2''''''''''''\)_-[2,8,14,20-tetrapentylpentacyclo[19.3.1.13,7.19,13.-115,19]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,5,6,-10,11,12,16,17,18,22,23,24-dodecayl]dodekakis(oxy)]dodecaacetate (74)

10.00 g (12.00 mmol) 62, 44.07 g (288.11 mmol) methyl bromoacetate (69) and 39.82 g (288.11 mmol) dry K\(_2\)CO\(_3\) were reacted as described in the general procedure GP II. The crude dodecamethyl acetate was further purified by dissolution in hot MeOH and crystallization at -30 °C. 16.55 g (81.2 % yield, m.p.: 124-125 °C) pure 74 were obtained as its \(rrcc\)-isomer as a colorless solid.

\(\text{H NMR} \) (500.1 MHz, CDCl\(_3\), r.t.): \(rrcc\)-isomer in cone conformation: \(\delta \) (ppm) = 6.40 (m, 4 H, H3/3*), 4.63-4.56 (m, 4 H, H1), 4.56-4.52 (s, 8 H, H4a), 4.49 (m, 8 H, H5a/5a*), 4.25-4.10 (m, 8 H, H4a*), 3.71 (s, 12 H, H5c/5c*), 3.69 (s, 24 H, H4c/4c*), 1.79 (m, 8 H, H6), 1.27 (br. s, 24 H, H7-9), 0.82 (t, \(J(H,H)=6.8\) Hz, 12 H, H10).

\(\text{C NMR} \) (125.7 MHz, CDCl\(_3\), r.t.): \(rrcc\)-isomer in cone conformation: \(\delta \) (ppm) = 169.54 (s, C4b), 169.50 (s, C4b*), 169.09 (s, C5b), 169.06 (s, C5b*), 147.92-147.78 (m, C4i/4i*), 142.92 (s, C5i/5i*), 133.88-133.79 (m, C3i/3i*), 121.41-121.31 (m, C2i/2i*), 69.83 (s, C5a/5a*), 69.54 (s, C4a/4a*), 51.66 (s, C4c/4c* and 5c/5c*), 36.96 (s, C1), 35.03 (s, C6), 31.97 (s, C8), 27.70 (s, C7), 22.59 (s, C9), 14.10 (s, C10).

\(\text{MALDI-TOF-MS} \) (4-NA): calcd. for C\(_{84}\)H\(_{112}\)O\(_{36}\): \(m/z = 1696.693 \) [M]\(^+\);
found: \(m/z = 1719.002\) [M+Na]\(^+\), 1736.040 [M+K]\(^+\).

\(\text{EA} \): calcd. for C\(_{84}\)H\(_{112}\)O\(_{36}\): C 59.43 %, H 6.65 %; found: C 59.43 %, H 6.84 %.

\(\text{SXD}:\)

\begin{align*}
\text{Empirical formula} & \quad \text{C}_{84}\text{H}_{112}\text{O}_{36} \\
\text{Moiety formula} & \quad \text{C}_{84}\text{H}_{112}\text{O}_{36} \cdot 0.10(\text{CH}_3\text{OH}) \\
\text{Formula weight} & \quad 1697.74 \\
\text{Temperature} & \quad 198(2)\ \text{K}
\end{align*}
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Figure 109. ORTEP-plot of the asymmetric unit of 74 with 50 % probability level. Hydrogen atoms omitted for clarity.

Figure 110. Packing diagram of 74. View along a-axis of unit cell (b: red, c: green).
10.1.1.6. Synthesis of dodecamethyl \(2,2',2'',2'''',2''''',2''''''',2''''''''',2'''''''''',2''''''''''',2''''''''''''',\[2,8,14,20\text{-}\text{tetraundecy}lpentacyclo[19.3.1.1\text{3,7}.,1\text{9,13}.,1\text{5,19}]\text{octacosa}\text{-}1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23\text{-}\text{dodecane}\text{-}4,5,6,10,11,12,16,17,18,22,23,24\text{-}\text{dodecay}l\text{dodekakis(oxy)}\text{dodecaacetate} (75)

10.00 g (12.00 mmol) 63, 44.07 g (288.11 mmol) methyl bromoacetate (69) and 39.82 g (288.11 mmol) dry K\(_2\)CO\(_3\) were reacted as described in the general procedure GP II. The crude dodecamethyl acetate was further purified by dissolution in hot MeOH and crystallization at -30 °C. 16.55 g (81.2 % yield, m.p.: 43-44 °C) pure 75 were obtained as its rc-cc-isomer as a colorless solid.

\(^1\)H NMR (500.1 MHz, CDCl\(_3\), r.t.): rc-cc-isomer in cone conformation: \(\delta\) (ppm) = 6.39 (m, 4 H, H3/3*), 4.70-4.52 (m, 12 H, H1 and H4a), 4.49 (s, 8 H, H5a/5a*), 4.15 (m, 8 H, H4a*), 3.71 (m, 36 H, H5c/5c* and H4c/4c*), 1.79 (m, 8 H, H6), 1.28, (br. s, 16 H, H7 and H8), 1.27-1.22 (m, 8 H, H15), 1.20 (br. s, 48 H, H9-14), 0.84 (t, \(J(H,H)=6.9\) Hz, 12 H, H16).

\(^{13}\)C NMR (125.7 MHz, CDCl\(_3\), r.t.): rc-cc-isomer in cone conformation: \(\delta\) (ppm) = 169.47 (s, C4b/4b*), 169.11 (s, C5b/5b*), 147.87 (s, C4i/4i*), 143.01 (s, C5i/5i*), 133.90 (s, C2i/2i*), 121.44 (s, C3/3*), 69.88 (s, C5a/5a*), 69.59 (s, C4a/4a*), 51.73 (s, C4c/4c* and C5c/5c*), 37.06 (s, C1), 35.16 (s, C6), 31.91 (s, C10), 29.99 (s, C8), 29.86-29.37 (m, C9 and C11-14), 28.17 (s, C7), 22.67 (s, C15), 14.09 (s, C16).

MALDI-TOF-MS (4-NA): calcd. for C\(_{108}\)H\(_{160}\)O\(_{36}\): \(m/z = 2033.069\) [M]\(^+\);
found: \(m/z = 2058.419\) [M+Na]\(^+\), 2073.327 [M+K]\(^+\).

EA: calcd. for C\(_{108}\)H\(_{160}\)O\(_{36}\): C 63.76 %, H 7.93 %; found: C 63.81 %, H 8.03 %.
10.1.1.7. **Synthesis of dodecamethyl 2,2',2'',2''',2'''',2''''',2''''''',2''''''''',2'''''''''''-
2'''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''''}

5.00 g (5.43 mmol) 66, 26.58 g (173.75 mmol) methyl bromoacetate (69) and 24.01 g (173.75 mmol) dry K₂CO₃ were reacted as described in the general procedure GP II. The crude hexadecamethyl acetate was further purified by dissolution in hot CHCl₃ and precipitation from MeOH at -30 °C. 10.78 g (95.7 % yield, m.p.: 170-171 °C) pure 76 were obtained as a mixture of its rccc- and rctt-isomers as a orange powder.

**1H NMR** (500.1 MHz, CDCl₃, r.t.): **rctt-isomer in chair conformation**: δ (ppm) = 6.58 (br. d, J(H,H) = 8.6 Hz, 16 H, H7/8), 6.03 (s, 4 H, H1), 5.82 (s, 2 H, H3), 5.42 (s, 2 H, H3*), 4.67 (s, 2 H, H4a*-1), 4.66 (s, 1 H, H5a*-1), 4.65 (s, 2 H, H4a*-1), 4.63 (s, 1 H, H5a*-1), 4.56 (s, 8 H, H9a), 4.48 (s, 4 H, H5a*-1 and H5a*-2), 4.46 (s, 3 H, H4a-1 and H5a-2), 4.43 (s, 3 H, H4a-1 and H5a-2), 4.22 (s, 2 H, H4a-2), 3.90 (s, 6 H, H5c*), 3.80 (s, 12 H, H9c), 3.70 (s, 12 H, H4c*), 3.67 (s, 6 H, H5c), 3.63 (s, 12 H, H4c). **rccc-isomer**: concentration too low for NMR correlation.

**13C NMR** (125.7 MHz, CDCl₃, r.t.): **rctt-isomer in chair conformation**: δ (ppm) = 169.52 (s, C4b), 169.42 (s, C9b), 169.31 (s, C4b*), 169.25 (s, C5b), 168.95 (s, C5b*), 156.06 (s, C9i*), 148.41 (s, C4i), 148.38 (s, C4i*), 143.62 (s, C5i), 142.27 (s, C5i*), 134.45 (s, C6i), 133.14 (s, C2i), 132.73 (s, C2i*), 129.83 (s, C7), 127.06 (s, C3*), 123.85 (s, C3), 114.09 (s, C8), 70.13 (s, C4b), 69.91 (s, C5b and C5b*), 69.78 (s, C4b*), 65.09 (s, C9b), 52.13 (s, C5c*), 52.01 (s, C9c), 51.83 (s, C4c*), 51.76 (s, C5c), 51.67 (s, C4c), 43.06 (s, C1). **rccc-isomer**: concentration too low for NMR correlation.


**EA**: calcd. for C₁₀₀H₁₀₄O₄₈: C 57.91 %, H 5.05 %; found: C 57.92 %, H 5.04 %. 

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Practical part
10.1.2. Reduction of methyl acetates of resorcinarenes with the active metal hydride Li-AlH₄


0.50 g (0.30 mmol) 71 were weighted into a flame dried 500 ml three necked round bottom flask, equipped with a condenser and two septa, in an argon counter stream. 300 ml dry THF were added by syringe and the solution was cooled to 0 °C and flushed with argon for 10 minutes. Subsequently 3.10 ml (3.10 mmol) of a 1 M LiAlH₄ solution in THF were added by syringe under further cooling with an ice bath. The mixture was allowed to warm to room temperature and was further stirred for 24 h followed by refluxing for 2 h. After cooling to room temperature 10 ml of ethyl acetate were added to quench the excess of LiAlH₄ followed by 10 ml of H₂O. After evaporation to dryness, the residual solid was suspended in CHCl₃ and transferred to a dropping funnel. The suspension was washed extensively with 0.5 molar HCl solution and the resulting clear organic phase neutralized with sat. NaHCO₃ solution. After drying over MgSO₄ and evaporation of the solvent, the crude product was precipitated from a mixture of CHCl₃/n-pentane. 0.30 g (69.5 % yield, m.p.: 199-201 °C) pure 77 were obtained as its rcce-isomer as a colorless solid.

**¹H NMR** (500.1 MHz, CDCl₃, r.t.): *rcce-isomer in cone conformation*: δ (ppm) = 6.70 (br. s, 4 H, ArH), 6.27 (br. s, 4 H, ArH), 4.51 (br. s, 4 H, CH), 4.40-3.30 (br. m, 32 H, CH₂), 2.99 (br. s, 8 H, OH), 1.82 (br. s, 8 H, CH₂), 1.30 (br. m, 16 H, CH₂), 1.22 (br. s, 56 H, CH₂), 0.85 (t, 3 J(H,H)=6.9Hz, 12 H, CH₃).

**¹³C NMR** (125.7 MHz, CDCl₃, r.t.): *rcce-isomer in cone conformation*: δ (ppm) = 154.32 (s, ArC=O), 126.04 (s, ArCH), 122.60 (s, ArC), 98.01 (s, ArCH), 70.31 (s, OCH₂), 61.34 (s, CH₂OH), 35.03 (s, CH), 31.91 (s, CH₂), 30.31-29.36 (m, CH₂), 28.06 (s, CH₂), 22.67 (s, CH₂), 14.10 (s, CH₃).

**MALDI-TOF-MS** (4-NA): calcd. for C₈₈H₁₄₄O₁₆: m/z = 1457.045 [M]⁺;

**EA:** calcd. for C$_{88}$H$_{144}$O$_{16}$: C 72.49 %, H 9.95 %; found: C 72.45 %, H 10.06 %.

### 10.1.3. Reductive dimethylation of methyl acetates of resorcinarenes with the Grignard-reagent MeMgBr

#### 10.1.3.1. Synthesis of 1,1’,1”’,1’’’,1””’,1’’’’,1”’’’’’’-[[2,8,14,20-tetraundecylpentacyclo[19.3.1.1$^3$.7.9,13.1$^{15,19}$]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16-,18,21,23-dodecaene-4,6,10,12,16,18,22,24-octayl]octakis(oxy)]octakis(2-methylpropan-2-ol) (78)

1.00 g (0.59 mmol) 71 were weighted into a flame dried 100 ml three necked round bottom flask, equipped with a condenser and two septa, in an argon counter stream. 50 ml dry THF were added by syringe and the solution was flushed with argon for 10 minutes. Subsequently 3.96 ml (11.89 mmol) of a 3 M MeMgBr solution in THF were added by syringe and the mixture was refluxed for 2 h. After cooling to room temperature, NH$_4$Cl solution was added to quench the reaction and the mixture was extracted 4 times with 100 ml Et$_2$O. The combined organic layers were washed with sat. NaHCO$_3$ solution, brine and small amounts of H$_2$O. After drying over MgSO$_4$ the solvent was evaporated to dryness. The crude product was dissolved in $n$-hexane and precipitated at -30 °C. The hygroscopic solid was further dried in vacuum. 0.76 g (76.4 % yield, m.p.: 78-80 °C) pure 78 were obtained as its rcce-isomer as a slightly yellow solid.

$^1$H NMR (500.1 MHz, CDCl$_3$, r.t.): **rcce-isomer in boat conformation:** $\delta$ (ppm) = 7.22 (s, 2 H, H3*), 6.50 (s, 2 H, H5), 6.04 (s, 2 H, H3), 6.00 (s, 2 H, H5*), 4.53 (dd, $^3J(H,H)$=10.7 Hz, $^4J(H,H)$=3.8 Hz, 4 H, H1), 3.96 (d, $^2J(H,H)$=8.8 Hz, 4 H, H4a_1 or H4a_2), 3.85 (d, $^2J(H,H)$=8.5 Hz, 4 H, H4a_1 or H4a_2), 3.44 (d, $^2J(H,H)$=8.5 Hz, 4 H, H4a*_1 or H4a*_2), 3.27 (d, $^2J(H,H)$=8.5 Hz, 4 H, H4a*_1 or H4a*_2), 2.95-2.60 (br. d, 8 H, OH), 1.93 (br. m, 4 H, H6_1 or H6_2), 1.73 (br. m, 4 H, H6_1 or H6_2), 1.45 (br. m, 4 H, H7_1 or H7_2), 1.41 (s, 12 H, H4b_1 or H4b_2), 1.38 (s, 12 H, H4b_1 or H4b_2), 1.33-1.18 (br. m, 68 H, H7_1 or
H7_2 and H8-15), 1.17 (s, 12 H, H4b*_1 or H4b*_2), 1.08 (s, 12 H, H4b*_1 or H4b*_2), 0.85 (t, $^3J(H,H)=7.1$ Hz, 12 H, H16).

$^{13}$C NMR (125.7 MHz, CDCl$_3$, r.t.): \textit{rcce-isomer in boat conformation}: $\delta$ (ppm) = 155.34 (s, C4i*), 153.11 (s, C4i), 128.52 (s, C2i), 126.38 (s, C3*), 125.80 (s, C3), 122.39 (s, C2i*), 97.96 (s, C5*), 95.92 (s, C5), 76.35 (s, C4a*), 76.25 (s, C4a), 70.11 (s, C4ci), 69.71 (s, C4ci*), 36.37 (s, C1), 34.71 (s, C6), 31.88 (s, C14), 30.38 (s, C8), 29.81, 29.78, 29.69, 29.66, 29.34 (s, C9-13), 29.03 (s, C7), 26.53 (s, C4b_1 or C4b_2), 26.36 (s, C4b_1 or C4b_2), 25.96 (s, C4b*_1 or C4b*_2), 25.75 (s, C4b*_1 or C4b*_2), 22.65 (s, C15), 14.08 (s, C16).

MALDI-TOF-MS (4-NA): calcd. for C$_{104}$H$_{176}$O$_{16}$: $m/z$ = 1681.296 [M]$^+$; found: $m/z$ = 1704 [M+Na]$^+$, 1721 [M+K]$^+$.

EA: calcd. for C$_{104}$H$_{176}$O$_{16}$: C 74.24 %, H 10.54 %; found: C 74.10 %, H 10.61 %.
10.2. Modification of resorcin- and pyrogallolarenes by O-alkylation with N-bromo-propylphthalimide

10.2.1. General procedure for the O-alkylation of resorcin- and pyrogallolarenes with N-bromopropylphthalimide – GP III

1.00 g of resorcin- or pyrogallolarene were weighted into a flame dried 100 ml three necked round bottom flask in an argon counter stream. 2 equivalents of prior dried anhydrous K$_2$CO$_3$ were added, followed by 25 ml of dry acetonitrile. Under stirring 2 equivalents of N-(3-bromopropyl)phthalimide (79) per phenolic hydroxyl group were added. The mixture was
further flushed with argon for 10 minutes and afterwards heated to 90 °C for approx. 2 weeks. The course of the reaction was controlled by MALDI-TOF-MS. The reactions were stopped when only peaks of the fully substituted cores 80 to 85 could be observed. The mixture was then filtrated and the residual solid suspended in chloroform, refluxed for 10 minutes and again screened from the inorganic solids. The procedure was repeated two times more. The combined organic phases were evaporated to dryness and the residue re-dissolved in chloroform. The solution was washed with brine several times and dried over MgSO₄. After evaporation of the solvent, the crude product was dissolved in a small amount of chloroform and precipitated twice from EtOH at -30 °C. The pure octa-, dodeca- 80, 81, 83 and 84, and two rather impure dodeca- and hexadeca-N-propylphthalimide 82 to 85 derivatives of resorcin- and pyrogallolarenes respectively were obtained by flash-chromatography with 1:10 MeOH/CHCl₃.

10.2.1.1. Synthesis of 2,2',2'',2''',2''''',2'''''',2''''''',2''''''''-[[2,8,14,20-tetrapentylpentacyclo[19.3.1.13,7.19,13.115,19]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16-18,21,23-dodecaene-4,6,10,12,16,18,22,24-octayl]octakis(oxypropane-3,1-diyl)]octakis(1H-isooindole-1,3(2H)-dione) (80)

1.00 g (1.30 mmol) 59, 5.58 g (20.81 mmol) N-(3-bromopropyl)phthalimide (79) and 2.88 g (20.81 mmol) dry K₂CO₃ were reacted as described in the general procedure GP III. The crude octa-N-propylphthalimide derivative 80 was further purified by flash-chromatography with 1:10 MeOH/CHCl₃. 1.82 g (61.6 % yield, m.p.: 191-192 °C) pure 80 were obtained as its recce-isomer as a slightly yellow powder.

¹H NMR (500.1 MHz, CDCl₃, r.t.): *recce-isomer in boat conformation*; δ (ppm) = 7.90-7.50 (br. m, 32 H, H16/16* and H17/17*), 7.18 (br. s, 2 H, H3), 6.50 (br. s, 2 H, H5*), 6.17 (br. s, 2 H, H5), 5.95 (br. s, 2 H, H3*), 4.52 (t, 2J(H,H)=7.3 Hz, 4 H, H1), 4.20 (br. s, 4 H, H11_1 or H11*_1), 4.06 (br. s, 4 H, H11_2 or H11*_2), 3.94 (br. s, 8 H, H13 or H13*), 3.69 (br. s, 4 H, H11_1 or H11*_1), 3.64 (br. s, 4 H, H13_1 or H13*_1), 3.53 (br. s, 4 H, H13_2 or H13*_2), 3.32 (br. s, 4 H, H11_2 or H11*_2), 2.20 (br. s, 8 H, H12 or H12*), 1.84 (br. s, 8 H,
H6), 1.72 (br. s, 8 H, H12 or H12*), 1.38 (br. s, 8 H, H7), 1.27 (br. m, 16 H, H8/9), 0.80 (t, 
$3J(H,H)=6.9$ Hz, 12 H, H10).

