

Synthesis of Glyco-Substituted Tetrapyrroles and Expanded Porphyrinoids for Biomedical Applications

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—

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in memoriam.

Abstract

One of the objectives and the focal point of this thesis was the development of a library of *meta*- and *para*-glycosylated porphyrins using glycosyl trichloroacetimidates. The influence of their different substitution patterns (different polarities, carbohydrate moieties and lipophilic substituents) on the photodynamic activity was investigated in tests against several cancer cell lines. It turned out that most glyco-conjugates showed cytotoxicity, but especially glyco-substituted porphyrins with a *trans*-A₂B₂-substitution pattern showed very promising results. Selected mono- or *trans*-A₂B₂-glycosylated porphyrins which exhibited a good cytotoxicity but are rather lipophilic were re-synthesized (upscaling) and were successfully incorporated into pharmaceutical formulations. Besides the development of potential new photosensitizers, modifications and combinations of the trichloroacetimidate method were exemplified showing its broad scope of applicability.

Another aim of this thesis was the synthesis of glyco-porphyrinoids absorbing at other wavelengths than typical tetrapyrroles. In a first approach a synthetic protocol was developed to directly connect a carbohydrate with a porphyrin scaffold *via* a triple bond in a SONOGASHIRA reaction (absorption shift to higher wavelengths). Since this worked only for mono-substitutions and partly for di-substitutions, the possibility of glycosylating new (expanded) porphyrinoid systems which strongly differ in their photophysical properties from porphyrins was investigated. Utilization of the glycosyl thiolate method (nucleophilic aromatic substitution) and PFP-substituted porphyrinoids led to novel glycosylated dipyrromethane, *trans*-A₂B-corrole, calix[4]phyrin(1.1.1.1), calix[6]phyrin(1.1.1.1.1.1) and [28]hexaphyrin(1.1.1.1.1.1) systems which are easily soluble in alcohol/water mixtures thus fulfilling a crucial requirement for biomedical applications. In the nucleophilic substitution reactions of challenging PFP-substituted porphyrinoids thiolates proved to be very precise and powerful tools regarding their high nucleophilicity leading to a controlled, regio- and stereoselective glycosylation.

Furthermore synthetic strategies for the rational access to heteroglycosylated tetrapyrroles were realized in 6 to 8 consecutive reaction steps for the first time. Basically, their synthesis was accomplished in two approaches: The combination of the glycosyl trichloroacetimidate method with thioglycosylation and the combination of Cu(I)-catalyzed 1,3-dipolar “click” chemistry and thioglycosylation. The resulting porphyrins with different carbohydrate moieties may be advantageous as compared to traditional tetrapyrroles for better binding to cell membranes and as a consequence leading to an improved targeting.

In the last project 4-azido-tetrafluorobenzaldehyde was employed in different condensation reactions with dipyrromethanes and pyrrole giving access to novel azido-porphyrinoids suitable for further functionalization reactions. Thus azido-substituted porphyrins (A₁B₃, A₂B₂, A₃B and A₄), corroles (A₃), calix[4]phyrins (A₂B₂), calix[6]phyrins (A₃B₃), *N-fused* pentaphyrins (A₅) and hexaphyrins (A₃B₃, A₆) can be synthesized in a straightforward way. Several of these azido-porphyrinoids are only accessible *via* the described route. Besides further possible glycosylation reactions for medical applications, they can also serve as valuable platforms in other research fields due to the versatile “click” chemistry.

Zusammenfassung

Ein Forschungsschwerpunkt innerhalb dieser vorliegenden Dissertation war die Erstellung einer Bibliothek von *meta*- und *para*-glycosylierten Porphyrinen unter Verwendung von Glycosyl-Trichloracetimidaten. Der Einfluss verschiedener Substitutionsmuster (unterschiedliche Polaritäten, Kohlenhydrate, lipophile Substituenten) wurde bezüglich der photodynamischen Aktivität in Tests gegen mehrere Tumorzelllinien untersucht. Es stellte sich heraus, dass die meisten Glykokonjugate eine gewisse Zytotoxizität zeigten, jedoch speziell die glyco-substituierten Porphyrine mit einem *trans*-A₂B₂ Substitutionsmuster sehr vielversprechende Resultate lieferten. Ausgewählte mono- oder *trans*-A₂B₂-glycosylierte Porphyrine, welche eine sehr gute Zytotoxizität zeigten, aber recht lipophil waren, wurden erneut in größeren Massstab synthetisiert und erfolgreich in eine erste pharmazeutischen Formulierung gebracht. Neben der Entwicklung potentieller Photosensibilisatoren, wurden auch Modifikationen sowie Kombinationen der Trichloracetimidat-Methode durchgeführt, die den breiten Anwendungsbereich dieser Methode unterstreichen.

Ein weiteres Ziel dieser Arbeit war die Synthese von Glyco-Porphyrinoiden, welche bei anderen Wellenlängen als typische Tetrapyrrole absorbieren. In einer ersten Annäherung wurde ein Syntheseprotokoll für die direkte Verknüpfung eines Kohlenhydrats mit einem Porphyringrundgerüst durch eine Dreifachbindung in einer SONOGASHIRA Reaktion (Verschiebung der Absorption zu höheren Wellenlängen) entwickelt. Da dies nur bei Monosubstitutionen und teilweise bei Disubstitutionen funktionierte, wurde die Möglichkeit untersucht, (expandierte) Porphyrinoidsysteme zu glycosylieren, die sich in ihren photophysikalischen Eigenschaften stark von den Porphyrinen unterscheiden. Mithilfe der Glycosyl-Thiolat Methode (nucleophile aromatische Substitution) und PFP-substituierten Porphyrinoiden konnten glycosylierte Dipyrromethan-, *trans*-A₂B-Corrol-, Calix[4]phyrin(1.1.1.1)-, Calix[6]phyrin(1.1.1.1.1.1)- and [28]Hexaphyrin(1.1.1.1.1.1)-Systeme hergestellt werden, die in alkoholisch/wässrigen Lösungsmittelgemischen gut löslich sind und somit eine wichtige Voraussetzung für biomedizinische Anwendungen erfüllen. In den nucleophilen Substitutionsreaktionen der PFP-substituierten Porphyrinoide erwiesen sich Glycosyl-Thiolate aufgrund ihrer hohen Nucleophilie als sehr präzise und nützliche Reagentien und führten zu einer kontrollierten, regio- und stereoselektiven Glycosylierung.

Weiterhin wurden synthetische Strategien für einen rationalen Zugang zu heteroglycosylierten Tetrapyrrolen entwickelt, die in 6 bis 8 konsekutiven Reaktionsschritten erstmalig realisiert werden konnten. Grundsätzlich wurde ihre Synthese auf zwei Wegen bewerkstelligt: Die Kombination der Trichloracetimidat- mit der Thiolat-Methode sowie die Kombination der Cu(I)-katalysierten 1,3-dipolaren „Click“ Reaktion mit der Thiolat-Methode. Die dabei entstehenden Porphyrine mit unterschiedlichen Kohlenhydrateinheiten können eine höhere Affinität zur Zellmembran als klassische Tetrapyrrole zeigen und somit zu einer verbesserten Targetierung beitragen.

Im letzten Projekt wurde 4-Azido-tetrafluorbenzaldehyd in verschiedenen Kondensationsreaktionen mit Dipyrromethan und Pyrrol eingesetzt, um so zu neuartigen Azido-Porphyrinoiden zu gelangen, die für weitere Funktionalisierungsreaktionen als interessante Plattformen dienen können. Auf diese Weise konnten azid-substituierte Porphyrine (A₁B₃, A₂B₂, A₃B and A₄), Corrole (A₃), Calix[4]phyrine (A₂B₂), Calix[6]phyrine (A₃B₃), *N-fused* Pentaphyrine (A₅) und Hexaphyrine (A₃B₃, A₆) auf direktem Weg synthetisiert werden. Mehrere dieser Azido-Porphyrinoide sind nur auf dem beschriebenen Weg zugänglich. Neben weiteren möglichen Glycosylierungsreaktionen für medizinische Anwendungen, könnten sie auch als wertvolle Plattformen in anderen Forschungsfeldern dienen, basierend auf der vielseitig einsetzbaren „Click“ Chemie.

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1 INTRODUCTION

1.1 Porphyrinoid Systems

1.1.1 Porphyrins and their Derivatives

Porphyrins are often titled 'colors of life'. These conjugated macrocycles consist of four pyrrole units which are connected by sp^2 methine bridges. These carbon bridges are called *meso*-positions while the α - and β -positions are located at the pyrrole units. Porphyrins possess 22 π -electrons whereof only 18 are necessary for the formation of the aromatic perimeter. Therefore this structure, fulfilling the HÜCKEL rule, is considered as typical aromatic structure. A comparison with [18]annulene systems seems reasonable. Other derivatives like the reduced porphyrins (chlorins, bacteriochlorins or isobacteriochlorins) where the pyrrole unit(s) are replaced by pyrroline unit(s) or porphyrins with differently connected pyrrole units (*N-confused* or *-fused* porphyrins) also follow the HÜCKEL rule and are therefore aromatic (Figure 1).

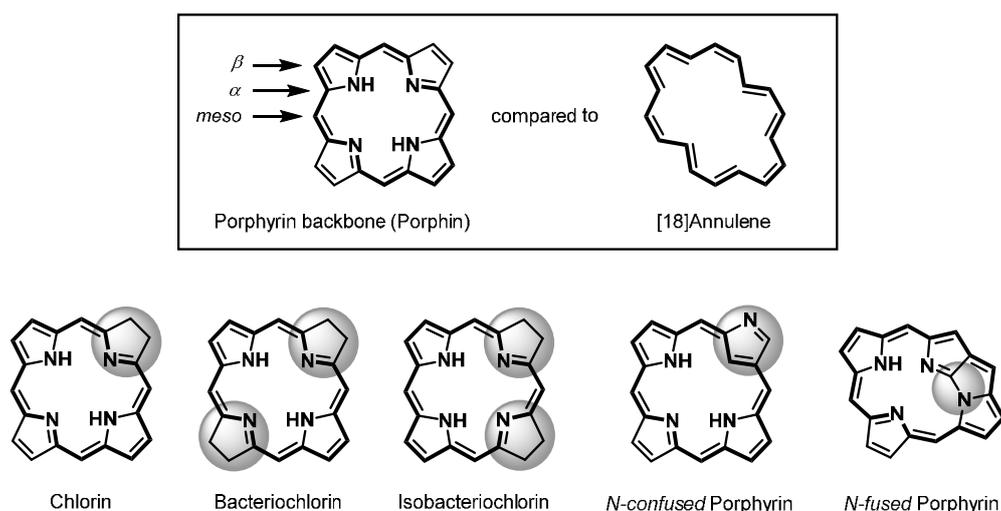


Figure 1. Structural comparison of porphyrin and its derivatives possessing an aromatic perimeter.

Changing the amount and hybridization state of the carbon bridges or the amount of pyrrole units leads to a variety of other interesting porphyrinoids like e.g. corroles, calixphyrins or expanded systems which will at a later stage be discussed in detail.

Due to their aromatic character, porphyrins show a similar manner of reaction like common aromatic compounds and, for instance, can undergo electrophilic substitution reactions. So, porphin (the basic chromophore) can be halogenated,^[1a] sulfonated,^[1b] nitrated,^[1c] acylated^[1d] or formylated^[1e] in β - or *meso*-position. A desired reaction in either β - or *meso*-position is accomplished best by blocking of the undesired position with a suitable substituent. On the other hand, it is also possible to attack the

macrocycle with nucleophilic reagents like lithiumorganic compounds.^[2] In addition, the two double bonds which are not necessary for formation of an aromatic perimeter act like olefinic double bonds. Possible reactions are reductions,^[3a] oxidations,^[3b] electrophilic additions^[3c] and cycloadditions^[3d,3e]. Tetrapyrroles can be complexed with various metal ions. Some of the stated reactions above can only be accomplished after precedent metallation.

In nature macrocyclic tetrapyrroles play a crucial role in fundamental biochemical processes and are also found as metal complexes. Typical, well-known representatives are chlorophyll A and B (Figure 2). Chlorophyll, a chlorin, has an additional five-membered ring at the scaffold and is complexed with magnesium. In photosynthesis this chlorin plays a crucial role because it absorbs the sunlight and forwards the energy to the photosynthetic reaction center, which itself contains chlorophyll molecules. Another important representative is the iron(II) complex of protoporphyrin IX, also called heme B or protoheme IX (Figure 2). This metallated porphyrin is part of the proteins hemoglobin and myoglobin which are essential for oxygen transport and storage in living organisms. It should be noted that chlorophyll is responsible for the green color of plants and heme for the red color of blood which underlines the term ‘colors of life’.

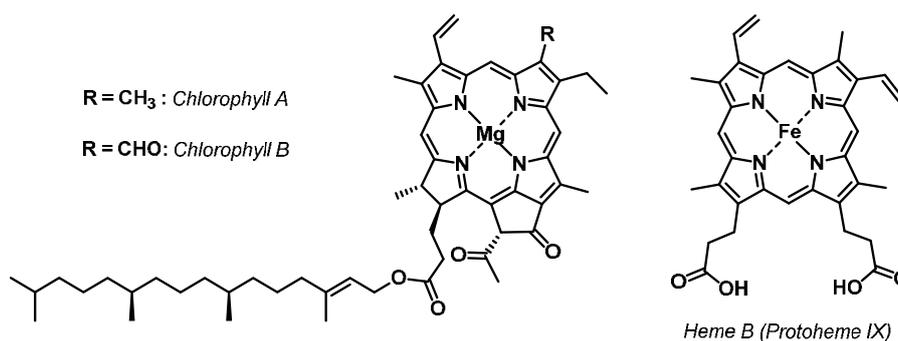
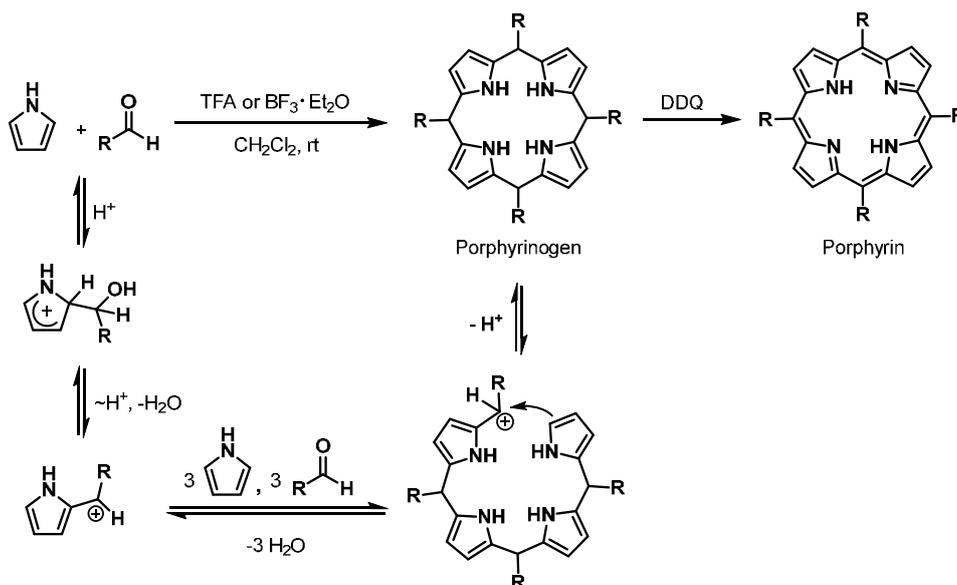


Figure 2. Structures of naturally occurring metallated tetrapyrroles: chlorophyll and heme.

The first synthesis of the simplest porphyrin (porphin) was reported by ROTHEMUND in 1936 using pyrrole and formaldehyde as starting materials in a condensation reaction.^[4] 30 years later ADLER and LONGO presented an improved synthetic protocol with shorter reaction times, higher yields and a slightly higher tolerance regarding substituted aldehydes.^[5] Still the reaction conditions were quite harsh (propionic acid, temperatures of 150 °C) and therefore aldehydes with sensitive functional groups were not tolerated. In 1987 LINDSEY presented the synthesis of porphyrins under mild reaction conditions (catalytic amounts of acid, room temperature) and set a new standard in porphyrin chemistry.^[6] In this acid-catalyzed (TFA or BF₃·OEt₂) equilibrium condensation reaction, pyrroles and the corresponding aldehydes are condensed to the thermodynamically favored porphyrinogen. In a second step this porphyrinogen is irreversible oxidized with DDQ to the desired porphyrin (Scheme 1). It is important to use a (relatively low) concentration of 10⁻² mol/l of the starting materials (pyrrole, aldehyde) to ensure a successful synthesis. While higher concentrations favor the formation of oligo- and polymers, lower concentrations lead to shorter chain lengths than necessary.



Scheme 1. Mechanism for the synthesis of A_4 -porphyrins according to LINDSEY.^[6]

Due to the mild conditions more sensitive aldehydes were utilizable. This resulted in a broad variety of novel *meso*-substituted porphyrins. High yields of up to 40% conducted to the success of this method and make it indispensable for current porphyrin chemistry.

It should be noted that not only A_4 -, but also A_3B -, A_2B_2 - or AB_3 -porphyrins can be synthesized using a second aldehyde. The mixed condensation with two different aldehydes (1:1 ratio) and pyrrole would result in six possible products with the following statistical distribution (Figure 3).

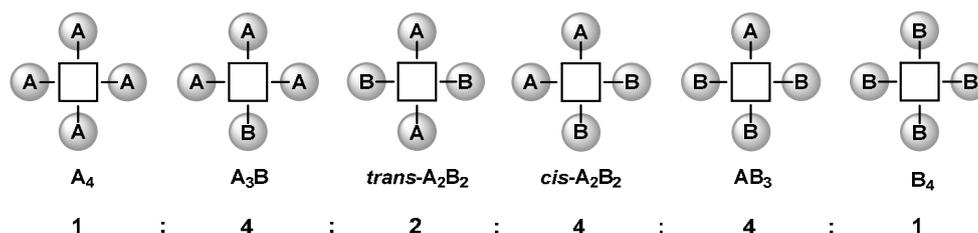
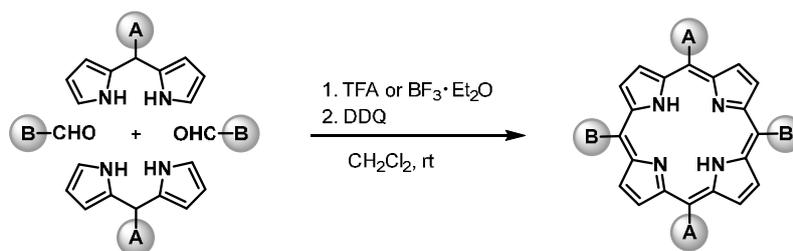


Figure 3. Statistical distribution for a mixed condensation using aldehydes A and B in a 1:1 ratio.

Due to the unfavorable statistical distribution regarding the *trans*- A_2B_2 -porphyrin, which is a quite interesting substitution pattern in porphyrin chemistry, another synthetic strategy was developed by LINDSEY and co-workers. Instead of two different aldehydes A/B and pyrrole, aldehyde A can be first reacted with pyrrole to obtain the corresponding dipyrromethane. Then this building block with the fixed aldehyde A can react with aldehyde B in an acid-catalyzed condensation reaction according to LINDSEY (Scheme 2).



Scheme 2. Synthesis of *trans*-A₂B₂-porphyrins *via* dipyrromethanes.

The yields of the *trans*-A₂B₂-porphyrin are usually high if the dipyrromethane has either electron-withdrawing *meso*-substituents or is sterically hindered. Otherwise acid-catalyzed scrambling can occur,^[7] leading to products with substitution patterns in a distribution similar to that of the mixed condensation.

Synthetic as well as naturally occurring porphyrins or derivatives thereof have manifold applications in the field of medicine as for instance in photodynamic therapy of malignant cancer^[8] or ophthalmology (age-related macular degeneration),^[9] skin (severe acne, psoriasis),^[10] cardiovascular and infectious diseases (antiviral or -bacterial)^[11]. In addition these systems are also of high interest in other research fields like catalysis,^[12] molecular electronics (solar cells),^[13] supramolecular chemistry (host-guest complexes)^[14] or exotic applications like ‘smart tattoos’.^[15]

1.1.2 Corroles

Corroles are ring-contracted representatives of the tetrapyrrole family. These conjugated macrocycles, in contrast to porphyrins, only possess three sp^2 methine bridges, one direct pyrrole-pyrrole linkage and three inner nitrogen protons (Figure 4). Corroles are aromatic systems because out of their overall 20 π -electrons, only 18 are needed for the aromatic perimeter. While porphyrins serve as dianionic ligands, corroles are trianionic ligands that support metals in higher oxidation states, main group elements,^[16a] actinides^[16b] and lanthanides.^[16c]

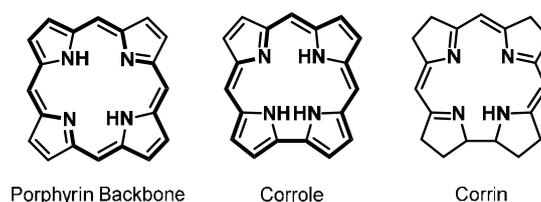


Figure 4. Structural comparison of aromatic porphyrin, corrole and non-aromatic corrin.

The contraction of the system, caused by the mentioned direct pyrrole-pyrrole linkage, is responsible for further specific properties like a nonplanar structure, a higher electron density and therefore a higher susceptibility to possible oxidation in the *meso*-position. Therefore, corroles are less stable compounds than their porphyrin analogues. Stabilization of the electron rich macrocycle is generally possible with the introduction of electron-withdrawing groups like in one of the most stable corroles: the tris(pentafluorophenyl)-substituted corrole.

Another interesting difference between porphyrins and corroles is found in their copper complexes regarding their NMR spectra. In contrast to copper(II)-complexed porphyrins which are paramagnetic, the copper-complexed corroles proved to be diamagnetic which allows the measurement of well-resolved NMR spectra. HOLTHAUSEN and co-workers showed that copper-corroles contain a rather well-hidden Cu(II)-ion instead of a Cu(III)-ion and it is suggested that the divalent state is stabilized through a saddling distortion of the corrole ligand.^[17]

Corrin is a non-aromatic derivative of corrole capable of binding cobalt and due to its high number of sp^3 carbon centers it is relatively flexible. In nature the corrinoid system forms the skeleton of cobalamins, also known as vitamin B₁₂ group (Figure 5). In living organism this vitamin is important for cell division, hematopoiesis (formation of blood cellular components) and the nervous system. It is the structurally most complicated and largest of all vitamins. The term ‘vitamin B₁₂’ is reserved for the biologically inactive cyanocobalamin only. In the organism it is transferred into the biologically active adenosylcobalamin (coenzyme B₁₂).

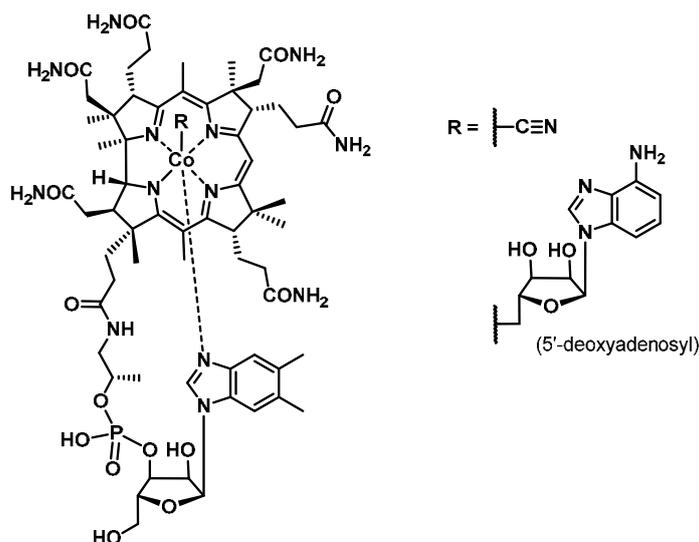
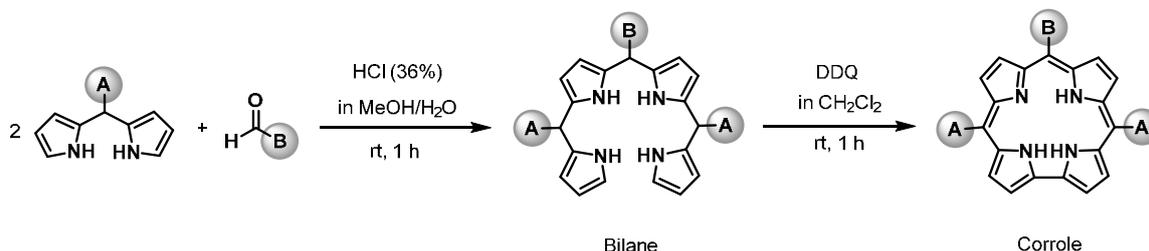


Figure 5. Structure of cyanocobalamin (vitamin B₁₂) and adenosylcobalamin (coenzyme B₁₂).

In comparison to porphyrins, for a long time an efficient synthesis for corroles was missing. The first synthesis of a corrole was accomplished by JOHNSON and KAY in 1965.^[18] Other strategies towards this macrocycle were also developed, but it took until the end of the 1990s when research groups like GROSS^[19] and PAOLESSE^[20] presented straightforward synthetic protocols. In 2006 GRYKO *et al.*^[21] published a new method for the synthesis of corroles which nowadays is a landmark in this research field (Scheme 3). In this approach, the different solubilities of the starting materials and the corrole precursor, the bilane, are exploited. While dipyrromethanes and aldehydes are soluble in the 1:1 mixture of water and methanol, the bilane precipitates and is thus removed from the condensation equilibrium. In the second step the bilane is oxidized to the corrole using DDQ. The yields of up to 56% are the best in literature so far and have been reproduced by a number of research groups.



Scheme 3. Two-step synthesis of A₂B-corroles according to GRYKO.^[21]

Due to these efficient synthetic protocols new applications for corroles could be investigated. They are e.g. used as catalysts,^[22] in medicine,^[23] and for dye-sensitized solar cells.^[22,24]

1.1.3 Partially Conjugated Porphyrinoids

In this chapter the focus is set on the *meso*-positions of tetrapyrrolic systems and their hybridization. For a better understanding, it is necessary to take a closer look at the different possible classifications (Figure 6). On the one hand, there are non-conjugated systems like the *meso*-unsubstituted porphyrinogen or *meso*-substituted calix[4]pyrrole each bearing exclusively sp^3 -hybridized carbon centers and, on the other hand, there is the porphyrin backbone (porphin) which is fully conjugated and possesses four sp^2 -hybridized carbon centers in *meso*-position. In between these two systems there are also partially conjugated tetrapyrroles with sp^3 - and sp^2 -hybridized *meso*-positions. These fascinating macrocycles are at the interface between **calixpyrroles** and **porphyrins** and are therefore described as ‘calixphyrins’.^[25]

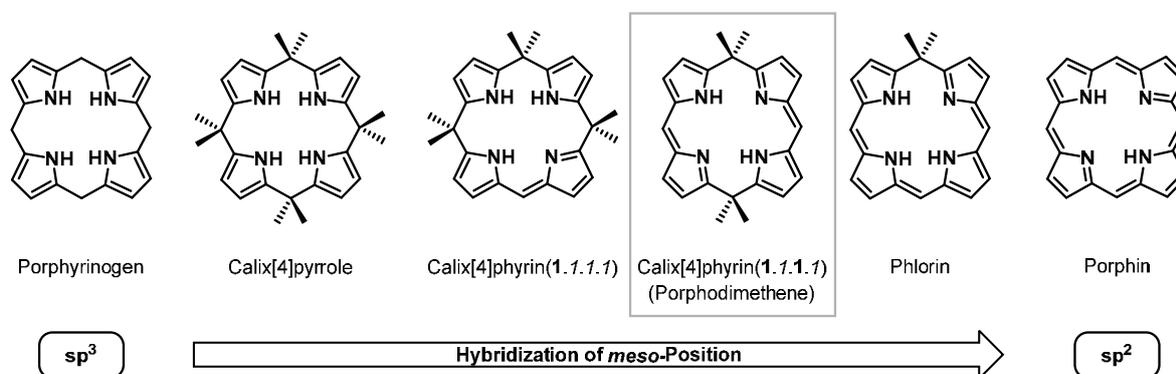
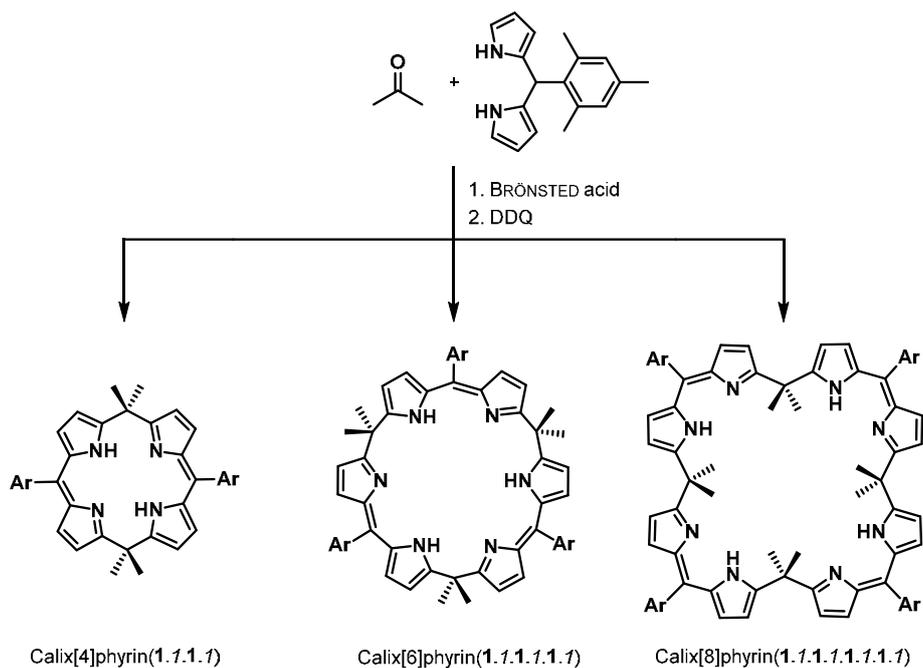


Figure 6. Series of non-conjugated, partially conjugated and fully conjugated tetrapyrroles.

The term ‘calixphyrin’ is typically used for the calix[4]phyrin(1.1.1.1), also known as porphodimethene. The alternating sp^3 - (**bold numbers**) and sp^2 -hybridized (*italic numbers*) *meso*-positions lead to far-reaching conformational changes (roof-shaped structure) and finally to their unique physicochemical properties. They were studied in the field of coordination chemistry, catalysis or as ion sensors.^[26]

Calix[*n*]phyrins exist in their tetrapyrrolic form ($n = 4$, four pyrrole units, four carbon-bridges), but also higher homologues are known. Unfortunately, efficient synthetic protocols for their preparation were not available for a long time. In 2000 SESSLER and co-workers reported the first simple and rational synthesis of calix[*n*]phyrins ($n = 4, 6$ and 8). The acid-catalyzed condensation reaction of mesityldipyrromethane and acetone proceeds in a range of solvents and BRÖNSTED acids (trifluoroacetic acid (TFA), methane sulfonic acid (MSA), 4-methylphenylsulfonic acid (*p*-TSA), HCl).^[26b] It should be noted that the specific reaction conditions strongly affect the outcome. While the use of acetone as the reagent and solvent, TFA as the catalyst and 24 h stirring at rt results in the formation of all three calix[*n*]phyrins with yields of 44% ($n = 4$), 23% ($n = 6$) and 9% ($n = 8$), the use of pure dichloromethane as the solvent leads to the formation of calix[4]phyrin exclusively.



Scheme 4. First rational synthesis of calix[*n*]phyrins (*n* = 4, 6 and 8) according to SESSLER.^[26b]

Unfortunately calixphyrin systems, especially those carrying hydrogen at their sp^3 -hybridized *meso*-positions, are generally unstable towards light or air oxidation making them less attractive for further applications. This problem was overcome i.a. in 2013 by REISSIG, WIEHE and co-workers, presenting stable PFP-substituted calix[4]- and calix[6]phyrins which were synthesized according to a novel synthetic protocol.^[27] Here the strategy was the use of a sterically congested dipyrromethane (with one *meso*-CH hydrogen atom) to avoid a full oxidation. Advantages, interesting side-products and details of this method will be discussed in the course of this thesis.

1.1.4 Expanded Porphyrinoids

The term ‘expanded porphyrinoids’ is defined as “macrocycles that contain pyrrole, furan, thiophene, or other heterocyclic subunits linked together either directly or through one or more spacer atoms in such a manner that the internal ring pathway contains a minimum of 17 atoms” according to SESSLER and SEIDEL.^[28] Since the big variety of possible macrocycles fitting in this general definition can be confusing, we will focus on pyrrole-containing systems. Also partially conjugated systems like expanded calix[*n*]phyrins are excluded (as they are already discussed in the previous chapter). Nevertheless, there is still a huge amount of expanded porphyrinoids left, possessing pyrrole units which are connected by sp^2 methine bridges (Figure 7).

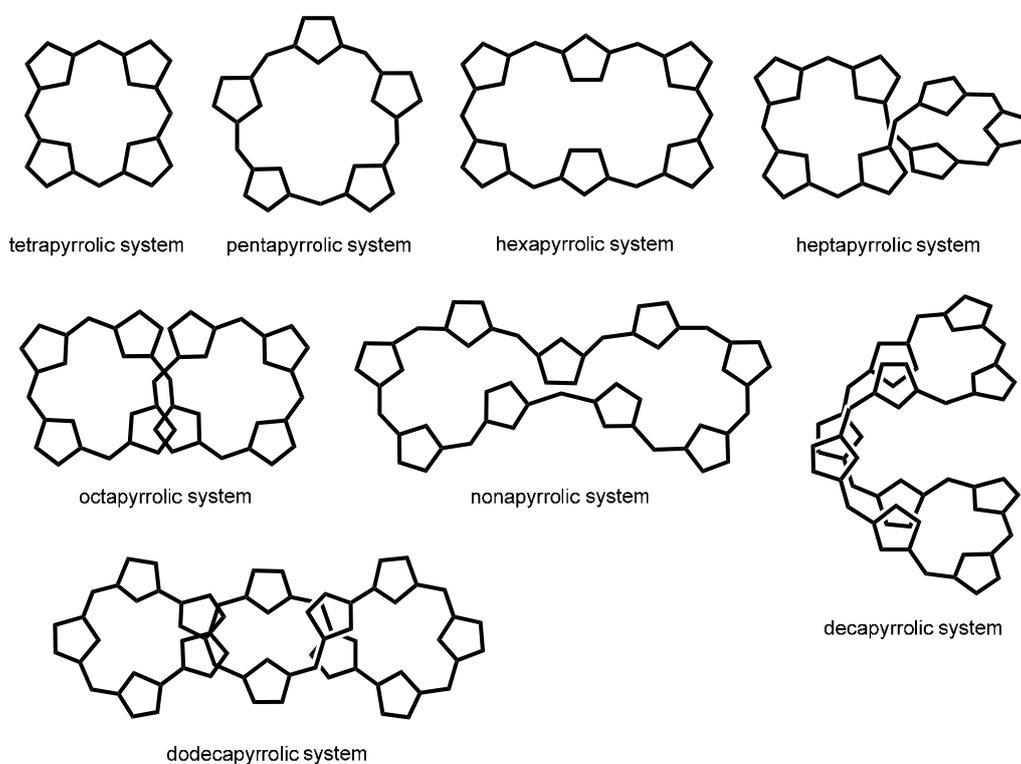


Figure 7. Series of all-pyrrole containing expanded porphyrinoid structures.^[29]

We focused on the next higher porphyrin homologues, the penta- and hexaphyrins, due to their interesting photophysical (red-shifted absorption spectra) and -chemical properties regarding possible biomedical applications, but also their non-distorted planar structures in contrast to their higher homologues. The systematic nomenclature for all above mentioned expanded porphyrinoids is accomplished as shown for the [26]hexaphyrin(1.1.1.1.1.1) system (Figure 8).

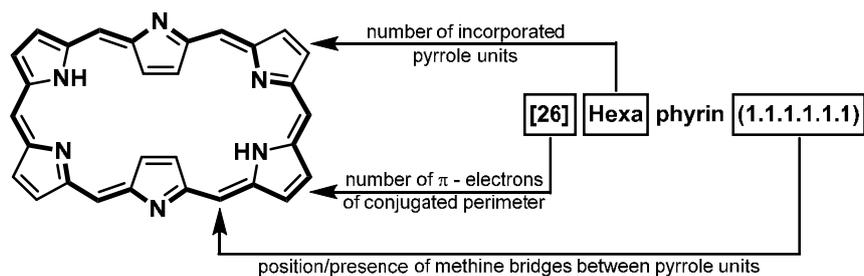


Figure 8. Systematic nomenclature for the hexaphyrin system.

According to FRANCK and NONN^[30] as well as others, an individual name for each of these expanded macrocycles can be generated in three steps. (a) The number of π -electrons in macrocyclic conjugation is put in square-brackets as the prefix of the name. (b) The number of pyrrole units in the macrocycle gives the first part of the name (pyrrole units: 5 = penta-, 6 = hexa-, 7 = hepta-, ...) which is completed with the suffix '-phyrin'. (c) Starting from the largest unit, the position and/or presence of methine bridges between pyrrole units or direct pyrrole-pyrrole linkages are given by the numbers in round-brackets (1 = methine bridge, 0 = direct linkage). For a simple porphyrin this specific nomenclature e.g. results in '[18]tetraphyrin(1.1.1.1)'. Since all expanded porphyrinoids shown in figure 7 possess larger conjugated π -systems, each of them has its specific absorption wavelengths and color. Some expanded systems with one or more direct pyrrole-pyrrole linkages even have color-related names like [22]pentaphyrin(1.1.1.1.0) is called sapphyrin (blue sapphire), [24]hexaphyrin(1.0.0.1.0.0) is called amethyrin (violet amethyst) or [26]hexaphyrin(1.1.0.1.1.0) is called rubyrin (pink to blood-red ruby).

Historically, the chemistry of all-pyrrole containing expanded porphyrinoids started in 1966 when WOODWARD and co-workers discovered sapphyrin by a coincidence (comprehensive publication finally in 1983).^[31] Other exotic structures like uranyl superphthalocyanine by DAY and MARKS (1978)^[32] or texaphyrin synthesized by SESSLER and co-workers (1988),^[33] although not directly referred to our focus of research, are worth to be mentioned (Figure 9).

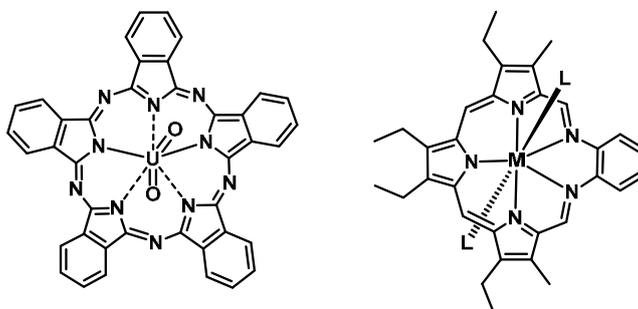
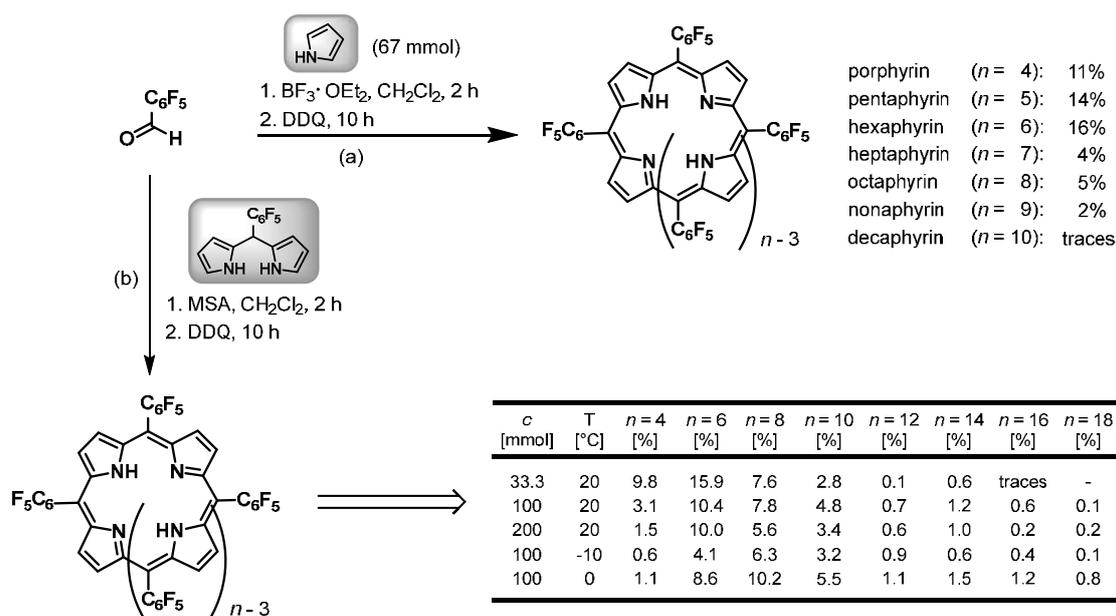


Figure 9. Structures of uranyl superphthalocyanine and texaphyrin.

Except GOSSAUER and co-workers who presented the first synthesis of penta- and hexaphyrins and metal complexes thereof (1983 and 1993, respectively),^[34] CAVALEIRO and co-workers who reported the formation of [26]hexaphyrin during a ROTHEMUND condensation reaction of tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrin (1999),^[35] it took until 2001 when OSUKA and co-workers finally reported a facile one-pot reaction for the synthesis of *meso*-aryl-substituted expanded porphyrinoids.^[36] Their systematic studies laid the foundations for further investigations regarding the unique structures, modifications, reactivities and applications of expanded porphyrinoids.

In summary, OSUKA and co-workers presented two approaches: (a) a mixed condensation using aldehyde, pyrrole and BF₃·OEt₂ with a reaction time of only two hours (Scheme 5) resulting in the formation of expanded macrocycles with up to 10 pyrrole units (even and uneven pyrrole units formed).^[36a] (b) In another protocol by OSUKA *et al.* from 2008, instead of an aldehyde, pyrrole and BF₃·OEt₂, the authors used an aldehyde, the building block dipyrromethane and methanesulfonic acid as catalyst (Scheme 5) to obtain expanded macrocycles with even pyrrole units only.^[37] This second size-selective approach allows the formation of higher expanded porphyrinoids with better yields and enables the synthesis of expanded macrocycles bearing two different *meso*-substituents.^[38]



Scheme 5. Synthesis of expanded porphyrinoids with even and uneven or only even pyrrole units.

These two approaches differ from the synthesis of the corresponding porphyrins according to LINDSEY in some conditions which favor the formation of the expanded porphyrinoids: (1) A much higher molar concentration of the starting materials (optimized 67 mmol), (2) longer condensation reaction times after addition of corresponding acid, (3) shorter oxidation reaction times and (4) use of different acids as the catalyst depending on the desired macrocycle.

It is noteworthy that electron-withdrawing substituents in the *meso*-position, like pentafluorophenyl groups, are favorable since they stabilize the partly huge electron-rich π -systems. The destabilizing influence of these electron-withdrawing substituents on the carbocations which occur in the course of the condensation reaction also hinder a re-opening of the primary condensation products favoring non-equilibrium expanded porphyrinoid structures. The slightly higher steric demand of the *ortho*-fluorines also favors larger (then porphyrinogen) ring condensation products.

Expanded porphyrins, including hexaphyrins, exhibit unique properties with respect to their optical, structural, electrochemical or coordination behavior.^[29,39] These features improve their potential as oxidation catalysts,^[40a] multi-metal coordination ligands,^[40b] nonlinear optical (NLO) materials^[40c] or near infrared (NIR) dyes.^[40d] Another very interesting property can be found in their large two-photon absorption (TPA) cross-sections ($\sigma^{(2)}$)^[41] which make them potential candidates for deeper-penetrating PDT agents. In the 1930s the simultaneous absorption of two photons by the same molecule was first described by later Nobel Prize winner GÖPPERT-MAYER ($\sigma^{(2)}$ values are therefore given in GM units).^[41]

A normal porphyrin possesses a $\sigma^{(2)}$ value lower than 100 GM^[42] whereas i.e. [28]hexaphyrin exhibits a ~20-fold larger and [26]hexaphyrin a ~100-fold larger $\sigma^{(2)}$ value^[43] (Figure 10). For a better understanding of these data it is noteworthy to mention that ‘medium’ $\sigma^{(2)}$ values are considered < 50 GM while values of 10000 GM are considered as ‘very large’.

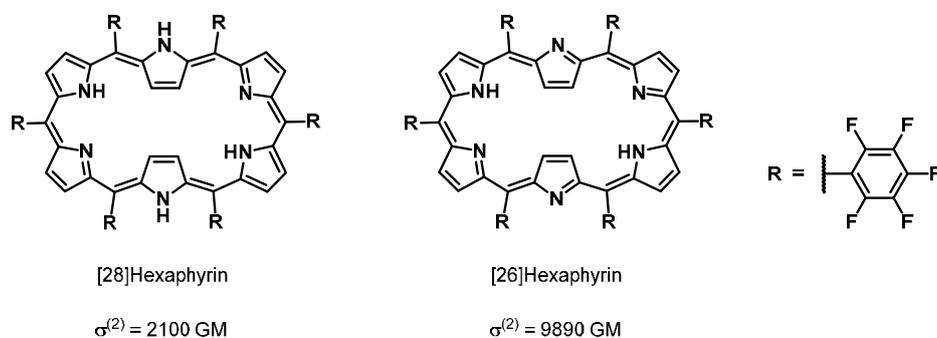


Figure 10. TPA cross-sections ($\sigma^{(2)}$) values of [28]- and [26]hexaphyrins.

1.2 Carbohydrates and Their Derivatives

Carbohydrates, along with nucleic acids, lipids and proteins, belong to the major classes of organic molecules which can be found in living systems. Since almost all organisms produce or metabolize them, carbohydrates are ubiquitously found in nature. Carbohydrates, also called saccharides, can be divided into monosaccharides, disaccharides, oligosaccharides and polysaccharides. Monosaccharides are the simplest units of carbohydrates. The different representation of structures for saccharides is exemplary shown for α -D-glucopyranose (Figure 11).

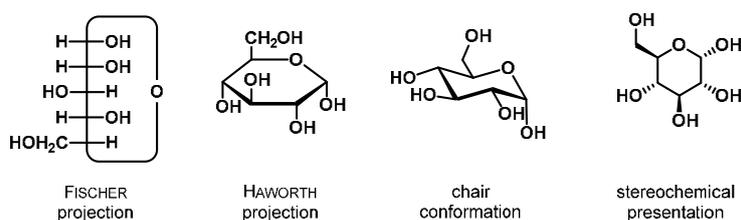


Figure 11. Different representations for α -D-glucopyranose.

How is the name ' α -D-glucopyranose' generated? First of all this monosaccharide possesses six carbon atoms and therefore belongs to the hexoses or more specifically to the aldoses since it carries an aldehyde group in its open-chain form which explains the suffix '-ose'. The open-chain form of glucose can cyclize *via* an intramolecular hemiacetal formation (Figure 12) which either leads to its pyranose (carbon 1 and 5: six-membered ring) or its less common furanose (carbon 1 and 4: five-membered ring) form.

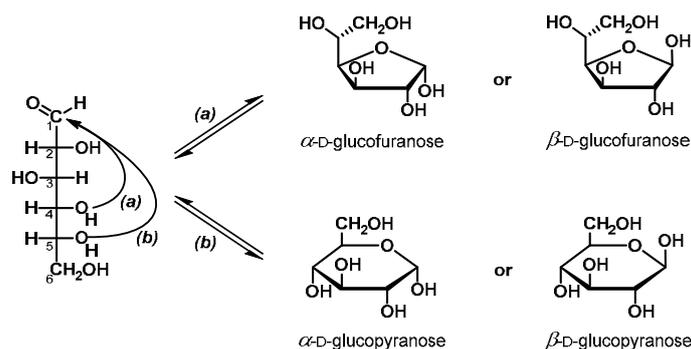
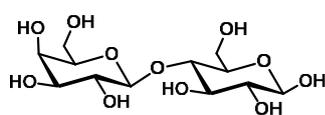


Figure 12. Open-chain form and possible intramolecular cyclization forms (furanose and pyranose form).

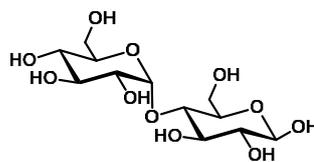
Furthermore, *via* cyclization (intramolecular hemiacetal formation) the first carbon atom becomes a new chiral center. Two possible anomers are possible which either give the prefix ' α ' or ' β '. The last information for the complete name of ' α -D-glucopyranose' is the stereodescriptor '-D-' which describes in this case the absolute configuration of the fifth carbon atom referring to *dexter* (opposite: L for *laevus*).

Monosaccharides (e.g. glucose, galactose or fructose) are also building blocks for disaccharides (e.g. sucrose, lactose or maltose) and polysaccharides (e.g. cellulose, starch or chitin) which are formed by condensation reactions. The polysaccharide starch is due to its tightly packed structure (helical amylose, highly branched amylopectin) ideal for energy storing in plants (Figure 13). The extensively branched analogue in animals and fungi is called glycogen. Cellulose on the other hand is a polysaccharide which also consists of glucose units, but has a linear structure. It is used as important structural component for cell walls in plants. For animals and fungi this stabilizing function is accomplished by chitin (linear polysaccharide consisting of *N*-acetylglucosamine units).

Disaccharides:

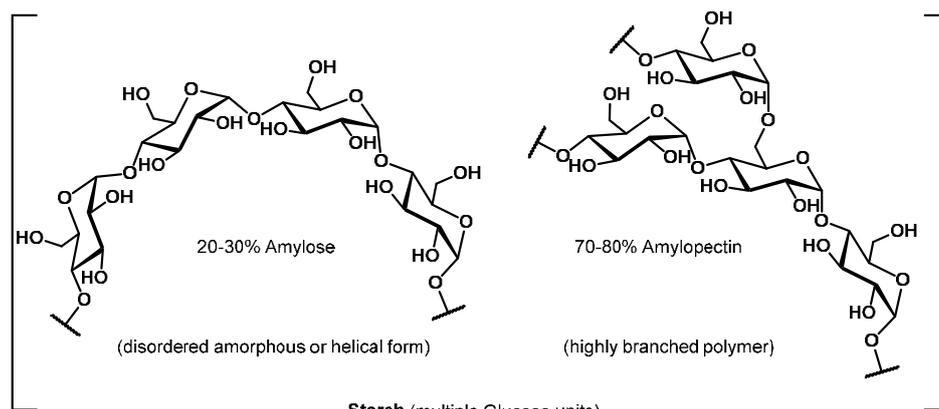


Lactose (Galactose + Glucose)

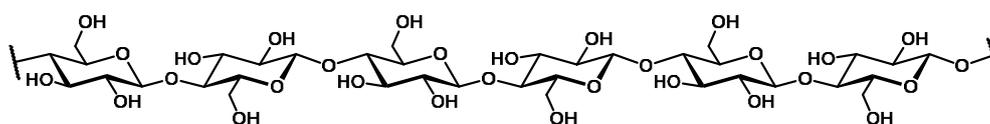


Maltose (Glucose + Glucose)

Polysaccharides:



Starch (multiple Glucose units)



Cellulose (multiple Glucose units)

Figure 13. Examples of di- and polysaccharides structures consisting of glucose and/or galactose units.

In nature apart from carbohydrate-carbohydrate linkages also carbohydrate containing biomolecules like glycoproteins and glycolipids are found where the carbohydrate is connected to a non-carbohydrate structure (the aglycon) which are involved in many molecular recognition processes like intermolecular cell communication or signal transduction. These properties are crucial for the regulation of biological functions and an interference can lead to a variety of diseases.

Hence, carbohydrates became highly interesting subunits for potential medicinal applications. Elucidating and analyzing the structures of naturally occurring glyco-conjugates, e.g. Vancomycin, Tunicamycin, Calicheamycin γ 1 or Avilamycin A, and clinical studies led to novel pharmaceuticals in the field of anticarcinogens, antibiotics, enzyme inhibitors and antibiotic growth promoters (Figure 14).^[44]

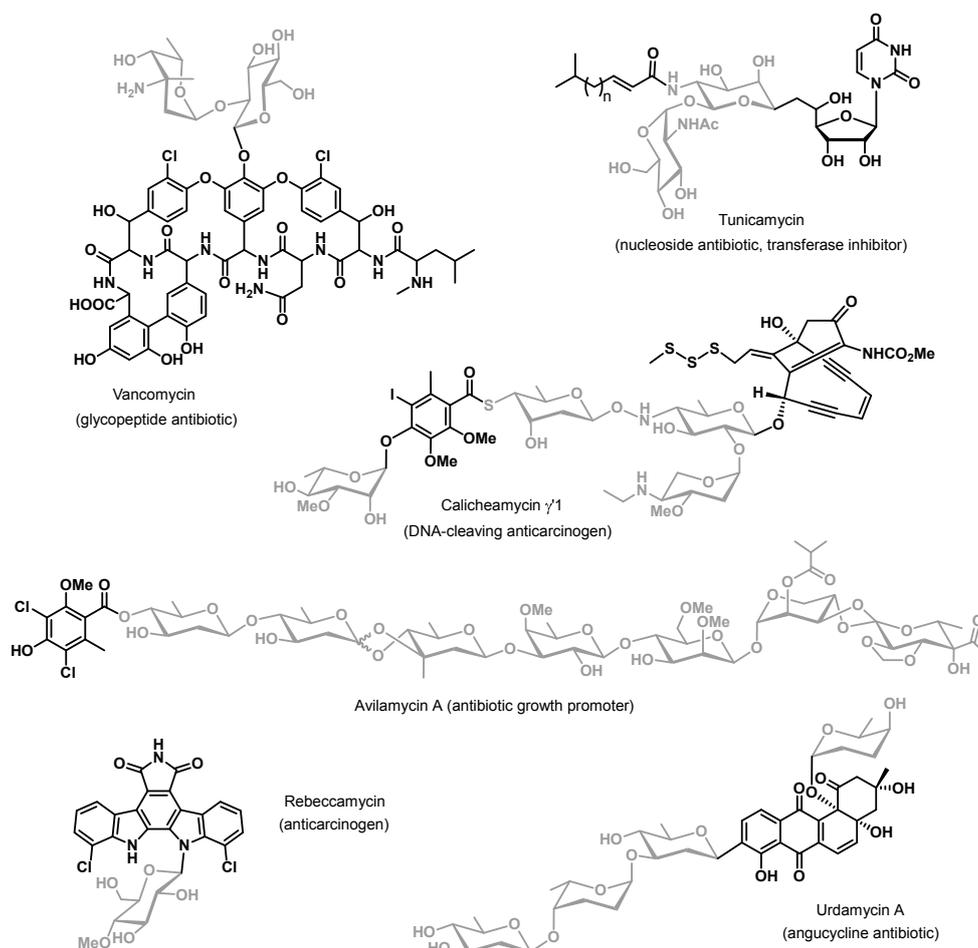


Figure 14. Naturally occurring glyco-conjugates with important biological activity used as pharmaceuticals.

Over time many synthetic glycosylated pharmaceuticals have been developed. Carbohydrates are hydrophilic biomolecules and they play an important role in cell recognition processes which makes them perfect substituents for many rather lipophilic substances with interesting features (so far unusable in biological environments) because they improve their solubility in aqueous media plus they serve as a targeting molecule and can navigate the substance to its destination, e.g. malignant tumor tissue.

There are multiple important coupling reactions (glycosylations) in literature to obtain the corresponding glyco-conjugates which may serve for potential novel medicinal applications. Some of them will be mentioned in the following chapter.

1.3 Glycosylation Methods

In this chapter selected glycosylation methods will be described, focusing on their applicability for porphyrinoids. Again, carbohydrate moieties not only transfer amphiphilic properties to extremely lipophilic compounds like porphyrinoids, but also serve as targeting molecules. Many cancer cells have over-expressed carbohydrate receptors due to their higher metabolic rate and the increased levels of carbohydrate uptake and their metabolism can facilitate the uptake of glyco-porphyrinoids.^[45] Several glycosylation protocols mainly for porphyrins were reported and the potential applications of the respective conjugates were investigated.^[46,47]

A glycosylation reaction involves the combination of a glycosyl donor and a glycosyl acceptor. The resulting glycoside has a glycone and an aglycone part (Figure 15).

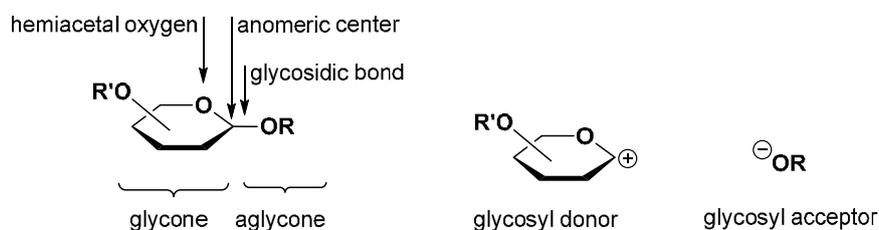
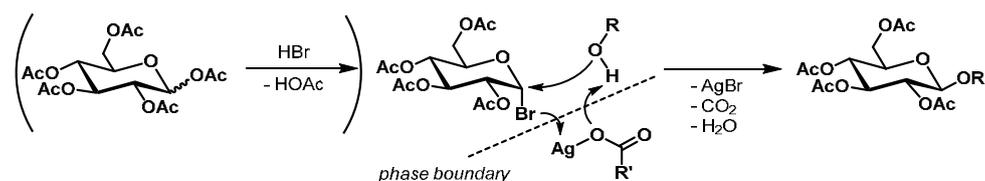


Figure 15. Structure of *O*-glycosides.

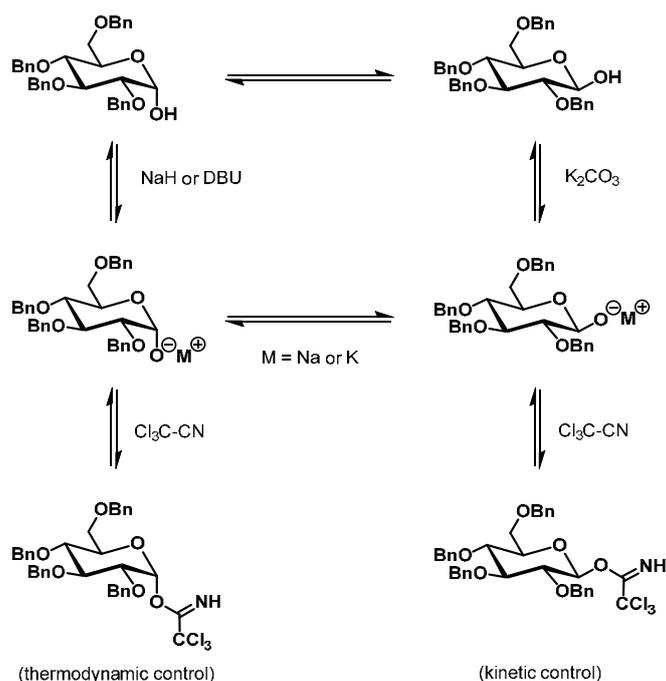
Due to the great importance of glycosides many glycosylation methods have been developed. In 1880 FISCHER started his first fundamental studies on carbohydrates (e.g. identification of their configuration) and also reported a method for the synthesis of glycosides.^[48] In this classical FISCHER synthesis, the unprotected monosaccharide is dissolved in an excess of alcohol and the catalyst HCl is added leading to a glycoside in an anomeric mixture. Here the higher reactivity of the hemiacetal hydroxyl group is utilized. Generally, most of the common glycosylations require an excess of the alcohol (aglycone). In our case a tetrapyrrole which has to be prepared in a multi-step synthesis. High costs of the aglycone and also the acidic conditions may be seen as disadvantageous.

In modern synthetic protocols the number of reactive hydroxyl groups is reduced by the introduction of protection groups which also improve the reactivity of the anomeric hydroxyl group of the glycone. One of these methods is the well-established KÖNIGS-KNORR glycosylation where mono-halogenated acetoxy-protected monosaccharides are reacted with alcohols in the presence of mostly silver carbonate. Thermodynamically controlled and stabilized by the anomeric effect the introduction of the halogen leads to the favored formation of the halogenated α -anomer which then can react with the aglycone to the corresponding β -glycoside (Scheme 6).^[49] Advantages are the good availability of the glycosyl donors (one-step synthesis) and the efficiency of the glycosylation whereas the harsh conditions for the synthesis of the glycosyl halides, their low thermal stability and sensitivity towards hydrolysis and the use of expensive and toxic heavy metal salts can be considered as disadvantages.



Scheme 6. General approach towards *O*-glycosides using KÖNIGS-KNORR glycosylation.

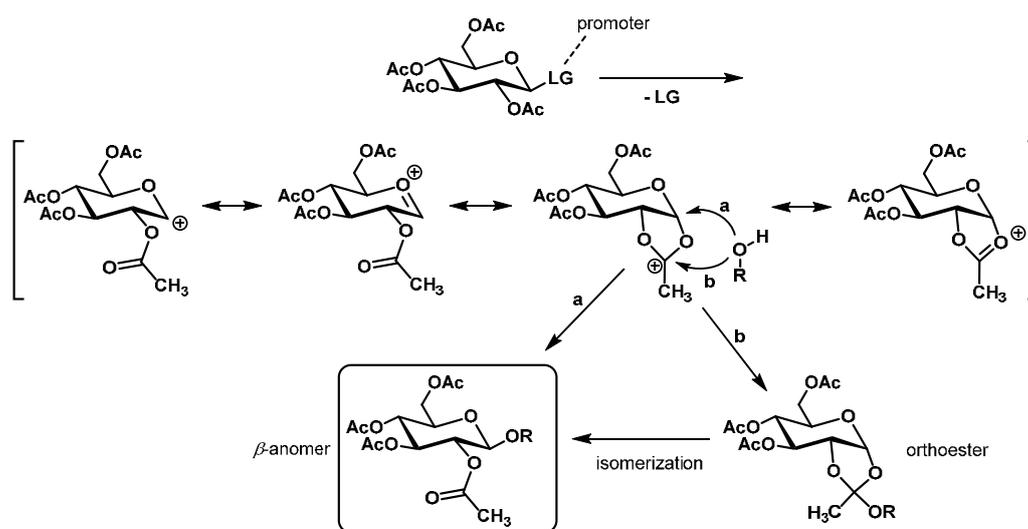
Nowadays, the trichloroacetimidate method, a glycosylation method propelled by SINAY^[50] and SCHMIDT,^[51] is very popular for the synthesis of carbohydrates, due to the high thermal and chemical stability and stereoselectivity of the respective glycosyl trichloroacetimidates. The base-catalyzed addition of protected carbohydrates, possessing an anomeric hydroxyl group, with trichloroacetonitrile leads to their corresponding imidates. Depending on the utilized base for deprotonation it is possible to selectively obtain the α - or β -trichloroacetimidates.^[52] This is shown for the case of the benzylated glucose (Scheme 7).



Scheme 7. Synthetic approaches towards α - or β -trichloroacetimidates.

For example, the β -glucosyl trichloroacetimidate is rapidly formed under kinetic control, but it can slowly anomerize in a base-catalyzed back-reaction. The anomerization of the β -glucosylate to the α -glucosylate and a renewed addition of trichloroacetonitrile leads to the more stable α -glucosyl trichloroacetimidate (thermodynamic control). Stronger bases like NaH or DBU can accelerate the equilibrium leading to the formation of pure α -anomers whereas the weaker base K_2CO_3 is used for the formation of β -anomers.

The corresponding glycosyl trichloroacetimidates are excellent leaving groups (LG) and with the addition of a promoter, e.g. catalytic amounts of $\text{BF}_3 \cdot \text{OEt}_2$, and an alcohol the glycosides can be generated under very mild conditions. The glycosylation mechanism is described for a tetraacetylated glucose molecule also to illustrate the neighboring group effect. First the leaving group is activated and cleaved. The carbonyl oxygen from the acetyl group in C-2 position attacks the pseudoaxial position of the anomeric center. Now the formed acetoxonium ion can be attacked in C-1 position by the alcohol *via* a $\text{S}_{\text{N}}2$ mechanism (a) or directly at the carbonyl carbon (b). This attack leads to the formation of an orthoester which isomerizes to the β -anomer.



Scheme 8. Mechanism of the trichloroacetimidate method including the neighboring group effect.

Recently, this trichloroacetimidate method was developed by AICHER and co-workers for a group of *meta*-substituted glyco-tetrapyrroles^[53] and is one focal point of this thesis for the development of a library of *meta*- and *para*-glycosylated porphyrins.

Thioglycosides, first reported in 1909 by FISCHER and co-workers,^[54] are possibly the most versatile family of glycosyl donors to date. Many are synthesized for polysaccharide formation or as glycosylation reagent.^[55] Thioglycosylated porphyrins, in comparison to their *O*-glycosylated analogues, are more resistant to endogenous hydrolysis catalyzed by glycosidases and stable in basic and acidic media (also stable under physiological conditions which includes the environment of cancer cells with a reduced pH value).^[56] Since thioglycosylations work metal-free and with unprotected carbohydrates, these reactions are also very interesting for the synthesis of glyco-porphyrinoids.

It is noteworthy that the Cu(I)-catalyzed 1,3-dipolar “click” reaction, proposed by SHARPLESS and co-workers in 2001,^[57] is an effective modern method which is also used for the introduction of carbohydrate moieties. This method is not in the focus of this thesis since examples in literature indicate a decreased phototoxicity of glyco-porphyrins with a triazole-linkage in *in vitro* experiments.^[46b,46d,58]

1.4 Photodynamic Therapy

1.4.1 Theory

Photodynamic Therapy (PDT) is an alternative mild method for the treatment of malignant and non-malignant diseases where in contrast to other therapies the damage of healthy tissue is avoided or largely reduced.^[8b] Three components are crucial for this method: light of a defined wavelength, a light activatable substance (photosensitizer, e.g. a porphyrin) and oxygen which is present in all living cells. In the first step, the photosensitizer (PS) is administered to the patient. In the absence of light the PS should not possess any toxicity. After a certain time, the PS has accumulated in the tumor tissue and stays there inactive. Irradiation of the tumor tissue with light of a defined wavelength causes a series of photophysical processes, resulting in the formation of reactive oxygen species (ROS). These ROS react with biochemical components of a tumor cell like e.g. aromatic amino acids, lipids, flavonoids, heterocyclic bases and nucleic acids causing oxidative damage of the cell, finally resulting in apoptosis or necrosis.^[59] In the first step, as shown in the modified JABLONSKI diagram (Figure 16), the PS absorbs light and is excited from the ground state (S_0) to the excited singlet state (S_1).

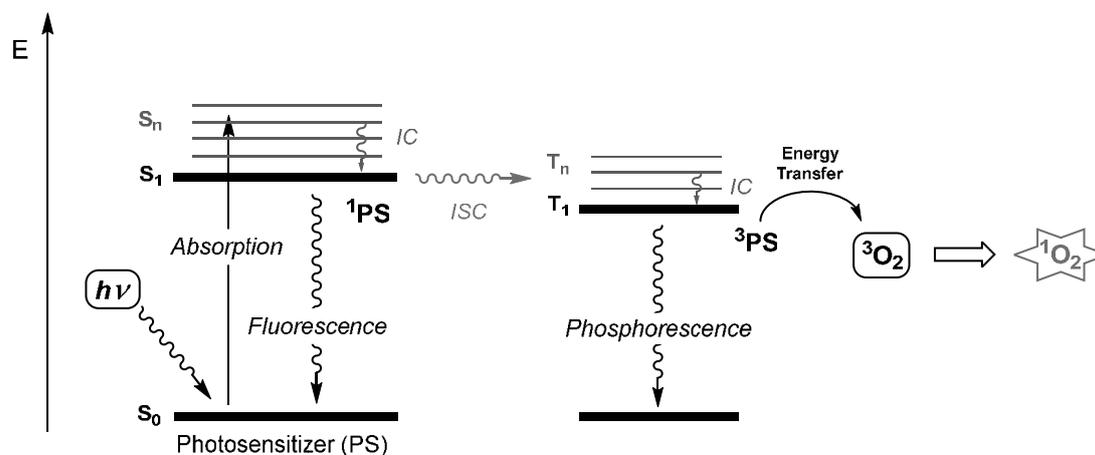


Figure 16. Modified JABLONSKI diagram showing generation of reactive singlet oxygen.

The PS in its first excited singlet state (S_1) can now return to the ground state exhibiting fluorescence or pass into a triplet state (T_1) through intersystem crossing (ISC). The triplet state (T_1) can return to the ground state exhibiting phosphorescence or it can participate in an electron-transfer process with the surrounding biological structures producing radical ions or radicals which in combination with present oxygen results in the formation of superoxides (type I reaction). Also possible is a photochemical process (type II reaction) where the PS (e.g. porphyrin) transfers the energy onto the stable triplet oxygen (ground state) which results in the short-lived highly reactive singlet oxygen which is believed to be the most important cytotoxic agent for cell death in PDT.^[8b]

The short lifetime of singlet oxygen (100 ns in lipid regions, 250 ns in cytoplasm) leads to a short diffusion rate which is approximately 45 nm in cellular media.^[60] This ensures that the cytotoxic effect is limited to the direct surrounding. The confinement of the effect to the desired area is assured by site-specific illumination.

Photosensitizers and their properties are crucial in PDT and are therefore discussed in the following chapter.

1.4.2 Photosensitizers

In the course of time certain requirements were found which a perfect PS should fulfill. Among them is the efficient generation of singlet oxygen since it is the most important cytotoxic species. Furthermore it should have a strong absorption in wavelength regions from 600-800 nm to penetrate into deeper situated tissues. Porphyrin-based PS possess a strong absorption band around 400 nm (Soret band) and less intensive absorption bands between 500 and 800 nm (Q-bands). The long-wavelength region of the Q-bands is of special interest in PDT, their absorption ranging from 600-650 nm for porphyrins, 630-700 nm for chlorins and 700-800 nm for bacteriochlorins. Chlorins and bacteriochlorins also have a higher absorbance maximum in this region. They are well studied, but nowadays also stable expanded porphyrinoids with extended π -systems are in the focus of research. Another important requirement for a perfect PS is its high toxicity in combination with light and at the same time a low dark toxicity. The PS should be also stable and chemically pure. An amphiphilic structure (hydrophilic and hydrophobic substituents) proved to be advantageous for a good distribution within the organism and a selective accumulation in the malignant tissue, assuring accumulation in membrane structures of tumor cells where the generated singlet oxygen is most effective in damaging the tumor cells.

The first clinically approved photosensitizer for PDT is Photofrin[®] (porfimer sodium). It is a photosensitizer of the first generation which consists of oligomeric hematoporphyrin derivatives. This PS possesses a couple of discussed advantages like an amphiphilic structure, an absorption at 630 nm (within the PDT window) and a quite good quantum yield of ISC (and singlet oxygen), but unfortunately a crucial disadvantage which can be found in its lower extinction coefficient making it less effective for PDT.

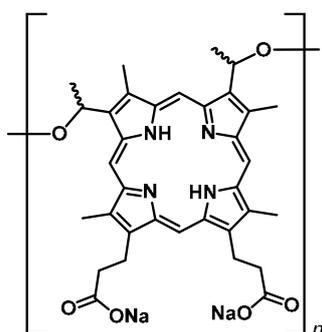


Figure 17. Structure of Photofrin[®] ($n = 1-9$).

Improved PS have been developed which led to the so-called second generation PS. One famous representative is Temoporfin and its medicinal formulation under the brand name Foscan[®]. In contrast to Photofrin[®], Temoporfin is a single compound with a defined structure. In detail, it has a chlorin

structure with an absorption at 650 nm and a higher extinction coefficient making it up to six times more efficient than Photofrin®.^[61]

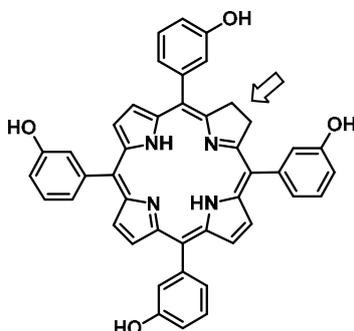


Figure 18. Structure of Temoporfin.

Besides all progresses and improvements which were made so far regarding the development of photosensitizers, one of the main problems is still a more selective accumulation of the PS in the corresponding malignant tumor or non-malignant target tissue. Here tetrapyrrolic systems with carbohydrate moieties seem very promising candidates to overcome this problem. Moreover, a certain substitution pattern (A_4 -, A_3B -, *trans*- A_2B_2 -, *cis*- A_2B_2 - or AB_3 -substituted porphyrins with A = carbohydrate moiety and B = other unpolar substituent) may be beneficial for a more selective accumulation.^[62] Both will be examined in the course of this thesis. Apart from this novel glycosylated expanded porphyrinoid systems with their unique photophysical properties could be promising as two-photon absorption photosensitizers leading into the new field of two-photon-PDT or 'PDT 2.0'. Other approaches towards increased accumulation in tumor tissue that are currently investigated comprise passive targeting *via* liposomal encapsulations or nanoparticle formulations exploiting the EPR effect and active targeting *via* antibody labelling or tumor-selective boron cluster derivatives.^[63]

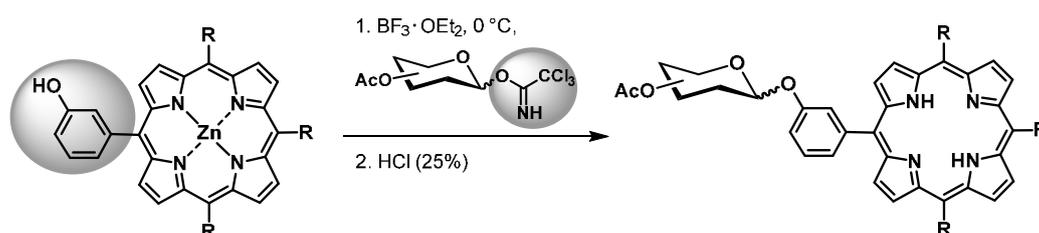
2. AIM OF WORK

Nowadays cancer is one of the most challenging diseases in the world which led to a multitude of different treatment strategies. Established, conventional methods for the treatment of cancer are surgery, chemotherapy and/or radiation therapy.^[8b,64] Besides high strain on the body, keloids, infections or infertility, one of the general side-effects is the damage of healthy tissues. To overcome this problem there is a constant interest in new treatment options. In recent research alternatives like the antibody therapy, the boron-neutron capture therapy and the photodynamic therapy (PDT) have been explored.^[63,65] As mentioned before, this doctoral thesis is a collaboration between Universität Hamburg and the biolitec research GmbH. Here the basic idea was to combine the expertise of a company in the field of PDT (laser systems, fibers, PS Temoporfin, active substance in the medicinal product "Foscan"), supervised by Dr. WIEHE, with the knowledge and experience of the research group of Prof. Dr. STARK in the field of target oriented synthetic organic chemistry (novel hybrid natural products, functional conjugates with tailored biochemical properties).

The essential aim of the work is the synthesis of porphyrinoids, their functionalization with carbohydrates and the evaluation of selected glyco-conjugates regarding their potential in *in vitro* tests against cancer cell lines. Challenging, less-explored porphyrinoid systems with their unique properties, very unpolar and therefore hardly used in biological or aqueous environments, should be glycosylated to make them accessible for potential medicinal applications.