$^{13}$C NMR (125.7 MHz, CDCl$_3$, r.t.): **rcce-isomer in boat conformation**: $\delta$ (ppm) = 168.07 (s, C14i/14i*), 155.60 (s, C4i*), 153.95 (s, C4i), 133.52 (s, C16/16* or C17/17*), 132.21 (s, C15i/15i*), 128.25 (s, C2i), 126.51 (s, C3*), 125.80 (s, C3), 124.29 (s, C2i*), 122.96 (s, C16/16* or C17/17*), 100.86 (s, C5*), 96.23 (s, C5), 66.84 (m, C11 or C11*), 65.62 (m, C11 or C11*), 36.08 (s, C1), 35.54 (s, C13/13*), 34.44 (s, C6), 32.40 (s, C8), 28.89 (m, C12 or C12*), 28.44 (m, C12 or C12*), 28.20 (s, C7), 22.67 (s, C9), 14.18 (s, C10).

MALDI-TOF-MS (4-NA): calcd. for C$_{136}$H$_{136}$N$_8$O$_{24}$: $m/z = 2264.967$ [M$^+$];

EA: calcd. for C$_{136}$H$_{136}$N$_8$O$_{24}$: C 72.07 %, H 6.05 %, N 4.94 %; found: C 72.23 %, H 6.15 %, N 4.72 %.

10.2.1.2. Synthesis of 2,2',2'',2''',2'''',2''''',2'''''''-[2,8,14,20-tetraundecylpentacyclo-[19.3.1.1$^{3,7}$.1$^{9,13}$.1$^{15,19}$]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,-18,21,23-dodecaene-4,6,10,12,16,18,22,24-octayl]octakis(oxypropane-3,1-diy1]octakis(1H-isoindole-1,3(2H)-dione) (81)

1.00 g (0.90 mmol) 60, 3.88 g (14.47 mmol) N-(3-bromopropyl)phthalimide (79) and 2.00 g (14.47 mmol) dry K$_2$CO$_3$ were reacted as described in the general procedure **GP III**. The crude octa-N-proplyphthalimide derivative 81 was further purified by flash-chromatography using 1:10 MeOH/CHCl$_3$. 1.64 g (69.7 % yield, m.p.: 142-143 °C) pure 81 were obtained as its rcce-isomer as a slightly yellow powder.

$^1$H NMR (500.1 MHz, CDCl$_3$, r.t.): **rcce-isomer in boat conformation**: $\delta$ (ppm) = 7.90-7.50 (br. m, 32 H, H22/22* and H23/23*), 7.18 (br. s, 2 H, H3), 6.50 (br. s, 2 H, H5*), 6.16
Practical part

1H NMR (400 MHz, CDCl 3, 100 MHz, CDOD 3): resonances are listed as follows: 5.95 (br. s, 2 H, H5), 4.52 (t, $^3J(H,H)=7.4$ Hz, 4 H, H1), 4.21 (br. s, 4 H, H17_1 or H17*_1), 4.06 (br. s, 4 H, H17_2 or H17*_2), 3.95 (br. s, 8 H, H19 or H19*), 3.69 (br. s, 4 H, H17_1 or H17*_1), 3.64 (br. s, 4 H, H19_1 or H19*_1), 3.53 (br. s, 4 H, H19_2 or H19*_2), 3.32 (br. s, 4 H, H17_2 or H17*_2), 2.21 (br. s, 8 H, H18 or H18*), 1.84 (br. s, 8 H, H6), 1.72 (br. s, 8 H, H18 or H18*), 1.38 (br. s, 8 H, H7), 1.29 (br. m, 8 H, H8), 1.24 (s, 8 H, H15), 1.24-1.09 (br. m, 48 H, H9-14), 0.81 (t, $^3J(H,H)=7.1$ Hz, 12 H, H16).

$^{13}$C NMR (125.7 MHz, CDCl 3, r.t.): $rcce$-isomer in boat conformation: $\delta$ (ppm) = 168.07 (s, C20i/20i*), 155.65 (s, C4i*), 153.93 (s, C4i), 133.57 (m, C22/22* or C23/23*), 132.25 (s, C21i/21i*), 128.33 (s, C2i), 126.65 (s, C3*), 125.84 (s, C3), 124.12 (s, 2i*), 122.96 (s, C22/22* or C23/23*), 100.86 (s, C5*), 96.31 (s, C5), 66.78 (s, C17 or C17*), 65.56 (s, C17 or C17*), 36.19 (s, C1), 35.57 (s, C19/19*), 34.51 (s, C6), 31.89 (s, C14), 30.33 (s, C8), 29.03, 29.81, 29.70 (s, C9-13), 28.93 (m, C18 or C18*), 28.60 (s, C7), 28.46 (m, C18 or C18*), 22.65 (s, C15), 14.09 (s, C16).

**MALDI-TOF-MS (4-NA):** calcd. for C$_{160}$H$_{184}$N$_8$O$_{24}$: $m/z = 2601.342$ [M]$^+$;
found: $m/z = 2603.422$ [M+H]$^+$, 2625.602 [M+Na]$^+$

**EA:** calcd. for C$_{160}$H$_{184}$N$_8$O$_{24}$: C 73.82 %, H 7.12 %, N 4.30 %; found: C 73.96 %, H 7.24 %, N 4.25 %.
10.2.1.3. Synthesis of \(\text{2,2}',\text{2''}',\text{2''''},\text{2'''''},\text{2'''''},\text{2''''''},\text{2'''''''},\text{2'''''''},\text{2''''''''}\)-[[2,8,14,20-tetrakis{4-[3-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)propoxy]phenyl}pentacyclo[19.3.1.1^{3,7}.-1^{9,13}.1^{15,19}]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,6,10,12,16,18,22,24-octayl]octakis(oxypropane-3,1-diyl]octakis(1H-isoindole-1,3(2H)-dione) (82)

\[\text{1.00 g (1.17 mmol) 65, 7.51 g (28.01 mmol) N-(3-bromopropyl)phthalimide (79) and 3.87 g (28.01 mmol) dry K}_2\text{CO}_3\] were reacted as described in the general procedure GP III. The crude dodeca-N-propyl-phthalimide 82 derivative was further purified by flash-chromatography using 1:10 MeOH/CHCl\(_3\). 2.12 g (58.5 % yield) rather impure 82 were obtained as a mixture of its \text{recc-} and \text{rett-} isomers as a orange solid.

\(\text{\(^1\text{H NMR}\) and \(^{13}\text{C NMR}:\)\) not significant, because the product obtained was a mixture of the dodecasubstituted resorcinarene with octa-, nona-, deca- and undecasubstituted byproducts.}

\(\text{EA: calcd. for C}_{184}\text{H}_{148}\text{N}_{12}\text{O}_{36}:\) C 71.22 %, H 4.81 %, N 5.42 %; found: not performed.

\(\text{MALDI-TOF-MS (4-NA):\) calcd. for C}_{184}\text{H}_{148}\text{N}_{12}\text{O}_{36}:\) m/z = 3101.012 [M]\(^+\); found: m/z = 2355[M-4xNphth+H]\(^+\), 2542[M-3xNphth+H]\(^+\), 2729 [M-2xNphth+H]\(^+\), 2916 [M-1xNphth+H]\(^+\), 3102 [M+H]\(^+\), 3141 [M+K]\(^+\).
10.2.1.4. Synthesis of \(2,2',2'',2''',2''''',2'''''',2''''''',2''''''''',2'''''''''',\ldots\)-\([2,8,14,20\text{-tetrapentylpentacyclo[19.3.1.1^{3,7,1^{9,13,1^{15,19}}]}\text{octacosa-1}(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23\text{-dodecaene-4,5,6,10,11,12,16,-17,18,22,23,24\text{-dodecayl}]dodecakis(\text{oxypropane-3,1-diyl]}\text{dodecakis(1H}

\text{isoindole-1,3(2H)-dione})\) (83)

1.00 g (1.20 mmol) 62, 7.72 g (28.81 mmol) \(N\)-(3-bromopropyl)phthalimide (79) and 3.98 g (28.81 mmol) dry \(K_2CO_3\) were reacted as described in the general procedure GP III. The crude dodeca-\(N\)-propyl-phthalimide derivative 83 was further purified by flash-chromatography using 1:10 MeOH/CHCl\(_3\). 3.02 g (81.7 % yield, m.p.: 79-81 °C) pure 83 were obtained as its \(rccc\)-isomers as a slightly yellow solid.

\(\text{\textsuperscript{1}H NMR}\) (500.1 MHz, CDCl\(_3\), r.t.): \(rccc\)-isomer in boat conformation: \(\delta\) (ppm) = 7.80-7.40 (br. m, 48 H, H16/16* and H17/17* and H23/23* and H24/24*), 6.93 (br. s, 2 H, H3), 5.74 (br. s, 2 H, H3*), 4.49 (t, \(^3J(H,H)\)=7.3 Hz, 4 H, H1), 4.45-3.20 (br. m, 48 H, H11/11* and H13/13* and H18/18* and H20/20*), 2.40-2.10 (br. m, 8 H, H12*), 2.10-2.00 (br. m, 8 H, H19/19*), 2.00-1.65 (br. m, 16 H, H12 and H6), 1.45-1.14 (br. m, 24 H, H7-9), 0.77 (t, \(^3J(H,H)\)=6.6 Hz, 12 H, H10).

\(\text{\textsuperscript{13}C NMR}\) (125.7 MHz, CDCl\(_3\), r.t.): \(rccc\)-isomer in boat conformation: \(\delta\) (ppm) = 168.20, 168.02, 167.98, 167.91 (s, C14i/14i* and C21i/21i*), 149.36-144.44 (m, C4i/4i* and C5i/5i*), 133.75-132.80 (m, C16/16* and C23/23* or C17/17* and C24/24*), 132.50-132.10 (m, C15i/15i* and C22i/22i*), 131.98 (s, C2i), 125.79 (s, C2i*), 123.25 (s, C3*), 123.10-122.65 (m, C16/16* and C23/23* or C17/17* and C24/24*), 121.25 (s, C3), 71.80-70.47 (s, C11/11* and C18/18*), 37.73 (s, C1), 35.70-35.45 (m, C13/13* and C20/20*), 35.32 (s, C6), 32.39 (s, C8), 30.04-29.00 (m, C12/12* and C19/19*), 28.51 (s, C7), 22.68 (s, C9), 14.16 (s, C10).

\textbf{MALDI-TOF-MS (4-NA):} calcd. for C\(_{180}\)H\(_{172}\)N\(_12\)O\(_{36}\): \(m/z = 3077.200\) [M\(^+\)]; found: \(m/z = 3101\) [M+Na\(^+\)], 3117 [M+K\(^+\)].
EA: calcd. for C_{180}H_{172}N_{12}O_{36}: C 70.21 %, H 5.63 %, N 5.46 %; found: C 70.32 %, H 5.75 % N 5.40 %.

10.2.1.5. **Synthesis of 2,2',2'',2''',2'''',2''''',2''''''',2''''''''',2'''''''''',2'''''''''''-2''''''''''''-[2,8,14,20-tetraundecylpentacyclo[19.3.1.1^3,7.1^9,13.1^15,19]octacosa-1(25),3(28),4,6,-9(27),10,12,15(26),16,18,21,23-dodecaene-4,5,6,10,11,12,16,17,-18,22,23,24-dodecayl]-dodekakis(oxypropane-3,1-diyl)dodekakis(1H-isoindole-1,3(2H)-dione) (84)**

1.00 g (0.85 mmol) 63, 5.50 g (20.52 mmol) N-(3-bromopropyl)phthalimide (79) and 2.84 g (20.52 mmol) dry K\textsubscript{2}CO\textsubscript{3} were reacted as described in the general procedure GP III. The crude dodeca-N-propyl-phthalimide derivative 84 was further purified by flash-chromatography using 1:10 MeOH/CHCl\textsubscript{3}. 2.52 g (86.3 % yield) pure 84 were obtained as its rcce-isomers as a slightly yellow oil.

\textsuperscript{1}H NMR (500.1 MHz, CDCl\textsubscript{3}, r.t.): **rcce-isomer in boat conformation:** \(\delta\) (ppm) = 7.80-7.40 (br. m, 48 H, H16/16* and H17/17* and H23/23* and H24/24*), 6.93 (br. s, 2 H, H3), 5.74 (br. s, 2 H, H3*), 4.49 (t, \(^3J(H,H)=7.1\) Hz, 4 H, H1), 4.45-3.20 (br. m, 48 H, H11/11* and H13/13* and H18/18* and H20/20*), 2.40-2.10 (br. m, 8 H, H12*), 2.10-2.00 (br. m, 8 H, H19/19*), 2.00-1.65 (br. m, 16 H, H12 and H6), 1.50-0.90 (br. m, 72 H, H7-15), 0.82 (t, \(^3J(H,H)=7.1\) Hz, 12 H, H16).

\textsuperscript{13}C NMR (125.7 MHz, CDCl\textsubscript{3}, r.t.): **rcce-isomer in boat conformation:** \(\delta\) (ppm) = 168.01, 167.95 (s, C20i and C27i), 149.36-144.55 (m, C4i/4i* and C5i/5i*), 133.75-132.80 (m, C22/22* and C29/29* or C23/23* and C30/30*), 132.50-132.10 (m, C21i/21i* and C28i/28i*), 129.95 (br. s, C2i), 125.65 (s, C2i*), 123.38 (br. s, C3*), 122.92 (m, C22/22* and C29/29* or C23/23* and C30/30*), 121.32 (br. s, C3), 71.81-70.38 (m, C17/17* and C24/24*), 37.81 (s, C1), 35.71-35.40 (m, C19/19* and C26/26*), 35.34 (s, C6), 31.89 (s,
C14), 29.98-29.55 (m, C8-13), 29.50-29.28 (m, C18/18* and C25/C25*), 28.90 (s, C7), 22.65 (s, C15), 14.09 (s, C16).

**MALDI-TOF-MS (4-NA):** calcd. for C_{204}H_{220}N_{12}O_{36}: \textit{m/z} = 3413.575 [M]^+; found: \textit{m/z} = 3436 [M+Na]^+, 3452 [M+K]^+.

**EA:** calcd. for C_{204}H_{220}N_{12}O_{36}: C 71.73 %, H 6.49 %, N 4.92 %; found: C 71.85 %, H 6.54 %, N 4.78 %.

**10.2.1.6. Synthesis of 2,2',2'',2''',2''''',2'''''',2''''''',2''''''''',2'''''''''',2''''''''''',2''''''''''''',2''''''''''''''',2'''''''''''''''\text{-}2'''''''''''''''\text{-}[\text{2,8,14,20-tetrakis{4-}{[3-(1,3-dioxo-1,3-dihydro-2H-isooindol-2-yl)-propoxyl}phenyl]}\text{-pentacyclo[19.3.1.1^3,7.1^9,1^3,1^5,1^9]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,5,6,10,11,12,16,17,18,22,23,24-dodecayl\text{-dodecakis(oxypropane-3,1-diyl)dodecakis(1H-isooindole-1,3(2H)-dione]} (85)

1.00 g (1.09 mmol) 66, 9.12 g (34.75 mmol) \textit{N}-(3-bromopropyl)phthalimide (79) and 4.80 g (34.75 mmol) dry K_2CO_3 were reacted as described in the general procedure GP III. The crude hexadeca-\text{-}N-propylphthalimide 85 derivative was further purified by flash-chromatography using 1:10 MeOH/CHCl_3. 3.19 g (75.1 % yield,) rather impure 85 were obtained as a mixture of its \textit{rcctt}- and \textit{rccee}-isomers as a orange solid.

**1H NMR** and **13C NMR:** not significant, because the product obtained was a mixture of the dodecasubstituted pyrogallolarene with octa-, nona-, deca- and undeca-substituted byproducts.

**EA:** calcd. for C_{228}H_{184}N_{16}O_{48}: C 69.93 %, H 4.74 %, N 5.72 %; found: not performed.

**MALDI-TOF-MS (4-NA):** calcd. for C_{228}H_{184}N_{16}O_{48}: \textit{m/z} = 3913.245 [M]^+; found: \textit{m/z} = 2980 [M-5xNphth+H]^+, 3167 [M-4xNphth+H]^+, 3355 (M-3xNphth+H)^+, 3542 [M-2xNphth+H]^+, 3730 [M-1xNphth+H]^+, 3934 [M+Na]^+, 3953 [M+K]^+.
10.3. Modification of resorcin- and pyrogallolarenes by O-alkylation with propargyl bromide

10.3.1. General procedure for the O-alkylation of resorcin- and pyrogallolarenes with propargyl bromide – GP IV

0.50 g of resorcin- or pyrogallolarene 59 and 62 were weighted into a flame dried 100 ml three necked round bottom flask in an argon counter stream. 2 equivalents of prior dried anhydrous K₂CO₃ were added, followed by 50 ml of dry acetonitrile. Under stirring 2 equivalents of propargylbromide (86) per phenolic hydroxyl group were added by syringe. The mixture was further flushed with argon for 5 minutes and afterwards heated to 90 °C for approx. 1 day. The course of the reaction was controlled by MALDI-TOF-MS. The reactions were stopped when only peaks of the fully substituted cores could be observed. The mixture was then filtrated and the residual solid suspended in chloroform, refluxed for 10 minutes and again screened from the inorganic solids. The procedure was repeated two times more. The combined organic phases were evaporated to dryness and the residue re-dissolved in chloroform. The solution was washed with brine several times and dried over MgSO₄. After evaporation of the solvent, educts and side products were removed under high vacuum. The resulting solid has been transferred to a 100 ml round bottom flask and dissolved in chloroform. The desired octa- and dodecapropargyl derivatives of the resorcin- and pyrogallolarenes 87 and 88, respectively, were then precipitated twice at -30 °C.

Figure 112. Synthesis and obtained yields of propyne functionalized C-alkylresorcin- and -pyrogallolarenes.
10.3.1.1. Synthesis of 2,8,14,20-tetrapentyl-4,6,10,12,16,18,22,24-octakis(prop-2-yn-1-yloxy)pentacyclo[19.3.1.13,7.19,13.115,19]octacosa-1(25),3(28),4,6,9(27),10,12,15-(26),16,18,21,23-dodecaene (87)

0.50 g (0.65 mmol) 59, 1.24 g (10.40 mmol) propargyl bromide (86) and 1.44 g (10.40 mmol) dry K₂CO₃ were reacted as described in the general procedure GP IV. The crude octapropargyl resorcin[4]arene 87 was further purified by dissolution in chloroform and precipitation from MeOH at -30 °C. 0.63 g (89.5 % yield, m.p.: 116-117 °C) pure 87 were obtained as its rcce-isomer as a yellow solid.²⁵⁶

¹H NMR (500.1 MHz, DMSO, r.t.): rcce-isomer in cone conformation: δ (ppm) = 6.69 (s, 4 H, H5), 6.68 (s, 4 H, H3), 4.60, 4.56, 4.52, 4.49 (qd, 4J(H,H)=2.2 Hz, 16 H, H4a), 4.46 (t, 3J(H,H)=7.6 Hz, 4 H, H1), 3.47 (t, 4J(H,H)=2.4 Hz, 8 H, H4c), 1.75 (br. q, 8 H, H6), 1.27-1.17 (br. m, 24 H, H7-9), 0.82 (t, 3J(H,H)=6.6 Hz, 12 H, H10).

¹³C NMR (125.7 MHz, DMSO, r.t.): rcce-isomer in cone conformation: δ (ppm) = 153.56 (s, C4i), 126.22 (s, C2i), 125.61 (s, C3), 100.50 (s, C5), 79.65 (s, C4bi), 77.74 (s, C4c), 56.60 (s, C4a), 34.69 (s, C6), 34.28 (s, C1), 31.50 (s, C8) 27.29 (s, C7), 22.17 (s, C9), 14.01 (s, C10).


EA: calecd. for C₇₂H₈₀O₈: C 80.56 %, H 7.51 %; found: C 80.61 %, H 7.57 %.

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b = 13.775(1) Å  $\beta = 88.73(1)^{\circ}$.
c = 19.735(2) Å  $\gamma = 64.08(1)^{\circ}$.

Volume 3095.3(5) Å³
Z 2
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Absorption coefficient 0.074 mm⁻¹
F(000) 1152
Crystal size 0.61 x 0.14 x 0.14 mm³
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Index ranges -18<=h<=18, -19<=k<=19, -28<=l<=28
Reflections collected 108141
Independent reflections 18839 [R(int) = 0.0305]
Completeness to theta = 30.51° 99.7 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.9898 and 0.9565
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 14502 / 12 / 774
Goodness-of-fit on F² 1.031
Final R indices [I>2sigma(I)] R1 = 0.0593, wR2 = 0.1544
R indices (all data) R1 = 0.0796, wR2 = 0.1707
Largest diff. peak and hole 0.528 and -0.345 e.Å⁻³
**Figure 113.** ORTEP-plot of the asymmetric unit of 87 with 50 % probability level. Hydrogen atoms omitted for clarity.

**Figure 114.** Packing diagram of 87. View along a-axis of unit cell (b: red, c: green).
10.3.1.2. Synthesis of 2,8,14,20-tetrapentyl-4,5,6,10,11,12,16,17,18,22,23,24-dodecakis-(prop-2-yn-1-yloxy)pentacyclo[19.3.1.1³,7.1⁹,13.1¹⁵,1⁹]octacosa-1(25),3(28),4,6,-9(27),10,12,15(26),16,18,21,23-dodecaene (88)

0.50 g (0.60 mmol) 62, 1.71 g (14.41 mmol) propargyl bromide (86) and 1.99 g (14.41 mmol) dry K₂CO₃ were reacted as described in the general procedure GP IV. The crude dodecapropargyl pyrogallol[4]arene 88 was further purified by dissolution in chloroform and precipitation from MeOH at -30 °C. 0.74 g (95.1 % yield, m.p.: 95-96 °C) pure 88 were obtained as its rccc-isomer as a yellow solid.²⁵⁶

¹H NMR (500.1 MHz, CDCl₃, r.t.): rccc-isomer in boat conformation δ (ppm) = 6.35 (s, 4 H, H3/3*), 4.75 (d, ²J(H,H)=2.5 Hz, 4 H, H4a1 or H4a2 or H4a1* or H4a2*), 4.72 (d, ³J(H,H)=2.2 Hz, 4 H, H5a1/5a2), 4.57 (t, ⁴J(H,H)=7.4 Hz, 4 H, H1), 4.39 (s, 4 H, H4a1 or H4a2 or H4a1* or H4a2*), 2.51 (t, ⁴J(H,H)=2.5 Hz, 8 H, H5c), 1.81 (br. m, 8 H, H6), 1.40-1.20 (br. m, 24 H, H7-9), 0.84 (t, ³J(H,H)=6.9 Hz, 12 H, H10).

¹³C NMR (125.7 MHz, CDCl₃, r.t.): rccc-isomer in boat conformation δ (ppm) = 147.84 (s, C4i/4i*), 144.03 (s, C5i/5i*), 134.08 (s, C2i/2i*), 121.41 (s, C3/3*), 79.70 (s, C4bi/4bi*), 79.03 (s, C5bi/5bi*), 75.39 (s, C5c/5c*), 74.94 (s, C4c/4c*), 60.73 (s, C5a/5a*), 60.47 (s, C4a/4a*), 37.34 (s, C1), 35.14 (s, C6), 31.96 (s, C8), 27.79 (s, C7), 22.71 (s, C9), 14.14 (s, C10).

MALDI-TOF-MS (4-NA): calcd. for C₈₄H₈₈O₁₂: m/z = 1288.628 [M]⁺;
found: m/z = 1289 [M+H]⁺, 1312 [M+Na]⁺.

EA: calcd. for C₈₄H₈₈O₁₂: C 78.23 %, H 6.88 %; found: C 78.45 %, H 6.92 %.
10.3.1.3. Synthesis of 2,2′,2″,2‴,2‴′,2‴‴,2‴‴′-,2‴‴‴,2‴‴‴′,2‴‴‴″-
[2,8,14,20-tetrakis[4-(prop-2-yn-1-yl-oxy)phenyl]pentacyclo[19.3.1.13,7.19,13.115,19]octacosa-1(25),3(28),4,6,-9(27),10,12,15(26),16,18,21,23-dodecaene-4,6,10,12,16,18,22,24-octayl]octakis-
(oxy]octaethanol (89)

15.00 g (12.40 mmol) 68, 14.67 g (99.23 mmol) propargyl bromide (86) and 13.71 g (99.23 mmol) dry K₂CO₃ were reacted as described in the general procedure GP IV. The crude tertapropargyl resorcinarene 89 was further purified by dissolution in chloroform/MeOH and precipitation at -30 °C. 3.40 g (20.1 % yield, m.p.: 160-161 °C and 226-225 °C) pure 89 were obtained as mixture of its rettt- and rccc-isomer as a yellow solid.²⁵⁶

¹H NMR (500.1 MHz, DMSO, r.t.): rettt-isomer in chair conformation: δ (ppm) = 6.72 (br. s, 2 H, H5*), 6.58 (br. m, 10 H, H5 and H7), 6.53 (br. m, 8 H, H8), 6.10 (br. s 2 H, H3), 5.60 (br. s, 2 H, H3*), 5.52 (br. s, 4 H, H1), 4.72 (br. d, 8 H, H9a), 4.03 (br. m, 4 H, H4a*₁), 3.92 (br. m, 4 H, H4a₂), 3.57 (br. m, 12 H, H4b₁/4b₂ and H4a*₂), 3.53 (br. m, 4 H, H9c), 3.31 (br. m, 8 H, H4b*₁ and H4b*₂).

rccc-isomer: concentration too low for NMR correlation.

¹³C NMR (125.7 MHz, DMSO, r.t.): rettt-isomer in chair conformation: δ (ppm) = 155.06 (s, C4i*), 154.90 (s, C9i), 154.45 (s, C4i), 135.27 (s, C6i), 130.73 (s,C3*), 129.88 (s, C7), 129.76 (s, C3), 126.92 (s, C2i), 123.91 (s, C2i*), 113.85 (s, C8), 100.00 (s, C5), 98.02 (s, C5*), 80.00 (s, C9bi), 77.97 (s, C9c), 70.30 (s, C4a), 69.50 (s, C4a*), 59.87 (s, C4b), 59.71 (s, C4b*), 55.44 (s, C9a), 40.15 (s, C1).

rccc-isomer: concentration too low for NMR correlation.

MALDI-TOF-MS (4-NA): calcld. for C₈₀H₈₀O₂₀: m/z = 1360.524 [M]+;
found: m/z = 1362 [M+H]+, 1383 [M+Na]+,

EA: calcld. for C₈₀H₈₀O₂₀: C 70.57 %, H 5.92; found: C 68.81 %, H 5.43 %.
11. Star polymers based on resorcin- and pyrogallololarenes

11.1. Synthesis of mono-, di- and trifunctional ATRP-initiators based on phenol, oligophenols, resorcin and pyrogallol

11.1.1. General procedure for the O-acylation of phenol, oligophenols, resorcin and pyrogallol with 2-bromo-isobutyryl bromide – GP V

1.00 g of either phenol (1), resorcinol (2), pyrogallol (5), or the oligophenols 93 and 94 were weighted into a 100 ml three necked round bottom flask in an argon counter stream. 50 ml of dry THF were added, followed by 2 equivalents of pyridine per phenolic hydroxyl group. After complete dissolution of the solid, the mixture was cooled to 0 °C. Under stirring subsequently 2 equivalents of 2-bromo-isobutyryl bromide (53) per phenolic hydroxyl group were slowly added under stirring by syringe. Stirring was continued for 1 h and the reactions were controlled by MALDI-TOF-MS. The reactions were stopped when only peaks of the fully substituted initiators could be observed. The solvent and educts were removed under high vacuum by Kugel-Rohr distillation and the residues were dissolved in chloroform. After washing the organic phase with sat. K₂CO₃ solution and NaCl solution, the separated organic

Figure 115. Synthesis and obtained yields of mono-, di- and trifunctional initiators 90 to 92, 95 and 96.
phase was dried over MgSO₄ and concentrated to 10 ml. The desired mono-, di-, and trifunctional initiators 90 to 92, 95 and 96 were precipitated twice from an excess of cold methanol and further purified by flash-chromatography.

11.1.1.1. Synthesis of phenyl 2-bromo-2-methylpropanoate (90)

1.00 g (10.63 mmol) phenol (1), 1.71 ml (21.25 mmol) pyridine and 2.63 ml (21.25 mmol) 2-bromo-isobutryl bromide (53) were reacted as described in the general procedure GP V. The crude product was further purified by flash chromatography using chloroform. 2.36 g (91.6 % yield) pure 90 were obtained as colorless oil.255

\[ ^1H \text{NMR (300.1 MHz, CDCl}_3, \text{r.t.}): \delta (\text{ppm}) = 7.42 (t, \frac{3}{2}J(H,H)=7.9 \text{ Hz, 2 H, H3}), 7.27 (t, \frac{3}{2}J(H,H)=7.4 \text{ Hz, 1 H, H4}), 7.15 (d, \frac{3}{2}J(H,H)=7.7 \text{ Hz, 2 H, H2}), 2.08 (s, 12 H, H7/8). \]

\[ ^13C \text{NMR (75.5 MHz, CDCl}_3, \text{r.t.}): \delta (\text{ppm}) = 170.15 (s, C5i), 150.70 (s, C1i), 129.43 (s, C2), 126.08 (s, C4), 120.96 (s, C3), 55.36 (s, C6i), 30.56 (s, C7/8). \]

\[ \text{GC-MS: calcd. for C}_{10}H_{11}BrO_2: m/z = 241.994 [M]^+; \]
\[ \text{found: m/z = 242 [M+H]^+}. \]

\[ \text{EA: calcd. for C}_{10}H_{11}BrO_2: C 49.41 \%, H 4.56 \%; \text{found: C 49.40 \%, H 4.53 \%}. \]

11.1.1.2. Synthesis of 1,3-phenylene bis(2-bromo-2-methylpropanoate) (91)

1.00 g (9.08 mmol) resorcinol (2), 2.92 ml (36.33 mmol) pyridine and 4.49 ml (36.33 mmol) 2-bromo-isobutryl bromide (53) were reacted as described in the general procedure GP V. The crude product was further purified by flash chromatography using chloroform. 3.68 g (99.3 % yield) pure 91 were obtained as colorless oil.255

\[ ^1H \text{NMR (300.1 MHz, CDCl}_3, \text{r.t.}): \delta (\text{ppm}) = 7.43 (t, \frac{3}{2}J(H,H)=8.1 \text{ Hz, 1 H, H4}), 7.06 (dd, \frac{3}{2}J(H,H)=8.3 \text{ Hz, }^4J(H,H)=2.0 \text{ Hz, 2 H, H3}), 7.00 (t, \frac{4}{2}J(H,H)=2.2 \text{ Hz, 1 H, H1}), 2.05 (s, 12 H, H7/8). \]
$^{13}$C NMR (75.5 MHz, CDCl$_3$, r.t.): $\delta$ (ppm) = 169.80 (s, C5i), 151.17 (s, C2i), 129.70 (s, C1), 118.87 (s, C3), 114.62 (s, C4), 55.06 (s, C6i), 30.54 (s, C7/8).

GC-MS: calcd. for C$_{14}$H$_{16}$Br$_2$O$_4$: $m/z = 407.939$ [M]$^+$; found: $m/z = 408$ [M+H]$^+$.

EA: calcd. for C$_{14}$H$_{16}$Br$_2$O$_4$: C 41.20 %, H 3.95 %; found: C 41.24 %, H 3.91 %.

### 11.1.1.3. Synthesis of benzene-1,2,3-triyl tris(2-bromo-2-methylpropanoate) (92)

1.00 g (7.93 mmol) pyrogallol (5), 3.83 ml (47.58 mmol) pyridine and 5.88 ml (47.58 mmol) 2-bromo-isobutyryl bromide (53) were reacted as described in the general procedure GP V. The crude product was further purified by flash chromatography using chloroform. 4.13 g (90.8 % yield, m.p.: 76 °C) pure 92 were obtained as colorless solid.

$^1$H NMR (300.1 MHz, CDCl$_3$, r.t.): $\delta$ (ppm) = 7.33 (t, $^3J(H,H)$=8.5 Hz, 1 H, H4), 7.17 (d, $^3J(H,H)$=8.1 Hz, 2 H, H3), 2.05 (s, 12 H, H7/8), 1.99 (s, 6 H, H11/12).

$^{13}$C NMR (125.7 MHz, CDCl$_3$, r.t.): $\delta$ (ppm) = 168.84 (s, C5i), 167.69 (s, C5i), 165.72 (s, C9i), 143.56 (s, C2i), 134.62 (s, C1i), 126.48 (s, C4), 120.44 (s, C3), 55.00 (s, C6i), 54.73 (s, C6i), 53.39 (s, C10i), 31.02 (s, C11/12), 30.65 (s, C11/12), 29.99 (s, C7/8).

GC-MS: calcd. for C$_{18}$H$_{21}$Br$_3$O$_6$: $m/z = 571.887$ [M]$^+$; found: $m/z = 572$ [M+H]$^+$.

EA: calcd. for C$_{18}$H$_{21}$Br$_3$O$_6$: C 37.73 %, H 3.69 %; found: C 37.79 %, H 3.65 %.

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</tr>
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<td>Index ranges</td>
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</tr>
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<td>Reflections collected</td>
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<td>Independent reflections</td>
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<td>Completeness to theta = 26.30°</td>
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<tr>
<td>Absorption correction</td>
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</tr>
<tr>
<td>Max. and min. transmission</td>
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</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on F$^2$</td>
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</tr>
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<td>Final R indices [I&gt;2sigma(I)]</td>
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</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0460, wR2 = 0.0575</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.510 and -0.587 e.Å$^{-3}$</td>
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</tbody>
</table>
Figure 116. ORTEP-plot of the asymmetric unit of 92 with 50 % probability level. Hydrogen atoms omitted for clarity.

11.1.1.4. Synthesis of 2,6-bis(3,5-di-tert-butyl-2-hydroxybenzyl)-4-methylphenyl 2-bromo-2-methylpropanoate (96)

1.00 g (1.84 mmol) 94, 0.89 ml (11.01 mmol) pyridine and 1.36 ml (11.01 mmol) 2-bromo-isobutyryl (53) bromide were reacted as described in the general procedure GP V. The crude product was further purified by flash chromatography using chloroform. 1.31 g (72.0 % yield, m.p.: 78 °C) pure 96 were obtained as colorless solid.

$^1$H NMR (500.1 MHz, CDCl$_3$, r.t.): $\delta$ (ppm) = 7.25 (d, $^4J(H,H)$=2.2 Hz, 2 H, H5), 6.96 (d, $^4J(H,H)$=2.2 Hz, 2 H, H7), 6.72 (s, 2 H, H10), 4.93 (s, 2 H, OH), 3.83 (d, $^4J(H,H)$=9.1 Hz, 4 H, H1), 2.15 (s, 3 H, H12), 1.97 (s, 6 H, H19), 1.40 (s, 18 H, H14 or H16), 1.30 (s, 18 H, H14 or H16).

$^{13}$C NMR (125.7 MHz, CDCl$_3$, r.t.): $\delta$ (ppm) = 170.50 (s C17i), 150.51 (s C3i), 144.52 (s, C9i), 142.26 (s, C6i), 136.95 (s, C11i), 135.73 (s, C4i), 131.36 (s, C8i), 129.03 (s, C10),
125.82 (s, C7), 123.85 (s, C2i), 122.84 (s, C5), 54.89 (s, C18i), 34.82 (s, C13i), 34.26 (s, C15i), 31.62 (s, C16), 31.30 (s, C1), 30.59 (s, C19), 29.86 (s, C16), 21.09 (s, C12).

**ESI-MS** (MeOH/NH₄OAc) : calcd. for C₄₁H₅₇BrO₄: \( m/z = 692.334 \) [M]+;
found: \( m/z = 691.0 \) [M-H]-, 712.4 [M+Na]+.

**EA**: calcd. for C₄₁H₅₇BrO₄: C 70.98 %, H 8.82 %; found: C 71.02 %, H 8.84 %.

**SXD**:
Empirical formula \( C_{41}H_{57}BrO_4 \)
Moiety formula \( C_{41}H_{57}BrO_4 \)
Formula weight 693.78
Temperature 198(2) K
Wavelength 0.71073 Å
Crystal system Monoclinic
Space group C2/c (No. 15)
Unit cell dimensions \( a = 34.757(1) \) Å \( \alpha = 90^\circ \).
\( b = 11.699(1) \) Å \( \beta = 108.13(1)^\circ \).
\( c = 20.320(1) \) Å \( \gamma = 90^\circ \).
Volume 7852.3(8) Å³
Z 8
Density (calculated) 1.174 Mg/m³
Absorption coefficient 1.084 mm⁻¹
F(000) 2960
Crystal size 0.53 x 0.28 x 0.23 mm³
Theta range for data collection 3.41 to 25.41°.
Index ranges \(-41\leq h \leq 41, -13\leq k \leq 14, -24\leq l \leq 24\)
Reflections collected 75201
Independent reflections 7206 \( [R(int) = 0.0531] \)
Completeness to theta = 25.41° 99.6 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7887 and 0.5974
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 4704 / 46 / 474

159
Goodness-of-fit on $F^2$ 1.052
Final R indices [I>2sigma(I)] $R_1 = 0.0746$, $wR_2 = 0.1832$
R indices (all data) $R_1 = 0.1174$, $wR_2 = 0.2096$
Largest diff. peak and hole 0.644 and -0.572 e.Å$^{-3}$

Figure 117. ORTEP-plot of the asymmetric unit of 96 with 50 % probability level. Hydrogen atoms omitted for clarity.

Figure 118. Packing diagram of 96.
11.1.1.5. Synthesis of 2,6-bis{2-[(2-bromo-2-methylpropanoyl)oxy]-5-tert-butylbenzyl}-4-methylphenyl 2-bromo-2-methylpropanoate (95)

1.00 g (2.31 mmol) 93, 1.12 ml (13.87 mmol) pyridine and 1.71 ml (13.87 mmol) 2-bromo-isobutyryl bromide (53) were reacted as described in the general procedure GP V. The crude product was further purified by flash chromatography using chloroform. Only 0.15 g (7.4 % yield, m.p.: not determined) pure 95 were obtained as colorless solid. A better separation from the di-substituted byproduct could not be achieved.

$^1$H NMR (500.1 MHz, CDCl₃, r.t.): $\delta$ (ppm) = 7.31 (dd, $^3J(H,H)$=8.5 Hz, $^4J(H,H)$=2.5 Hz, 2 H, H3), 7.15 (d, $^4J(H,H)$=2.2 Hz, 2 H, H4), 7.06 (d, $^3J(H,H)$=8.5 Hz, 2 H, H2), 6.69 (s, 2 H, H5), 3.85 (br. s, 4 H, H1), 2.16 (s, 3 H, H6), 1.95 (s, 12 H, H8), 1.92 (s, 6 H, H9), 1.28 (s, 18 H, H7).

$^{13}$C NMR (125.7 MHz, CDCl₃, r.t.): $\delta$ (ppm) = 169.99 (s, C10i), 169.31 (s, C11i), 149.31 (s, C12i), 146.62 (s, C16i), 144.71 (s, C17i), 136.08 (s, C13i), 131.48 (s, C15i), 130.10 (s, C14i), 129.01 (s, C5), 128.20 (s, C4), 124.68 (s, C3), 120.91 (s, C2), 55.47 (s, C18i) 55.43 (s, C18i), 55.06 (s, C19i), 34.50 (s, C20i), 31.34 (s, C7), 30.59 (s, C9), 30.53 (s, C8), 30.22 (s, C1), 20.91 (s, C6).

ESI-MS (MeOH/NH₄OAc): calcd. for C₄₁H₅₁Br₃O₆: $m/z = 876.124$ [M]$^+$; found: $m/z = 898.2$ [M+Na]$^+$.

EA: calcd. for C₄₁H₅₁Br₃O₆: C 55.99 %, H 5.84 %; found: not performed.
11.2. Synthesis of octa-, dodeca- and hexadecafunctional ATRP-initiators based on resorcin- and pyrogallolarenes

11.2.1. General procedure of the \(O\)-acylation of resorcin- and pyrogallolarenes with 2-bromo-isobutyryl bromide – GP VI

1.00 g of resorcin- or pyrogallolarene were weighted into a 100 ml three necked round bottom flask in an argon counter stream. 50 ml of dry THF were added, followed by 4 equivalents of pyridine per phenolic hydroxyl group. After complete dissolution of the solid, the mixture was cooled to 0 °C. Under stirring subsequently 4 equivalents of 2-bromo-isobutyryl bromide (53) per phenolic hydroxyl group were slowly added under stirring by syringe. Stirring was continued for 1 h and the reactions were controlled by MALDI-TOF-MS. The solvent and educts were removed under high vacuum by Kugel-Rohr distillation and the residues were dissolved in chloroform. After washing the organic phase with sat. \(K_2CO_3\) solution and NaCl solution, the separated organic phase was dried over \(MgSO_4\) and concentrated to 10 ml. The desired octa-, dodeca- and hexadeca-2-bromo-2-methylpropanoate derivatives 97 to 102 of resorc-
and pyrogallolarenes respectively were precipitated twice from an excess of cold methanol and further purified by flash-chromatography.