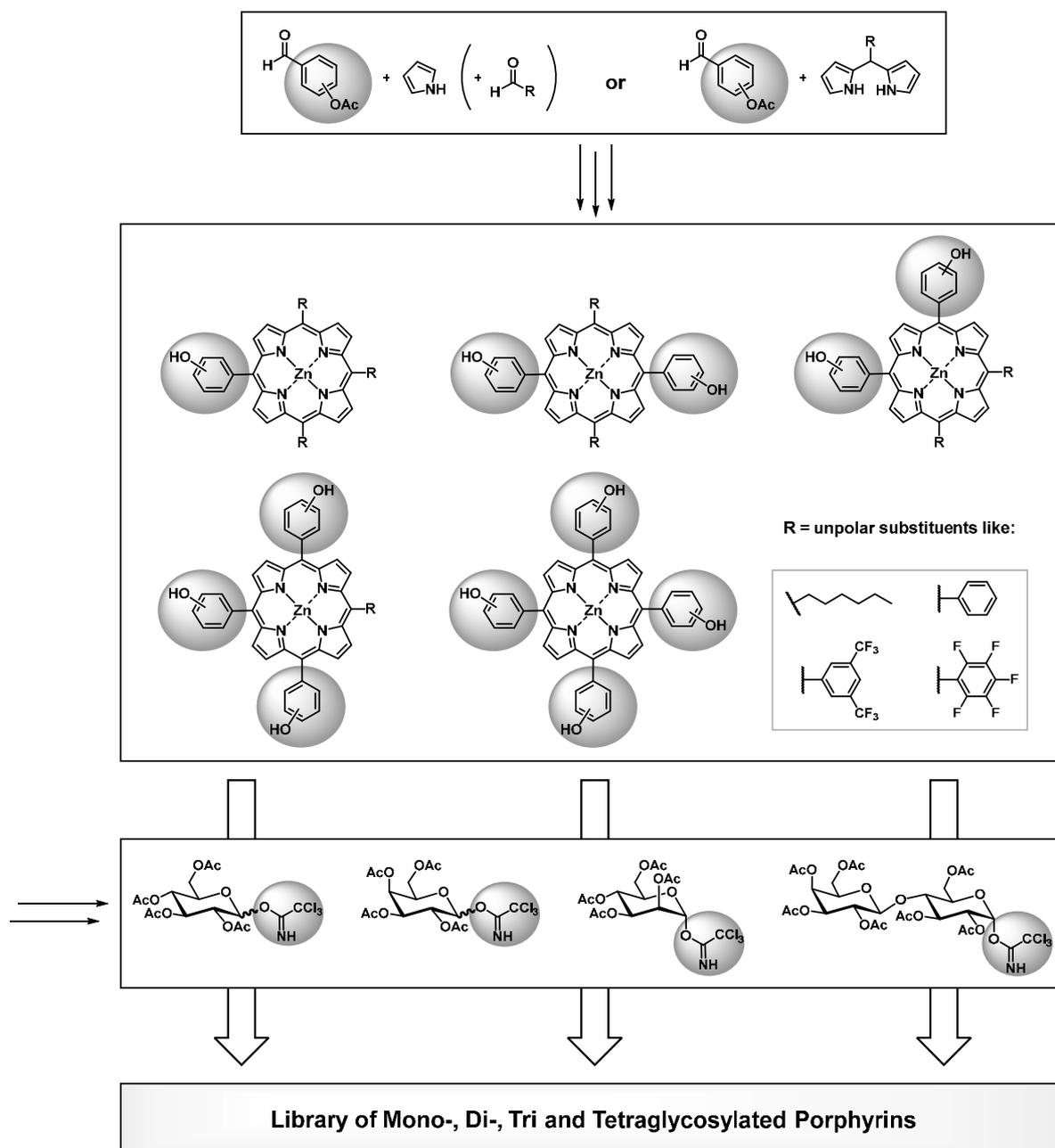
This task can be separated into four main objectives: (1) the generation of a library of glyco-porphyrins using glycosyl trichloroacetimidates and their evaluation in several cancer cell lines, (2) the synthesis of glyco-porphyrinoids absorbing at wavelengths different from a typical porphyrin to explore their use in PDT and other medical applications (3) the development of tetrapyrroles containing two different carbohydrate moieties and (4) the use of azidated aldehydes as building blocks for the synthesis of novel azide-containing porphyrinoids which then again can serve as precursors for further modifications (inclusively glycosylations).

One of the objectives and the focal point of this thesis was the development of a library of *meta*- and *para*-glycosylated porphyrins *via* the trichloroacetimidate method which was developed by AICHER and co-workers^[53] for a group of *meta*-substituted derivatives.



Scheme 9. Trichloroacetimidate method for glycosylations of porphyrins according to AICHER.^[53]

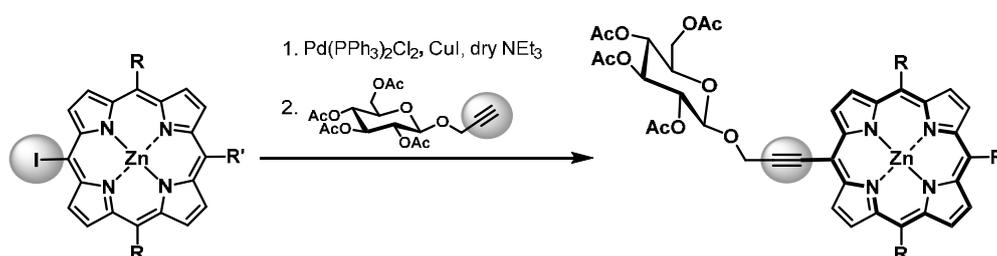
Two components are essential for this method: a Zn(II)-complexed tetrapyrrole with a phenolic hydroxyl group and a carbohydrate bearing a trichloroacetimidate moiety. As substrates a variety of zinc-metallated *meta*- and *para*-hydroxysubstituted A₄-, A₃B-, *trans*-A₂B₂-, *cis*-A₂B₂- and AB₃-porphyrins were selected (A = phenolic hydroxyl group, B = different unpolar substituents). After applying the glycosylation method (incl. demetallation and deprotection) and receiving a library of mostly novel glyco-derivatives, the influence of their different substitution patterns and polarities should be investigated in tests against cancer cell lines.



Scheme 10. Schematic representation of the development of the library of glyco-porphyrins.

In this context, modifications and combinations of the trichloroacetimidate method should be also explored to check its applicability and limitation.

Another aim of this thesis was the synthesis of glyco-porphyrinoids absorbing at longer wavelengths than a “typical” porphyrin. Two basic approaches were explored: (a) the introduction of substituents exerting a bathochromic shift, directly connected to the aromatic perimeter of the porphyrin and as a consequence a change in its absorption properties or (b) the use of a substrate possessing different absorption properties, e.g. an expanded porphyrinoid, which could then be glycosylated by an appropriate method. During the master thesis^[66] the development of a synthetic protocol for a glyco-porphyrin with a bathochromically shifted absorption was already started. In this case a Zn(II)-complexed, *meso*-iodinated porphyrin was reacted with a carbohydrate alkyne in a SONOGASHIRA reaction.



Scheme 11. First synthesis of glyco-porphyrin *via* Pd-catalyzed cross-coupling (SONOGASHIRA reaction).

Alternatively, porphyrinoid systems or precursors with different photophysical properties could be glycosylated. Here the focus lies on a glycosylation method which also works for more sensitive and challenging systems. It should be noted that glycosylations of calixphyrin or expanded porphyrinoid systems have not been examined so far.

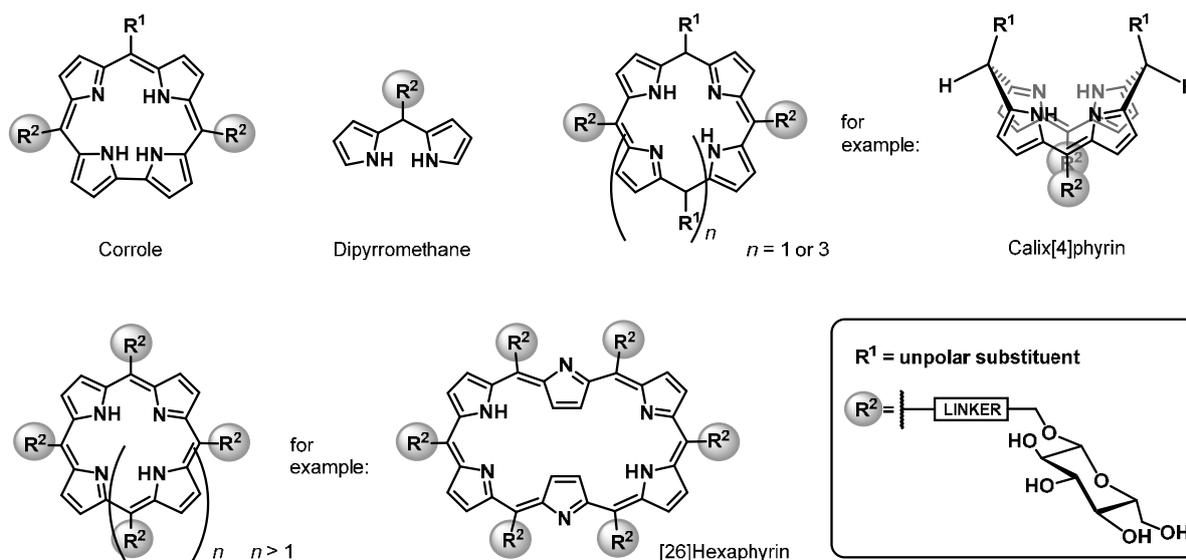


Figure 19. Target structure of novel glycosylated porphyrinoids.

The last aim regarding glyco-porphyrinoids, was the development of tetrapyrroles containing two different carbohydrate moieties, e.g. a mono- and a disaccharide moiety. These potentially bioactive tetrapyrrolic systems are hitherto unknown because synthetic strategies are missing. Thus, it was tried to find some strategic prospects.

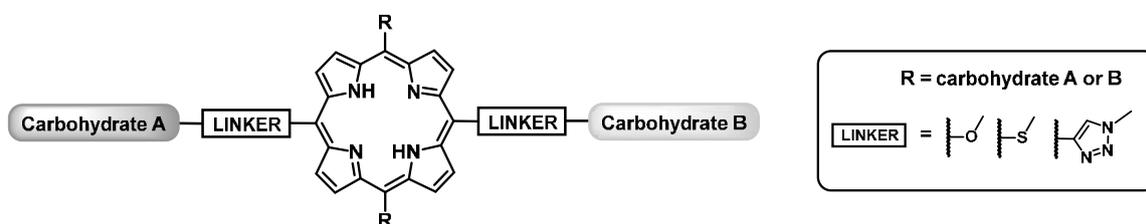


Figure 20. Schematic representation of heteroglycosylated tetrapyrrole.

An aim, not directly related to glycosylations, was the one-pot azido-aldehyde condensation which gives access to novel azido-porphyrinoids suitable for further functionalization reactions. For the relatively unexplored calix[*n*]phyrins and [*n*]hexaphyrins species especially in the field of biomedicine few applications are known today. Using a consecutive reaction, like the 1,3-dipolar “click” reaction, a variety of available alkyne-containing substrates can be chosen to synthesize customized porphyrinoids (including glycosylations with alkyne-substituted glycons).

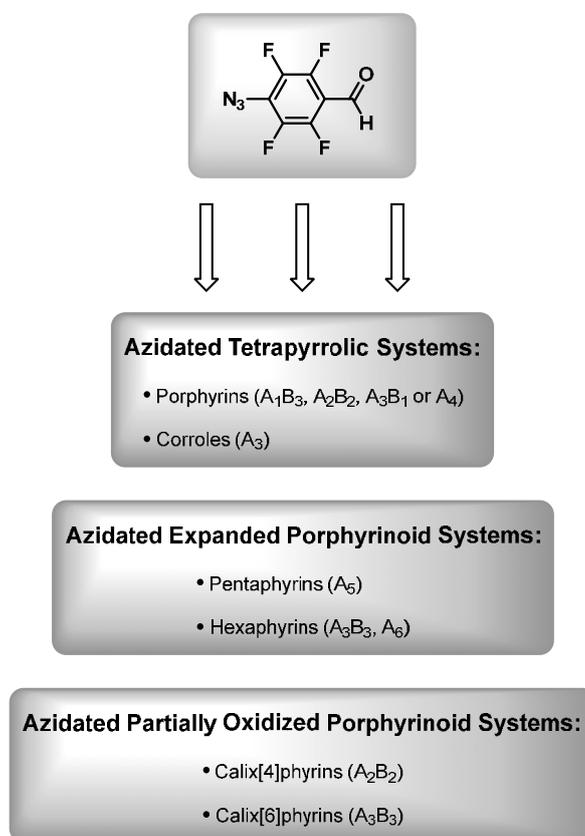


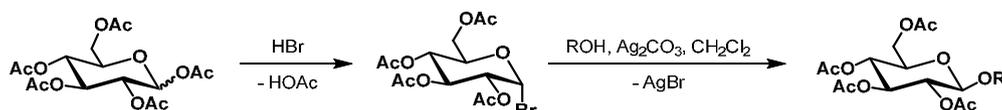
Figure 21. Schematic representation of the synthesis of azide-containing porphyrinoids.

3 RESULTS AND DISCUSSION

3.1 Library of Glyco-Porphyrins Using Glycosyl Trichloroacetimidates

3.1.1 Synthesis of Mono- and Diglycosylated Tetrapyrroles

As already outlined in chapter 1.4.2, the perfect PS should fulfill certain criteria for PDT. One of these criteria is the (passive) targeting of tumors. Herein glyco-porphyrins are a promising compound class. On one hand, carbohydrates improve the solubility of the porphyrin in aqueous media and, on the other hand, they play an important role in cell recognition processes and could help to bring the porphyrins to its target, e.g. malignant tumor tissue.^[67] Early attempts towards the synthesis of glyco-substituted tetrapyrroles were based on condensation reactions between glycosylated aldehydes and pyrroles according to LINDSEY.^[46e,46f,68] Unfortunately, these condensation reactions are low-yielding, as well as the synthesis of the corresponding glycosylated aldehydes with a yield of only 21%.^[69] KÖNIGS-KNORR reactions are an alternative path to glycosylated porphyrins (Scheme 12). Here a glycosyl halide reacts with the corresponding hydroxy-substituted porphyrin in the presence of silver carbonate.^[70] Disadvantages are the partial complexation of the porphyrin with silver, long reaction times, large excess of glycosyl halides and, in some cases, the formation of anomeric mixtures. Furthermore glycosyl halides are less stable which is unfavorable for their storage and they have to be freshly prepared if needed.

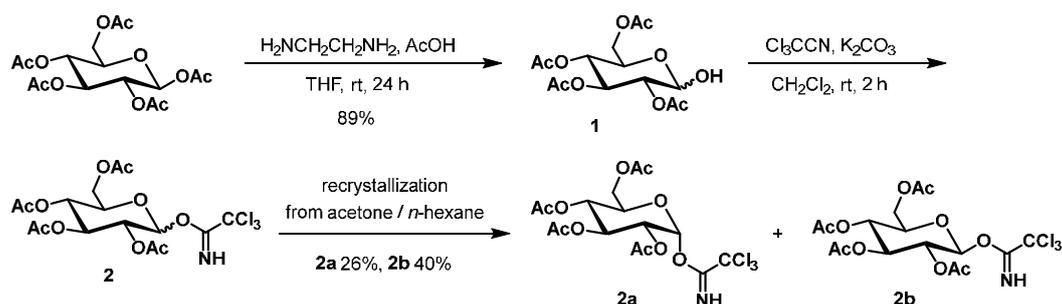


Scheme 12. General reaction pathway for the KÖNIGS-KNORR reaction.

Some other methods and strategies for the functionalization of porphyrins with carbohydrates have been investigated which are discussed in detail in reviews of CAVALEIRO and NIFANTIEV.^[46a,46b] In cell tests, glycosylated tetrapyrroles showed significant phototoxicity against tumor cells and also against bacteria in antibacterial PDT.^[71] Therefore glycosylated porphyrinoids are in the focus of further investigations.

Due to the existent partly inefficient synthetic strategies, a new strategy was developed by AICHER *et al.*^[53] which is based on a subsequent glycosylation of the already assembled porphyrin scaffold. In summary, the strategy is based on the conversion of hydroxyphenyl-substituted porphyrins with the corresponding trichloroacetimidates serving as glycosyl donors. The crucial step is the combination of different LEWIS and BRÖNSTED acids plus the metallation of the porphyrin. This strategy which was used for *meta*-hydroxyphenyl-substituted porphyrins so far should now be utilized for the preparation of the corresponding *para*-substituted derivatives and further *meta*-substituted derivatives to build up a library of glyco-porphyrins.

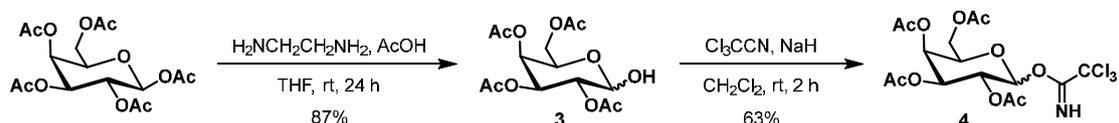
At first the trichloroacetimidates, which have been introduced to glycosylation chemistry by SINAÏ and SCHMIDT as glycosyl donors,^[50,51] were synthesized. This two-step reaction is shown for the glucosyl trichloroacetimidate in the scheme below (Scheme 13). Here the peracetylated glucose was deprotected selectively at the anomeric center with a very good yield using ethylenediamine and acetic acid.^[72] The selectively deprotected glucose **1** was then treated with trichloroacetonitrile and potassium carbonate to obtain the anomeric mixture of the trichloroacetimidate **2** (α -/ β -anomer = 1:1.6).^[73] *Via* recrystallization from acetone/hexane β -anomer **2b** (crystalline solid) and α -anomer **2a** (yellow oil) could be separated.



Scheme 13. Preparation of glucosyl trichloroacetimidate.

At the beginning, glycosylations were carried out using the pure β -anomer. However, use of the anomeric mixture resulted in identical yields with only the β -anomer being obtained. This is due to the neighboring group participation of the acetyl protecting group which leads exclusively to the formation of one glycosylated porphyrin anomer (see chapter 1.3).

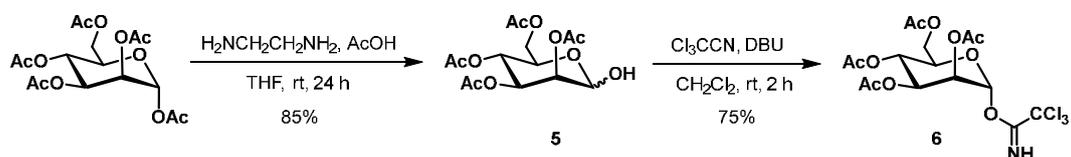
In a similar fashion, further trichloroacetimidates could be synthesized. For instance the galactosyl trichloroacetimidate which was received in two steps (Scheme 14). The peracetylated galactose was selectively deprotected at the anomeric center using ethylenediamine and acetic acid^[72] to then add trichloroacetonitrile and the base sodium hydride.^[73] Trichloroacetimidate **4** was obtained as an anomeric mixture (α -/ β -anomer = 10:1).



Scheme 14. Preparation of galactosyl trichloroacetimidate (anomeric mixture).

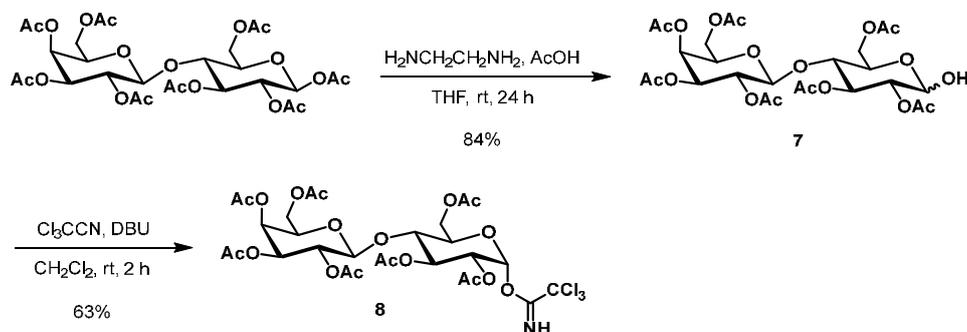
Another glycosyl donor synthesized was mannosyl trichloroacetimidate (Scheme 15).^[74] The procedure was similar to the above mentioned, but in the last step DBU serves as the base (in chapter 1.3 the use of the different bases is explained).

Here, the neighboring group effect of the axial acetyl group in C-2 position leads to the pure α -anomer of trichloroacetimidate **6** during the glycosylation.



Scheme 15. Preparation of mannosyl trichloroacetimidate.

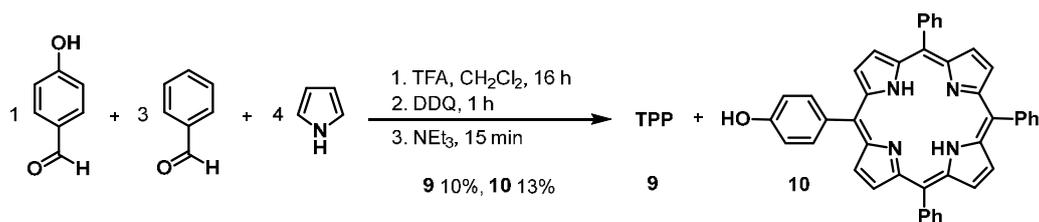
Due to their high hydrophilicity, disaccharides also seem to be promising glycosylation substituents for porphyrin photosensitizers. Hence the lactosyl trichloroacetimidate was synthesized according to the above-mentioned procedure. Only the pure α -anomer of trichloroacetimidate **8** was obtained.



Scheme 16. Preparation of lactosyl trichloroacetimidate.

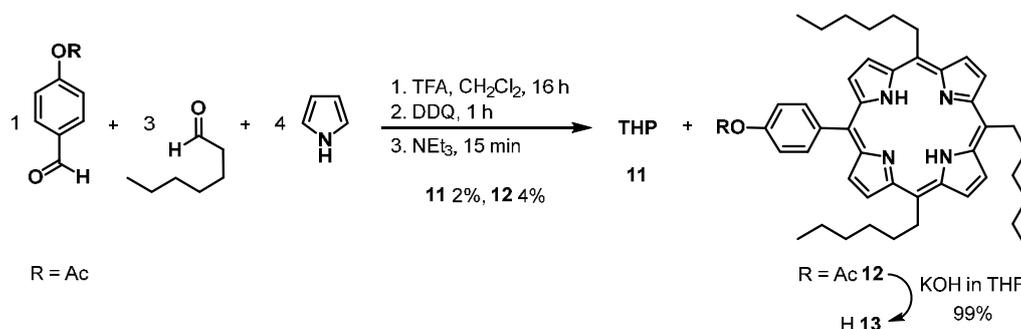
With the first component in hand (the glycosyl donors), the synthesis of the second component (hydroxyphenyl-substituted porphyrins) was the subsequent step for the imminent glycosylation. This was accomplished by a mixed condensation with the corresponding aldehydes and pyrrole according to LINDSEY.

For the phenyl-substituted porphyrin **10**, 4-hydroxybenzaldehyde and benzaldehyde were reacted with pyrrole in an acid-catalyzed condensation in 13% yield (Scheme 17). Furthermore, 5,10,15,20-tetraphenyl-porphyrin **9** was isolated as a side-product. This (low) yield of 13% is typical for mixed condensation reactions of porphyrins, as all possible combinatorial products are formed, A_4 , A_3B (the desired compound), A_2B_2 etc. (A and B representing the aldehyde moieties), apart from long-chain polymeric side products. For certain combinations (e.g. *trans*- A_2B_2 porphyrins) more specific condensation reactions are available (see below). However, specifically A_3B -porphyrins are difficult to synthesize otherwise.^[75]



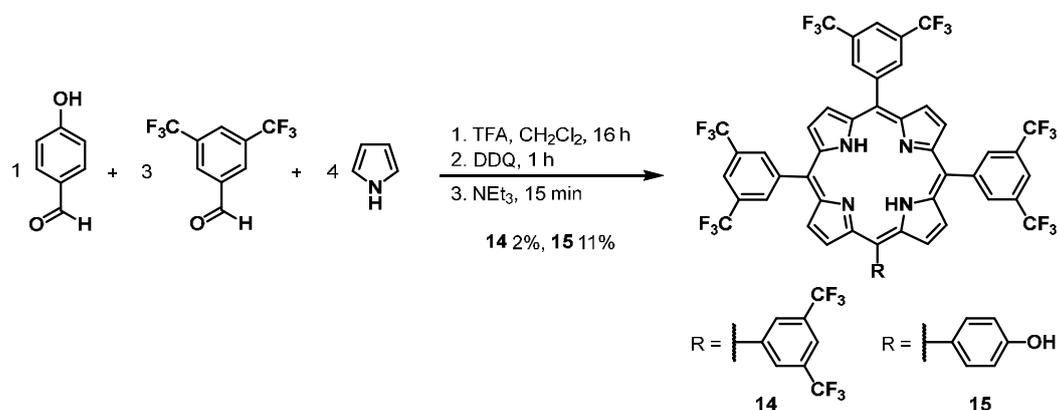
Scheme 17. Synthesis of the hydroxyphenyl-substituted porphyrin **10**.

The *n*-hexyl-substituted porphyrin **12** was synthesized in 4% yield using 4-acetoxybenzaldehyde, heptanal and pyrrole (Scheme 18). 5,10,15,20-Tetrahexyl-porphyrin **11** could be isolated as a side-product. The work-up showed various polymeric side products which accounts for the low yield. In a second step, the 4-acetoxy group was cleaved using potassium hydroxide in THF to give deprotected porphyrin **13** in 99% yield.



Scheme 18. Synthesis of the acetoxyphenyl-substituted porphyrin **12** and its deprotection.

Due to the interest in fluorinated structures of biologically active compounds, we decided to introduce trifluoromethyl groups as substituents. To this end, 4-hydroxybenzaldehyde, 3,5-bis-(trifluoromethyl)benzaldehyde and pyrrole were reacted to obtain fluorinated porphyrin **15** in 11% yield (Scheme 19). Again the A₄-porphyrin **14** could be isolated as a side-product.



Scheme 19. Synthesis of the hydroxyphenyl-substituted porphyrin **15**.

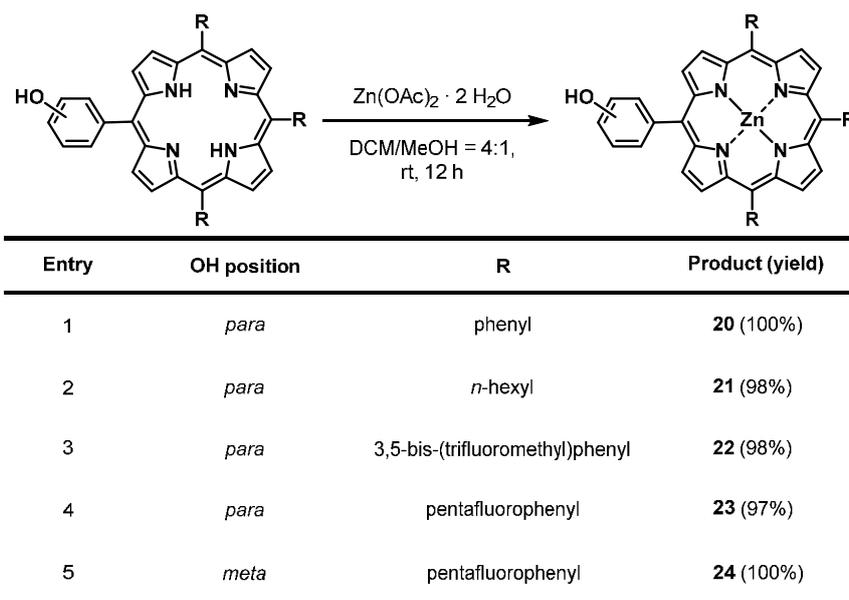


Table 1. Zinc-complexation of the porphyrin.

All necessary glycosylation substrates, the hydroxyphenyl-substituted zinc porphyrins (glycosyl acceptors) as well as the corresponding carbohydrate trichloroacetimidates (glycosyl donors), were now available for the glycosylation reactions.

Both starting materials were treated with catalytic amounts of boron trifluoride diethyl etherate at 0 °C. In a subsequent step, the obtained product was demetallated by treatment with hydrochloric acid (25%) for 10 min. The overall yields were good to very good for all monoglycosylations (Table 2). In comparison to the glucosyl trichloroacetimidate, the galactosyl, mannosyl and lactosyl trichloroacetimidates were less reactive. Instead of 2 equivalents glucose, 5 equivalents galactose and even 12 equivalents for mannose and lactose had to be used. In addition to that, the solvent dichloromethane and additional small amounts of acetonitrile were necessary because in contrast to the 3-hydroxyphenyl-substituted porphyrins, the *para*-substituted porphyrins are significantly less soluble. Due to neighboring group participation of the acetyl protecting group, both the α - and β -trichloroacetimidate led exclusively to formation of one glyco-porphyrin anomer. The glyco-conjugates **25**, **26** and **28** were β -linked, while the mannosyl-substituted porphyrin **27**, as expected, was α -linked. In ¹H-NMR spectra, H-1 gives a doublet with a coupling constant ~ 2 Hz at 6.0 ppm (α -anomer) or 7-8 Hz at 5.4 ppm (β -anomer).

The next step was the glucosylation of porphyrins, containing substituents like *n*-hexyl, 3,5-bis-(trifluoromethyl)phenyl, or perfluorinated phenyl groups which might be interesting regarding their potential biological activity. The catalyst promoted glucosylation with subsequent demetallation resulted in a variety of glyco-porphyrins with yields between 44% and 87% (Table 3).

Entry	R	Product (yield)
1		25 (89%) β-anomer
2		26 (83%) β-anomer
3		27 (78%) α-anomer
4		28 (54%) β-anomer

Table 2. Monoglycosylation of porphyrins containing phenyl groups with trichloroacetimidates.

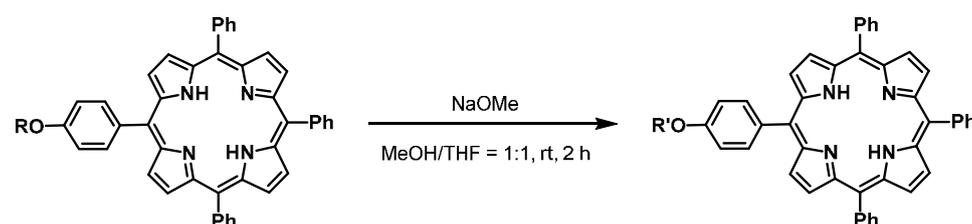
Entry	OH position	R	Product (yield)
1	<i>para</i>	<i>n</i> -hexyl	29 (87%)
2	<i>para</i>	3,5-bis-(trifluoromethyl)phenyl	30 (83%)
3	<i>para</i>	pentafluorophenyl	31 (48%)
4	<i>meta</i>	pentafluorophenyl	32 (44%)

Table 3. Monoglycosylation of porphyrins with trichloroacetimidates (all β-anomers).

Again it is observed that glucosyl trichloroacetimidates are more reactive than the other carbohydrate trichloroacetimidates. With 2-4 equivalents of glycosyl donor quite good yields could be obtained. Lower yields were observed for entry 3 and 4 (Table 3). This is not due to the glycosylation step which worked out similarly well as compared to the other conjugates, but due to the demetallation step. In pentafluorophenyl-substituted porphyrins the insertion of a metal like zinc works very nicely because

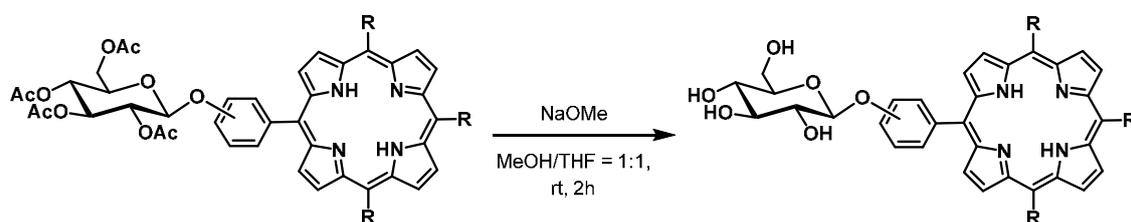
of their electron-withdrawing property. More problematic is the demetallation which could only be accomplished for these examples by repeating the demetallation step two more times. Of course it was also tried to demetallate with a higher concentration of hydrochloric acid and longer reaction times, but the isolated fraction showed unusual peaks in the “typical carbohydrate region” of the $^1\text{H-NMR}$ spectrum suggesting side-reactions of the glycosyl moiety under these conditions.

All synthesized glyco-porphyrins were obtained as acetoxy-protected products and had finally to be deacetylated. This was accomplished using sodium methanolate and resulted in very good yields for all the different carbohydrate conjugates (Table 4).



Entry	R	Starting material	R'	Product (yield)
1	Glc(OAc)	25	Glc(OH)	33 (98%)
2	Gal(OAc)	26	Gal(OH)	34 (99%)
3	Man(OAc)	27	Man(OH)	35 (98%)
4	Lac(OAc)	28	Lac(OH)	36 (98%)

Table 4. Deacetylation of monoglycosylated porphyrins.



Entry	Glucosyl position	R	Product (yield)
1	<i>para</i>	<i>n</i> -hexyl	37 (97%)
2	<i>para</i>	3,5-bis-(trifluoromethyl)phenyl	38 (99%)
3	<i>para</i>	pentafluorophenyl	39 (93%)
4	<i>meta</i>	pentafluorophenyl	40 (84%)

Table 5. Deprotection of glucosylated porphyrins.

The deacetylation for the glucosylated porphyrins bearing different functional groups worked without any problems (Table 5). Even the deacetylation of the pentafluorophenyl-substituted glycoporphyrins (*meta*, *para*) gave no side-products. Theoretically, a nucleophilic aromatic substitution (S_NAr) in the *para*-position of the pentafluorophenyl substituents can occur with methanolate as the corresponding nucleophile. Fortunately, this did not happen – probably due to the only catalytic amounts of sodium methanolate – and allowed further interesting modifications which will be discussed later in detail.

Another aim of this work was the synthesis of *trans*- A_2B_2 -substituted PS^[62] which showed promising activity in *in vitro* tests and are, at the moment, in the focus of further *in vivo* examinations. These porphyrins, in contrast to porphyrin condensations mentioned above, were synthesized *via* a modified LINDSEY protocol. The statistical distribution for a standard condensation with two aldehydes and pyrrole (ratio 1:1) would result in six possible products (Figure 3). To avoid this, it was necessary to synthesize the corresponding dipyrromethanes first. The dipyrromethanes were synthesized in an acid-catalyzed reaction of the corresponding aldehyde and pyrrole in good yields in a multigram-scale (Table 6).

Entry	R	Product (yield)
1		41 (71%)
2		42 (60%)
3		43 (56%)

Table 6. Synthesis of dipyrromethanes.

On one hand, pyrrole was used as a reactant and, on the other hand, it also served as the solvent. This large excess of pyrrole suppresses the condensation reaction leading to further oligomers and polymers. The purification was accomplished either by a Kugelrohr distillation or a column chromatography and subsequent recrystallization.

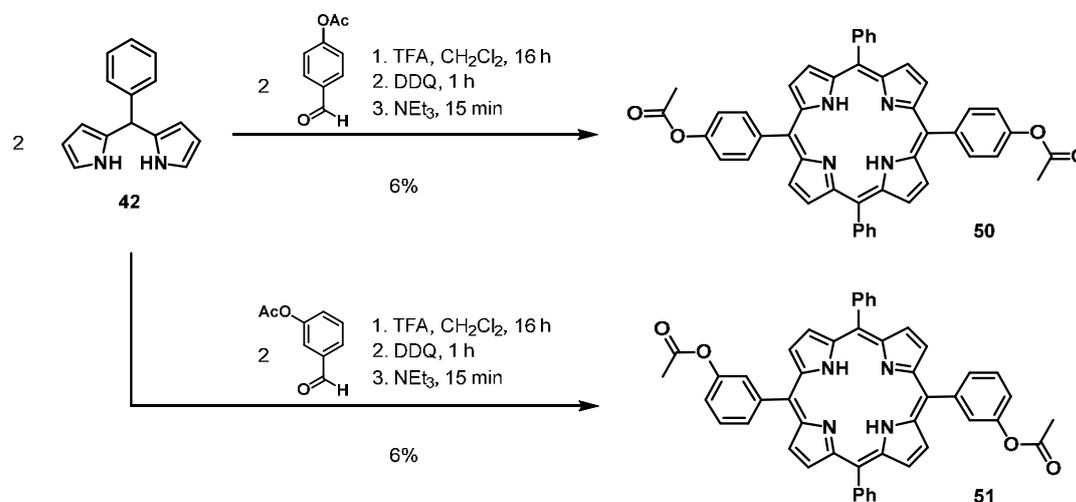
As explained previously, with these dipyrromethanes the *trans*- A_2B_2 -porphyrin can specifically be synthesized in higher yields. However the examples (Table 7) show that the *trans*-product is not formed exclusively. The reason is a reversible opening of the dipyrromethane during the acid-catalyzed condensation, called “scrambling”. Nevertheless, in the condensation reaction with *para*-substituted

benzaldehyde the desired product **44** could be isolated with a yield of 9% and in the condensation reaction with *meta*-substituted benzaldehyde the desired product **48** could be isolated with a yield of 8%. The yields justify this modified synthetic route.

Entry	R ¹	R ²	R ³	R ⁴	<i>para</i> -Product	<i>meta</i> -Product
1	<i>n</i> -hexyl	<i>n</i> -hexyl	<i>n</i> -hexyl	<i>n</i> -hexyl	11 (2%)	11 (1%)
2	acetoxyphenyl	<i>n</i> -hexyl	<i>n</i> -hexyl	<i>n</i> -hexyl	12 (10%)	47 (9%)
3	acetoxyphenyl	<i>n</i> -hexyl	acetoxyphenyl	<i>n</i> -hexyl	44 (9%)	48 (8%)
4	acetoxyphenyl	acetoxyphenyl	<i>n</i> -hexyl	<i>n</i> -hexyl	45 (4%)	49 (2%)
5	acetoxyphenyl	acetoxyphenyl	acetoxyphenyl	<i>n</i> -hexyl	46 (2%)	---

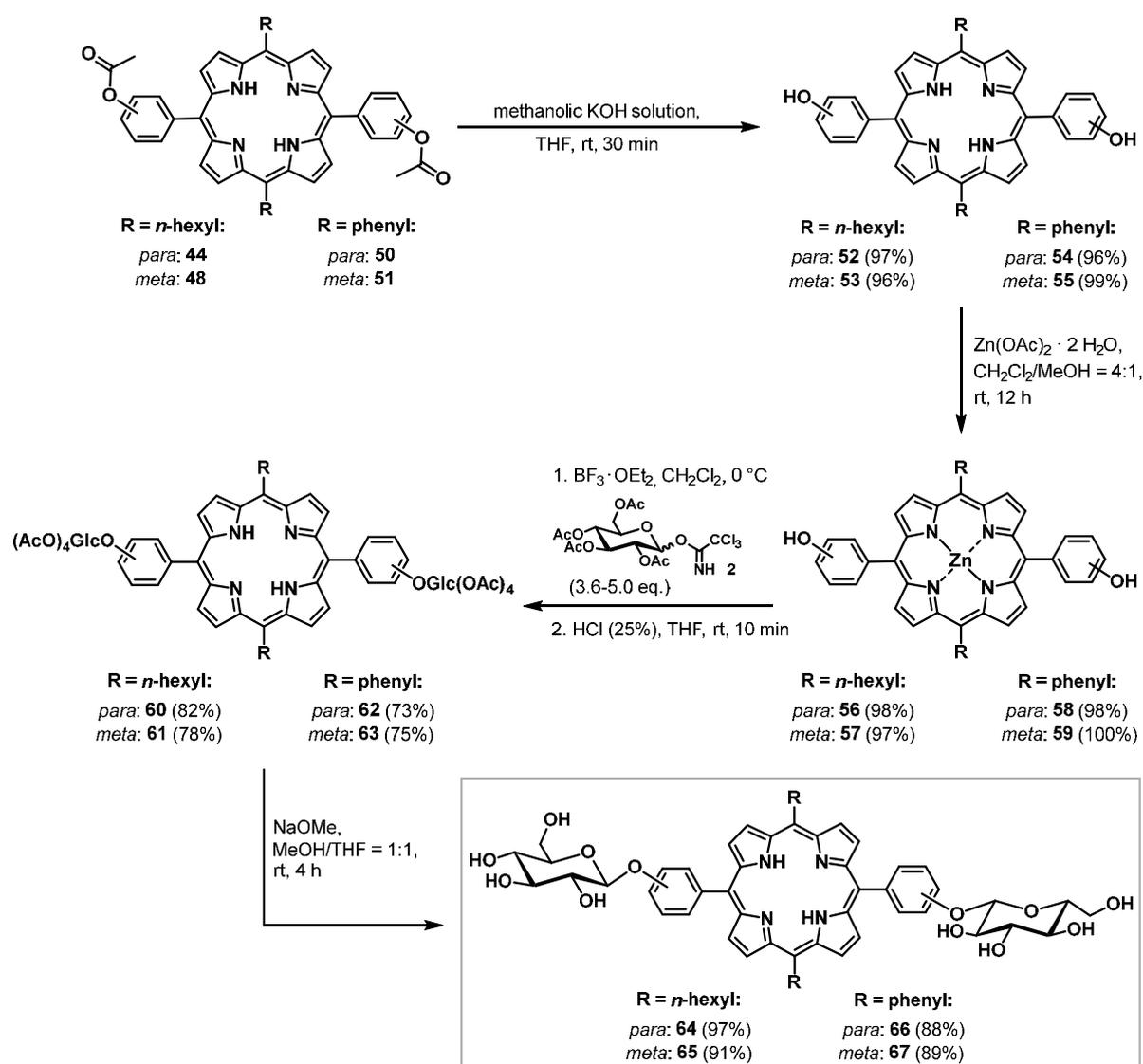
Table 7. Synthesis of *trans*-substituted porphyrins (for *para* and *meta* derivatives) and side-products.

Because of the high potential of *trans*-A₂B₂-substituted glyco-porphyrins regarding PDT, alternatively to the alkyl chain, phenyl substituents were introduced. The synthesis is analogous to the one shown before and therefore is only briefly described (Scheme 21). Due to the tedious and difficult separation by column chromatography, in this case the side-products (e.g. A₃B-, A₄-porphyrins) were not isolated.



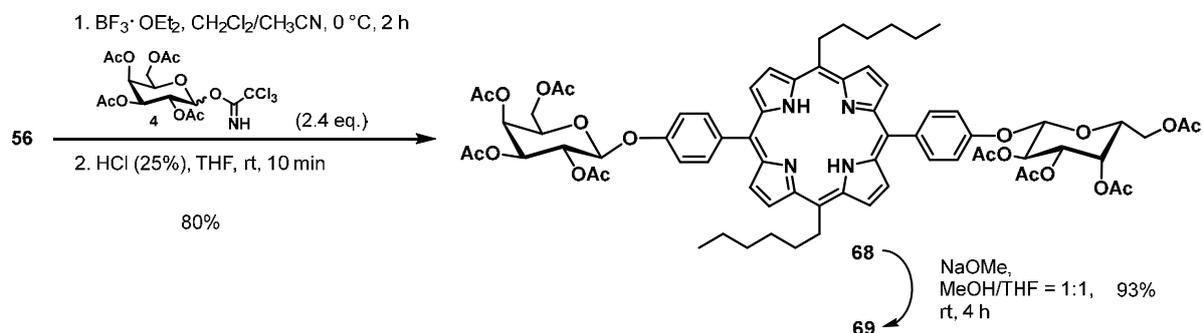
Scheme 21. Synthesis of *trans*-substituted porphyrin (for *para*- and *meta*-derivatives).

Then, following the synthetic protocol, the *trans*-A₂B₂-substituted porphyrins were deprotected with a methanolic potassium hydroxide solution, complexed with zinc and finally glycosylated with glucose trichloroacetimidate. After demetallation with hydrochloric acid (25%) and deacetylation with sodium methanolate, the desired glycosylated porphyrins (*para* and *meta*) could be isolated in good to very good yields (Scheme 22). For each of these four substances, 9 synthetic steps were necessary to obtain these made-to-measure photosensitizers: (1) Regioselective, anomeric deacetylation of the peracetylated carbohydrate, (2) synthesis of the corresponding carbohydrate trichloroacetimidate, (3) synthesis of the (5-substituted) dipyrromethane, (4) synthesis of *trans*-A₂B₂-porphyrin *via* condensation of the dipyrromethane, (5) hydrolysis of the porphyrin esters under basic conditions, (6) metallation of the free base porphyrin with zinc acetate, (7) glycosylation of the porphyrin *via* the trichloroacetimidate method, (8) demetallation of the glyco-porphyrin with hydrochloric acid (25%) and (9) deacetylation of glycosylated tetrapyrrole with sodium methanolate.



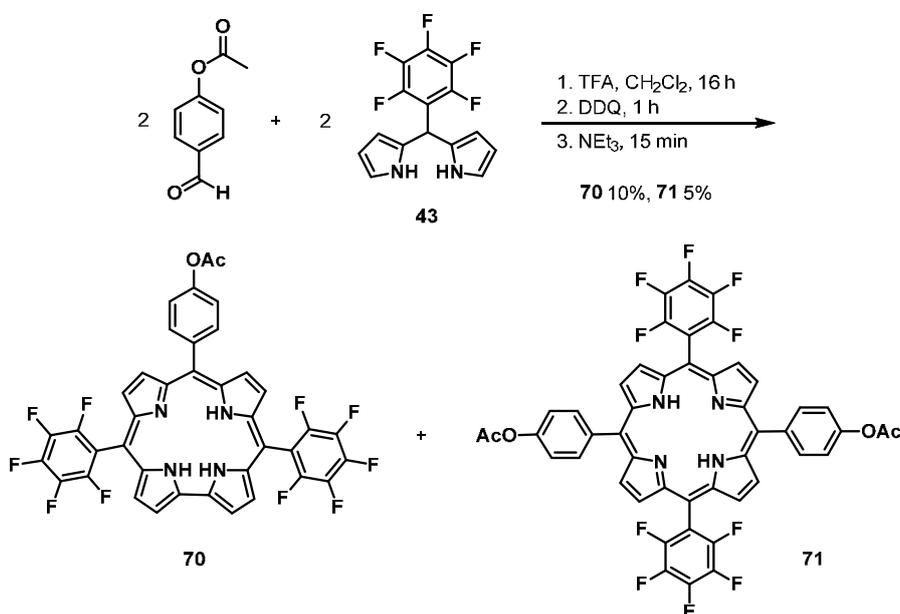
Scheme 22. Synthesis of *para*- and *meta*-derivatives of *trans*-A₂B₂-substituted glyco-porphyrins bearing *n*-hexyl or phenyl groups.

Metallated porphyrin **56** also served as a precursor for the synthesis of galactosyl-substituted porphyrin **69** (Scheme 23).



Scheme 23. Synthesis of *trans*- A_2B_2 -substituted glyco-porphyrin **69** containing two galactose subunits.

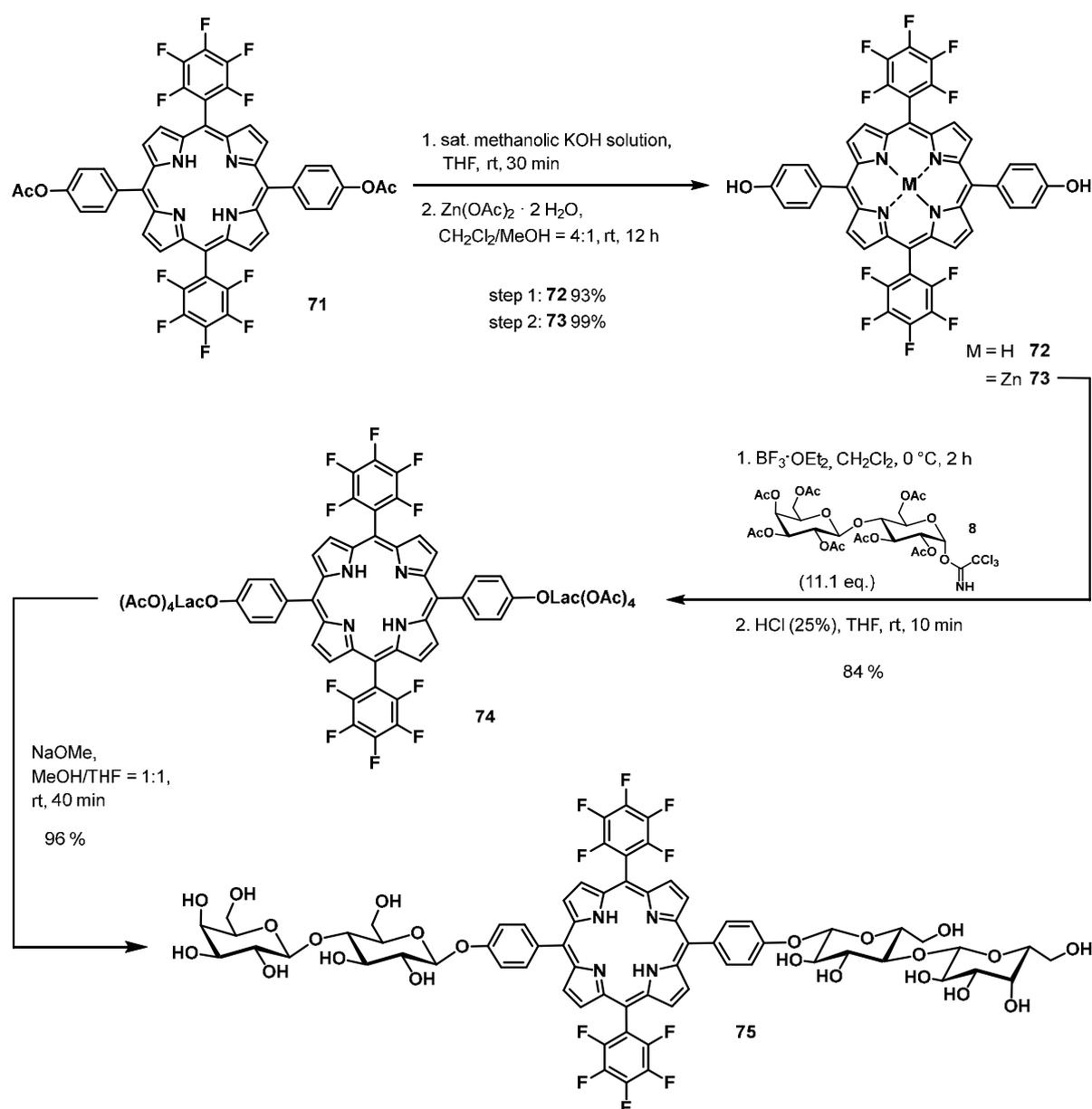
The condensation to the fluorinated *trans*- A_2B_2 -substituted porphyrin, following the modified LINDSEY method, resulted in the formation of the desired porphyrin (5% yield), but another green substance could also be isolated (10% yield). This substance turned out to be an A_2B -substituted corrole (Scheme 24).



Scheme 24. Synthesis of *trans*-substituted porphyrin **71** and corrole **70** as a side-product.

This reaction was repeated several times and always led to a different outcome in the ratio between porphyrin and corrole, sometimes not even traces of corrole could be found. Due to this bad reproducibility, another more reliable method for corrole synthesis had to be applied. This method following GRYKO is discussed later in detail.

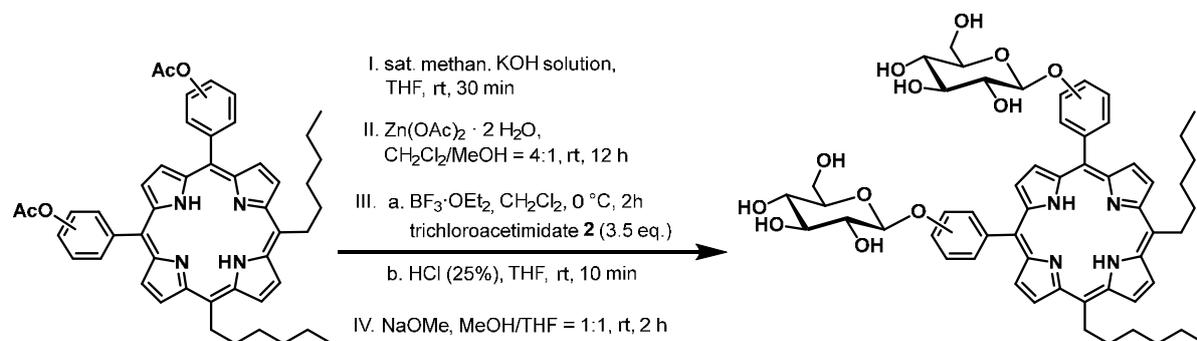
The synthesis of the corresponding *trans*-A₂B₂-substituted glyco-porphyrins was similar to other already mentioned *trans*-porphyrins. One important difference is that due to the pentafluorophenyl substituent and a possible nucleophilic aromatic substitution (S_NAr) either the reaction times had to be shortened or the concentration of the bases during the deprotection reactions had to be decreased. For both cases – the deprotection of the acetoxy groups as well as the deprotection of the protected glyco-porphyrins – these reactions were therefore done twice for short time periods.



Scheme 25. Synthesis of *trans*-A₂B₂-substituted glyco-porphyrin **75** containing two disaccharide subunits.

The deprotected lactosylated porphyrin is not only another interesting example as a photosensitizer candidate for a possible PDT application, but also served as a starting material for the development of a porphyrin containing two monosaccharides and two disaccharides. This will be discussed later in detail.

Beside the effects of different substituents (*n*-hexyl, phenyl, 3,5-bis-(trifluoromethyl)phenyl, pentafluorophenyl) regarding to PDT, another task was to find out, if the position of the substituents of the promising A_2B_2 -substituted glyco-porphyrins lead to different or similar cell test results. To make this comparison possible, *cis*- A_2B_2 -substituted glyco-porphyrins were synthesized analogously to the existing synthetic protocol (Table 8).



Entry	Reaction step	Position of substituent	Product (yield)
1	step I	<i>para</i>	76 (99%)
2		<i>meta</i>	77 (98%)
3	step II	<i>para</i>	78 (95%)
4		<i>meta</i>	79 (96%)
5	step III	<i>para</i>	80 (64%)
6		<i>meta</i>	81 (68%)
7	step IV	<i>para</i>	82 (86%)
8		<i>meta</i>	83 (83%)

Table 8. Synthesis of *cis*- A_2B_2 -substituted glyco-porphyrins (for *para* and *meta* derivatives).

The *cis*- and *trans*- A_2B_2 -porphyrins can unambiguously be distinguished *via* NMR spectroscopy which will be shown in detail in chapter 3.7.1.

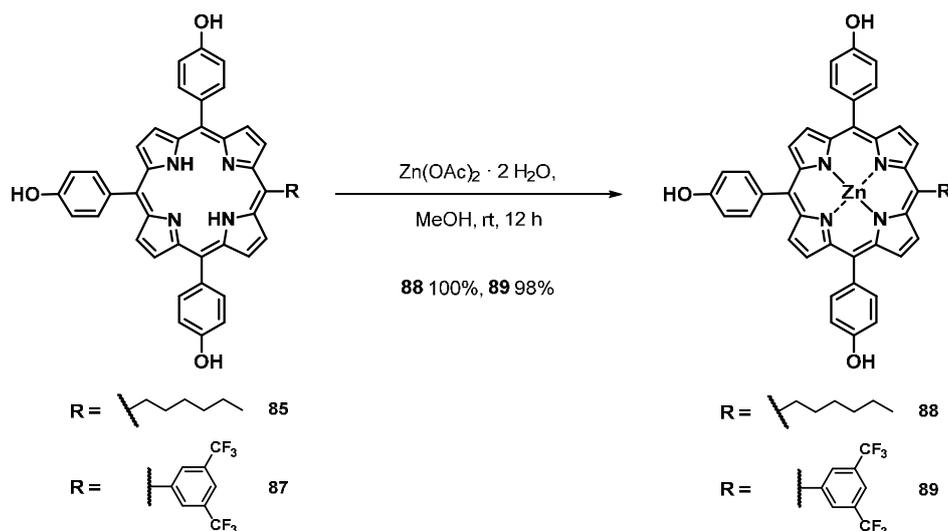
3.1.2 Synthesis of Tri- and Tetraglycosylated Tetrapyrroles

Literature^[47d] shows that triglycosylated tetrapyrroles are very promising candidates as PS against tumor cells. Unfortunately, as already shown by AICHER *et al.*,^[77] the synthesis of the corresponding glycosylated benzaldehydes is quite tricky, especially their purification by column chromatography. Another issue is the loss of aldehyde during the subsequent low-yielding condensation reactions. This encouraged us to apply the trichloroacetimidate method, successfully used for mono- and disubstituted derivatives, also for the *para*-hydroxylated porphyrins carrying three aromatic phenol groups. For this purpose we selected two porphyrins each one bearing a specific substituent. In one case we chose a *n*-hexyl group for the completion of the substitution pattern (mono-, bis-*trans*- and bis-*cis*-*n*-hexyl already synthesized) to judge their different behaviour in cell tests and to check how the non-glycosylated part of the porphyrin influences the biological activity. The other selected substituent was the 3,5-bis-(trifluoromethyl)phenyl group. This is due to the good *in vitro* efficiency which this porphyrin showed even without any glyco-substitution.^[77] Both porphyrins were synthesized in mixed condensation reactions in quite good yields (Table 9) and were subsequently deprotected at their phenolic hydroxyl groups.

Entry	Reaction step	R ¹	R ²	Product (yield)
1	step I			84 (11%)
	step II			85 (94%)
2	step I			86 (14%)
	step II			87 (96%)

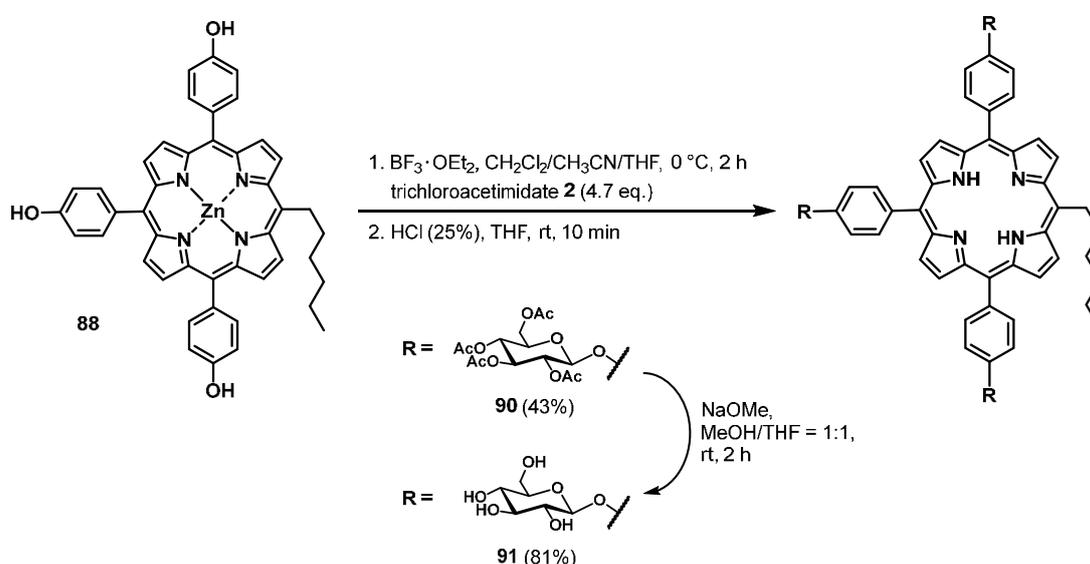
Table 9. Condensation reactions of porphyrins and their subsequent deprotections.

In the next step, both tetrapyrroles were metallated in nearly quantitative yields using zinc acetate.



Scheme 26. Zinc-complexation of porphyrins **85** and **87**.

Then the metallated, trishydroxyphenyl-substituted porphyrins were ready for glycosylation with the corresponding carbohydrate. First the derivative with the *n*-hexyl moiety was reacted with protected glucosyl trichloroacetimidate (Scheme 27) which resulted in a moderate yield of 43%.



Scheme 27. Glycosylation of a porphyrin and following deprotection.

On repetition, the glycosylation delivered similar results. One reason could be that the metallated *para*-substituted derivative (more rigid than *meta*-substituted derivatives) with three hydroxyphenyl substituents is hard to dissolve. Therefore, in addition to dichloromethane and acetonitrile, THF is needed to dissolve this derivative. Maybe this different solvent mixture is partially responsible for the lower yield. The subsequent deacetylation proceeded in good yield.

As mentioned before, the “pure” non-glycosylated porphyrin with trifluoromethyl substituents already possesses good *in vitro* efficiency. The interesting point was now to introduce different carbohydrates to improve its *in vitro* efficiency and to enhance its solubility in polar solvents. The glucosyl- and galactosyl-substituted porphyrins were obtained in good yields (85% and 73%, respectively) and the mannosyl- and lactosyl-substituted porphyrins were obtained in moderate yields (36% and 51%, respectively, see Table 10). The moderate yield of the mannosylated and lactosylated porphyrins fit in the experience we gained during the mono-glycosylations where mannose was the lowest-yielding monosaccharide and lactose also delivered ~ 50%; the deprotections worked with 78% and 97% yield, respectively (Table 11).

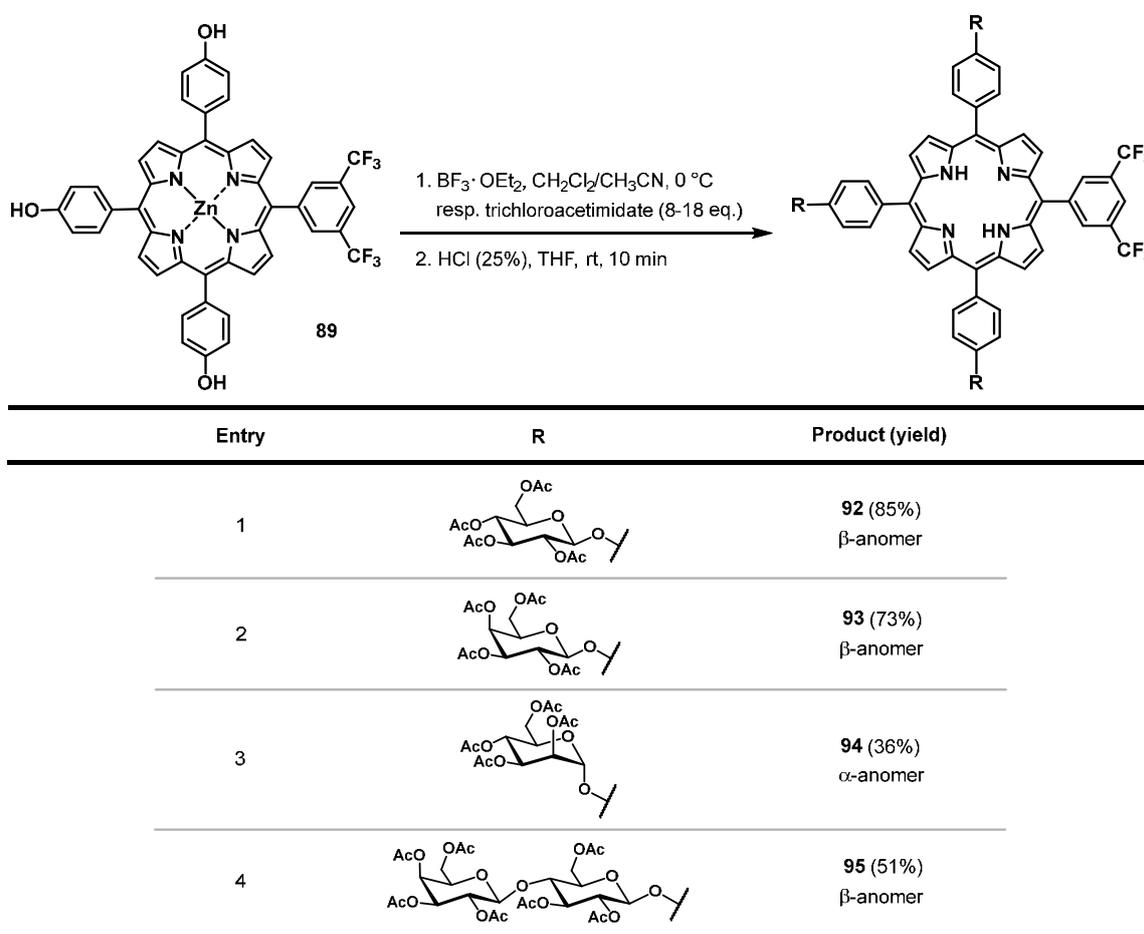


Table 10. Glycosylations of a porphyrin with various trichloroacetimidates.

The last examples for the library of glyco-porphyrins were the tetraglycosylated porphyrins and the examination of their possible applicability as PS for PDT. In contrast to the other glyco-porphyrins they possess a much lower amphiphilicity due to the lack of lipophilic substituents. It should be noted that the route to the metallated hydroxy-substituted porphyrin was much easier than for the mono-, di- and trihydroxy-substituted derivatives. Time-consuming separation processes were not needed anymore because the A₄-porphyrin was exclusively formed (apart from long-chain polymeric side products). In this case the corresponding acetoxybenzaldehyde was used for the condensation *via* LINDSEY. This led

to yields of 43% for the *para*-substituted derivative and 39% for the *meta*-substituted derivative (Scheme 28). Deacetylation reactions with potassium hydroxide and metallation reactions with zinc acetate proceeded both rapidly and in nearly quantitative yield.

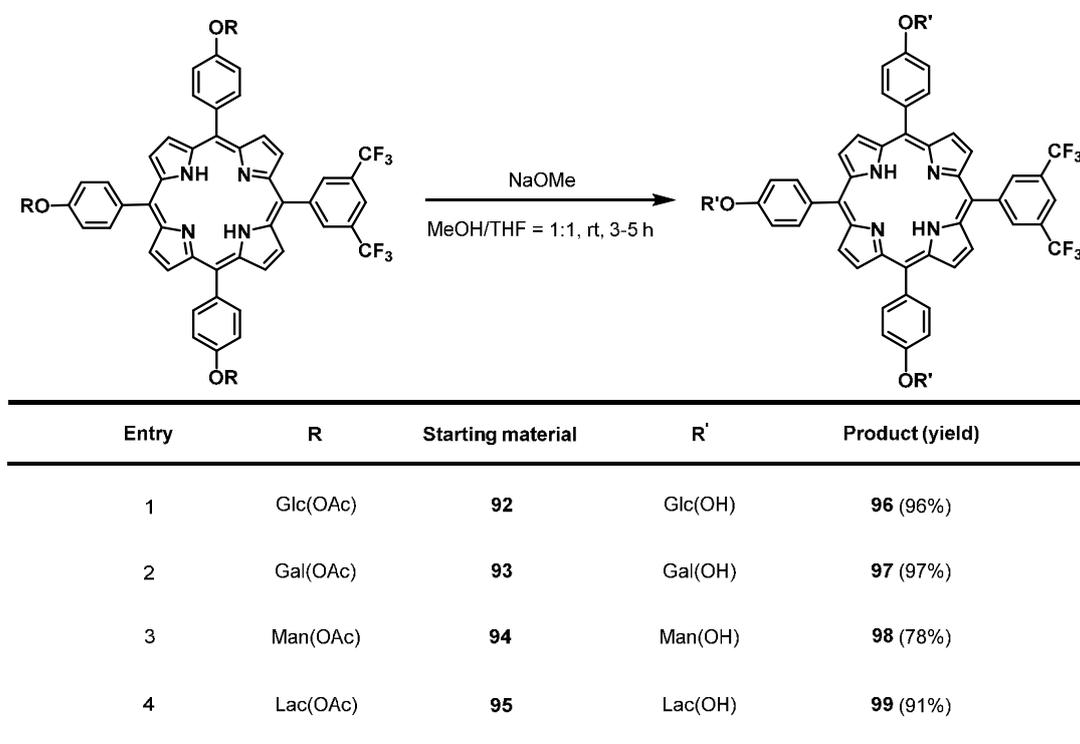
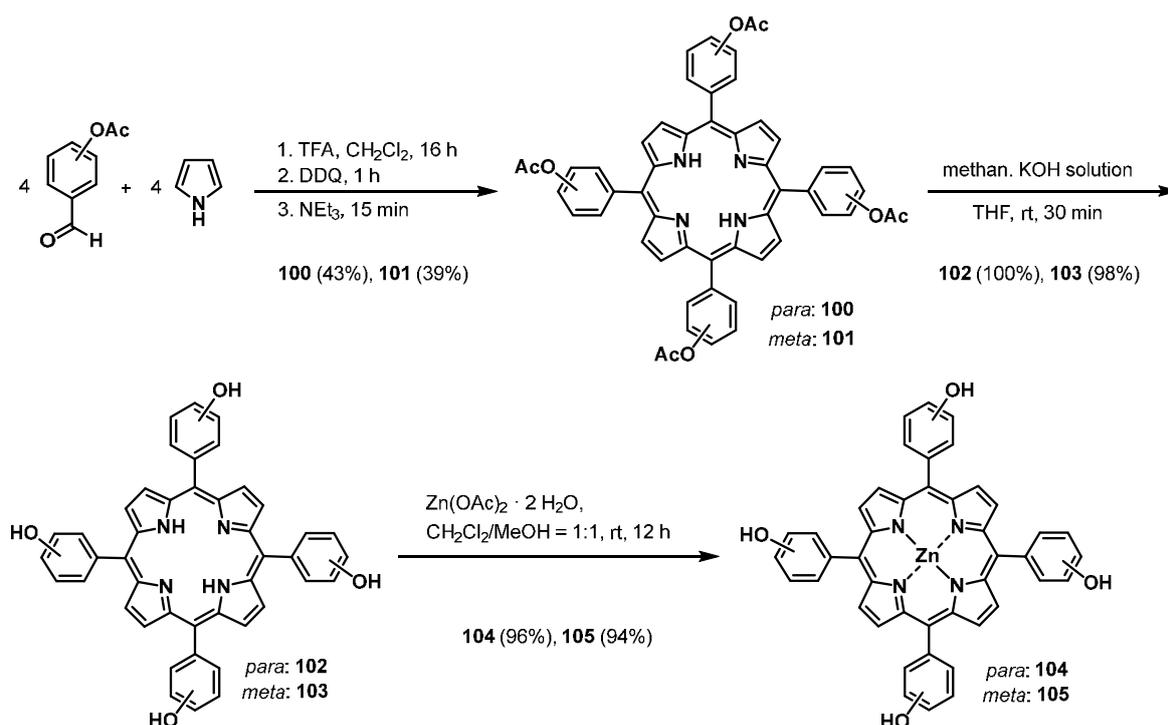
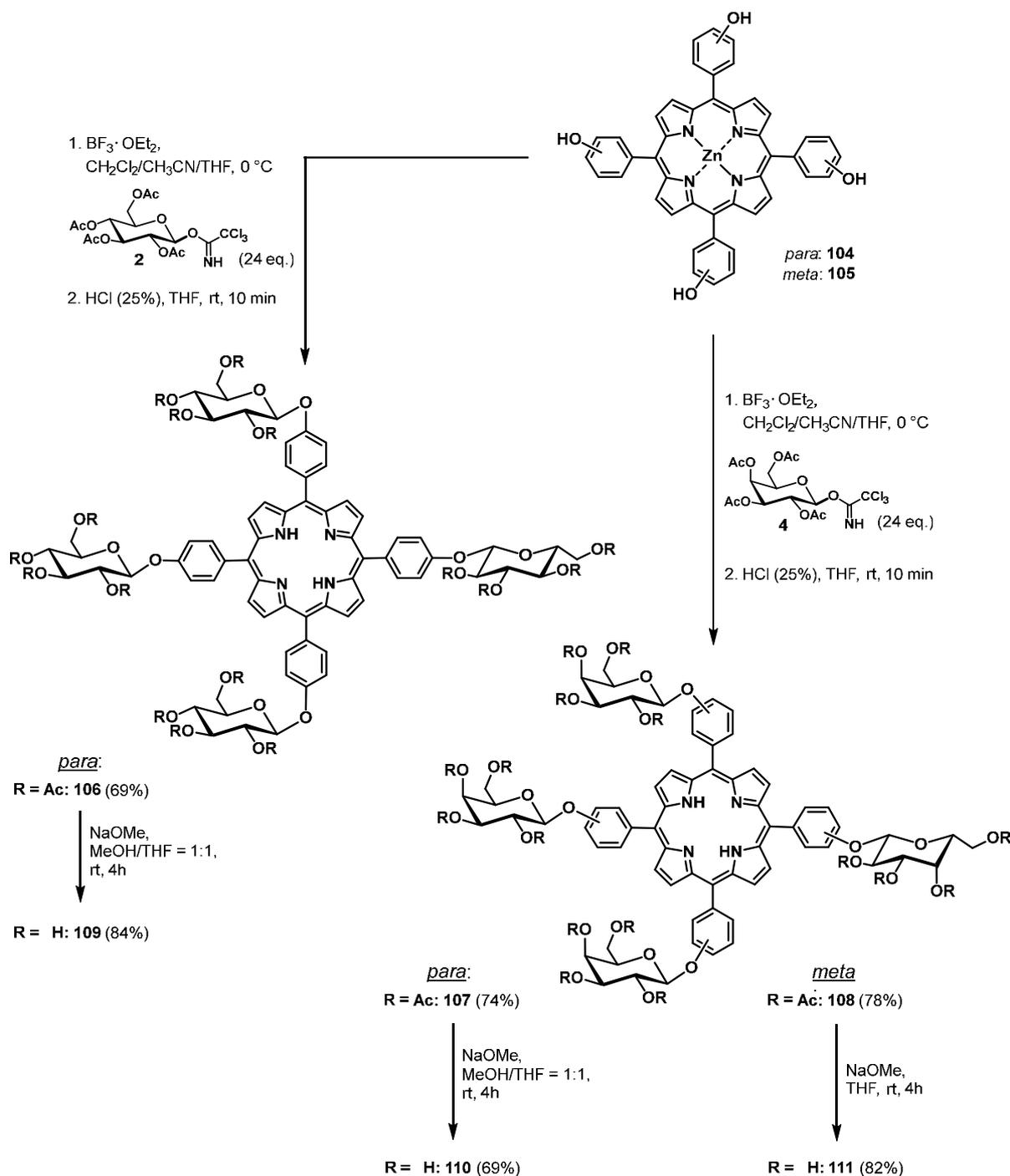


Table 11. Deacetylation of glyco-porphyrins.



Scheme 28. Synthesis, deprotection and zinc-complexation of acetoxyphenyl-substituted A₄-porphyrins.



Scheme 29. Synthesis of tetraglycosylated porphyrins (glucosylation of **104**, galactosylation of **104** and **105**).

The different glycosylations with the corresponding trichloroacetimidates resulted in good yields (Scheme 29). Deacetylations of the protected sugar subunits were accomplished with sodium methanolate in good yields. In comparison to the *meta*-substituted derivatives, the *para*-substituted derivatives were less soluble. During the deprotection processes, especially for the galactosyl conjugate, the incompletely deprotected product precipitated from the reaction mixture and so no further deprotection was possible. Due to this problem, the deprotection was completed in the sonication bath at 40°C . Final purification was performed by filtration of the product, washing with unpolar solvents and a column chromatography with reversed phase silica gel.