11.2.1.1. Synthesis of 2,8,14,20-tetrapentylpentacyclo[19.3.1.1\textsuperscript{3,7}.1\textsuperscript{9,13}.1\textsuperscript{15,19}]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,6,10,12,16,18,22,24-octayl octakis-(2-bromo-2-methylpropanoate) (97)

1.00 g (1.30 mmol) \textit{59}, 3.35 ml (41.61 mmol) pyridine and 5.14 ml (41.61 mmol) 2-bromo-isobutyryl bromide (\textit{53}) were reacted as described in the general procedure \textit{GP VI}. The crude octabromo resorcinarene \textit{97} was further purified by flash chromatography using chloroform (R\textsubscript{f} = 0.61). 2.10 g (82.4 \% yield, m.p.: 287-288 °C decom.) pure \textit{97} as its \textit{rcce}-isomer were obtained as a colorless solid.

\textbf{\textsuperscript{1}H NMR} (500.1 MHz, CDCl\textsubscript{3}, r.t.): \textit{rcce}-isomer in boat conformation: \(\delta\) (ppm) = 7.37 (s, 2 H, H3*), 7.01 (s, 2 H, H5), 6.80 (s, 2 H, H5*), 6.15 (s, 2 H, H3), 4.33 (dd, \(^3J(H,H)=11.0\) Hz, \(^4J(H,H)=3.5\) Hz, 4 H, H1), 2.08 (s, 12 H, H4b2), 2.07 (s, 12 H, H4b1), 1.91 (s, 12 H, H4b1*), 1.88 (m, 8 H, H6), 1.84 (s, 12 H, H4b2*), 1.30 (br. m, 8 H, H7), 1.23 (br. m, 16 H, H8/9), 0.82 (t, \(^3J(H,H)=6.8\) Hz, 12 H, H10).

\textbf{\textsuperscript{13}C NMR} (125.7 MHz, CDCl\textsubscript{3}, r.t.): \textit{rcce}-isomer in boat conformation: \(\delta\) (ppm) = 169.75 (s, C4a), 168.99 (s, C4a*), 148.68 (s, C4i*), 145.87 (s, C4i), 134.97 (s, C2i), 129.59 (s, C2i*), 127.75 (s, C3*), 126.67 (s, C3), 115.92 (s, C5*), 115.26 (s, C5), 55.73 (s, C4c*), 55.05 (s, C4c), 38.22 (s, C1), 34.81 (s, C6), 32.36 (s, C8), 30.82 (s, C4b1/4b2), 30.55 (s, C4b1*), 30.45 (s, C4b2*), 28.26 (s, C7), 22.61 (s, C9), 14.19 (s, C10).

\textbf{MALDI-TOF-MS} (Dithranol): calcd. for C\textsubscript{80}H\textsubscript{104}Br\textsubscript{8}O\textsubscript{16}: \(m/z = 1960.071\) [M]\textsuperscript{+};

found: \(m/z = 1983.370\) [M+Na]\textsuperscript{+}, 1999.330 [M+K]\textsuperscript{+}.

\textbf{EA}: calcd. for C\textsubscript{80}H\textsubscript{104}Br\textsubscript{8}O\textsubscript{16}: C 49.00 \%, H 5.35 \%; found: C 48.99 \%, H 5.37 \%.
11.2.1.2. Synthesis of 2,8,14,20-tetraundecylpentacyclo[19.3.1.1\(^3\)7.1\(^9\)13.1\(^{15}\)19\]octacosa-
1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,6,10,12,16,18,22,24-
octyl octakis-(2-bromo-2-methylpropanoate) (98)

1.00 g (0.90 mmol) 60, 2.33 ml (28.94 mmol) pyridine and 3.58 ml (28.94 mmol) 2-bromo-isobutyryl bromide (53) were reacted as described in the general procedure GP VI. The crude octabromo resorcinarene 98 was further purified by flash chromatography using chloroform (R\(_f\) = 0.68). 1.79 g (86.2 % yield, m.p.: 135-136 °C) pure 98 were obtained as its \textit{rcce}-isomer as a colorless solid.

\(^1\)H NMR (500.1 MHz, CDCl\(_3\), r.t.): \textit{rcce}-isomer in boat conformation: \(\delta\) (ppm) = 7.37 (s, 2 H, H3*), 7.02 (s, 2 H, H5), 6.80 (s, 2 H, H5*), 6.15 (s, 2 H, H3), 4.32 (dd, \(^3J(H,H)=10.9\) Hz, \(^4J(H,H)=3.3\) Hz, 4 H, H1), 2.08 (s, 12 H, H4b2), 2.07 (s, 12 H, H4b1), 1.91 (s, 12 H, H4b1*), 1.88 (m, 8 H, H6), 1.84 (s, 12 H, H4b2*), 1.32 (br. m, 8 H, H7), 1.21 (br. m, 8 H, H15), 1.19 (br. m, 56 H, H8-14), 0.85 (t, \(3J(H,H)=6.9\) Hz, 12 H, H16).

\(^{13}\)C NMR (125.7 MHz, CDCl\(_3\), r.t.): \textit{rcce}-isomer in boat conformation: \(\delta\) (ppm) = 169.74 (s, C4a), 168.99 (s, C4a*), 148.67 (s, C4i*), 145.86 (s, C4i), 134.97 (s, C2i), 129.55 (s, C2i*), 127.80 (s, C3*), 126.66 (s, C3), 115.90 (s, C5*), 115.24 (s, C5), 55.69 (s, C4c*), 55.01 (s, C4c), 38.23 (s, C1), 34.81 (s, C6), 31.90 (s, C14), 30.80 (s, C4b1/4b2), 30.53 (s, C4b1*), 30.43 (s, C4b2*), 30.20 (s, C8), 29.84-29.35 (s, C9-13), 28.54 (s, C7), 22.66 (s, C15), 14.09 (s, C16).

MALDI-TOF-MS (Dithranol): calcd. for C\(_{104}\)H\(_{152}\)Br\(_8\)O\(_{16}\): \(m/z = 2297.450\) [M]\(^+\);
found: \(m/z = 2320.247\) [M+Na]\(^+\), 2336.266 [M+K]\(^+\).

EA: calcd. for C\(_{104}\)H\(_{152}\)Br\(_8\)O\(_{16}\): C 54.37 %, H 6.67 %; found: C 54.34 %, H 6.71 %.

1.00 g (1.16 mmol) 65, 4.50 ml (56.02 mmol) pyridine and 6.92 ml (56.02 mmol) 2-bromo-isobutyryl bromide (53) were reacted as described in the general procedure GP VI. The crude dodecabromo resorcinarene 99 was further purified by flash chromatography using chloroform (Rf = 0.27).

2.92 g (94.6 % yield, m.p.:  210 °C decomp.) pure 99 as a mixture of its rccc- and rctt-isomer were obtained as a colorless solid.

\[ ^1H \text{NMR} \] (500.1 MHz, CDCl\textsubscript{3}, r.t.): rctt-isomer in chair conformation: $\delta$ (ppm) = 7.09 (s, 2 H, H5), 6.96 (s, 4 H, H8a), 6.91 (s, 2 H, H5*), 6.90 (br. s, 8 H, H7), 6.40 (br. s, 4 H, H8b), 6.38 (s, 2 H, H3), 6.07 (s, 2 H, H3*), 5.72 (s, 4 H, H1), 2.07 (d, $^4J(H,H)=2.8$ Hz, 24 H, H9b), 1.97 (s, 12 H, H4b1*), 1.89 (s, 12 H, H4b2*), 1.67 (s, 12 H, H4b1), 1.65 (s, 12 H, H4b2).

rccc-isomer in boat conformation: $\delta$ (ppm) = 7.03 (s, 2 H, H5*), 6.96 (s, 2 H, H5), 6.81 (d, $^3J(H,H)=8.5$ Hz, 8 H, H7), 6.70-6.48 (br. s, 8 H, H8), 6.32 (s, 2 H, H3), 6.12 (s, 2 H, H3*), 5.85 (s, 4 H, H1), 2.05 (d, $^4J(H,H)=2.8$ Hz, 24 H, H9b), 1.94 (s, 12 H, H4b1*), 1.84 (s, 12 H, H4b2*), 1.70 (s, 12 H, H4b1), 1.64 (s, 12 H, H4b2).

\[ ^13C \text{NMR} \] (125.7 MHz, CDCl\textsubscript{3}, r.t.): rctt-isomer in chair conformation: $\delta$ (ppm) = 169.92 (s, C9a), 169.28 (s, C4a*), 168.74 (s, C4a), 149.45 (s, C9i), 147.29 (s, C4i* and C4i), 138.70 (s, C6i), 134.40 (s, C3*), 131.72 (s, C2i*), 130.80 (s, C2i), 129.97 (s, C3), 121.22 (s, C7), 116.28 (s, C5), 115.79 (s, C5*), 55.82 (s, C4c*), 55.66 (s, C9c), 55.02 (s, C4c), 43.36 (s, C1), 30.87-30.68 (s, C9b), 30.42 (s, C4b2*), 30.31 (s, C4b1* and C4b1 and C4b2).

rccc-isomer in boat conformation: $\delta$ (ppm) = 169.95 (s, C9a), 169.24 (s, C4a*), 168.70 (s, C4a), 149.64 (s, C9i), 147.53 (s, C4i*), 147.03 (s, C4i), 136.33 (s, C6i), 132.68 (s, C2i*), 132.34 (s, C3*), 131.77 (s, C2i), 130.73 (s, C3), 120.83 (s, C7), 116.58 (s, C5), 115.79 (s, C5*), 55.53 (s, C9c), 55.14 (s, C4c*), 55.07 (s, C4c), 43.36 (s, C1), 30.87-30.68 (s, C9b), 30.52 (s, C4b1), 30.31 (s, C4b1* and C4b2* and C4b2).

\[ \text{MALDI-TOF-MS (Dithranol)}: \text{ calcd. for C}_{100}H_{100}Br_{12}O_{24}: m/z = 2644.672 [M]^+; \text{ found: m/z = 2667.204 [M+Na]^+}, 2683.181 [M+K]^+. \]
11.2.1.4. Synthesis of $2,8,14,20$-tetrapentylpentacyclo[19.3.1.1$^3$.7.$^{13}$].9.$^{13}$.1$^{15}$.1$^{19}$]octacosa-1$(25)$.3$(28)$.4$.6$.9$(27)$.10$.12$.15$(26)$.16$.18$.21$.23$-dodecaene-4$.5$.6$.10$.11$.12$.16$.17$.-18$.22$.23$.24$-dodecayl dodekakis(2-bromo-2-methylpropanoate) (100)

1.00 g (1.20 mmol) 62, 4.63 ml (57.62 mmol) pyridine and 7.12 ml (57.62 mmol) 2-bromo-isobutyryl bromide (53) were reacted as described in the general procedure GP VI. The crude dodecabromo pyrogallolarene 100 was further purified by flash chromatography using chloroform ($R_f$ = 0.56). 2.87 g (91.3 % yield, m.p.: 186-187 °C) pure 100 were obtained as its $rccc$-isomer as a colorless solid.

$^1$H NMR (500.1 MHz, TCI, r.t.): $rccc$-isomer in boat conformation: $\delta$ (ppm) = 7.23 (s, 2 H, H3*), 6.15 (s, 2 H, H3), 4.26 (d, $^3J(H,H)$=12.9 Hz, 4 H, H1), 2.05 (s, 12 H, H4b2), 2.03 (s, 12 H, H4b1), 1.97 (s, 12 H, H5b), 1.95 (s, 12 H, H5b*), 1.91 (s, 12 H, H4b1*), 1.80 (s, 12 H, H4b2*), 1.77-1.55 (br. m, 8 H, H6), 1.17 (br. m, 8 H, H7), 1.11 (br. m, 16 H, H8/9), 0.74 (t, $^3J(H,H)$=6.6 Hz, 12 H, H10).

$^{13}$C NMR (125.7 MHz, TCI, r.t.): $rccc$-isomer in boat conformation: $\delta$ (ppm) = 168.80 (s, C4a), 167.28 (s, C4a*), 167.30 (s, C5a/5a*), 142.03 (s, C4i*), 138.99 (s, C4i), 137.13 (s, C5i*), 136.15 (s, C2i), 136.02 (s, C5i), 130.97 (s, C2i*), 125.67 (s, C3*), 124.10 (s, C3), 56.20 (s, C5c*), 56.06 (s, C4c*), 55.88 (s, C5c), 55.13 (s, C4c), 39.27 (s, C1), 35.27 (s, C6), 32.50 (s, C8), 31.77 (s, C5b*), 31.64 (s, C4b2), 31.60 (s, C4b1), 31.54 (s, C4b1*), 31.43 (s, C4b2*), 31.14 (s, C5b), 28.27 (s, C7), 22.91 (s, C9), 14.61 (s, C10).

MALDI-TOF-MS (Dithranol): calcd. for C$_{96}$H$_{124}$Br$_{12}$O$_{24}$: $m/z$ = 2620.859 [M]$^+$; found: $m/z$ = 2644.143 [M+Na]$^+$, 2660.139 [M+K]$^+$.

EA: calcd. for C$_{96}$H$_{124}$Br$_{12}$O$_{24}$: C 43.99 %, H 4.77 %; found: C 43.85 %, H 4.70 %.
11.2.1.5. Synthesis of 2,8,14,20-tetraundecylpentacyclo[19.3.1.1^3,7.1^9,13.1^15,19]octacosa-
1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,5,6,10,11,12,16,17,-
18,22,23,24-dodecayl dodecakis(2-bromo-2-methylpropanoate) (101)

1.00 g (0.85 mmol) 63, 3.30 ml (41.04 mmol) pyridine and 5.07 ml 
(41.04 mmol) 2-bromo-isobutyryl bromide (53) were reacted like de-
scribed in the general procedure GP VI. The crude dodecabromo py-
rogallolarene 101 was further purified by flash chromatography using 
a 1:5 mixture of n-pentane/chloroform ($R_f = 0.64$). 2.23 g (88.1 %
yield, m.p.: 95-96 °C) pure 101 were obtained as its recce-isomer as a colorless solid.

$^1$H NMR (500.1 MHz, TCI, r.t.): recce-isomer in boat conformation: $\delta$ (ppm) = 7.23 (s, 2 
H, H3*), 6.14 (s, 2 H, H3), 4.25 (d, $^3J(H,H)$=12.9 Hz, 4 H, H1), 2.05 (s, 12 H, H4b2), 2.03 (s, 
12 H, H4b1), 1.97 (s, 12 H, H5b), 1.94 (s, 12 H, H5b*), 1.91 (s, 12 H, H4b1*), 1.79 (s, 12 H, 
H4b2*), 1.78-1.55 (br. m, 8 H, H6), 1.17 (br. m, 8 H, H15), 1.13 (br. m, 64 H, H7-14), 0.78 (t, 
$^3J(H,H)$=6.9 Hz, 12 H, H16).

$^{13}$C NMR (125.7 MHz, TCI, r.t.): recce-isomer in boat conformation: $\delta$ (ppm) = 168.80 (s, 
C4a), 168.30 (s, C4a*), 167.27 (s, C5a/5a*), 142.01 (s, C4i*), 138.95 (s, C4i), 137.11 (s, 
C5i*), 136.17 (s, C2i), 135.99 (s, C5i), 130.95 (s, C2i*), 125.60 (s, C3*), 124.05 (s, C3), 
56.20 (s, C5e*), 56.07 (s, C4e*), 55.90 (s, C5c), 55.10 (s, C4c), 39.27 (s, C1), 35.26 (s, C6), 
32.21 (s, C14), 31.77 (s, C5b*), 31.62 (s, C4b2), 31.58 (s, C4b1), 31.54 (s, C4b1*), 31.42 (s, 
C4b2*), 31.11 (s, C5b), 30.44 (s, C8), 30.26-29.65 (s, C9-13), 28.59 (s, C7), 23.02 (s, C15), 
14.55 (s, C16).

MALDI-TOF-MS (Dithranol): calcd. for C$_{120}$H$_{172}$Br$_{12}$O$_{24}$: $m/z = 2957.235$ [M]$^+$; 

EA: calcd. for C$_{120}$H$_{172}$Br$_{12}$O$_{24}$: C 48.73 %, H 5.86 %; found: C 48.85 %, H 5.94 %.
11.2.1.6. Synthesis of 2,8,14,20-tetrakis{4-[(2-bromo-2-methylpropanoyl)oxy]phenyl}-pentacyclo[19.3.1.1^{3,7,1}^{9,13,1}^{15,19}]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,-18,21,23-dodecaene-4,5,6,10,11,12,16,17,18,22,23,24-dodecayl dodekas(2-bromo-2-methylpropanoate) (102)

1.00 g (1.09 mmol) 66, 5.59 ml (69.50 mmol) pyridine and 8.59 ml (69.50 mmol) 2-bromo-isobutyryl bromide (87) were reacted as described in the general procedure GP VI. 2.82 g (78.7 % yield) crude 102 were obtained as a slightly orange solid. The crude hexadecabromo pyrogallolarene 102 was further purified by flash chromatography using chloroform (Rf = 0.35). Only the rctt-isomer of 102 could be isolated, the rccc-isomer precipitated on the silica column. 1.73 g (48.2 % yield, m.p.: 220 °C decomp.) pure 102 were obtained as its rctt-isomer as a slightly orange solid.

\[
\text{1H-NMR} \ (500.1 \text{ MHz, TCl, r.t.}) \ rctt\text{-isomer in chair conformation:} \quad \delta \ (\text{ppm}) = 6.87 \ (\text{br. d, 4 H, H7a}), \ 6.75 \ (\text{br. d, 4 H, H8a}), \ 6.70 \ (\text{br. d, 4 H, H8b}), \ 6.31 \ (\text{br. s, 4 H, H7b}), \ 6.20 \ (\text{s, 2 H, H3}), \ 6.04 \ (\text{s, 2 H, H3*}), \ 5.68 \ (\text{br. s, 4 H, H1}), \ 2.01 \ (\text{s, 12 H, H4b1*}), \ 1.98 \ (\text{s, 12 H, H9b1 or H9b2}), \ 1.97 \ (\text{s, 12 H, H9b2 or H9b1}), \ 1.95 \ (\text{s, 12 H, H5b*}), \ 1.94 \ (\text{s, 6 H, H5b1}), \ 1.91 \ (\text{s, 6 H, H5b2}), \ 1.89 \ (\text{s, 12 H, H4b2*}), \ 1.54 \ (\text{s, 12 H, H4b1}), \ 1.43 \ (\text{s, 12 H, H4b2}).
\]

\[
\text{13C-NMR} \ (125.7 \text{ MHz, TCl, r.t.}) \ rctt\text{-isomer in chair conformation:} \quad \delta \ (\text{ppm}) = 170.33 \ (\text{s, C9a}), \ 168.90 \ (\text{s, C4a*}), \ 168.02 \ (\text{s, C5a*}), \ 167.34 \ (\text{s, C4a}), \ 166.27 \ (\text{s, C5a}), \ 149.99 \ (\text{s, C9i}), \ 140.93 \ (\text{s, C4i*}), \ 140.45 \ (\text{s, C4i}), \ 137.37 \ (\text{s, C2i}), \ 136.52 \ (\text{s, C2i*}), \ 135.22 \ (\text{br. s, C6i}), \ 134.72 \ (\text{s, C5i* or C5i}), \ 133.51 \ (\text{s, C5i or C5i*}), \ 131.16 \ (\text{s, C7a}), \ 130.38 \ (\text{s, C7b and C3*}), \ 127.80 \ (\text{s, C3}), \ 121.71 \ (\text{s, C8b}), \ 120.98 \ (\text{s, C8a}), \ 56.17 \ (\text{s, C5c*}), \ 56.12 \ (\text{s, C9c}), \ 55.87 \ (\text{s, C4c*}), \ 55.72 \ (\text{s, C5c}), \ 55.41 \ (\text{s, C4c}), \ 44.33 \ (\text{s, C1}), \ 31.80 \ (\text{s, C5b1}), \ 31.40 \ (\text{s, C4b1*}), \ 31.25 \ (\text{s, C9b1 or C9b2}), \ 31.17 \ (\text{s, C4b1 and C5b2}), \ 31.14 \ (\text{s, C4b2}), \ 30.99 \ (\text{s, C4b2* and C9b2 or C9b1}).
\]

MALDI-TOF-MS (Dithranol): calcld. for C_{116}H_{120}Br_{16}O_{32}: m/z = 3304.457 [M]^+; found: m/z = 3327.652 [M+Na]^+, 3343.564 [M+K]^+.

EA: calcld. for C_{116}H_{120}Br_{16}O_{32}: C 42.16 %, H 3.66 %; found: C 42.18 %, H 3.67 %.
11.3. Atom transfer radical polymerization of styrene using mono-, di-, tri-, octa-, dodeca- and hexadecafunctional initiators

11.3.1. General procedure for the atom transfer radical polymerization of styrene using mono-, di-, tri-, octa-, dodeca- and hexadecafunctional initiators – GP VII

According to Table 12 and Table 13 accurate amounts of initiators 90 to 92, 95 to 102, CuBr, bpy (e. g. 2,2'-bbpy) and styrene (29) were weighted into a 25 ml Schlenk tube equipped with a magnetic stir bar. The mixture was flushed with argon for 1 minute and further degassed by four freeze-thaw cycles (10^{-4} mbar, liquid N_2). After sealing the tube by a plug in an argon counter stream and fixation by a clamp, the mixture was transferred to a 120°C preheated oil bath. Exactly after 4 h the polymerization reaction was immediately quenched by transferring the tube to an ice bath. The mixture was diluted by adding 5.00 ml chloroform-\textit{d}_1 (CDCl_3) and stirred until homogenization was achieved. A NMR sample was taken to determine the reaction conversion. The residual mixture was purified from the catalyst by filtration over a short plug filled with neutral aluminum oxide and eluting with CH_2Cl_2. The resulting clear solution was evaporated to approx. 10 ml and the desired polymer was precipitated from cold MeOH, filtrated and dried in high vacuum over night.

97

\[ \text{L} = 2,2'\text{-bpy or} \]
\[ 4,4'\text{-di-}^{\prime}\text{Bu-2,2'-bpy} \]

Figure 120. Bulk-ATRP of styrene conducted with octafunctional initiator 97, as example.
Table 12. Amounts of octa-, dodeca- and hexadecafunctional initiators 97 to 102 (I), monomer (M), ligand (L) and CuBr (Cu) used for ATRP of styrene (29) in bulk with CuBr/tbbpy and CuBr/bpy system as atom transfer agent at 120 °C.

<table>
<thead>
<tr>
<th>Initiator</th>
<th>$M_I$ (g/mol)</th>
<th>$n(I):n(M):n(L):n(Cu)$</th>
<th>Ligand</th>
<th>$m(I)$ (mg)</th>
<th>$m(M)$ (mg)</th>
<th>$m(L)$ (mg)</th>
<th>$m(Cu)$ (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>97-Br$_8$</td>
<td>1961</td>
<td>1:100:3:1</td>
<td>tbbpy</td>
<td>24.5</td>
<td>1041.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>97-Br$_8$</td>
<td>1961</td>
<td>1:250:3:1</td>
<td>tbbpy</td>
<td>24.5</td>
<td>2603.8</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>97-Br$_8$</td>
<td>1961</td>
<td>1:500:3:1</td>
<td>tbbpy</td>
<td>24.5</td>
<td>5207.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>97-Br$_8$</td>
<td>1961</td>
<td>1:500:3:1</td>
<td>bpy</td>
<td>24.5</td>
<td>5207.5</td>
<td>46.9</td>
<td>14.4</td>
</tr>
<tr>
<td>97-Br$_8$</td>
<td>1961</td>
<td>1:1000:3:1</td>
<td>tbbpy</td>
<td>24.5</td>
<td>10415.0</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>98-Br$_8$</td>
<td>2298</td>
<td>1:100:3:1</td>
<td>tbbpy</td>
<td>28.7</td>
<td>1041.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>98-Br$_8$</td>
<td>2298</td>
<td>1:500:3:1</td>
<td>tbbpy</td>
<td>28.7</td>
<td>5207.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>98-Br$_8$</td>
<td>2298</td>
<td>1:500:3:1</td>
<td>bpy</td>
<td>28.7</td>
<td>5207.5</td>
<td>46.9</td>
<td>14.4</td>
</tr>
<tr>
<td>99-Br$_{12}$</td>
<td>2645</td>
<td>1:100:3:1</td>
<td>tbbpy</td>
<td>22.0</td>
<td>1041.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>99-Br$_{12}$</td>
<td>2645</td>
<td>1:500:3:1</td>
<td>tbbpy</td>
<td>22.0</td>
<td>5207.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>99-Br$_{12}$</td>
<td>2645</td>
<td>1:500:3:1</td>
<td>bpy</td>
<td>22.0</td>
<td>5207.5</td>
<td>46.9</td>
<td>14.4</td>
</tr>
<tr>
<td>100-Br$_{12}$</td>
<td>2621</td>
<td>1:100:3:1</td>
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<td>21.8</td>
<td>1041.5</td>
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<td>14.4</td>
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<tr>
<td>100-Br$_{12}$</td>
<td>2621</td>
<td>1:500:3:1</td>
<td>tbbpy</td>
<td>21.8</td>
<td>5207.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>100-Br$_{12}$</td>
<td>2621</td>
<td>1:500:3:1</td>
<td>bpy</td>
<td>21.8</td>
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</tr>
<tr>
<td>101-Br$_{12}$</td>
<td>2958</td>
<td>1:100:3:1</td>
<td>tbbpy</td>
<td>24.7</td>
<td>1041.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>101-Br$_{12}$</td>
<td>2958</td>
<td>1:500:3:1</td>
<td>tbbpy</td>
<td>24.7</td>
<td>5207.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>101-Br$_{12}$</td>
<td>2958</td>
<td>1:500:3:1</td>
<td>bpy</td>
<td>24.7</td>
<td>5207.5</td>
<td>46.9</td>
<td>14.4</td>
</tr>
<tr>
<td>102-Br$_{16}$</td>
<td>3305</td>
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<td>tbbpy</td>
<td>20.7</td>
<td>1041.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>102-Br$_{16}$</td>
<td>3305</td>
<td>1:500:3:1</td>
<td>tbbpy</td>
<td>20.7</td>
<td>5207.5</td>
<td>80.4</td>
<td>14.4</td>
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<tr>
<td>102-Br$_{16}$</td>
<td>3305</td>
<td>1:500:3:1</td>
<td>bpy</td>
<td>20.7</td>
<td>5207.5</td>
<td>46.9</td>
<td>14.4</td>
</tr>
</tbody>
</table>
Table 13. Amounts of mono-, di- and trifunctional initiators 90 to 92, 95 and 96 (I), monomer (M), ligand (L) and CuBr (Cu) used for ATRP of styrene (29) at 120 °C.

<table>
<thead>
<tr>
<th>Initiator</th>
<th>M&lt;sub&gt;i&lt;/sub&gt; (g/mol)</th>
<th>n(I):n(M):n(L):n(Cu)</th>
<th>Ligand</th>
<th>m(I) (mg)</th>
<th>m(M) (mg)</th>
<th>m(L) (mg)</th>
<th>m(Cu) (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90-Br&lt;sub&gt;1&lt;/sub&gt;</td>
<td>242</td>
<td>1:500:3:1</td>
<td>t&lt;sub&gt;bbpy&lt;/sub&gt;</td>
<td>24.2</td>
<td>5207.5</td>
<td>46.9</td>
<td>14.4</td>
</tr>
<tr>
<td>90-Br&lt;sub&gt;1&lt;/sub&gt;</td>
<td>242</td>
<td>1:500:3:1</td>
<td>bpy</td>
<td>24.2</td>
<td>5207.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>96-Br&lt;sub&gt;1&lt;/sub&gt;</td>
<td>694</td>
<td>1:500:3:1</td>
<td>t&lt;sub&gt;bbpy&lt;/sub&gt;</td>
<td>69.4</td>
<td>5207.5</td>
<td>46.9</td>
<td>14.4</td>
</tr>
<tr>
<td>96-Br&lt;sub&gt;1&lt;/sub&gt;</td>
<td>694</td>
<td>1:500:3:1</td>
<td>bpy</td>
<td>69.4</td>
<td>5207.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>91-Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>408</td>
<td>1:500:3:1</td>
<td>t&lt;sub&gt;bbpy&lt;/sub&gt;</td>
<td>20.4</td>
<td>5207.5</td>
<td>46.9</td>
<td>14.4</td>
</tr>
<tr>
<td>91-Br&lt;sub&gt;2&lt;/sub&gt;</td>
<td>408</td>
<td>1:500:3:1</td>
<td>bpy</td>
<td>20.4</td>
<td>5207.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>92-Br&lt;sub&gt;3&lt;/sub&gt;</td>
<td>573</td>
<td>1:500:3:1</td>
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<td>5207.5</td>
<td>46.9</td>
<td>14.4</td>
</tr>
<tr>
<td>92-Br&lt;sub&gt;3&lt;/sub&gt;</td>
<td>573</td>
<td>1:500:3:1</td>
<td>bpy</td>
<td>19.1</td>
<td>5207.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
<tr>
<td>95-Br&lt;sub&gt;3&lt;/sub&gt;</td>
<td>879</td>
<td>1:500:3:1</td>
<td>t&lt;sub&gt;bbpy&lt;/sub&gt;</td>
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<td>5207.5</td>
<td>46.9</td>
<td>14.4</td>
</tr>
<tr>
<td>95-Br&lt;sub&gt;3&lt;/sub&gt;</td>
<td>879</td>
<td>1:500:3:1</td>
<td>bpy</td>
<td>29.3</td>
<td>5207.5</td>
<td>80.4</td>
<td>14.4</td>
</tr>
</tbody>
</table>

11.3.1.1. Results of atom transfer radical polymerization of styrene in bulk using mono-, di- and trifunctional initiators and either CuBr/bpy or CuBr/t<sub>bbpy</sub> as atom transfer agent with [I]:[M] = 1:500

Table 14. Results of NMR- and SEC-RI measurements of mono-, di- and triarm PS stars for n(I):n(M) = 1:500 using CuBr/t<sub>bbpy</sub> and CuBr/bpy at 120 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Ligand</th>
<th>&lt;sup&gt;1&lt;/sup&gt;H&lt;sub&gt;mono&lt;/sub&gt; integral</th>
<th>&lt;sup&gt;1&lt;/sup&gt;H&lt;sub&gt;poly&lt;/sub&gt; integral</th>
<th>Conv. %</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (g/mol)</th>
<th>M&lt;sub&gt;w&lt;/sub&gt; (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90-Br&lt;sub&gt;1&lt;/sub&gt;</td>
<td>bpy</td>
<td>1.00</td>
<td>0.95</td>
<td>24</td>
<td>9170</td>
<td>12250</td>
<td>1.34</td>
</tr>
<tr>
<td>2</td>
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<td>t&lt;sub&gt;bbpy&lt;/sub&gt;</td>
<td>1.00</td>
<td>0.93</td>
<td>24</td>
<td>5540</td>
<td>6150</td>
<td>1.11</td>
</tr>
<tr>
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<td>bpy</td>
<td>1.00</td>
<td>0.81</td>
<td>21</td>
<td>11730</td>
<td>13760</td>
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</tr>
<tr>
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<td>0.48</td>
<td>14</td>
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<td>5710</td>
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<td>1.00</td>
<td>0.87</td>
<td>22</td>
<td>16040</td>
<td>19300</td>
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</tr>
<tr>
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<td>t&lt;sub&gt;bbpy&lt;/sub&gt;</td>
<td>1.00</td>
<td>0.65</td>
<td>18</td>
<td>13340</td>
<td>14900</td>
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<tr>
<td>7</td>
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<td>20</td>
<td>23390</td>
<td>28830</td>
<td>1.23</td>
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<tr>
<td>8</td>
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<td>t&lt;sub&gt;bbpy&lt;/sub&gt;</td>
<td>1.00</td>
<td>0.25</td>
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<td>24880</td>
<td>30130</td>
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Table 15. Results of SEC-MALLS and MALDI-TOF-MS measurements of mono-, di- and triarm PS stars for n(I):n(M) = 1:500 using CuBr/bbpy and CuBr/bpy at 120 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Ligand</th>
<th>(M_n) g/mol</th>
<th>(M_w) g/mol</th>
<th>PDI</th>
<th>(M_n) g/mol</th>
<th>(M_w) g/mol</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90-Br1</td>
<td>bpy</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>5300</td>
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</tr>
<tr>
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<td>96-Br1</td>
<td>bpy</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7900</td>
<td>10000</td>
<td>1.26</td>
</tr>
<tr>
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<td>96-Br1</td>
<td>'bbpy'</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4600</td>
<td>5100</td>
<td>1.11</td>
</tr>
<tr>
<td>5</td>
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<td>bpy</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20100</td>
<td>22500</td>
<td>1.12</td>
</tr>
<tr>
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<td>'bbpy'</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<td>-</td>
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<td>-</td>
<td>8400</td>
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11.3.1.2. Results of atom transfer radical polymerization of styrene in bulk using octa-, dodeca- and hexadecafunctional initiators and CuBr/\textit{bbpy} as atom transfer agent with \([I]:[M] = 1:100\)

Table 16. Results of NMR- and SEC-RI measurements of octa-, dodeca- and hexadecaarm PS stars for \(n(I):n(M) = 1:100\) using CuBr/\textit{bbpy} at 120 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Ligand</th>
<th>(^1\text{H}^{\text{monomer}}) integral</th>
<th>(^1\text{H}^{\text{polymer}}) integral</th>
<th>Conv. %</th>
<th>(M_n ) g/mol</th>
<th>(M_w ) g/mol</th>
<th>PDI</th>
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<td>81</td>
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<td>122800</td>
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1 ml DMF added to polymerization mixture

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<th>(^1\text{H}^{\text{monomer}}) integral</th>
<th>(^1\text{H}^{\text{polymer}}) integral</th>
<th>Conv. %</th>
<th>(M_n ) g/mol</th>
<th>(M_w ) g/mol</th>
<th>PDI</th>
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<td>13800</td>
<td>1.06</td>
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1 drop CHCl\(_3\) added to polymerization mixture

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<th>(^1\text{H}^{\text{monomer}}) integral</th>
<th>(^1\text{H}^{\text{polymer}}) integral</th>
<th>Conv. %</th>
<th>(M_n ) g/mol</th>
<th>(M_w ) g/mol</th>
<th>PDI</th>
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<td>-</td>
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<td>7400</td>
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11.3.1.3. Results of atom transfer radical polymerization of styrene in bulk using octa-, dodeca- and hexadecafunctional initiators and CuBr/\(t^\text{bpy}\) as atom transfer agent with [I]:[M] = 1:500

Table 17. Results of NMR- and SEC-RI measurements of octa-, dodeca- and hexadecaarm PS stars for n(I):n(M) = 1:500 using CuBr/\(t^\text{bpy}\) at 120 °C.

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<th>(\text{^1H}_{\text{poly}}\text{ integral})</th>
<th>Conv. %</th>
<th>(M_n) g/mol</th>
<th>(M_w) g/mol</th>
<th>PDI</th>
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<td>52400</td>
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<td>31100</td>
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<td>23800</td>
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<td>28800</td>
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<td>36000</td>
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<td>23000</td>
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<td>21500</td>
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<td>21500</td>
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<td>4600</td>
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11.3.1.4. Results of atom transfer radical polymerization of styrene in bulk using octa-, dodeca- and hexadeca-functional initiators and CuBr/bpy as atom transfer agent with $[I] : [M] = 1:500$

Table 18. Results of NMR- and SEC-RI measurements of octa-, dodeca- and hexadecaarm PS stars for $n(I):n(M) = 1:500$ using CuBr/bpy at 120 °C.

<table>
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<th>Initiator</th>
<th>Ligand</th>
<th>$^1$H mono integral</th>
<th>$^1$H poly integral</th>
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<th>$M_w$ g/mol</th>
<th>PDI</th>
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<td>74200</td>
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<td>14</td>
<td>54500</td>
<td>59300</td>
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<td>63700</td>
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11.3.1.5. Results of atom transfer radical polymerization of styrene in bulk using octa-functional initiator 97 and CuBr/tbbpy as atom transfer agent with [I]:[M] = 1:100 – 1:1000

Table 19. Results of SEC-RI measurements for octaarm star polymers based on 97-Br₈ for n(I): n(M) = 1:100 – 1:1000 using CuBr/tbbpy and DMF as solvent at 120 °C.

<table>
<thead>
<tr>
<th>Entry</th>
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<th>Ligand</th>
<th>n(I):n(M):n(L):n(Cu)</th>
<th>Vₛ₀вл</th>
<th>Mₙ</th>
<th>Mₘ</th>
<th>PDI</th>
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<td>67100</td>
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<tr>
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<td>-</td>
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</table>
11.3.1.6. Results of kinetical investigation of atom transfer radical polymerization of styrene in bulk using dodecafunctional initiators and CuBr/\(\text{bbpy}\) or CuBr/bpy as atom transfer agent with \([I]:[M] = 1:500\)

Table 20. Results of SEC-RI measurements for dodecaarm star polymers based on \(99\text{-Br}_{12}\) and \(100\text{-Br}_{12}\) for \(n(I) : n(M) = 1:500\) using CuBr/\(\text{bbpy}\) at 120 °C.

<table>
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<tr>
<th>Initiator</th>
<th>Ligand</th>
<th>(n(I):n(M):n(L):n(Cu))</th>
<th>Time</th>
<th>Conv.</th>
<th>(M_n)</th>
<th>(M_w)</th>
<th>PDI</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>g/mol</td>
<td>g/mol</td>
<td></td>
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<tr>
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<td>bpy</td>
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<td>6</td>
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<td>10</td>
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<td>22000</td>
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<td>39</td>
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<td>167700</td>
<td>2.11</td>
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</table>
11.4. Cleavage of polymer arms from octa-, dodeca and hexadecabifunctional star polymers by alkaline saponification

11.4.1. General procedure for the cleavage of polymer arms from octa-, dodeca and hexadecabifunctional star polymers by alkaline saponification – GP VIII

20.00 mg of the polymer was weighted into a 10 ml round bottom flask. 2.50 ml THF followed by 2.50 ml 2.0 molar KOH-solution. The flask was sealed with a plug which was fixed by a clamp and heated to 80 °C for 24 h. After cooling to room temperature the mixture was evaporated to dryness and the residual solid suspended in chloroform. After washing with 0.5 molar HCl-solution followed by sat. NaHCO₃-solution the organic layer was separated and evaporated to dryness. Complete evaporation of residual water was achieved at 50 °C in high vacuum.

**Figure 121.** Cleavage of the PS arms by alkaline saponification of the ester-linkages giving resorcinarene-core 59 and individual arms of the star polymers shown for a octaarm-star polymer derived from 97 as example.
12. Dendrimers based on plurifunctional resorcin- and pyrogallolarenes

12.1. Synthesis of AB$_2$-monomers and dendrons suitable for the convergent approach towards dendrimers via Williamson etherification and “click”-reaction

12.1.1. Synthesis of methyl 3,5-dihydroxybenzoate (104)

100.00 g (648.84 mmol) dihydroxybenzoic acid (103, DHB) were weighted into a 1000 ml three necked round bottom flask. 600 ml MeOH were added and the mixture was stirred until complete dissolution of the solid. The solution was flushed with N$_2$ for 10 minutes. 50 ml (981.36 mmol) conc. H$_2$SO$_4$ were added and the solution has been heated under reflux for 48 h. After cooling to room temperature the solution was neutralized with sat. NaHCO$_3$-solution and extracted 4 times with Et$_2$O. The combined organic phases were dried over MgSO$_4$ and evaporated to dryness. The crude product was crystallized several times from H$_2$O. 98.47 g (90.3 % yield, m.p.: 168 °C) of 104 were obtained as slightly yellow solid.\[256\]

$^{1}$H NMR (300.1 MHz, DMSO, r.t.): $\delta$ (ppm) = 9.61 (s, 2 H, OH), 6.81 (s, 2 H, H2), 6.47 (t, $\delta J(H,H)$=2.2 Hz, 1 H, H4), 3.78 (s, 3 H, H6).