RESULTS AND DISCUSSION

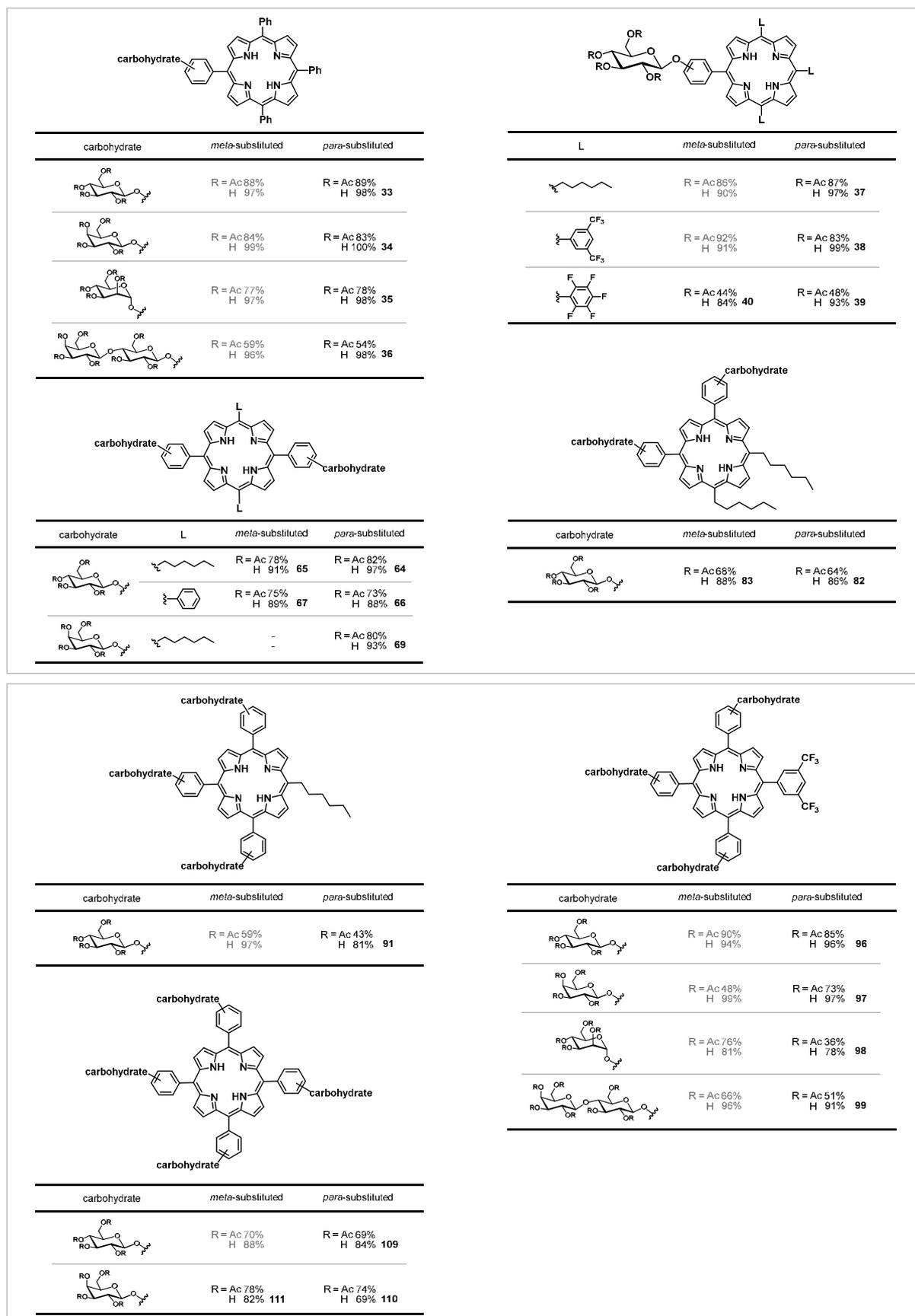


Figure 22. Overview of synthesized glyco-porphyrins via the trichloroacetimidate method (*meta*-substituted substances in grey were previously synthesized by AICHER).

3.1.3 *In Vitro* Photodynamic Effect of Glyco-Porphyrins Against (Carcinoma) Cell Lines

One of the main prospects of this thesis was the development of a library of *meta*- and *para*-glycosylated porphyrins *via* the trichloroacetimidate method and to study their different substitution patterns – A₄-, A₃B-, *trans*-A₂B₂-, *cis*-A₂B₂- and AB₃-substituted glyco-porphyrins – on the photodynamic activity against several cancer cell lines. All the mentioned mono-, di-, tri- and tetraglycosylated porphyrins were tested by Dr. GRÄFE (biolitec research GmbH) against A431 cells (epidermoid carcinoma cells from skin/epidermis), A253 cells (submandibular carcinoma cells), CAL-27 cells (squamous cell carcinoma from tongue), L929 (subcutaneous connective tissue, areolar and adipose) and resistant HT29 cells (colorectal adenocarcinoma cells from colon). For *in vitro* tests, the corresponding cells were incubated for 24 hours in 10% fetal calf serum (FCS) with the photosensitizers. Then the samples were irradiated with laser light ($\lambda = 652$ nm) and a radiation energy of 50 J/cm² and the cell viability was colorimetrically determined. In detail the cells were treated with the tetrazolium salt XTT which is segregated by dehydrogenases of metabolic active cells under formation of a strongly colored product.^[78a] The dark toxicity and phototoxicity were determined for concentrations of 0 μ mol (reference sample), 2 μ mol and 10 μ mol.

First of all the dark toxicity was verified. Therefore the corresponding cell lines were treated with the mentioned different concentrations of the photosensitizer in the absence of light. Ideally no cell growth or cell damage should occur at this point. Furthermore it had to be verified that the laser *per se* does not lead to a cell damage. Therefore the cells were irradiated with laser light in the absence of the photosensitizer. The following pages will first show all *in vitro* assays and then a table which gives a summary and a better overview regarding the activity of the different PS.

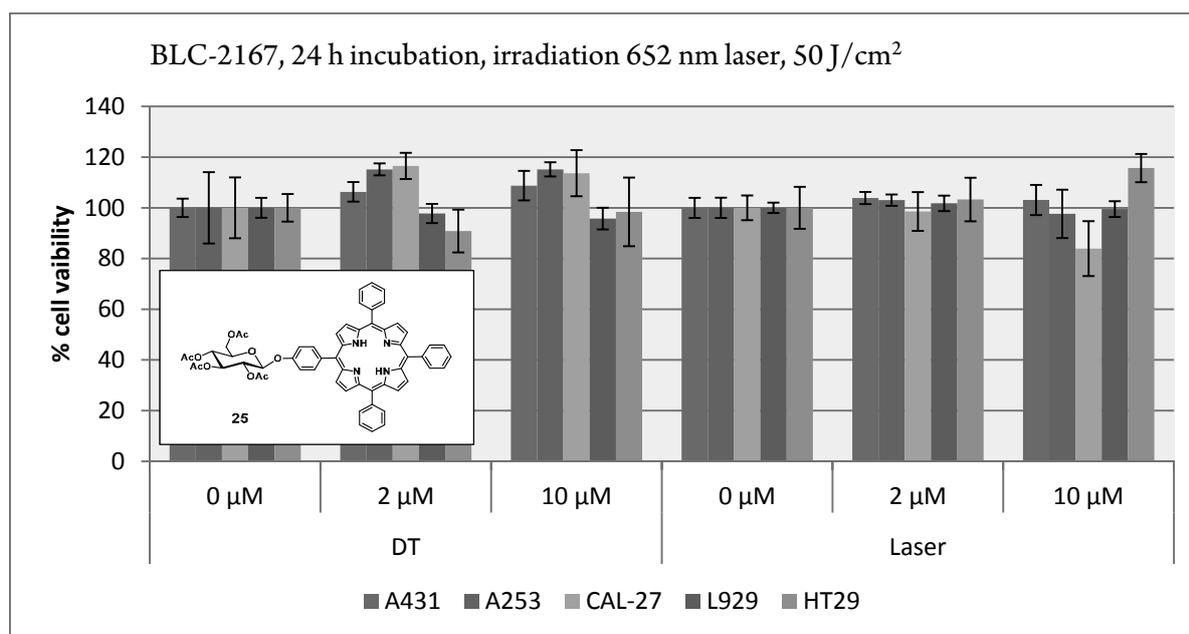


Figure 23. Photodynamic activity of BLC-0167 (24 h incubation with photosensitizer, DT = dark toxicity, Laser = irradiation with laser light ($\lambda = 652$ nm) and a radiation energy of 50 J/cm²).

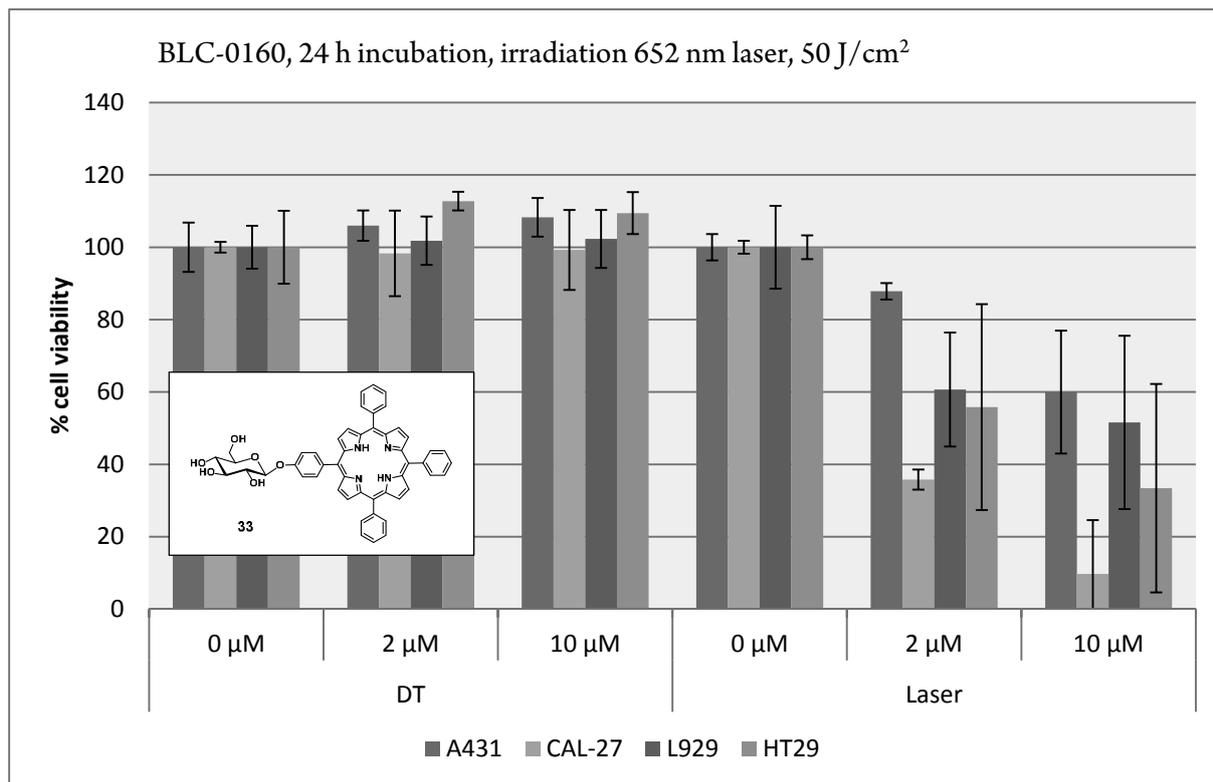


Figure 24. Photodynamic activity of BLC-0160.

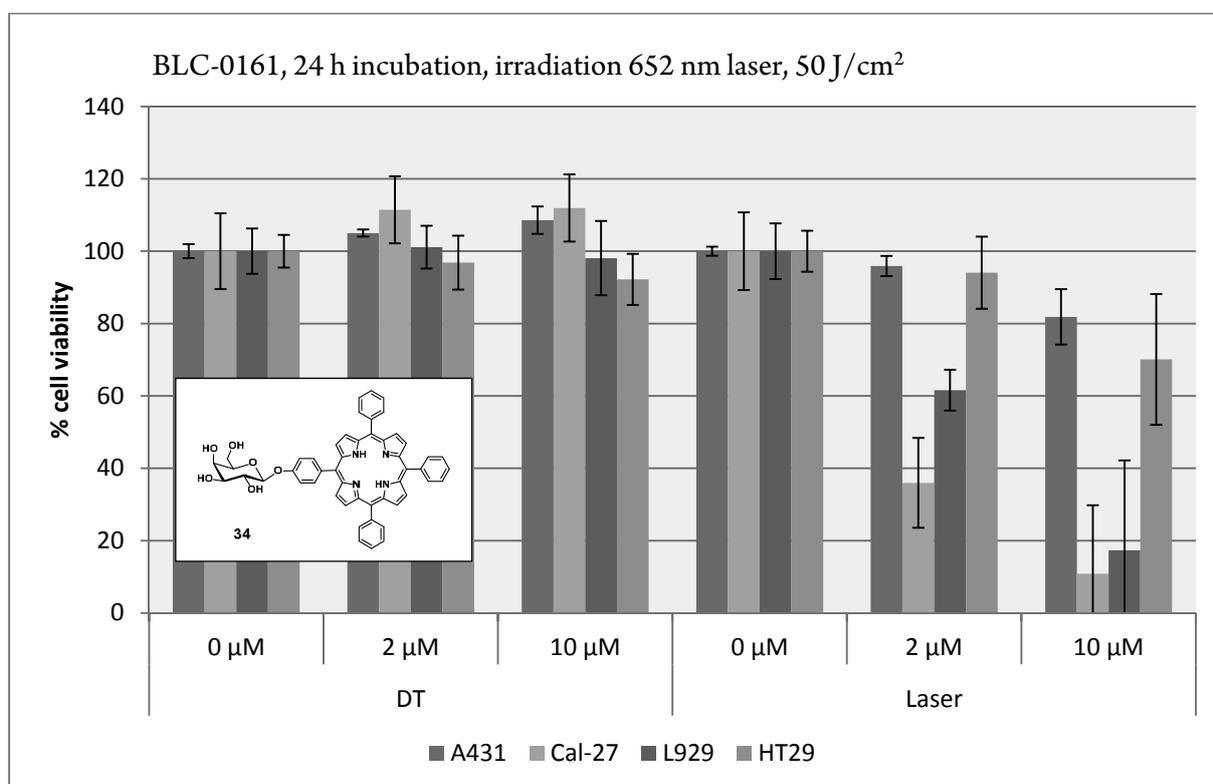


Figure 25. Photodynamic activity of BLC-0161.

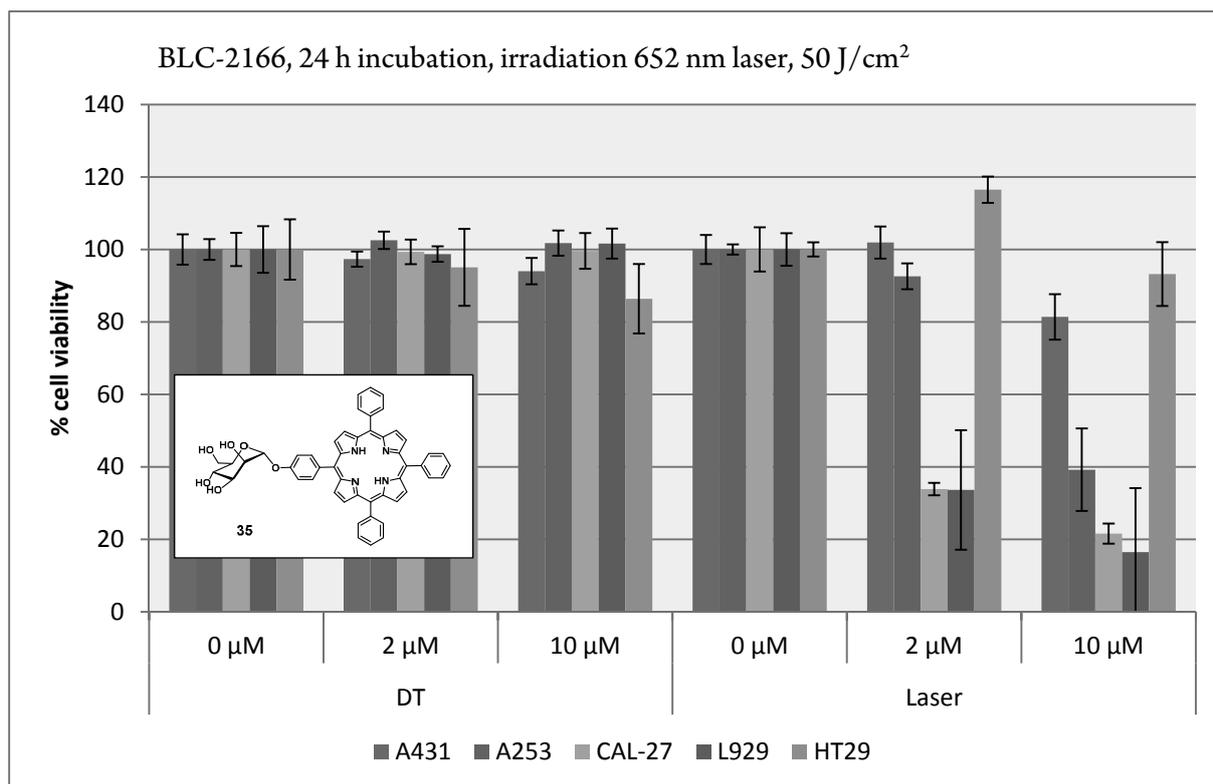


Figure 26. Photodynamic activity of BLC-2166.

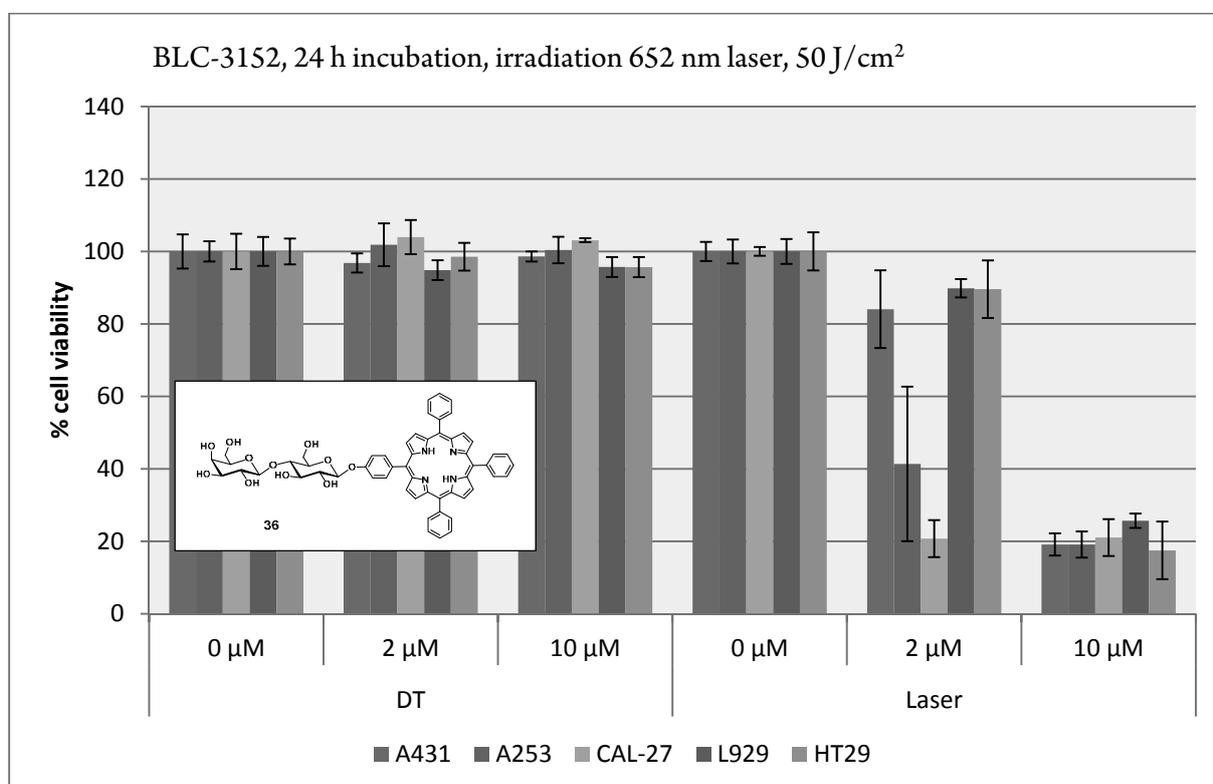


Figure 27. Photodynamic activity of BLC-3152.

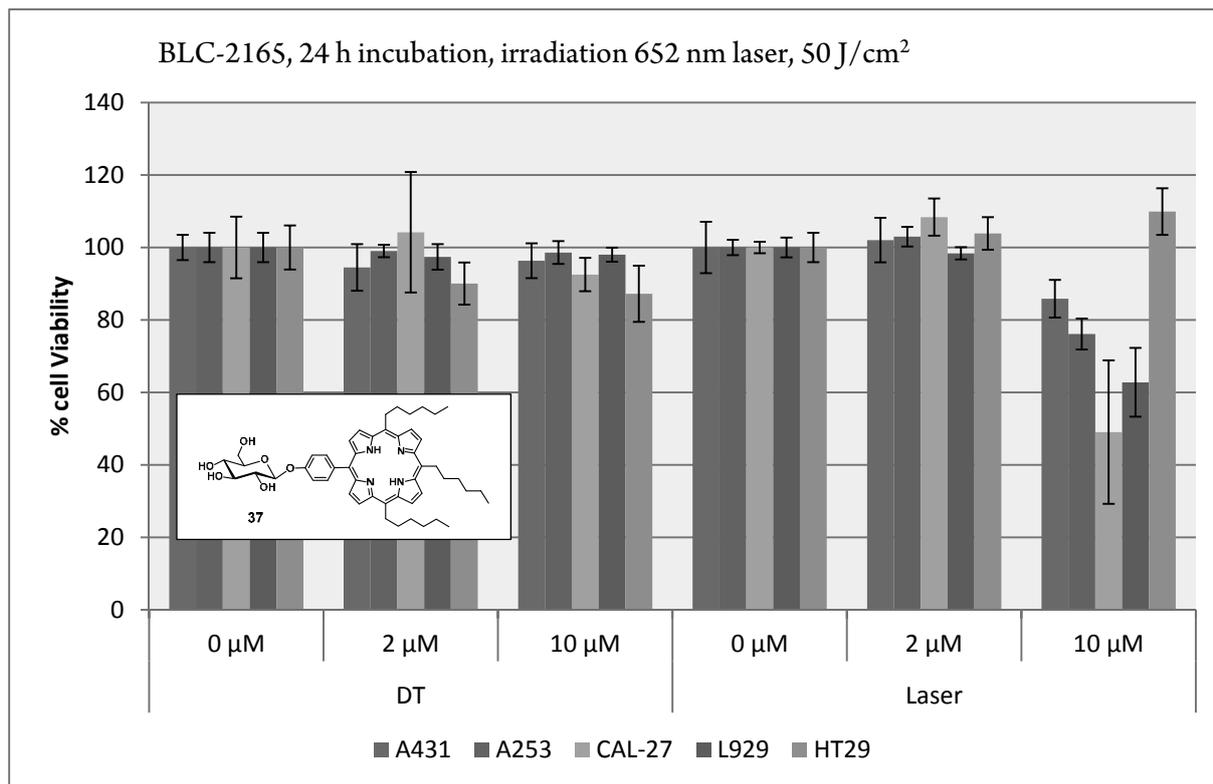


Figure 28. Photodynamic activity of BLC-2165.

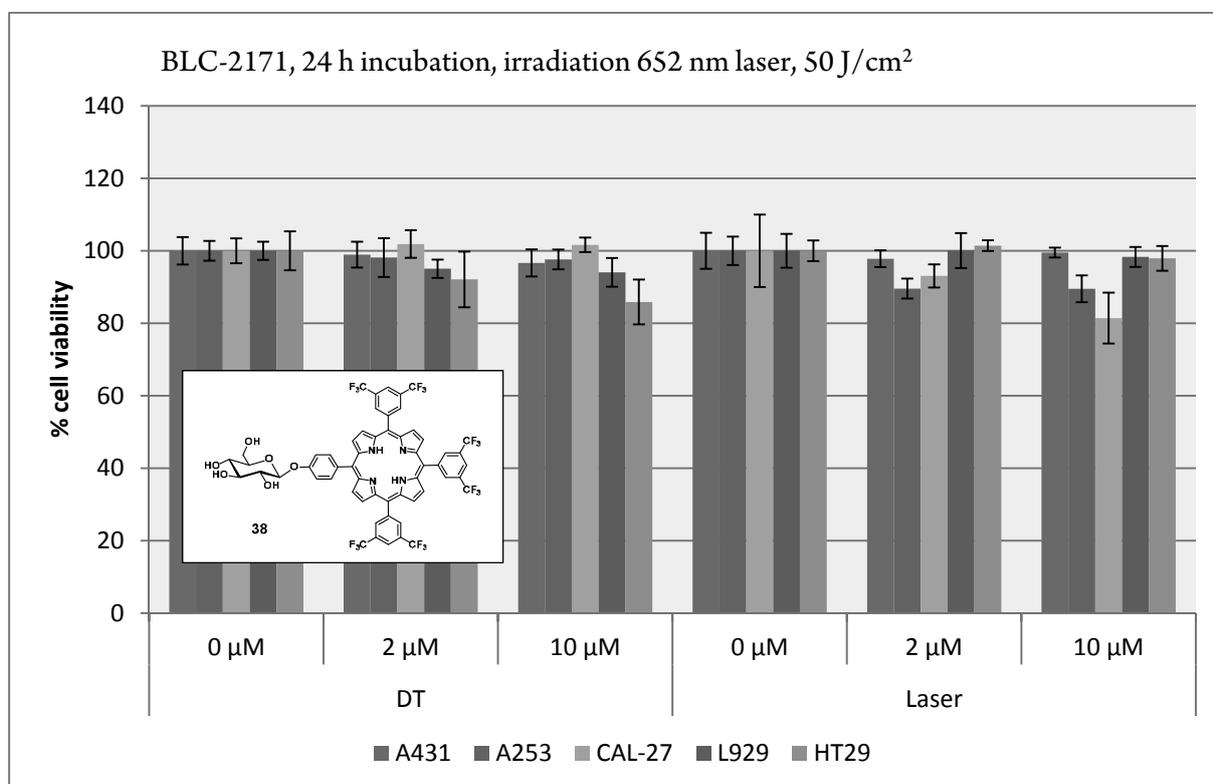


Figure 29. Photodynamic activity of BLC-2171.

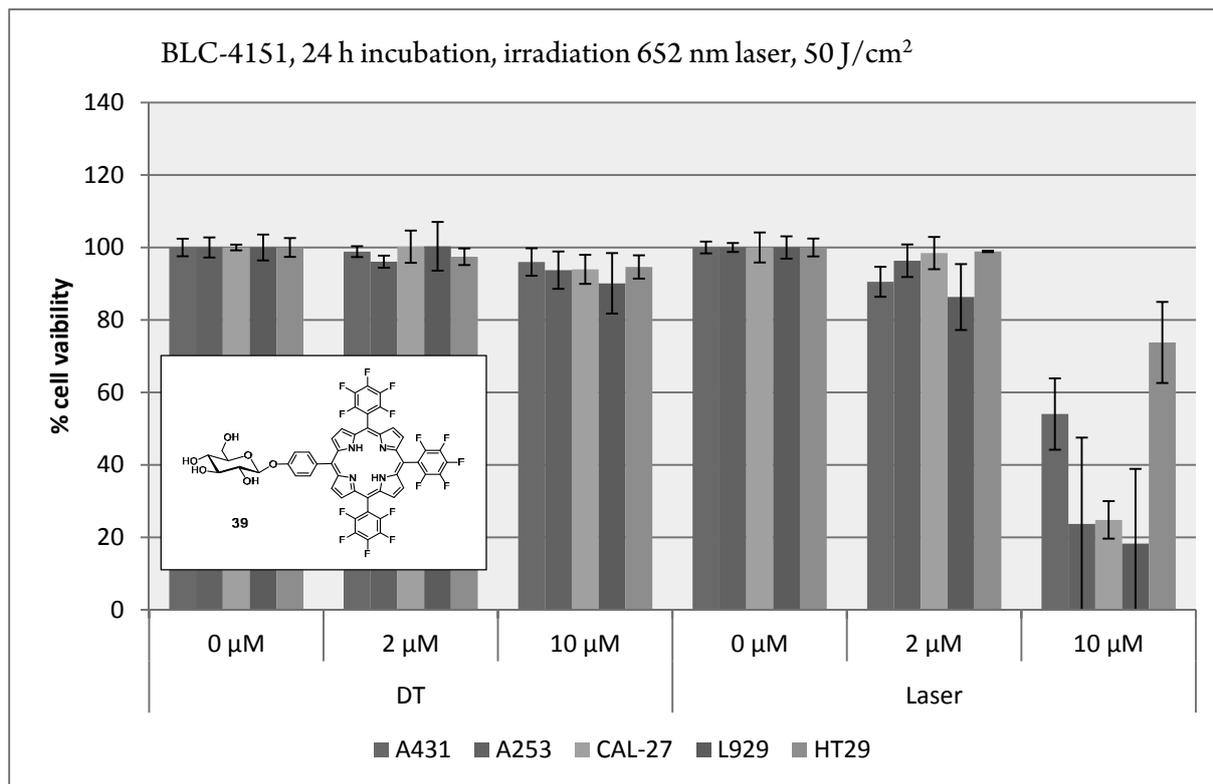


Figure 30. Photodynamic activity of BLC-4151.

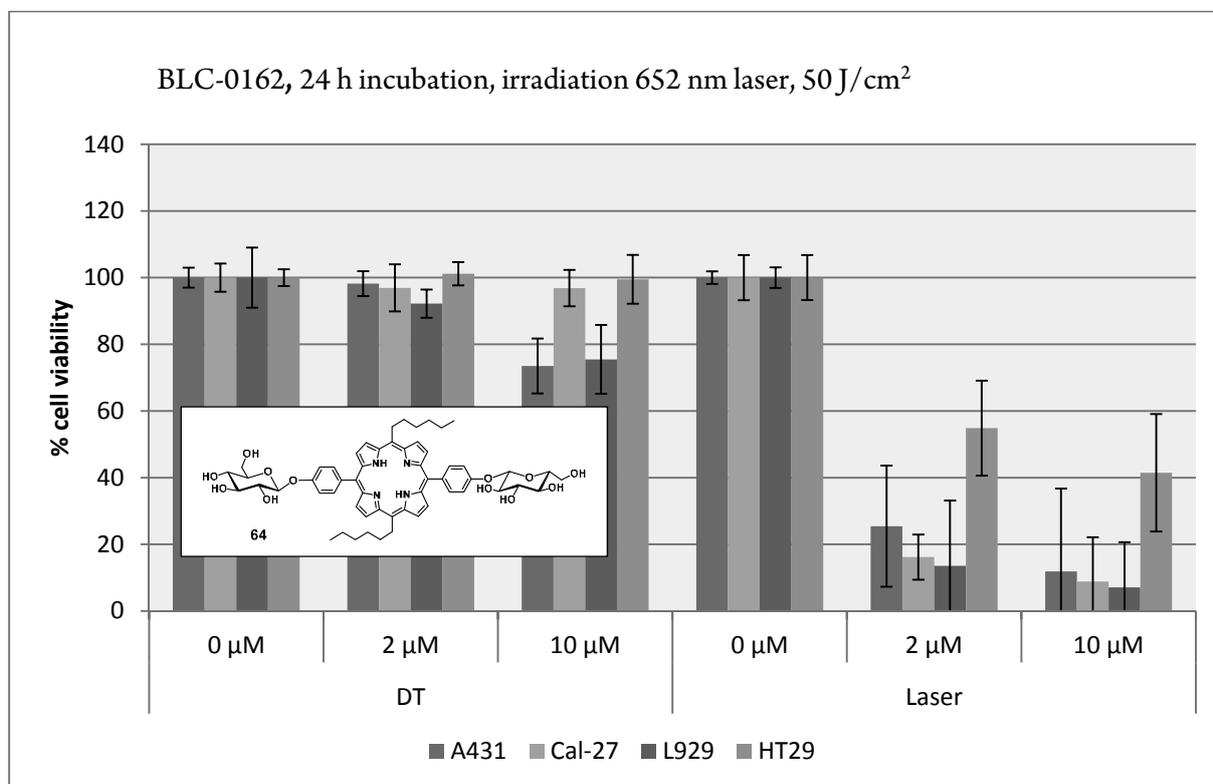


Figure 31. Photodynamic activity of BLC-0162.

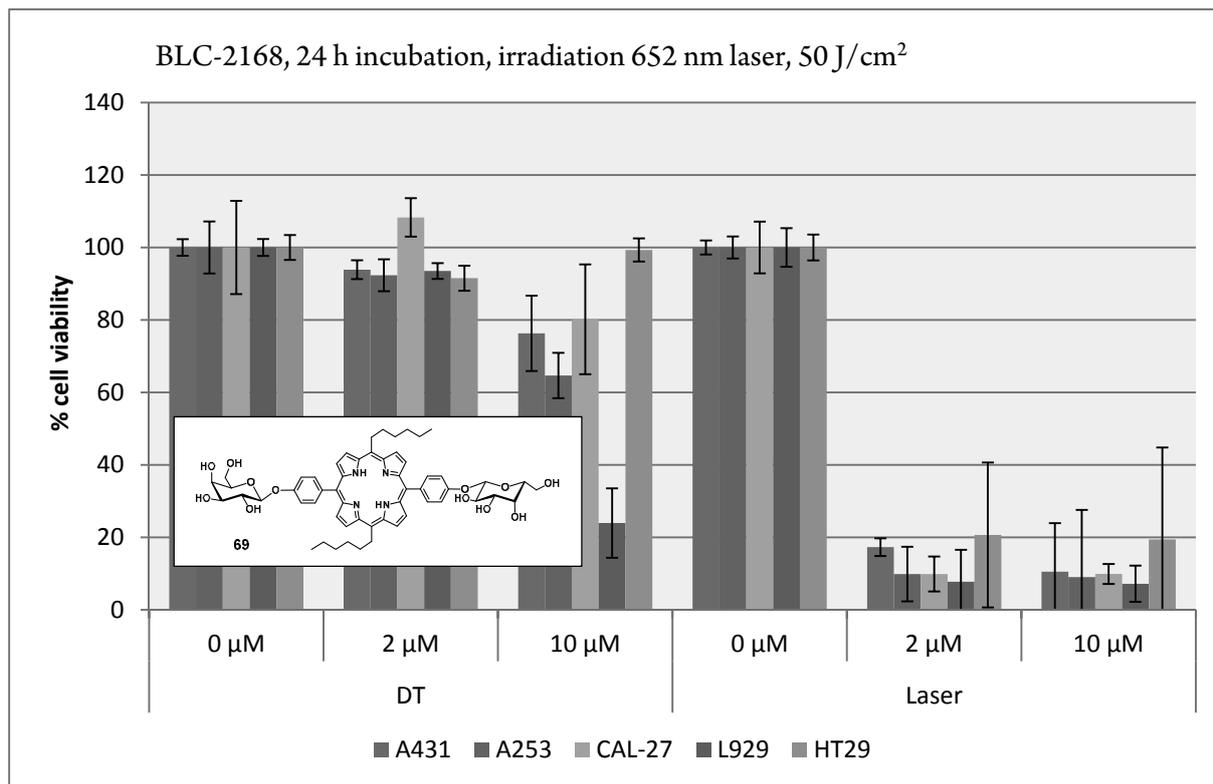


Figure 32. Photodynamic activity of BLC-2168.

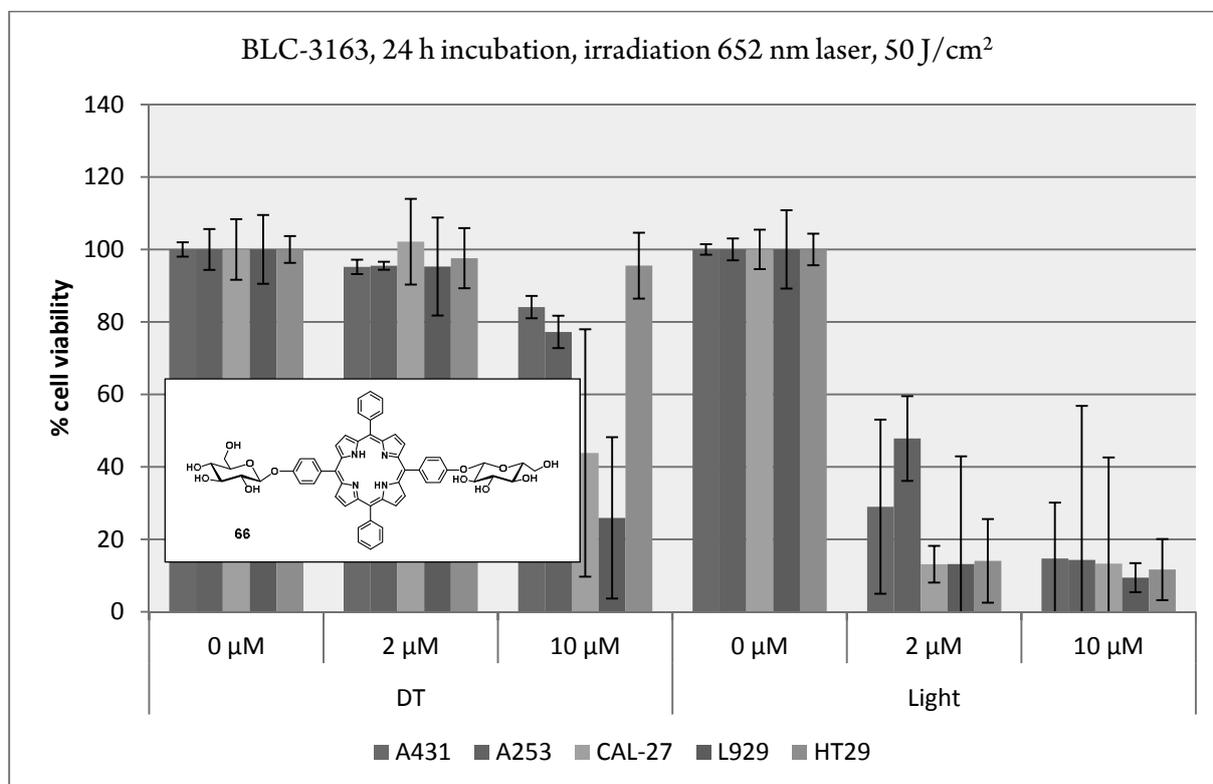


Figure 33. Photodynamic activity of BLC-3163.

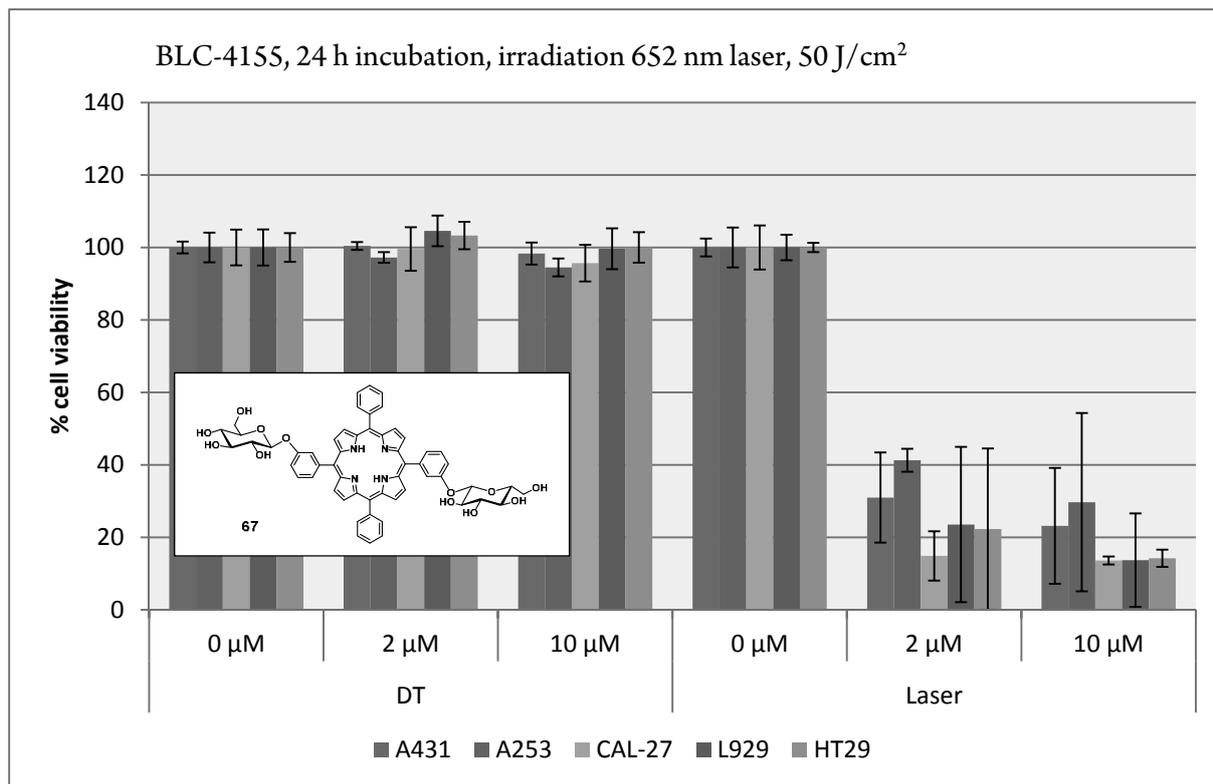


Figure 34. Photodynamic activity of BLC-4155.

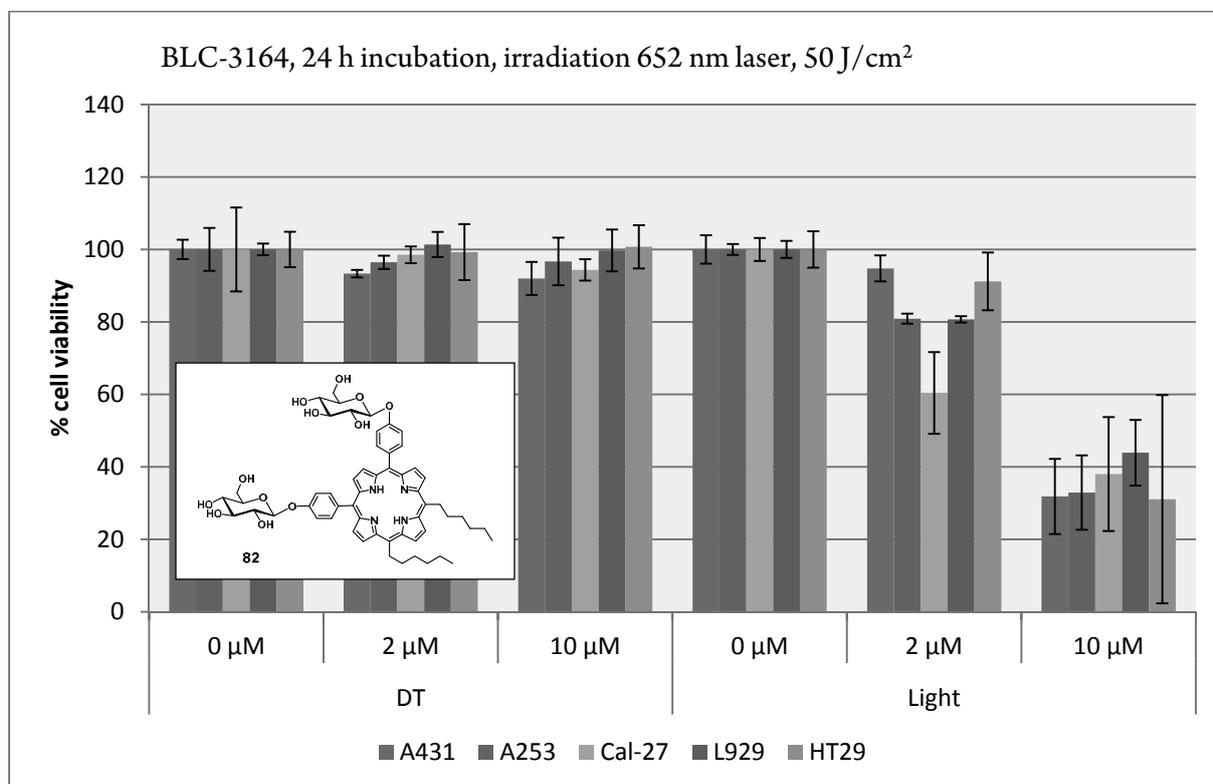


Figure 35. Photodynamic activity of BLC-3164.

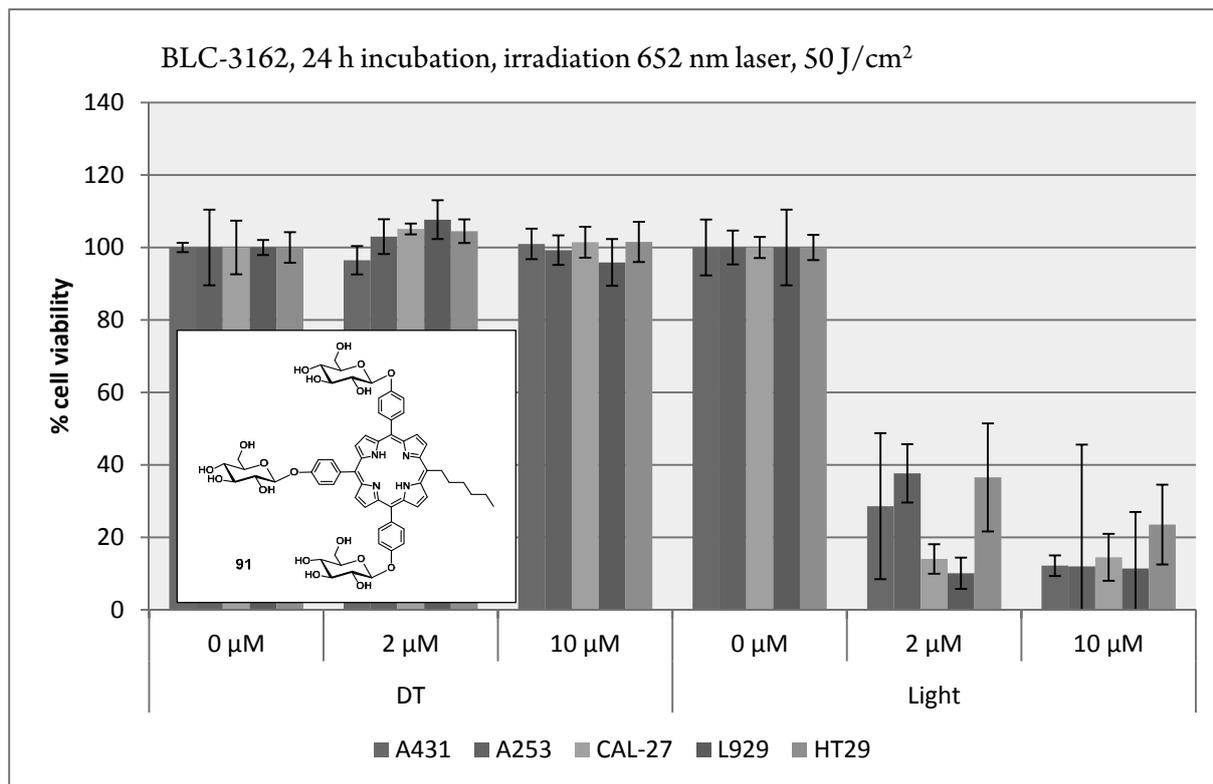


Figure 36. Photodynamic activity of BLC-3162.

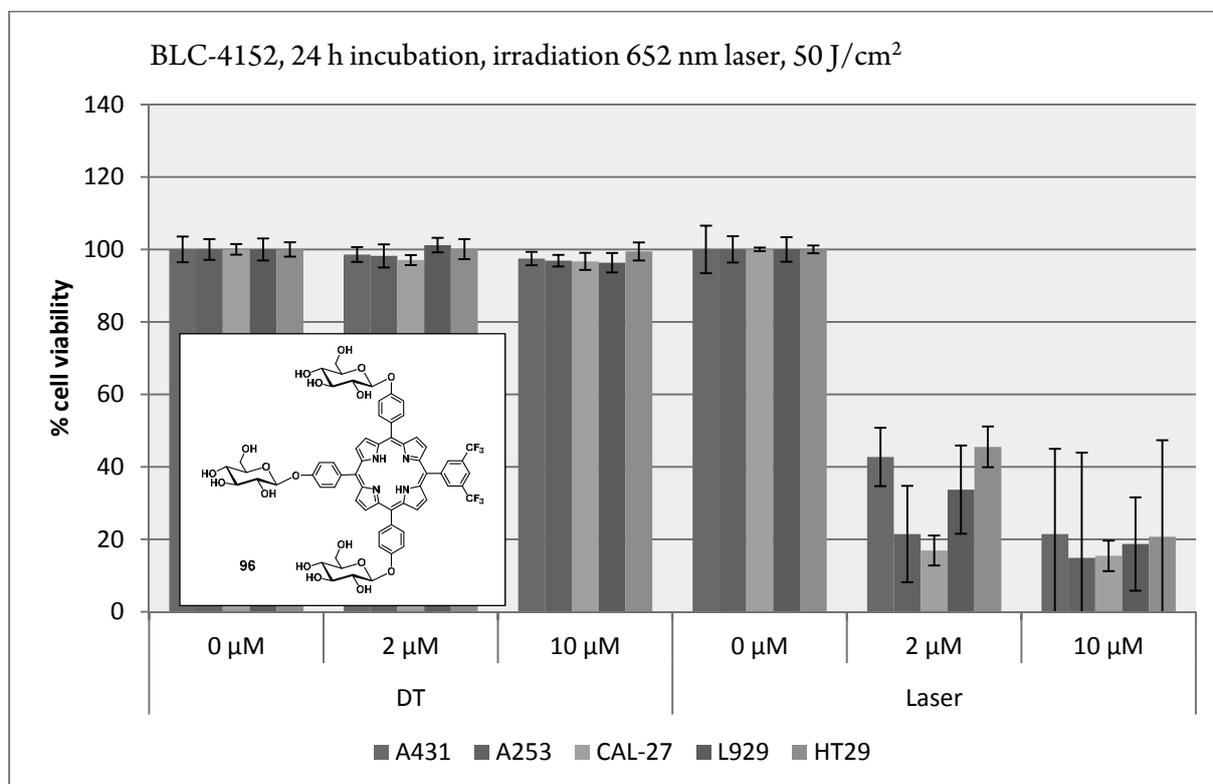


Figure 37. Photodynamic activity of BLC-4152.

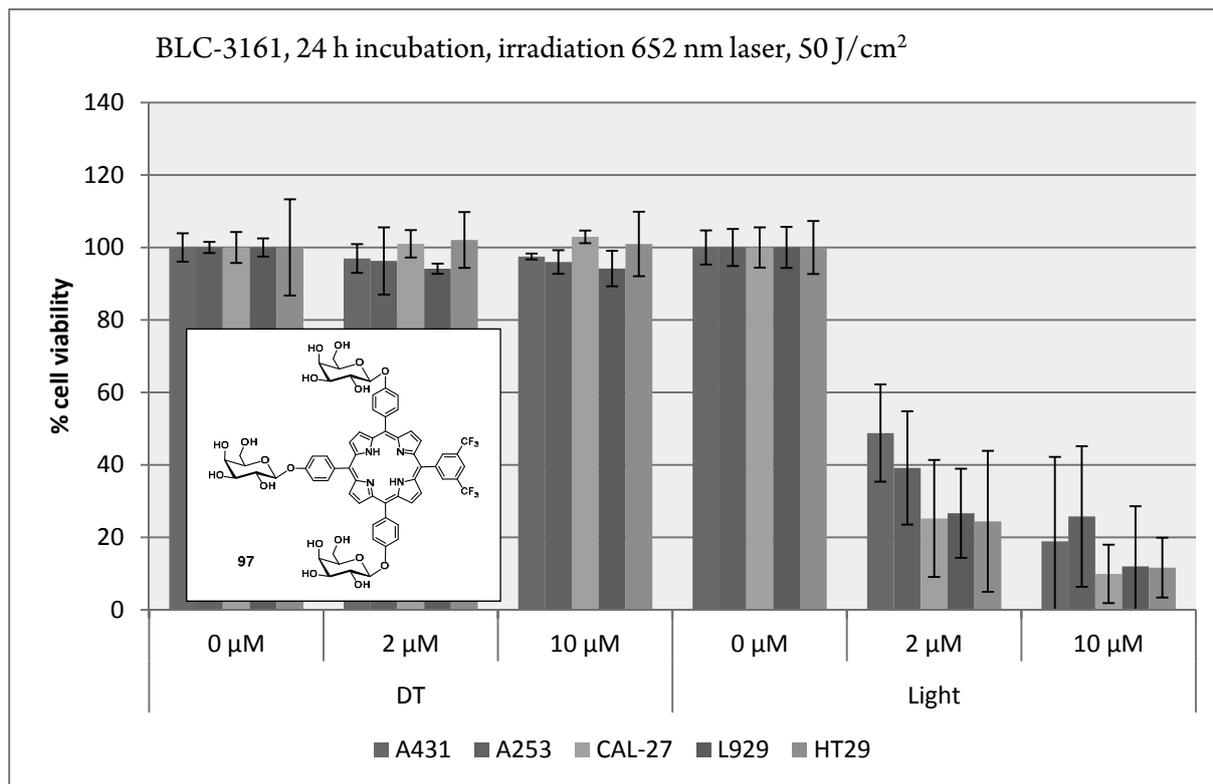


Figure 38. Photodynamic activity of BLC-3161.

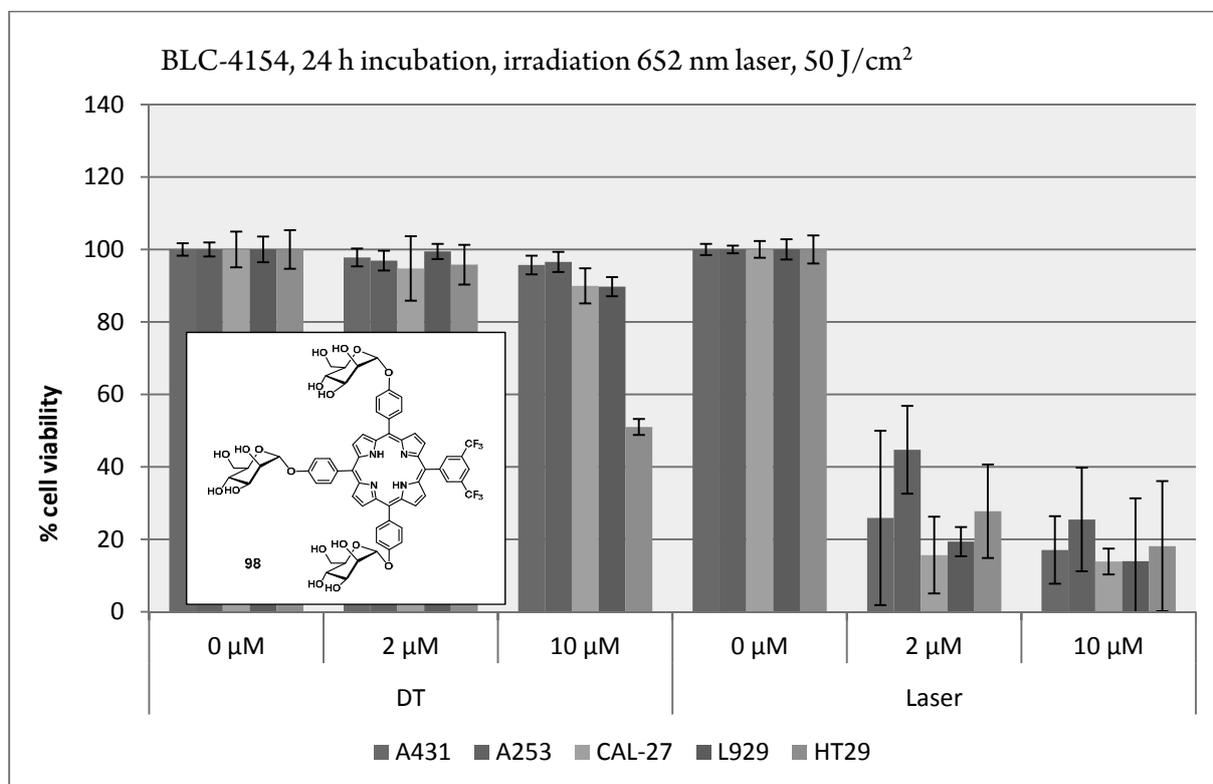


Figure 39. Photodynamic activity of BLC-4154.

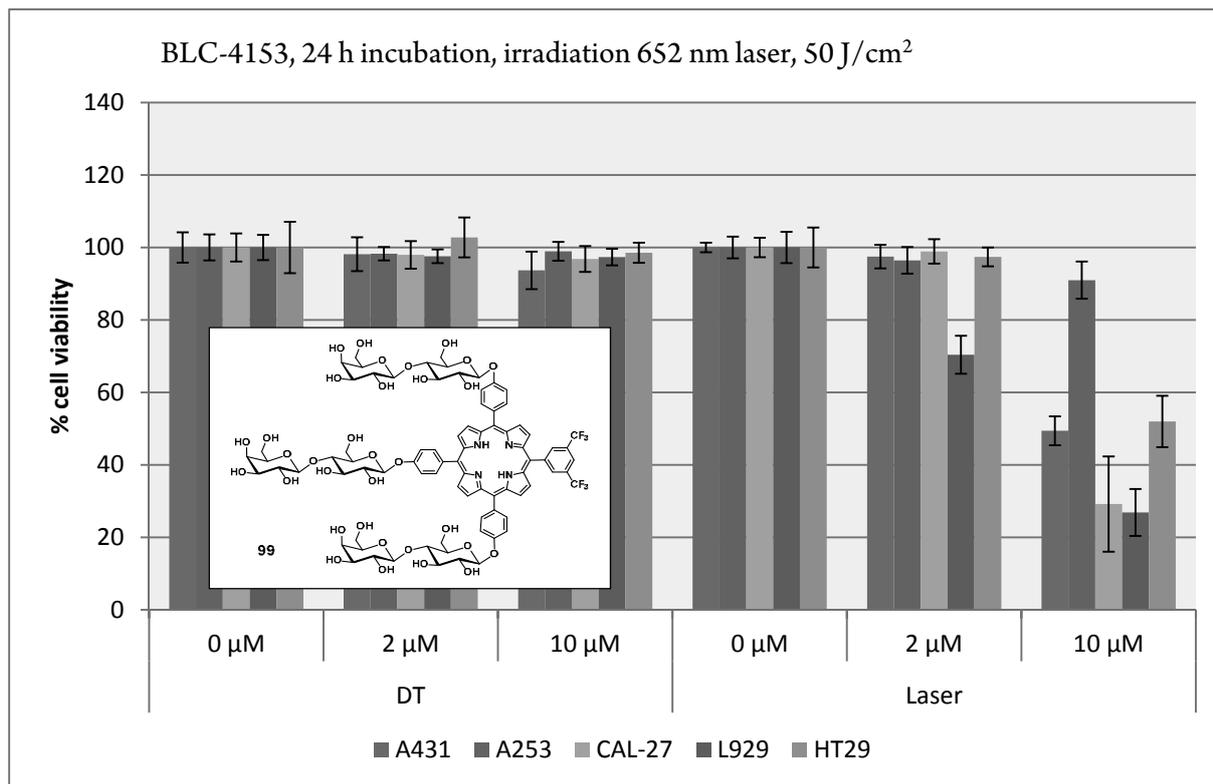


Figure 40. Photodynamic activity of BLC-4153.

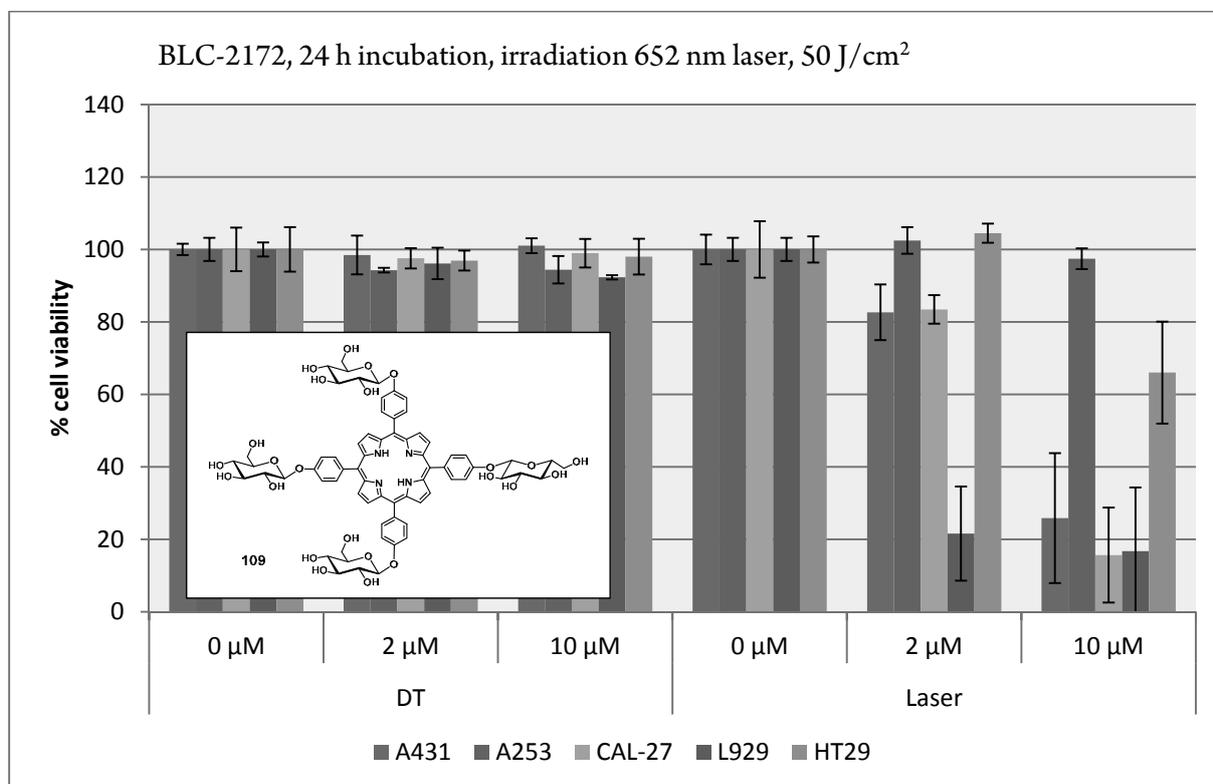


Figure 41. Photodynamic activity of BLC-2172.

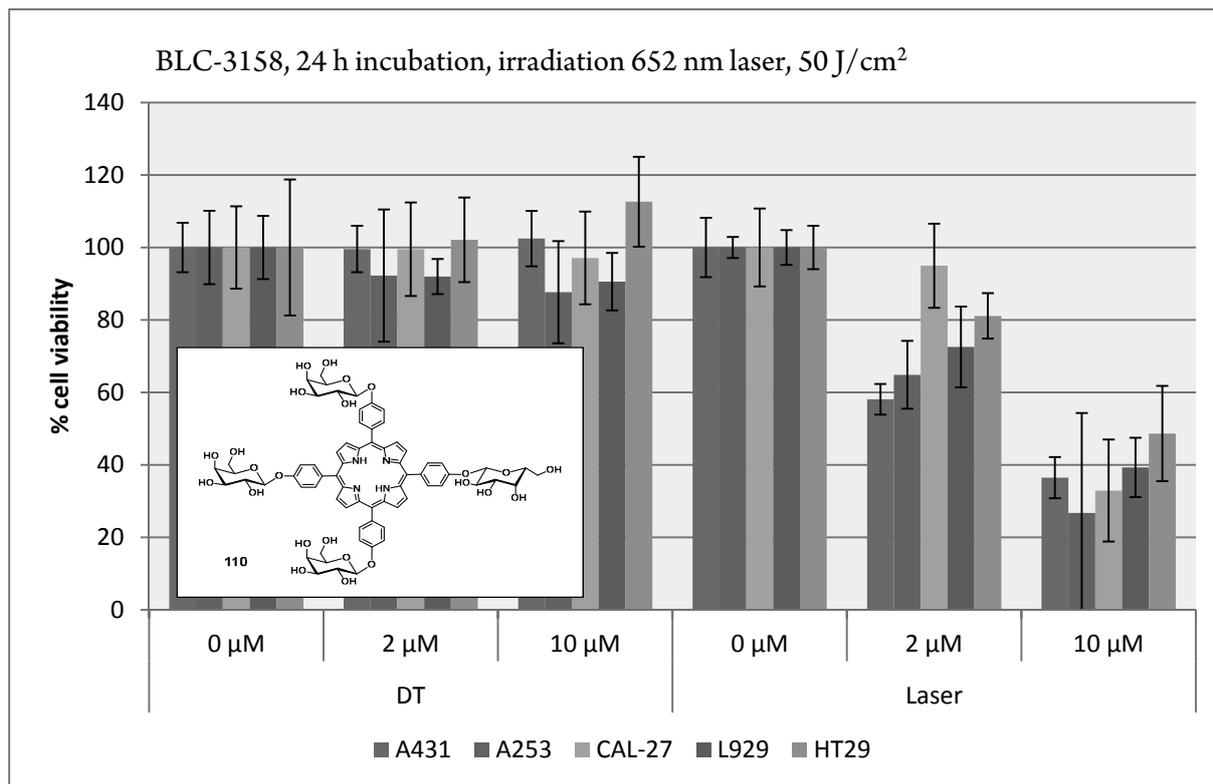


Figure 42. Photodynamic activity of BLC-3158.

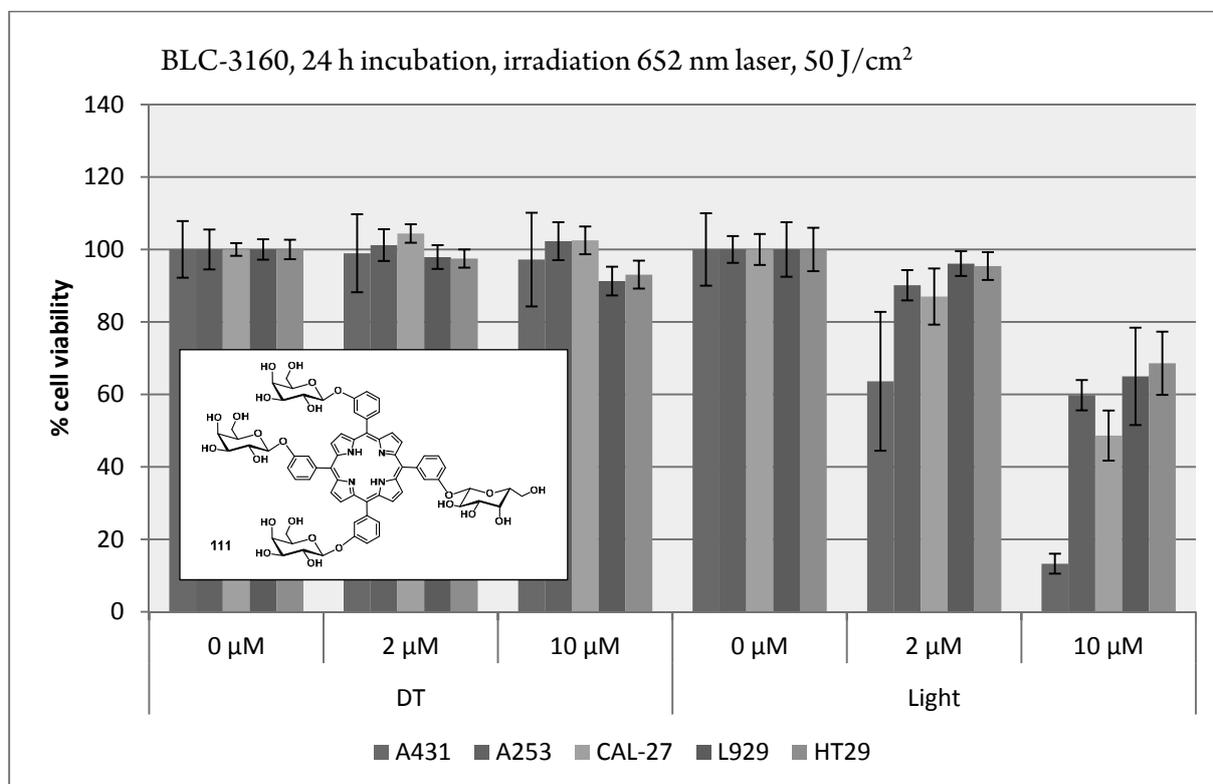


Figure 43. Photodynamic activity of BLC-3160.

RESULTS AND DISCUSSION

The following table summarizes all PS and their activity against the corresponding cells:

Substitution Patterns	Photosensitizer (conc.)		cell viability in %				
			A431	A253	CAL-27	L929	HT29
MONO (Test)	BLC-2167	2 μ mol	>100	>100	>100	>100	>100
		10 μ mol	>100	100	85	100	>100
MONO	BLC-0160	2 μ mol	90	n.d.	35	60	55
		10 μ mol	60	n.d.	10	50	30
	BLC-0161	2 μ mol	95	n.d.	35	60	95
		10 μ mol	80	n.d.	10	15	70
	BLC-2166	2 μ mol	100	90	35	35	>100
		10 μ mol	80	40	20	15	95
	BLC-3152	2 μ mol	80	40	20	90	90
		10 μ mol	20	20	20	25	20
	BLC-2165	2 μ mol	100	100	100	100	>100
		10 μ mol	85	75	50	60	>100
	BLC-2171	2 μ mol	100	90	90	100	100
		10 μ mol	100	90	80	100	100
	BLC-4151	2 μ mol	90	95	100	85	100
		10 μ mol	55	20	25	20	75
DI	BLC-2168	2 μ mol	20	10	10	<10	20
		10 μ mol	10	<10	10	<10	20
	BLC-0162	2 μ mol	25	n.d.	15	10	55
		10 μ mol	10	n.d.	<10	<10	40
	BLC-3163	2 μ mol	30	50	15	10	10
		10 μ mol	15	15	15	<10	10
	BLC-4155	2 μ mol	30	40	15	20	20
		10 μ mol	20	30	15	10	15
	BLC-3164	2 μ mol	95	80	60	80	90
		10 μ mol	30	30	40	40	30
TRI	BLC-3162	2 μ mol	30	35	15	<10	40
		10 μ mol	10	10	15	10	20
	BLC-4152	2 μ mol	40	20	15	30	45
		10 μ mol	20	15	15	20	20
	BLC-3161	2 μ mol	50	40	25	30	20
		10 μ mol	20	25	10	10	10
	BLC-4154	2 μ mol	25	45	15	20	30
		10 μ mol	15	25	15	10	20
	BLC-4153	2 μ mol	100	95	100	70	100
		10 μ mol	50	90	30	25	50
TETRA	BLC-2172	2 μ mol	80	100	80	20	>100
		10 μ mol	25	100	15	15	65
	BLC-3158	2 μ mol	60	65	95	70	80
		10 μ mol	35	25	30	40	50
	BLC-3160	2 μ mol	60	90	85	95	95
		10 μ mol	15	60	50	65	70

0-15	20-30	35-55	60-100
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Table 12. Different Photosensitizer and their activity against the corresponding cell lines: dark green = excellent, light green = good, yellow = medium, red = bad.

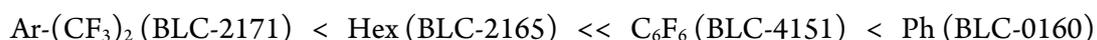
All mentioned PS were tested against A431 cells (epidermoid carcinoma cells from skin/epidermis), A253 cells (submandibular carcinoma cells), CAL-27 cells (squamous cell carcinoma from tongue), L929 (subcutaneous connective tissue, areolar and adipose) and resistant HT29 cells (colorectal adenocarcinoma cells from colon). The PS BLC-0160, BLC-0161 and BLC-0162 were synthesized when A253 cell lines were not yet available in the biolitec labs so their activity could not be determined (n.d.). The classification in four colors (dark green = excellent, light green = good, yellow = medium, red = bad) was chosen for a better overview and easier evaluation.

General remarks:

A first look at the table shows that generally most of the PS show the best activity against squamous cell carcinoma from the tongue while they are generally less active against colorectal adenocarcinoma cells from colon and submandibular carcinoma cells. The table also shows that monoglycosylated porphyrins (AB₃) with three 3,5-bis-(trifluoromethyl)-phenyl- and three *n*-hexyl substituents show no activity at any concentration (2 μmol or 10 μmol) or even lead to tumor growth. Contrary to our expectation, some rather lipophilic monoglycosylated porphyrins (AB₃) with three phenyl substituents show quite promising results. As a blank test the acetoxy-protected glyco-porphyrins BLC-2167, the precursor of the active and deprotected BLC-0160, was tested and, as expected, showed no activity against the cell lines. Another conclusion which can be derived from the table is the very good activity of the diglycosylated porphyrins. A difference between the very active *trans*-A₂B₂- and the less active *cis*-A₂B₂-substituted glyco-porphyrins can be observed and indicates the importance of the structure motif. The differences between *meta*- and *para*-substituted glyco-porphyrins regarding their activity seems to be negligible (BLC-3163 vs BLC-4155 and BLC-3158 vs BLC-3160). Furthermore, for the A₃B-substituted glyco-porphyrins, it turns out that all PS with three monosaccharides (glucose, galactose and mannose) show a good activity against the cell lines whereas the one with three disaccharides is not or less active. In general the A₄-substituted glyco-porphyrins are less active, except the photosensitizer BLC-2172.

influence of lipophilic substituent(s):

The glycosylated tetrapyrroles can be evaluated with respect to their lipophilic substituents. Therefore monoglycosylated porphyrins, all possessing one glucosyl substituent, but different lipophilic substituents (phenyl, *n*-hexyl, 3,5-bis-(trifluoromethyl)-phenyl and pentafluorophenyl substituents) are observed first. The result is the following (activity increases from left to right):



In detail, for monoglycosylated porphyrins the lipophilic substituents play a crucial role regarding their activity against the cell lines evaluated. In this screening, phenyl groups gave promising results while *n*-hexyl- and 3,5-bis-(trifluoromethyl)-phenyl groups show an unsatisfactory activity or even no

cytotoxic activity at all. It should be also noted that the impact of the lipophilic substituent(s) in di- (BLC-0162 vs BLC-3163) and triglycosylated (BLC-3162 vs BLC-4152) porphyrins decreases.

influence of carbohydrate(s):

Here, we focus on the influence of carbohydrate subunits in glycosylated tetrapyrroles regarding their activity against the cell lines evaluated. Monoglycosylated porphyrins, all possessing three phenyl substituents, but different carbohydrate-substituents (glucose, galactose, mannose and lactose) were studied. It turns out that the lactosyl derivative BLC-3152 possesses a good activity against all cell lines investigated (~ 80% activity). The monosaccharide-containing PS have a lower 'overall' activity, but among these especially the glucosyl- and galactosyl-substituted derivatives (BLC-0160 and BLC-0161) show a very promising activity of 90% against CAL-27 cancer cells. Despite that it seems that monoglycosylated PS with disaccharides subunits are generally more active (against all cell lines studied). Because of the rather high lipophilicity, a disaccharide leads to a higher polarity of the PS than a monosaccharide. Again, this proves the general assumption that amphiphilicity plays a crucial role for the activity of a PS. The amphiphilic and very active *trans*-A₂B₂-substituted glyco-porphyrins (ratio of lipophilic substituents and glycosylic units = 1:1) underline this. The same trend is also observed for the rather polar A₃B-substituted glyco-porphyrins: while the monosaccharide-containing PS show very promising activities, the disaccharide-containing PS BLC-4153 is less active. Here, due to three carbohydrate units and only one lipophilic substituent, the PS generally possesses a higher polarity and an introduction of three lactosyl units probably makes it too polar and lowers its activity. In general the A₄-substituted glyco-porphyrins are less active, probably due to their high polarity and the lack of amphiphilicity. An exception is BLC-2172 with a higher activity against CAL-27 and L929 cells.

HT-29 tumor cells as a special case:

The HT-29 tumor cell line is known to be one of the most resistant cancer cell lines and it is significantly harder to find appropriate candidates against this cell line. Table 12 shows that there are some promising candidates among the tested PS. Especially among the *trans*-A₂B₂-substituted glyco-porphyrins, one of the promising candidates is BLC-3163 with an activity of 90% even at low concentrations of 2 µmol (10 µmol: 90% activity). But also the corresponding *meta*-derivative BLC-4155 shows a good activity of 80% at low concentrations of 2 µmol (10 µmol: 85% activity). Another good candidate is *trans*-A₂B₂-substituted BLC-2168 with an activity of 80%. Also A₃B-substituted glyco-porphyrins may be interesting candidates for further investigations, one of the most promising is BLC-3161 (3 x galactose units, 1 x 3,5-bis-(trifluoromethyl)-phenyl substituent) with an activity of 80% at concentrations of 2 µmol (10 µmol: 90% activity). The corresponding mannosyl derivative BLC-4154 also shows a good activity against the resistant HT-29 cells (2 µmol: 70%, 10 µmol: 80% activity). Again, the corresponding disaccharide containing derivative BLC-4153 is less active or not active at all.