$^{13}$C NMR (75.5 MHz, DMSO, r.t.): $\delta$ (ppm) = 166.26 (s, C5i), 158.53 (s, C3i), 131.32 (s, C1i), 107.20 (s, C2), 107.13 (s, C4), 51.92 (s, C6).

ESI-MS (MeOH/NH$_4$OAc) : calcd. for C$_8$H$_8$O$_4$: m/z = 168.042 [M]$^+$; found: m/z = 169.0 [M+H]$^+$. 

EA: calcd. for C$_8$H$_8$O$_4$: C 57.14 %, H 4.80 %; found: C 57.02 %, H 4.88 %.

12.1.2. Synthesis of methyl 3,5-bis(prop-2-yn-1-yloxy)benzoate (105)

40.00 g (237.89 mmol) 104 and 82.13 g (594.69 mmol) prior dried K$_2$CO$_3$ were weighted into a 1000 ml three necked round bottom flask equipped with a condenser. 600 ml dry acetonitrile were added and the reaction mixture was flushed with N$_2$ for 10 minutes.
Practical part

with argon for 10 minutes. After sealing the equipment with an argon-balloon, 66.24 ml (594.69 mmol) 80% propargylbromide solution (86) in toluene were added by syringe. The mixture was heated to 90 °C for 3 days. After cooling to room temperature, the mixture was filtered and the solid residue was washed with 200 ml hot chloroform. The combined organic phases were evaporated to dryness and the residue was dissolved in the appropriate amount of hot MeOH to yield a saturated solution. The desired product was obtained through purification by repeated crystallization from MeOH at -30 °C followed by drying under high vacuum. 57.99 g (99.8% yield, m.p.: 108 °C) pure 105 were obtained as slightly yellow solid.

\[^1\text{H NMR}\ (300.1 \text{ MHz, CDCl}_3, \text{ r.t.}): \delta \ (\text{ppm}) = 7.28 \ (d, J(H,H)=2.3 \text{ Hz}, 2 \text{ H}, H2), 6.80 \ (t, J(H,H)=2.3 \text{ Hz}, 1 \text{ H}, H4), 4.70 \ (d, J(H,H)=2.3 \text{ Hz}, 4 \text{ H}, H7), 3.89 \ (s, 3 \text{ H}, H6), 2.53 \ (t, J(H,H)=2.4 \text{ Hz}, 2 \text{ H}, H9).\]

\[^{13}\text{C NMR}\ (75.5 \text{ MHz, CDCl}_3, \text{ r.t.}): \delta \ (\text{ppm}) = 166.40 \ (s, C5i), 158.55 \ (s, C3i), 132.20 \ (s, C1i), 108.99 \ (s, C2), 107.58 \ (s, C4), 77.99 \ (s, C8i), 75.91 \ (d, C9), 56.15 \ (t, C7), 52.28 \ (q, C6).\]

\[^{\text{ESI-MS}}\ (\text{MeOH/\text{NH}_4\text{OAc}}): \text{calcd. for C}_{14}\text{H}_{12}\text{O}_4: m/z = 244.074 [M]^+;\]
\ndefound: m/z = 245.0 [M+H]^+.\]

\[^{\text{EA}}:\ \text{calcd. for C}_{14}\text{H}_{12}\text{O}_4: \text{ C 68.85 \%}, \text{ H 4.95 \%}; \text{found: C 68.53 \%}, \text{ H 4.97 \%}.\]

\[^{\text{SXD}}:\]

Empirical formula C_{14}H_{12}O_{4}
Moiety formula C_{14}H_{12}O_{4}
Formula weight 244.24
Temperature 193(2) K
Wavelength 0.71073 Å
Crystal system Orthorhombic
Space group Pca2_1 (No. 29)
Unit cell dimensions $a = 21.402(2)$ Å, $\alpha = 90.00^\circ$
$\beta = 90.00^\circ$
$\gamma = 90.00^\circ$
Volume 1212.6(3) Å$^3$
Z 4
Density (calculated) 1.338 Mg/m³
Absorption coefficient 0.098 mm⁻¹
F(000) 512
Crystal size 0.60 x 0.49 x 0.16 mm³
Theta range for data collection 3.40 to 35.00°.
Index ranges -33 <= h <= 33, -5 <= k <= 6, -33 <= l <= 33
Reflections collected 17235
Independent reflections 4987 [R(int) = 0.0240]
Completeness to theta = 35.00° 97.0 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.9844 and 0.9433
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 4223 / 1 / 164
Goodness-of-fit on F² 1.052
Final R indices [I > 2σ(I)] R1 = 0.0374, wR2 = 0.0917
R indices (all data) R1 = 0.0495, wR2 = 0.0980
Absolute structure parameter 0.2(5)
Largest diff. peak and hole 0.403 and -0.184 e.Å⁻³

Figure 122. ORTEP-plot of the asymmetric unit of 105 with 50 % probability level. Hydrogen atoms omitted for clarity.
12.1.3. Synthesis of [3,5-bis(prop-2-yn-1-yloxy)phenyl]methanol (106)

20.00 g (81.89 mmol) 105 were weighted into a flame dried 500 ml three necked round bottom flask, equipped with a condenser and two septa, in an argon counter stream. By syringe 250 ml dry THF were added. After complete dissolution, subsequently 49.13 ml (49.13 mmol) of a 1 M LiAlH₄-solution in THF were added slowly by syringe under cooling with an ice bath. The mixture was stirred for 24 h and refluxed for 2 h. After quenching with ethyl acetate and 50 ml 1.0 M HCl-solution, the liquid was transferred to a 1 l separating funnel and diluted with 250 ml Et₂O. Washing twice with sat. NaHCO₃-solution and brine afforded a yellow solution, which was dried over MgSO₄ and evaporated to dryness. The crude product was dissolved in a mixture of EtOH/n-pentane and recrystallized several times at – 30 °C. 15.12 g (85.4 % yield, m.p.: 70 °C) pure 106 were obtained as slightly yellow solid.

$^1$H NMR (300.1 MHz, CDCl₃, r.t.): $\delta$ (ppm) = 6.59 (d, $^4$J(H,H)=2.3 Hz, 2 H, H2), 6.51 (t, $^4$J(H,H)=2.3 Hz, 1 H, H4), 4.64 (d, $^4$J(H,H)=2.4 Hz, 4 H, H6), 4.60 (s, 2 H, H5), 2.51 (t, $^4$J(H,H)=2.4 Hz, 2 H, H8), 2.08 (br. s, 1 H, OH).

$^{13}$C NMR (75.5 MHz, CDCl₃, r.t.): $\delta$ (ppm) = 158.84 (s, C3i), 143.60 (s, C1i), 106.28 (s, C2), 101.55 (s, C4), 78.40 (s, C7i), 75.61 (d, C8), 64.99 (s, C5), 55.93 (d, C6).

ESI-MS (MeOH/NH₄OAc): calcd. for C₁₃H₁₂O₃: $m/z = 216.079$ [M]$^+$;
found: $m/z = 217.2$ [M+H]$^+$.

EA: calcd. for C₁₃H₁₂O₃: C 72.21 %, H 5.59 %; found: 72.24 C %, H 5.61 %.

SXD:

Empirical formula C₁₃H₁₂O₃
Formula weight 216.23
Temperature 198(2) K
Wavelength 0.71073 Å
Crystal system Monoclinic
Space group P2₁/c (No. 14)
Unit cell dimensions $a = 15.559(2)$ Å, $\alpha = 90^\circ$. 
b = 4.4853(3) Å \hspace{1cm} \beta = 104.54(1)°.
\[ \text{Volume} \hspace{1cm} 1155.4(2) \text{ Å}^3 \]
\[ \text{Z} \hspace{1cm} 4 \]
\[ \text{Density (calculated)} \hspace{1cm} 1.243 \text{ Mg/m}^3 \]
\[ \text{Absorption coefficient} \hspace{1cm} 0.088 \text{ mm}^{-1} \]
\[ \text{F}(000) \hspace{1cm} 456 \]
\[ \text{Crystal size} \hspace{1cm} 0.54 \times 0.19 \times 0.10 \text{ mm}^3 \]
\[ \text{Theta range for data collection} \hspace{1cm} 3.17 \text{ to } 30.00°. \]
\[ \text{Index ranges} \hspace{1cm} -18 \leq h \leq 18, -5 \leq k \leq 5, -20 \leq l \leq 20 \]
\[ \text{Reflections collected} \hspace{1cm} 30164 \]
\[ \text{Independent reflections} \hspace{1cm} 3322 \ [R(\text{int}) = 0.0414] \]
\[ \text{Completeness to theta = 30.00°} \hspace{1cm} 98.5 \% \]
\[ \text{Absorption correction} \hspace{1cm} \text{Semi-empirical from equivalents} \]
\[ \text{Max. and min. transmission} \hspace{1cm} 0.9912 \text{ and } 0.9540 \]
\[ \text{Refinement method} \hspace{1cm} \text{Full-matrix least-squares on } F^2 \]
\[ \text{Data / restraints / parameters} \hspace{1cm} 2313 / 0 / 145 \]
\[ \text{Goodness-of-fit on } F^2 \hspace{1cm} 1.043 \]
\[ \text{Final R indices [I>2sigma(I)]} \hspace{1cm} R1 = 0.0455, wR2 = 0.0965 \]
\[ \text{R indices (all data)} \hspace{1cm} R1 = 0.0786, wR2 = 0.1123 \]
\[ \text{Largest diff. peak and hole} \hspace{1cm} 0.301 \text{ and } -0.198 \text{ e.Å}^{-3} \]

**Table 21.** Hydrogen-bonds for 106 [Å and °].

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<th>D-H...A</th>
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<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
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<td>0.84</td>
<td>1.89</td>
<td>2.717(1)</td>
<td>166.4</td>
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</table>

Symmetry transformations used to generate equivalent atoms:
#1 -x,y-1/2,-z-1/2
**Figure 123.** ORTEP-plot of the asymmetric unit of 106 with 50 % probability level. Hydrogen atoms omitted for clarity.

**Figure 124.** Packing diagram of 106 showing the intermolecular hydrogen bonds and weak CH···O interactions.
12.1.4. Synthesis of 1-(chloromethyl)-3,5-bis(prop-2-yn-1-yloxy)benzene (107)

15.00 g (69.37 mmol) 106 were weighted into a 500 ml three necked round bottom flask. 250 ml dry CH₂Cl₂ followed by 8.40 ml (104.10 mmol) dry pyridine were added. The mixture was cooled to 0 °C and flushed with argon for 10 min. Afterwards subsequently a solution of 7.57 ml (104.10 mmol) thionylchloride in 25 ml CH₂Cl₂ were added through a 50 ml dropping funnel. Stirring for 1 week at room temperature followed by quenching with H₂O afforded a brownish mixture, which was separated from the aqueous phase. Washing twice with H₂O, NaHCO₃-solution and brine, gave a slightly brighter solution, which was dried over MgSO₄ and evaporated to dryness. The crude product was distillated by Kugel-Rohr distillation under high vacuum. The resulting yellow oil was dissolved in Et₂O and precipitated at -30 °C. 9.90 g (60.8 % yield, m.p.: 53 °C) pure 107 were obtained as colorless powder.

**¹H NMR** (300.1 MHz, CDCl₃, r.t.): δ (ppm) = 6.64 (d, 4J(H,H)=2.3 Hz, 2 H, H2), 6.57 (t, 4J(H,H)=2.3 Hz, 1 H, H4), 4.67 (d, 4J(H,H)=2.4 Hz, 4 H, H6), 4.51 (s, 2 H, H5), 2.54 (t, 4J(H,H)=2.4 Hz, 2 H, H8).

**¹³C NMR** (75.5 MHz, CDCl₃, r.t.): δ (ppm) = 158.83 (s, C3i), 143.89 (s, C1i), 139.69 (s, C1i), 108.27 (s, C2), 102.37 (s, C4), 78.20 (s, C7i), 75.76 (s, C8), 56.02 (s, C6), 46.00 (s, C5).

**GC-MS**: calcd. for C₁₃H₁₁ClO₂: m/z = 234.045 [M]+;
found: m/z = 234 [M+H]+.

**EA**: calcd. for C₁₃H₁₁ClO₂: C 66.53 %, H 4.72 %; found: C 66.48 %, H 4.67 %.

12.1.5. Synthesis of (azidomethyl)benzene (109)

A stock solution of 0.5 mol NaN₃ in DMSO was prepared by stirring 8.13 g (125.00 mmol) NaN₃ in 250 ml DMSO in a 500 ml round bottom flask for 24 h at 25 °C. 242.00 ml (121.00 mmol) of the solution were transferred to a 500 ml round bottom flask equipped with a magnetic stir bar, condenser and a 25 ml dropping funnel. 18.81 g (110.00 mmol) benzyl bromide (108) were added dropwise over a period of 10 min. The mix-
ture was heated to 80 °C and stirred for 24 h. The complete conversion to benzyl azide (109) was confirmed by TLC analysis. The reaction was quenched with H2O (slightly exothermic) and stirred until cooling to r.t. The mixture was extracted with Et2O (3x 100 ml) and the combined organic layers were washed with H2O and brine. After drying over MgSO4 and removal of the solvent by evaporation at low temperature, the crude product was purified by flash-chromatography using CH2Cl2. 14.62 g (99.8 % yield) benzyl azide (109) were obtained as yellow oil.253

\[
^{1}H \text{ NMR (300.1 MHz, CDCl}_3, \text{ r.t.}): \delta \text{ (ppm) = 7.45-7.29 (m, 5 H, H2-4), 4.35 (s, 2 H, H5).}
\]

\[
^{13}C \text{ NMR (75.5 MHz, CDCl}_3, \text{ r.t.}): \delta \text{ (ppm) = 135.32 (s, C1i), 128.78 (s, C2), 128.25 (s, C4), 128.16 (s, C3), 54.73 (s, C5).}
\]

ESI-MS (MeOH/NH4OAc) : calcd. for C7H7N3: \( m/z = 133.064 \) [M]+; found: \( m/z = 133 \) [M+H]+.

EA: calcd. for C43H55Br3O6: C 63.14 %, H 5.30 %, N 31.56%; found: C 63.20 %, H 5.34 %, N 31.51 %.

12.1.6. Synthesis of bromotris(triphenylphosphine)copper (110)

5.00 g (19.06 mmol) PPh3 and 0.91 g (6.35 mmol) CuBr were weighted into a 100 ml round bottom flask equipped with a condenser. 50 ml chloroform were added and the mixture was refluxed for 4 h. After cooling to room temperature, the clear solution was evaporated to approx. 25 ml and cooled to -30 °C. The colorless precipitate was filtered and further purified by recrystallization from chloroform. 5.53 g (92.4 % yield, 166-167 °C) pure 110 were obtained as colorless solid.257,258

SXD:

<p>| Empirical formula | ( \text{C}<em>{56}\text{H}</em>{47}\text{BrCl}<em>{5}\text{CuP}</em>{3} ) |
| Moiety formula | ( \text{C}<em>{54}\text{H}</em>{45}\text{BrCuP}<em>{3} \cdot 2(\text{CHCl}</em>{3}) ) |
| Formula weight | 1169.00 |
| Temperature | 198(2) K |</p>
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<th>Property</th>
<th>Value</th>
</tr>
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<tr>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/n$ (No. 14)</td>
</tr>
</tbody>
</table>
| Unit cell dimensions           | $a = 11.690(3)$ Å, $\alpha = 90^\circ$.  
|                                | $b = 22.678(3)$ Å, $\beta = 91.32(1)^\circ$.  
|                                | $c = 20.080(8)$ Å, $\gamma = 90^\circ$.  |
| Volume                         | 5322(3) Å³                      |
| $Z$                            | 4                               |
| Density (calculated)           | 1.459 Mg/m³                     |
| Absorption coefficient         | 1.590 mm⁻¹                      |
| $F(000)$                       | 2376                            |
| Crystal size                   | 0.30 x 0.30 x 0.25 mm³          |
| Theta range for data collection| 3.17 to 30.01°                  |
| Index ranges                   | $-16 \leq h \leq 16$, $-31 \leq k \leq 31$, $-27 \leq l \leq 28$ |
| Reflections collected          | 124981                          |
| Independent reflections        | 15505 [R(int) = 0.0703]         |
| Completeness to theta = 30.01° | 99.8 %                          |
| Absorption correction          | Semi-empirical from equivalents |
| Max. and min. transmission     | 0.6920 and 0.6470               |
| Refinement method              | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 10136 / 0 / 604                 |
| Goodness-of-fit on $F^2$       | 1.017                           |
| Final R indices [I>2sigma(I)]  | $R1 = 0.0437$, $wR2 = 0.0766$   |
| R indices (all data)           | $R1 = 0.0893$, $wR2 = 0.0899$   |
| Largest diff. peak and hole    | 0.832 and -0.891 e.Å⁻³          |
**Figure 125.** ORTEP-plot of the asymmetric unit of Cu(PPh₃)₃Br (110) with 50 % probability level. Hydrogen atoms omitted for clarity.

**Figure 126.** Packing diagram of 110 showing the weak CH···Br interaction.
12.1.7. Synthesis of 4,4'-[[5-(chloromethyl)-1,3-phenylene]bis(oxymethylene)]bis(1-benzyl-1H-1,2,3-triazole) (111)

5.00 g (21.31 mmol) 107, 6.24 g (46.87 mmol) benzylazide (109), 0.42 g (2.13 mmol) sodium ascorbate and 0.21 g (1.07 mmol) CuSO$_4$ were weighted into a 250 ml round bottom flask. 150 ml 1:1 THF/H$_2$O mixture were added and an immediate reaction was observed for the heterogeneous system. The mixture was stirred for 24 h at room temperature. 100 ml H$_2$O were added and the aqueous phase was extracted three times with 100 ml CH$_2$Cl$_2$. The organic phase was dried over MgSO$_4$ and evaporated to dryness. Flash-chromatography with CH$_2$Cl$_2$ followed by EtOAc gave an orange oil which was dissolved in 75 ml CH$_2$Cl$_2$. Another 75 ml of $n$-pentane were added and the solution was cooled to -30 °C. After 24 h a colorless precipitate formed which was filtered. 9.03 g (84.6 % yield, m.p.: 68 °C) pure 111 were obtained as colorless solid.

$^1$H NMR (500.1 MHz, CDCl$_3$, r.t.): δ (ppm) = 7.54 (s, 2 H, H8), 7.40-7.34 (m, 6 H, H12/13), 7.30-7.25 (m, 4 H, H11), 6.59 (d, $^4$J(H,H)=1.9 Hz, 2 H, H2), 6.54 (t, $^4$J(H,H)=2.0 Hz, 1 H, H4), 5.52 (s, 4 H, H9), 5.14 (s, 4 H, H6), 4.46 (s, 2 H, H5).

$^{13}$C NMR (125.7 MHz, CDCl$_3$, r.t.): δ (ppm) = 159.35 (s, C3i), 144.05 (s, C7i), 139.71 (s, C1i), 134.25 (s, C10i), 129.17 (s, C12), 128.88 (s, C13), 128.15 (s, C11), 122.78 (s, C8), 107.95 (s, C2), 101.84 (s, C4), 62.04 (s, C6), 54.35 (s, C9), 46.05 (s, C5).

ESI-MS (MeOH/NH$_4$OAc) : calcd. for C$_{27}$H$_{25}$ClN$_6$O$_2$: $m/z$ = 500.173 [M]$^+$;
found: $m/z$ = 501.2 [M+H]$^+$.