The given conclusions are based upon the *in vitro* assays and give a better understanding of structure motifs and substitution patterns (different polarities, carbohydrate moieties and lipophilic substituents) on the photodynamic activity for further *in vivo* research and possible pharmaceutical formulations. Selected mono- or *trans*-A₂B₂-glycosylated porphyrins (BLC-0160, BLC-0161 and BLC-0162), which exhibited a good cytotoxicity but are rather lipophilic, were re-synthesized (upscaling) and successfully incorporated into pharmaceutical formulations in the group of Prof. FAHR from the Friedrich-Schiller-Universität in Jena (Germany). Thus, in combination with such carrier systems these compounds are interesting for further *in vivo* investigations.

3.1.4 Liposomal Formulations of Selected Compounds

The three compounds selected for liposomal formulations had shown promising cell test results, but also possess an insufficient solubility in polar solvents which would make them less interesting for PDT in *in vivo* applications (Figure 44).

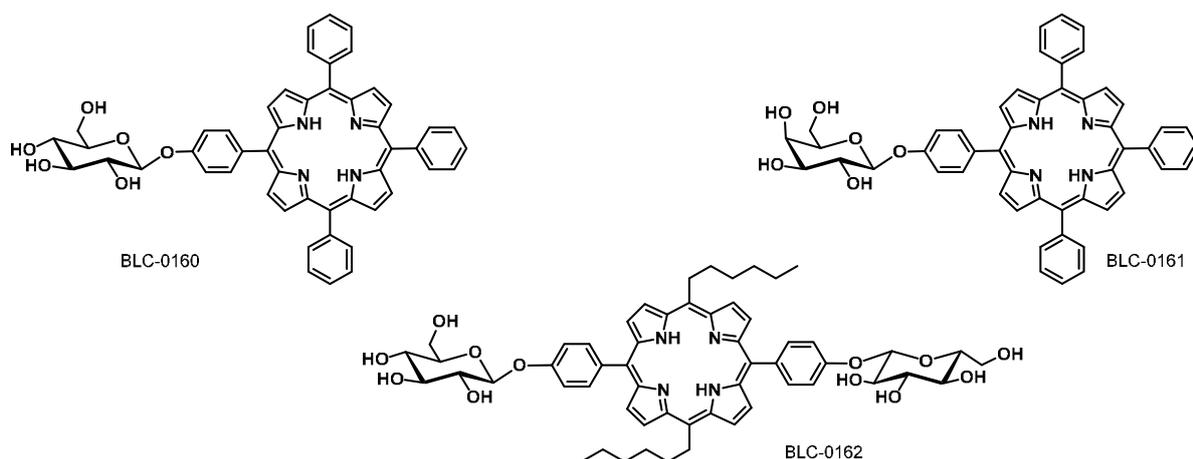


Figure 44. Three candidates for liposomal formulations.

One possibility to overcome this poor solubility is the incorporation of these photosensitizers in carrier systems like liposomes. After encapsulation in a liposome, the conjugates can be transported in the blood to their final destination, e.g. a tumor, where they can unfold their potential. Moreover liposomal formulations could benefit from the EPR effect leading to an increased (passive) accumulation of particles of a certain size in tumorous tissue.

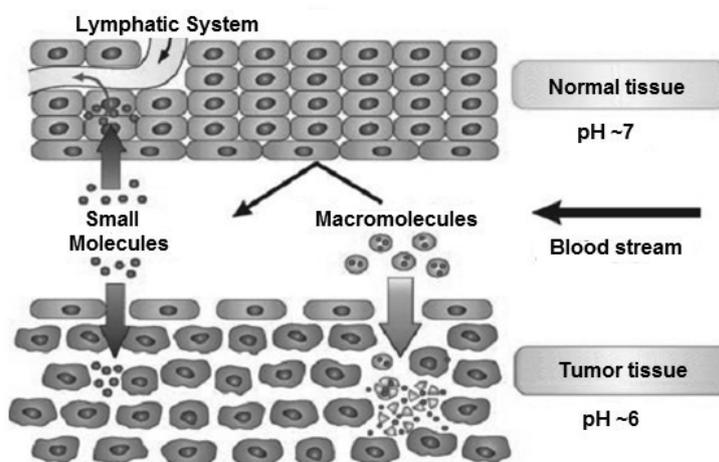


Figure 45. Schematic representation of the physiological and anatomical characteristics of normal and tumor tissue regarding the vascular permeability and retention of small and large molecules (EPR effect).^[79] Copyright 2006 Wiley-VCH Verlag.

There are several reasons for this effect which can be found in the malign tumor tissue which is biochemically and physiologically different from healthy tissue. For example a tumor needs an extensive formation of new blood vessels to ensure a rapid growth. Typically these formed vessels possess a different architecture and form than in normal tissue, e.g. the endothelial cells of tumor tissue have wider fenestrations and they do not have an effective lymphatic drainage (Figure 45). So macromolecules, like e.g. liposomes, can enter the tumor tissue much better than normal tissue. The ineffective lymphatic system leads to a longer duration of the macromolecule.

To prepare these liposomal formulations, larger amounts of the deprotected glycosylated porphyrins were needed (approximately 200 mg). It should be noted, that each of them required 6-7 synthetic steps; starting with a two to four liter flask for condensation and ending up with a 20 milliliter flask for the deprotection of the glycosylated porphyrins, clearly illustrates the dimensions. In comparison to the small amounts synthesized before, the yields in the scale-up were similar in all steps, but the purification processes were more tricky and time-consuming than before. Finally, with the suitable amount of all conjugates in hand they were successfully incorporated into pharmaceutical formulations in the group of Prof. Fahr from the Friedrich-Schiller-Universität in Jena (Germany) using DPPC (Dipalmitoylphosphatidylcholine) and DPPG (Dipalmitoylphosphatidylglycerol) as liposomal components. Again, the liposomal formulations of the glycosylated porphyrins were tested *in vitro* like the pure conjugates before and showed a similarly good activity against the different carcinoma cell lines. Thus, in combination with this carrier system these compounds are interesting for further investigations.

Since the three photosensitizer BLC-0160, BLC-0161 and BLC-0162 had shown promising photodynamic activity against several cancer cell lines, we examined their impact on caspase activity. Caspases (**cysteine-aspatic proteases**) are protease enzymes which play crucial roles in programmed cell death and can be subclassified into three types (initiator, executioner, inflammatory).^[78b] The process of programmed cell death (apoptosis, pyroptosis and necroptosis) depends on the corresponding caspase. In our case, we examined the activity of Caspase 3/7 which are executioner type of caspases leading to apoptosis.^[78b] Therefore, A431 cells (epidermoid carcinoma cells from skin/epidermis) and CAL-27 cells (squamous cell carcinoma from tongue) were incubated for 24 hours with the photosensitizers. Then the samples were irradiated with laser light ($\lambda = 652 \text{ nm}$) and a radiation energy of 24 J/cm^2 .

The assays show that the activation of apoptic caspases 3/7 *via* a photosensitizer (BLC-0160, BLC-0161 or BLC-0162) is strongly associated with the cell viability (here: CAL-27 and A431 cells). Higher concentrations of caspases 3/7 lead to an increased cell death.

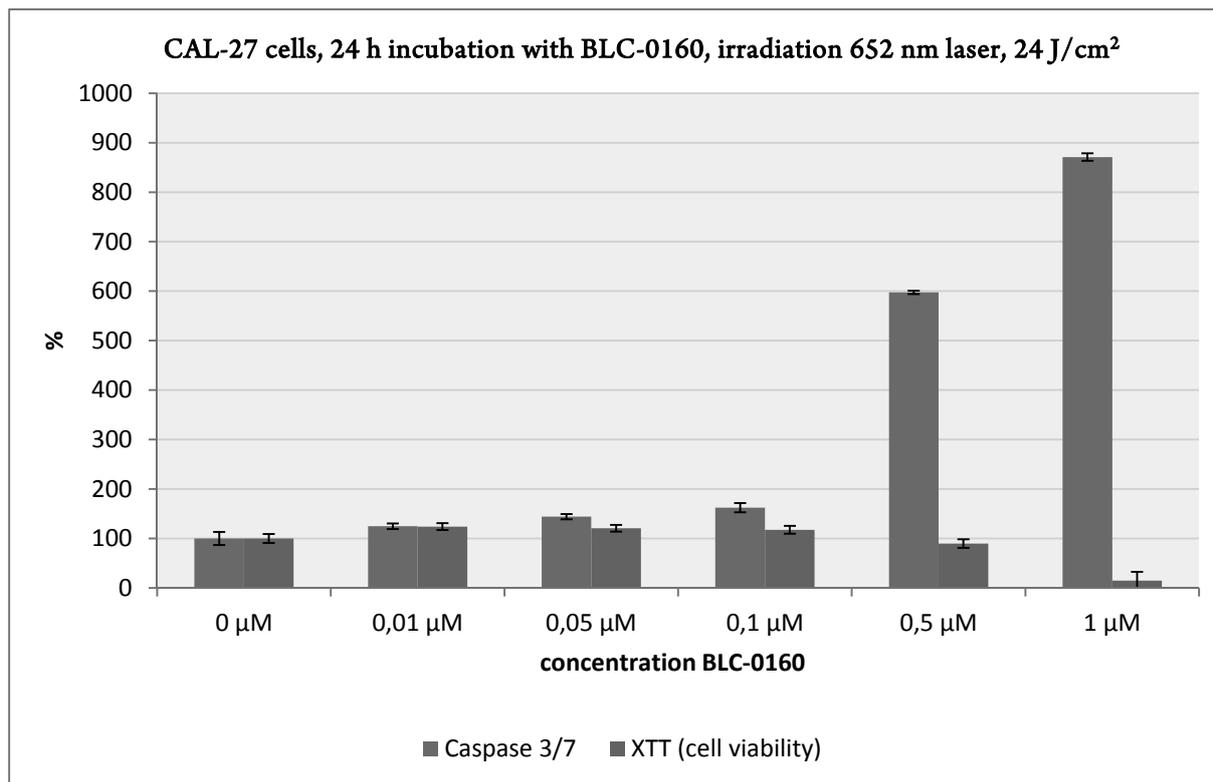


Figure 46. Caspase activity assay for photosensitizer BLC-0160 (CAL-27 cells).

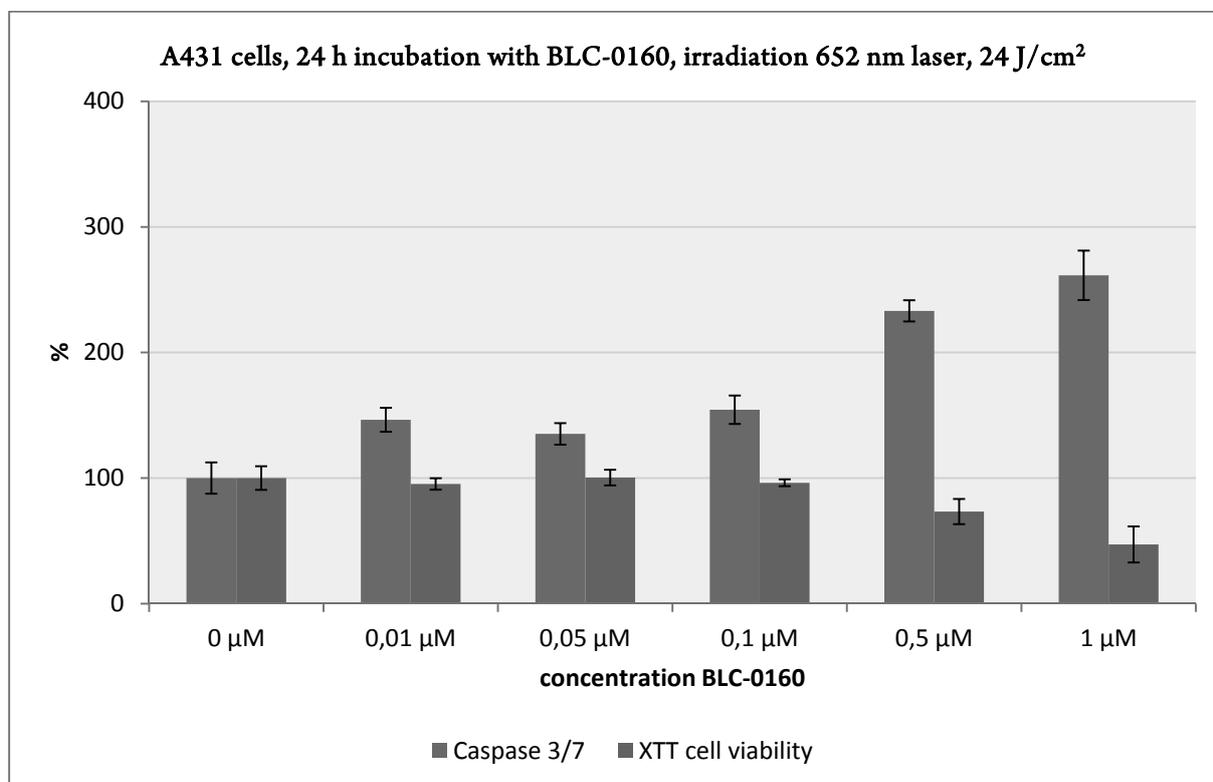


Figure 47. Caspase activity assay for photosensitizer BLC-0160 (A431 cells).

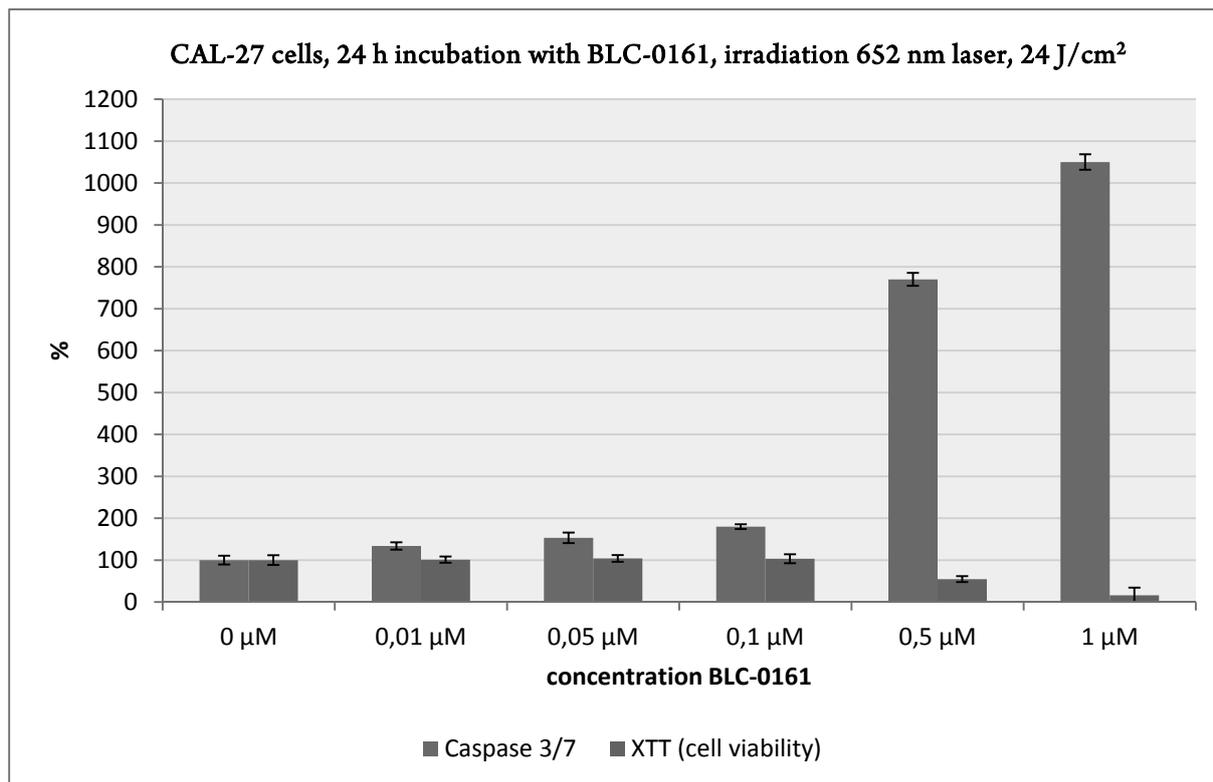


Figure 48. Caspase activity assay for photosensitizer BLC-0161 (CAL-27 cells).

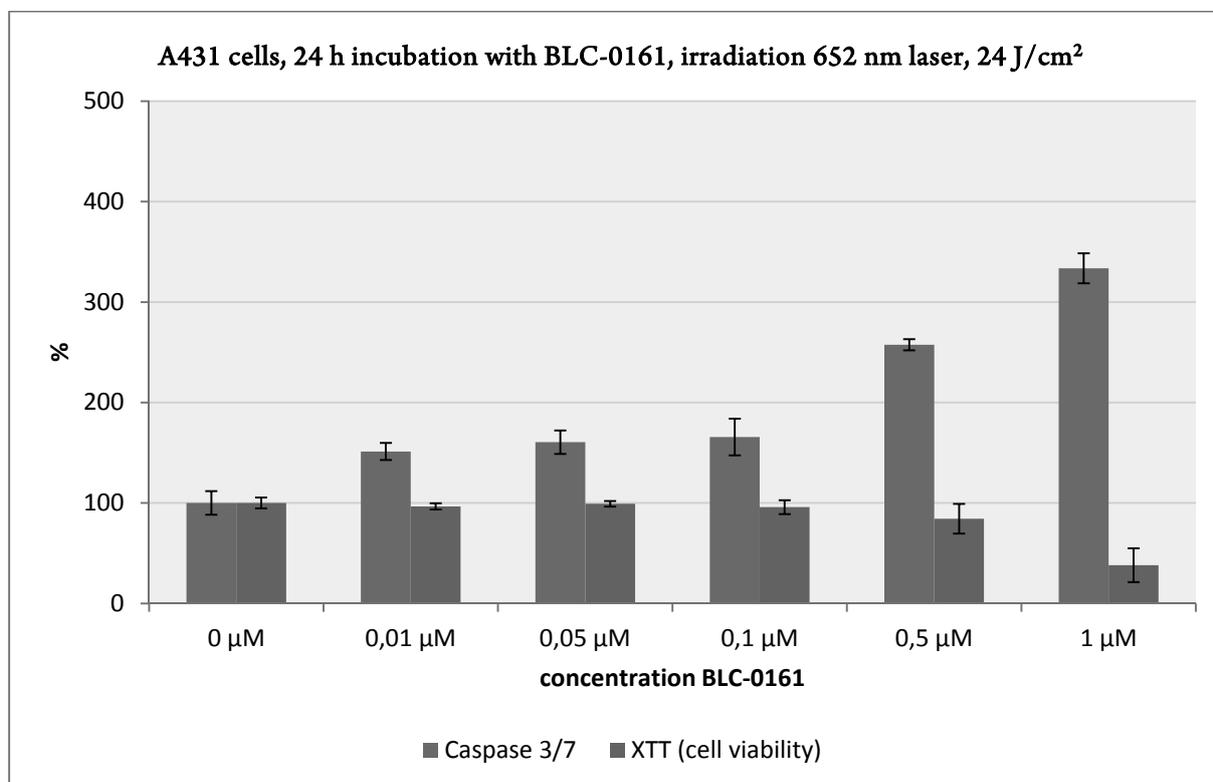


Figure 49. Caspase activity assay for photosensitizer BLC-0161 (A431 cells).

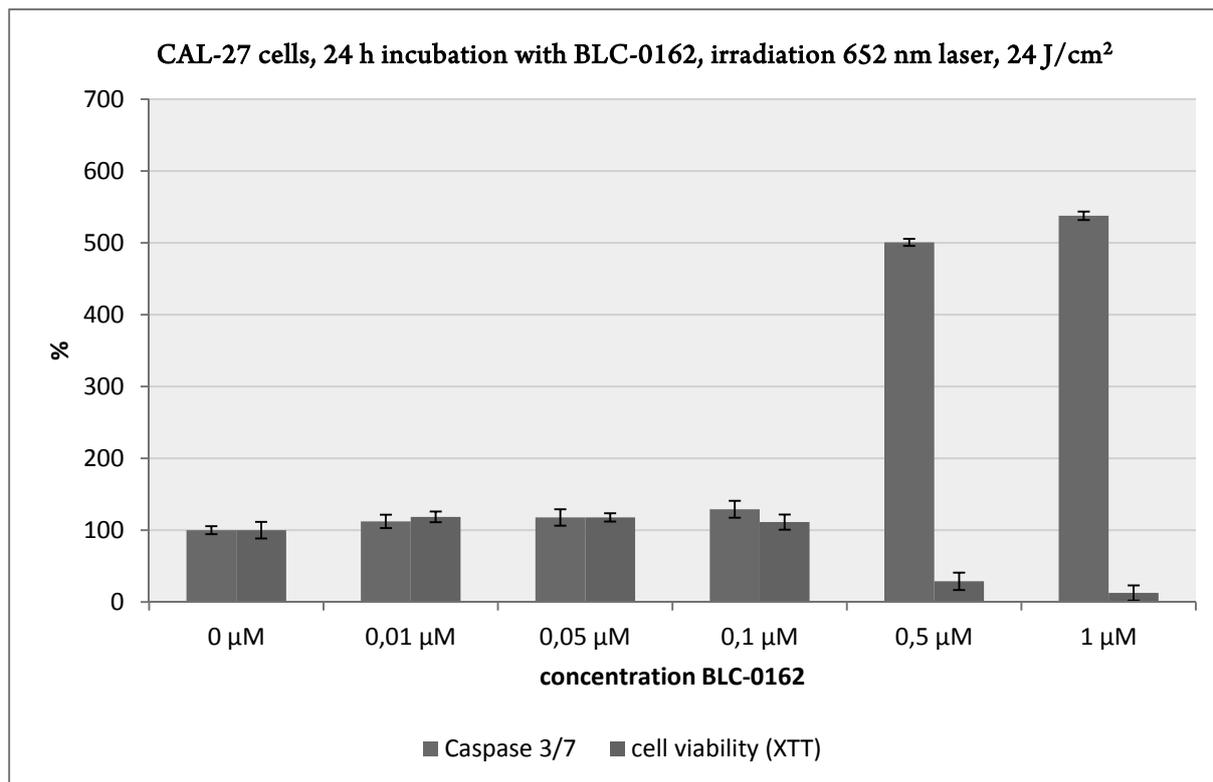


Figure 50. Caspase activity assay for photosensitizer BLC-0162 (CAL-27 cells).

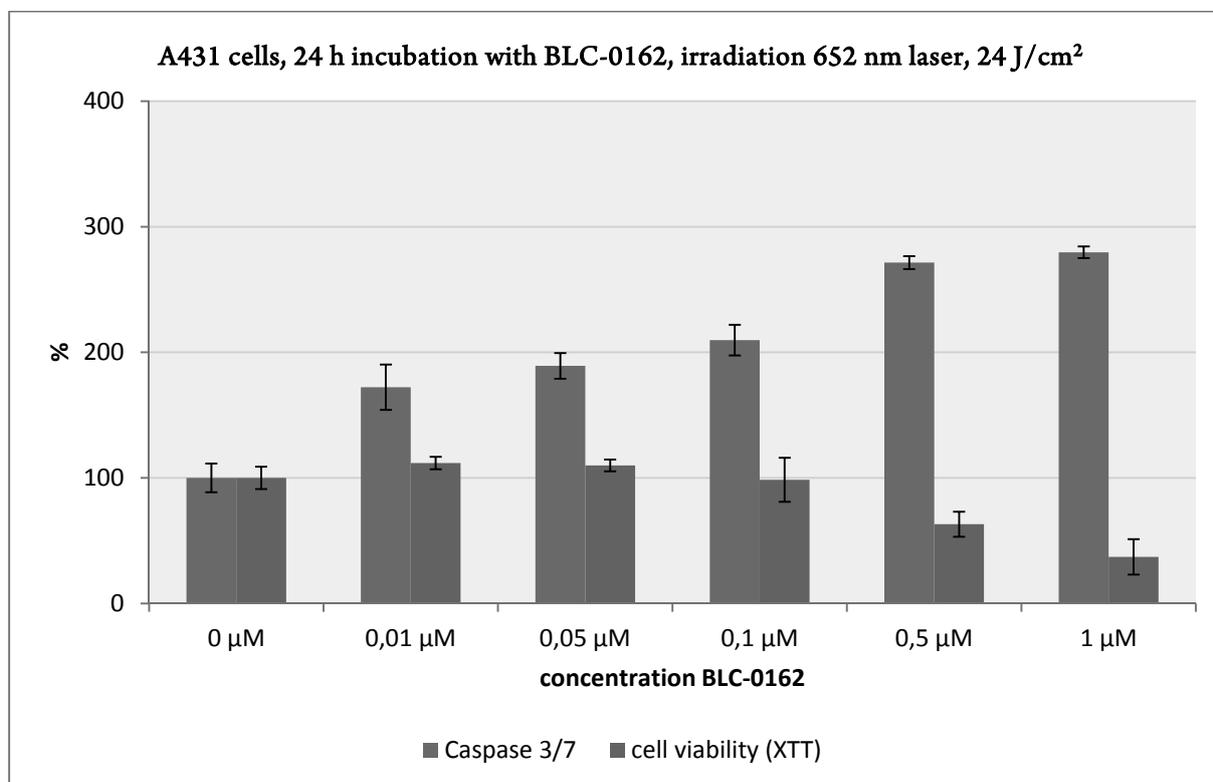
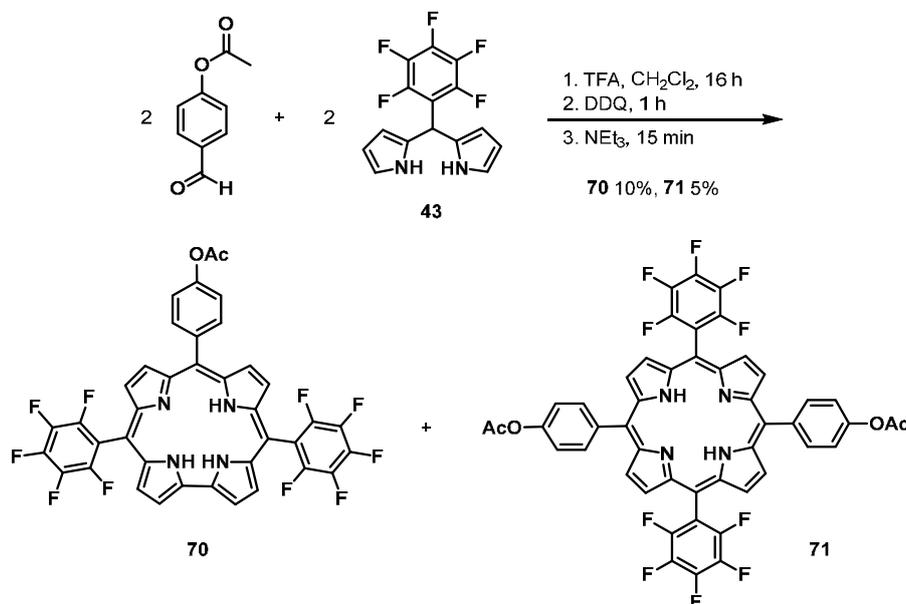


Figure 51. Caspase activity assay for photosensitizer BLC-0162 (A431 cells).

3.2 Modifications and Combinations of the Trichloroacetimidate Method

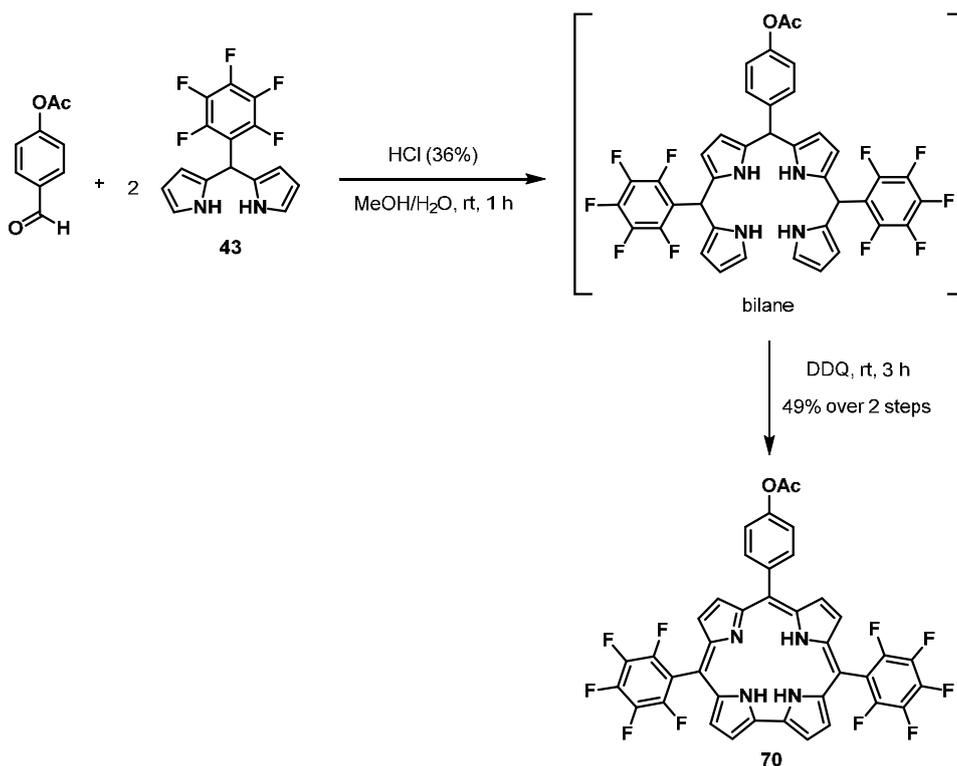
3.2.1 Lactosylation of a Corrole

Encouraged by the synthesis of the library of *meta*- and *para*-substituted glyco-porphyrins *via* the trichloroacetimidate method, we tried to transfer this method to a corrole system to smooth the way for the synthesis of novel glyco-corroles. For this purpose, it was necessary to find a reproducible synthetic route for the condensation to corroles. As mentioned before, the condensation to the fluorinated *trans*-A₂B₂-substituted porphyrin, following LINDSEY, resulted in the formation of the desired porphyrin, but surprisingly also the corresponding corrole could be isolated (Scheme 30). This good yield for the formation of corrole was very satisfying, unfortunately the yields were fluctuating as described above. So an alternative method had to be found.



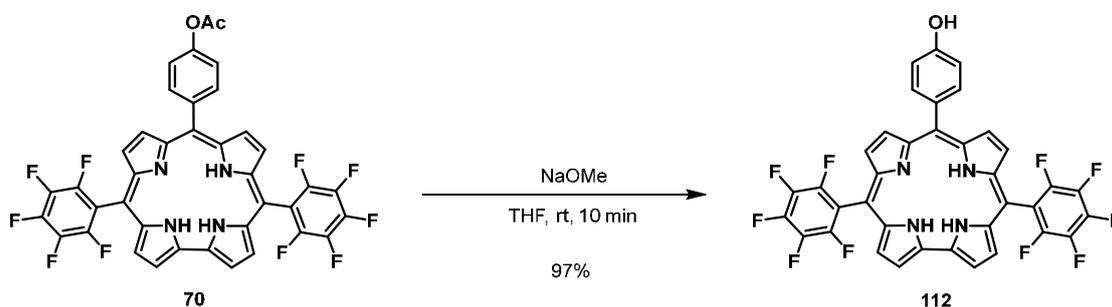
Scheme 30. Synthesis of *trans*-A₂B-substituted corrole (as a side-product) *via* LINDSEY.

A new method for the synthesis of corroles was published in 2006 by GRYKO *et al.*^[21] Instead of the unpolar dichloromethane a mixture of water and methanol was chosen here. In this approach, the different solubilities of the starting materials and the corrole precursor, the bilane, are exploited. Moreover, as opposed to the condensation reaction in dichloromethane this reaction is carried out under non-equilibrium conditions. While dipyrromethanes and aldehydes are soluble in the 1:1 mixture of water and methanol, the bilane precipitates and is thus removed from the condensation equilibrium. In the second step the bilane is oxidized to the corrole with DDQ. The overall yield of 49% for the GRYKO method (Scheme 31) is much higher in comparison to the LINDSEY method and on repetitions of this synthesis the yield was also reproducible.



Scheme 31. Synthesis of *trans*-A₂B-substituted corrole via GRYKO.

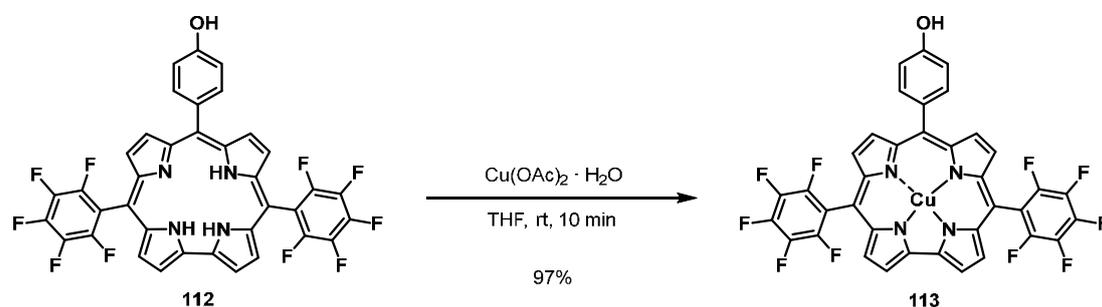
The trichloroacetimidate method needs a glycosyl trichloroacetimidate and a tetrapyrrole (in this case the corrole) with phenolic hydroxyl group and the insertion of a metal to avoid a LEWIS acid/base complex with the free nitrogen of the tetrapyrrole during the glycosylation process. The last two steps had to be accomplished. While the removal of the protecting group with sodium methanolate, analogous to porphyrins, was nearly quantitative (Scheme 32), the insertion of a metal proved to be more problematic.



Scheme 32. Copper-complexation of corrole.

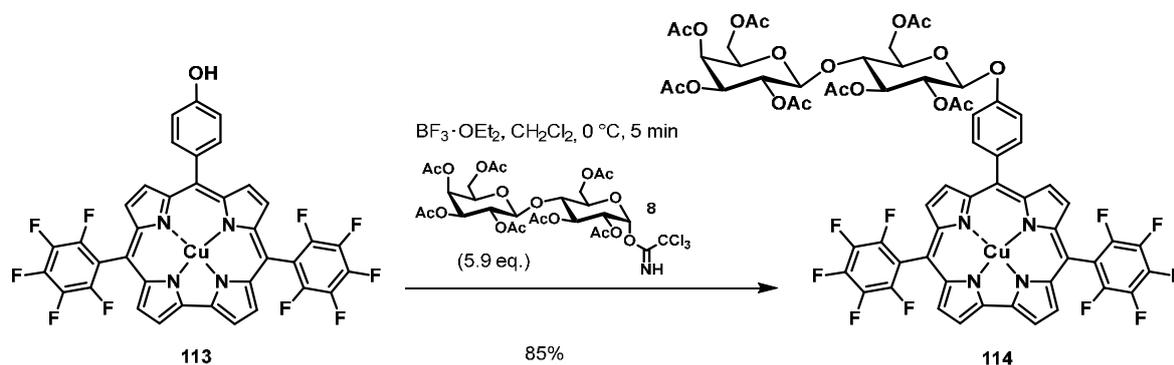
For porphyrins the metal of choice is zinc because it can be easily complexed/removed. Since the synthesis of a corrole-zinc-complex analogous to the porphyrin procedure is not possible (corrole acts as trianionic ligand) we decided to choose copper as an alternative metal.

The complexation with copper acetate worked, as described for similar systems by MAES *et al.*,^[80] almost quantitatively.



Scheme 33. Copper-complexation of corrole.

Now, all tools for the glycosylation with the trichloroacetimidate method were available. Apart from the different metal, the glycosylation conditions for the corrole were identical to those of the porphyrins. The reaction was very fast and the lactosylated copper-corrole could be isolated in 85% yield. Not only the speed of this reaction, but also the high yield was surprising.



Scheme 34. Glycosylation of *trans*-A₂B-substituted corrole.

We thus could show that the developed protocol can also be applied for corrole systems. The example shown is the first disaccharide corrole reported in the literature. In contrast to copper-porphyrins which are paramagnetic, the copper-corrole proved to be diamagnetic which allowed the measurement of this neat NMR spectrum (Figure 52).

First it was suggested that copper-corroles exist as an equilibrium between a diamagnetic Cu(III)-complex and the corresponding Cu(II) radical cation, but in a comparative crystallographic and theoretical study HOLTHAUSEN and co-workers showed that copper-corroles contain a rather well-hidden Cu(II)-ion instead of a Cu(III)-ion and it is suggested that the divalent state is stabilized through a saddling distortion of the corrole ligand.^[17]

RESULTS AND DISCUSSION

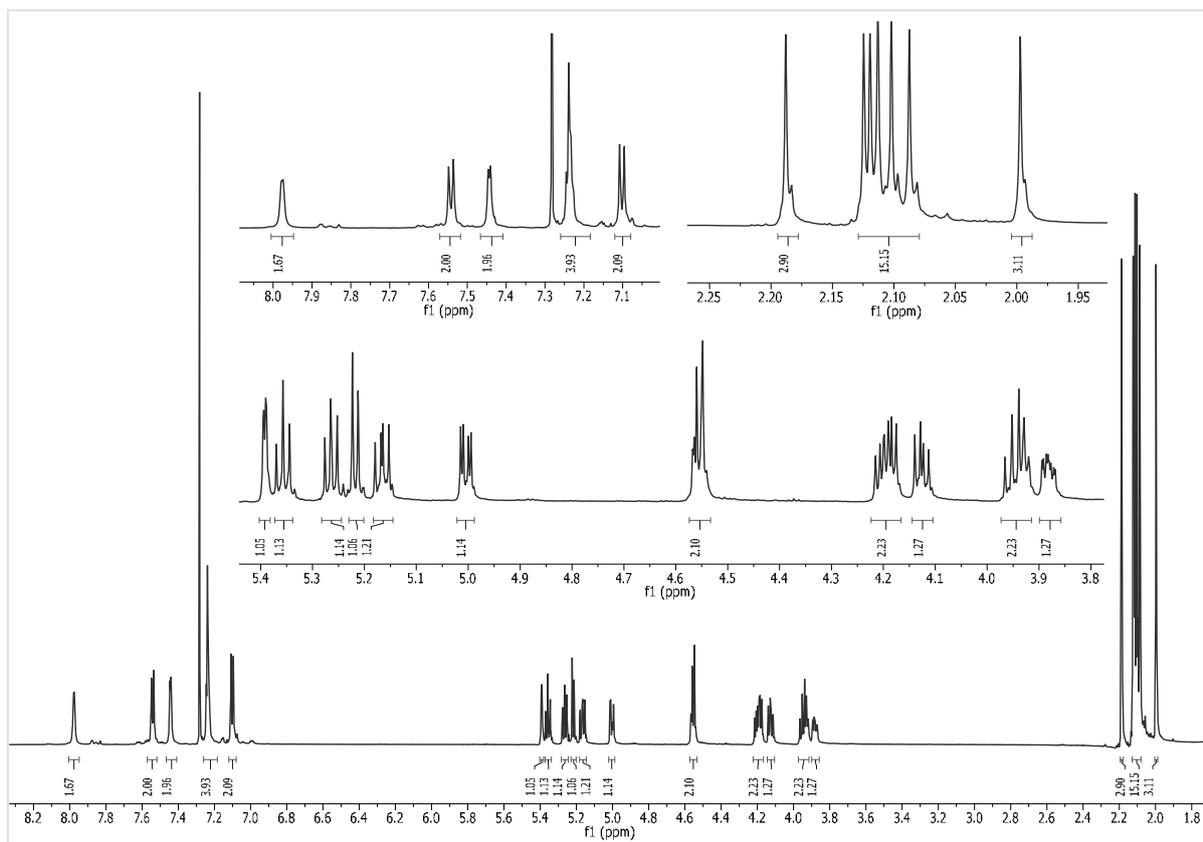
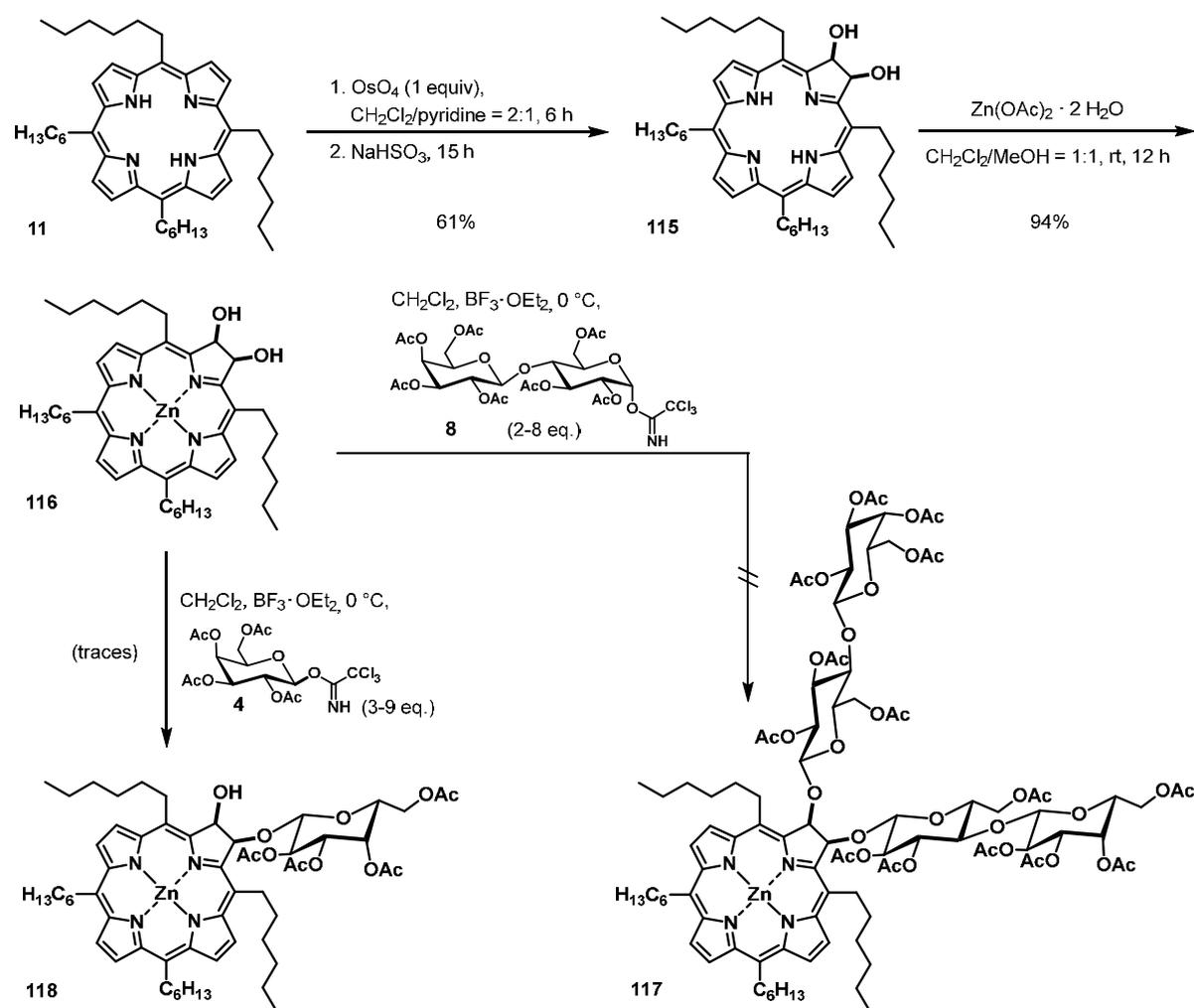


Figure 52. ¹H-NMR spectrum of lactosylated corrole.

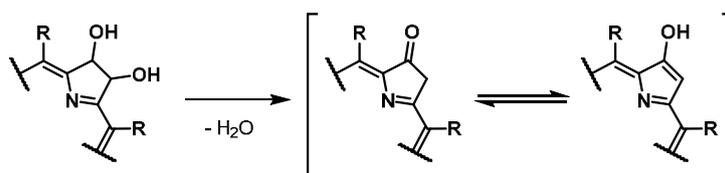
3.2.2 Attempted Glycosylation of a Chlorin

Encouraged by these results, we next tried to apply the trichloroacetimidate method to β -dihydroxychlorins. These tetrapyrrolic systems possess interesting photophysical properties regarding PDT due to their higher absorption coefficient at higher wavelengths (630-700 nm) in comparison to their porphyrin analogues (600-650 nm). As light of higher wavelength can penetrate into deeper parts of the tissue these compounds are highly interesting as photosensitizers (see above discussion in chapter 1.4.2). So theoretically, the introduction of carbohydrates in the oxidized β -position(s) would lead to a promising glyco-chlorin which, on the one hand, possesses improved photophysical properties (bathochromic shift) and, on the other hand, a moiety for a better targeting. Since 5,10,15,20-tetrahexyl-porphyrin **11** was isolated as a side-product in some condensation reactions and it also has flexible alkyl chains which, in contrast to substituted phenyl moieties, may allow an easier access to the β -position(s), we found it a suitable candidate.



Scheme 35. Lactosylation and galactosylation attempts for A₄-chlorins.

In the first step, this A₄-porphyrin was oxidized with the help of osmium tetroxide in a mixture of dichloromethane/pyridine = 2:1 following the protocol of BRÜCKNER and co-workers.^[81a,81b] After this *cis*-dihydroxylation of the porphyrin (61% yield) and subsequent metallation with zinc, the conjugate was ready for the reaction with the corresponding glycosyl trichloroacetimidate. Unfortunately, neither the full-glycosylation attempts with lactosyl nor with galactosyl trichloroacetimidate were successful. Only traces of mono-galactosylated chlorin 118 could be found in the mass spectrum. Reasons for this outcome could be the different positions of the hydroxyl groups: in comparison to the aryl hydroxyl groups of the various porphyrins or the corrole which mainly reacted without bigger complications with the corresponding trichloroacetimidate, here the hydroxyl groups are aliphatic. Nevertheless, the outcome should not be so different. Maybe the *n*-hexyl groups of chlorin 116 block the hydroxyl groups which then cannot react with the carbohydrate(s). Another possible reason could be a water elimination from the vicinal hydroxyl unit resulting in the formation of a ketone moiety (keto-enol tautomerism). The formed water could then deactivate the catalyst (boron trifluoride) making a glycosylation impossible.

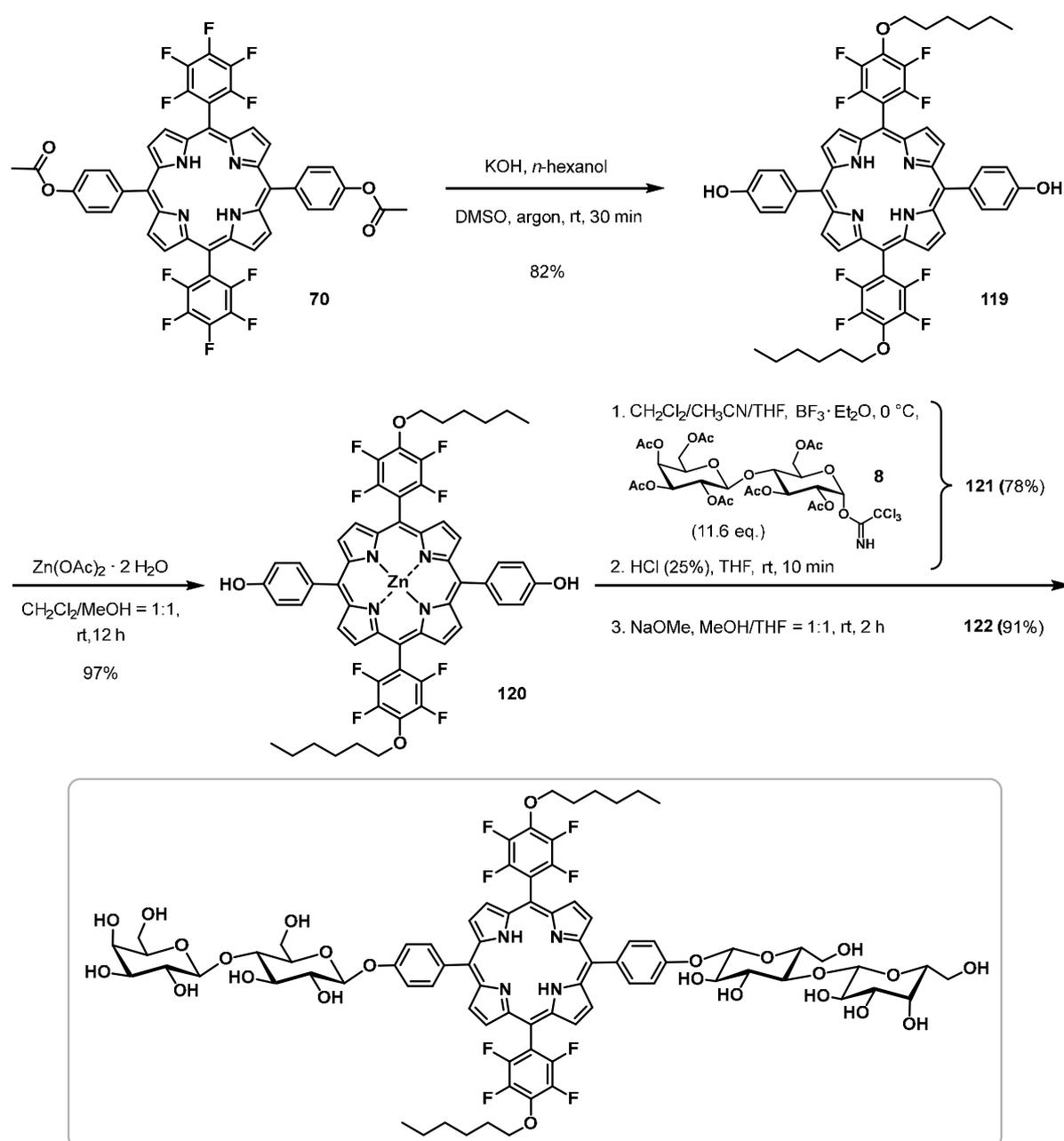


Scheme 36. Loss of hydroxyl group by dehydration and formation of ketone/enol.

But surprisingly, dehydration and rearrangement only take place under harsh conditions using concentrated sulfuric acid^[81c,81d] or perchloric acid^[81a] in boiling benzene. This is unexpected since the molecule could reconstitute its porphyrin resonance structure as the enolic tautomer (fully conjugated) *via* water elimination (Scheme 36).

3.2.3 Combinations with Nucleophilic Aromatic Substitution Reactions

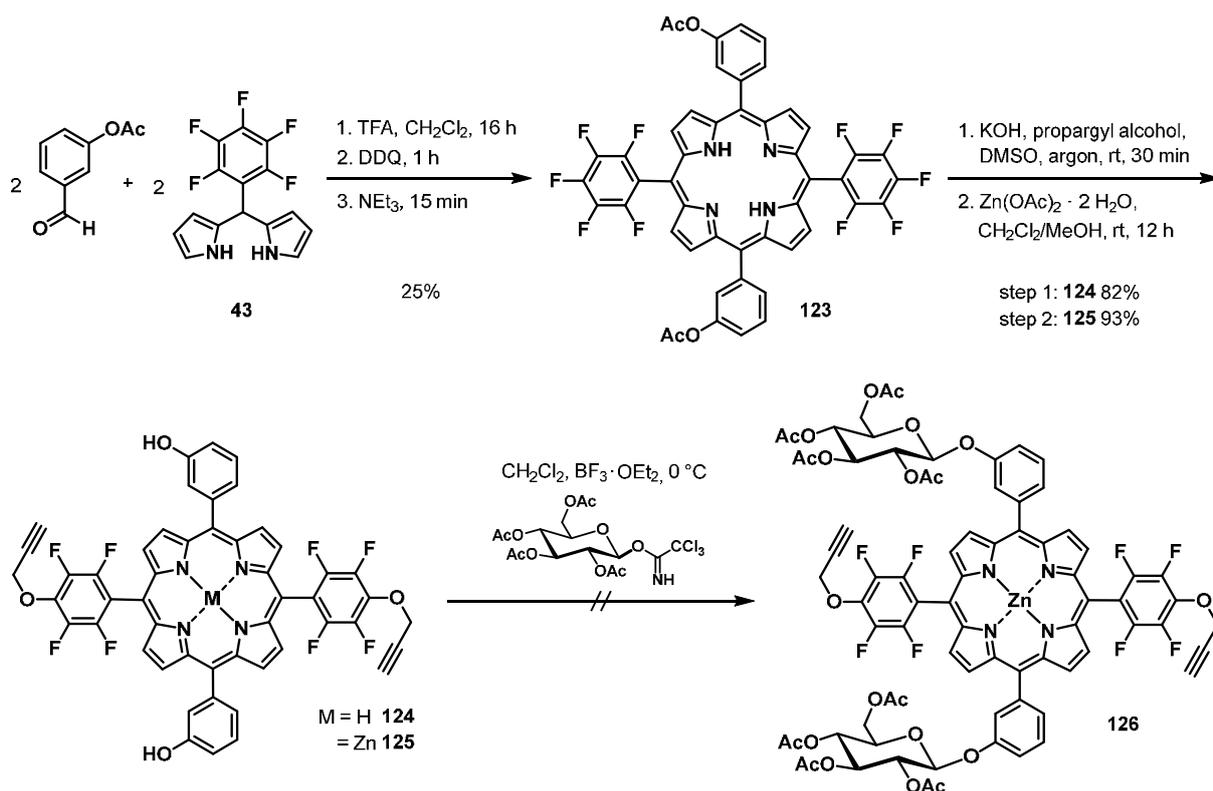
We also tried to combine the developed and tested trichloroacetimidate method with another known method from literature, the high-yielding regioselective nucleophilic aromatic substitution (S_NAr) reaction of alcoholates with pentafluorophenyl units.^[76] Therefore, the protected *trans*-A₂B₂-porphyrin was reacted first with an excess of *in situ* generated *n*-hexanolate. On the one hand, this led to the deacetylation of the alcohols and, on the other hand, to the regioselective substitution in the *para*-position yielding 82% of the desired diether. After zinc-complexation the carbohydrate moiety could be installed in good yield.



Scheme 37. Combination of S_NAr reaction with the trichloroacetimidate method.

This combination allowed the access of a quite nice glyco-substituted *trans*-porphyrin bearing two opposite polar lactosyl rests and two opposite unpolar *n*-hexyl groups. During the last years, this type of amphiphilic structure motif turned-out to be promising for photosensitizers regarding PDT.^[62] It should be stated that, due to its amphiphilic structure, the solubility of the final compound in polar as well as unpolar solvents and mixtures thereof was difficult and led to problems during the purification process. Because of this problem, the crude product was purified by washing with dichloromethane and THF.

Also the combination of the trichloroacetimidate method with the installation of an alkyne moiety seems to be interesting due to a possible further modifications using Cu(I)-catalyzed 1,3-dipolar “click” or SONOGASHIRA reactions. Therefore, the protected *trans*-A₂B₂-porphyrin was reacted first with an excess of *in situ* generated propargyl alcoholate. On the one hand, this led to the deacetylation of the alcohols and, on the other hand, to the regioselective substitution in the *para*-position yielding 82% of the desired diether **124**. While the zinc-complexation was successful (93% yield), the subsequent glycosylation of **125** failed.

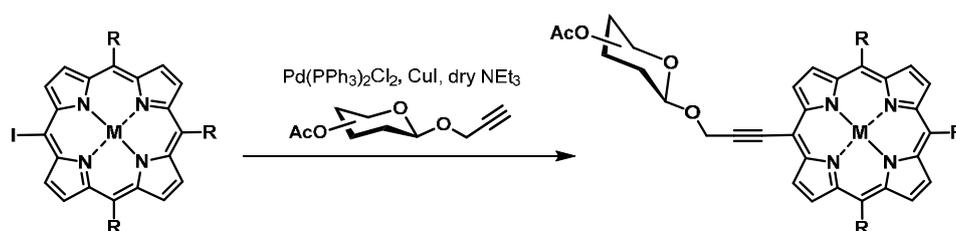


Scheme 38. Failed combination of S_NAr reaction with trichloroacetimidate method.

One possible reason for this unsuccessful glycosylation attempt could be found in a direct reaction of the trichloroacetimidate moiety with the alkyne similar to a reaction described by HII and co-workers.^[82] So in this case it would be a better strategy to do modifications at the alkyne moiety, e.g. “click” chemistry, before the carbohydrate moieties are connected to the porphyrin.

3.3 Synthesis of Glyco-Porphyrins *via* Pd-Catalyzed Cross-Coupling (SONOGASHIRA)

The developed protocol for the synthesis of glyco-substituted porphyrins, using an iodide-containing porphyrin and an alkyne-containing carbohydrate in a SONOGASHIRA reaction, was already started during the master thesis.^[66]

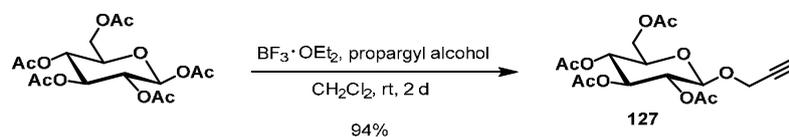


Scheme 39. Developed protocol for the synthesis of glyco-substituted porphyrins *via* SONOGASHIRA reaction.

This cross-coupling has two advantages: on the one hand, a moiety for a better (tumor) targeting is introduced and, on the other hand, the triple bond directly connected to the tetrapyrrole leads to a bathochromic shift of the Q-bands. This bathochromic shift as explained above is favorable for the treatment of tumors in deeper tissues with PDT.

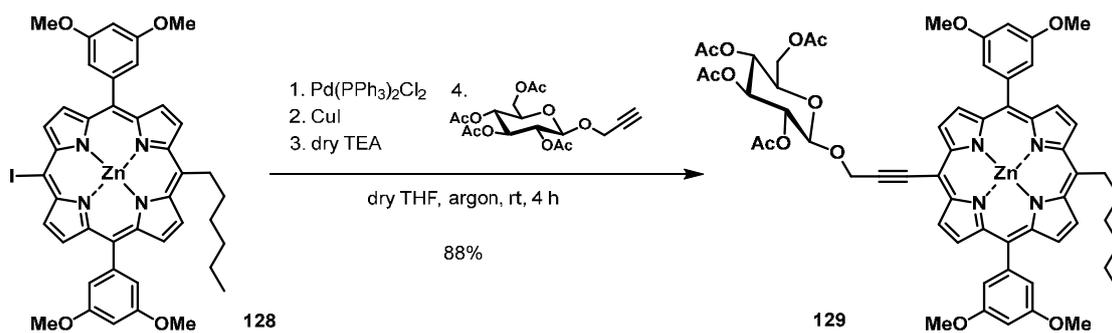
3.3.1 Monoglycosylations

The first building block for this SONOGASHIRA reaction, an alkyne-containing carbohydrate, was synthesized following a known protocol.^[83] To this end peracetylated β -D-glucose was reacted with boron trifluoride diethyl etherate and propargyl alcohol yielding 94% of the β -anomer. The product did not need an extensive purification and could be synthesized in a gram-scale.



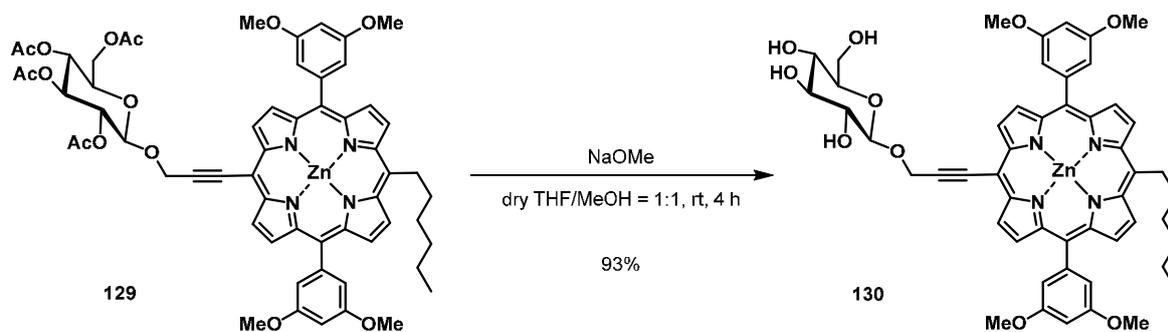
Scheme 40. Synthesis of glycosyl alkyne.

To connect the porphyrin with a carbohydrate *via* SONOGASHIRA reaction for the first time, monoiodinated porphyrin **128**, the second building block for this SONOGASHIRA reaction and provided by biolitec research GmbH, was dissolved in dry THF and the palladium catalyst, copper iodide, dry triethyl amine and finally the glucosyl alkyne were added under an argon atmosphere. Glyco-porphyrin **129** was obtained in a very good yield of 88%. The product is a green-violet solid.



Scheme 41. First synthesis of glyco-porphyrin *via* Pd-catalyzed cross-coupling (SONOGASHIRA reaction).

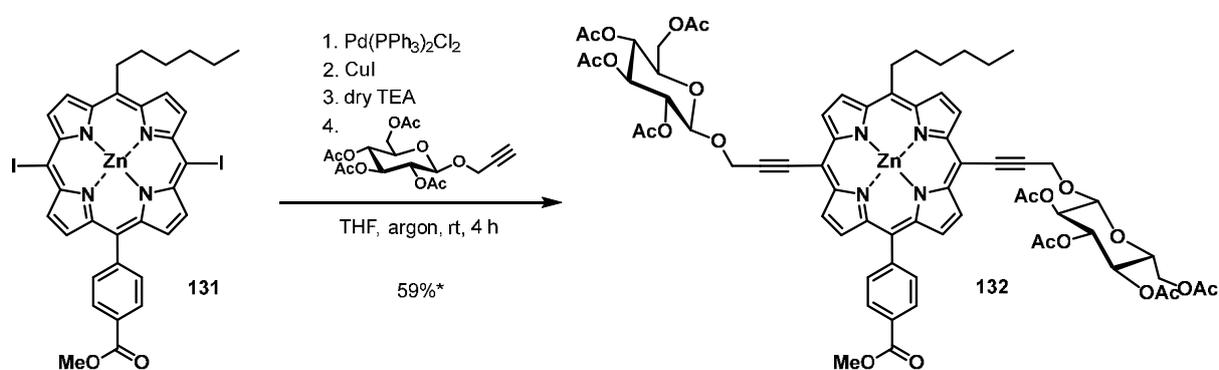
The subsequent deacetylation with sodium methanolate in methanol/THF = 1:1 delivered the deprotected glyco-porphyrin in a yield of 93%. It should be noted that impurities were found which could not be separated.



Scheme 42. Deprotection of glycosylated porphyrin 129.

3.3.2 Diglycosylations Attempts and Resulting Problems

Motivated by the straightforward synthesis of the monoglycosylated porphyrin, the developed protocol was attempted using diiodinated porphyrin **131**, provided by biolitec research GmbH, as the substrate. Unfortunately, this coupling turned out to be more difficult than expected. Basically, the SONOGASHIRA reaction worked, but led to a moderate yield and a highly impure product (green solid) which could not be purified after several successive column chromatographies. This diglycosylation was repeated under different reaction conditions: variation of parameters like reaction time (up to 2 d stirring), amount of alkyne (up to 30 equivalents) and temperature (up to 50 °C) were examined. The outcome was similar and unfortunately the unknown impurities were formed in each reaction. The ¹H-NMR spectrum indicates that the impurities also possess a porphyrin backbone.



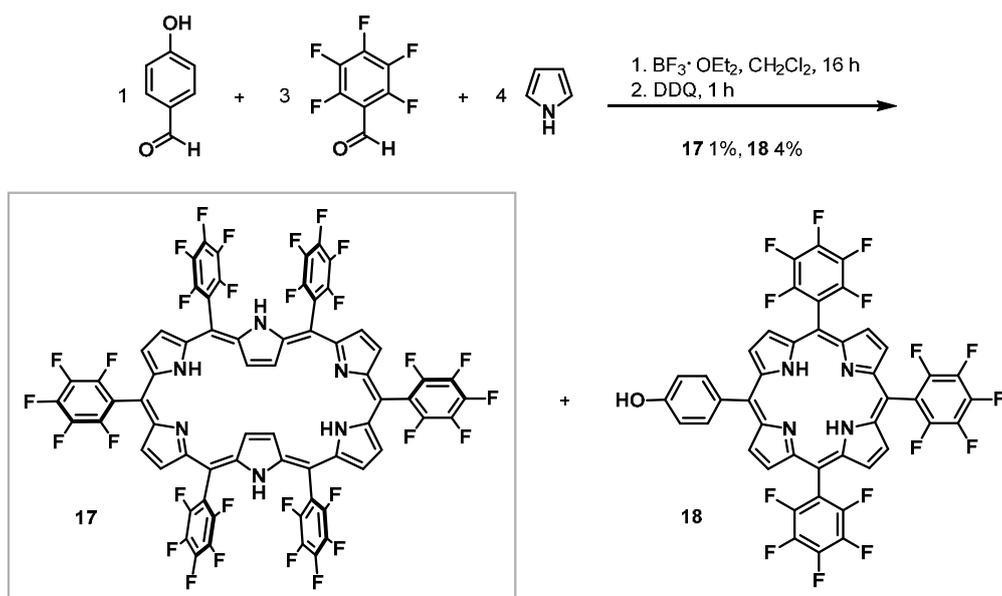
Scheme 43. Diglycosylations attempts *via* Pd-catalyzed cross-coupling (SONOGASHIRA reaction).

An explanation for the unsatisfying results of the diglycosylation experiments, in contrast to the unproblematic monoglycosylation, may be found in the direct connection of the porphyrin backbone with the triple bond. Since one direct alkyne moiety is already increasing the electron density in the system, the installation of a second electron donating alkyne moiety could be too much.

3.4 Synthesis of Glyco-Porphyrinoids Using Glycosyl Thiolates

In this chapter the utilization of carbohydrate thiolates for facile, high-yielding regioselective nucleophilic substitution reactions with challenging pentafluorophenyl-substituted porphyrinoids is reported. The obtained novel glyco-porphyrinoids with their specific photophysical properties and extraordinary structures can serve as platforms for possible new applications in biomedicine, catalysis, coordination or redox chemistry. This work represents the first thiolation of the mentioned pyrrole-containing macrocycles and therefore can serve as a model for the synthesis of further customized sulfur-linked conjugates thereof.

As described in the previous chapter on the trichloroacetimidate method, during the condensation reaction of a pentafluorophenyl-substituted porphyrin the unexpected formation of a [28]hexaphyrin was observed (Scheme 44).



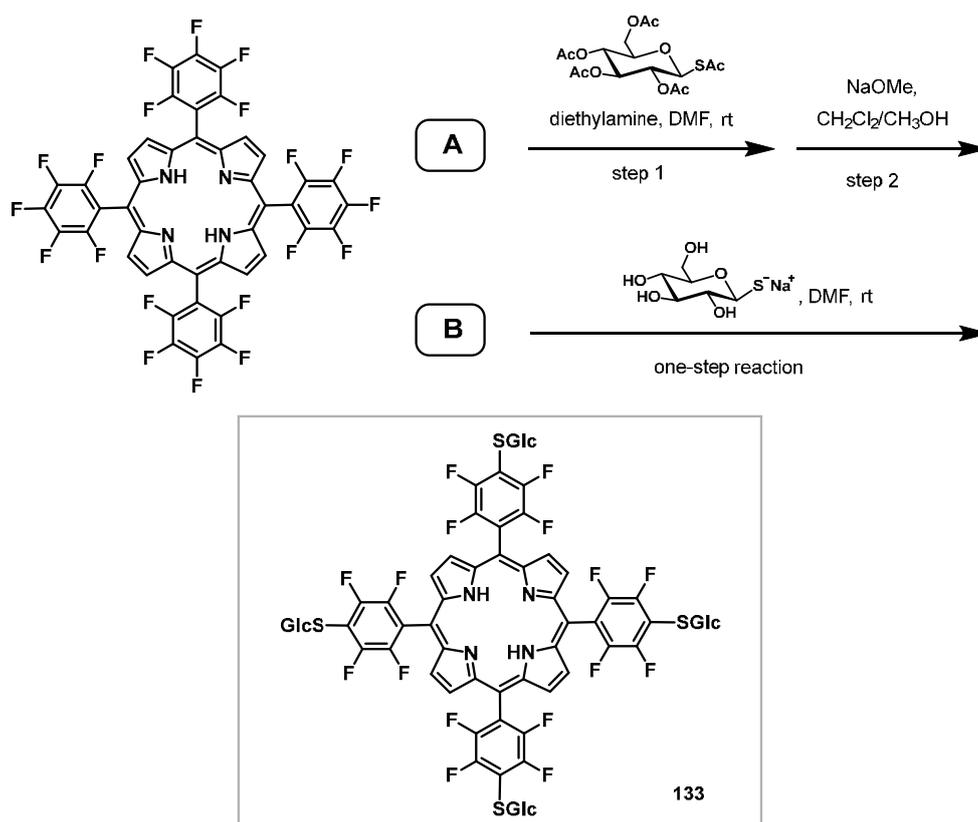
Scheme 44. Unexpected formation of PFP-substituted [28]hexaphyrin.

While the trichloroacetimidate method was successfully used for the synthesis of various glyco-substituted porphyrins and a corrole, it was also clear that this method would not be suitable for hexaphyrins. Also the protocol developed for monoglycosylations *via* SONOGASHIRA reactions failed for multiple glycosylations and was therefore no alternative. Therefore, the idea was born to develop a protocol for synthesizing glyco-substituted hexaphyrins and other interesting porphyrinoids like corroles, calix[4]-, calix[6]phyrins and the precursor dipyrromethane for the first time in order to be able to evaluate their photophysical and chemical properties. To this end, the first step was to search for an established, straightforward and metal-free glycosylation method which could match the different porphyrinoid systems. The focus on a metal-free process was based on expected problems of complexation of the metal and/or potential problems during the deprotection/demetallation step of

the final glyco-conjugate. So basically, the Cu(I)-catalyzed 1,3-dipolar “click” reaction or multi-step reactions were not suitable here.

Our hexaphyrin side product – as most published hexaphyrins – possesses pentafluorophenyl substituents. Such substituents are known to result in a higher probability of formation of the unusual macrocycle and a higher product stability.^[29] Analyzing the exotic structure of hexaphyrins, there are only two reasonable positions for a glycosylation: either a multi-step glycosylation at the β -position(s) or the direct glycosylation at the *para*-position(s) of the pentafluorophenyl substituents. A simple and yet effective protocol reported by DRAIN and co-workers describes the thioglycosylation of tetrakis(pentafluorophenyl)porphyrins^[47i] and -chlorins^[47f] with a fully unprotected glycosyl thiolate in DMF. These results served as a starting point for our investigations.

To get familiar with this method, we investigated the thioglycosylation of an A₄-porphyrin (Scheme 45). It should be noted that there were two different thioglycosylations reported, one with the acetoxy-protected carbohydrate and another one with an unprotected carbohydrate.



Scheme 45. Synthetic routes A and B to thioglycosylated A₄-porphyrins according to DRAIN.^[47i]

We chose the protocol using unprotected carbohydrates (synthetic route B) in order to avoid further deprotection steps. This procedure seemed particularly adequate as hexaphyrins in general possess some unusual properties which will be discussed in detail in this chapter. The repetition of the reaction according to DRAIN *et al.* did not result in the published 92% yield for tetra-thioglycosylated porphyrin 133, probably due to the formation of another more polar product, e.g. a penta-

thioglycosylated porphyrin. After another precise repetition of the DRAIN procedure with a similar outcome, the reported ratio of equivalents was adjusted (thiolate/PFP-unit from 2:1 to 1.2:1) in the course of various reactions. The final almost equimolar use of the reaction components led to a similar outcome as that reported by DRAIN and co-workers (82% yield for tetra-thioglycosylated porphyrin **133**), minimizing the formation of side products. With this change and inert reaction conditions (heated reaction flask, dry solvent and argon atmosphere) we had a powerful, highly precise tool which allowed for a controlled nucleophilic attack of the hexaphyrin system. It has to be noted that a clean reaction is the prerequisite to isolate pure products as separation from side products is generally difficult with this class of compounds.

As a second building block, it was necessary to install PFP-substituents in all porphyrinoid systems. Literature procedures were found for each of these, including corroles,^[21] calix[4]-, calix[6]phyrins,^[27] [26]hexaphyrins^[35,36a,37b] and the precursor dipyrromethane.^[84] All of these classes with pentafluorophenyl substituents have the advantage of higher stability as opposed to their differently substituted analogues. The electron-withdrawing PFP-substituents lead to quite stable corroles, dipyrromethanes, hexaphyrins and calix[*n*]phyrins (with bridging *meso*-CH moieties).

3.4.1 Dipyrromethanes

The respective dipyrromethane was synthesized according to a known protocol, described above. We started, according to the slightly adapted protocol (ratio of thiolate/PFP-unit = 1.2:1) with the mono-thioglycosylation of this potential porphyrinoid precursor. In several test reactions, we found out that the reaction time had to be reduced from 12 hours to 30 min to finally obtain the product in 72% yield (Table 13). At prolonged reaction times, we observed the formation of multiple, unidentifiable side-products with similar polarities like the product which made a separation very difficult.

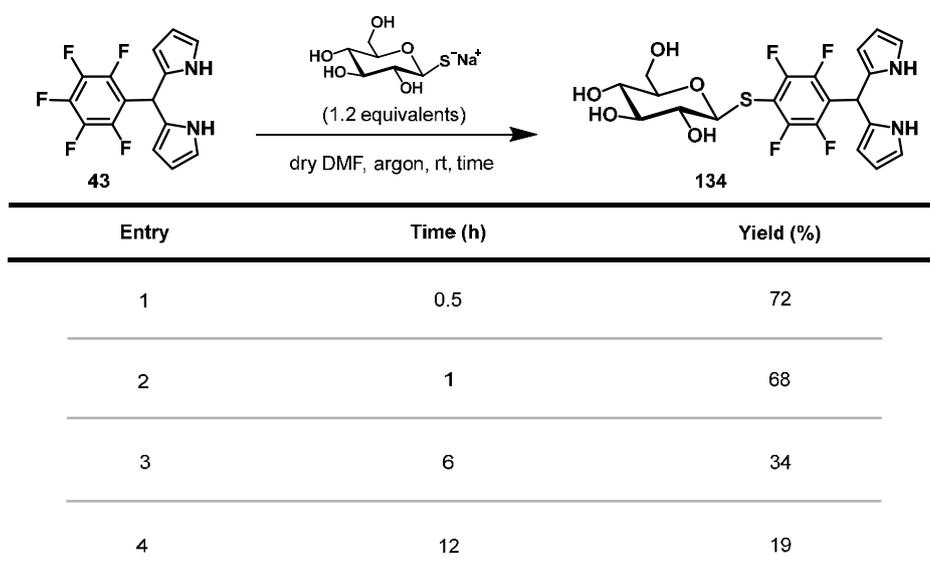
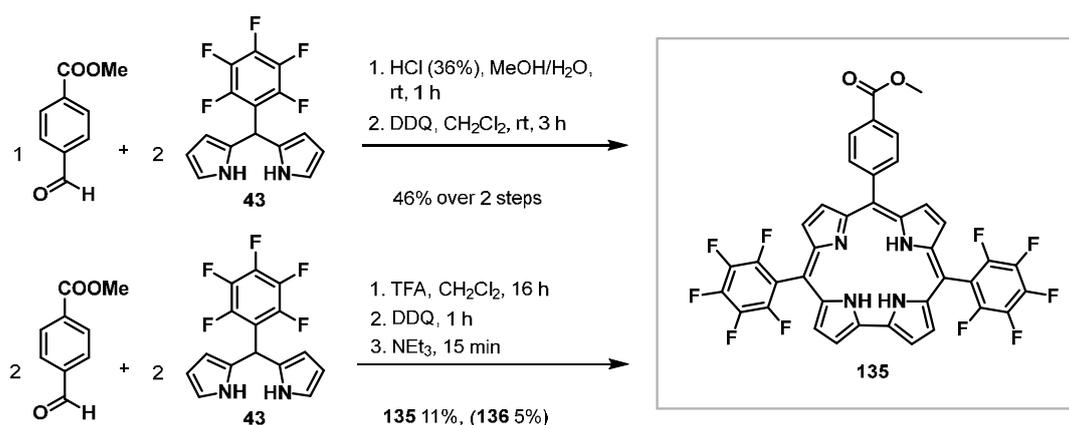


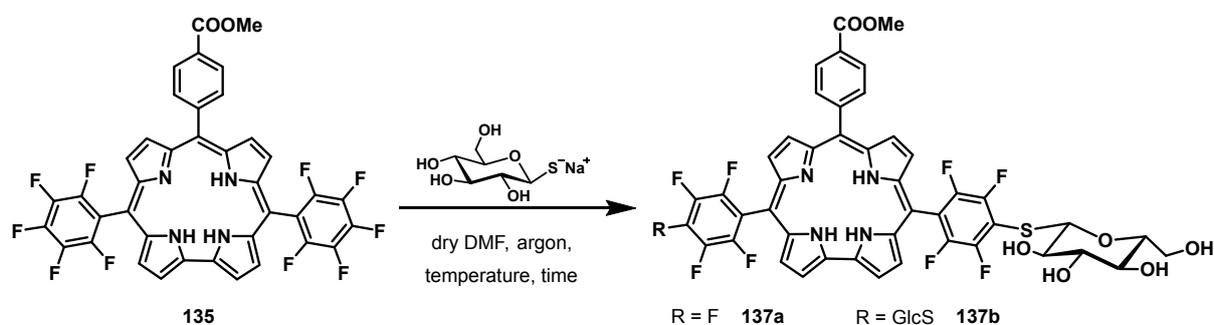
Table 13. Thioglycosylation of dipyrromethane showing the dependence of yield on reaction time.

3.4.2 A₂B- and A₃-Corroles

With this improved protocol in hand, we tried to thioglycosylate another tetrapyrrole for the first time: an A₂B-corrole **135** (Scheme 46). The corrole was synthesized, on the one hand, in a standard condensation reaction in dichloromethane (side product: corresponding *trans*-A₂B₂-porphyrin **136**) and, on the other hand, in a reaction following GRYKO. Again, the method of GRYKO proved to be superior with respect to reproducibility.



Scheme 46. Synthesis of *trans*-A₂B-substituted corrole *via* standard condensation and according to GRYKO.

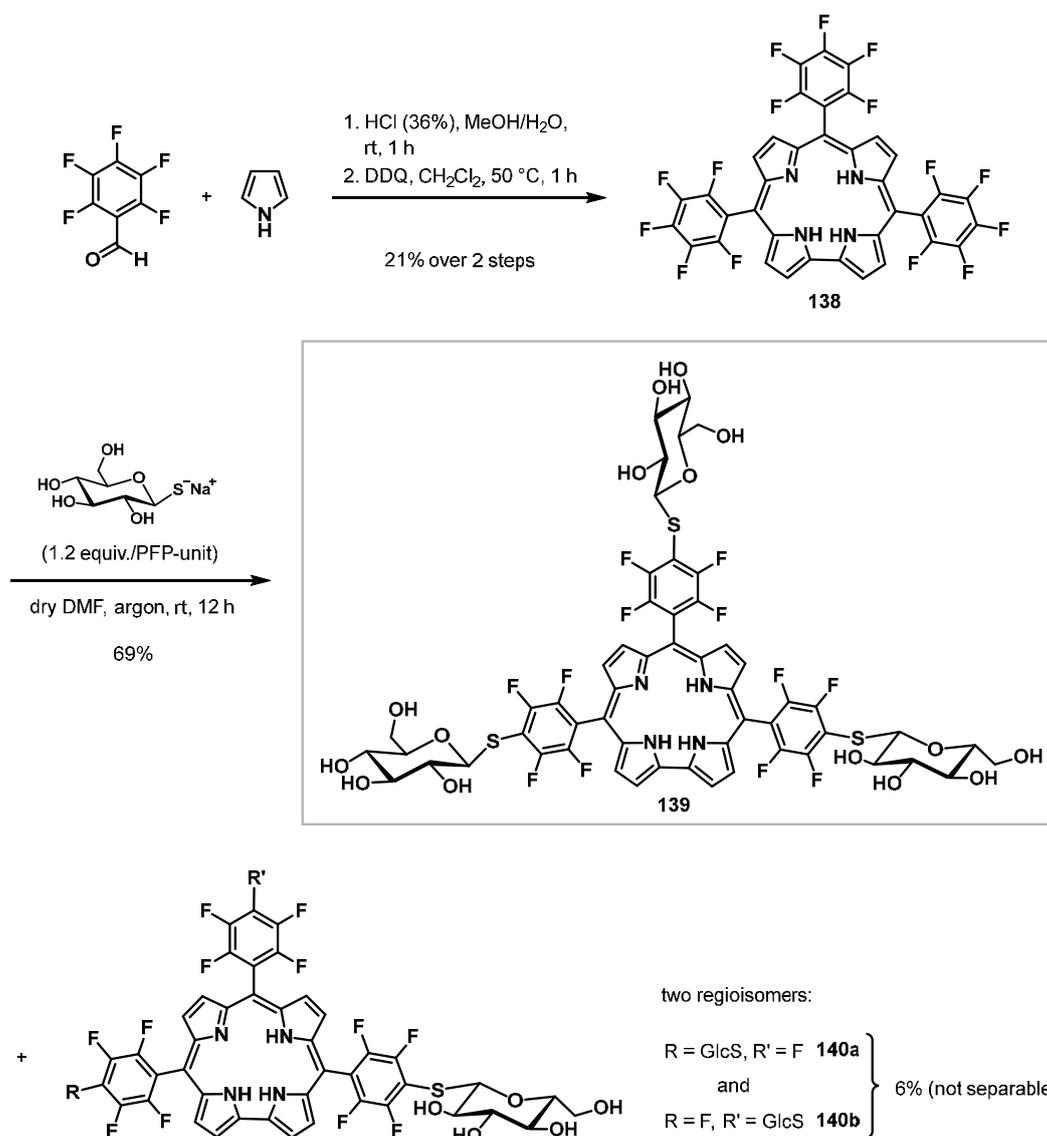


Entry	Equivalents	T (°C)	Time (h)	Yield (%) [*]
1	2.4	rt	1	44 / 37
2	2.4	rt	12	16 / 69
3	3.2	rt	12	14 / 73
4	4.2	rt	12	14 / 71
5	4.2	50	12-24	12 / 64

Table 14. Thioglycosylation of corrole **135** (* ratio of mono- and diglycosylated corroles **137a**/**137b**).

For the glycosylation of corrole **135**, in contrast to dipyrromethane **43**, longer reaction times were beneficial for the reaction, but as opposed to the substitution of a porphyrin, it was not possible to fully glycosylate the corrole. Even with an excess amounts of thiolate (thiolate/PFP-unit = 4.8:1), heating at temperatures of 50 °C and longer reaction times (24 h) no full conversion could be achieved. The bis-thioglycosylated corrole **137b** was isolated in an optimized yield of 73% and, as a side-product, mono-thioglycosylated corrole **137a** was isolated in 14% yield. Still these yields are superior in comparison to another method reported previously.^[85]

We next tried to thioglycosylate an A₃-corrole using the optimized reaction conditions (Scheme 47). Again, this corrole was synthesized according to the procedure of GRYKO. The desired product **139** was isolated in a yield of 69%. The bis-thioglycosylated corrole was obtained as a mixture of the two regioisomers **140a** and **140b** (6% yield) which could not be separated due to their very similar chromatographic properties.

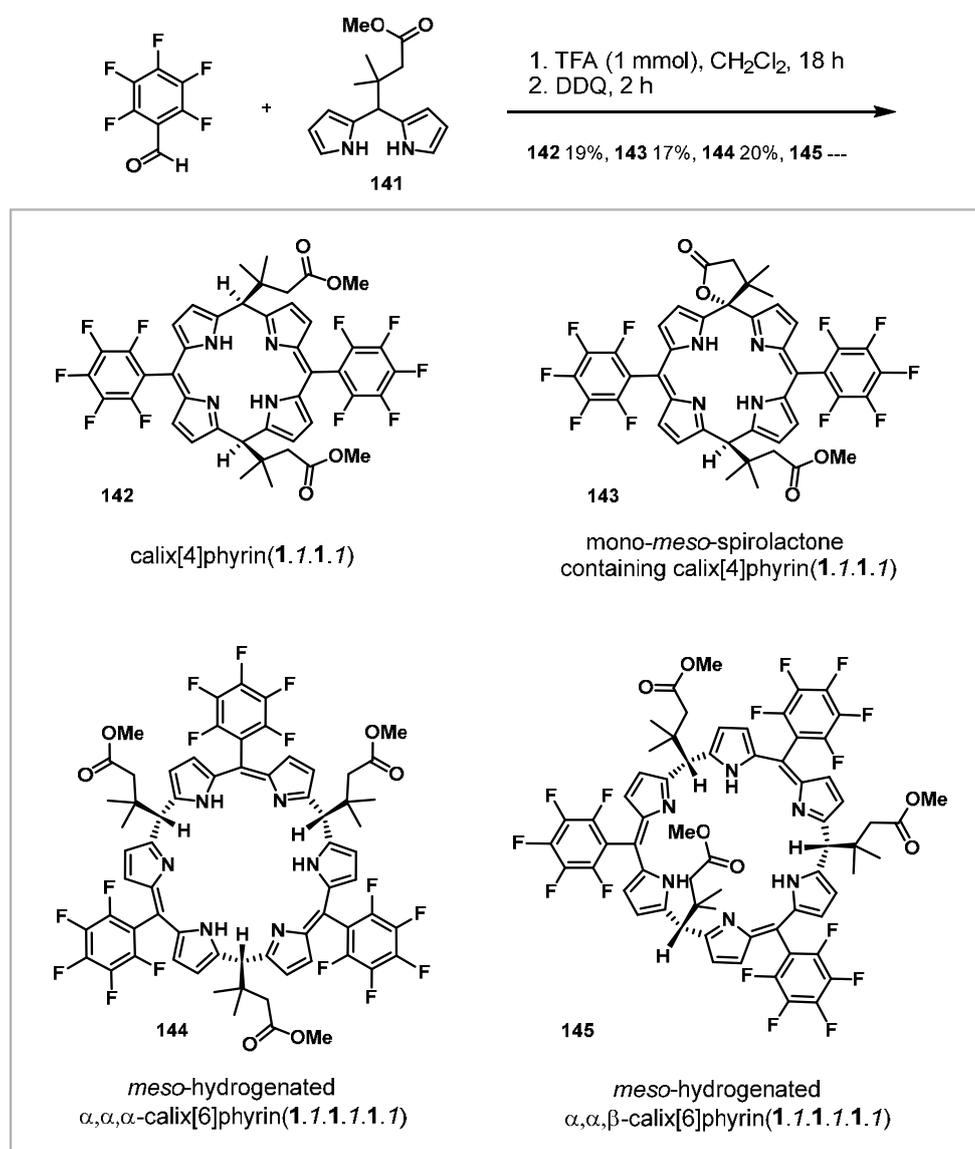


Scheme 47. Synthesis of an A₃-substituted corrole *via* GRYKO.

3.4.3 Calix[*n*]phyrin Systems

The next class of compounds were PFP-substituted calix[*n*]phyrins which were first synthesized in 2013 by REISSIG, WIEHE and co-workers.^[27a] Basically, this synthesis is similar to the standard condensation reaction of porphyrins reported by LINDSEY, except that the use of a sterically congested dipyrromethane and a higher concentration of starting materials (dipyrromethane and aldehyde) is needed. Dipyrromethane **141** was provided by biolitec research GmbH.

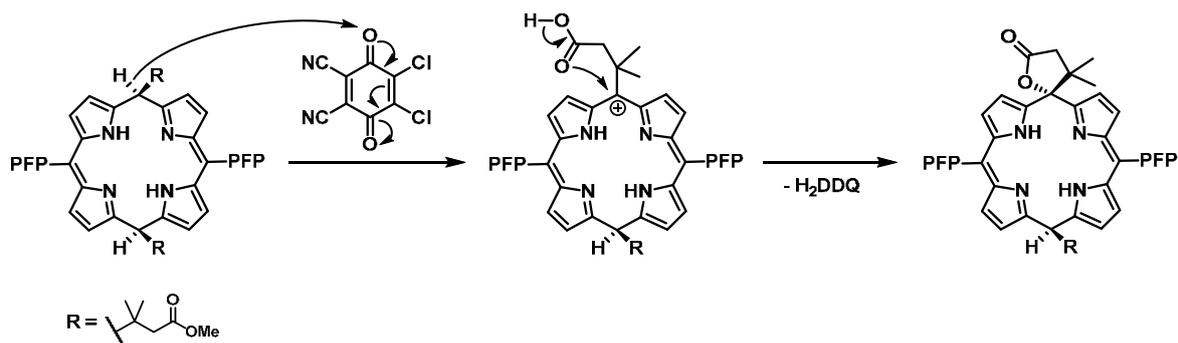
It should be noted that the choice of acid (TFA, boron trifluoride diethyl etherate, *p*-TSA, Sc(OTf)₃ or PPA) and acid loading determines the ratio of the formed calix[*n*]phyrins. Based on the bad separation of the α,α,α - and α,α,β -calix[6]phyrins, we chose TFA (100 mol-%) where the authors did not observe the formation of the α,α,β species **145**. The reaction worked as reported with similar ratios and yields (Scheme 48).



Scheme 48. Synthesis of calix[*n*]phyrin macrocycles using sterically congested dipyrromethane.

Due to the steric hindrance of the dipyrromethane building blocks in the porphyrinogen (resp. hexaphyrinogen), the oxidation with DDQ is only possible at the position of the PFP-aldehyde building blocks, leading to these interesting non-aromatic, yellow-orange (calix[4]phyrins) to orange-red (calix[6]phyrin) structures.

The formation of mono-*meso*-spirolactone containing calix[4]phyrin is described in the proposed mechanistic considerations (Scheme 49).



Scheme 49. Proposed mechanism for TFA/DDQ mediated formation of mono-*meso*-spirolactone containing calix[4]phyrin(1.1.1.1)s.

After the condensation, the porphyrinogen is formed and usually oxidized with DDQ. However, as a side-reaction, here the *meso*-hydrogen of the porphyrinogen can interact with the oxidizing reagent. Precisely, in a LINSTEAD dehydrogenation there is a hydride shift to DDQ^[86] which results in the formation of a carbenium ion. Due to the presence of TFA and water which are still in the reaction mixture from the condensation reaction, the methoxycarbonyl group is partially hydrolyzed. In molecules with hydrolyzed methoxycarbonyl groups, the neighboring carboxylic acid unit can intramolecularly attack the carbenium ion.

It should be noted that calix[*n*]phyrins, in contrast to porphyrins, possess non-planar structures. For example a calix[4]phyrin has a roof-shaped structure where the two PFP-substituted moieties pointing down while the two ester groups are *syn*-axial and pointing up (Figure 53).

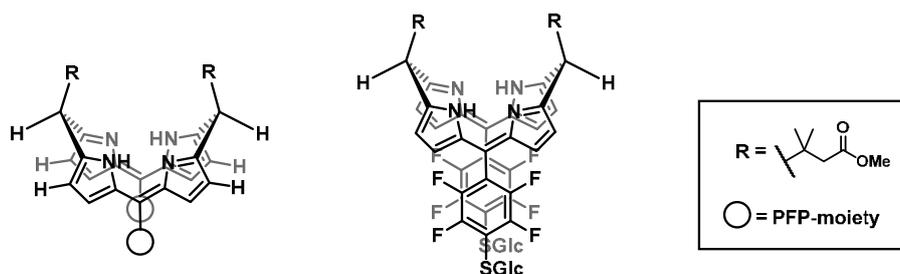


Figure 53. Side-view of calix[4]phyrin for clarification of roof-shaped structure.

First we tried to substitute the roof-shaped calix[4]phyrin **142** and the mono-*meso*-spirolactone containing calix[4]phyrin **143** systems, using a ratio of thiolate/PFP-unit = 1.2:1 and a reaction time of 12 hours. Both thioglyco-conjugates **146** and **147** were obtained in very good yields (85%, resp. 83%) without the formation of undesired products *via* additional attacks at the PFP-unit (Figure 54).

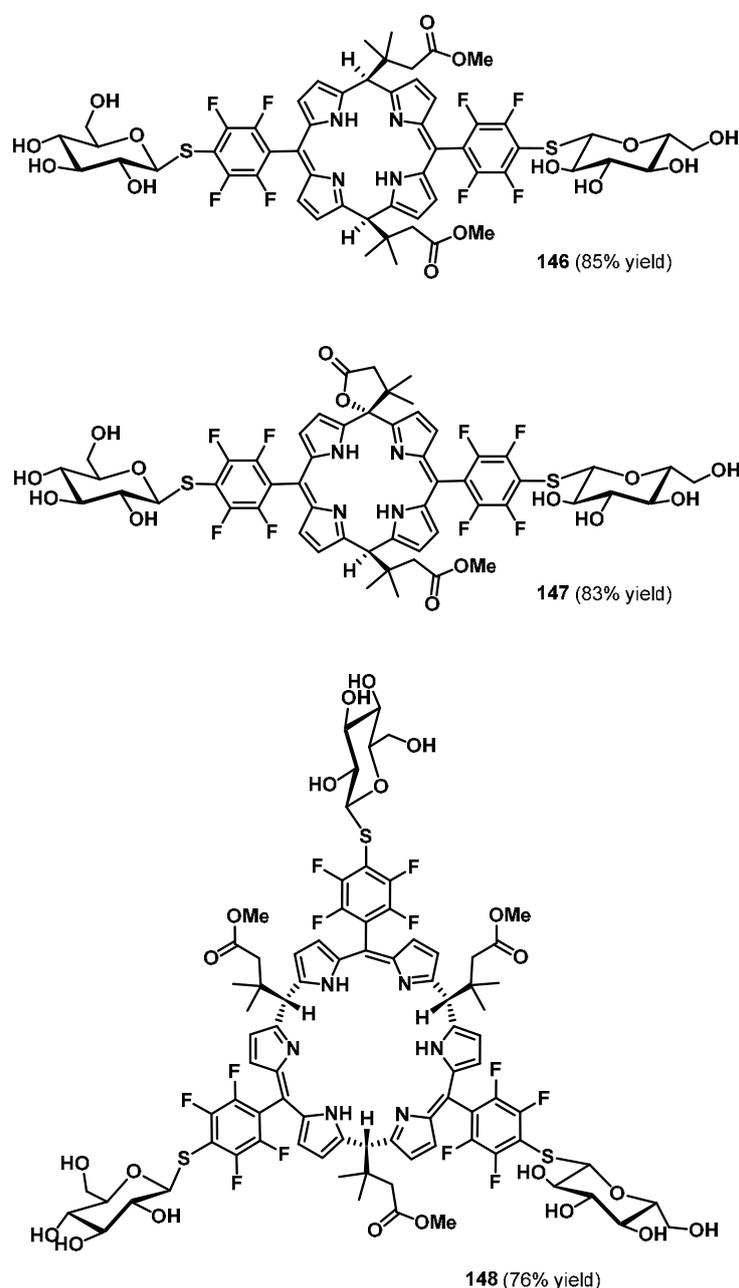


Figure 54. Final yields for the thioglycosylation of the calix[*n*]phyrins under optimized reaction conditions: GlcSNa (1.2 equiv./PFP-unit), dry DMF, argon, room temperature and 1 h reaction time.

A stepwise reduction of the reaction time already showed a full conversion after one hour. Then, with this knowledge in mind, we thioglycosylated the most unusual calix[*n*]phyrin: the relatively unexplored calix[6]phyrin **144**. Using the same nucleophilic substitution reaction conditions, we obtained the thioglycosylated calix[6]phyrin **148** in 76% yield. It should be noted, that all three

calix[*n*]phyrins could be thioglycosylated in a straightforward fashion by using the same “standard” reaction conditions. Only the purification *via* reverse phase column chromatography was tricky, due to a strong tailing effect of these compounds. The successful thioglycosylation of these challenging PFP-substituted macrocycles can be easily seen in a ^{19}F -NMR spectrum (Figure 55). The substitution in *para*-position can clearly be seen by the disappearance of the respective *para*-fluorine signal.

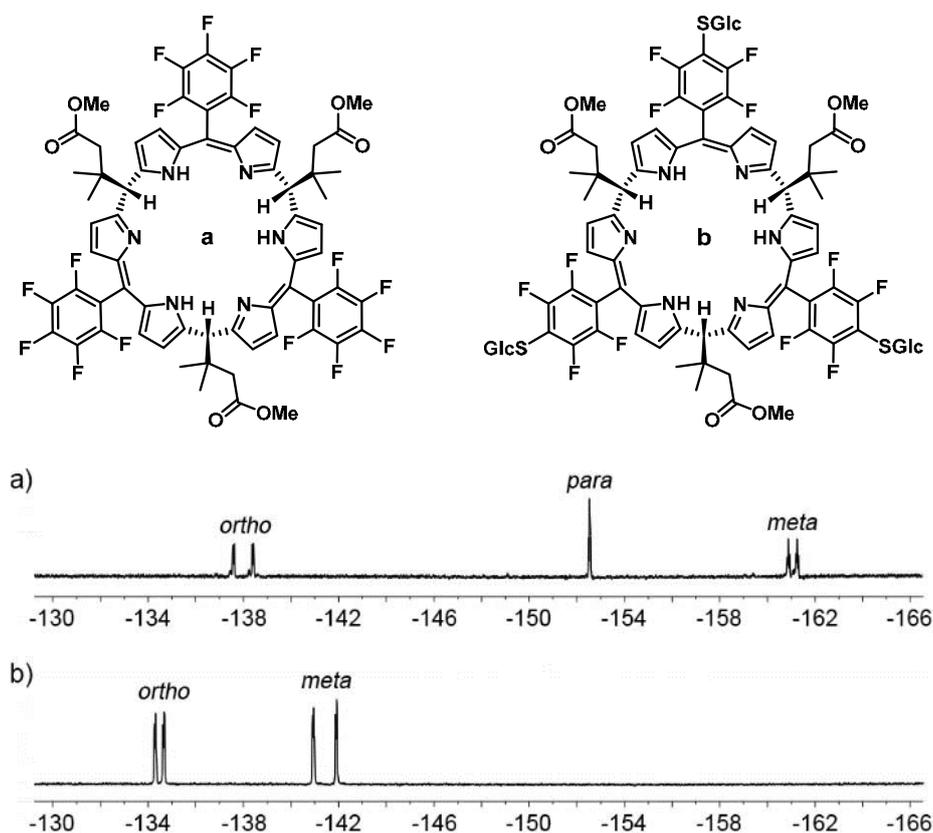
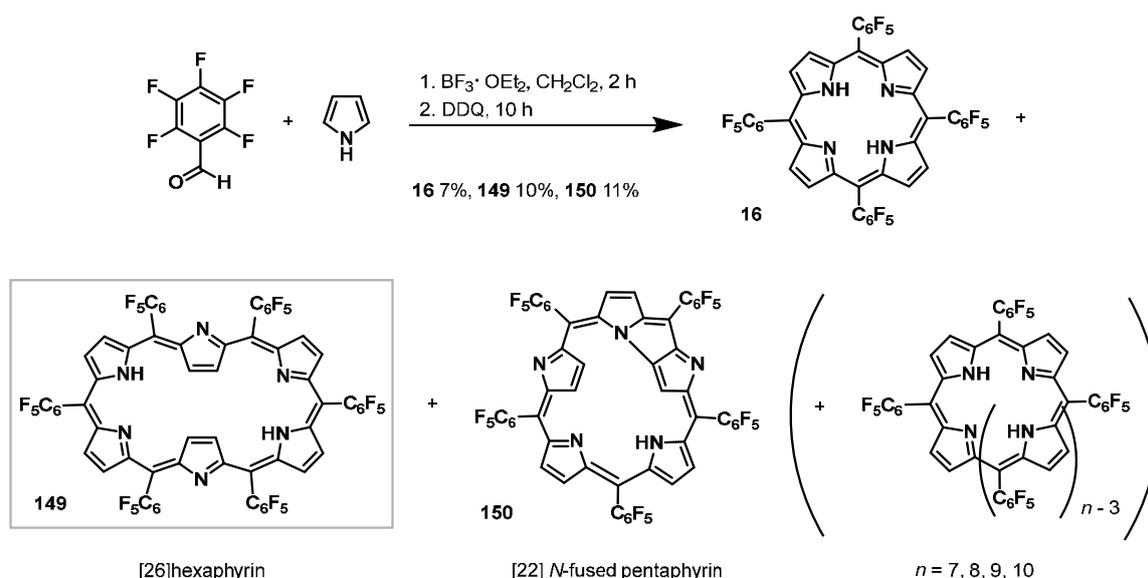


Figure 55. ^{19}F -NMR spectra comparison between unsubstituted (a) and substituted calix[6]phyrin (b) in *para*-position.

With all experiences gained in the thioglycosylation of porphyrins, dipyrromethane, corroles, calix[4]phyrins and calix[6]phyrins, the next challenge was the utilization of this thioglycosylation protocol for the class of expanded aromatic porphyrins.

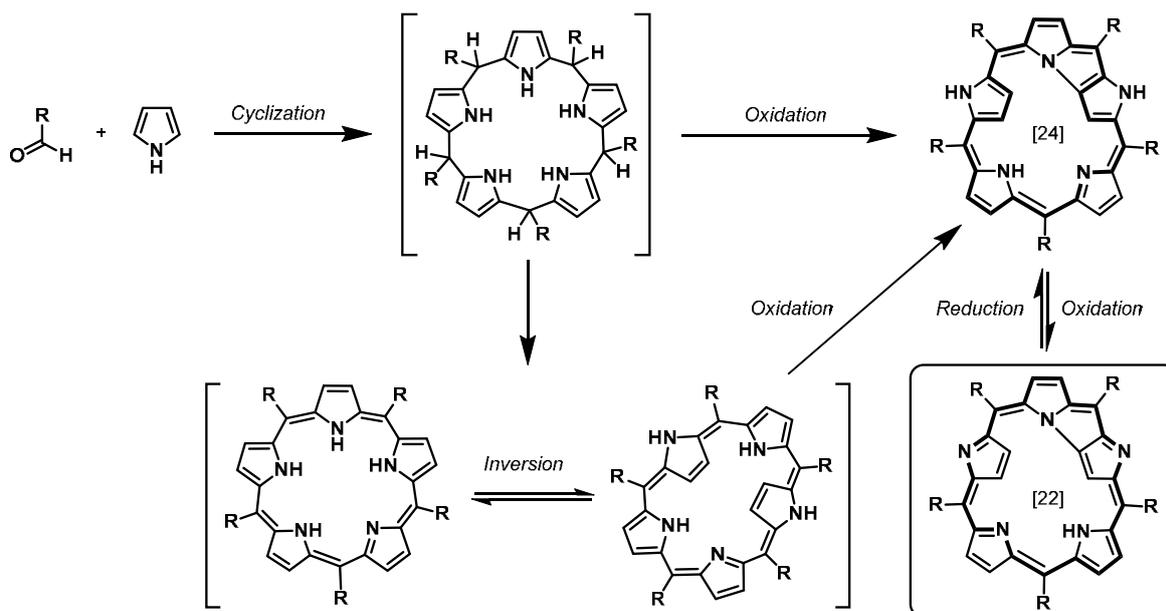
3.4.4 Oxidized and Reduced Hexaphyrins

Due to the small amounts of hexaphyrins obtained as a side-product during a standard condensation following the LINDSEY procedure, we searched for more efficient protocols to hexaphyrins in order to obtain sufficient starting material for the subsequent thioglycosylation attempts. First, we applied a protocol by OSUKA *et al.*^[36a] dealing with a mixed condensation by using aldehyde, pyrrole and boron trifluoride diethyl etherate with a reaction time of only two hours (Scheme 50). This reaction led to the formation of a porphyrin and a broad selection of different, partly bizarre, expanded macrocycles possessing up to 10 pyrrole units. The main problem, using the aldehyde, pyrrole and the LEWIS acid, is the formation of macrocycles with an even and uneven number of pyrrole units ($n = 4, 5, 6, 7, \dots, 10$) resulting in a difficult and tedious separation by column chromatography which had to be repeated up to six times. In particular, a *N-fused* pentaphyrin and the desired [26]hexaphyrin possess almost the same polarity and thus their separation was one of the major challenges.



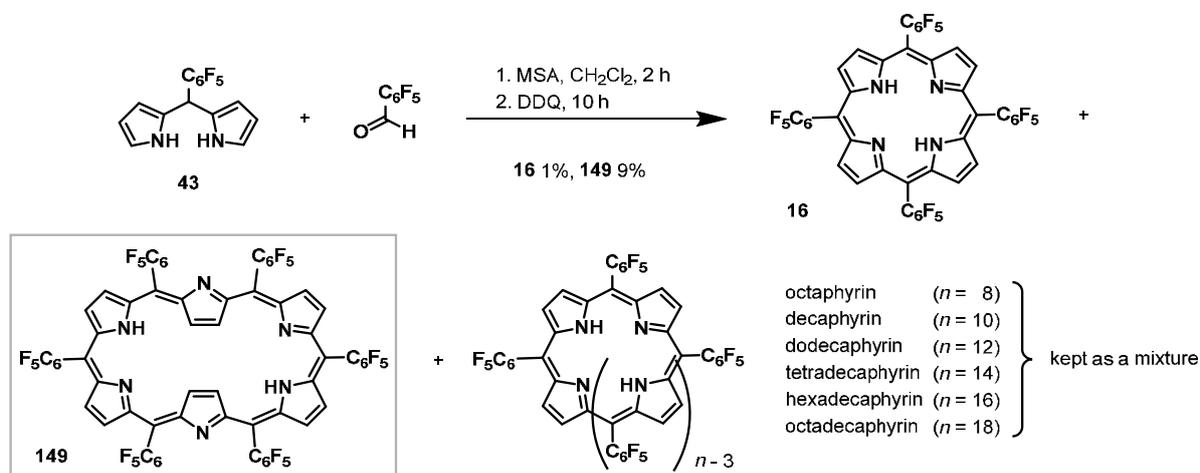
Scheme 50. Mixed condensation reaction generating expanded porphyrinoids with even and uneven pyrrole units.

A possible reaction mechanism for the formation of *N-fused* [22]pentaphyrin is shown in scheme 51. According to condensation reactions of porphyrins *via* the unoxidized porphyrinogen, it is suggested that *N-fused* [24]- and [22]pentaphyrins are derived from the putative precursor pentaphyrinogen. According to FURUTA and OSUKA^[36b] oxidation may proceed *via* two different routes: (1) direct oxidation of pentaphyrinogen to *N-fused* [24]pentaphyrin and (2) oxidation of pentaphyrinogen to putative *meso*-pentaaryl]pentaphyrin (not synthesized so far) which is a highly strained molecule and would invert one or two of the pyrrole moieties; a subsequent oxidation would lead to *N-fused* [24]pentaphyrin.



Scheme 51. A possible reaction mechanism for the formation of *N-fused* pentaphyrins.

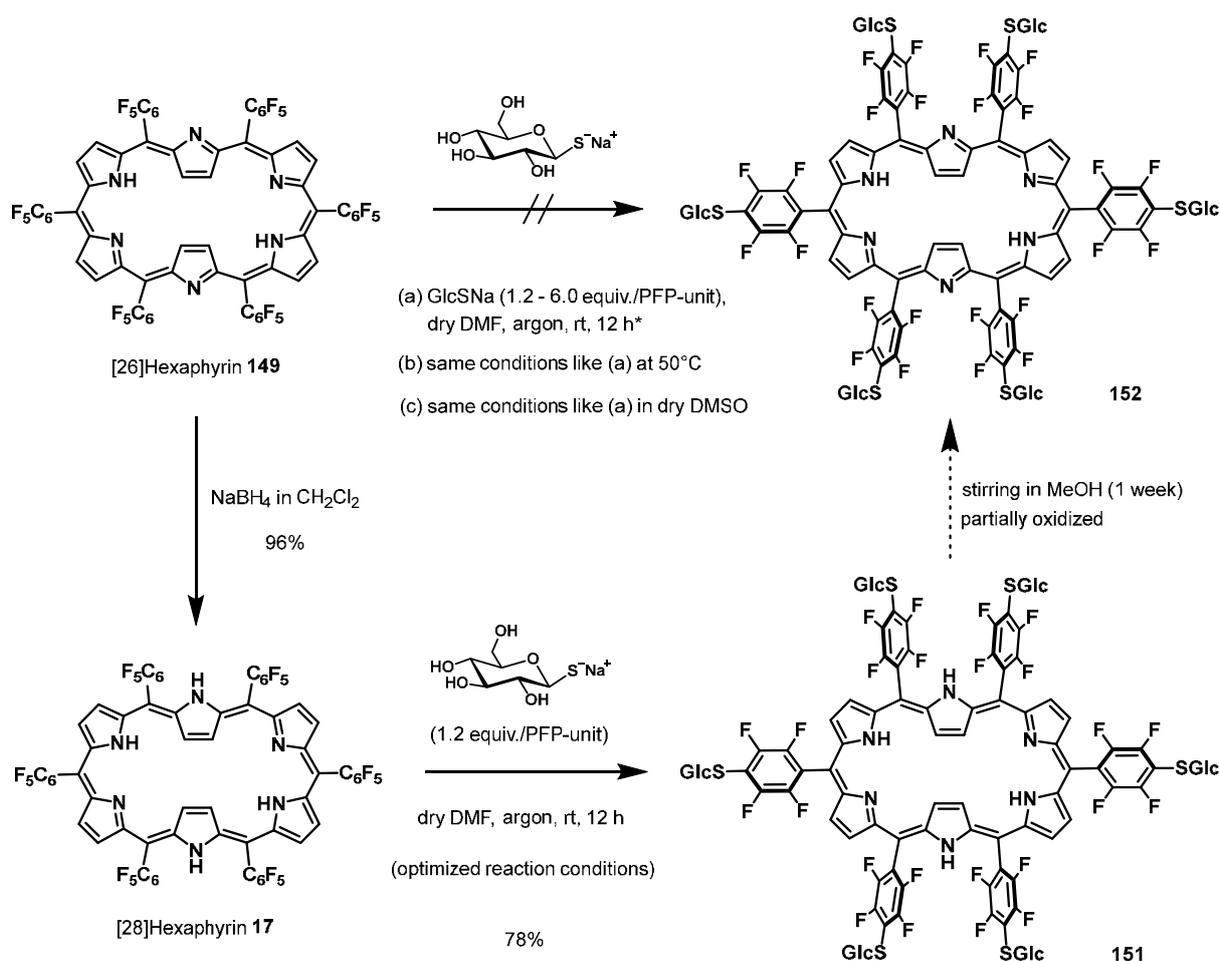
In another protocol by OSUKA *et al.* from 2008,^[37b] instead of an aldehyde, pyrrole and boron trifluoride diethyl etherate, the authors used an aldehyde, the building block dipyrromethane and methanesulfonic acid as catalyst (Scheme 52).



Scheme 52. Facile synthesis of expanded porphyrinoids with only even pyrrole units.^[37b]

This change in the protocol does not allow the formation of the *N-fused* pentaphyrin. Only macrocycles with an even number of pyrrole units, like [18]porphyrin ($n = 4$), [26]hexaphyrin ($n = 6$), [36]octaphyrin ($n = 8$), ... [80]octadecaphyrin ($n = 18$) were formed due to the dipyrromethane building block. This simplified the whole separation process and an increased amount of [26]hexaphyrin could be isolated. It should be noted that larger porphyrinoids with pyrrole units $n = 12-18$ were kept as a mixture and not further separated due to their similar polarities and/or poor yield.

From the beginning of our synthesis plan, the hexaphyrin seemed to be the most interesting, but also the most challenging candidate for a glycosylation. It should be noted that neither a nucleophilic substitution with a thiol nor a glycosylation of a hexaphyrin has been reported so far. Following our modified protocol, we tried to thioglycosylate the [26]hexaphyrin, using a ratio of thiolate/PFP-unit = 1.2:1. TLC analysis indicated formation of multiple glycosylations at the [26]hexaphyrin and partially also its conversion in the corresponding reduced form, the [28]hexaphyrin. We tested different parameters like reaction time, amount of thiolate, temperature and use of a different appropriate solvent to completely thioglycosylate the [26]hexaphyrin, but all attempts were unsatisfactory (Scheme 53). In the course of these experiments, the major problem proved to be a partial reduction of the [26]hexaphyrin to the [28]hexaphyrin. Such a reduction was first observed by OSUKA and co-workers for a nucleophilic substitution reaction with an amine.^[87] However in this case, the excess of amine led to a full reduction to the [28]hexaphyrin and did not lead to any additional attacks at one PFP-unit since amines are less nucleophilic than the corresponding thiolates. Even an excess of thiolate (thiolate/PFP-unit = 6:1) could not ensure a complete reduction of the [26]hexaphyrin before an additional attack at the *ortho*- or *meta*-position of a PFP-unit occurred. Consequently, another strategy had to be found.



Scheme 53. Route to the first thioglycosylated hexaphyrin 151.

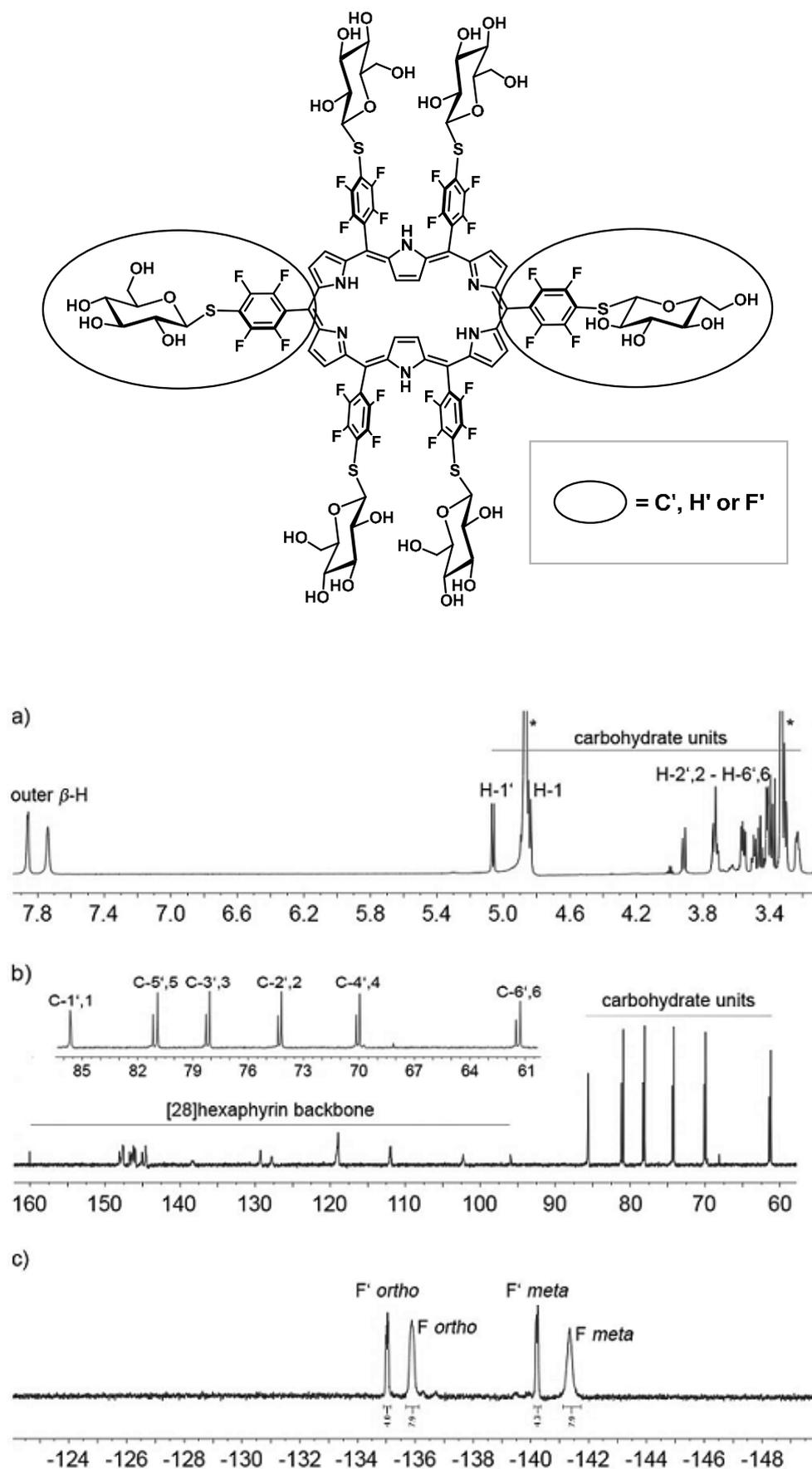
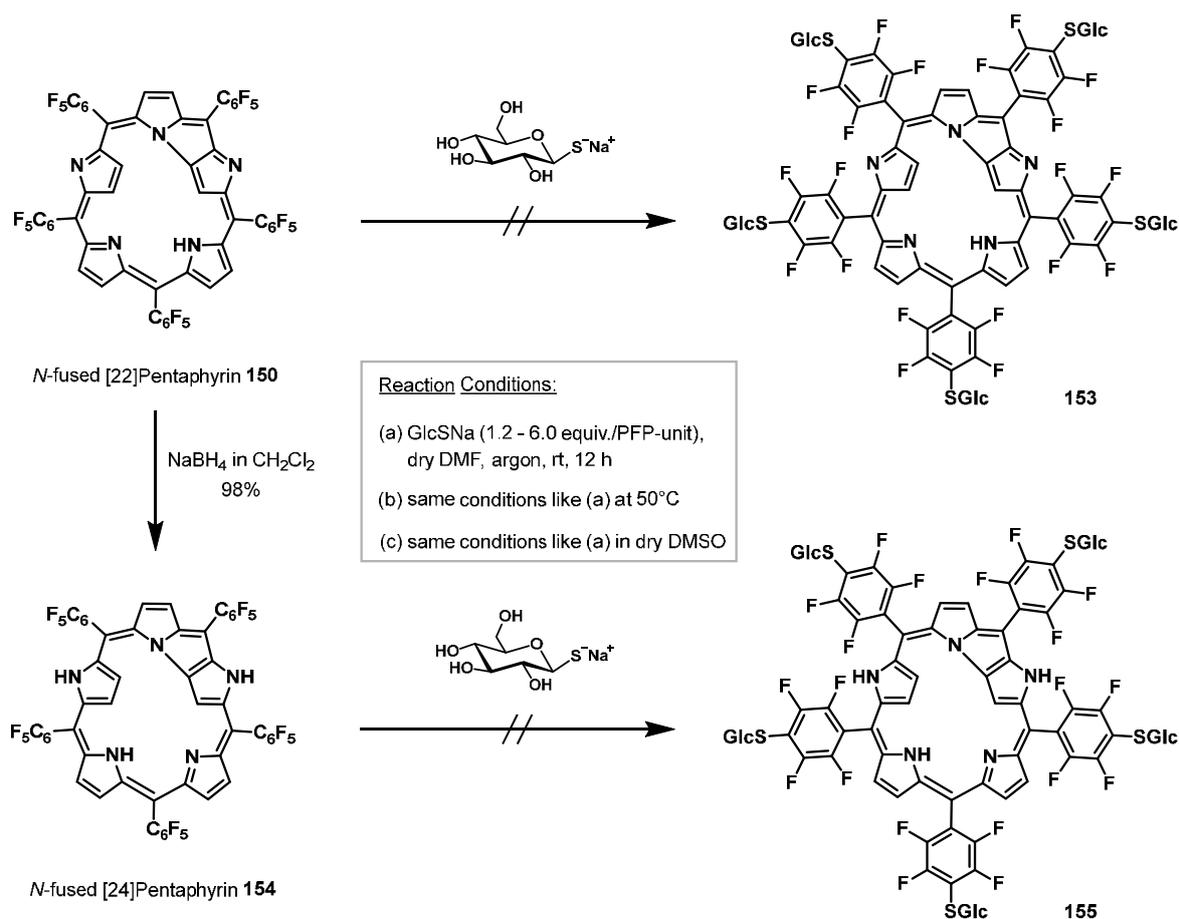


Figure 56. ^1H -, ^{13}C - and ^{19}F -NMR spectra of thioglycosylated [28]hexaphyrin 151.

Finally, we reduced the [26]hexaphyrin **149** with NaBH₄ to the corresponding [28]hexaphyrin species **17** (with almost quantitative yield) prior to the thioglycosylation, thus avoiding a deactivation of the glycosyl thiolate. This strategy proved to be successful and after optimizations the nucleophilic substitution at all six PFP-units led to the first glycosylated [28]hexaphyrin **151** in 78% yield (Scheme 53). This excellent yield corresponds to 96% yield for each substitution event. Since extraction is not possible and dialysis attempts were unsuccessful, purification of this highly polar conjugate was finally accomplished by multiple reverse phase column chromatographies using methanol/water 50:50 to 65:35. Fortunately, this porphyrinoid gave analyzable ¹H-, ¹³C- and ¹⁹F-NMR spectra which provide evidence for the desired structure (Figure 56). Even the different carbohydrate positions (e.g. 4 x C-1, 2 x C-1') could be differentiated, especially in the ¹³C-NMR spectrum. We noticed, that the thioglycosylated [28]hexaphyrin, dissolved in methanol, with its typical blue color slowly changed its color to purple after being exposed to air. This is indicative of a re-oxidation to the glycosylated [26]hexaphyrin **152**, as also described in literature for other derivatives.^[40a] However, this oxidation remained unfortunately incomplete (1 week stirring) and a separation of the oxidized and reduced form was not possible due to their similar polarities.

3.4.5 Oxidized and Reduced *N*-fused Pentaphyrins

From the mixed condensation reactions generating expanded porphyrinoids with even and uneven pyrrole units, we had also obtained small amounts of the *N*-fused pentaphyrin (NFP). We therefore tried to apply the thioglycosylation protocol to this unusual compound. Similar to the [26]hexaphyrin, the *N*-fused [22]pentaphyrin can also be reduced to its 24- π -electron form (Scheme 51). Nevertheless we first tried to thioglycosylate 22- π -electron NFP in the same manner as we did for the [26]hexaphyrin. It turned out that the result was similar: multiple glycosylations at the [22]NFP together with partial conversion to the corresponding reduced form. Following the hexaphyrin strategy, we almost quantitatively reduced the [22]NFP **150** with NaBH₄ to the corresponding [24]NFP species **154**. Again we tried the glycosylation, testing and verifying possible parameters like reaction time, amount of thiolate, temperature and use of a different appropriate solvent (Scheme 54), but in contrast to the [28]hexaphyrin the thioglycosylation of the [24]NFP could not be accomplished.

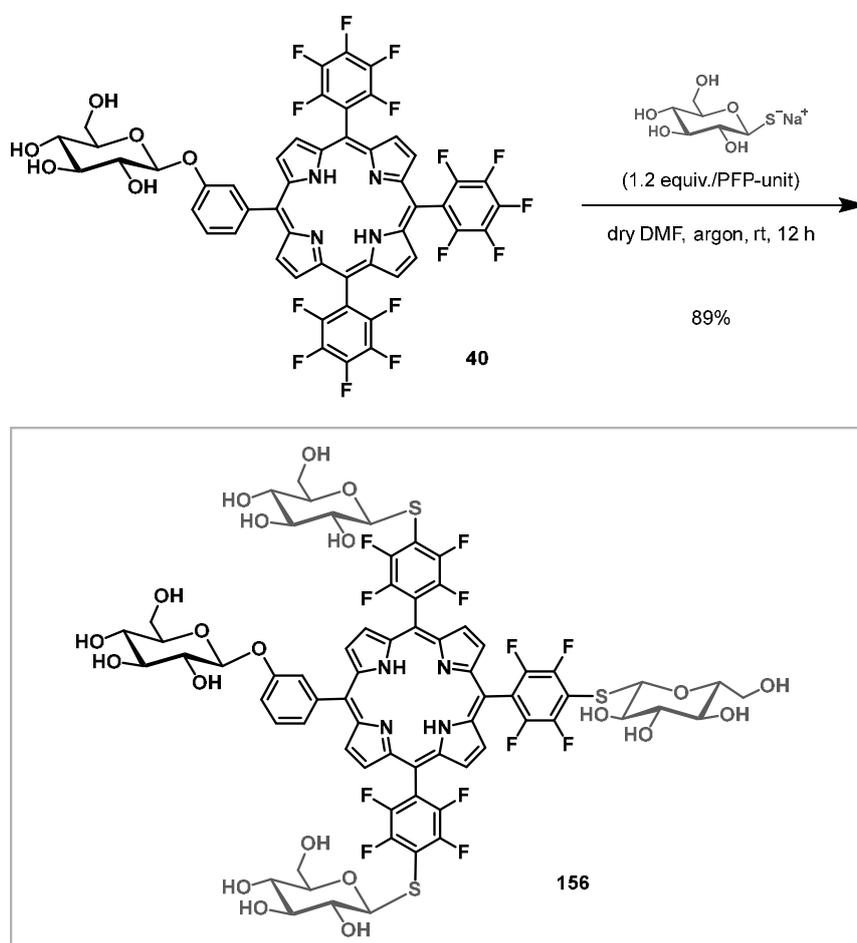


Scheme 54. Attempts to create the first thioglycosylated *N*-fused pentaphyrin.

3.5 Synthesis of Porphyrins Containing Different Carbohydrate Moieties

3.5.1 Combination of Trichloroacetimidate and Thiolate Method

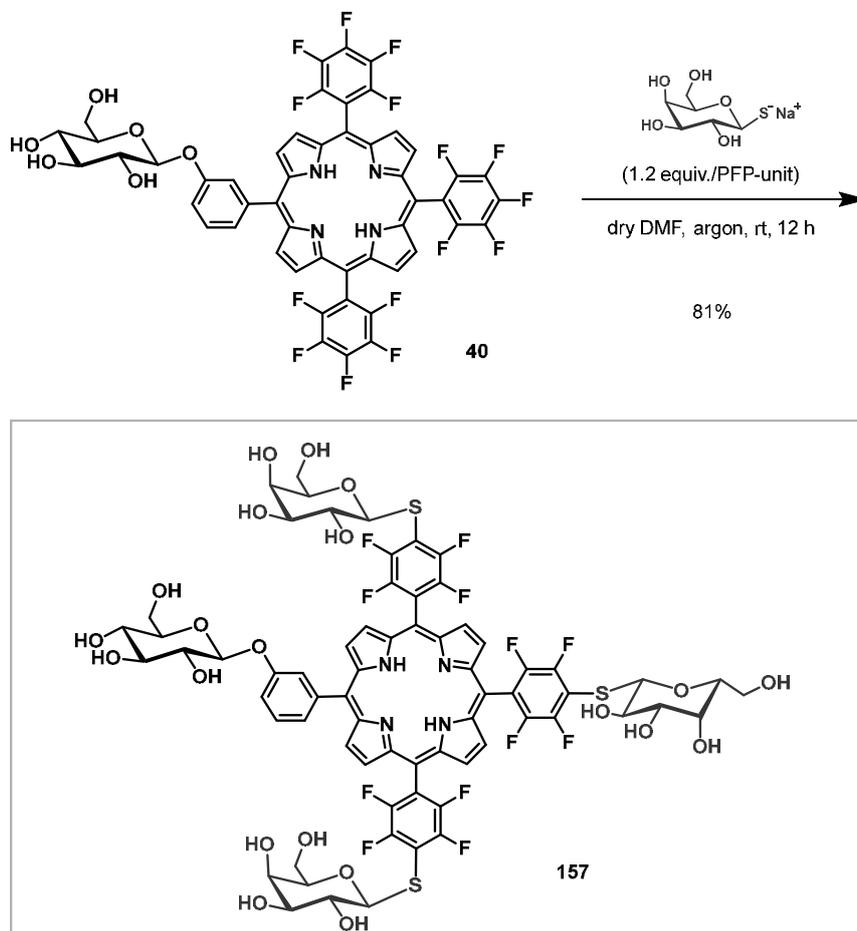
Based on the findings acquired during the glycosylation of porphyrinoids *via* the trichloroacetimidate and thiolate method, the next logical step was the combination of these two methods in order to obtain for the first time tetrapyrroles with different carbohydrate moieties in a rational synthetic approach. The synthesis of the deprotected, monoglucosylated porphyrin **40**, following the trichloroacetimidate method, has already been described in chapter 3.1. In the current study this compound served as starting material. We decided to first install another glucosyl moiety to the monoglucosylated porphyrin in order to investigate if the thiolate method is suitable to this class of substrates as well.



Scheme 55. Thioglycosylation of glucosylated porphyrin **40**.

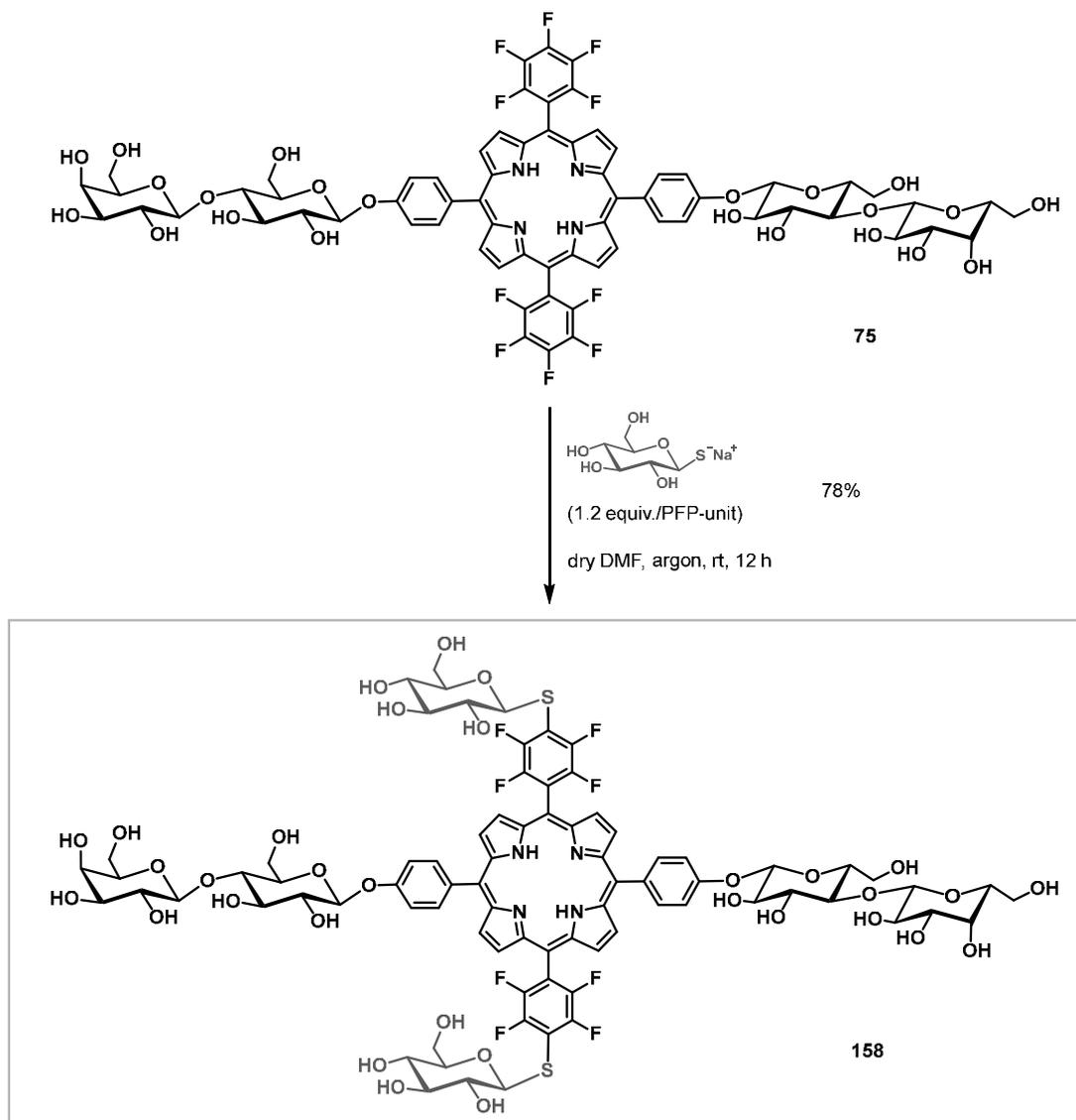
Therefore the deprotected, monoglucosylated tetrapyrrole was dissolved in dry DMF and for each PFP-unit an almost equimolar amount of 1-thio- β -D-glucose sodium salt was added. After 12 h stirring at rt, a tetrapyrrole containing two differently connected glucosyl moieties, was isolated in a very good yield of 89% (Scheme 55).

Due to this straightforward and controlled introduction of a second glucosyl moiety, we tried to install a different second carbohydrate: galactose. Under the same reaction conditions, the glucosylated tetrapyrrole was reacted with 1-thio- β -D-galactose sodium salt and yielded a tetrapyrrole with two different carbohydrate moieties in 81% (Scheme 56).



Scheme 56. Synthesis of first tetrapyrrole carrying glucosyl and galactosyl moieties.

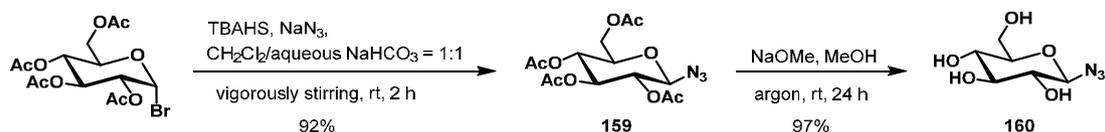
Since the synthesis of a tetrapyrrole bearing two different monosaccharides was successful, we next tried to apply this strategy to install a monosaccharide moiety to a substrate which already contained a disaccharide. The synthesis of the *trans*-A₂B₂-substituted glyco-porphyrin **75** had been described previously in chapter 3.1. The glycosylation reaction was carried out under standard conditions and yielded the desired product in 78% (Scheme 57). Compound **158** is the first porphyrinoid bearing mono- and disaccharide moieties at the same time. It is obtained in 8 consecutive reaction steps starting from simple commercially available compounds.



Scheme 57. Synthesis of first tetrapyrrole carrying mono- and disaccharide moieties.

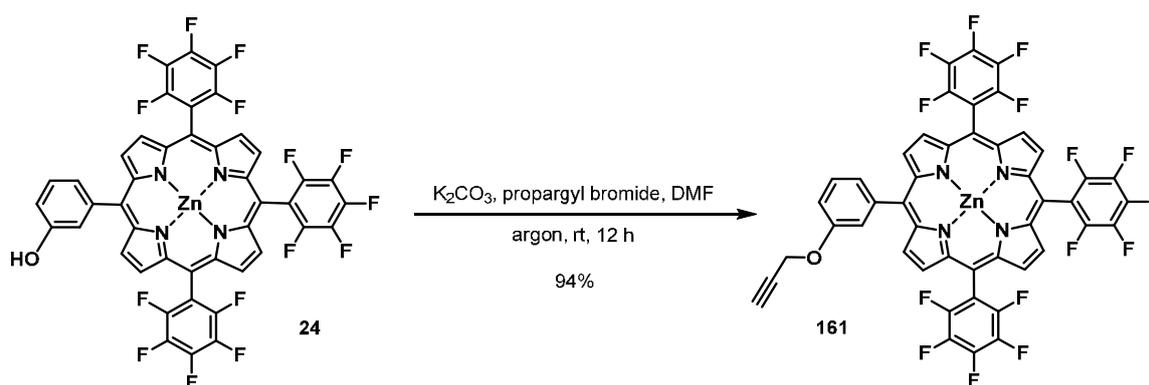
3.5.2 Combination of 1,3-Dipolar “Click” Reaction and Thiolate Method

Based on investigations during the master thesis,^[66] dealing with the introduction of a carbohydrate moiety to a tetrapyrrolic system *via* 1,3-dipolar “click” reactions, we decided to also combine this approach with the thiolate method to prepare porphyrins with two different carbohydrate moieties. Initially, we had to synthesize the two main components for the 1,3-dipolar “click” reaction: an azidated carbohydrate and an alkyne-substituted porphyrin. The carbohydrate component was synthesized according to a protocol by ROY and co-workers.^[88] Accordingly, α -glucosyl bromide was reacted with TBAHS and sodium azide in a biphasic reaction mixture consisting of dichloromethane and NaHCO₃ yielding 92% of the β -anomer. The product did not need an extensive purification and could be synthesized on a gram-scale. The deprotection of the peracetylated glucosyl azide was accomplished almost quantitatively in dry methanol using sodium methanolate.



Scheme 58. Synthesis of glycosyl azide and its subsequent deprotection.

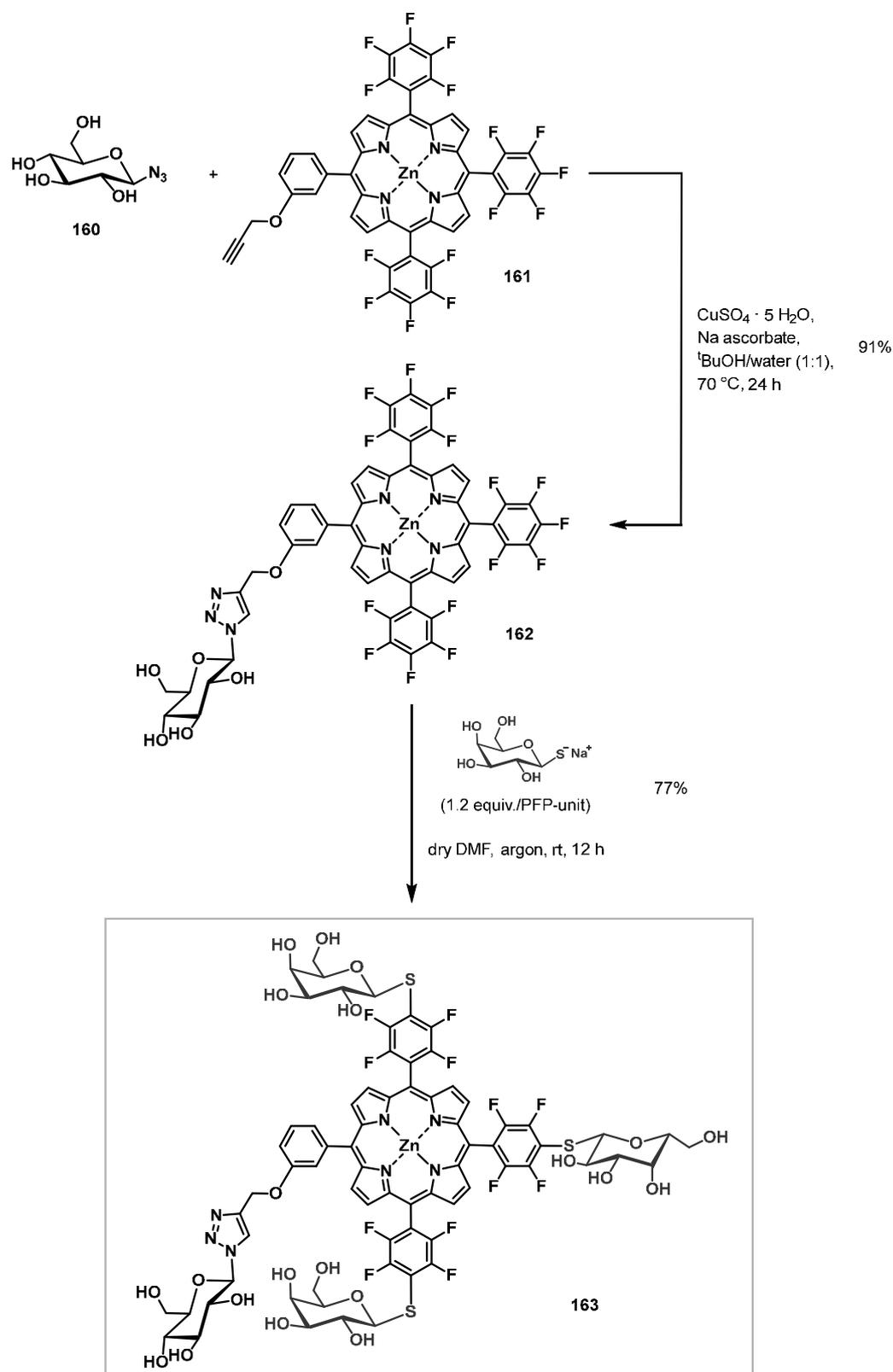
The second component for the 1,3-dipolar “click” reaction was the alkyne-substituted porphyrin. The condensation reaction and metallation for the synthesis of the zinc porphyrin **24** was already described in a previous chapter. The alkyne moiety was installed by using propargyl bromide and K₂CO₃ in DMF. Thus, the alkyne-substituted porphyrin was synthesized in a very good yield of 94%.



Scheme 59. Introduction of an alkyne moiety into porphyrin **24**.

Now, the azidated carbohydrate and the alkyne-substituted porphyrin were ready for the 1,3-dipolar “click” reaction. To this end, both components were reacted in a *tert*-butanol/water mixture with catalytic amounts of copper sulfate and sodium ascorbate at a temperature of 70 °C yielding 91%. This monoglucosylated porphyrin serves as the platform for the introduction of another different

carbohydrate moiety. Therefore, the glucosylated porphyrin was reacted with 1-thio- β -D-galactose sodium salt under the same conditions as shown above and gave porphyrin **163** in a yield of 77%.



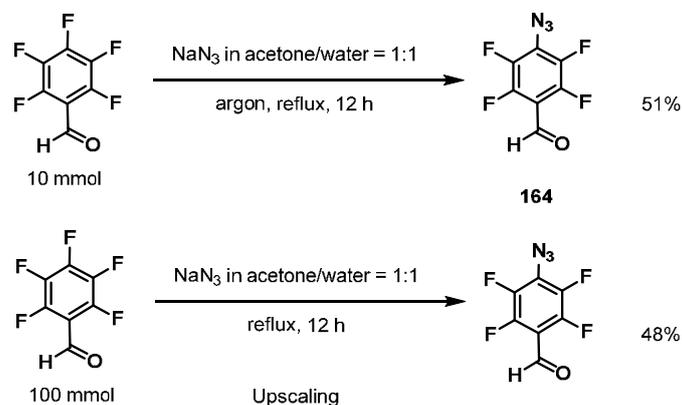
Scheme 60. Combination of 1,3-dipolar “click” reaction and thiolate method.

The synthesis of a porphyrin with two different monosaccharides, combining the “click” reaction and the regioselective nucleophilic substitution reaction, was realized in 7 consecutive reaction steps. In summary, the first rational synthesis of porphyrins carrying two different carbohydrate moieties was exemplified using two different pathways: The combination of the trichloroacetimidate method with thioglycosylation and the combination of “click” chemistry and thioglycosylation.

3.6 Azido-Aldehyde as a Versatile Building Block for Azide-Containing Porphyrinoids

Expanded porphyrins, including hexaphyrins, offer particularly fascinating properties regarding their optical, structural, electrochemical and their coordination behavior.^[29,39] These properties make them interesting for oxidation catalysts,^[40a] multi-metal coordination ligands,^[40b] nonlinear optical (NLO) materials,^[40c] near-IR dyes^[40d] or deeper-penetrating PDT regarding to their large two-photon absorption (TPA) cross-sections ($\sigma^{(2)}$).^[41] Calix[*n*]phyrin(1.1.1)s are macrocycles at the interface of porphyrins and calixpyrroles.^[25a,c] In contrast to the roof-like calix[4]phyrin systems which are well studied and established in the field of coordination chemistry, catalysis or ion sensoric, the calix[6]phyrins and especially their possible applications are relatively unexplored.^[26] Based on this reasonings, we decided to incorporate an azide moiety to such porphyrinoids serving as a platform for further modifications to study these classes of compounds in detail and uncover their potential.

Our idea was to install the azide moiety before the condensation reaction to the corresponding porphyrinoid. So basically, after this one-pot reaction one would have the azide-containing macrocycle in hand without further modifications. Another advantage would be the broad range of existing alkynes which could be connected either in a Cu(I)-catalyzed or copper-free 1,3-dipolar “click” reaction. A simple yet effective protocol for the synthesis of an azide-containing precursor is described by MOERNER and co-workers with a nucleophilic azidation of pentafluorobenzaldehyde in an acetone/water mixture.^[89]



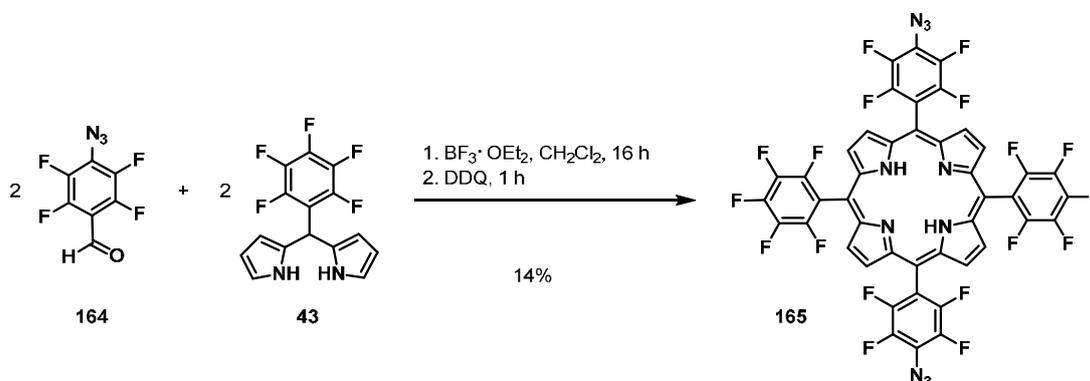
Scheme 61. Synthesis of azide-containing aldehyde **164** and its upscaling.

The MOERNER protocol could be reproduced without any difficulties and with a similar outcome. In the next step we upscaled this reaction and cut out the argon atmosphere. The yield for the upscaling was with 48% similar to the standard one and provided enough starting material for the synthesis of the azido-porphyrinoids.

3.6.1 Tetrapyrroles (Porphyrins and Corroles)

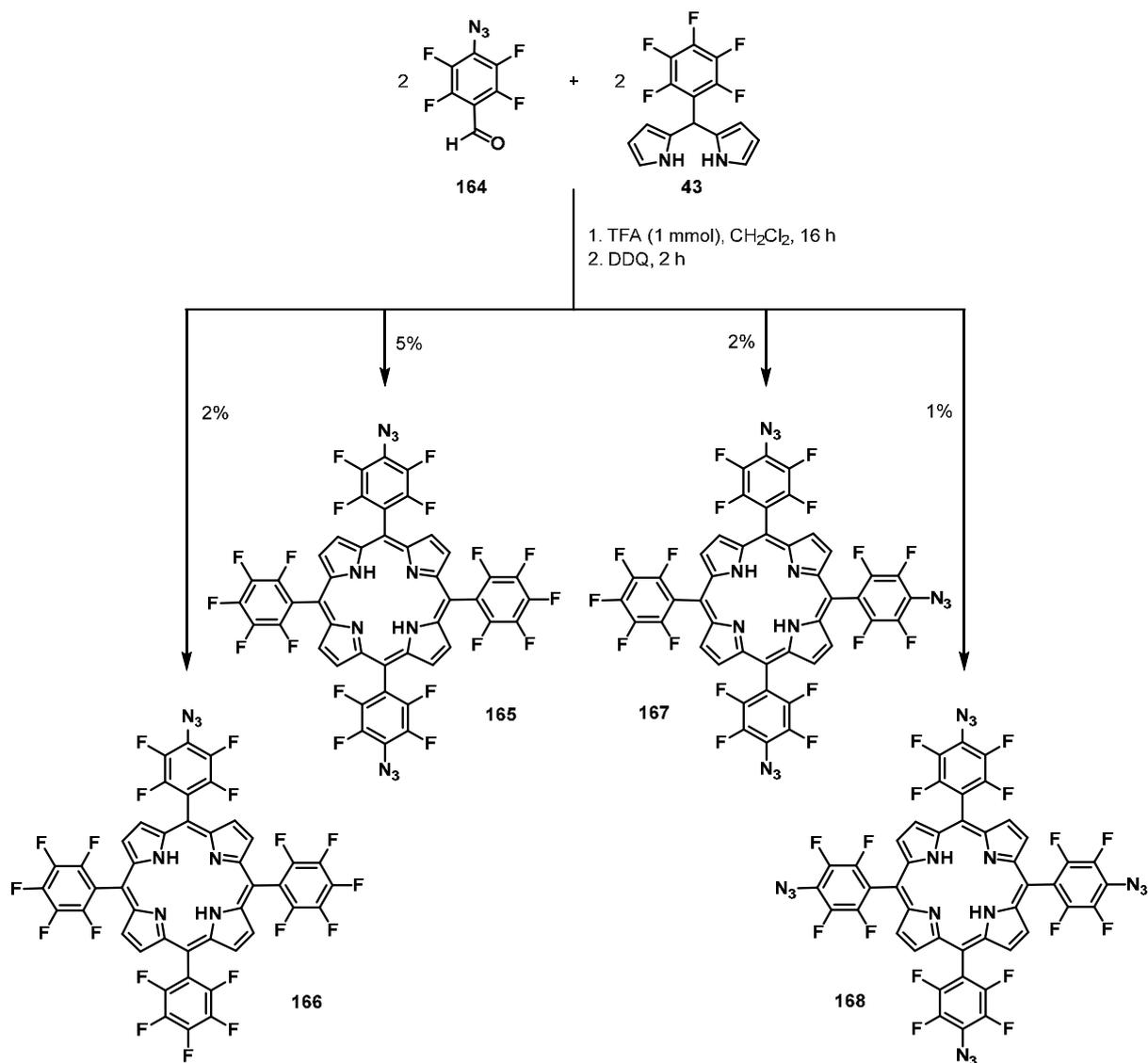
The first class of porphyrinoids that was explored were the porphyrins. The azidation of a PFP-substituted porphyrin with NaN_3 *via* a nucleophilic aromatic substitution is a known reaction,^[76a] however it has the disadvantage of uncontrolled substitution: For this azidation an excess of NaN_3 is required leading to a complete nucleophilic substitution in the *para*-position of the PFP-units and further additional, undesired substitutions. The synthesis of azide-substituted porphyrins with customized substitution patterns, for example a *trans*- A_2B_2 -substituted porphyrin, is thus not possible or very low-yielding. Using our strategy, this is basically possible because an azidated aldehyde can react with an unsubstituted PFP-dipyrromethane in a standard condensation reaction.

With this in mind, we reacted the 4-azido-2,3,5,6-tetrafluorobenzaldehyde with PFP-dipyrromethane (ratio 1:1) in the presence of the LEWIS acid $\text{BF}_3 \cdot \text{OEt}_2$ to synthesize the *trans*- A_2B_2 -substituted porphyrin in a yield of 14% (Scheme 62). This is the first straightforward synthesis of a *trans*- A_2B_2 -azidated porphyrin in literature so far. Since a *trans*- A_2B_2 -structural motif showed to be very promising regarding targeting, azidated porphyrin **165** could serve as a valuable platform for corresponding functionalizations (e.g. 1,3-dipolar “click”, $\text{S}_{\text{N}}\text{Ar}$ or STAUDINGER reactions).



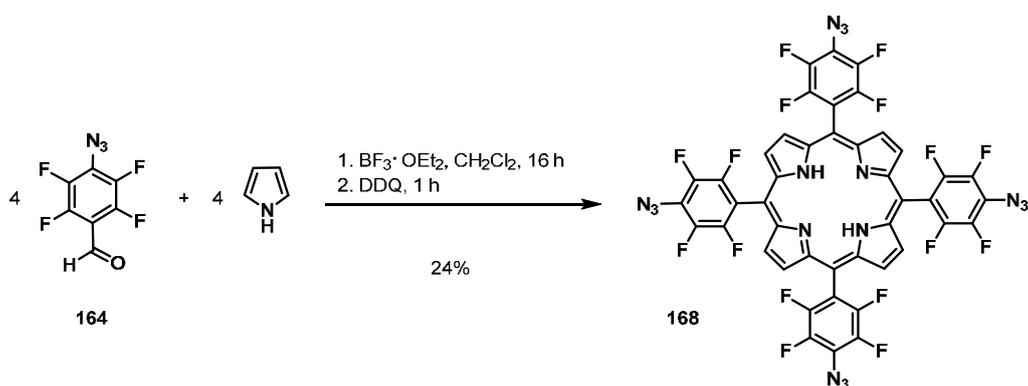
Scheme 62. Synthesis of *trans*- A_2B_2 -porphyrin using a PFP-substituted DPM and an azidated aldehyde.