EA: calcd. for C$_{27}$H$_{25}$ClN$_6$O$_2$: C 64.73 %, H 5.03 %, N 16.78 %; found: C 63.75 %, H 5.02 %, N 16.38 %.
12.1.8. Synthesis of 4,4’-[[5-(azidomethyl)-1,3-phenylene]bis(oxymethylene)]bis(1-benzyl-1\(H\)-1,2,3-triazole) (112)

2.50 g (4.99 mmol) 111 were weighted into a 100 ml round bottom flask. 14.99 ml (7.49 mmol) of a stock solution of 0.5 M NaN\(_3\) in DMSO were added. The mixture was heated to 80 °C and stirred for 3 h. The complete conversion to azide 112 was confirmed by TLC analysis and MALDI-TOF-MS. The reaction was quenched with H\(_2\)O (slightly exothermic) and stirred until cooling to r.t. The mixture was extracted with CHCl\(_3\) (4x 50 ml) and the combined organic layers were washed with H\(_2\)O and brine. After drying over MgSO\(_4\) and evaporation to 25 ml, the chloroform solution was poured into cold MeOH. The colorless precipitate was filtered and dried under high vacuum. 2.34 g (92.6 % yield, m.p.: 138-139 °C) 112 were obtained as colorless powder.\(^{208}\)

\(^1\)H NMR (500.1 MHz, CDCl\(_3\), r.t.): \(\delta\) (ppm) = 7.55 (s, 2 H, H8), 7.40-7.34 (m, 6 H, H12/13), 7.30-7.25 (m, 4 H, H11), 6.55 (t, \(^4\)\(J(H,H)=2.0\) Hz, 1 H, H4), 6.52 (d, \(^4\)\(J(H,H)=1.9\) Hz, 2 H, H2), 5.52 (s, 4 H, H9), 5.14 (s, 4 H, H6), 4.22 (s, 2 H, H5).

\(^{13}\)C NMR (125.7 MHz, CDCl\(_3\), r.t.): \(\delta\) (ppm) = 159.57 (s, C3i), 144.08 (s, C7i), 137.73 (s, C1i), 134.30 (s, C10i), 129.14 (s, C12), 128.83 (s, C13), 128.12 (s, C11), 122.74 (s, C8), 107.45 (s, C2), 101.62 (s, C4), 62.05 (s, C6), 54.59 (s, C5), 54.28 (s, C9).

ESI-MS (MeOH/NH\(_4\)OAc) : calcd. for C\(_{27}\)H\(_{25}\)N\(_9\)O\(_2\): \(m/z = 507.213\) [M]\(^+\); found: \(m/z = 508.2\) [M+H]\(^+\).

MALDI-TOF-MS (4-NA): found: \(m/z = 508\) [M+H]\(^+\), 531 [M+Na]\(^+\), 548 [M+K]\(^+\).

EA: calcd. for C\(_{27}\)H\(_{25}\)N\(_9\)O\(_2\): C 63.89 %, H 4.96 %, N 24.84 %; found: C 64.38 %, H 5.03 %, N 24.79 %.
12.1.9. Synthesis of \(4,4',4'',4'''-\{[5-(chloromethyl)-1,3-phenylene]bis[oxymethylene-1H-1,2,3-triazole-4,1-diylmethylenebenzene-5,1,3-triylbis(oxymethylene)]\}tetrakis(1-benzyl-1H-1,2,3-triazole)\) (113)

\[
\begin{align*}
46.24 \text{ mg (197.00 } \mu\text{mol) 107, 200.00 \text{ mg (394.10 } \mu\text{mol) 112,}
\end{align*}
\]

10.19 \(\mu\text{l (78.81 } \mu\text{mol) DIPEA and 36.66 \text{ mg (39.41 } \mu\text{mol) Cu(PPh}_3\text{)Br (110) were reacted like described in the GP IX. The crude product was purified by extensive flash-chromatography using CHCl}_3 followed by EtOAc as eluent. Compound 113 could not by isolated, only a byproduct with m/z = 1955.863 was obtained.}^{208}

\(^1\text{H NMR and }^{13}\text{C NMR were not performed.}\)

MALDI-TOF-MS (4-NA): calcd. for \(C_{67}H_{61}ClN_{18}O_6\): \(m/z = 1248.471 [M]^+\]; found: \(m/z = 1249 [M+H]^+, 1261 [M+Na]^+, 1288 [M+K]^+\), before purification by flash-chromatography; found: \(m/z = 1955.863 (1960)\) after purification by flash-chromatography.

EA: calcd. for \(C_{67}H_{61}ClN_{18}O_6\): C 64.39 %, H 4.92 %, N 20.17 %; found: not performed.

12.1.10. Synthesis of \([3,5\text{-bis([3,5-bis[(1-benzyl-1H-1,2,3-triazol-4-yl)methoxy]benzyl]-oxy)phenyl}methanol (115)

\[
\begin{align*}
1.00 \text{ g (2.00 mmol) 111, 0.13 \text{ g (0.91 mmol) 5-(hydroxymethyl)benzene-1,3-diol (114), 1.10 \text{ g (7.89 mmol) dry K}_2\text{CO}_3, 0.20 \text{ g (2.00 mmol) NaI and catalytic amounts of 18-crown-6 were weighted into a flame dried 100 ml three-necked round bottom flask equipped with a condenser. 50 ml dry acetonitrile were added and the suspension was flushed with argon for 5 minutes. The equipment was sealed with an argon-balloon and heated to 90 °C for 24 h. After cooling to room tem-
\end{align*}
\]
perature, the mixture was filtered and the residual solid suspended in 50 ml chloroform, refluxed for 10 minutes and again screened from the inorganic solids. The combined organic phases were evaporated to dryness and dissolved in chloroform. After washing twice with brine, the separated organic phase was dried over MgSO₄ and evaporated to dryness. The crude product was purified by flash-chromatography using EtOAc followed by 1:1 MeOH/CHCl₃ as eluent. 0.61 g (62.8 % yield, m.p.: 97-98 °C) pure 115 were obtained as colorless solid.

1H NMR (500.1 MHz, CDCl₃, r.t.): δ (ppm) = 7.50 (s, 4 H, H13), 7.34-7.31 (m, 12 H, H17 and H18), 7.24 (dd, 3J(H,H)=7.7 Hz, 4J(H,H)=2.0 Hz, 8 H, H16), 6.60 (d, 4J(H,H)=2.2 Hz, 4 H, H8), 6.56 (d, 4J(H,H)=2.2 Hz, 2 H, H2), 6.49 (t, 4J(H,H)=2.0 Hz, 2 H, H10), 6.40 (t, 4J(H,H)=2.2 Hz, 1 H, H4), 5.48 (s, 8 H, H14), 5.09 (s, 8 H, H11), 4.91 (s, 4 H, H6), 4.59 (d, 3J(H,H)=5.0 Hz, 2 H, H5), 2.35 (t, 3J(H,H)=6.0 Hz, 1 H, OH).

13C NMR (125.7 MHz, CDCl₃, r.t.): δ (ppm) = 159.78 (s, C3i), 159.47 (s, C9i), 144.23 (s, C12i), 143.72 (s, C1i), 139.52 (s, C7i), 134.42 (s, C15i), 129.12 (s, C17), 128.78 (s, C18), 128.10 (s, C16), 122.74 (s, C13), 106.39 (s, C8), 105.83 (s, C2), 101.39 (s, C10), 101.18 (s, C4), 69.95 (s, C6), 65.07 (s, C5), 62.05 (s, C11), 54.19 (s, C14).


EA: calcd. for C₆₁H₅₆N₁₂O₇: C 68.53 %, H 5.28 %, N 15.72 %; found: C 68.41 %, H 5.32 %, N 15.67 %.

12.1.11. Synthesis of methyl 3,5-bis[(4-vinylbenzyl)oxy]benzoate (118)

25.00 g (148.68 mmol) methyl 3,5-dihydroxybenzoate (104), 55.47 g (327.10 mmol) 4-vinylbenzyl chloride (117) and 45.21 g (327.10 mmol) prior to use dried anhydrous K₂CO₃ were weighted into a 1 l three necked round bottom flask. 500 ml dry acetonitrile were added followed by 5.00 g (33.36 mmol) NaI, catalytic amounts of 18-crown-6 and a spattle of BHT to prevent polymerization. The suspen-
sion was flushed with argon for 15 minutes and the flask sealed with an argon-balloon. Stir-
ring for 1 week and filtration from the inorganic solids afforded a yellow solution which was
evaporated to dryness at room temperature under high vacuum and further purified by Kugel-
Rohr distillation at temperatures not exceeding 30 °C. The residual oil was dissolved in chlo-
roform and washed with H₂O and brine. After drying over MgSO₄ and evaporation to approx.
100 ml the desired product was purified by precipitation from methanol at -30 °C. 36.31 g
(61.0 %, m.p.: 75 °C) pure 118 were obtained as colorless powder.²⁵⁹,²⁶⁰

¹H NMR (500.1 MHz, acetone, r.t.): δ (ppm) = 7.47 (d, ³J(H,H)=8.2 Hz, 4 H, H10), 7.43 (d, ³J(H,H)=8.2 Hz, 4 H, H9), 7.21 (d, ⁴J(H,H)=2.2 Hz, 2 H, H2), 6.89 (t, ⁴J(H,H)=2.4 Hz, 1 H, H4), 6.74 (dd, ³J(H,H)=17.8 Hz, ²J(H,H)=10.9 Hz, 2 H, H12), 5.80 (dd, ³J(H,H)=17.7 Hz, ²J(H,H)=0.9 Hz, 2 H, H13), 5.22 (dd, ³J(H,H)=11.0 Hz, ²J(H,H)=0.9 Hz, 2 H, H13), 5.13 (s, 4 H, H7), 3.83 (s, 3 H, H6).

¹³C NMR (125.7 MHz, acetone, r.t.): δ (ppm) = 166.79 (s, C5i), 160.80 (s, C3i), 138.14 (s, C8i), 137.50 (s, C12), 137.39 (s, C11i), 133.06 (s, C1i), 128.70 (s, C9), 127.12 (s, C10), 114.37 (s, C13), 109.03 (s, C2), 107.50 (s, C4), 70.47 (s, C7), 52.45 (s, C6).

ESI-MS (MeOH/NH₄OAc) : calcd. for C₂₆H₂₄O₄: m/z = 400.167 [M]+;
found: m/z = 401.2 [M+H]+, 418.2 [M+NH₄]+,
423.2 [M+Na]+.

EA: calcd. for C₂₆H₂₄O₄:  C 77.98 %, H 6.04 %; found:  C 78.04 %, H 6.11 %.

12.1.12. Synthesis of {3,5-bis[(4-vinylbenzyl)oxy]phenyl}methanol (119)

15.00 g (37.46 mmol) 118 were weighted into a flame dried 500 ml three necked
round bottom flask equipped with a condenser and two septa. By syringe 300 ml
dry THF were added and the solution was flushed with argon for 20 minutes.
After cooling the solution to 0 °C with an ice bath, subsequently 22.47 ml (22.47
mmol) 1.0 molar LiAlH₄-solution in THF were added to the reaction mixture over a period of
30 minutes. The mixture was stirred for 24 h at room temperature and the reaction quenched
with EtOAc followed by 100 ml H₂O. The mixture was screened from inorganic solids and
the volume reduced to 200 ml. After transfer to a 1 l separating funnel the crude product was diluted with 200 ml chloroform and washed with brine several times. After drying over MgSO₄ and evaporation of the solvent at room temperature under high vacuum, the resulting solid was dissolved in chloroform and precipitated from methanol at -30 °C. 10.49 g (75.2 % yield, m.p.: 61 °C) pure 119 were obtained as colorless powder.²⁵⁹,²⁶⁰

¹H NMR (300.1 MHz, CDCl₃, r.t.): δ (ppm) = 7.42 (d, ³J(H,H)=8.3 Hz, 4 H, H9), 7.36 (d, ²J(H,H)=8.3 Hz, 4 H, H8), 6.72 (dd, ³J(H,H)=17.6 Hz, ²J(H,H)=10.9 Hz, 2 H, H11), 6.61 (d, ⁴J(H,H)=2.2 Hz, 2 H, H2), 6.52 (t, ⁴J(H,H)=2.2 Hz, 1 H, H4), 5.75 (d, ³J(H,H)=17.6 Hz, 2 H, H12), 5.25 (d, ³J(H,H)=10.8 Hz, 2 H, H12), 5.02 (s, 4 H, H6), 4.62 (d, ³J(H,H)=6.1 Hz, 2 H, H5), 1.66 (t, ³J(H,H)=6.0 Hz, 1 H, OH).

¹³C NMR (75.5 MHz, CDCl₃, r.t.): δ (ppm) = 160.18 (s, C3i), 143.47 (s, C7i), 137.40 (s, C10i), 136.47 (s, C11), 136.43 (s, C1i), 127.67 (s, C8), 126.42 (s, C9), 114.08 (s, C12), 105.88 (s, C2), 101.46 (s, C4), 69.89 (s, C6), 65.32 (s, C5).

ESI-MS (MeOH/NH₄OAc) : calcd. for C₂₅H₂₄O₃: m/z = 372.137 [M]+; found: m/z = 373.3 [M+H]+, 391.3[M+NH₄]⁺.

EA: calcd. for C₂₅H₂₄O₃: C 80.62 %, H 6.49 %; found: C 80.58 %, H 6.53 %.

12.1.13. Synthesis of 1-(bromomethyl)-3,5-bis[(4-vinylbenzyl)oxy]benzene (120)

10.00 g (26.85 mmol) 119 and 8.80 g (33.56 mmol) triphenylphosphine were weighted into a 250 ml three necked round bottom flask. 75 ml dry THF were added, followed by 11.13 g (33.56 mmol) tetrabromomethane. The solution was stirred for 4 h and quenched with 50 ml H₂O. The mixture was transferred to a 500 ml separating funnel and extracted 4 times with 100 ml chloroform. After drying the combined organic phases over MgSO₄ the solvent was evaporated at room temperature under high vacuum. The crude product was further purified by flash-chromatography using CH₂Cl₂. 1.51 g (12.9 % yield, m.p.: 83 °C) pure 120 were obtained as colorless solid.²⁵⁹,²⁶⁰
**1H NMR** (300.1 MHz, CDCl$_3$, r.t.): $\delta$ (ppm) = 7.42 (d, $^3$J(H,H)=8.2 Hz, 4 H, H9), 7.36 (d, $^3$J(H,H)=8.2 Hz, 4 H, H8), 6.72 (dd, $^3$J(H,H)=17.6 Hz, $^2$J(H,H)=10.9 Hz, 2 H, H11), 6.62 (d, $^4$J(H,H)=2.2 Hz, 2 H, H2), 6.52 (t, $^4$J(H,H)=2.2 Hz, 1 H, H4), 5.75 (d, $^3$J(H,H)=17.6 Hz, 2 H, H12), 5.26 (d, $^3$J(H,H)=10.9 Hz, 2 H, H12), 5.01 (s, 4 H, H6), 4.40 (s, 2 H, H5).

**13C NMR** (75.5 MHz, CDCl$_3$, r.t.): $\delta$ (ppm) = 160.08 (s, C3i), 139.81 (s, C7i), 137.49 (s, C10i), 136.46 (s, C11), 136.20 (s, C1i), 127.73 (s, C8), 126.54 (s, C9), 114.15 (s, C12), 108.29 (s, C2), 102.31 (s, C4), 69.98 (s, C6), 33.46 (s, C5).

**ESI-MS** (MeOH/NH$_4$OAc): calcd. for C$_{25}$H$_{23}$BrO$_2$: $m/z$ = 434.088 [M$^+$];

found: $m/z$ = 435.0 [M$+$H$^+$].

**EA**: calcd. for C$_{25}$H$_{23}$BrO$_2$: C 68.97 %, H 5.33 %; found: C 69.05 %, H 5.35 %.

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**12.2. Core-coupling of convergent grown dendrons with resorcin- and pyrogallolarene cores via “click”-reaction**

**12.2.1. General procedure for the convergent, non-aqueous Cu-catalyzed synthesis of 1,4-disubstituted 1H-1,2,3-triazole-dendrimers under microwave irradiation – GP IX**

100.00 mg (1.1 equiv.) of the azide functionalized dendritic component and 0.125 equiv. of octapropyneresorcinarene, e. g. 0.08 equiv. dodecapropynepyrogallolarene were weighted into a 10 ml reaction vessel followed by 0.22 equiv. $N,N$-diisopropylethylamine (DIPEA) and 0.11 equiv. Cu(PPh$_3$)$_3$Br (110). After dissolving in approx. 5-8 ml dry THF the reaction vessel was submitted to microwave irradiation at 140 °C (nominal temperature) for 10 minutes and completeness of conversion was confirmed by MALDI-TOF-MS. The mixture was evaporated to dryness, dissolved in a small amount of chloroform and precipitated from cold n-pentane. After filtration of the crude product, the resulting solid was dissolved in chloroform and further purified by flash-chromatography using first chloroform as eluent followed by either mixtures of CHCl$_3$/MEOH or pure ethyl acetate.
12.2.1.1. **Synthesis of** 4,4',4'',4''',4''''',4'''''',4''''''-[[2,8,14,20-tetrapentylpentacyclo[19.3.1.13.7.15.19.13.115.19]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,-23-dodecaene-4,6,10,12,16,18,22,24-octayl]octakis(oxymethylene)]octakis(1-benzyl-1H-1,2,3-triazole) (121)

0.25 mg (0.23 mmol) 87 were weighted into a 100 ml round bottom flask. 0.07 g (0.37 mmol) sodium ascorbate and 0.06 g (0.37 mmol) dry CuSO₄ were added followed by 50 ml 1:1 THF/H₂O and 0.50 g (3.73 mmol) benzylazide (109) by syringe. The mixture was stirred at room temperature for 24 h and evaporated to dryness. The excess of benzylazide was removed under high vacuum by Kugel-Rohr distillation. The residual solid was dissolved in chloroform and washed extensively with H₂O and brine. After phase separation the organic layer was dried over MgSO₄ and evaporated to dryness. 0.49 g (98.9 % yield, m.p.: 145-146 °C) pure 121 were obtained as its *rcce*-isomer as a slightly brown solid.

**¹H NMR** (500.1 MHz, CDCl₃, r.t.): *rcce*-isomer in cone conformation: δ (ppm) = 7.38 (s, 8 H, H13/13*), 7.32-7.20 (m, 40 H, H16/16* and H17/17* and H18/18*), 6.45 (s, 8 H, H3/3* and H5/5*), 5.44 (q, 16 H, H14/14*), 4.75 (br. s, 8 H, H11_1 and H11*_1), 4.44 (br. s, 8 H, H11_2 and H11*_2), 4.37 (t, ³J(H,H)=7.4 Hz, 4 H, H1), 1.69 (br. s, 8 H, H6), 1.11 (br. s, 24 H, H7-9), 0.73 (t, ³J(H,H)=6.5 Hz, 12 H, H10).

**¹³C NMR** (125.7 MHz, CDCl₃, r.t.): *rcce*-isomer in cone conformation: δ (ppm) = 154.62 (s, C4i/4i*), 144.72 (s, C12i/12i*), 134.95 (s, C15i/15i*), 128.98 (s, C17/17*), 128.56 (s, C18/18*), 128.05 (s, C16/16*), 126.23 (s, C2i/2i*), 123.04 (s, C13/13*), 99.46 (br. s, C3/3*), 92.17 (br. s, C5/5*), 63.09 (s, C11/11*), 53.93 (s, C14/14*), 35.77 (s, C1), 34.30 (s, C6), 31.99 (s, C8), 27.80 (s, C7), 22.51 (s, C9), 14.09 (s, C10).

**EA:** calcd. for C\textsubscript{128}H\textsubscript{136}N\textsubscript{24}O\textsubscript{8}: C 71.89 %, H 6.41, N 15.72 %; found: C 70.73 %, H 6.77 %, N 14.96 %.

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<td>Largest diff. peak and hole</td>
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Figure 127. ORTEP-plot of the asymmetric unit of 121 with 50 % probability level. Hydrogen atoms and disorder omitted for clarity.

Figure 128. CPK-model of 121, blue: nitrogen; black: carbon; red: oxygen.
12.2.1.2. Synthesis of \( 4,4',4'',4''',4''''',4''''''',4'''''''',4''''''''',4'''''''''',4''''''''''',4'''''''''''',4''''''''''''',4'''''''''''''',4''''''''''''''\)\([2,8,14,20\text{-tetra-pan-}
\text{petylpentacyclo}[19.3.1.1\text{3,7.1\text{9,13.1\text{15,19}}\text{octacosa-1(25),3(28),4,6,9(27),10,12,15-}
\text{(26),16,18,21,-23-dodecaene-4,6,10,12,16,18,22,24octayl]octakis[oxymethylen-}
\text{e-1H-1,2,3-triazole-4,1-diyl-methylenebenzene-5,1,3-triylbis(oxymethylene)]-}
\text{hexadecakis(1-benzyl-1H-1,2,3-triazole)}\) (122)

24.03 mg (22.39 \( \mu \)mol) 87, 100.00 mg (197.03 \( \mu \)mol) 112, 6.13 \( \mu \)l (35.82 \( \mu \)mol) DIPEA and 16.66 mg (17.91 \( \mu \)mol) Cu(PPh\(_3\))\(_3\)Br (110) were re-
acted as described in the GP IX. The crude product was purified by exten-
sive flash-chromatography using CHCl\(_3\) followed by EtOAc as eluent.
112.70 mg (98 % yield, m.p.: 84-85 °C) pure 122 were obtained as its
\( rccc \)-isomer as a colorless solid.