In an earlier attempt, we reacted the 4-azido-2,3,5,6-tetrafluorobenzaldehyde with PFP-dipyrromethane (ratio 1:1) in the presence of the BRÖNSTEDT acid TFA (Scheme 63). The result was a broad variety of mono-, di-, tri- and tetra-azidated porphyrins. It is remarkable that the formation of the *cis*- A_2B_2 -substituted porphyrin was not observed. All other derivatives, although possessing very similar polarities, could be separated in a column chromatography without considerable problems. The desired *trans*- A_2B_2 -porphyrin was isolated in only 5% which shows that the LEWIS acid is more suitable here.



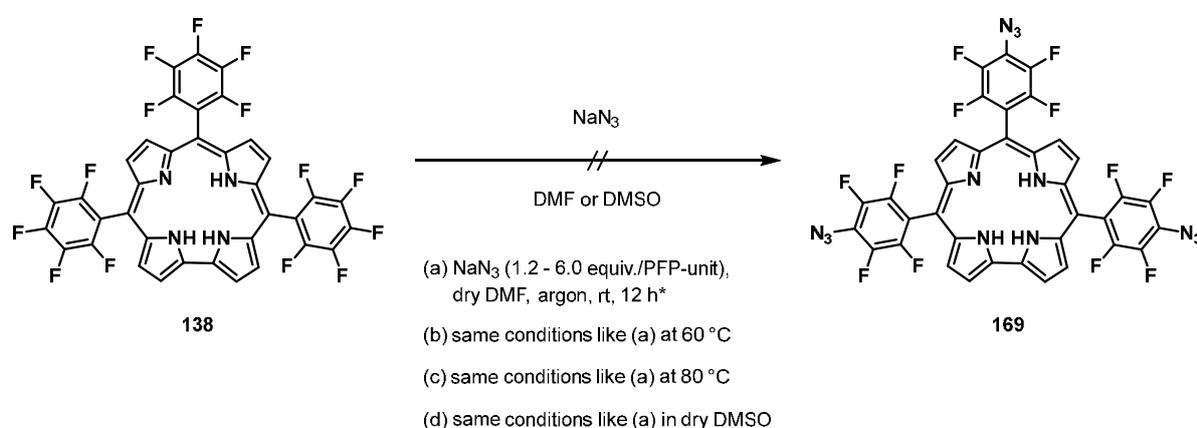
Scheme 63. Synthesis of *trans*-A₂B₂-porphyrin using a PFP-substituted DPM and an azidated aldehyde.

In the presence of the LEWIS acid BF₃·OEt₂, a direct synthesis^[6] of the azidated A₄-porphyrin was also realized in a yield of 24% which is superior to the known two-step synthesis.^[76a]



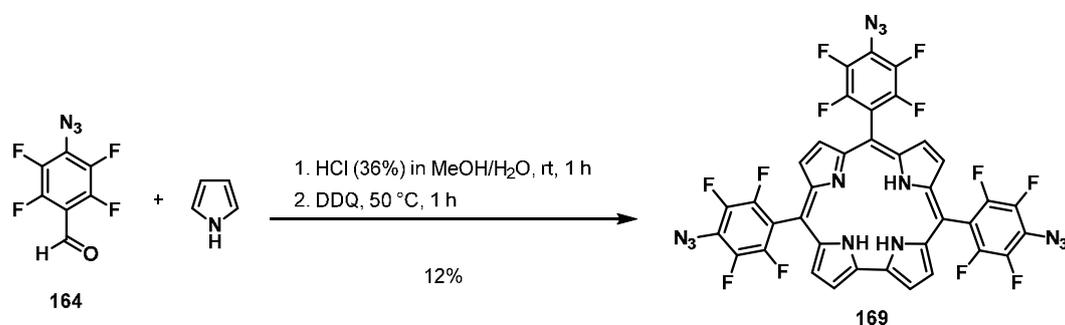
Scheme 64. Synthesis of azide-containing A₄-porphyrin.

The next class of porphyrinoids investigated were corroles which due to improved synthetic protocols (cf. also above) have found interest for a variety of applications. They were studied in detail as key compounds in coordination chemistry, electrochemistry, catalysis or medicine-oriented research.^[22] The synthesis of corroles has been improved in the course of time since initial reports by GROSS and PAOLESSE which have been already discussed in detail. Especially the synthesis of *meso*-substituted corroles in a water/methanol mixture, developed by GRYKO and co-workers, present an efficient and reproducible route.^[21] This route was also chosen for the introduction of the azide moieties *via* the azido-aldehyde. It should be noted, that all attempts (higher temperature, excess of sodium azide, different solvent) to introduce an azide to the PFP-substituted corrole in a nucleophilic substitution reaction failed (Scheme 65).



Scheme 65. Attempts to create the first azide-containing A_3 -corrole (* regularly monitored by TLC).

Due to these results, we started the condensation reaction of the azido-aldehyde with pyrrole and HCl in a water/methanol mixture. After the oxidation of the bilane with DDQ at 50 °C, we obtained the desired azido-corrole in an overall yield of 12% for the first time (Scheme 66). It turned out that this compound decomposes if kept in solution longer than 7 days.



Scheme 66. First Synthesis of azide-containing A_3 -corrole.

Furthermore we detected a new side-product (4% yield) which strongly differs from the observed side-products described by GROSS and GRYKO.^[19b,21] Although we obtained a quite nice ¹H- and ¹⁹F-NMR spectrum (Figure 57) we could not clearly identify the formed compound.

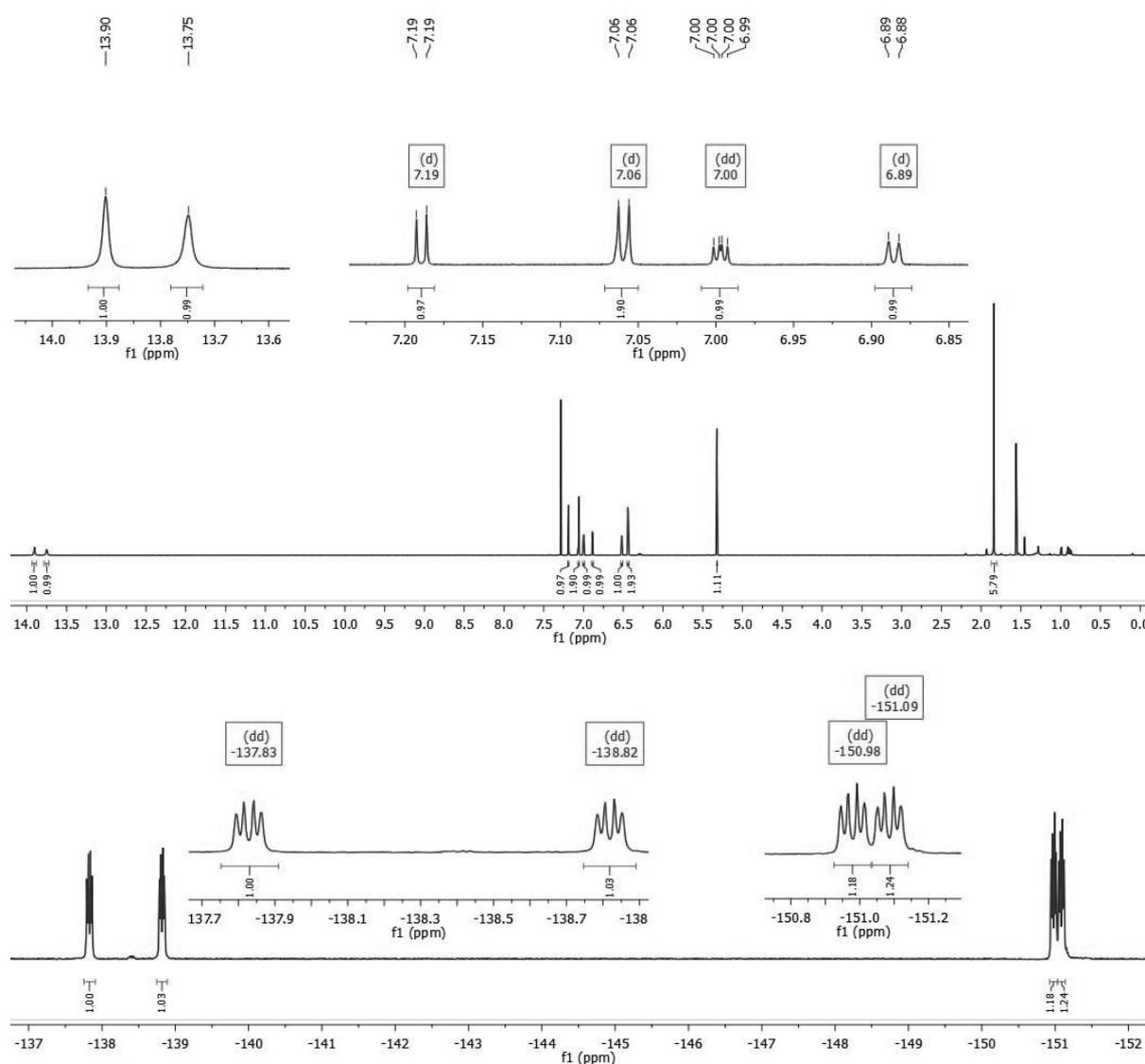
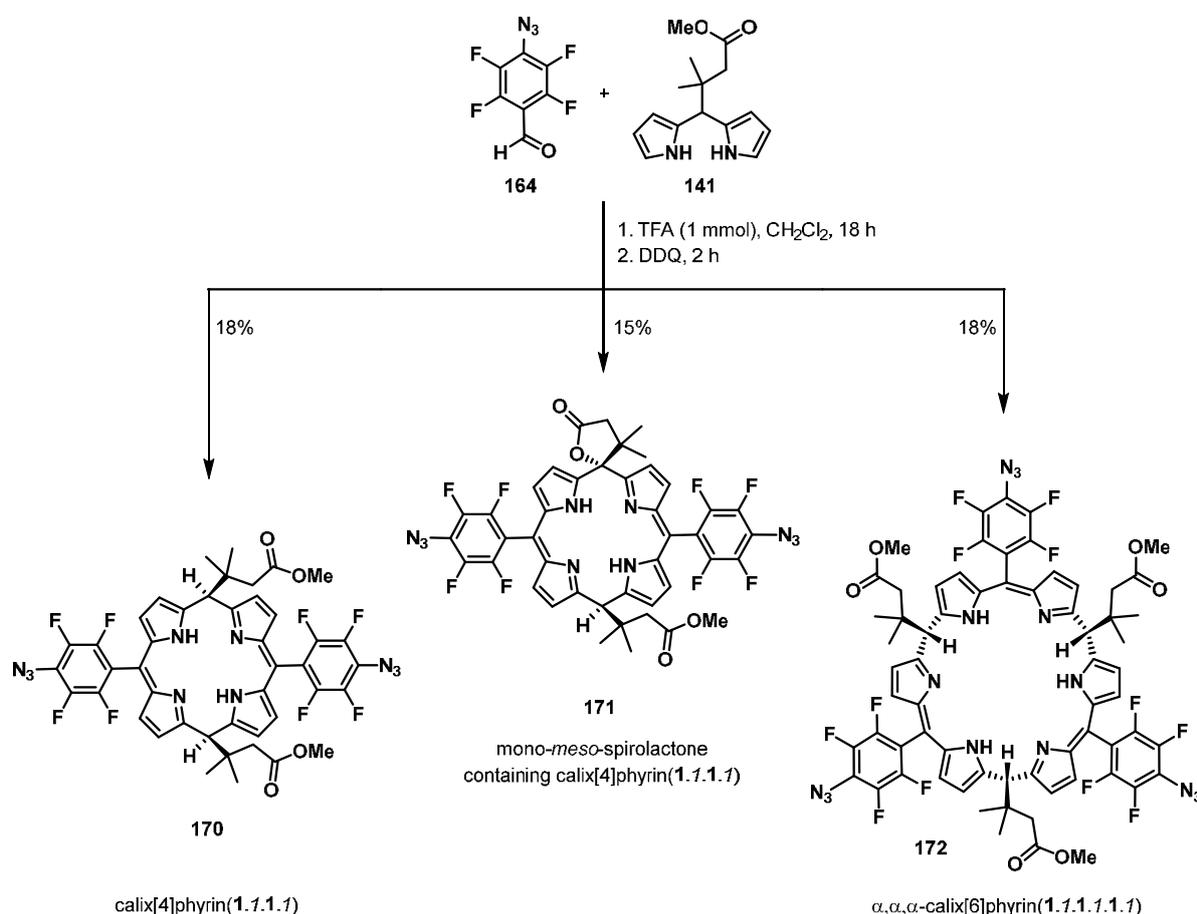


Figure 57. ¹H- (above) and ¹⁹F-NMR spectrum (below) in CDCl₃ of unknown side-product.

GROSS and co-workers also found another unknown side-product during their studies. First they hypothesized that it can be a radical cation of corrole,^[90] but this has been criticized by PAOLESSE and co-workers.^[91] The structure remains unsolved, but it is believed that this unknown side-product cannot be an open-chain compound.

3.6.2 Calix[4]- and Calix[6]phyrin Systems

As mentioned before, stable pentafluorophenyl-substituted calix[*n*]phyrins bearing *meso*-CH moieties were recently synthesized by REISSIG, WIEHE and co-workers.^[27] Calix[4]phyrins are hybrid compounds at the interface between porphyrins (sp²-hybridized *meso*-carbon bridges) and calixpyrroles (sp³-hybridized *meso*-carbon bridges). They contain sp²- and sp³-hybridized *meso*-carbon bridges resulting in a rather rigid π -conjugated and a more flexible subunit. Thereby these compounds are unique and promising candidates e.g. as catalysts, as sensors for cations and anions or neutral substrate recognition in supramolecular chemistry. To obtain their azide-analogues, we used our own procedure and tried to install the azide moiety *via* the azido-aldehyde route (Scheme 67). The respective aldehyde was reacted with the sterically congested dipyrromethane in dichloromethane and TFA for 16 hours without any problems.



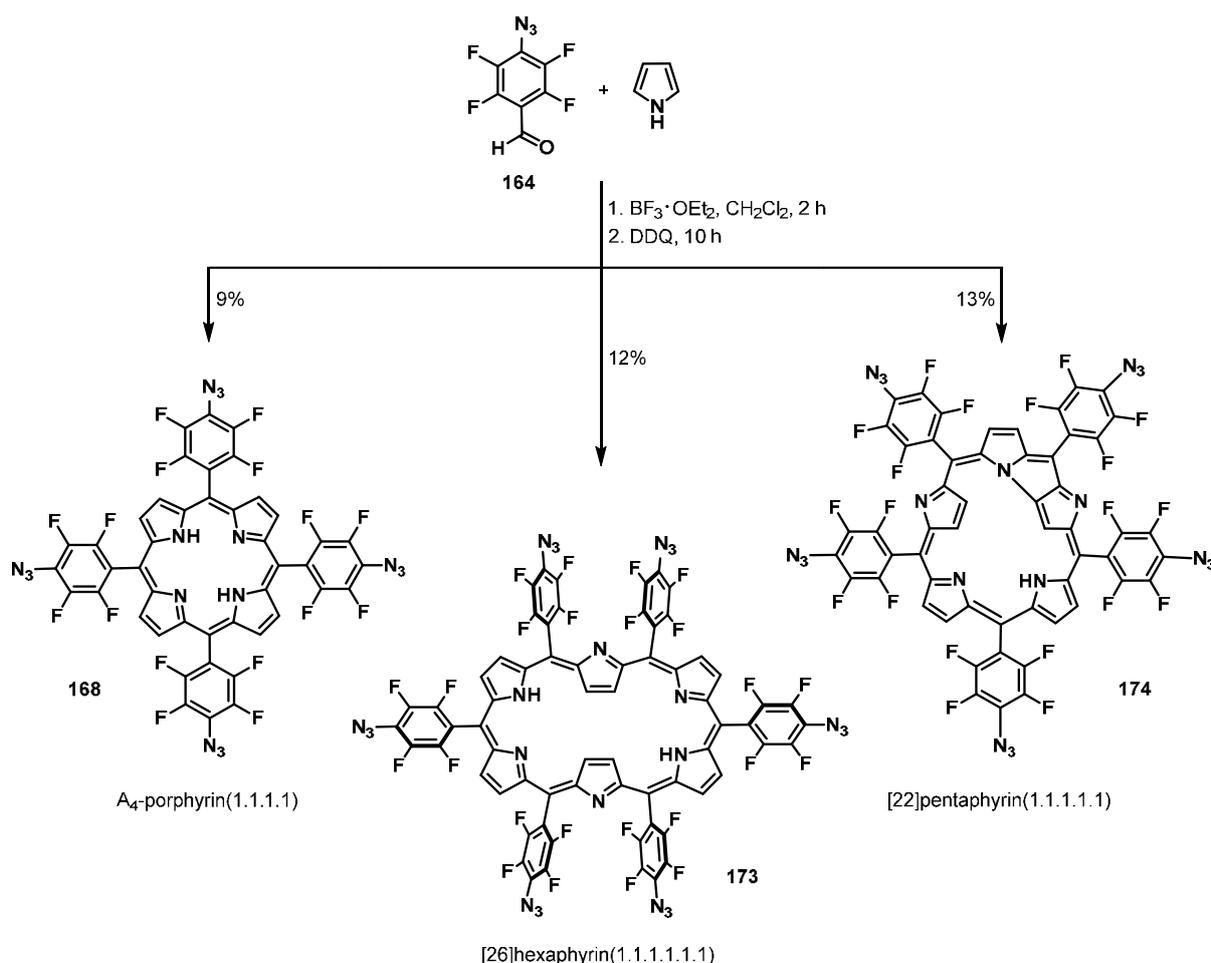
Scheme 67. Synthesis of azide-containing calix[*n*]phyrin macrocycles by using a sterically congested DPM.

After oxidation with DDQ, the azido-substituted calix[4]phyrin, mono-*meso*-spirolactone calix[4]phyrin and α, α, α -calix[6]phyrin were obtained in similar yields as their azide-free analogues. Fortunately, purification and separation of these three azido-calix[*n*]phyrins *via* column chromatography was easier than for their PFP-substituted analogues.

3.6.3 *N*-fused [22]Pentaphyrins and [26]Hexaphyrins

As the last class of compounds to implement our azido-aldehyde, we chose expanded porphyrinoids focusing on *N*-fused [22]pentaphyrins and [26]hexaphyrins. It should be stated that azidated species of *N*-fused pentaphyrins and hexaphyrins are thus far unknown compounds. We chose two different approaches to obtain different azide-substitution patterns.

In a first approach, we reacted exclusively the azido-aldehyde with pyrrole in the presence of the LEWIS acid to ensure the desired formation of the azido-substituted *N*-fused pentaphyrin (five azide moieties in *meso*-position) and [26]hexaphyrin (six azide moieties in *meso*-position). This condensation reaction was stirred for 2 h, following a protocol by OSUKA and co-workers.^[36a] The result was the formation of azido-substituted macrocycles with even and uneven pyrrole units ($n = 4, 5, 6, 7, \dots 18$). After using the mentioned reaction conditions we could isolate the fully azidated porphyrin **168** in a yield of 9%, [26]hexaphyrin **173** in a yield of 12% and *N*-fused [22]pentaphyrin **174** in a yield of 13%.



Scheme 68. Synthesis of azide-containing expanded porphyrinoids with even and uneven pyrrole units.

In contrast to the PFP-substituted *N-fused* pentaphyrin and [26]hexaphyrin, which required a difficult and extensive separation by column chromatography (repeated up to six times), purification of their azide-containing analogues was found to be easier. In dichloromethane both azidated compounds possess a characteristic color: [26]hexaphyrin has an intense purple hue while *N-fused* [22]pentaphyrin is red. Furthermore azidated [26]hexaphyrin **173**, in contrast to its unsubstituted form, was isolated as a shiny gold-metallic solid (Figure 58).

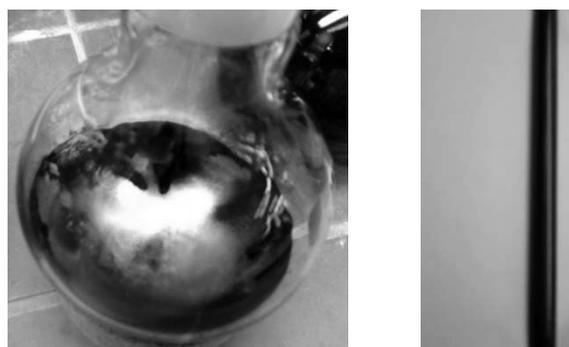


Figure 58. Colors of azidated [26]hexaphyrin **173** in its solid form and in solution (dichloromethane).

Since **174** is the first known PFP-substituted *N-fused* pentaphyrin, it is also interesting to inspect its NMR spectra more closely. In contrast to a porphyrin this macrocycle possesses no mirror planes resulting in a complex ^1H - and ^{13}C -NMR spectra. More interesting and informative is its very unique ^{19}F -NMR spectrum (Figure 59).

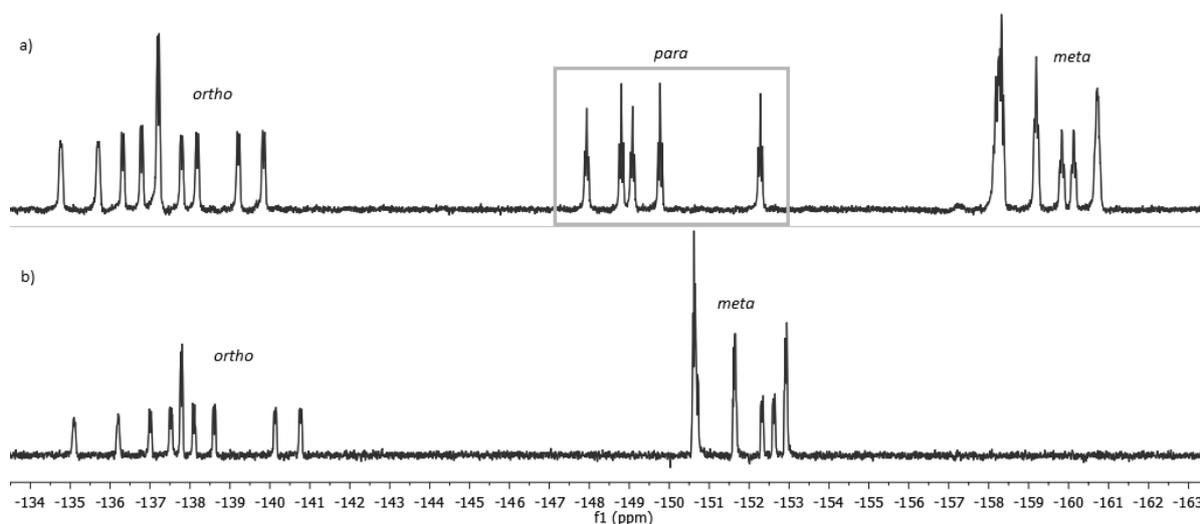
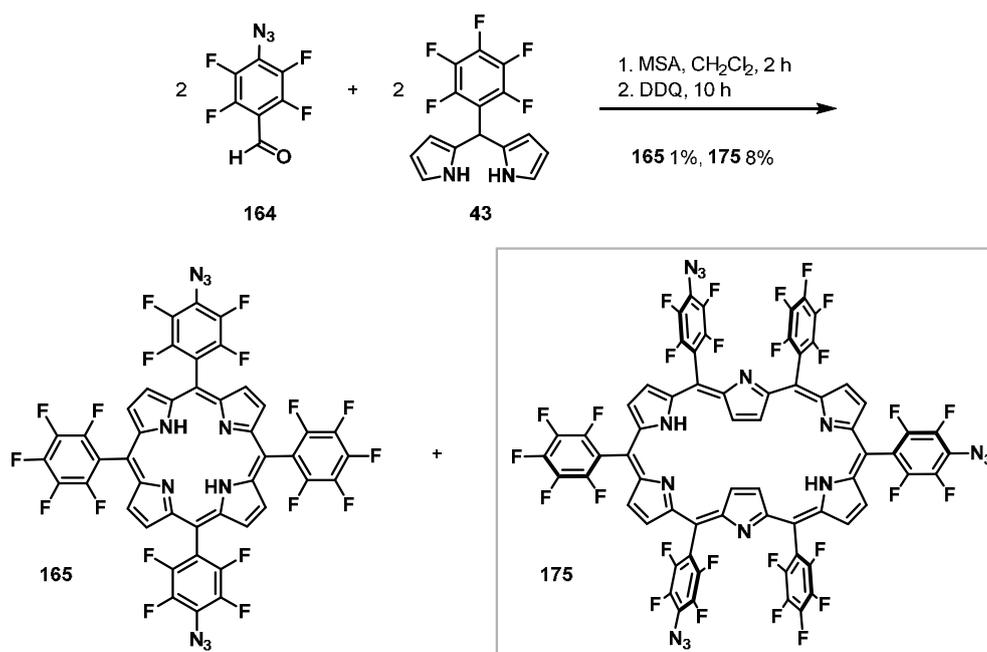


Figure 59. ^{19}F -NMR spectra comparison between a) the unsubstituted and b) the azidated *N-fused* [22]pentaphyrin showing the substitution in *para*-position.

A comparison of the ^{19}F -NMR spectrum of an unsubstituted *N-fused* [22]pentaphyrin (a) with the azide-containing *N-fused* [22]pentaphyrin (b) clearly shows the complete disappearance of the five *para*-fluorine signals (between -148 and -154 ppm) due to the substitution at each *para*-position.

In a second approach, avoiding the formation of *N-fused* pentaphyrin, we used another protocol by OSUKA and co-workers.^[37] Here, instead of the azido-aldehyde and pyrrole, we used the building block PFP-dipyrromethane and the azido-aldehyde (Scheme 69). The main aim was the controlled formation of a [26]hexaphyrin possessing alternating PFP- and azide units. As an expected side-product, the *trans*-A₂B₂-substituted porphyrin could be isolated, too. The azidated [26]hexaphyrin could be isolated in a yield of 8% as a gold-metallic shiny solid.



Scheme 69. Synthesis of alternating PFP- and azide-containing porphyrinoids with even pyrrole units

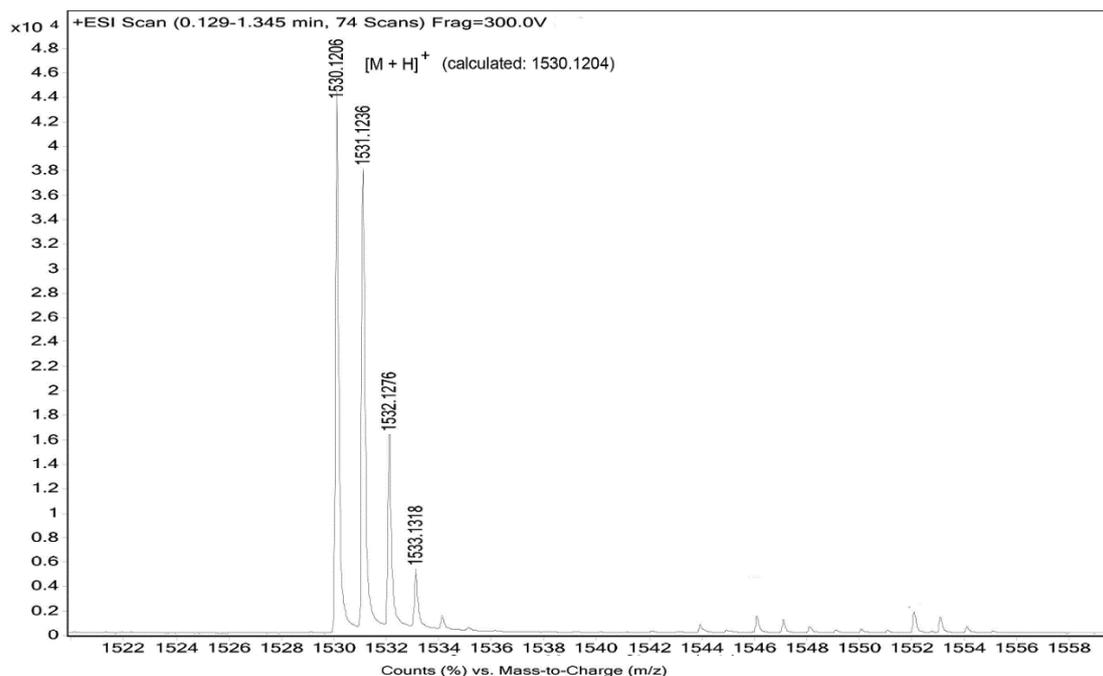


Figure 60. HRMS (ESI-TOF) of A₃B₃-[26]hexaphyrin 175.

Unfortunately, the NMR spectra of [26]hexaphyrin **175** are poorly resolved. This is a known phenomenon in the characterization of hexaphyrins.^[92] and was also confirmed during the course of this thesis. Reasons are related to their rectangular, flat and rigid structure and possible π -stacking. A mass spectrometric analysis, however shows formation of the desired compound (Figure 60).

3.7 NMR Considerations

One interesting aspect in tetrapyrrole analytics are their unique NMR spectra. The current chapter displays and discusses mono-, di- (*cis*, *trans*), tri- and tetra-substitution patterns in ^1H -NMR spectra, shows the monitoring of *para*-substituted PFP-porphyrinoids by ^{19}F -NMR spectroscopy, and compares different porphyrinoid systems with regard to their spectra.

3.7.1 Mono-, Di- (*cis*, *trans*), Tri- and Tetra-Substitution Patterns in ^1H -NMR Spectra

Due to their symmetry, porphyrin systems, especially the hydrogens in β -position, provide quite characteristic substitution patterns in their ^1H -NMR spectra. The following examples, extracted from analytics obtained during this thesis are chosen to exemplify this issue (Figure 61).

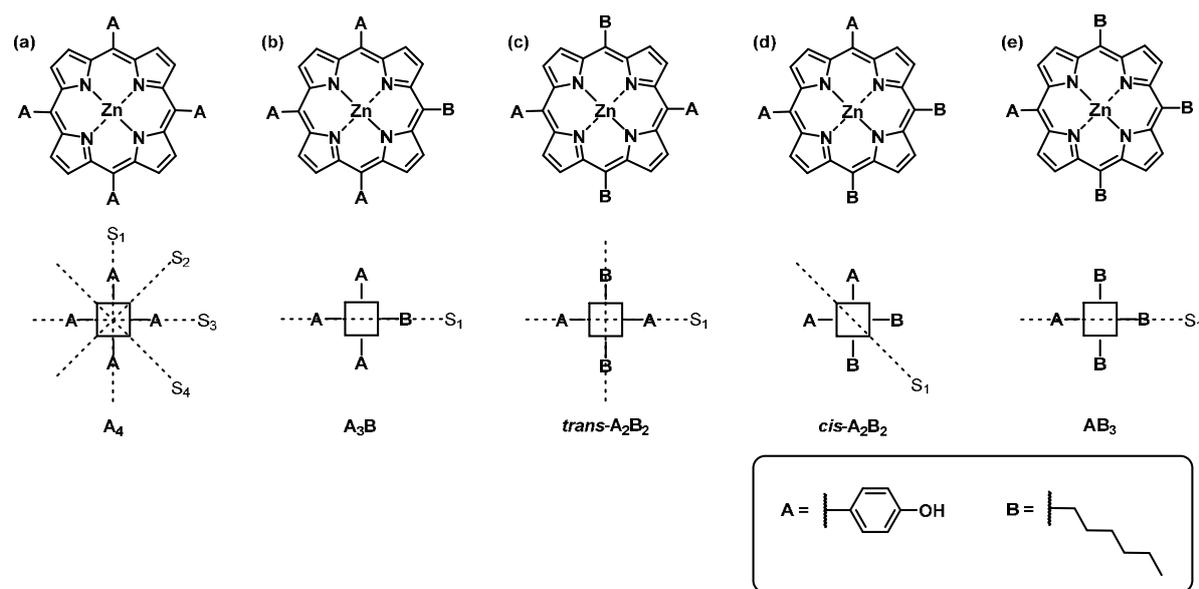


Figure 61. Selected A_4 -, A_3B -, *cis*- A_2B_2 -, *trans*- A_2B_2 -, AB_3 -porphyrins and their mirror planes.

While an A_4 -porphyrin (a) gives a singlet peak for all 8 pyrrole-H (each H has the same chemical environment), the A_3B -porphyrin (b) gives two doublets (each 2 H) and a multiplet (4 H) in a proton NMR. Since the *cis*- and *trans*- A_2B_2 -porphyrin, both with the same molecular mass, cannot be distinguished by HRMS, their ^1H -NMR spectra are crucial for structural elucidation. The substitution patterns for the 8 pyrrole-Hs of the *cis*-porphyrin (d) give two doublets (each 4 H) while the *trans*-porphyrin (c) gives two singlets and two doublets (each 2H). The AB_3 -porphyrin (e) has a similar substitution pattern like the A_3B -porphyrin, only the two doublets are shifted due to their different chemical environment.

Inspection of the *ortho*- and *meta*-positions of the aryl rings also indicates a certain substitution pattern. The A_4 -porphyrin with four aryl substituents (a) gives two doublets (each 8 H), the *cis*- (d) and *trans*-porphyrin (c) with two aryl substituents give two sharp doublets (each 4 H) whereas an A_3B - (b) and AB_3 -porphyrin (e) shows multiplets for these protons. It is noteworthy that *cis*- and *trans*-porphyrins can be distinguished based on their chemical shifts: a *trans*-porphyrin (c) as compared to the *cis*-form is shifted upfield by about 0.3-0.4 ppm.

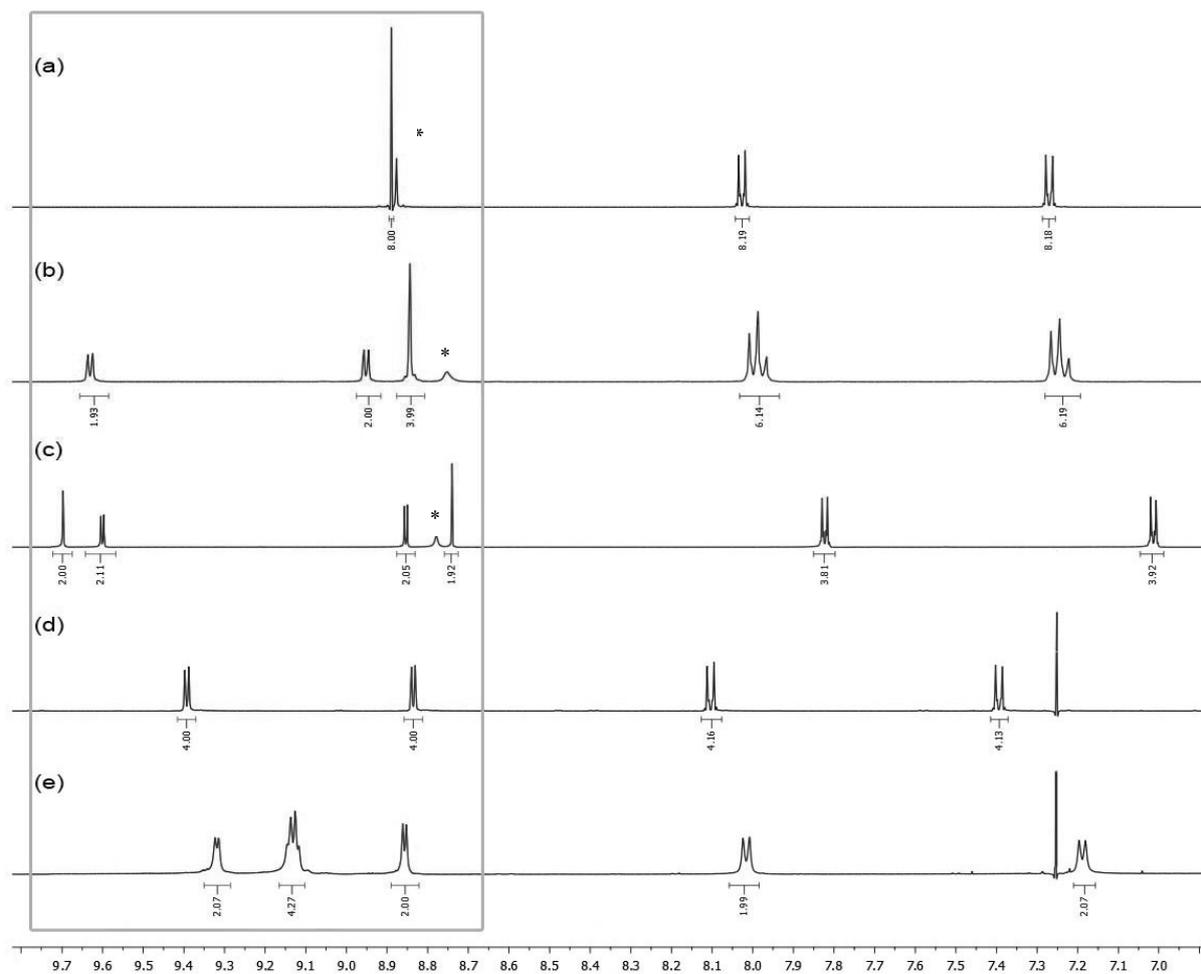


Figure 62. ^1H -NMR spectra comparison showing the characteristic substitution patterns of pyrrole protons due to their symmetry (OH peaks are marked with asterisk).

3.7.2 Monitoring of *para*-substituted PFP-Porphyrinoids by ^{19}F -NMR Spectroscopy

Mono-, di- (*cis*, *trans*), tri- and tetra-substituted PFP-porphyrins also provide quite characteristic substitution patterns in their ^{19}F -NMR spectra. The following examples from this thesis are chosen to highlight this issue (Figure 63).

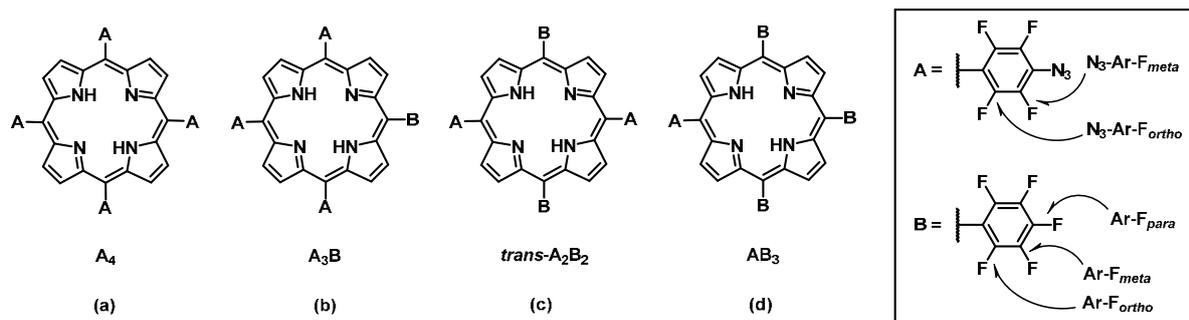


Figure 63. Selected A_4 -, A_3B -, *trans*- A_2B_2 - and AB_3 -PFP-substituted porphyrins from this thesis.

Analysis of the ^{19}F -NMR spectra (Figure 64) shows that every single Ar-F of each derivative can be identified. With each additional N_3 -substitution in *para*-position the fluorine substituents in *ortho*- and *meta*-position (Ar-F_{ortho} and Ar-F_{meta}) decrease (-2F) while the N_3 -fluorines in *ortho*- and *meta*-position ($\text{N}_3\text{-Ar-F}_{ortho}$ and $\text{N}_3\text{-Ar-F}_{meta}$) increase by the same value ($+2\text{F}$). Figure 64 also shows the stepwise decrease of fluorine in *para*-position (-1F).

Furthermore, the spectra show how easily e.g. $\text{S}_{\text{N}}\text{Ar}$ -reactions can be monitored. This was also a very useful tool for monitoring of the thioglycosylations of the corresponding PFP-substituted porphyrinoids (see chapter “Synthesis of Glyco-Porphyrinoids Using Glycosyl Thiolates” and “Synthesis of Porphyrins Containing Different Carbohydrate Moieties”). Porphyrinoids with incomplete thioglycosylation (mono- and/or dithioglycosylation) can easily be distinguished.

The same analytical tool can also be employed for more complicated and complex systems like *N*-fused [22]pentaphyrin, the mono-*meso*-spirolactone containing calix[4]phyrin and [26]- or [28]hexaphyrins. Here, a glance at the ^{19}F -NMR spectrum is usually more meaningful than any attempt at a full interpretation of the corresponding ^1H - or ^{13}C -NMR spectra.

Some of these ^{19}F -NMR spectra are e.g. shown and discussed in chapters 3.4.3, 3.4.4 or 3.6.3.

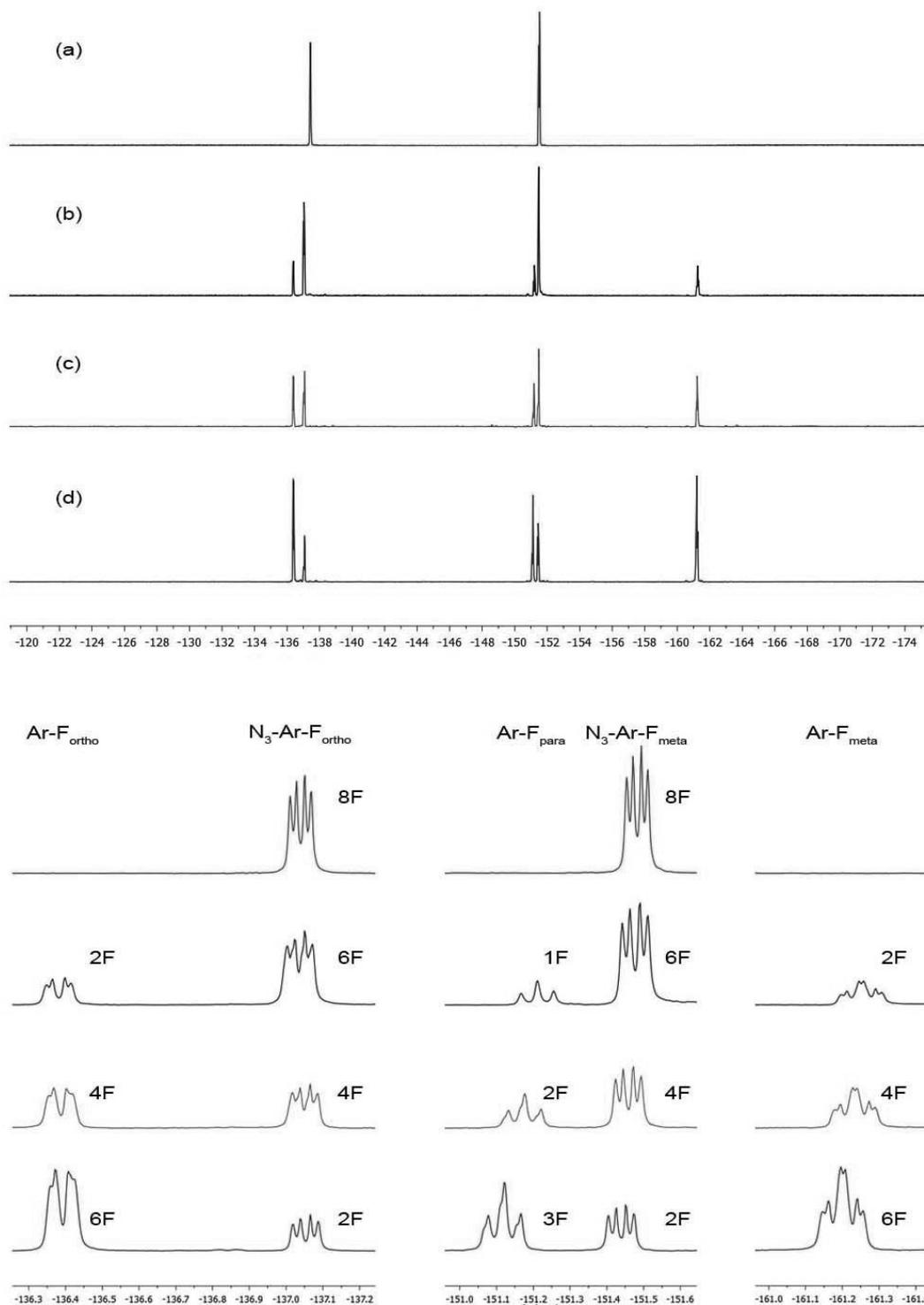


Figure 64. ¹⁹F-NMR spectra comparison showing the characteristic substitution patterns.

3.7.3 Comparison of Porphyrinoid Systems and Discussion of Their Spectra

The following porphyrinoids possess different symmetries and aromatic perimeters which directly influence their spectra. We will take a closer look at their $^1\text{H-NMR}$ spectra, focusing on the hydrogens in β -position and the NH-protons. The following porphyrinoids were selected:

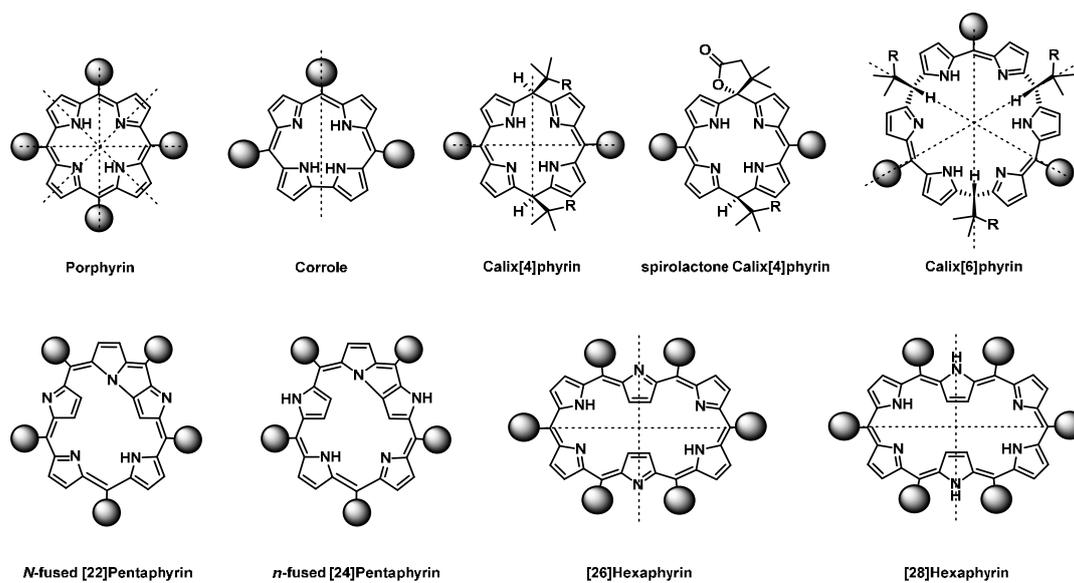


Figure 65. Selected porphyrinoids and their mirror planes (dots = PFP-units).

For porphyrins, as well as for corroles, the β -protons at the outer aromatic ring give signals which are strongly downfield shifted (between 8 and 10 ppm) due to their strong aromatic ring current effect. In contrast to the β -protons, the inner NH-protons are strongly upfield shifted (between 8 and 10 ppm). The presented A_4 -porphyrin gives a neat spectrum with a singlet (8H) for the β -protons and a singlet (2H) for the inner NH-protons due to its four mirror planes. The A_3 -corrole is less symmetric (only one mirror plane) resulting in a more complicated NMR spectrum with three doublets (each 2H) and a broad singlet (2H).

In contrast to these two compounds, the calix[n]phyrin systems are different because of the interrupted aromatic perimeter. While the β -protons are also shifted downfield (between 6 and 7 ppm), the NH-protons are strongly shifted downfield (between 12 and 14 ppm) which is significantly different as compared to porphyrins or corroles. The calix[4]- (two mirror planes) and calix[6]- (three mirror planes) basically have the same NMR spectrum albeit with a different integration pattern. Both have two doublets for the β -protons and a broad singlet for the inner NH-protons. The spectra of this compound class are similar to dipyrromethenes.

porphyrinoid system	NH-protons	β -protons
porphyrin	-2.90 br s, 2 H	8.94 s, 8 H
corrole		8.57 br s, 2 H 8.59 d, $J=4.6$ Hz, 2 H 8.77 d, $J=4.4$ Hz, 2 H 9.11 d, $J=4.1$ Hz, 2 H
calix[4]phyrin	12.92 br s, 2 H	6.32 d, $J=4.2$ Hz, 4 H 6.34 d, $J=4.3$ Hz, 4 H
meso-spirolactone calix[4]phyrin	12.79 br s, 2 H	6.35 d, $J=4.1$ Hz, 2 H 6.37 d, $J=3.9$ Hz, 2 H 6.38 d, $J=3.8$ Hz, 2 H 6.52 d, $J=4.0$ Hz, 2 H
calix[6]phyrin	13.34 br s, 3 H	6.38 d, $J=4.3$ Hz, 6 H 6.44 d, $J=4.3$ Hz, 6 H
<i>N</i> -fused [22]pentaphyrin	1.27 br s, 1 H	-2.22 s, 1 H (inner β -H) 1.74 d, $J=4.4$ Hz, 1 H (inner β -H) 2.23 d, $J=4.4$ Hz, 1 H (inner β -H) 8.37 d, $J=4.6$ Hz, 1 H (outer β -H) 8.41 d, $J=4.6$ Hz, 1 H (outer β -H) 8.44 d, $J=4.6$ Hz, 1 H (outer β -H) 8.63 d, $J=4.6$ Hz, 1 H (outer β -H) 9.16-9.19 m, 2 H (outer β -H)
<i>N</i> -fused [24]pentaphyrin	6.62 br s, 1 H (outer NH) 6.76 br s, 1 H (outer NH) 13.76 br s, 1 H (inner NH)	5.60 d, $J=5.9$ Hz, 1 H 5.87 d, $J=4.9$ Hz, 1 H 6.02 d, $J=4.9$ Hz, 1 H 6.05 d, $J=5.4$ Hz, 1 H 6.18 d, $J=5.9$ Hz, 1 H 6.21 d, $J=5.3$ Hz, 1 H 7.88 d, $J=1.9$ Hz, 1 H (inner β -H) 8.12 dd, $J=2.2, 3.9$ Hz, 1 H 8.19 dd, $J=2.2, 3.9$ Hz, 1 H
[26]hexaphyrin	-2.00 br s, 2 H	-2.41 br s, 4 H (inner β -H) 9.11 d, $J=4.6$ Hz, 4 H (outer β -H) 9.45 d, $J=4.6$ Hz, 4 H (outer β -H)
[28]hexaphyrin	4.57 br s, 4 H	2.63 s, 4 H (inner β -H) 7.61 d, $J=4.9$ Hz, 4 H (outer β -H) 7.70 d, $J=4.9$ Hz, 4 H (outer β -H)

Table 15. Comparison of NH- and β -protons of different porphyrinoid systems.

4. CONCLUSION AND OUTLOOK

4.1. Conclusion

(a) Library of Glyco-Porphyrins Using Glycosyl Trichloroacetimidates

One of the objectives and the focal point of this thesis was the development of a library of *meta*- and *para*-glycosylated porphyrins *via* the trichloroacetimidate method which was developed by AICHER and co-workers for a group of *meta*-substituted derivatives.^[53] In the course of this thesis different glycosyl trichloroacetimidates (glucosyl, galactosyl, mannosyl and lactosyl donors) have been synthesized as the functionalized glycone part. To obtain the aglycone part, Zn(II)-complexed hydroxyphenyl-substituted tetrapyrroles carrying additional lipophilic substituents were synthesized in 5-7 synthetic steps [lipophilic moieties: 3,5-bis-(trifluoromethyl)-phenyl, PFP, *n*-hexyl or phenyl substituents]. About 80 mostly new porphyrins were synthesized as precursors for the glycosylation reactions. The glycone and the aglycone then underwent the glycosylation promoted by the LEWIS acid BF₃·OEt₂. Thus, utilizing the trichloroacetimidate method (incl. demetallation and deprotection) a library of 25 predominantly novel *meta*- or *para*-substituted glyco-derivatives was obtained.

The influence of their different substitution patterns (different polarities, carbohydrate moieties and lipophilic substituents) on the photodynamic activity was investigated in tests against several cancer cell lines. It turned out that most glyco-conjugates showed cytotoxicity, but especially the glyco-substituted porphyrins with a *trans*-A₂B₂-substitution pattern showed very promising results. Selected mono- or *trans*-A₂B₂-glycosylated porphyrins which exhibited a very good cytotoxicity but are rather lipophilic were re-synthesized on a larger scale and were successfully incorporated into pharmaceutical formulations in the group of Prof. Fahr from the Friedrich-Schiller-Universität in Jena (Germany). Thus, in combination with such carrier systems these compounds are interesting for further *in vivo* investigations.

Besides the development of potential new photosensitizers another aim of this thesis was a more detailed investigation of the trichloroacetimidate method. During the preparation of the library of different glyco-porphyrins this method already proved its broad scope of applicability. Furthermore modifications and combinations of the trichloroacetimidate method were exemplified. While the lactosylation of a Cu-complexed corrole or the synthesis of a twofold functionalized, highly amphiphilic lactosylated *trans*-A₂B₂-porphyrin were successful, it should be noted that the OH-glycosylation of a β -dihydroxychlorin could not be accomplished *via* the trichloroacetimidate method.

(b) Glycosylations of Challenging Porphyrinoids Using Glycosyl Thiolates

Another aim of this thesis was the synthesis of glyco-porphyrinoids absorbing at other wavelengths than typical tetrapyrroles. The first approach of directly connecting a carbohydrate with a porphyrin scaffold *via* a triple bond in a SONOGASHIRA reaction (to enhance its absorption at higher wavelengths) worked only in the case of a mono-substitution, but not for a bis-substitution. Several optimization attempts did not change the outcome. Then the possibility of glycosylating new (expanded) porphyrinoid systems which strongly differ in their photophysical properties from porphyrins was investigated. Utilization of the thiolate method (nucleophilic aromatic substitution) led to (deprotected) glycosylated PFP-substituted dipyrromethane, *trans*-A₂B-corrole, calix[4]phyrin(1.1.1.1), calix[6]phyrin(1.1.1.1.1) and [28]hexaphyrin(1.1.1.1.1.1) systems which are the first reported in literature.

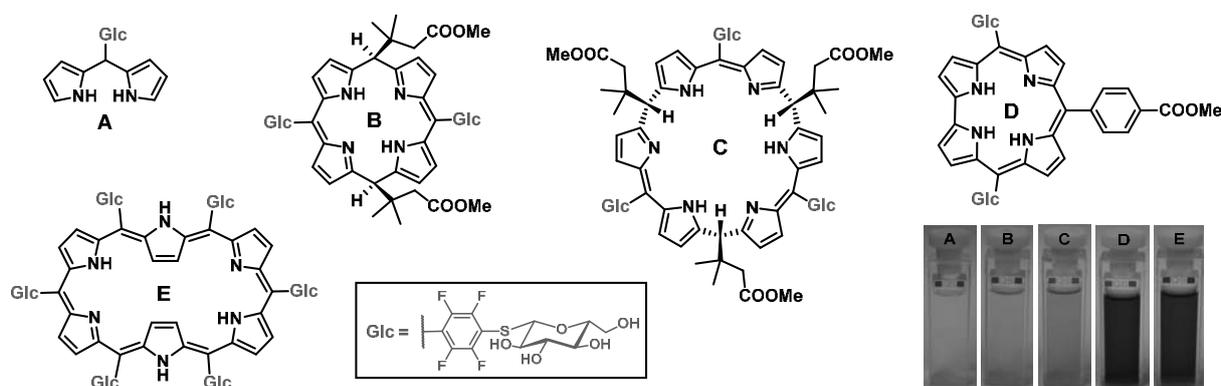


Figure 66. Novel thioglycosylated porphyrinoid systems and dipyrromethane precursor (A).

It is important to note that all new glycosylated porphyrinoids are easily soluble in alcohol/water mixtures thus fulfilling a crucial requirement for biomedical applications: the better compatibility with the aqueous biological environment. In the nucleophilic substitution reactions of challenging PFP-substituted porphyrinoids thiolates proved to be very precise and powerful tools regarding their high nucleophilicity leading to a controlled, regio- and stereoselective glycosylation. The *para*-substituted products were obtained as the only regioisomer with the expected β -orientation of the glycosidic bond. There is no need to use an excess of the nucleophile (which was found to cause undesired additional substitutions). No base was required so that the reaction proceeds under milder conditions making it also interesting for the coupling of other base-labile compounds. The reaction conditions described herein can be also used for the incorporation of other polar (bioactive) thiolates to prepare customized complex porphyrinoids and other macrocycles.

(c) Synthesis of Tetrapyrroles Containing Different Carbohydrate Moieties

Based on the knowledge gained during the synthesis of glyco-porphyrins *via* the trichloroacetimidate and thiolate method as well as using 1,3-dipolar “click” reactions in the course of the master thesis^[66] we undertook to combine these methods in order to obtain for the first time tetrapyrroles with different carbohydrate moieties in a rational synthetic approach. The synthesis of porphyrins carrying two different carbohydrate moieties was accomplished in two ways: The combination of the trichloroacetimidate method with thioglycosylation and the combination of “click” chemistry and thioglycosylation. The combination of the trichloroacetimidate method with thioglycosylation leads to A_3B -substituted porphyrins (A = *S*-monosaccharide, B = *O*-monosaccharide) in 6 consecutive reaction steps and to *trans*- A_2B_2 -substituted porphyrins (A = *S*-monosaccharide, B = *O*-disaccharide) in 8 consecutive reaction steps. The first synthesis of an A_3B -substituted porphyrin with two different monosaccharides, combining “click” reaction and the regioselective nucleophilic substitution reaction (A = *S*-monosaccharide, B = *triazole*-monosaccharide), was realized in 7 consecutive reaction steps. Thus it could be shown that these synthetic pathways provide a rational access to heteroglycosylated tetrapyrroles. Such mixed-glycosylation porphyrins may be advantageous for better binding to the cell membrane.^[47f]

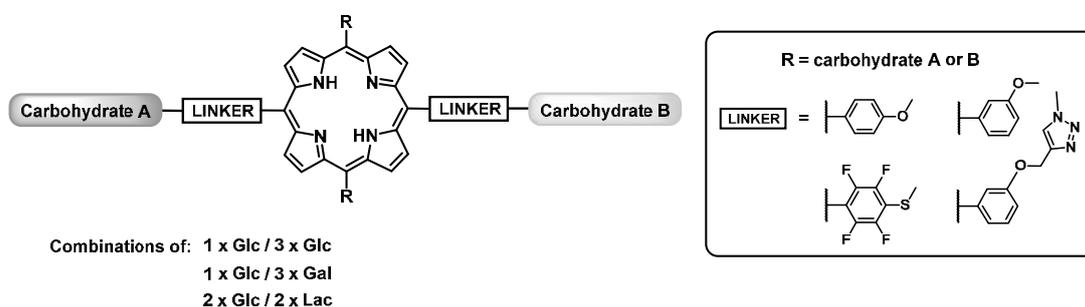


Figure 67. Representation of heteroglycosylated tetrapyrroles.

(d) Azido-Aldehydes as a Versatile Building Block for Novel Azide-Containing Porphyrinoids

In the last project the 4-azido-tetrafluorobenzaldehyde – accessible through the known nucleophilic substitution of pentafluorobenzaldehyde with sodium azide – was employed in different condensation reactions with dipyrromethanes and pyrrole leading to novel azido-porphyrinoids suitable for further functionalization reactions. Thus azido-substituted porphyrins, corroles, calix[*n*]phyrins, *N*-fused pentaphyrins and [*n*]hexaphyrins can be synthesized in a straightforward way starting from the azido-substituted aldehyde. If a pentafluorophenyl-substituted dipyrromethane is used in the condensation reaction porphyrins and hexaphyrins with a mixed substitution pattern are available (see Figure 68) which are susceptible to further nucleophilic functionalization reactions. Using these azido-substituted compounds in a consecutive reaction, like the 1,3-dipolar “click” reaction, a variety of available alkyne-containing substrates can be chosen to synthesize customized porphyrinoids for biomedical applications, catalysis or supramolecular assemblies.

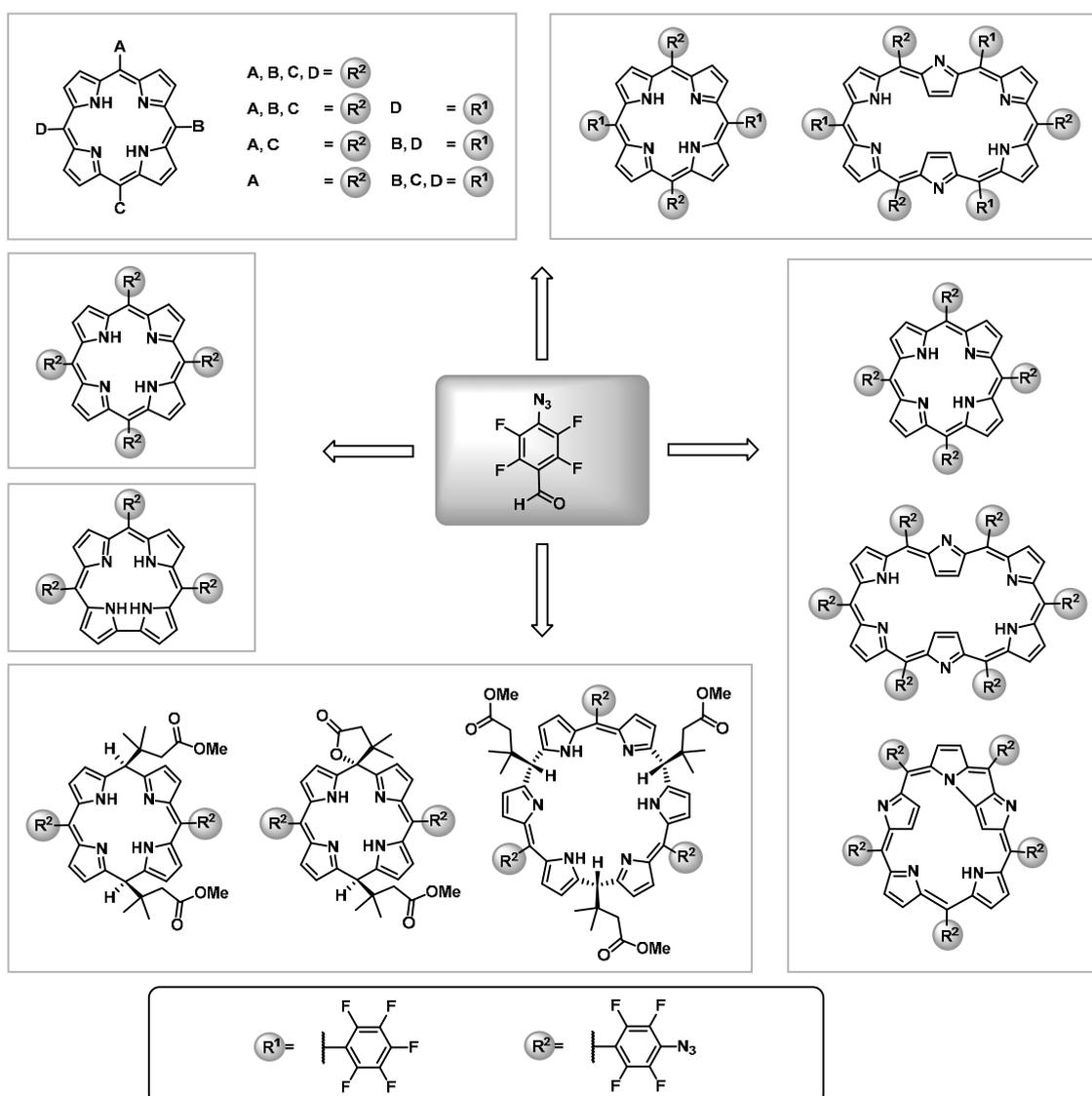


Figure 68. 4-Azido-tetrafluorobenzaldehyde as a building block for azide-containing porphyrinoids.

4.2. Outlook

The large variety of properties of porphyrinoids like porphyrins, corroles, calix[*n*]phyrins and [*n*]hexaphyrin systems or precursors like dipyrromethane has already been discussed in this thesis. Generally, it can be stated that most of these applications can now be transferred to more polar or even aqueous media because of the introduction of different carbohydrate moieties *via* combination of different strategies or methods investigated as part of the present work. Furthermore the introduced carbohydrate moieties usually give these porphyrinoids a better (tumor) targeting. Based on these two major properties, novel applications or future trends of these glyco-porphyrinoids are possible and will be depicted in this chapter.

Biomedical applications:

Glyco-porphyrins possess a huge potential for PDT. This has also been shown in this thesis regarding their evaluation against several cancer cell lines. Although various modifications have been exemplified, there are still other modifications conceivable like e.g. the *O*-sulfatation of the carbohydrate moieties leading to an even higher hydrophilicity (Figure 69).

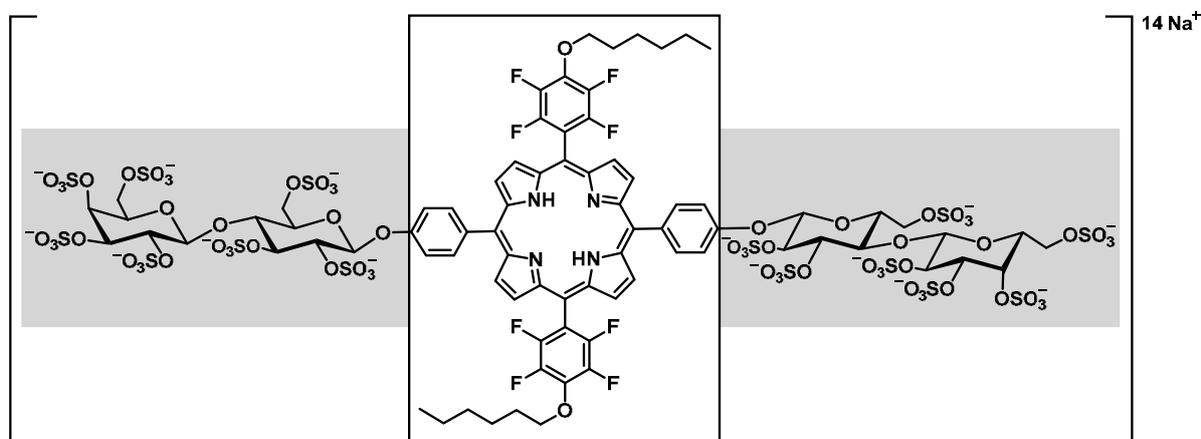


Figure 69. Hydrophilic porphyrin with *O*-sulfated carbohydrate moieties.

Instead of mono- or disaccharide moieties it would also be possible to introduce α -, β -, γ - or δ -cyclodextrins into tetrapyrroles. These moieties could be used as targeting groups, but also possess the property to act as a carrier for drugs (Figure 70). For treatment of malignant tumor cells this bears two advantages: on the one hand a drug (e.g. a cytostatic compound) for chemotherapy can be carried within the cyclodextrin unit to the tumor cell and on the other hand the cyclodextrin unit acts as targeting group for the tetrapyrrole for PDT. Such a combination of chemotherapy and photodynamic therapy was described by KRÁL and co-workers for porphyrins,^[93] but could be also applied to other

porphyrinoids like corroles, calix[*n*]phyrins or hexaphyrins based on our modified protocol for thioglycosylations.

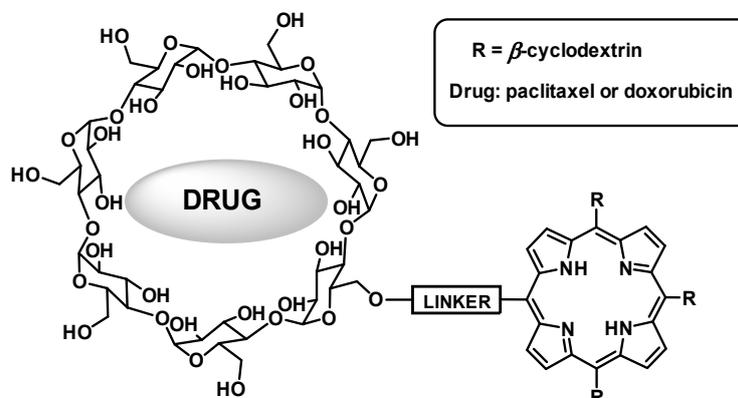


Figure 70. Cyclodextrin-substituted tetrapyrrole as possible carrier for drugs.

Furthermore with the novel thioglycosylated [28]hexaphyrin, a step towards PDT 2.0 is possible. It is one of the first hexaphyrins with biomolecule moieties and therefore a promising two-photon absorber (TPA) for biological environments. This property does not only make it an interesting candidate for an effective treatment of malignant cancer, but it could also be a candidate for the treatment of the common age-related macular degeneration (AMD). In the latter blood-vessels of the eyes grow in an uncontrolled manner which leads to severe impaired vision and finally to blindness.

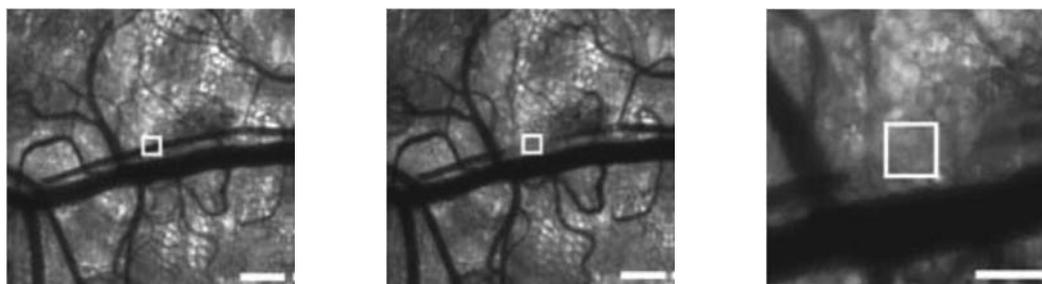


Figure 71. *In vivo* two-photon blood-vessel closure with another TPA (porphyrin-dimer) by ANDERSON and co-workers (scale bar, 200 μm). Left picture shows blood-vessel before treatment, middle and right pictures clearly shows the closure.^[94] Copyright 2008 Nature Publishing Group (Nature Photonics).

Here TPA is in current focus because the dye simultaneously absorbs two lower energy photons to arrive at the same excited state as in single photon absorptions making three-dimensional manipulation of treatments volumes possible, in case of AMD to precisely close the corresponding vessel.^[94] For this purpose our developed thioglycosylated hexaphyrin could be an interesting candidate.

In contrast to porphyrins, corroles are trianionic ligands and can stabilize high valent metal ions like e.g. Ga(III)^[95] making them suitable as MRI contrast agents. The chances to obtain potential contrast

reagents *via* re-synthesizing the two glyco-corroles, already prepared in this thesis, in their Ga(III)-metallized form should be examined in the future.

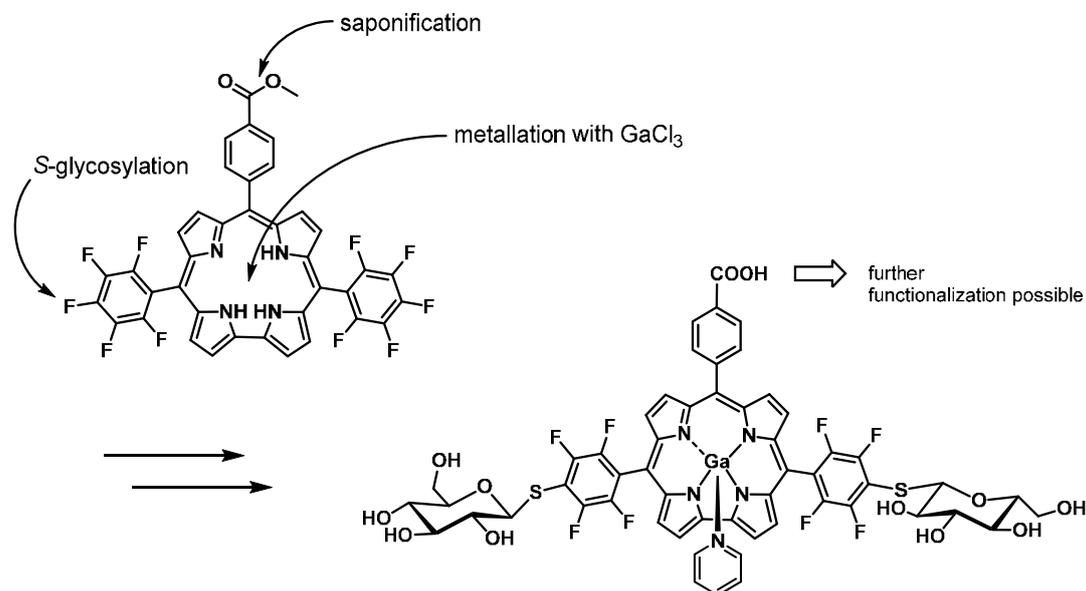


Figure 72. Possible thioglycosylated Ga(III)-metallated corrole as potential MRI contrast reagent.

Furthermore, it should be noted that most of the synthesized glyco-porphyrinoids also have the potential for utilization as antibacterial or antiviral compounds.^[96] Especially, the glyco-calix[*n*]phyrins could be interesting for antimicrobial treatment of Leishmaniasis. This effect has already been shown for dipyrromethenes^[97] and since calixphyrins can be considered as methane-bridged dipyrromethenes it would be interesting to study their antileishmanial activity. Another prospect would be the thioglycosylation of a PFP-substituted BODIPY. Here the modified glycothiolate protocol could be used to prepare a fluorescence marker with a promising targeting motif.

Applications in Catalysis:

The focal point of this thesis is mainly related to biomedical aspects, so this outlook on applications in catalysis is less extensively discussed.

It is well known that most of the porphyrinoids are capable of binding various metals. Referring to a recent publication about Ru-metallated glyco-porphyrins and their application as catalysts,^[12g] it is possible to use our trichloroacetimidate or slightly adapted thioglycosylation protocol to efficiently build similar water-soluble systems for catalysis (Figure 73). This shows the potential of glyco-porphyrins, synthesized *via* the trichloroacetimidate method originally for PDT purposes, which can be easily converted to their metal complexes, e.g. ruthenium, directly leading to highly interesting compounds for catalysis. Some of them could also lead to potent catalysts for carbenoid transfer

reactions like e.g. inter- or intramolecular cyclopropanations, [2,3]-sigmatropic rearrangements of diazoketones or intermolecular carbenoid *N*-H insertions.

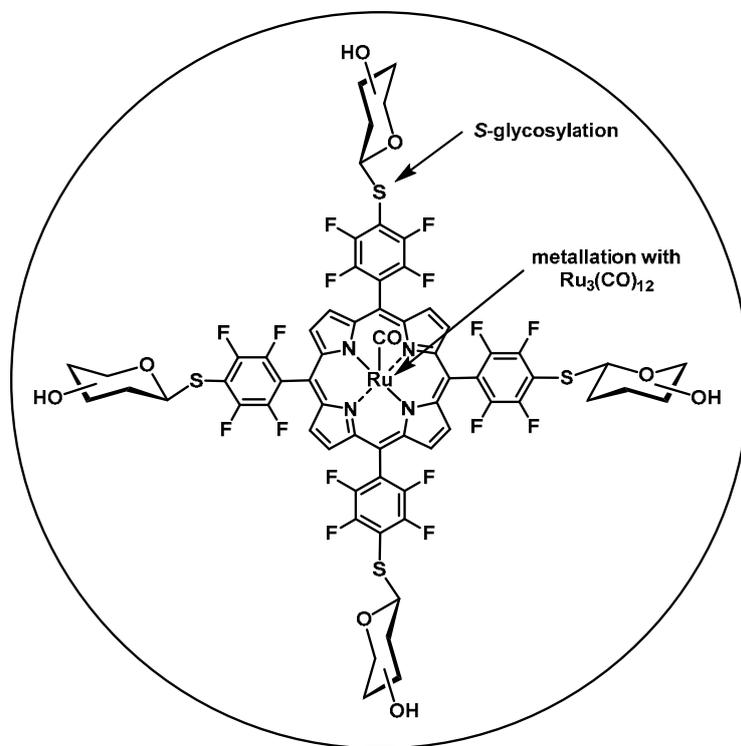


Figure 73. Ru-metallated glyco-porphyrin as water-soluble catalyst for carbenoid transfer reactions.