\( ^1\)H NMR (500.1 MHz, CDCl\(_3\), r.t.): \( rccc \)-isomer in cone conformation: \( \delta \) (ppm) = 7.53 (s, posture 16 H, H21/21*), 7.37 (m, 32 H, H25/25*), 7.36 (s, 8 H, H13/13*), 7.28 (m, 16 H, H26/26*), 7.26 (m, 32 H, H24/24*), 6.67 (s, 4 H, H3/3*), signal (s, 4 H, H5/5* not visible), 6.56 (t, \( ^4J(H,H)=2.2 \) Hz, 8 H, H16/16*), 6.52 (d, \( ^4J(H,H)=2.2 \) Hz, 16 H, H18/18*), 5.52 (s, 32 H, H22/22*), 5.14 (s, 32 H, H19/19*), signal (s, 16 H, H11/11* not visible), 4.48 (m, 4 H, H1), 4.22 (s, 16 H, H14/14*), 1.80 (br. m, 8 H, H6), 1.27 (br. m, 24 H, H7-9), 0.87 (t, \( ^3J(H,H)=7.3 \) Hz, 12 H, H10).

\( ^13\)C NMR (125.7 MHz, CDCl\(_3\), r.t.): \( rccc \)-isomer in cone conformation: \( \delta \) (ppm) = 159.59 (s, C17/17i*), 146.23 (s, C12i/12i*), signal (s, C4/i/4i* not visible), 144.11 (s, C20i/20i*), 137.75 (s, C15i/15i*), 134.33 (s, C23i/23i*), 129.15 (s, C25/25*), 128.85 (s, C26/26*), 128.14 (s, C24/24*), signal (s, C2i/2i* not visible), 124.79 (s, C13/13*), 122.70 (s, C21/21*), 107.48 (s, C18/18*), 101.65 (s, C16/16*), signal (s, C3/3* not visible), signal (s, C5/5* not
visible), 63.38 (s, C11/11*), 62.10 (s, C19/19*), 54.62 (s, C14/14*), 54.29 (s, C22/22*), signal (s, C1 not visible), 34.77 (s, C6), 32.04 (s, C8), 27.58 (s, C7), 22.62 (s, C9), 14.04 (s, C10).

**MALDI-TOF-MS (4-NA):** calcd. for C_{288}H_{280}N_{72}O_{24}: \[m/z = 5133.300 \ [M]^+; \]
found: \[m/z = 5135.929 \ [M+H]^+, 5155.697 \ [M+Na]^+.\]

12.2.1.3. **Synthesis of** 4,4',4'',4''',4'''',4''''',4''''''',4''''''''',4''''''''''',4'''''''''''',4''''''''''''',4''''''''''''''',4''''''''''''''''''',4'''''''''''''''''''''''\[2,8,14,20-tetrapentylpentacyclo[19.3.1.1^3.7.1^9.1^3.1^5.1^9]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-4,5,6,10,11,12,16,17,18,22,23,24-dodecayl]dodekakis[oxymethylene-1H-1,2,3-triazole-4,1-diyl-methylene-benzene-5,1,3-triylbis(oxymethylene)]-tetracosakis(1-benzyl-1H-1,2,3-triazole) (123)

19.25 mg (14.93 μmol) 88, 100.00 mg (197.03 μmol) 112, 6.13 μl (35.82 μmol) DIPEA and 16.66 mg (17.91 μmol) Cu(PPh_3)_3Br were reacted as described in the GP IX. The crude product was purified by extensive flash-chromatography using a sequence of eluents: CHCl_3 - 20:1 CHCl_3/MeOH - EtOAc. 66.20 mg (59% yield) pure 123 were obtained as mixture with its of partially substituted nona-, deca- and undeca-analogues.

\[^1H \text{NMR}\] and \[^{13}C \text{NMR}\] not significant, because the product obtained was a mixture of the nona-, deca-, undeca- and dodecafunctional pyrogallolarene-dendrimers.

**MALDI-TOF-MS (4-NA):** calcd. for C_{420}H_{412}N_{108}O_{36}: \[m/z = 7547.386 \ [M]^+; \]
found: \[m/z = 7546.244 \ [M-H]^-.\]
Conclusions

In the frame of this thesis different calix[4]resorcin- and calix[4]pyrogallol derivatives were used as platform for the synthesis of novel star polymers and dendritic structures.

Synthesis and modification of resorcin- and pyrogallolarenes

The synthesis of C-alkyl- and C-arylresorcin- and -pyrogallolarenes was achieved in multi-gram scale by the acid-catalyzed cyclotetramerization of either resorcinol (2) or pyrogallol (5) with acetaldehyde (6), n-hexanal (7), n-dodecanal (8) and p-hydroxybenzaldehyde (64). C-alkylresorcin- and pyrogallolarenes 59 to 63 were obtained as their pure rccc-isomers, in contrast to C-arylresorcin- and –pyrogallolarenes 65 and 66, which were preserved as mixtures of their rccc- and rctt-isomers. Upon utilization of 2,2’-[1,3-phenylenebis(oxy)]diethanol (67) and p-hydroxybenzaldehyde (64), a prefunctionalized C-arylresorcinarene core 68 with aliphatic as well as phenolic hydroxyl groups was prepared, which offers the possibility for regiospecific functionalization by Williamson etherification.

Figure 129. Overview about the synthesized and further modified resorcin- and pyrogallolarenes.
Modification of the acquired resorcin- and pyrogallolarenes \(59\) to \(63, 65, 66,\) and \(68\) through \(O\)-alkylation via Williamson etherification yielded methyl acetate-derivatives \(70\) to \(76,\) \(N\) -propylphthalimido-derivatives \(80\) to \(85\) and propyne-derivatives \(87\) to \(89\) of resorcin- and pyrogallolarenes respectively (Figure 129).

The methyl acetate derivatives \(70\) to \(76\) were further transformed into the corresponding water-soluble alcohols upon reduction with \(\text{LiAlH}_4\). Difficulties which arose from the water-solubility exacerbated the purification of these compounds.

Reaction of the same octamethyl acetate precursor \(71\) with \(\text{MeMgBr}\) afforded a resorcinarene \(78\) functionalized with iso-butanol groups.

Both, the primary \(77,\) as well as, the tertiary alcohol derivative \(78\) might prove to be efficient initiators for the anionic polymerization of oxiranes, or effective ligands towards complexation and recognition of aminoacids and even metallic species.

The one-step access towards \(N\)-propylphthalimido-derivatives \(80\) to \(85\) via Williamson etherification and subsequent cleavage of the protective group allows the preparation of cores with amine functions, which can be utilized for the divergent growth of polyamidoamine dendrimers as well as for complexation with transition metals to achieve supramolecular assemblies.

\(O\)-alkylation of resorcin- and pyrogallolarenes with propargyl bromide (86) afforded cores \(87\) to \(89\) with reactive propyne functions in high yield, which served starting materials for the convergent access towards polyaryl ether dendrimers with triazole units.

Especially 2D-NMR techniques, MALDI-TOF-MS and single crystal X-ray diffraction were used to investigate and prove the structures of the products obtained. Thus six up to now unknown crystal structures of resorcin- and pyrogallolarenes were obtained.

### Star polymers based on resorcin- and pyrogallolarenes

The initiators for the envisaged ATRP polymerization reaction were synthesized in high yield by \(O\)-acylation of different phenols (phenol (1) itself, resorcinol (2), pyrogallol (5), oligophenols 93 and 94) and resorcin- and pyrogallolarenes (59, 60, 62, 63, 65 and 66) with 2-bromo-isobutyryl bromide (53). Two new crystal structures were for the mono- and trifunctional initiators 92 and 96 obtained by SXD, and 2D NMR and dynamic NMR was used to determine the conformations of the octa-, dodeca- and hexadecafunctional initiators 97 to 102 (Figure 130).
All initiators (Figure 130) proved to be efficient in the initiation of ATRP of styrene in bulk, using either the Cu/tbbpy catalytic system or the usually applied CuBr/bpy system. With both catalytic systems star polymers with different molecular weight and narrow molecular weight distribution could be achieved. The obtained polymers were investigated by means of SEC-RI, SEC-MALLS and MALDI-TOF-MS.

Good control over molecular weight and molecular weight distribution was perceived for the commonly used CuBr/bpy atom transfer agent. A loss of reproducibility and control was observed for the CuBr/tbbpy system.

When using low ratios of monomer to initiator (1:100), massive star-star coupling was observed. Such dimers and trimers and even higher coupling products are mainly the result of intermolecular radical-coupling of active growing chains. MALDI-TOF-MS proved to be the method of choice to investigate the population of single-star polymers besides their intermolecular coupled byproducts.
Using higher monomer to initiator ratios (1:500), star-star coupling could be avoided to a great extend. Especially with the CuBr/bpy catalytic system, well-defined and narrowly disperse star polymers were synthesized. In this case SEC-MALLS is the method of choice to investigate the content of star species (single stars, double stars, ...) in the product.

Molecular weights for octa-, dodeca- and hexadecaarm star polymers are generally determined too low using the SEC-RI technique. Minor impurities of coupled stars are not recognized by SEC-RI, and thus the results for molecular weight determination indicate rather low compositional heterogeneity. This was disproved when redetermination was done with SEC-MALLS. Results obtained from MALDI-TOF-MS indicate a rather low dispersity of the single-star polymers (PDI < 1.1) obtained with both atom transfer agents (CuBr/bpy and CuBr/tbbpy).

In all cases dodeca- and hexadecaarm star polymers could only be perceived together with impurities of coupled byproducts, which decreased with increasing monomer to initiator ratios. The calculation of the functionality of the star polymers, based on the molecular weight determination of the individual polymeric arms, received by the hydrolysis of the star polymers, gave results close to the theoretical values of $f = 8, 12$ and $16$ for octa-, dodeca- and hexadecaarm star polymers. Therefore it can be concluded that all 2-bromo-isobutyro-substituents took part in the initiation and led to the propagation of a polymer arm, giving rise to precise octa-, dodeca- and hexadecaarm star polymers.

**Dendrimers based on resorcin- and pyrogallolarenes**

For the build-up of dendritic structures based on resorcin- and pyrogallolarenes with eight and twelve reactive groups 59, 62 and 87, 88, the convergent approach was selected. Two G1-poly(arylether)-dendrons with benzyl 111, as well as, styrene end-groups 120 and reactive benzyl halides at the focal point were synthesized. In both cases, core-coupling via Williamson etherification with resorcin- and pyrogallolarenes 59 and 62 did not afford the corresponding G1-dendrimers. In these cases only incomplete G1-dendrimers were obtained, as indicated by MALDI-TOF-MS measurements at intermediate reaction times.

The convergent approach towards G1-dendrimers 122 and 123 based on resorcin- and pyrogallolarenes 87 and 88 was achieved via preparation of a bis-propyne functional AB$_2$-monomer 107 starting from commercially available 3,5-dihydroxybenzoic acid (103). End-capping of the propyne functions via copper-mediated $(3+2)$ cycloaddition between benzyl
azide (109) and the AB₂-monomer 107 resulted in the corresponding G1-dendron 111, which, after subsequent activation of the focal benzyl chloride by azidification with NaN₃ to benzyl azide 112, was coupled with a resorcinarene core 87 bearing eight propyne substituents, as well as, with a pyrogallolarene core 88 bearing twelve propyne functions.

The pure G1-dendrimer 122 of the resorcinarene 87 could be obtained in nearly quantitative yield via a microwave assisted copper-mediated (3+2) cycloaddition between the core and the G1-azide 112. In the case, when the G1-azide 112 was coupled with the pyrogallolarene core 88, the pure G1-dendrimer could not be obtained. Only a mixture of the completed G1-dendrimer 123 with its incomplete analogues could be perceived.
References

References

<table>
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<th>Page</th>
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References
Cambridge Structural Database; Version 5.27 with update from May 06.
### Appendix

#### List of Abbreviations

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<tr>
<th>Abbreviation</th>
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<tr>
<td>18-C-6</td>
<td>18-crown-6</td>
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<tr>
<td>2D</td>
<td>two-dimensional</td>
</tr>
<tr>
<td>4-NA</td>
<td>4-nitroaniline</td>
</tr>
<tr>
<td>ATRP</td>
<td>atom transfer radical polymerization</td>
</tr>
<tr>
<td>BA</td>
<td>n-butyl acrylate</td>
</tr>
<tr>
<td>BHT</td>
<td>butylated hydroxytoluene</td>
</tr>
<tr>
<td>BMA</td>
<td>n-butyl methacrylate</td>
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<tr>
<td>bpy</td>
<td>2,2'-bipyridine</td>
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<tr>
<td>COSY</td>
<td>correlated spectroscopy</td>
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<tr>
<td>CRP</td>
<td>controlled radical polymerization</td>
</tr>
<tr>
<td>DHB</td>
<td>3,5-dihydroxybenzoic acid</td>
</tr>
<tr>
<td>DIPEA</td>
<td>N,N-diisopropylethylamine</td>
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<tr>
<td>DMA</td>
<td>dimethyl acetamide</td>
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<tr>
<td>DMF</td>
<td>dimethyl formamide</td>
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<td>DMSO</td>
<td>dimethyl sulfoxide</td>
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<td>DOSY</td>
<td>diffusion-ordered spectroscopy</td>
</tr>
<tr>
<td>DPMK</td>
<td>diphenylmethyl potassium</td>
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<tr>
<td>EA</td>
<td>elemental analysis</td>
</tr>
<tr>
<td>ESI</td>
<td>electro-spray ionization</td>
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<tr>
<td>EtOH</td>
<td>ethanol</td>
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<tr>
<td>EXAFS</td>
<td>extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>FG</td>
<td>functional group</td>
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<tr>
<td>GC</td>
<td>gas chromatography</td>
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<td>HMBC</td>
<td>heteronuclear multiple bond connectivity</td>
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<td>HMTETA</td>
<td>1,1,4,7,10,10-hexamethylenehexamethylenetetraamine</td>
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<tr>
<td>HSQC</td>
<td>heteronuclear single quantum coherence</td>
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<tr>
<td>I</td>
<td>initiator</td>
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<tr>
<td>IB</td>
<td>isobutylene</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>L</td>
<td>ligand</td>
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<td>LC</td>
<td>liquid chromatography</td>
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<tr>
<td>M</td>
<td>monomer</td>
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<td>MALDI</td>
<td>matrix assisted LASER desorption/ionization</td>
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<td>MALLS</td>
<td>multi angle laser light scattering</td>
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<td>MMA</td>
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<td>weight average molecular weight</td>
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<tr>
<td>MW</td>
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<tr>
<td>NBS</td>
<td>N-bromosuccinimide</td>
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<td>NMP</td>
<td>nitrooxide-mediated polymerization</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>NOESY</td>
<td>nuclear Overhauser enhancement spectroscopy</td>
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<td>N-propylphthalimide</td>
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<td>polydispersity index</td>
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<td>polyethylene oxide</td>
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<td>protective group</td>
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<td>polyisobutylene</td>
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<td>polymethyl methacrylate</td>
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<td>persistent radical effect</td>
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<td>pyridine</td>
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<td>RAFT</td>
<td>reversible addition fragmentation chain-transfer polymerization</td>
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<td>radius of gyration</td>
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<td>glass transition temperature</td>
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<td>tetrahydrofurane</td>
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<td>thin-layer chromatography</td>
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<td>TOF</td>
<td>time of flight</td>
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<tr>
<td>tren</td>
<td>tris(2-aminoethyl)amine</td>
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</tbody>
</table>
Tilo Krause

Diplomchemiker

*15.02.1978 in Leipzig

Education

06/1984 - 06/1991  86. Polytechnische Oberschule, Leipzig

Major subjects:  Mathematics, Biology
Certificate:  Abitur

Military service

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Study

09/1997 - 08/1999  Food-chemistry study, Technische Universität Dresden
09/1999 - 08/2002  Chemistry study, Technische Universität Dresden

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Second subject:  Analytical chemistry
Certificate:  Diplomchemiker
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09/2002 -

Postgraduate study, Technische Universität Dresden
Fellowship of German Research Foundation (DFG) within “European Graduate Collage 720 - Advanced Materials”
Thesis:  “Star polymers and dendrimers based on highly functional resorcin- and pyrogallolarenes”
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02/2002 - 06/2002
Student assistant in laboratory course for medicine students, Technische Universität Dresden

04/2003 - 07/2003
Scientific assistant in laboratory course for advanced chemistry students, Technische Universität Dresden

04/2004 - 07/2004
Scientific assistant in laboratory course for advanced chemistry students, Technische Universität Dresden

01/2005 - 02/2005
Scientific assistant in X-ray laboratory, Westfälische-Wilhelms-Universität, Münster

**Experience**

Organic synthesis, especially macrocyclic, supramolecular hosts, dendritic architectures and initiators for controlled radical polymerization techniques.

Application of controlled radical polymerization techniques, especially ATRP and NMP in the synthesis of linear and star-shaped polymer architectures.

Single crystal X-ray diffraction of small molecules.

**Language Skills**

English (fluently)
Russian (elementary)

**Private Interests**

Computer, Programming, Raytracing, Snow-boarding
List of scientific publications

1. Leuteritz, A.; Messerschmidt, M.; Voit; B. I.; Krause, T.; Habicher, W. D.
   “Synthesis of orthogonally protected narrowly distributed block copolymers of hydroxystyrene.”
   *Polymer Preprints (ACS, Division of Polymer Chemistry)* **2002**, *43*, 283-284.

   “Synthesis of boc-protected block copolymers based on para-hydroxystyrene via NMP.”

   “A novel method for the synthesis of alkoxyamine initiators for nitroxide-mediated radical polymerization using Mn(OAc)₃ as electron-transfer reagent.”


   “Nitroxide-mediated homo and block copolymerization of styrene and multifunctional acryl- and methacryl derivatives.”


   „ESR studies on hydroxylamine (HMPAP) in DMF and tert-butylbenzene.”

   „First total synthesis of the 7-oxygenated carbazole alkaloids clauszoline-K, 3-formyl-7-hydroxycarbazole, clausine M, clausine N and the anti-HIV active siamenol using a highly efficient palladium-catalyzed approach”
List of poster presentations

1. “Synthesis and polymerization of functional methacrylamides and methacrylates”
   Yin, M.; Krause, T.; Habicher, W. D.

2. “Synthesis of orthogonally protected narrowly distributed block copolymers of hydroxystyrene”
   Leuteritz, A.; Messerschmidt, M.; Voit, B. I.; Krause, T.; Habicher, W. D.
   224th ACS National Meeting 2002, Boston, US.

3. „Novel synthesis of alkoxyamine initiators for the nitroxide-mediated radical polymerization – star polymers on the basis of calixarenes“
   Krause, T.; Yin, M.; Habicher, W. D.; Messerschmidt, M.; Voit, B.
   5th International Polymer Seminar 2003, Gliwice, Poland. Book of Abstracts P27.

4. Synthesis of boc-protected block copolymers based on para-hydroxystyrene via NMRP“


6. “Atom transfer radical polymerization with resorcin- and pyrogallolarene derived plurifunctional initiators”
   Krause, T.; Gruner, M.; Habicher, W. D.

   Krause, T.; Gruner, M.; Habicher, W. D.
8. “Resorcin- and pyrogallolarenes as platform for novel star polymers and dendrimers”
Krause, T.; Gruner, M.; Habicher, W. D.
10th International Seminar on Inclusion Compounds (ISIC-10) 2005, Kazan, Russia.
Book of Abstracts p.102, P-44.

Krause, T.; Gruner, M.; Kataeva, O.; Habicher, W. D.

10. “Synthesis, structure and anion binding properties of different N-benzylated TREN-derivatives”

Versicherung

Hiermit versichere ich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht. Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.


Erklärung

Frühere Promotionsverfahren haben nicht stattgefunden.

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