It should be stated that basically all synthesized glyco-porphyrinoids in this thesis can be complexed with diverse metals. Dependent on the metal and the chosen glyco-porphyrinoid system, customized catalytic systems can be generated (aerobic oxidation,^[98] oxygen transfer,^[99] water oxidation^[100] or hydrogen generation.^[101]

Supramolecular Chemistry and Other Complex Molecular Architectures:

In the research field of supramolecular chemistry, especially the novel azide-containing porphyrinoids with different substitution patterns could serve as valuable precursors for complex architectures which then can fulfill new functions. Dimeric, trimeric, tetrameric up to oligomeric porphyrin-, corrole-, calixphyrin-, pentaphyrin- or hexaphyrin-systems are possible using the azido-porphyrinoids as a tool kit (Figure 74), as well as combinations of these subclasses of porphyrinoids. For example hetero-tetrameric calix[*n*]systems (azidated calix[6]phyrin as precursor and three triple bond containing calix[4]phyrins) could be synthesized *via* Cu(I)-catalyzed ‘click’ chemistry without insertion of copper because these systems with their non-planar and unique roof-type structure are not able to complex this metal.^[27b] Further functionalizations are possible by S_nAr into PFP-substituents to manipulate their polarity for the corresponding medium (Figure 75). They could be studied regarding their applicability as ion sensors.^[26a]

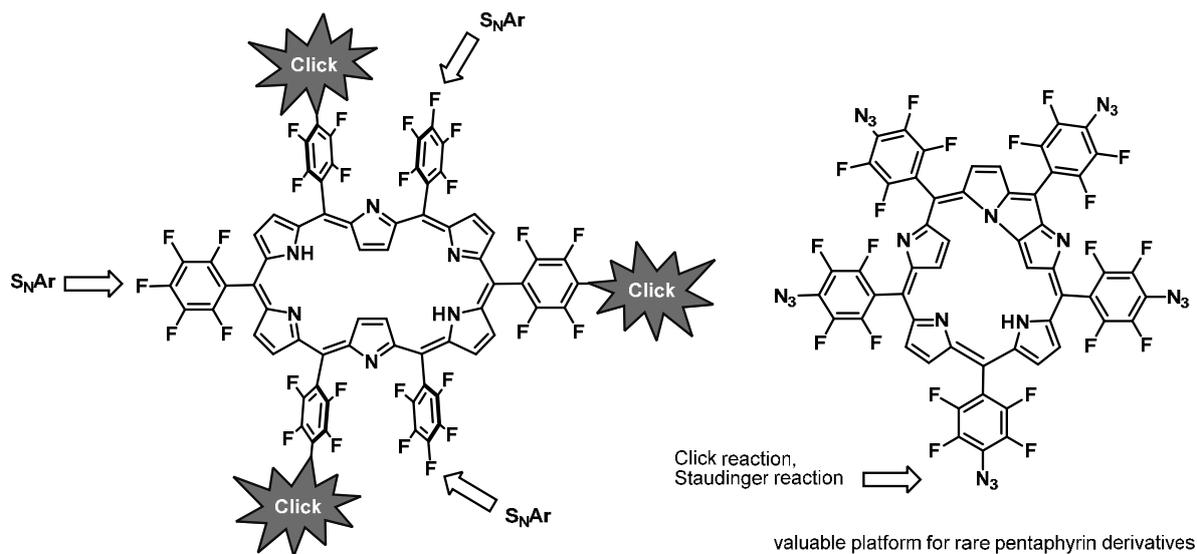


Figure 74. Novel azide-containing A_3B_3 -[26]hexaphyrin and A_5 -[22]NFP systems as valuable precursors

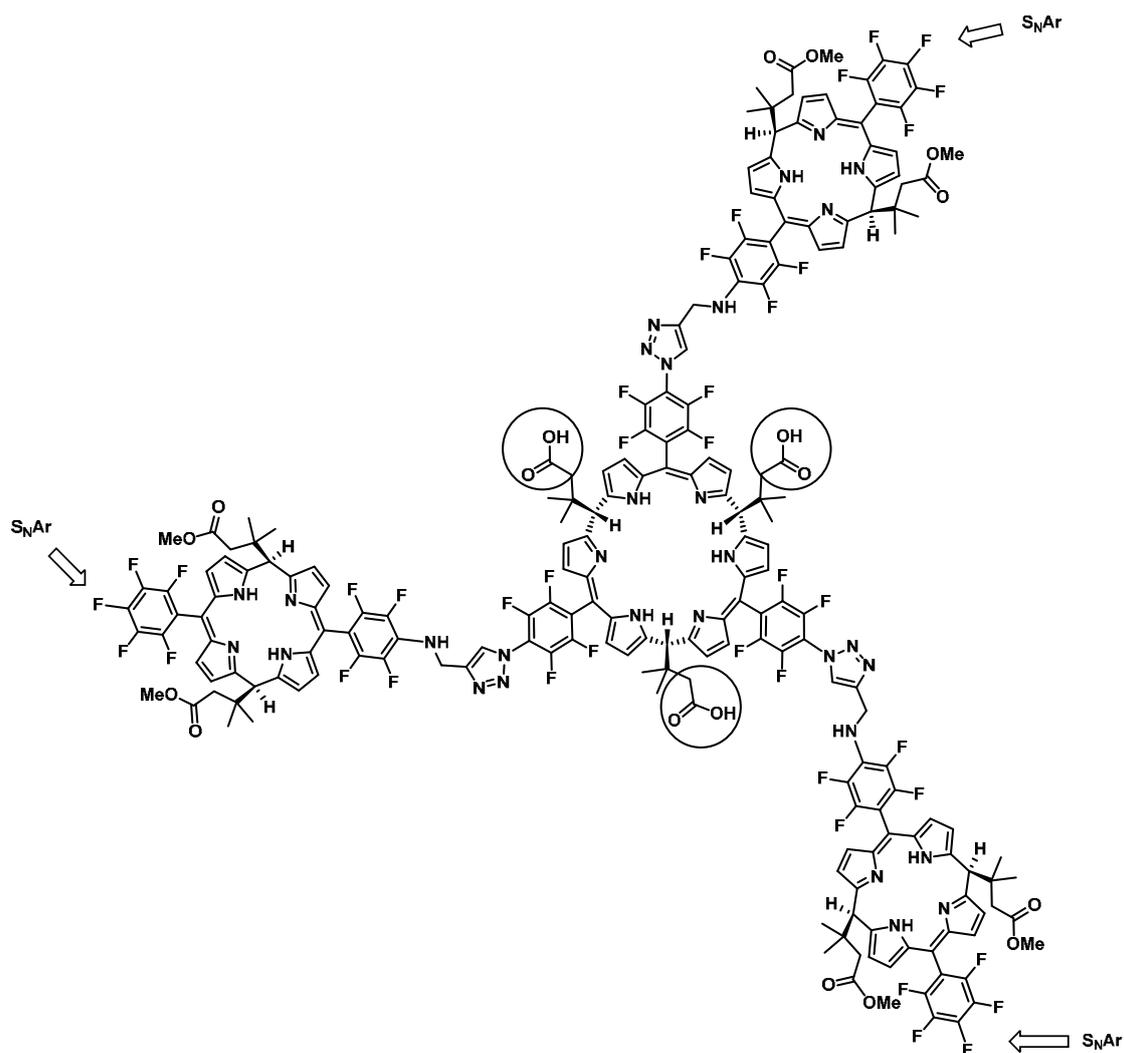


Figure 75. Azide-containing porphyrinoids as valuable precursors for hetero-tetrameric calix[n] systems

Furthermore the azido-porphyrinoids can be used in “click” reactions for the preparation of so-called supramolecular cages where other molecules like e.g. a Buckyball can be trapped and to study the guest-host behavior. Similar to ANDERSON and co-workers^[102] the azido-porphyrinoids could be used for the synthesis of nanorings or -tubes. They could also be valuable precursors for Pacman or Hangman porphyrins,^[103] efficient light harvesting antenna or artificial photosynthesis systems^[104] or simply the introduction of other functional groups (e.g. biomolecules). It is also noteworthy to mention that the azide moieties can be reduced, e.g. in a STAUDINGER reaction, to the corresponding amines and then these amino-porphyrinoids could react with a range of carboxylic acid-containing molecules.

5 EXPERIMENTAL SECTION

5.1 Materials and Methods

Chemical Names of compounds and their numbering were determined with due regard to the IUPAC nomenclature. The *cis/trans* notation was used to describe the substitution pattern of A₂B₂ porphyrins in *meso*-position.

Solvents used in this work were distilled prior to use. For porphyrin condensations dichloromethane was freshly distilled from potassium carbonate. Extra-dry solvents, stored over molecular sieves, like dichloromethane, tetrahydrofuran, methanol, dimethylformamide and dimethyl sulfoxide were purchased commercially.

Chemicals used in this work were purchased from *Merck*, *Fluka*, *Sigma-Aldrich*, *Acros Organics* and *Alfa Aesar* and were used without any further purification.

Melting Points were measured with a *Reichert* ThermoVar apparatus and are uncorrected.

Thin Layer Chromatography (TLC) was carried out on *Merck* silica gel 60 (with fluorescence indicator F₂₅₄ or without fluorescence indicator) or reversed phase *Merck* silica gel 60 (with fluorescence indicator F₂₅₄) pre-coated on aluminium sheets. For porphyrins and chlorins visualization was achieved with a CAMAG variable UV detector ($\lambda = 254/366$ nm) because of their inherent fluorescence. For other substances visualization was performed by using wavelength $\lambda = 254$ nm or by treatment with solutions of potassium permanganate, anisaldehyde or cerium(IV) sulfate.

Column Chromatography was accomplished on *Fluka* silica gel 60, 0.040-0.063 mm (230-400 mesh), neutral *Fluka* aluminium oxide gel (0.05-0.15 mm, pH 7.0 \pm 0.5) or on reversed phase *Sigma Aldrich* silica gel 60, 0.035-0.070 mm (220-400 mesh). Purification of the eluents was done as mentioned above.

Elemental Analysis (EA) was generally not performed and was substituted by high-resolution mass spectrometry because solvents or impurities can be trapped *via* recrystallization of tetrapyrroles and due to this fact the results of elemental analysis are inaccurate.^[105]

High-Resolution Mass Spectrometry (HRMS) analyses were recorded with an Agilent 6210 ESI-TOF (ESI-TOF = electrospray ionization/time of flight) instrument from Agilent Technologies, Santa Clara, CA, USA. The spray voltage was 4 kV and the solvent flow rate was adjusted to 4 μ Lmin⁻¹. The drying gas flow rate was 15 psi (1 bar)

NMR Spectroscopy was conducted on machines from *Bruker* (AC 250, AC 500, AVIII 700) and *JEOL* (Eclipse 500). The dimension of the chemical shift δ is given in ppm with the used solvents as references (chloroform- d_1 : $\delta = 7.26$ ppm for ^1H or $\delta = 77.16$ ppm for ^{13}C ; methanol- d_4 : $\delta = 3.31$ and 4.78 ppm for ^1H or $\delta = 49.00$ ppm for ^{13}C ; acetone- d_6 : $\delta = 2.05$ ppm for ^1H or $\delta = 29.84$ and 206.26 ppm for ^{13}C ; DMSO- d_6 : $\delta = 2.50$ ppm for ^1H or $\delta = 39.52$ ppm for ^{13}C ; tetrahydrofuran- d_8 : $\delta = 1.73$ and 3.58 ppm for ^1H or $\delta = 25.37$ and 67.57 ppm for ^{13}C). Multiplicities in ^1H -NMR spectra are labelled as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, m = multiplet and m_c = centered multiplet. Signals denoted "br = broad" are significantly broadened or not clearly resolved. For an unambiguous assignment two-dimensional COSY, HMQC and HMBC spectra were used.

UV/Vis Spectroscopy was conducted on a Specord S 300 spectrophotometer from *Analytik Jena* using dichloromethane, acetone, methanol, ethanol or DMSO as solvents and quartz cuvettes of 1 cm path length.

Optical rotations were measured with the polarimeter *POLAR L μ P* from *IBZ Messtechnik* ($\lambda = 589$ nm, sodium D-emission, quartz cuvette, layer width: 1 dm) and are given in $^\circ$ (angle). The concentration (c) is given in g/100 ml. The measuring mistake from this apparatus is $\pm 5^\circ$. It should be noted that the optical rotation cannot be determined for porphyrins, corroles, pentaphyrins and hexaphyrins (absorption of light by the dye even at high dilutions).

Yield Calculations of mixed porphyrin condensations are based on pyrrol for each resulting structural isomer. Hence the reaction is considered as an overall reaction. All single yields can thus be summed up to a theoretical total yield of 100%. Yield calculations based on the aldehyde would not lead to a useful total yield.

5.2 General Procedures

GP I: Regioselective, anomeric deacetylation of peracetylated carbohydrates^[72]

Glacial acetic acid is added dropwise to a solution of ethylenediamine in THF. After the addition of the peracetylated carbohydrate, the reaction mixture is stirred overnight. Water is added and the aqueous layer is extracted with dichloromethane. The combined organic layers are washed four times with water, dried over sodium sulfate and the solvent is evaporated under reduced pressure. Further purification is achieved by column chromatography and recrystallization, if necessary.

GP II: Synthesis of (5-substituted) dipyrromethanes^[84]

The appropriate aldehyde is dissolved in an excess of pyrrole at room temperature under an argon atmosphere. Then TFA is added and the reaction is stirred for 30 min. The reaction mixture is treated with a 0.1 N NaOH solution. Then the aqueous layer is extracted three times with ethyl acetate. The combined organic layers are washed three times with water, dried over sodium sulfate and the solvent plus the residual pyrrole is evaporated under reduced pressure. Further purification is achieved by column chromatography and/or a Kugelrohr distillation.

GP III: Synthesis of porphyrins according to LINDSEY^[6]

Pyrrole and the appropriate aldehyde are dissolved in freshly distilled dichloromethane under an argon atmosphere and subsequently TFA is added. The reaction is stirred at room temperature and exclusion of light for 12 hours. Then a suspension of DDQ in dichloromethane is added and the reaction mixture is stirred for an additional hour. After neutralization with triethylamine, the mixture is filtered through silica gel and the solvent is removed *in vacuo*. Further purification is achieved by column chromatography and recrystallization.

GP IV: Synthesis of *trans*-A₂B₂-porphyrins *via* condensation of dipyrromethanes^[84b]

The (5-substituted) dipyrromethane and the appropriate aldehyde are dissolved in freshly distilled dichloromethane under an argon atmosphere and subsequently TFA is added. The reaction is stirred at room temperature and exclusion of light for 12 hours. Then a suspension of DDQ in dichloromethane is added and the reaction mixture is stirred for an additional hour. After neutralization with triethylamine, the mixture is filtered through silica gel and the solvent is removed *in vacuo*. Further purification is achieved by column chromatography and recrystallization.

GP V: Hydrolysis of porphyrin esters under basic conditions

The appropriate tetrapyrrole is dissolved in THF and a solution of methanolic potassium hydroxide is added. After full conversion, water and HCl (25%) are added to the reaction mixture until the pH value reached 4-5. Then the aqueous layer is extracted with either dichloromethane or ethyl acetate. The combined organic layers are washed three times with water, dried over sodium sulfate and the solvent is evaporated under reduced pressure. Further purification is achieved by column chromatography and recrystallization.

GP VI: Metallation of the free base porphyrins with zinc acetate

The tetrapyrrole is dissolved in a mixture of dichloromethane/methanol and zinc acetate dihydrate is added. The reaction is stirred overnight. After the addition of water, the aqueous layer is extracted three times with either dichloromethane or ethyl acetate. The combined organic layers are washed three times with water, dried over sodium sulfate and the solvent is evaporated under reduced pressure. Further purification is achieved by column chromatography and recrystallization.

GP VII: Glycosylation of peripheral hydroxyl groups with trichloroacetimidates^[53]

The metallated hydroxyporphyrin is dissolved in dry dichloromethane under an argon atmosphere and the appropriate trichloroacetimidate followed by catalytic amounts of boron trifluoride etherate are added subsequently at 0 °C. After full conversion, water is added to the reaction mixture. Then the aqueous layer is extracted with dichloromethane. The combined organic layers are washed two times with water, dried over sodium sulfate and the solvent is evaporated under reduced pressure. For demetallation the residue is dissolved in THF and HCl (25%) is added. After full conversion, water is added to the reaction mixture. The aqueous layer is extracted with dichloromethane. The combined organic layers are washed two times with water, dried over sodium sulfate and the solvent is evaporated under reduced pressure. Further purification is achieved by column chromatography and recrystallization.

GP VIII: Deacetylation of glycosylated tetrapyrrools with sodium methanolate

The glycosylated tetrapyrrole derivative is dissolved in dry methanol or dry THF/methanol (1:1) under an argon atmosphere and a solution of sodium methanolate in dry methanol is added. After full conversion, the solvent is evaporated under reduced pressure and purification is achieved by column chromatography and recrystallization or, if too polar, by washing with unpolar solvents.

GP IX: Synthesis of corroles *via* condensation of dipyrromethanes

The (5-substituted) dipyrromethane and the appropriate aldehyde are dissolved in freshly distilled dichloromethane under an argon atmosphere and subsequently TFA is added. The reaction is stirred at room temperature and exclusion of light for 12 hours. Then a suspension of DDQ in dichloromethane is added and the reaction mixture is stirred for six hours. After neutralization with triethylamine, the mixture is filtered through silica gel and the solvent is removed *in vacuo*. Further purification is achieved by column chromatography and recrystallization.

GP X: Synthesis of corroles according to GRYKO^[21]

The (5-substituted) dipyrromethane and the appropriate aldehyde (for A₂B-corroles) or pyrrole and the appropriate aldehyde (for A₃-corroles) are dissolved in a methanol/water mixture (1:1) without using inert reaction conditions. Subsequently HCl (36%) is added. The reaction is stirred at room temperature for 1 hour. Then the mixture is extracted three times with dichloromethane. The combined organic layers are washed three times with water, dried over sodium sulfate and the solvent is evaporated under reduced pressure. The residue is dissolved in dichloromethane and DDQ is added. After 4 hours stirring at room temperature (for A₂B-corroles) or 1 hour at 50 °C (for A₃-corroles), purification is achieved by column chromatography and a recrystallization from dichloromethane/*n*-pentane.

GP XI: Synthesis of calix[*n*]phyrins *via* sterically congested dipyrromethanes^[27a]

The sterically congested (5-substituted) dipyrromethane and the appropriate aldehyde are dissolved in freshly distilled dichloromethane under an argon atmosphere and subsequently TFA (acid loading: 100 mol-%) is added. The reaction is stirred at room temperature and exclusion of light for 18 hours. Then a suspension of DDQ in dichloromethane is added and the reaction mixture is stirred for 2 additional hours. After neutralization with triethylamine, the mixture is filtered through silica gel and the solvent is removed *in vacuo*. Further purification is achieved by column chromatography and recrystallization.

GP XII: Synthesis of expanded porphyrinoids^[37b,106]

For the synthesis of expanded porphyrinoids with an even number of pyrrole units (pathway A), the (5-substituted) dipyrromethane and the appropriate aldehyde are dissolved in freshly distilled dichloromethane under an argon atmosphere at 0 °C and subsequently MSA (2.5 N in CH₂Cl₂, acid loading: 10 mol-%) is added. Alternatively for the synthesis of expanded porphyrinoids with even and uneven number of pyrrole units (pathway B), pyrrole and the appropriate aldehyde are dissolved in

freshly distilled dichloromethane under an argon atmosphere at room temperature and subsequently $\text{BF}_3 \cdot \text{OEt}_2$ (2.5 N in CH_2Cl_2 , acid loading: 16 mol-%) is added. In both cases the resulting mixture is stirred for only 2 hours, then a suspension of DDQ in dichloromethane is added and the reaction mixture is stirred for another 10 hours. For both pathways the mixture is passed through a short alumina column to remove the tar and the solvent is removed *in vacuo*. Further purification is achieved by column chromatography (dichloromethane/*n*-hexane) and recrystallization (*n*-pentane or *n*-hexane).

GP XIII: Synthesis of thioglycosylated porphyrinoids

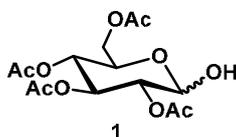
A standard reaction was performed in a heated 10ml two-necked round-bottom flask which was fitted with an inlet port for argon and a septum port. Under an argon atmosphere, the corresponding PFP-substituted porphyrinoid or porphyrin precursor was dissolved in dry DMF. After the starting material was fully dissolved, the carbohydrate thiolate (mostly 1.2 equivalents per PFP-unit) was added. The reaction mixture was stirred in the dark at room temperature for a specific time as indicated for each individual experiment. The progress of nucleophilic substitutions was monitored by TLC. After the times indicated, the glycosylated calix[6]phyrin and [28]hexaphyrin, due to their high polarity and poor separation in the separation funnel, were quenched with water and directly evaporated to dryness using a rotary evaporator. For all other porphyrinoids, the reaction mixtures were quenched with water, after the time indicated, and transferred to a separatory funnel. Ethyl acetate was added and the organic phases were washed with water, dried over anhydrous sodium sulfate and the solvent was evaporated to dryness using a rotary evaporator. Finally all porphyrins were applied to silica gel column chromatography using dichloromethane/methanol mixtures or reverse phase silica gel chromatography using methanol/water mixtures.

5.3 Experimental Data

2,3,4,6-Tetra-*O*-acetyl-D-glucopyranosyl trichloroacetimidate (2):

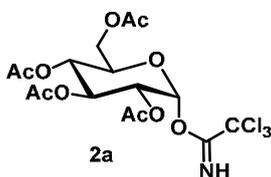
According to the general procedure I, β -D-glucose pentaacetate (3.90 g, 9.99 mmol), ethylenediamine (0.80 ml, 12.0 mmol) and glacial acetic acid (0.80 ml, 14.0 mmol) were reacted in THF (250 ml). Purification was achieved by column chromatography on silica using *n*-hexane/acetone (3:2) as the eluent to obtain tetraacetylated glucose **1** (3.08 g, 89%).

Subsequently, tetraacetylated glucose **1** (3.00 g, 8.61 mmol) was dissolved in dry dichloromethane (20 ml) under an argon atmosphere and trichloroacetonitrile (2.50 ml, 24.9 mmol) was added, followed by potassium carbonate (2.10 g, 15.2 mmol). The reaction mixture was stirred for 2 h. Then dichloromethane (100 ml) was added and remaining potassium carbonate was filtered off. After the solvent was evaporated under reduced pressure, purification was achieved by column chromatography on silica using *n*-hexane/acetone (3:2) as the eluent. The anomeric mixture **2** could be separated by recrystallization from *n*-hexane/acetone. The β -anomer **2b** (1.68 g, 40%) precipitated as a colorless solid which was filtered off. The resulting filtrate gave the α -anomer **2a** (1.08 g, 26%) as a yellow oil.

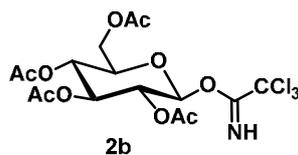


¹H-NMR (250 MHz, CDCl₃): δ = 2.00 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 3.86-3.92 (m, 1 H, H'ose'), 4.23-4.30 (m, 1 H, H'ose'), 5.24-5.34 (m, 3 H, H'ose'), 6.07 (d, J = 2.7 Hz, 1 H, H-1'ose') ppm.

HRMS (ESI-TOF): m/z calcd. for C₁₄H₂₀O₁₀Na [M + Na]⁺: 371.0954, found: 371.0964.



¹H-NMR (250 MHz, CDCl₃): δ = 2.00 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 3.89 (ddd, J = 2.7, 4.5, 10.0 Hz, 1 H, H-5'ose'), 4.14 (ddd, J = 2.2, 4.6, 10.3 Hz, 1 H, H-6_A'ose'), 4.24 (dd, J = 4.6, 12.8 Hz, 1 H, H-6_B'ose'), 5.10 (dd, J = 3.6, 10.3 Hz, 1 H, H-2'ose'), 5.16 (dd, J = 9.8, 10.3 Hz, 1 H, H-3'ose'), 5.55 (dd, J = 9.8, 10.3 Hz, 1 H, H-4'ose'), 6.54 (d, J = 3.6 Hz, 1 H, H-1'ose'), 8.67 (s, 1 H, NH) ppm.



¹H-NMR (250 MHz, CDCl₃): δ = 2.00 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 3.89 (ddd, J = 2.7, 4.5, 10.0 Hz, 1 H, H-5'ose'), 4.14 (dd, J = 2.7, 12.7 Hz, 1 H, H-6_A'ose'), 4.30 (dd, J = 4.5, 12.7 Hz, 1 H, H-6_B'ose'), 5.16-5.23 (m, 1 H, H-4'ose'), 5.26-5.32 (m, 2 H, H'ose'), 5.83-5.87 (m, 1 H, H-1'ose'), 8.70 (s, 1 H, NH) ppm.

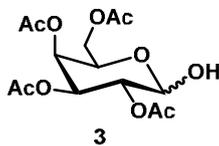
HRMS (ESI-TOF): m/z calcd. for C₁₆H₂₀Cl₃NO₁₀Na [M + Na]⁺: 516.0046, found: 516.0019.

Analytical data are in accordance with published data.^[107]

2,3,4,6-Tetra-*O*-acetyl-D-galactopyranosyl trichloroacetimidate (4):

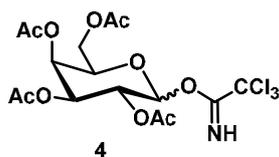
According to the general procedure I, β -D-galactose pentaacetate (7.80 g, 20.0 mmol), ethylenediamine (1.60 ml, 24.0 mmol) and glacial acetic acid (1.60 ml, 28.0 mmol) were reacted in THF (400 ml). Purification was achieved by column chromatography on silica using *n*-hexane/acetone (3:2) as the eluent to obtain tetraacetylated galactose **3** (6.03 g, 87%).

Subsequently, tetraacetylated galactose **3** (6.00 g, 17.2 mmol) was dissolved in dry dichloromethane (75 ml) under an argon atmosphere and trichloroacetonitrile (7.50 ml, 74.8 mmol) was added, followed by a dispersion of 60% NaH in mineral oil (0.60 g, 15.1 mmol). The reaction mixture was stirred for 2 h. Then dichloromethane (80 ml) was added and remaining NaH was filtered off. After the solvent was evaporated under reduced pressure, purification was achieved by column chromatography on silica using *n*-hexane/acetone (3:2) as the eluent to obtain trichloroacetimidate **4** (6.24 g, 63%) as a yellow solid. The α -/ β -anomeric ratio is 10:1.



¹H-NMR (250 MHz, CDCl₃): δ = 1.97 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), 2.08 (s, 3 H, OAc), 2.12 (s, 3 H, OAc), 3.05 (br s, 1 H, OH), 4.06-4.14 (m, 2 H, H'ose'), 4.42-4.47 (m, 1 H, H'ose'), 5.11-5.17 (m, 1 H, H'ose'), 5.36-5.51 (m, 3 H, H'ose') ppm.

HRMS (ESI-TOF): m/z calcd. for C₁₄H₂₀O₁₀Na [M + Na]⁺: 371.0954, found: 371.0967.



$^1\text{H-NMR}$ (250 MHz, CDCl_3): δ = 1.98 (s, 3 H, OAc), 1.99 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 2.14 (s, 3 H, OAc), 4.02-4.18 (m, 3 H, H'ose'), 4.38-4.44 (m, 1 H, H'ose'), 5.33-5.42 (m, 2 H, H'ose'), 5.53-5.56 (m, 1 H, H'ose'), 6.58 (d, J = 3.6 Hz, 1 H, H-1'ose'), 8.64 (s, 1 H, NH) ppm.

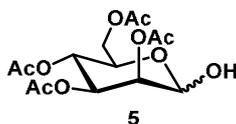
HRMS (ESI-TOF): m/z calcd. for $\text{C}_{16}\text{H}_{20}\text{Cl}_3\text{NO}_{10}\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 516.0046, found: 516.0050.

Analytical data are in accordance with published data.^[74]

2,3,4,6-Tetra-*O*-acetyl- α -D-mannopyranosyl trichloroacetimidate (6):

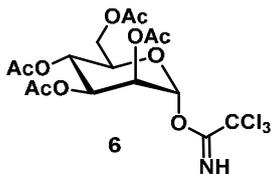
According to the general procedure I, α -D-mannose pentaacetate (10.0 g, 25.8 mmol), ethylenediamine (2.10 ml, 31.5 mmol) and glacial acetic acid (2.10 ml, 36.8 mmol) were reacted in THF (500 ml). Purification was achieved by column chromatography on silica using *n*-hexane/acetone (3:2) as the eluent to obtain tetraacetylated mannose **5** (7.66 g, 85%).

Subsequently, tetraacetylated mannose **5** (1.90 g, 5.45 mmol) was dissolved in dry dichloromethane (40 ml) under an argon atmosphere and trichloroacetonitrile (2.90 ml, 28.9 mmol) was added, followed by DBU (0.16 ml, 1.08 mmol). The reaction mixture was stirred for 2 h. After the solvent was evaporated under reduced pressure, purification was achieved by column chromatography on silica using *n*-hexane/acetone (3:2) as the eluent to obtain trichloroacetimidate **6** (2.03 g, 75%) as a yellow solid. The α -anomer was formed exclusively.



$^1\text{H-NMR}$ (250 MHz, CDCl_3): δ = 1.98 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.08 (s, 3 H, OAc), 2.14 (s, 3 H, OAc), 3.36 (br s, 1 H, OH), 4.10-4.18 (m, 1 H, H'ose'), 4.20-4.27 (m, 2 H, H'ose'), 5.22-5.32 (m, 3 H, H'ose'), 5.37-5.43 (m, 1 H, H'ose') ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{14}\text{H}_{21}\text{O}_{10}$ [$\text{M} + \text{H}$] $^+$: 371.0949, found: 371.0954.



¹H-NMR (250 MHz, CDCl₃): δ = 2.00 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 2.18 (s, 3 H, OAc), 4.12-4.21 (m, 2 H, H'ose'), 4.23-4.29 (m, 1 H, H'ose'), 5.37-5.40 (m, 2 H, H'ose'), 5.43-5.46 (m, 1 H, H'ose'), 6.26 (d, J = 1.8 Hz, 1 H, H-1'ose'), 8.76 (s, 1 H, NH) ppm.

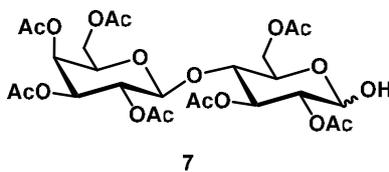
HRMS (ESI-TOF): m/z calcd. for C₁₆H₂₀Cl₃NO₁₀Na [M + Na]⁺: 516.0046, found: 516.0051.

Analytical data are in accordance with published data.^[108]

2,3,4,6,2',3',6'-Hepta-*O*-acetyl- α -D-lactosyl trichloroacetimidate (8):

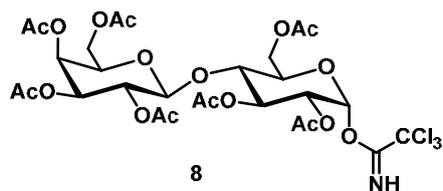
According to the general procedure I, β -D-lactose octaacetate (6.12 g, 9.02 mmol), ethylenediamine (0.73 ml, 11.0 mmol) and glacial acetic acid (0.73 ml, 12.8 mmol) were reacted in THF (200 ml). Purification was achieved by column chromatography on silica using dichloromethane/acetone (75:25) as the eluent to obtain heptaacetylated lactose 7 (4.82 g, 84%).

Subsequently, heptaacetylated lactose 7 (4.70 g, 6.93 mmol) was dissolved in dry dichloromethane (60 ml) under an argon atmosphere and trichloroacetonitrile (7.52 ml, 74.9 mmol) was added, followed by DBU (0.22 ml, 1.49 mmol). The reaction mixture was stirred for 2 h. After the solvent was evaporated under reduced pressure, purification was achieved by column chromatography on silica using dichloromethane/acetone (75:25) as the eluent to obtain trichloroacetimidate 8 (3.40 g, 63%) as a yellow solid. The α -anomer was formed exclusively.



¹H-NMR (250 MHz, CDCl₃): δ = 1.94 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 2.10 (s, 3 H, OAc), 2.13 (s, 3 H, OAc), 3.72-3.79 (m, 1 H, H'ose'), 3.84-3.87 (m, 1 H, H'ose'), 4.03-4.16 (m, 4 H, H'ose'), 4.43-4.49 (m, 2 H, H'ose'), 4.79 (dd, J = 3.4, 10.2 Hz, 1 H, H'ose'), 4.93 (dd, J = 3.4, 10.4 Hz, 1 H, H'ose'), 5.08 (ddd, J = 6.4, 7.9, 10.4 Hz, 1 H, H-5'ose'), 5.30-5.35 (m, 2 H, H'ose'), 5.47-5.51 (m, 1 H, H'ose') ppm.

HRMS (ESI-TOF): m/z calcd. for C₂₆H₃₇O₁₈ [M + H]⁺: 637.1980, found: 637.1952.



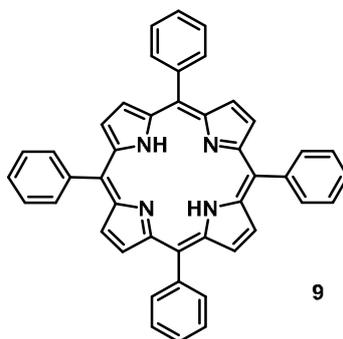
$^1\text{H-NMR}$ (250 MHz, CDCl_3): δ = 1.94 (s, 3 H, OAc), 1.98 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.04 (s, 6 H, 2 x OAc), 2.08 (s, 3 H, OAc), 2.13 (s, 3 H, OAc), 3.80-3.88 (m, 2 H, H'ose'), 4.02-4.17 (m, 4 H, H'ose'), 4.42-4.51 (m, 2 H, H'ose'), 4.93 (dd, J = 3.4, 10.4 Hz, 1 H, H'ose'), 5.00-5.15 (m, 2 H, 2 x H'ose'), 5.33 (d, J = 3.4 Hz, 1 H, H-1'ose'), 5.54 (dd, J = 9.6, 9.6 Hz, 1 H, H'ose'), 6.46 (d, J = 3.9 Hz, 1 H, H-1''ose'), 8.63 (s, 1 H, NH) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{28}\text{H}_{36}\text{Cl}_3\text{NO}_{18}\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 802.0896, found: 802.0881.

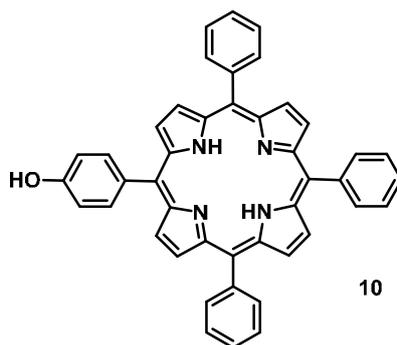
Analytical data are in accordance with published data.^[109]

5-(4-Hydroxyphenyl)-10,15,20-triphenylporphyrin (10):

According to the general procedure III, 4-hydroxybenzaldehyde (620 mg, 5.08 mmol), benzaldehyde (1.00 ml, 9.81 mmol), pyrrole (1.04 ml, 15.0 mmol), TFA (1.16 ml, 15.1 mmol), DDQ (2.55 g, 11.3 mmol) and triethylamine (3.00 ml, 21.5 mmol) were reacted in dry dichloromethane (1500 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (99:1) as the eluent and subsequent recrystallization from dichloromethane/methanol. The first band gave 5,10,15,20-tetraphenylporphyrin (232 mg, 10%) in form of violet crystals, and the second gave the desired product (295 mg, 13%) in form of violet crystals.



$^1\text{H-NMR}$ (250 MHz, CDCl_3): δ = -2.76 (br s, 2 H, NH), 7.73-7.77 (m, 12 H, 8 x Ph- H_{meta} , 4 x Ph- H_{para}), 8.21-8.24 (m, 8 H, 8 x Ph- H_{ortho}), 8.86 (s, 8 H, β -H) ppm.



Melting Point: > 300 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.79 (br s, 2 H, NH), 5.05 (br s, 1H, OH), 7.16 (d, J = 8.4 Hz, 2 H, Ar-H_{meta}), 7.69-7.77 (m, 9 H, 6 x Ph-H_{meta}, 3 x Ph-H_{para}), 8.05 (d, J = 8.4 Hz, 2 H, Ar-H_{ortho}), 8.19-8.22 (m, 6 H, Ph-H_{ortho}), 8.82-8.85 (m, 6 H, β -H), 8.87 (d, J = 4.8 Hz, 2 H, β -H) ppm.

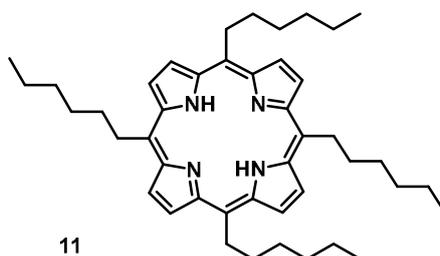
¹³C-NMR (126 MHz, CDCl₃): δ = 113.76 (Ar-C_{meta}), 119.93 (Ar-C_{meso}), 120.10 (Ph-C_{meso}), 120.18 (Ph-C_{meso}), 126.77 (Ph-C_{meta}), 127.79 (Ph-C_{para}), 134.65 (Ph-C_{ortho}), 135.79 (Ar-C_{ortho}), 142.28 (Ph-C_{ipso}), 155.46 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₃₁N₄O [M + H]⁺: 631.2498, found: 631.2521.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 419 (5.46), 516 (4.22), 551 (3.92), 592 (3.76), 648 (3.70) nm.

5-(4-Acetoxyphenyl)-10,15,20-trihexylporphyrin (12):

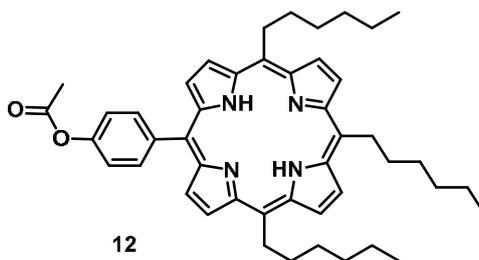
According to the general procedure III, 4-acetoxybenzaldehyde (1.59 ml, 11.3 mmol), heptanal (4.71 ml, 33.8 mmol), pyrrole (3.12 ml, 45.1 mmol), TFA (3.48 ml, 45.3 mmol), DDQ (7.65 g, 33.9 mmol) and triethylamine (9.00 ml, 64.5 mmol) were reacted in dry dichloromethane (3000 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (99:1) as the eluent and subsequent recrystallization from dichloromethane/methanol. The first band gave 5,10,15,20-tetrahexylporphyrin (132 mg, 2%) in form of violet crystals, and the second gave the desired product (296 mg, 4%) in form of violet crystals.



Melting Point: 121 °C

¹H-NMR (250 MHz, CDCl₃): δ = -2.65 (br s, 2 H, NH), 0.93 (t, J = 7.3 Hz, 12 H, 4 x CH₃), 1.32-1.55 (m, 16 H, 8 x CH₂), 1.74-1.86 (m, 8 H, 4 x CH₂), 2.44-2.56 (m, 8 H, 4 x CH₂), 4.88-4.94 (m, 8 H, 4 x CH₂), 9.44 (s, 8 H, β -H) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₆₃N₄ [M + H]⁺: 647.5052, found: 647.5049.



Melting Point: 88 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.68 (br s, 2 H, NH), 0.90-0.99 (m, 9 H, 3 x CH₃), 1.34-1.56 (m, 12 H, 6 x CH₂), 1.73-1.88 (m, 6 H, 3 x CH₂), 2.43-2.56 (m, 6 H, 3 x CH₂), 2.50 (s, 3 H, OCH₃), 4.89-4.99 (m, 6 H, 3 x CH₂), 7.48 (d, J = 8.2 Hz, 2 H, Ar-H_{meta}), 8.16 (d, J = 8.2 Hz, 2 H, Ar-H_{ortho}), 8.81 (d, J = 4.6 Hz, 2 H, β -H), 9.37 (d, J = 4.6 Hz, 2 H, β -H), 9.47-9.53 (m, 4 H, β -H) ppm.

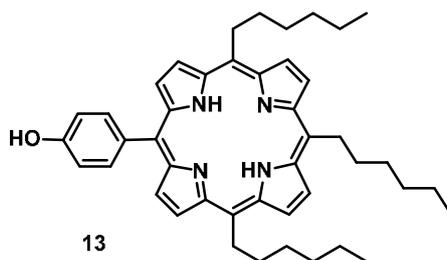
¹³C-NMR (126 MHz, CDCl₃): δ = 14.25 (CH₃), 21.50 (OCH₃), 22.83 (CH₂), 30.35 (CH₂), 32.01 (CH₂), 35.55 (CH₂), 38.78 (CH₂), 116.85 (Ar-C_{meso}), 119.20 (Alkyl-C_{meso}), 119.31 (Alkyl-C_{meso}), 119.77 (Ar-C_{meta}), 135.24 (Ar-C_{ortho}), 140.28 (Ar-C_{ipso}), 150.49 (Ar-C_{OAc}), 169.73 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₆H₅₇N₄O₂ [M + H]⁺: 697.4481, found: 697.4495.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 416 (5.34), 518 (4.09), 553 (3.89), 598 (3.42), 654 (3.57) nm.

5-(4-Hydroxyphenyl)-10,15,20-trihexylporphyrin (13):

According to the general procedure V, acetylated porphyrin **12** (60 mg, 86 μ mol) was dissolved in THF (50 ml) and saturated methanolic KOH solution (20 ml) was added. After full conversion, purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent followed by recrystallization from dichloromethane/methanol to obtain the desired product (56 mg, 99%) as a violet solid.



Melting Point: 79 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.68 (br s, 2 H, NH), 0.89-0.97 (m, 9 H, 3 x CH₃), 1.33-1.55 (m, 12 H, 6 x CH₂), 1.73-1.88 (m, 6 H, 3 x CH₂), 2.44-2.60 (m, 6 H, 3 x CH₂), 4.89-5.00 (m, 6 H, 3 x CH₂), 7.12 (d, J = 8.2 Hz, 2 H, Ar-H_{meta}), 7.99 (d, J = 8.2 Hz, 2 H, Ar-H_{ortho}), 8.81 (d, J = 4.6 Hz, 2 H, β -H), 9.36 (d, J = 4.6 Hz, 2 H, β -H), 9.47-9.52 (m, 4 H, β -H) ppm.

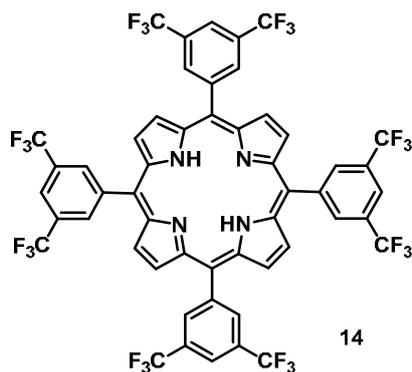
¹³C-NMR (176 MHz, CDCl₃): δ = 14.27 (CH₃), 14.30 (CH₃), 22.84 (CH₂), 22.90 (CH₂), 30.32 (CH₂), 30.43 (CH₂), 31.99 (CH₂), 32.04 (CH₂), 35.44 (CH₂), 35.84 (CH₂), 38.74 (CH₂), 38.96 (CH₂), 113.43 (Ar-C_{meta}), 117.97 (Ar-C_{meso}), 119.12 (Alkyl-C_{meso}), 119.29 (Alkyl-C_{meso}), 134.80 (Ar-C_{ipso}), 135.42 (Ar-C_{ortho}), 155.08 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₅₅N₄O [M + H]⁺: 655.4370, found: 655.4416.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 416 (5.46), 517 (4.21), 553 (3.86), 595 (3.57), 653 (3.67) nm.

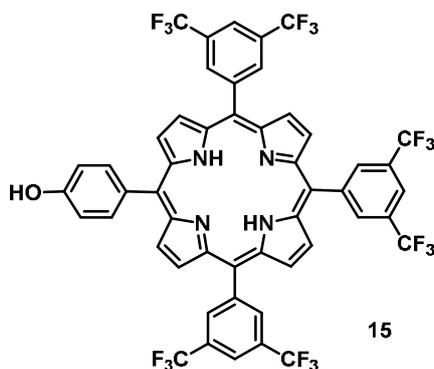
5-(4-Hydroxyphenyl)-10,15,20-tris[3,5-bis(trifluoromethyl)phenyl]porphyrin (15):

According to the general procedure III, 4-hydroxybenzaldehyde (260 mg, 2.13 mmol), 3,5-bis(trifluoromethyl)benzaldehyde (0.70 ml, 4.25 mmol), pyrrole (0.44 ml, 6.41 mmol), TFA (0.50 ml, 6.51 mmol), DDQ (1.45 g, 6.41 mmol) and triethylamine (1.30 ml, 9.27 mmol) were reacted in dry dichloromethane (750 ml). Purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (2:1) as the eluent and subsequent recrystallization from dichloromethane/methanol. The first band gave 5,10,15,20-tetrakis[3,5-bis(trifluoromethyl)phenyl]porphyrin (42 mg, 2%) in form of violet crystals, and the second gave the desired product (185 mg, 11%) in form of violet crystals.



$^1\text{H-NMR}$ (250 MHz, CDCl_3): δ = -2.89 (br s, 2 H, NH), 8.37 (br s, 4 H, 4 x $\text{Ar}_\text{F}\text{-H}_\text{para}$), 8.68 (br s, 8 H, 8 x $\text{Ar}_\text{F}\text{-H}_\text{ortho}$), 8.79 (br s, 8 H, $\beta\text{-H}$) ppm.

Analytical data are in accordance with published data.^[110]



Melting Point: 294 °C

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = -2.84 (br s, 2 H, NH), 5.27 (br s, 1 H, Ar-OH), 7.22 (d, J = 8.4 Hz, 2 H, 2 x Ar-H_meta), 8.07 (d, J = 8.4 Hz, 2 H, 2 x Ar-H_ortho), 8.37 (br s, 3 H, 3 x $\text{Ar}_\text{F}\text{-H}_\text{para}$), 8.70 (br s, 6 H, 6 x $\text{Ar}_\text{F}\text{-H}_\text{ortho}$), 8.73 (d, J = 4.8 Hz, 2 H, $\beta\text{-H}$), 8.78 (s, 4 H, $\beta\text{-H}$), 9.00 (d, J = 4.8 Hz, 2 H, $\beta\text{-H}$) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ = 114.08 (Ar-C_meta), 116.58 ($\text{Ar}_\text{F}\text{-C}_\text{meso}$), 117.10 ($\text{Ar}_\text{F}\text{-C}_\text{meso}$), 122.24 ($\text{Ar}_\text{F}\text{-C}_\text{para}$), 122.31 ($\text{Ar}_\text{F}\text{-C}_\text{para}$), 122.49 (Ar-C_meso), 124.66, 126.83, 130.59 (CF_3), 130.63 (CF_3), 133.79 ($\text{Ar}_\text{F}\text{-C}_\text{ortho}$), 133.86 (Ar-C_ipso), 135.94 (Ar-C_ortho), 143.89 ($\text{Ar}_\text{F}\text{-C}_\text{ipso}$), 143.98 ($\text{Ar}_\text{F}\text{-C}_\text{ipso}$), 155.96 (Ar-C_OH) ppm.

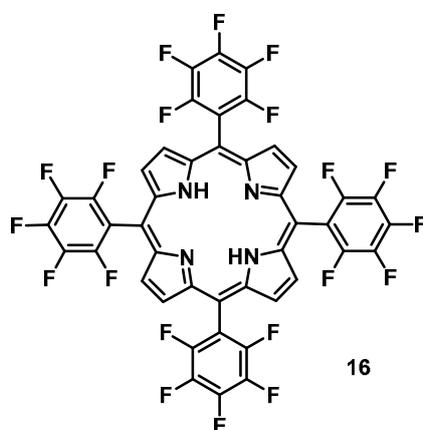
$^{19}\text{F-NMR}$ (471 MHz, CDCl_3): δ = -62.25 (s, 18 F, 6 x CF_3) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{50}\text{H}_{25}\text{F}_{18}\text{N}_4\text{O}$ [$\text{M} + \text{H}$] $^+$: 1039.1741, found: 1039.1851.

UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 408 (5.59), 514 (4.35), 548 (3.87), 589 (3.88), 645 (3.49) nm.

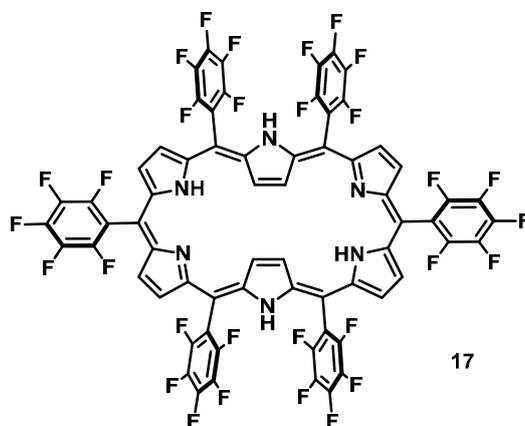
5-(4-Hydroxyphenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (18):

According to the general procedure III, 4-hydroxybenzaldehyde (525 mg, 4.29 mmol), pentafluorobenzaldehyde (1.06 ml, 8.59 mmol), pyrrole (0.88 ml, 12.7 mmol), $\text{BF}_3 \cdot \text{OEt}_2$ (0.45 ml, 3.61 mmol), DDQ (2.91 g, 12.8 mmol) and triethylamine (3.00 ml, 21.5 mmol) were reacted in dry dichloromethane (1500 ml). Purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (1:1) as the eluent and subsequent recrystallization from dichloromethane/methanol. The first band gave 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (1.10 g, 36%) in form of violet crystals, the second blue band gave [28]hexaphyrin (31 mg, 1%) in form of shiny crystals after recrystallization from dichloromethane/*n*-pentane and the third band gave the desired product (120 mg, 4%) in form of violet crystals.



$^1\text{H-NMR}$ (250 MHz, CDCl_3): $\delta = -2.90$ (br s, 2 H, NH), 8.94 (s, 8 H, $\beta\text{-H}$) ppm.

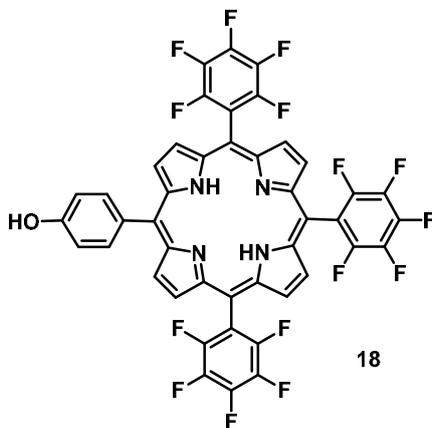
Analytical data are in accordance with published data.^[47c]



Melting Point: > 300 °C

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 2.63 (s, 4 H, inner $\beta\text{-H}$), 4.57 (br s, 4 H, NH), 7.61 (d, J = 4.9 Hz, 4 H, outer $\beta\text{-H}$), 7.70 (d, J = 4.9 Hz, 4 H, outer $\beta\text{-H}$) ppm.

Analytical data are in accordance with published data.^[35]



Melting Point: > 300 °C

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = -2.85 (br s, 2 H, NH), 5.30 (br s, 1H, Ar-OH), 7.23 (d, J = 8.3 Hz, 2 H, Ar- H_{meta}), 8.07 (d, J = 8.3 Hz, 2 H, Ar- H_{ortho}), 8.82 (d, J = 4.8 Hz, 2 H, $\beta\text{-H}$), 8.89 (d, J = 4.8 Hz, 4 H, $\beta\text{-H}$), 9.01 (d, J = 4.8 Hz, 2 H, $\beta\text{-H}$) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ = 101.75 (Ar_F-C_{meso}), 103.01 (Ar_F-C_{meso}), 114.08 (Ar-C_{meta}), 115.70-116.25 (Ar_F-C_{ipso}), 123.21 (Ar-C_{meso}), 133.53 (Ar-C_{ipso}), 135.95 (Ar-C_{ortho}), 136.47-136.79 (Ar_F-C), 138.47-138.82 (Ar_F-C), 141.06-141.36 (Ar_F-C), 143.00-143.42 (Ar_F-C), 145.54-145.74 (Ar_F-C), 147.50-147.71 (Ar_F-C), 156.02 (Ar-C_{OH}) ppm.

$^{19}\text{F-NMR}$ (471 MHz, CDCl_3): δ = -161.53 (dt, J = 6.9, 23.3 Hz, 4 F, Ar-F_{meta}), -161.43 (dt, J = 6.9, 23.3 Hz, 2 F, Ar-F_{meta}), -151.67 (t, J = 20.9 Hz, 2 F, Ar-F_{para}), -151.59 (t, J = 20.9 Hz, 1 F, Ar-F_{para}), -136.56 (dd, J = 7.9, 23.8 Hz, 4 F, Ar-F_{ortho}), -136.43 (dd, J = 7.9, 23.8 Hz, 2 F, Ar-F_{ortho}) ppm.

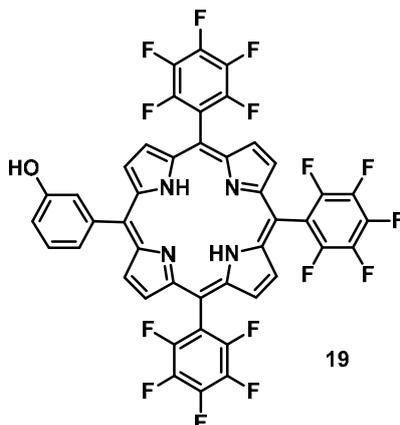
HRMS (ESI-TOF): m/z calcd. for $\text{C}_{44}\text{H}_{16}\text{F}_{15}\text{N}_4\text{O}$ $[\text{M} + \text{H}]^+$: 901.1085, found: 901.1067.

UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 414 (5.49), 510 (4.28), 586 (3.91), 642 (3.43) nm.

5-(3-Hydroxyphenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (19):

According to the general procedure III, 3-hydroxybenzaldehyde (525 mg, 4.29 mmol), pentafluorobenzaldehyde (1.06 ml, 8.59 mmol), pyrrole (0.88 ml, 12.7 mmol), $\text{BF}_3 \cdot \text{OEt}_2$ (0.45 ml, 3.61 mmol), DDQ (2.91 g, 12.8 mmol) and triethylamine (3.00 ml, 21.5 mmol) were reacted in dry dichloromethane (1500 ml). Purification was achieved by column chromatography on silica using

dichloromethane/*n*-hexane (1:1) as the eluent and subsequent recrystallization from dichloromethane/methanol. The first band gave 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (1.04 g, 34%) in form of violet crystals, the second blue band gave [28]hexaphyrin (19 mg, < 1%) in form of shiny crystals and the third band gave the desired product (142 mg, 5%) in form of violet crystals.



Melting Point: > 300 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.87 (br s, 2 H, NH), 5.11 (br s, 1H, Ar-OH), 7.27-7.31 (m, 1 H, Ar-H), 7.61-7.65 (m, 1 H, Ar-H), 7.67-7.70 (m, 1 H, Ar-H), 7.77-7.81 (m, 1 H, Ar-H), 8.82 (d, J = 4.6 Hz, 2 H, β -H), 8.87-8.92 (m, 4 H, β -H), 9.02 (d, J = 4.6 Hz, 2 H, β -H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 102.03 (Ar_F-C_{meso}), 115.57 (Ar-C), 116.05-116.42 (Ar_F-C_{ipso}), 122.04 (Ar-C), 122.58 (Ar-C_{meso}), 127.86 (Ar-C), 128.14 (Ar-C), 135.08-135.46 (Ar_F-C), 138.51-138.76 (Ar_F-C), 140.26-141.50 (Ar_F-C), 142.50 (Ar-C_{ipso}), 145.42-145.72 (Ar_F-C), 147.41-147.71 (Ar_F-C), 154.13 (Ar-C_{OH}) ppm.

¹⁹F-NMR (471 MHz, CDCl₃): δ = -161.57 – -161.39 (m, 6 F, Ar-F_{meta}), -151.67 – -151.52 (m, 3 F, Ar-F_{para}), -136.60 – -136.52 (m, 4 F, Ar-F_{ortho}), -136.47 – -136.39 (m, 2 F, Ar-F_{ortho}) ppm.

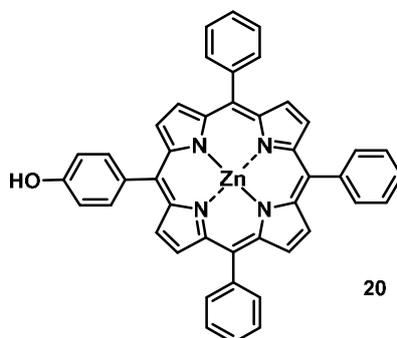
HRMS (ESI-TOF): m/z calcd. for C₄₄H₁₆F₁₅N₄O [M + H]⁺: 901.1085, found: 901.1086.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 415 (5.51), 508 (4.44), 586 (3.94), 640 (3.21) nm.

[5-(4-Hydroxyphenyl)-10,15,20-triphenylporphyrinato]zinc(II) (20):

According to the general procedure VI, a mixture of porphyrin 10 (288 mg, 457 μ mol) and Zn(OAc)₂ · 2 H₂O (300 mg, 1.37 mmol) was reacted in dichloromethane/methanol (20 ml, 4:1). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate

(95:5) as the eluent and subsequent recrystallization from dichloromethane/methanol to obtain the desired product (317 mg, 100%) as a pink solid.



Melting Point: > 300 °C

¹H-NMR (500 MHz, CDCl₃): δ = 5.21 (br s, 1H, OH), 7.18 (d, J = 8.3 Hz, 2 H, Ar-H_{meta}), 7.72-7.78 (m, 9 H, 6 x Ph-H_{meta}, 3 x Ph-H_{para}), 8.07 (d, J = 8.3 Hz, 2 H, Ar-H_{ortho}), 8.20-8.24 (m, 6 H, Ph-H_{ortho}), 8.93 (s, 4 H, β -H), 8.94 (d, J = 4.6 Hz, 2 H, β -H), 8.98 (d, J = 4.6 Hz, 2 H, β -H) ppm.

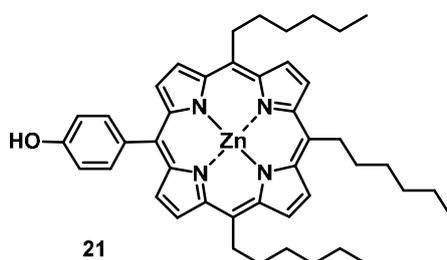
¹³C-NMR (126 MHz, CDCl₃): δ = 113.63 (Ar-C_{meta}), 120.93 (Ar-C_{meso}), 121.13 (Ph-C_{meso}), 121.19 (Ph-C_{meso}), 126.64 (Ph-C_{meta}), 127.58 (Ph-C_{para}), 132.02 (β -C), 132.05 (β -C), 132.08 (β -C), 134.51 (Ph-C_{ortho}), 135.43 (Ar-C_{ipso}), 135.60 (Ar-C_{ortho}), 142.90 (Ph-C_{ipso}), 150.25 (α -C), 150.30 (α -C), 150.32 (α -C), 155.32 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₂₉N₄OZn [M + H]⁺: 693.1633, found: 693.1589.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 419 (5.60), 548 (4.39), 587 (3.72) nm.

[5-(4-Hydroxyphenyl)-10,15,20-trihexylporphyrinato]zinc(II) (21):

According to the general procedure VI, a mixture of porphyrin 13 (80 mg, 122 μ mol) and Zn(OAc)₂ · 2 H₂O (100 mg, 457 μ mol) was reacted in dichloromethane/methanol (10 ml, 4:1). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent and subsequent recrystallization from dichloromethane/methanol to obtain the desired product (86 mg, 98%) as a pink solid.



Melting Point: 132 °C

¹H-NMR (500 MHz, CDCl₃): δ = 0.95 (t, J = 7.5 Hz, 6 H, 2 x CH₃), 0.96 (t, J = 7.5 Hz, 3 H, CH₃), 1.38-1.54 (m, 12 H, 6 x CH₂), 1.73-1.83 (m, 6 H, 3 x CH₂), 2.29-2.36 (m, 2 H, CH₂), 2.39-2.45 (m, 4 H, 2 x CH₂), 4.46-4.50 (m, 2 H, CH₂), 4.62-4.65 (m, 4 H, 2 x CH₂), 7.19 (d, J = 8.0 Hz, 2 H, Ar-H_{meta}), 8.02 (d, J = 8.0 Hz, 2 H, Ar-H_{ortho}), 8.86 (d, J = 4.4 Hz, 2 H, β -H), 9.08-9.11 (m, 4 H, β -H), 9.32 (d, J = 4.4 Hz, 2 H, β -H) ppm.

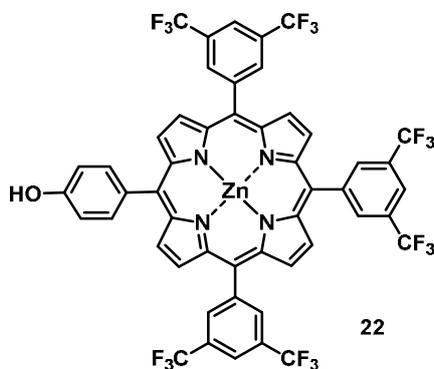
¹³C-NMR (126 MHz, CDCl₃): δ = 14.28 (CH₃), 22.87 (CH₂), 30.50 (CH₂), 31.99 (CH₂), 32.02 (CH₂), 35.56 (CH₂), 38.92 (CH₂), 38.92 (CH₂), 113.51 (Ar-C_{meta}), 118.59 (Ar-C_{meso}), 119.81 (Alkyl-C_{meso}), 119.87 (Alkyl-C_{meso}), 128.42 (β -C), 128.44 (β -C), 128.60 (β -C), 131.79 (β -C), 135.53 (Ar-C_{ortho}), 135.81 (Ar-C_{ipso}), 148.66 (α -C), 149.21 (α -C), 149.60 (α -C), 149.64 (α -C), 155.14 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₅₂N₄OZn [M]⁺: 716.3433, found: 716.3261.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 418 (5.24), 551 (3.56), 591 (3.54) nm.

[5-(4-Hydroxyphenyl)-10,15,20-tris{3,5-bis(trifluoromethyl)phenyl}porphyrinato]zinc(II)
(22):

According to the general procedure VI, a mixture of porphyrin 15 (180 mg, 174 μ mol) and Zn(OAc)₂ · 2 H₂O (200 mg, 914 μ mol) was reacted in dichloromethane/methanol (7 ml, 4:1). Purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (2:1) as the eluent and subsequent recrystallization from dichloromethane/methanol to obtain the desired product (187 mg, 98%) as a pink solid.



Melting Point: > 300 °C

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 5.25 (br s, 1 H, Ar-OH), 7.22 (d, J = 8.1 Hz, 2 H, 2 x Ar- H_{meta}), 8.07 (d, J = 8.1 Hz, 2 H, 2 x Ar- H_{ortho}), 8.36 (br s, 3 H, 3 x Ar $_F$ - H_{para}), 8.69 (br s, 6 H, 6 x Ar $_F$ - H_{ortho}), 8.82 (d, J = 4.6 Hz, 2 H, β -H), 8.87 (s, 4 H, β -H), 9.10 (d, J = 4.6 Hz, 2 H, β -H) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ = 113.90 (Ar- C_{meta}), 117.57 (Ar $_F$ - C_{meso}), 118.02 (Ar $_F$ - C_{meso}), 120.36, 122.00 (Ar $_F$ - C_{para}), 122.54, 123.06, 124.71, 126.87, 130.35 (CF_3), 130.38 (CF_3), 131.69 (β -C), 132.19 (β -C), 132.34 (β -C), 133.64 (Ar $_F$ - C_{ortho}), 133.83 (β -C), 134.50 (Ar- C_{ipso}), 135.70 (Ar- C_{ortho}), 144.58 (Ar $_F$ - C_{ipso}), 144.63 (Ar $_F$ - C_{ipso}), 149.67 (α -C), 149.90 (α -C), 150.02 (α -C), 151.42 (Ar- C_{OH}) ppm.

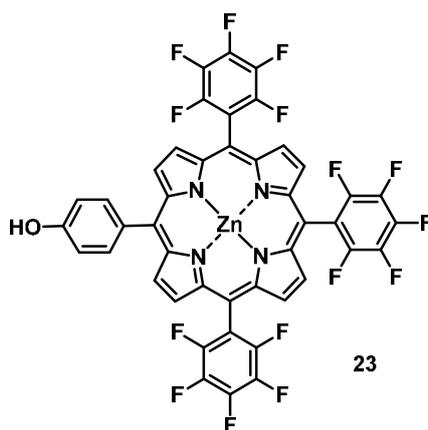
$^{19}\text{F-NMR}$ (471 MHz, CDCl_3): δ = -62.26 (s, 18 F, 6 x CF_3) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{50}\text{H}_{23}\text{F}_{18}\text{N}_4\text{OZn}$ [$\text{M} + \text{H}$] $^+$: 1101.0876, found: 1101.0663.

UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 421 (5.55), 549 (4.41) nm.

[5-(4-Hydroxyphenyl)-10,15,20-tris(pentafluorophenyl)porphyrinato]zinc(II) (23):

According to the general procedure VI, a mixture of porphyrin 18 (107 mg, 119 μmol) and $\text{Zn}(\text{OAc})_2 \cdot 2 \text{H}_2\text{O}$ (100 mg, 457 μmol) was reacted in dichloromethane/methanol (7 ml, 4:1). Purification was achieved by column chromatography on silica using pure dichloromethane as the eluent and subsequent recrystallization from dichloromethane/methanol to obtain the desired product (113 mg, 97%) as a pink solid.



Melting Point: > 300 °C

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 7.17 (d, J = 8.3 Hz, 1 H, Ar- H_{meta}), 8.05 (d, J = 8.3 Hz, 1 H, Ar- H_{ortho}), 8.90 (d, J = 4.7 Hz, 2 H, β -H), 8.96-8.99 (m, 4 H, β -H), 9.09 (d, J = 4.7 Hz, 2 H, β -H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 102.60 (Ar-F-C_{meso}), 103.75 (Ar-F-C_{meso}), 113.84 (Ar-C_{meta}), 116.49-116.60 (Ar-F-C_{ipso}), 123.86 (Ar-C_{meso}), 130.54 (β -C), 131.58 (β -C), 131.94 (β -C), 134.34 (Ar-C_{ipso}), 134.44 (β -C), 135.76 (Ar-C_{ortho}), 136.44-136.78 (Ar-F-C), 138.46-138.75 (Ar-F-C), 140.87-141.15 (Ar-F-C), 142.95-143.26 (Ar-F-C), 145.50-145.72 (Ar-F-C), 147.51-147.76 (Ar-F-C), 149.69 (α -C), 149.97 (α -C), 150.30 (α -C), 151.46 (α -C), 155.64 (Ar-C_{OH}) ppm.

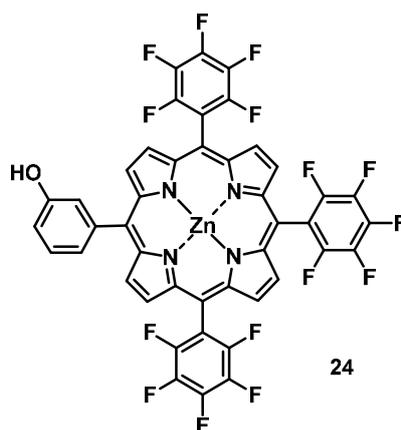
¹⁹F-NMR (471 MHz, CDCl₃): δ = -161.85 (dt, J = 9.0, 23.9 Hz, 4 F, Ar-F_{meta}), -161.77 (dt, J = 9.0, 23.9 Hz, 2 F, Ar-F_{meta}), -152.26 (t, J = 20.8 Hz, 2 F, Ar-F_{para}), -152.19 (t, J = 20.8 Hz, 1 F, Ar-F_{para}), -136.84 (dd, J = 8.2, 24.3 Hz, 4 F, Ar-F_{ortho}), -136.72 (dd, J = 8.2, 24.3 Hz, 2 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₁₂F₁₅N₄OZn [M - H]⁺: 961.0063, found: 961.0195.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 417 (5.51), 546 (4.34) nm.

[5-(3-Hydroxyphenyl)-10,15,20-tris(pentafluorophenyl)porphyrinato]zinc(II) (24):

According to the general procedure VI, a mixture of porphyrin 19 (90 mg, 100 μ mol) and Zn(OAc)₂ · 2 H₂O (100 mg, 457 μ mol) was reacted in dichloromethane/methanol (7 ml, 4:1). Purification was achieved by column chromatography on silica using pure dichloromethane as the eluent and subsequent recrystallization from dichloromethane/methanol to obtain the desired product (102 mg, 100%) as a pink solid.



Melting Point: > 300 °C

¹H-NMR (500 MHz, CDCl₃): δ = 4.89 (br s, 1H, Ar-OH), 7.11-7.14 (m, 1 H, Ar-H), 7.47-7.50 (m, 1 H, Ar-H), 7.56 (m, 1 H, Ar-H), 7.73-7.75 (m, 1 H, Ar-H), 8.89 (d, J = 4.6 Hz, 2 H, β -H), 8.97 (d, J = 4.6 Hz, 2 H, β -H), 8.99 (d, J = 4.6 Hz, 2 H, β -H), 9.06 (d, J = 4.6 Hz, 2 H, β -H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 102.76 (Ar_F-C_{meso}), 103.76 (Ar_F-C_{meso}), 115.10 (Ar-C), 116.31-116.97 (Ar_F-C_{ipso}), 121.91 (Ar-C_{meso}), 123.27 (Ar-C), 127.80 (Ar-C), 127.84 (Ar-C), 130.59 (β -C), 131.60 (β -C), 131.91 (β -C), 134.34 (β -C), 136.40-136.75 (Ar_F-C), 138.36-138.77 (Ar_F-C), 140.81-141.23 (Ar_F-C), 143.20 (Ar-C_{ipso}), 145.47-145.78 (Ar_F-C), 147.37-147.78 (Ar_F-C), 149.76 (α -C), 150.04 (α -C), 150.25 (α -C), 150.94 (α -C), 153.67 (Ar-C_{OH}) ppm.

¹⁹F-NMR (471 MHz, CDCl₃): δ = -161.93 – -161.76 (m, 6 F, Ar-F_{meta}), -152.31 – -152.15 (m, 3 F, Ar-F_{para}), -136.90 – -136.68 (m, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₁₂F₁₅N₄OZn [M - H]⁺: 961.0063, found: 961.0134.

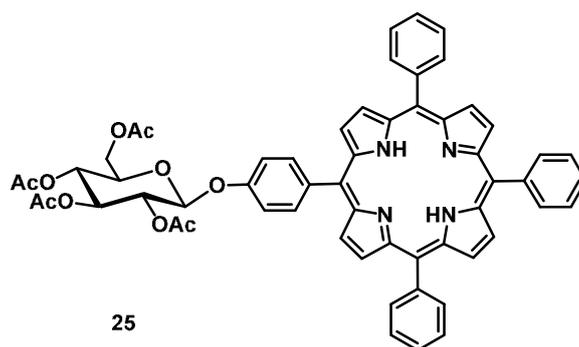
UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 415 (5.43), 545 (4.19) nm.

5-[4-(2,3,4,6-Tetraacetyl- β -D-glucosyl)phenyl]-10,15,20-triphenylporphyrin (25):

According to the general procedure VII, metallated hydroxyporphyrin **20** (50 mg, 72 μ mol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate **2** (65 mg, 132 μ mol) and BF₃·Et₂O (2.5 μ l, 20 μ mol) were reacted in a mixture of dry dichloromethane/acetonitrile (10 ml, 95:5) for 20 min. Demetallation was accomplished with HCl (0.3 ml, 25%) in THF (10 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired product (61 mg, 89%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.

Upscaled Reaction:

According to the general procedure VII, metallated hydroxyporphyrin **20** (180 mg, 259 μ mol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate **2** (200 mg, 407 μ mol) and BF₃·Et₂O (7.5 μ l, 60 μ mol) were reacted in a mixture of dry dichloromethane/acetonitrile (30 ml, 29:1) for 2 h. Demetallation was accomplished with HCl (2.0 ml, 25%) in THF (50 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired product (214 mg, 86%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: > 300 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.78 (br s, 2 H, NH), 2.10 (s, 3 H, OAc), 2.11 (s, 3 H, OAc), 2.12 (s, 3 H, OAc), 2.22 (s, 3 H, OAc), 4.06 (ddd, J = 2.6, 5.6, 10.1 Hz, 1 H, H-5'ose'), 4.30 (dd, J = 2.6, 12.3 Hz, 1 H, H-6_A'ose'), 4.42 (dd, J = 5.6, 12.3 Hz, 1 H, H-6_B'ose'), 5.31 (dd, J = 9.4, 10.1 Hz, 1 H, H-4'ose'), 5.45 (dd, J = 9.4, 9.4 Hz, 1 H, H-3'ose'), 5.47 (d, J = 7.5 Hz, 1 H, H-1'ose'), 5.49 (dd, J = 7.5, 9.4 Hz, 1 H, H-2'ose'), 7.38 (d, J = 8.6 Hz, 2 H, Ar-H_{meta}), 7.73-7.80 (m, 9 H, 6 x Ph-H_{meta} 3 x Ph-H_{para}), 8.14 (d, J = 8.6 Hz, 2 H, Ar-H_{ortho}), 8.20-8.22 (m, 6 H, Ph-H_{ortho}), 8.84-8.86 (m, 8 H, β -H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 20.71 (OCH₃), 20.75 (OCH₃), 20.84 (OCH₃), 20.88 (OCH₃), 62.20 (C-6'ose'), 68.51 (C-4'ose'), 71.44 (C-2'ose'), 72.39 (C-5'ose'), 72.96 (C-3'ose'), 99.29 (C-1'ose'), 115.14 (Ar-C_{meta}), 119.23 (Ar-C_{meso}), 120.27 (Ph-C_{meso}), 120.30 (Ph-C_{meso}), 126.77 (Ph-C_{meta}), 127.82 (Ph-C_{para}), 134.63 (Ph-C_{ortho}), 135.63 (Ar-C_{ortho}), 142.21 (Ph-C_{ipso}), 156.71 (Ar-C_{Oglc}), 169.54 (C=O), 170.40 (C=O), 170.70 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₈H₄₉N₄O₁₀ [M + H]⁺: 961.3448, found: 961.3480.

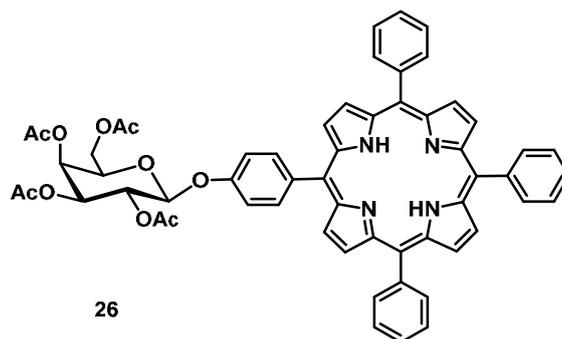
UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 415 (5.51), 513 (4.31), 547 (4.02), 591 (3.86), 647 (3.69) nm.

5-[4-(2,3,4,6-Tetraacetyl- β -D-galactosyl)phenyl]-10,15,20-triphenylporphyrin (26):

According to the general procedure VII, metallated hydroxyporphyrin **20** (50 mg, 72 μ mol), 2,3,4,6-tetraacetyl-D-galactose trichloroacetimidate **4** (175 mg, 355 μ mol) and BF₃·Et₂O (2.5 μ l, 20 μ mol) were reacted in a mixture of dry dichloromethane/acetonitrile (10 ml, 95:5) for 2 h. Demetallation was accomplished with HCl (0.3 ml, 25%) in THF (10 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired product (58 mg, 83%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.

Upscaled Reaction:

According to the general procedure VII, metallated hydroxyporphyrin **20** (180 mg, 259 μ mol), 2,3,4,6-tetraacetyl-D-galactose trichloroacetimidate **4** (530 mg, 1.08 mmol) and BF₃·Et₂O (7.5 μ l, 60 μ mol) were reacted in a mixture of dry dichloromethane/acetonitrile (30 ml, 29:1) for 2 h. Demetallation was accomplished with HCl (2.0 ml, 25%) in THF (50 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired product (202 mg, 81%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 293 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.79 (br s, 2 H, NH), 2.07 (s, 3 H, OAc), 2.08 (s, 3 H, OAc), 2.23 (s, 3 H, OAc), 2.26 (s, 3 H, OAc), 4.22-4.26 (m, 1 H, H-5'ose'), 4.27-4.30 (m, 1 H, H-6_A'ose'), 4.37 (dd, J = 6.7, 11.0 Hz, 1 H, H-6_B'ose'), 5.27 (dd, J = 3.5, 10.5 Hz, 1 H, H-3'ose'), 5.42 (d, J = 8.0 Hz, 1 H, H-1'ose'), 5.57 (dd, J = 0.9, 3.5 Hz, 1 H, H-4'ose'), 5.70 (dd, J = 7.9, 10.5 Hz, 1 H, H-2'ose'), 7.38 (d, J = 8.6 Hz, 2 H, Ar-H_{meta}), 7.73-7.80 (m, 9 H, 6 x Ph-H_{meta}, 3 x Ph-H_{para}), 8.14 (d, J = 8.6 Hz, 2 H, Ar-H_{ortho}), 8.20-8.22 (m, 6 H, Ph-H_{ortho}), 8.84-8.86 (m, 8 H, β -H) ppm.

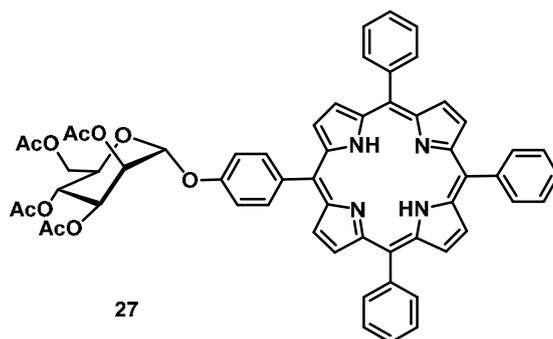
¹³C-NMR (126 MHz, CDCl₃): δ = 20.75 (OCH₃), 20.80 (OCH₃), 20.83 (OCH₃), 21.01 (OCH₃), 61.62 (C-6'ose'), 67.09 (C-4'ose'), 68.90 (C-2'ose'), 71.07 (C-3'ose'), 71.38 (C-5'ose'), 99.79 (C-1'ose'), 115.14 (Ar-C_{meta}), 119.26 (Ar-C_{meso}), 120.27 (Ph-C_{meso}), 120.29 (Ph-C_{meso}), 126.78 (Ph-C_{meta}), 127.83 (Ph-C_{para}), 134.64 (Ph-C_{ortho}), 135.64 (Ar-C_{ortho}), 142.21 (Ph-C_{ipso}), 156.72 (Ar-C_{OGal}), 169.65 (C=O), 170.31 (C=O), 170.41 (C=O), 170.51 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₈H₄₉N₄O₁₀ [M + H]⁺: 961.3448, found: 961.3500.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 418 (5.61), 515 (4.32), 550 (4.03), 591 (3.89), 647 (3.78) nm.

5-[4-(2,3,4,6-Tetraacetyl- α -D-mannosyl)phenyl]-10,15,20-triphenylporphyrin (27):

According to the general procedure VII, metallated hydroxyporphyrin **20** (100 mg, 144 μ mol), 2,3,4,6-tetraacetyl- α -D-mannose trichloroacetimidate **6** (862 mg, 1.75 mmol) and BF₃·Et₂O (7.5 μ l, 60 μ mol) were reacted in a mixture of dry dichloromethane/acetonitrile (20 ml, 19:1) for 3 h. Demetallation was accomplished with HCl (0.6 ml, 25%) in THF (20 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired product (108 mg, 78%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: > 300 °C

¹H-NMR (700 MHz, (CD₃)₂CO): δ = -2.73 (br s, 2 H, NH), 2.04 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 2.13 (s, 3 H, OAc), 2.24 (s, 3 H, OAc), 4.25 (dd, J = 2.8, 12.3 Hz, 1 H, H-6_A'ose'), 4.37 (dd, J = 6.4, 12.3 Hz, 1 H, H-6_B'ose'), 4.45 (ddd, J = 2.8, 6.4, 10.0 Hz, 1 H, H-5'ose'), 5.46 (dd, J = 10.0, 10.0 Hz, 1 H, H-4'ose'), 5.64 (dd, J = 1.9, 3.8 Hz, 1 H, H-2'ose'), 5.69 (dd, J = 3.8, 10.0 Hz, 1 H, H-3'ose'), 6.02 (d, J = 1.9 Hz, 1 H, H-1'ose'), 7.62 (d, J = 8.7 Hz, 2 H, Ar-H_{meta}), 7.79-7.82 (m, 9 H, 6 x Ph-H_{meta}, 3 x Ph-H_{para}), 8.21 (d, J = 8.7 Hz, 2 H, Ar-H_{ortho}), 8.23-8.25 (m, 6 H, Ph-H_{ortho}), 8.86 (s, 6 H, β -H), 8.90 (d, J = 4.3 Hz, 2 H, β -H) ppm.

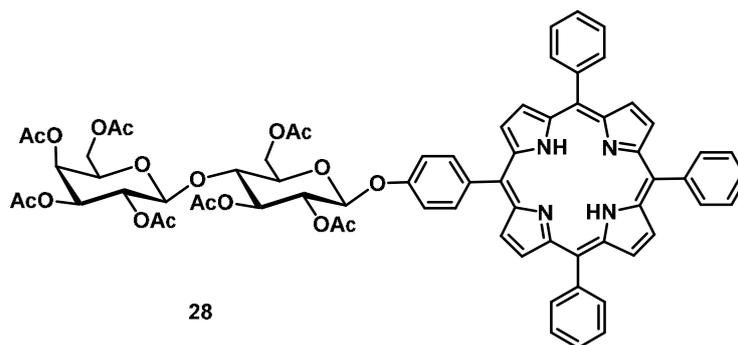
¹³C-NMR (176 MHz, (CD₃)₂CO): δ = 21.69 (OCH₃), 21.73 (OCH₃), 21.76 (OCH₃), 21.80 (OCH₃), 64.21 (C-6'ose'), 67.86 (C-4'ose'), 70.96 (C-3'ose'), 71.12 (C-5'ose'), 71.58 (C-2'ose'), 98.33 (C-1'ose'), 117.32 (Ar-C_{meta}), 121.51 (Ar-C_{meso}), 122.10 (Ph-C_{meso}), 122.14 (Ph-C_{meso}), 128.76 (Ph-C_{meta}), 129.86 (Ph-C_{para}), 136.32 (Ar-C_{ortho}), 137.37 (Ph-C_{ortho}), 144.88 (Ph-C_{ipso}), 157.82 (Ar-C_{OMan}), 171.36 (C=O), 170.45 (C=O), 170.51 (C=O), 170.71 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₈H₄₉N₄O₁₀ [M + H]⁺: 961.3448, found: 961.3444.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 415 (5.51), 513 (4.30), 547 (4.00), 591 (3.84), 647 (3.66) nm.

5-[4-(2,3,4,6,2',3',6'-Heptaacetyl- β -D-lactosyl)phenyl]-10,15,20-triphenylporphyrin (28):

According to the general procedure VII, metallated hydroxyporphyrin **20** (60 mg, 86 μ mol), 2,3,4,6,2',3',6'-heptaacetyl- α -D-lactose trichloroacetimidate **8** (800 mg, 1.02 mmol) and BF₃·Et₂O (10 μ l, 80 μ mol) were reacted in a mixture of dry dichloromethane/acetonitrile (10 ml, 19:1) for 2 h. Demetallation was accomplished with HCl (0.6 ml, 25%) in THF (20 ml). Purification was achieved by column chromatography on silica using dichloromethane/methanol (99:1) as the eluent. The desired product (58 mg, 54%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: > 300 °C

¹H-NMR (700 MHz, CDCl₃): δ = -2.80 (br s, 2 H, NH), 1.99 (s, 3 H, OAc), 2.09 (s, 3 H, OAc), 2.11 (s, 3 H, OAc), 2.13 (s, 3 H, OAc), 2.15 (s, 3 H, OAc), 2.19 (s, 3 H, OAc), 2.21 (s, 3 H, OAc), 3.96-4.04 (m, 3 H, H-5'ose', H-4'ose', H-5'ose'), 4.16 (dd, J = 7.3, 11.2 Hz, 1 H, H-6_A'ose'), 4.22 (dd, J = 6.3, 11.2 Hz, 1 H, H-6_B'ose'), 4.29 (dd, J = 5.7, 11.9 Hz, 1 H, H-6_B''ose'), 4.58 (d, J = 7.9 Hz, 1 H, H-1'ose'), 4.62 (dd, J = 2.0, 11.9 Hz, 1 H, H-6_A''ose'), 5.00 (dd, J = 3.4, 10.4 Hz, 1 H, H-3'ose'), 5.18 (dd, J = 8.0, 10.4 Hz, 1 H, H-2'ose'), 5.39-5.47 (m, 4 H, H-4'ose', H-1''ose', H-2'ose', H-3''ose'), 7.38 (d, J = 8.5 Hz, 2 H, Ar-H_{meta}), 7.76-7.83 (m, 9 H, 6 x Ph-H_{meta}, 3 x Ph-H_{para}), 8.15 (d, J = 8.5 Hz, 2 H, Ar-H_{ortho}), 8.21-8.24 (m, 6 H, Ph-H_{ortho}), 8.81-8.84 (m, 8 H, β -H) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 20.55 (CH₃), 20.68 (CH₃), 20.69 (CH₃), 20.71 (CH₃), 20.87 (CH₃), 20.89 (CH₃), 60.90 (C-6'ose'), 62.27 (C-6''ose'), 66.68 (C'ose'), 69.17 (C-2'ose'), 70.85 (C'ose'), 71.02 (C-3'ose'), 71.70 (C'ose'), 72.97 (C'ose'), 73.10 (C'ose'), 76.45 (C'ose'), 98.95 (C-1''ose'), 101.25 (C-1'ose'), 115.05 (Ar-C_{meta}), 119.17 (Ar-C_{meso}), 120.20 (Ph-C_{meso}), 120.22 (Ph-C_{meso}), 126.70 (Ph-C_{meta}), 127.75 (Ph-C_{para}), 134.56 (Ph-C_{ortho}), 135.56 (Ar-C_{ortho}), 137.25 (Ar-C_{ipso}), 142.14 (Ph-C_{ipso}), 156.64 (Ar-C_{OLac}), 169.15 (C=O), 169.78 (C=O), 169.84 (C=O), 170.08 (C=O), 170.17 (C=O), 170.37 (C=O), 170.40 (C=O) ppm.

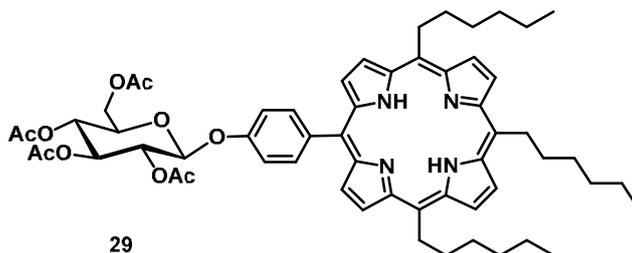
HRMS (ESI-TOF): m/z calcd. for C₇₀H₆₅N₄O₁₈ [M + H]⁺: 1249.4294, found: 1249.4248.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 418 (5.56), 515 (4.26), 550 (3.94), 590 (3.81), 647 (370) nm.

S-[4-(2,3,4,6-Tetraacetyl- β -D-glucosyl)phenyl]-10,15,20-trihexylporphyrin (29):

According to the general procedure VII, metallated hydroxyporphyrin **21** (50 mg, 69 μ mol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate **2** (80 mg, 162 μ mol) and BF₃·Et₂O (2.5 μ l, 20 μ mol) were reacted in a mixture of dry dichloromethane/acetonitrile (10 ml, 19:1) for 20 min. Demetallation was accomplished with HCl (0.5 ml, 25%) in THF (10 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired

product (60 mg, 87%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 132 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.67 (br s, 2 H, NH), 0.93 (t, J = 7.3 Hz, 6 H, 2 x CH₃), 0.96 (t, J = 7.3 Hz, 3 H, CH₃), 1.37-1.43 (m, 6 H, 3 x CH₂), 1.49-1.54 (m, 6 H, 3 x CH₂), 1.78-1.85 (m, 6 H, 3 x CH₂), 2.11 (s, 3 H, OAc), 2.12 (s, 3 H, OAc), 2.14 (s, 3 H, OAc), 2.24 (s, 3 H, OAc), 2.49-2.57 (m, 6 H, 3 x CH₂), 4.05 (ddd, J = 2.6, 5.6, 9.9 Hz, 1 H, H-5'ose'), 4.31 (dd, J = 2.6, 12.4 Hz, 1 H, H-6_A'ose'), 4.43 (dd, J = 5.6, 12.4 Hz, 1 H, H-6_B'ose'), 4.92-5.00 (m, 6 H, 3 x CH₂), 5.32 (dd, J = 9.4, 9.9 Hz, 1 H, H-4'ose'), 5.43-5.45 (m, 1 H, H-3'ose'), 5.44 (d, J = 7.7 Hz, 1 H, H-1'ose'), 5.50 (dd, J = 7.7, 9.4 Hz, 1 H, H-2'ose'), 7.35 (d, J = 8.6 Hz, 2 H, Ar-H_{meta}), 8.08 (d, J = 8.6 Hz, 2 H, Ar-H_{ortho}), 8.80 (d, J = 4.7 Hz, 2 H, β -H), 9.37 (d, J = 4.7 Hz, 2 H, β -H), 9.49 (d, J = 4.7 Hz, 2 H, β -H), 9.52 (d, J = 4.7 Hz, 2 H, β -H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 14.23 (CH₃), 14.25 (CH₃), 20.74 (OCH₃), 20.78 (OCH₃), 20.86 (OCH₃), 20.91 (OCH₃), 22.82 (CH₂), 22.86 (CH₂), 30.33 (CH₂), 30.41 (CH₂), 32.01 (CH₂), 32.03 (CH₂), 35.52 (CH₂), 35.91 (CH₂), 38.77 (CH₂), 38.97 (CH₂), 62.22 (C-6'ose'), 68.54 (C-4'ose'), 71.47 (C-2'ose'), 72.39 (C-5'ose'), 72.99 (C-3'ose'), 99.39 (C-1'ose'), 115.03 (Ar-C_{meta}), 117.07 (Ar-C_{meso}), 119.27 (Alkyl-C_{meso}), 119.60 (Alkyl-C_{meso}), 135.45 (Ar-C_{ortho}), 137.86 (Ar-C_{ipso}), 156.58 (Ar-C_{Oglc}), 169.56 (C=O), 170.43 (C=O), 170.73 (C=O) ppm.

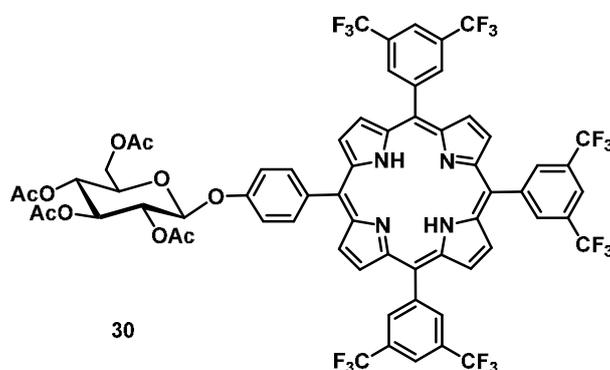
HRMS (ESI-TOF): m/z calcd. for C₅₈H₇₃N₄O₁₀ [M + H]⁺: 985.5327, found: 985.5318.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 418 (5.34), 519 (4.08), 553 (3.82), 601 (3.35), 657 (3.55) nm.

5-[4-(2,3,4,6-Tetraacetyl- β -D-glucosyl)phenyl]-10,15,20-tris[3,5-bis(trifluoromethyl)-phenyl]porphyrin (30):

According to the general procedure VII, metallated hydroxyporphyrin **22** (50 mg, 43 μ mol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate **2** (40 mg, 81 μ mol) and BF₃·Et₂O (2.5 μ l, 20 μ mol) were reacted in a mixture of dry dichloromethane/acetonitrile (10 ml, 19:1) for 20 min. Demetallation was

accomplished with HCl (1.0 ml, 25%) in THF (10 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired product (49 mg, 83%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 154 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.84 (br s, 2 H, NH), 2.11 (s, 3 H, OAc), 2.12 (s, 3 H, OAc), 2.13 (s, 3 H, OAc), 2.23 (s, 3 H, OAc), 4.08 (ddd, J = 2.5, 5.3, 10.0 Hz, 1 H, H-5'ose'), 4.33 (dd, J = 2.5, 12.4 Hz, 1 H, H-6_A'ose'), 4.43 (dd, J = 5.3, 12.4 Hz, 1 H, H-6_B'ose'), 5.33 (dd, J = 9.5, 10.0 Hz, 1 H, H-4'ose'), 5.47 (dd, J = 9.5, 9.5 Hz, 1 H, H-3'ose'), 5.49 (d, J = 7.7 Hz, 1 H, H-1'ose'), 5.50-5.53 (m, 1 H, H-2'ose'), 7.44 (d, J = 8.5 Hz, 2 H, 2 x Ar-H_{meta}), 8.16 (d, J = 8.5 Hz, 2 H, 2 x Ar-H_{ortho}), 8.38 (br s, 3 H, 3 x Ar_F-H_{para}), 8.70 (br s, 6 H, 6 x Ar_F-H_{ortho}), 8.75 (d, J = 4.8 Hz, 2 H, β -H), 8.79 (s, 4 H, β -H), 8.99 (d, J = 4.8 Hz, 2 H, β -H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 20.74 (OCH₃), 20.78 (OCH₃), 20.86 (OCH₃), 20.91 (OCH₃), 62.16 (C-6'ose'), 68.43 (C-4'ose'), 71.39 (C-2'ose'), 72.44 (C-5'ose'), 72.88 (C-3'ose'), 99.19 (C-1'ose'), 115.40 (Ar-C_{meta}), 116.77 (Ar_F-C_{meso}), 117.19 (Ar_F-C_{meso}), 120.31 (Ar_F-C_{meso}), 121.59 (Ar-C_{meso}), 122.27 (Ar_F-C_{para}), 122.48, 124.65, 126.82, 130.62 (CF₃), 130.65 (CF₃), 133.77 (Ar_F-C_{ortho}), 133.80 (Ar_F-C_{ortho}), 135.75 (Ar-C_{ortho}), 136.37 (Ar-C_{ipso}), 143.84 (Ar_F-C_{ipso}), 143.91 (Ar_F-C_{ipso}), 157.05 (Ar-C_{OGLc}), 169.56 (C=O), 170.44 (C=O), 169.56 (C=O) ppm.

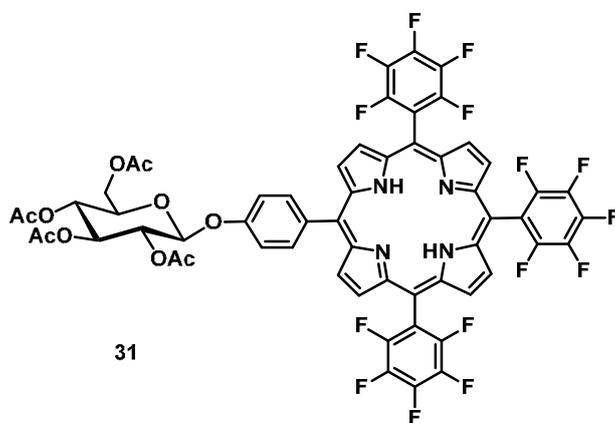
¹⁹F-NMR (471 MHz, CDCl₃): δ = -62.26 (s, 18 F, 6 x CF₃) ppm.

HRMS (ESI-TOF): m/z calcd. for C₆₄H₄₃F₁₈N₄O₁₀ [M + H]⁺: 1369.2692, found: 1369.2683.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 420 (5.50), 515 (3.93), 554 (4.53), 593 (4.20), 645 (3.84) nm.

5-[4-(2,3,4,6-Tetraacetyl- β -D-glucosyl)phenyl]-10,15,20-tris(pentafluorophenyl)porphyrin (31):

According to the general procedure VII, metallated hydroxyporphyrin **23** (30 mg, 31 μ mol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate **2** (66 mg, 134 μ mol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.4 μ l, 11 μ mol) were reacted in a mixture of dry dichloromethane/acetonitrile (5 ml, 19:1) for 20 min. Demetallation was accomplished with HCl (1.0 ml, 25%) in THF (6 ml); this step was repeated two more times. Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (98:2) as the eluent. The desired product (18 mg, 48%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 169 °C

$^1\text{H-NMR}$ (700 MHz, CDCl_3): δ = -2.82 (br s, 2 H, NH), 2.13 (s, 3 H, OAc), 2.14 (s, 3 H, OAc), 2.15 (s, 3 H, OAc), 2.24 (s, 3 H, OAc), 4.10 (ddd, J = 2.5, 5.5, 10.0 Hz, 1 H, H-5'ose'), 4.34 (dd, J = 2.5, 12.4 Hz, 1 H, H-6_A'ose'), 4.45 (dd, J = 5.5, 12.4 Hz, 1 H, H-6_B'ose'), 5.32-5.36 (m, 1 H, H-4'ose'), 5.48-5.53 (m, 3 H, H-3'ose', H-2'ose', H-1'ose'), 7.44 (d, J = 8.1 Hz, 2 H, 2 x Ar-H_{meta}), 8.16 (d, J = 8.1 Hz, 2 H, 2 x Ar-H_{ortho}), 8.82-8.85 (m, 2 H, β -H), 8.88-8.93 (m, 4 H, β -H), 8.99-9.01 (m, 2 H, β -H) ppm.

$^{13}\text{C-NMR}$ (176 MHz, CDCl_3): δ = 20.65 (OCH₃), 20.69 (OCH₃), 20.80 (OCH₃), 20.83 (OCH₃), 62.11 (C-6'ose'), 68.37 (C-4'ose'), 71.33 (C-2'ose'), 72.39 (C-5'ose'), 72.81 (C-3'ose'), 99.03 (C-1'ose'), 101.86 (Ar_F-C_{meso}), 103.03 (Ar_F-C_{meso}), 115.24 (Ar-C_{meta}), 115.63-116.06 (Ar_F-C_{ipso}), 122.39 (Ar-C_{meso}), 135.63 (Ar-C_{ortho}), 135.96 (Ar-C_{ipso}), 136.62-137.06 (Ar_F-C), 137.98-138.72 (Ar_F-C), 141.17-141.78 (Ar_F-C), 142.67-143.24 (Ar_F-C), 145.72-146.33 (Ar_F-C), 147.11-147.42 (Ar_F-C), 157.01 (Ar-C_{Oglc}), 169.45 (C=O), 170.32 (C=O), 170.59 (C=O) ppm.

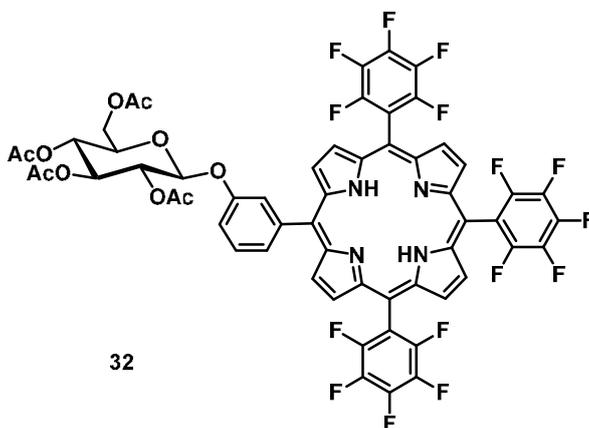
$^{19}\text{F-NMR}$ (471 MHz, CDCl_3): δ = -161.56 – -161.35 (m, 6 F, Ar-F_{meta}), -151.64 – -151.48 (m, 3 F, Ar-F_{para}), -136.62 – -136.39 (m, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{58}\text{H}_{33}\text{F}_{15}\text{N}_4\text{NaO}_{10}$ [$M + \text{Na}$]⁺: 1253.1855, found: 1253.1896.

UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 414 (5.36), 509 (4.30), 582 (3.81), 638 (3.11) nm.

5-[3-(2,3,4,6-Tetraacetyl- β -D-glucosyl)phenyl]-10,15,20-tris(pentafluorophenyl)porphyrin (32):

According to the general procedure VII, metallated hydroxyporphyrin **24** (30 mg, 31 μmol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate **2** (66 mg, 134 μmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.4 μl , 11 μmol) were reacted in a mixture of dry dichloromethane/acetonitrile (5 ml, 19:1) for 20 min. Demetallation was accomplished with HCl (1.0 ml, 25%) in THF (6 ml); this step was repeated two more times. Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (98:2) as the eluent. The desired product (16 mg, 44%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 190 °C

$^1\text{H-NMR}$ (700 MHz, CDCl_3): δ = -2.84 (m, 2 H, NH), 1.41 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 2.13 (s, 3 H, OAc), 3.83 (ddd, J = 2.4, 5.6, 10.1 Hz, 1 H, H-5'ose'), 4.11 (dd, J = 2.4, 12.2 Hz, 1 H, H-6_A'ose'), 4.18 (dd, J = 5.6, 12.2 Hz, 1 H, H-6_B'ose'), 5.21 (dd, J = 9.2, 10.1 Hz, 1 H, H-4'ose'), 5.35 (dd, J = 9.2, 9.2 Hz, H-3'ose'), 5.39 (d, J = 7.7 Hz, 1 H, H-1'ose'), 5.42 (dd, J = 7.7, 9.2 Hz, 1 H, H-2'ose'), 7.49-7.51 (m, 1 H, Ar-H), 7.73-7.76 (m, 1 H, Ar-H), 7.88-7.92 (m, 1 H, Ar-H), 7.95-7.98 (m, 1 H, Ar-H), 8.86-8.88 (m, 2 H, β -H), 8.91-8.94 (m, 4 H, β -H), 9.01-9.03 (m, 2 H, β -H) ppm.

$^{13}\text{C-NMR}$ (176 MHz, CDCl_3): δ = 19.87 (OCH₃), 20.53 (OCH₃), 20.60 (OCH₃), 20.72 (OCH₃), 61.94 (C-6'ose'), 68.26 (C-4'ose'), 71.23 (C-2'ose'), 72.19 (C-5'ose'), 72.70 (C-3'ose'), 99.07 (C-1'ose'), 102.07 (Ar_F-C_{meso}), 103.11 (Ar_F-C_{meso}), 115.60-115.94 (Ar_F-C_{ipso}), 117.21 (Ar-C), 122.12 (Ar-C_{meso}), 122.81 (Ar-C), 128.05 (Ar-C), 129.90 (Ar-C), 136.77-136.94 (Ar_F-C), 138.21-138.32 (Ar_F-C), 141.48-141.56 (Ar_F-C), 142.47 (Ar-C_{ipso}), 142.86-142.95 (Ar_F-C), 145.76-145.96 (Ar_F-C), 147.12-147.35 (Ar_F-C), 155.33 (Ar-C_{Oglc}), 169.34 (C=O), 169.35 (C=O), 170.21 (C=O), 170.31 (C=O) ppm.

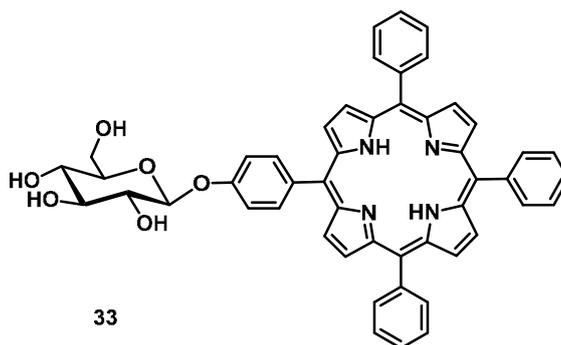
^{19}F -NMR (471 MHz, CDCl_3): $\delta = -161.54 - -161.27$ (m, 6 F, Ar-F_{meta}), $-151.57 - -151.42$ (m, 3 F, Ar-F_{para}), $-136.75 - -136.39$ (m, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{58}\text{H}_{33}\text{F}_{15}\text{N}_4\text{O}_{10}\text{Na}$ [$\text{M} + \text{Na}$]⁺: 1253.1855, found: 1253.1849.

UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 414 (5.50), 508 (4.33), 585 (3.83) 636 (3.02) nm.

5-(4- β -D-Glucosylphenyl)-10,15,20-triphenylporphyrin (33):

According to the general procedure VIII, acetylated glycoporphyrin 25 (74 mg, 77 μmol) was dissolved in a mixture of dry THF/methanol (14 ml, 1:1). Then a solution of sodium methanolate in dry methanol (2.20 ml, 0.02 N) was added. After 2 h, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, using dichloromethane/methanol (9:1) as the eluent. The desired product (60 mg, 98%) was obtained as a violet crystalline solid.



Melting Point: > 300 °C

^1H -NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$): $\delta = -2.91$ (s, 2 H, NH), 3.38-3.47 (m, 3 H, H'ose'), 3.49-3.52 (m, 1 H, H'ose'), 3.58-3.64 (m, 1 H, H-6'ose'), 3.79-3.85 (m, 1 H, H-6'ose'), 4.68 (dd, $J = 5.9, 5.9$ Hz, 1 H, OH-6'ose'), 5.08 (d, $J = 5.3$ Hz, 1 H, OH'ose'), 5.16 (d, $J = 5.1$ Hz, 1 H, OH'ose'), 5.23 (d, $J = 7.6$ Hz, 1 H, H-1'ose'), 5.48 (d, $J = 4.9$ Hz, 1 H, OH'ose'), 7.48 (d, $J = 8.7$ Hz, 2 H, Ar-H_{meta}), 7.81-7.85 (m, 9 H, 6 x Ph-H_{meta}, 3 x Ph-H_{para}), 8.14 (d, $J = 8.7$ Hz, 2 H, Ar-H_{ortho}), 8.20-8.24 (m, 6 H, Ph-H_{ortho}), 8.82 (s, 6 H, β -H), 8.88 (d, $J = 4.6$ Hz, 2 H, β -H) ppm.

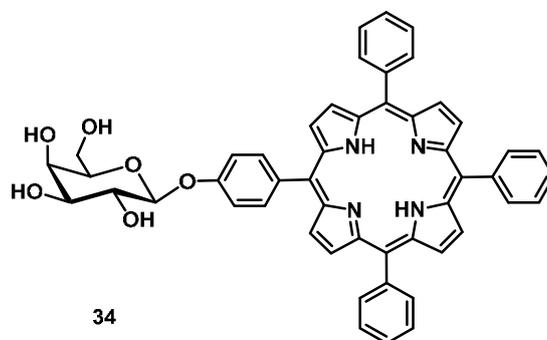
^{13}C -NMR (126 MHz, $(\text{CD}_3)_2\text{SO}$): $\delta = 61.18$ (C-6'ose'), 68.31 (C'ose'), 71.32 (C'ose'), 72.35 (C'ose'), 72.88 (C'ose'), 99.14 (C-1'ose'), 114.87 (Ar-C_{meta}), 119.23 (Ar-C_{meso}), 119.57 (Ph-C_{meso}), 120.23 (Ph-C_{meso}), 125.67 (Ph-C_{meta}), 126.84 (Ph-C_{para}), 132.93 (Ph-C_{ortho}), 135.63 (Ar-C_{ortho}), 140.31 (Ph-C_{ipso}), 156.43 (Ar-C_{Oglc}) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{50}\text{H}_{41}\text{N}_4\text{O}_6$ [$\text{M} + \text{H}$]⁺: 793.3021, found: 793.3046.

UV/Vis ((CH₃)₂SO): λ_{\max} (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 415 (5.41), 513 (4.12), 547 (3.80), 591 (3.62), 647 (3.51) nm.

5-(4- β -D-Galactosylphenyl)-10,15,20-triphenylporphyrin (34):

According to the general procedure VIII, acetylated glycoporphyrin 26 (74 mg, 77 μmol) was dissolved in a mixture of dry THF/methanol (14 ml, 1:1). Then a solution of sodium methanolate in dry methanol (2.20 ml, 0.02 N) was added. After 2 h, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, using dichloromethane/methanol (9:1) as the eluent. The desired product (61 mg, 99%) was obtained as a violet crystalline solid.



Melting Point: 297 °C

¹H-NMR (700 MHz, (CD₃)₂SO): δ = -2.89 (s, 2 H, NH), 3.57 (ddd, J = 3.3, 5.6, 9.3 Hz, 1 H, H-5'ose'), 3.66-3.70 (m, 2 H, H-6'ose'), 3.76-3.80 (m, 2 H, H'ose'), 3.81-3.84 (m, 1 H, H'ose'), 4.59 (d, J = 4.7 Hz, 1 H, OH'ose'), 4.74 (t, J = 5.6 Hz, 1 H, OH'ose'), 4.94 (d, J = 5.8 Hz, 1 H, OH'ose'), 5.19 (d, J = 7.7 Hz, 1H, H-1'ose'), 5.33 (d, J = 5.1 Hz, 1 H, OH'ose'), 7.49 (d, J = 8.4 Hz, 2 H, Ar-H_{meta}), 7.82-7.87 (m, 9 H, 6 x Ph-H_{meta}, 3 x Ph-H_{para}), 8.14 (d, J = 8.4 Hz, 2 H, Ar-H_{ortho}), 8.21-8.25 (m, 6 H, Ph-H_{ortho}), 8.83 (s, 6 H, β -H), 8.90 (d, J = 4.6 Hz, 2 H, β -H) ppm.

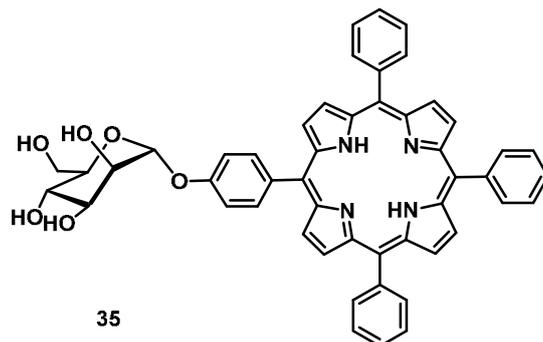
¹³C-NMR (176 MHz, (CD₃)₂SO): δ = 61.04 (C-6'ose'), 68.77 (C'ose'), 70.97 (C'ose'), 73.89 (C-5'ose'), 76.21 (C'ose'), 101.75 (C-1'ose'), 115.10 (Ar-C_{meta}), 120.34 (Ar-C_{meso}), 120.39 (Ph-C_{meso}), 120.43 (Ph-C_{meso}), 127.46 (Ph-C_{meta}), 128.55 (Ph-C_{para}), 134.67 (Ph-C_{ortho}), 135.69 (Ar-C_{ortho}), 141.71 (Ph-C_{ipso}), 158.10 (Ar-C_{OGal}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₀H₄₁N₄O₆ [M + H]⁺: 793.3021, found: 793.3054.

UV/Vis ((CH₃)₂SO): λ_{\max} (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 418 (5.48), 515 (4.20), 550 (3.91), 591 (3.76), 647 (3.65) nm.

5-(4- α -D-Mannosylphenyl)-10,15,20-triphenylporphyrin (35):

According to the general procedure VIII, acetylated glycoporphyrin **27** (40 mg, 42 μ mol) was dissolved in a mixture of dry THF/methanol (10 ml, 1:1). Then a solution of sodium methanolate in dry methanol (1.5 ml, 0.06 N) was added. After 2 h, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, using dichloromethane/methanol (9:1) as the eluent. The desired product (32 mg, 98%) was obtained as a violet crystalline solid.



Melting Point: 251 °C

$^1\text{H-NMR}$ (500 MHz, $(\text{CD}_3)_2\text{SO}$): δ = -2.91 (br s, 2 H, NH), 3.60-3.66 (m, 2 H, H-4'ose'), H-6_A'ose'), 3.68-3.72 (m, 1 H, H-5'ose'), 3.76-3.81 (m, 1 H, H-6_B'ose'), 3.86-3.90 (m, 1 H, H-3'ose'), 4.04-4.07 (m, 1H, H-2'ose'), 4.63 (dd, J = 5.9, 5.9 Hz, 1 H, OH-6'ose'), 4.87 (d, J = 5.6 Hz, 1 H, OH-3'ose'), 4.95 (d, J = 5.6 Hz, 1 H, OH-4'ose'), 5.17 (d, J = 4.6 Hz, 1 H, OH-2'ose'), 5.72 (d, J = 1.8 Hz, 1 H, H-1'ose'), 7.53 (d, J = 8.7 Hz, 2 H, Ar-H_{meta}), 7.80-7.85 (m, 9 H, 6 x Ph-H_{meta}, 3 x Ph-H_{para}), 8.13 (d, J = 8.7 Hz, 2 H, Ar-H_{ortho}), 8.20-8.23 (m, 6 H, Ph-H_{ortho}), 8.82 (s, 6 H, β -H), 8.88 (d, J = 4.6 Hz, 2 H, β -H) ppm.

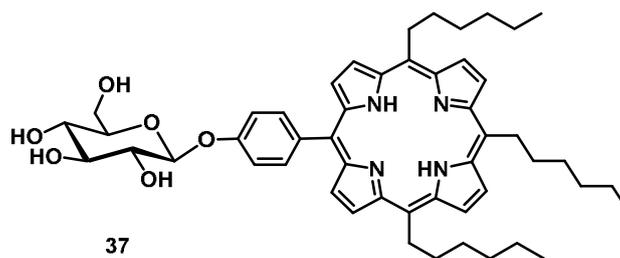
$^{13}\text{C-NMR}$ (126 MHz, $(\text{CD}_3)_2\text{SO}$): δ = 61.79 (C-6'ose'), 67.44 (C-4'ose'), 70.84 (C-2'ose'), 71.42 (C-3'ose'), 75.89 (C-5'ose'), 100.00 (C-1'ose'), 115.91 (Ar-C_{meta}), 120.43 (Ar-C_{meso}), 120.52 (Ar-C_{meso}), 127.56 (Ph-C_{meta}), 128.64 (Ph-C_{para}), 134.78 (Ph-C_{ortho}), 135.28 (Ar-C_{ipso}), 135.92 (Ar-C_{ortho}), 141.78 (Ph-C_{ipso}), 157.15 (Ar-C_{OMan}) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{50}\text{H}_{41}\text{N}_4\text{O}_6$ $[\text{M} + \text{H}]^+$: 793.3021, found: 793.3067.

UV/Vis ($(\text{CH}_3)_2\text{SO}$): λ_{max} ($\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 415 (5.38), 513 (4.10), 547 (3.77), 591 (4.01), 647 (3.40) nm.

5-(4- β -D-Lactosylphenyl)-10,15,20-triphenylporphyrin (36):

According to the general procedure VIII, acetylated glycoporphyrin **28** (37 mg, 30 μ mol) was dissolved in a mixture of dry THF/methanol (12 ml, 1:1). Then a solution of sodium methanolate in



Melting Point: 112 °C

¹H-NMR (500 MHz, (CD₃)₂SO): δ = -2.93 (s, 2 H, NH), 0.86 (t, J = 7.5 Hz, 6 H, 2 x CH₃), 0.87 (t, J = 7.5 Hz, 3 H, CH₃), 1.28-1.33 (m, 6 H, 3 x CH₂), 1.39-1.46 (m, 6 H, 3 x CH₂), 1.70-1.78 (m, 6 H, 3 x CH₂), 2.36-2.42 (m, 6 H, 3 x CH₂), 3.29-3.32 (m, 1 H, H'ose'), 3.39-3.47 (m, 2 H, H'ose'), 3.53 (ddd, J = 1.9, 5.7, 9.5 Hz, 1 H, H-5'ose'), 3.61 (dd, J = 5.7, 11.8 Hz, 1 H, H-6_B'ose'), 3.84 (dd, J = 1.9, 11.8 Hz, 1 H, H-6_A'ose'), 4.92-5.00 (m, 6 H, 3 x CH₂), 5.24 (d, J = 7.3 Hz, 1 H, H-1'ose'), 7.46 (d, J = 8.5 Hz, 2 H, Ar-H_{meta}), 8.05 (d, J = 8.5 Hz, 2 H, Ar-H_{ortho}), 8.78 (d, J = 4.8 Hz, 2 H, β -H), 9.59 (d, J = 4.8 Hz, 2 H, β -H), 9.66-9.70 (m, 4 H, β -H) ppm.

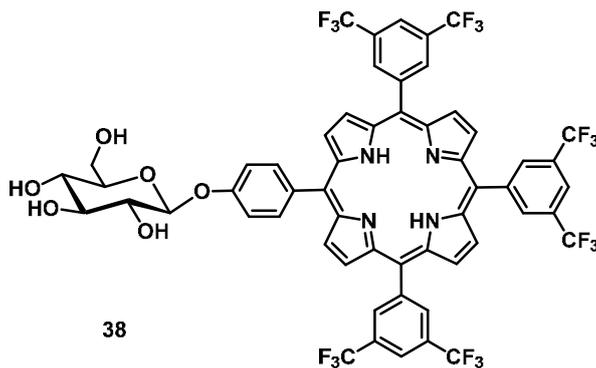
¹³C-NMR (126 MHz, (CD₃)₂SO): δ = 14.51 (CH₃), 21.58 (CH₂), 22.71 (CH₂), 29.91 (CH₂), 29.94 (CH₂), 30.98 (CH₂), 31.89 (CH₂), 34.94 (CH₂), 34.96 (CH₂), 39.16 (CH₂), 39.34 (CH₂), 61.40 (C-6'ose'), 70.41 (C'ose'), 74.03 (C'ose'), 77.32 (C-5'ose'), 77.82 (C'ose'), 101.19 (C-1'ose'), 115.02 (Ar-C_{meta}), 117.89 (Ar-C_{meso}), 119.69 (Alkyl-C_{meso}), 119.92 (Alkyl-C_{meso}), 125.47, 135.62 (Ar-C_{ortho}), 139.75 (Ar-C_{ipso}), 157.87 (Ar-C_{OGLc}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₀H₆₄N₄NaO₆ [M + Na]⁺: 839.4724, found: 839.4701.

UV/Vis (C₄H₈O): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 417 (5.35), 518 (4.10), 553 (3.89), 601 (3.42), 658 (3.61) nm.

5-(4- β -D-Glucosylphenyl)-10,15,20-tris[3,5-bis(trifluoromethyl)phenyl]porphyrin (38):

According to the general procedure VIII, acetylated glycoporphyrin **30** (30 mg, 22 μ mol) was dissolved in a mixture of dry THF/methanol (8 ml, 1:1). Then a solution of sodium methanolate in dry methanol (1.0 ml, 0.02 N) was added. After 2 h, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, using dichloromethane/methanol (9:1) as the eluent. The desired product (26 mg, 99%) was obtained as a violet crystalline solid.



Melting Point: 239 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = -2.80 (br s, 2 H, NH), 3.56-3.60 (m, 1 H, H'ose'), 3.63-3.71 (m, 3 H, H'ose'), 3.79-3.85 (m, 1 H, H-6'ose'), 3.84-3.87 (m, 1 H, H'ose'), 3.98-4.02 (m, 1 H, H'ose'), 4.40 (d, J = 3.9 Hz, 1 H, OH), 4.49 (br s, 1 H, OH), 4.86 (d, J = 2.5 Hz, 1 H, OH), 5.33 (d, J = 7.2 Hz, 1 H, H-1'ose'), 7.56 (d, J = 8.5 Hz, 2 H, 2 x Ar-H_{meta}), 8.19 (d, J = 8.5 Hz, 2 H, 2 x Ar-H_{ortho}), 8.58 (br s, 3 H, 3 x Ar_F-H_{para}), 8.91-8.97 (m, 6 H, β -H), 8.93 (br s, 6 H, 6 x Ar_F-H_{ortho}), 9.05 (d, J = 4.8 Hz, 2 H, β -H) ppm.

¹³C-NMR (126 MHz, (CD₃)₂CO): δ = 61.94 (C-6'ose'), 70.63 (C'ose'), 74.08 (C'ose'), 77.21 (C'ose'), 77.29 (C'ose'), 101.33 (C-1'ose'), 115.04 (Ar-C_{meta}), 116.69 (Ar_F-C_{meso}), 117.21 (Ar_F-C_{meso}), 120.70 (Ar_F-C_{meso}), 121.93 (Ar-C_{meso}), 122.28 (Ar_F-C_{para}), 122.87, 125.03, 127.19, 130.11 (CF₃), 130.14 (CF₃), 133.88 (Ar_F-C_{ortho}), 134.94 (Ar-C_{ipso}), 135.55 (Ar-C_{ortho}), 144.17 (Ar_F-C_{ipso}), 144.27 (Ar_F-C_{ipso}), 158.36 (Ar-C_{OGlc}) ppm.

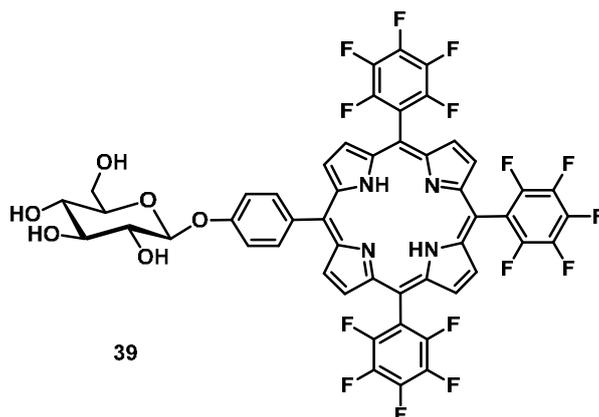
¹⁹F-NMR (471 MHz, (CD₃)₂CO): δ = -62.74 (s, 12 F, 4 x CF₃), -62.73 (s, 6 F, 2 x CF₃) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₆H₃₅F₁₈N₄O₆ [M + H]⁺: 1201.2269, found: 1201.2247.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 416 (5.45), 513 (4.30), 547 (3.93), 589 (3.91), 645 (3.70) nm.

5-(4- β -D-Glucosylphenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (39):

According to the general procedure VIII, acetylated glycoporphyrin **31** (13 mg, 11 μ mol) was dissolved in a mixture of dry THF/methanol (4 ml, 1:1). Then a solution of sodium methanolate in dry methanol (0.25 ml, 0.02 N) was added. After 2 h, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, using dichloromethane/methanol (9:1) as the eluent. The desired product (10 mg, 93%) was obtained as a violet crystalline solid.



Melting Point: > 300 °C

¹H-NMR (700 MHz, (CD₃)₂CO): δ = -2.81 (br s, 2 H, NH), 3.60-3.65 (m, 1 H, H'ose'), 3.69-3.72 (m, 2 H, 'ose'), 3.74-3.77 (m, 1 H, H'ose'), 3.84-3.88 (m, 2 H, H-6_A'ose', H'ose'), 4.02-4.06 (m, 1 H, H-6_B'ose'), 4.44 (br s, 1 H, OH'ose'), 4.54 (br s, 1 H, OH'ose'), 4.90 (br s, 1 H, OH'ose'), 5.39 (d, J = 7.4 Hz, 1 H, H-1'ose'), 7.59 (d, J = 8.4 Hz, 2 H, 2 x Ar-H_{meta}), 8.25 (d, J = 8.4 Hz, 2 H, 2 x Ar-H_{ortho}), 9.11-9.35 (m, 8 H, β -H) ppm.

¹³C-NMR (176 MHz, (CD₃)₂CO): δ = 61.88 (C-6'ose'), 70.57 (C'ose'), 74.02 (C'ose'), 77.13 (C'ose'), 101.19 (C-1'ose'), 101.80 (Ar_F-C_{meso}), 103.10 (Ar_F-C_{meso}), 114.92 (Ar-C_{meta}), 115.42-115.85 (Ar_F-C_{ipso}), 123.21 (Ar-C_{meso}), 134.43 (Ar-C_{ortho}), 135.55 (Ar-C_{ipso}), 137.14-137.43 (Ar_F-C), 138.55-138.78 (Ar_F-C), 141.58-141.86 (Ar_F-C), 143.07-143.30 (Ar_F-C), 145.98-146.20 (Ar_F-C), 147.33-147.58 (Ar_F-C), 158.36 (Ar-C_{Oglc}) ppm.

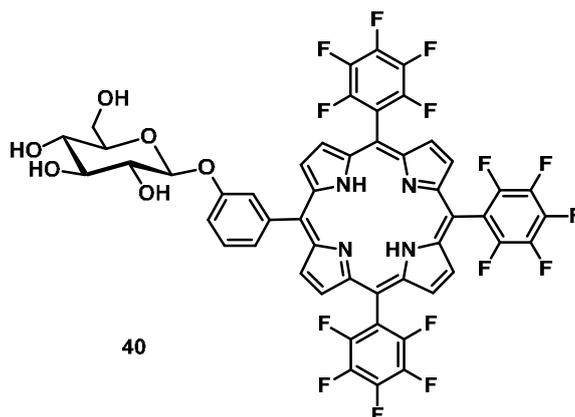
¹⁹F-NMR (471 MHz, (CD₃)₂CO): δ = -164.66 – -164.48 (m, 6 F, Ar-F_{meta}), -155.69 – -155.56 (m, 3 F, Ar-F_{para}), -139.99 – -139.79 (m, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₀H₂₆F₁₅N₄O₆ [M + H]⁺: 1063.1613, found: 1063.1622.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 415 (5.44), 508 (4.29), 586 (3.81), 637 (3.19) nm.

5-(3- β -D-Glucosylphenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (40):

According to the general procedure VIII, acetylated glycoporphyrin 32 (40 mg, 33 μ mol) was dissolved in a mixture of dry THF/methanol (10 ml, 1:1). Then a solution of sodium methanolate in dry methanol (1.0 ml, 0.02 N) was added. After 2 h, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, using dichloromethane/methanol (9:1) as the eluent. The desired product (30 mg, 84%) was obtained as a violet crystalline solid.



Melting Point: > 300 °C

¹H-NMR (700 MHz, (CD₃)₂CO): δ = -2.79 (s, 2 H, NH), 3.55-3.66 (m, 4 H, H-2'ose', H-3'ose', H-4'ose', H-5'ose'), 3.69-3.71 (m, 1 H, OH'ose'), 3.72-3.76 (m, 1 H, H-6_A'ose'), 3.87-3.91 (m, 1 H, H-6_B'ose'), 4.31-4.33 (m, 1 H, OH'ose'), 4.43-4.45 (m, 1 H, OH'ose'), 4.82 (d, J = 3.7 Hz, 1 H, OH'ose'), 5.38 (d, J = 7.6 Hz, 1 H, H-1'ose'), 7.63-7.66 (m, 1 H, Ar-H), 7.76-7.79 (m, 1 H, Ar-H), 7.95-7.98 (m, 1 H, Ar-H), 8.09-8.13 (m, 1 H, Ar-H), 9.13-9.17 (m, 2 H, β -H), 9.26-9.32 (m, 2 H, β -H), 9.35-9.39 (m, 4 H, β -H) ppm.

¹³C-NMR (176 MHz, (CD₃)₂CO): δ = 61.68 (C-6'ose'), 70.40 (C'ose'), 73.97 (C'ose'), 76.83 (C'ose'), 77.10 (C'ose'), 101.03 (C-1'ose'), 102.05 (Ar_F-C_{meso}), 103.17 (Ar_F-C_{meso}), 115.43-115.86 (Ar_F-C_{ipso}), 116.54 (Ar-C), 122.85 (Ar-C_{meso}), 122.95 (Ar-C), 127.90 (Ar-C), 128.78 (Ar-C), 137.22-137.39 (Ar_F-C), 138.64-138.81 (Ar_F-C), 141.69-141.85 (Ar_F-C), 142.07 (Ar-C_{ipso}), 143.12-142.28 (Ar_F-C), 146.03-146.16 (Ar_F-C), 147.37-147.53 (Ar_F-C), 156.46 (Ar-C_{Oglc}) ppm.

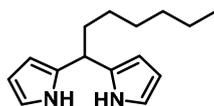
¹⁹F-NMR (471 MHz, (CD₃)₂CO): δ = -164.62 – -164.42 (m, 6 F, Ar-F_{meta}), -155.61 – -155.45 (m, 3 F, Ar-F_{para}), -139.93 – -139.77 (m, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₀H₂₆F₁₅N₄O₆ [M + H]⁺: 1063.1613, found: 1063.1614.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 410 (5.49), 506 (4.32), 581 (3.83), 635 (3.04) nm.

S-Hexyldipyrromethane (41):

According to the general procedure II, a mixture of heptanal (2.00 ml, 14.4 mmol) and pyrrole (30.0 ml, 432 mmol) was reacted in the presence of TFA (0.11 ml, 1.44 mmol). Purification was achieved by column chromatography on silica using *n*-hexane/ethyl acetate/triethylamine (80:20:0.1) as the eluent and a Kugelrohr distillation (250 °C, 10 mbar) to obtain the desired product (2.33 g, 71%) as a yellow oil.



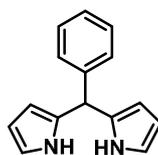
41

$^1\text{H-NMR}$ (250 MHz, CDCl_3): δ = 0.85 (t, J = 6.3 Hz, 3 H, CH_3), 1.24-1.27 (m, 8 H, CH_2), 1.87-1.96 (m, 2 H, CH_2), 3.95 (t, J = 7.1 Hz, 1 H, CH), 6.05-6.15 (m, 4 H, $\text{H}_{\text{Pyrrole}}$), 6.60-6.63 (m, 2 H, $\text{H}_{\text{Pyrrole}}$), 7.73 (br s, 2 H, NH) ppm.

Analytical data are in accordance with published data.^[111]

5-Phenyldipyrromethane (42):

According to the general procedure II, a mixture of benzaldehyde (6.00 ml, 59.4 mmol) and pyrrole (150 ml, 2.17 mol) was reacted in the presence of TFA (0.45 ml 5.84 mmol). Purification was achieved by column chromatography on silica using pure dichloromethane as the eluent and subsequent recrystallization from dichloromethane/*n*-pentane to obtain the desired product (7.89 g, 60%) as colorless crystals.



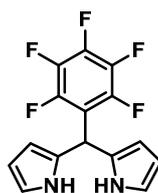
42

$^1\text{H-NMR}$ (250 MHz, CDCl_3): δ = 5.46 (s, 1 H, CH), 5.91 (br s, 2 H, $\text{H}_{\text{Pyrrole}}$), 6.15 (d, J = 2.9 Hz, 2 H, $\text{H}_{\text{Pyrrole}}$), 6.68 (br s, 2 H, $\text{H}_{\text{Pyrrole}}$), 7.19-7.35 (m, 5 H, Ph-H), 7.87 (br s, 2 H, NH) ppm.

Analytical data are in accordance with published data.^[84b]

5-(Pentafluorophenyl)dipyrromethane (43):

According to the general procedure II, a mixture of pentafluorobenzaldehyde (7.30 ml, 59.1 mmol) and pyrrole (150 ml, 2.17 mol) was reacted in the presence of TFA (0.45 ml 5.84 mmol). Purification was achieved by column chromatography on silica using pure dichloromethane as the eluent and subsequent recrystallization from dichloromethane/*n*-pentane to obtain the desired product (10.5 g, 56%) as colorless crystals.



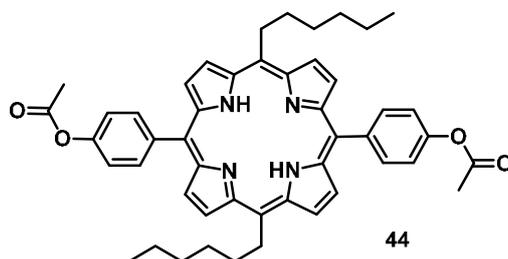
43

$^1\text{H-NMR}$ (250 MHz, CDCl_3): δ = 5.90 (s, 1 H, CH), 6.00-6.04 (m, 2 H, $\text{H}_{\text{pyrrole}}$), 6.19 (dd, J = 2.8, 5.9 Hz, 2 H, $\text{H}_{\text{pyrrole}}$), 6.71-6.74 (m, 2 H, $\text{H}_{\text{pyrrole}}$), 8.11 (br s, 2 H, NH) ppm.

Analytical data are in accordance with published data.^[84a]

5,10,15,20-Tetrahexylporphyrin (11), 5-(4-acetoxyphenyl)-10,15,20-trihexylporphyrin (12), 5,15-bis(4-acetoxyphenyl)-10,20-dihexylporphyrin (44), 5,10-bis(4-acetoxyphenyl)-15,20-dihexylporphyrin (45) and 5,10,15-tris(4-acetoxyphenyl)-20-hexylporphyrin (46):

According to the general procedure IV, 5-hexyldipyrromethane **41** (2.33 g, 10.1 mmol), 4-acetoxybenzaldehyde (1.73 g, 10.6 mmol), TFA (0.17 ml, 2.25 mmol), DDQ (5.56 g, 24.5 mmol) and triethylamine (1.37 ml, 9.85 mmol) were reacted in dry dichloromethane (2500 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (98:2) as the eluent. Five fractions could be isolated and were recrystallized from dichloromethane/methanol. The first fraction gave 5,10,15,20-tetrahexylporphyrin (45 mg, 2%), the second fraction gave trihexylporphyrin **12** (349 mg, 10%), the third fraction gave *trans*-porphyrin **44** (345 mg, 9%), the fourth fraction gave *cis*-porphyrin **45** (169 mg, 4%) and the fifth fraction gave mono-hexylporphyrin **46** (87 mg, 2%). All fractions were obtained as violet solids.



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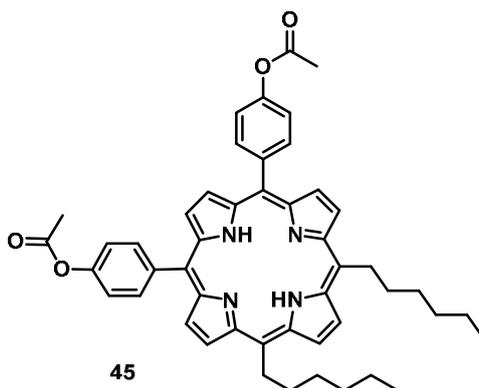
Melting Point: 93 °C

$^1\text{H-NMR}$ (700 MHz, CDCl_3): δ = -2.63 (br s, 2 H, NH), 0.98 (t, J = 7.4 Hz, 6 H, 2 x CH_3), 1.40-1.46 (m, 4 H, 2 x CH_2), 1.52-1.56 (m, 4 H, 2 x CH_2), 1.80-1.84 (m, 4 H, 2 x CH_2), 2.49-2.56 (m, 4 H, 2 x CH_2), 2.56 (s, 6 H, 2 x OCH_3), 4.94-4.97 (m, 4 H, 2 x CH_2), 7.55 (d, J = 8.2 Hz, 4 H, Ar- H_{meta}), 8.24 (d, J = 8.2 Hz, 4 H, Ar- H_{ortho}), 8.93 (d, J = 4.6 Hz, 4 H, $\beta\text{-H}$), 9.45 (d, J = 4.6 Hz, 4 H, $\beta\text{-H}$) ppm.

$^{13}\text{C-NMR}$ (176 MHz, CDCl_3): δ = 14.16 (CH_3), 21.44 (OCH_3), 22.73 (CH_2), 30.23 (CH_2), 31.92 (CH_2), 35.34 (CH_2), 38.72 (CH_2), 117.81 ($\text{Ar-C}_{\text{meso}}$), 119.68 ($\text{Ar-C}_{\text{meta}}$), 120.02 ($\text{Alkyl-C}_{\text{meso}}$), 135.18 ($\text{Ar-C}_{\text{ortho}}$), 140.21 ($\text{Ar-C}_{\text{ipso}}$), 150.52 (Ar-C_{OAc}), 169.61 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{48}\text{H}_{51}\text{N}_4\text{O}_4$ $[\text{M} + \text{H}]^+$: 747.3910, found: 747.3927.

UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 417 (5.26), 517 (4.31), 553 (3.81), 594 (3.62), 651 (3.64) nm.



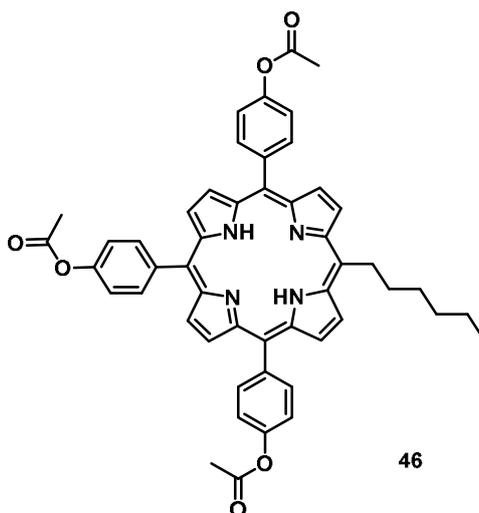
Melting Point: 94 °C

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = -2.73 (br s, 2 H, NH), 0.93 (t, J = 7.4 Hz, 6 H, 2 x CH_3), 1.22-1.37 (m, 4 H, 2 x CH_2), 1.38-1.41 (m, 4 H, 2 x CH_2), 1.71-1.85 (m, 4 H, 2 x CH_2), 2.48-2.58 (m, 4 H, 2 x CH_2), 2.50 (s, 6 H, 2 x OCH_3), 4.91-5.02 (m, 4 H, 2 x CH_2), 7.48 (d, J = 8.4 Hz, 4 H, $\text{Ar-H}_{\text{meta}}$), 8.17 (d, J = 8.4 Hz, 4 H, $\text{Ar-H}_{\text{ortho}}$), 8.74 (s, 1 H, $\beta\text{-H}$), 8.86 (d, J = 4.8 Hz, 2 H, $\beta\text{-H}$), 9.41 (d, J = 4.8 Hz, 2 H, $\beta\text{-H}$), 9.55 (s, 1 H, $\beta\text{-H}$) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ = 14.25 (CH_3), 21.50 (OCH_3), 22.84 (CH_2), 30.39 (CH_2), 32.01 (CH_2), 35.82 (CH_2), 38.99 (CH_2), 117.65 ($\text{Ar-C}_{\text{meso}}$), 119.87 ($\text{Ar-C}_{\text{meta}}$), 120.46 ($\text{Alkyl-C}_{\text{meso}}$), 135.30 ($\text{Ar-C}_{\text{ortho}}$), 139.92 ($\text{Ar-C}_{\text{ipso}}$), 150.63 (Ar-C_{OAc}), 169.69 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{48}\text{H}_{51}\text{N}_4\text{O}_4$ $[\text{M} + \text{H}]^+$: 747.3910, found: 747.3934.

UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 417 (5.19), 516 (4.22), 553 (3.71), 596 (3.61), 651 (3.49) nm.



Melting Point: 270 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.76 (s, 2 H, NH), 0.94 (t, J = 7.3 Hz, 3 H, CH₃), 1.36-1.44 (m, 2 H, CH₂), 1.48-1.53 (m, 2 H, CH₂), 1.77-1.84 (m, 2 H, CH₂), 2.50 (s, 3 H, OAc), 2.52 (s, 6 H, OAc), 2.53-2.58 (m, 2 H, CH₂), 4.99-5.02 (m, 2 H, CH₂), 7.50 (m, 6 H, Ar-H_{meta}), 8.20 (m, 6 H, Ar-H_{ortho}), 8.83 (s, 4 H, β -H), 8.94 (d, J = 4.7 Hz, 2 H, β -H), 9.50 (d, J = 4.7 Hz, 2 H, β -H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 14.05 (CH₃), 21.30 (OCH₃), 21.32 (OCH₃), 22.61 (CH₂), 30.14 (CH₂), 31.79 (CH₂), 35.47 (CH₂), 38.80 (CH₂), 118.16 (Ar-C_{meso}), 118.42 (Ar-C_{meso}), 119.68 (Ar-C_{meta}), 119.78 (Ar-C_{meta}), 121.00 (Alkyl-C_{meso}), 135.14 (Ar-C_{ortho}), 135.20 (Ar-C_{ortho}), 139.40 (Ar-C_{ipso}), 139.76 (Ar-C_{ipso}), 150.43 (Ar-C_{OH}), 150.45 (Ar-C_{OH}), 169.49 (C=O), 169.51 (C=O) ppm.

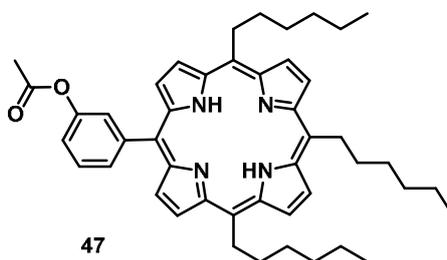
HRMS (ESI-TOF): m/z calcd. for C₅₀H₄₅N₄O₆ [M + H]⁺: 797.3339, found: 797.3348.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 418 (5.15), 516 (4.04), 551 (3.80), 593 (3.66), 650 (3.63) nm.

5,10,15,20-Tetrahexylporphyrin (11), 5-(3-acetoxyphenyl)-10,15,20-trihexylporphyrin (47), 5,15-bis(3-acetoxyphenyl)-10,20-dihexylporphyrin (48) and 5,10-bis(3-acetoxyphenyl)-15,20-dihexylporphyrin (49):

According to the general procedure IV, 5-hexyldipyrromethane **41** (1.90 g, 8.24 mmol), 3-acetoxybenzaldehyde (1.41 g, 8.64 mmol), TFA (0.14 mL, 1.85 mmol), DDQ (4.53 g, 20.0 mmol) and triethylamine (1.12 mL, 8.03 mmol) were reacted in dry dichloromethane (2000 mL). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (98:2) as the eluent. Four fractions could be isolated and were recrystallized from dichloromethane/methanol. The first fraction gave 5,10,15,20-tetrahexylporphyrin (32 mg, 1%), the second fraction gave

trihexylporphyrin **47** (249 mg, 9%), the third fraction gave *trans*-porphyrin **48** (253 mg, 8%) and the fourth fraction gave *cis*-porphyrin **49** (67 mg, 2%). All fractions were obtained as violet solids.

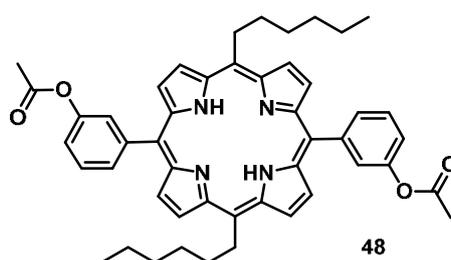


Melting Point: 83 °C

¹H-NMR (700 MHz, CDCl₃): δ = -2.67 (br s, 2 H, NH), 0.93 (t, J = 7.4 Hz, 6 H, 2 x CH₃), 0.96 (t, J = 7.4 Hz, 3 H, CH₃), 1.37-1.45 (m, 8 H, 4 x CH₂), 1.49-1.55 (m, 4 H, 2 x CH₂), 1.78-1.83 (m, 4 H, 2 x CH₂), 1.84-1.83 (m, 2 H, CH₂), 2.40 (s, 3 H, OCH₃), 2.49-2.54 (m, 4 H, 2 x CH₂), 2.55-2.59 (m, 2 H, CH₂), 4.93-4.96 (m, 4 H, 2 x CH₂), 4.99-5.02 (m, 2 H, CH₂), 7.53-7.56 (m, 1 H, Ar-H), 7.74-7.76 (m, 1 H, Ar-H), 7.90-7.94 (m, 1 H, Ar-H), 8.02-8.05 (m, 1 H, Ar-H), 8.85 (d, J = 4.7 Hz, 2 H, β -H), 9.40 (d, J = 4.7 Hz, 2 H, β -H), 9.51 (d, J = 4.7 Hz, 2 H, β -H), 9.54 (d, J = 4.7 Hz, 2 H, β -H) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 14.16 (CH₃), 21.29 (OCH₃), 22.75 (CH₂), 22.78 (CH₂), 30.27 (CH₂), 30.35 (CH₂), 31.94 (CH₂), 35.47 (CH₂), 35.86 (CH₂), 38.71 (CH₂), 38.91 (CH₂), 116.43 (Ar-C_{meso}), 119.28 (Alkyl-C_{meso}), 119.72 (Alkyl-C_{meso}), 120.76 (Ar-C), 127.40 (Ar-C), 127.69 (Ar-C), 132.10 (Ar-C), 144.00 (Ar-C_{ipso}), 149.18 (Ar-C_{OAc}), 169.70 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₆H₅₇N₄O₂ [M + H]⁺: 697.4481, found: 697.4423.



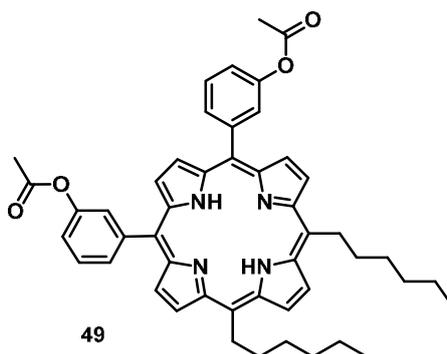
Melting Point: 98 °C

¹H-NMR (700 MHz, CDCl₃): δ = -2.71 (br s, 2 H, NH), 0.93 (t, J = 7.4 Hz, 6 H, 2 x CH₃), 1.36-1.42 (m, 4 H, 2 x CH₂), 1.48-1.53 (m, 4 H, 2 x CH₂), 1.77-1.82 (m, 4 H, 2 x CH₂), 2.42 (s, 6 H, 2 x OCH₃), 2.49-2.54 (m, 4 H, 2 x CH₂), 4.95-4.97 (m, 4 H, 2 x CH₂), 7.55-7.58 (m, 2 H, Ar-H), 7.74-7.78 (m, 2 H, Ar-H), 7.95-7.97 (m, 2 H, Ar-H), 8.05-8.08 (m, 2 H, Ar-H), 8.93 (d, J = 4.7 Hz, 4 H, β -H), 9.44 (d, J = 4.7 Hz, 4 H, β -H) ppm.

$^{13}\text{C-NMR}$ (176 MHz, CDCl_3): δ = 14.16 (CH_3), 21.30 (OCH_3), 22.73 (CH_2), 30.23 (CH_2), 31.93 (CH_2), 35.35 (CH_2), 38.74 (CH_2), 117.56 ($\text{Ar-C}_{\text{meso}}$), 120.10 ($\text{Alkyl-C}_{\text{meso}}$), 120.91 (Ar-C), 127.40 (Ar-C), 127.75 (Ar-C), 132.12 (Ar-C), 144.03 ($\text{Ar-C}_{\text{ipso}}$), 149.17 (Ar-C_{OAc}), 169.71 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{48}\text{H}_{51}\text{N}_4\text{O}_4$ $[\text{M} + \text{H}]^+$: 747.3910, found: 747.3954.

UV/Vis ($(\text{CH}_3)_2\text{CO}$): λ_{max} ($\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 418 (5.52), 516 (4.21), 552 (4.08), 594 (3.72), 653 (3.92) nm.



Melting Point: 101 °C

$^1\text{H-NMR}$ (700 MHz, CDCl_3): δ = -2.74 (br s, 2 H, NH), 0.93 (t, J = 7.4 Hz, 6 H, 2 x CH_3), 1.37-1.44 (m, 4 H, 2 x CH_2), 1.50-1.56 (m, 4 H, 2 x CH_2), 1.79-1.85 (m, 4 H, 2 x CH_2), 2.39 (s, 6 H, 2 x OCH_3), 2.51-2.56 (m, 4 H, 2 x CH_2), 4.98-5.02 (m, 4 H, 2 x CH_2), 7.51-7.54 (m, 2 H, Ar-H), 7.72-7.76 (m, 2 H, Ar-H), 7.91-7.94 (m, 2 H, Ar-H), 8.03-8.06 (m, 2 H, Ar-H), 8.81 (s, 2 H, β -H), 8.92 (d, J = 4.8 Hz, 2 H, β -H), 9.47 (d, J = 4.8 Hz, 2 H, β -H), 9.57 (s, 2 H, β -H) ppm.

$^{13}\text{C-NMR}$ (176 MHz, CDCl_3): δ = 14.15 (CH_3), 21.29 (OCH_3), 22.72 (CH_2), 30.28 (CH_2), 31.92 (CH_2), 35.63 (CH_2), 38.93 (CH_2), 118.31 ($\text{Ar-C}_{\text{meso}}$), 120.95 (Ar-C), 121.30 ($\text{Alkyl-C}_{\text{meso}}$), 127.50 (Ar-C), 127.83 (Ar-C), 132.15 (Ar-C), 143.66 ($\text{Ar-C}_{\text{ipso}}$), 149.21 (Ar-C_{OAc}), 169.66 (C=O) ppm.

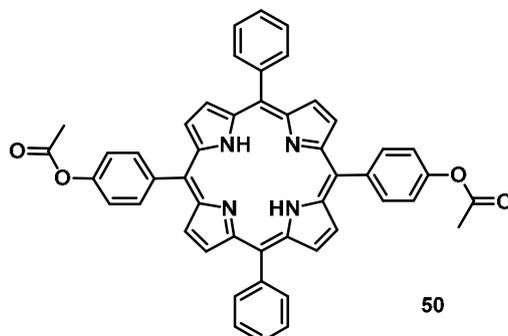
HRMS (ESI-TOF): m/z calcd. for $\text{C}_{48}\text{H}_{51}\text{N}_4\text{O}_4$ $[\text{M} + \text{H}]^+$: 747.3910, found: 747.3981.

UV/Vis ($(\text{CH}_3)_2\text{CO}$): λ_{max} ($\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 415 (5.39), 514 (4.12), 551 (4.16), 595 (3.69), 654 (3.83) nm.

5,15-Bis(4-acetoxyphenyl)-10,20-diphenylporphyrin (50):

According to the general procedure IV, 5-phenyldipyrromethane **42** (2.25 g, 10.1 mmol), 4-acetoxybenzaldehyde (1.48 ml, 10.5 mmol), TFA (0.17 mL, 2.25 mmol), DDQ (5.56 g, 25.0 mmol) and triethylamine (1.37 ml, 9.82 mmol) were reacted in dry dichloromethane (2500 ml). Purification

was achieved by column chromatography on silica using dichloromethane/methanol (99:1) as the eluent and subsequent recrystallization from dichloromethane/methanol to obtain the desired product (210 mg, 6%) as a violet solid.



Melting Point: > 300 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.77 (br s, 2 H, NH), 2.49 (br s, 6 H, 2 x OCH₃), 7.50 (d, J = 8.1 Hz, 4 H, Ar-H_{meta}), 7.71-7.79 (m, 6 H, 4 x Ph-H_{meta}, 2 x Ph-H_{para}), 8.19-8.25 (m, 4 H, Ph-H_{ortho}), 8.24 (d, J = 8.1 Hz, 2 H, Ar-H_{ortho}), 8.87-8.90 (m, 8 H, β -H) ppm.

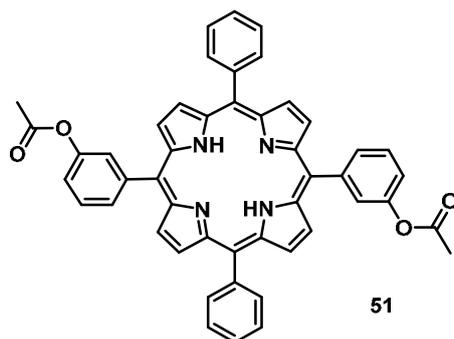
¹³C-NMR (126 MHz, CDCl₃): δ = 21.46 (CH₃), 119.13 (Ph-C_{meso}), 119.91 (Ar-C_{meta}), 120.40 (Ar-C_{meso}), 126.80 (Ph-C_{meta}), 127.86 (Ph-C_{para}), 134.64 (Ph-C_{ortho}), 135.39 (Ar-C_{ortho}), 139.75 (Ar-C_{ipso}), 142.16 (Ph-C_{ipso}), 150.70 (Ar-C_{OAc}), 169.63 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₈H₃₅N₄O₄ [M + H]⁺: 731.2653, found: 731.2594.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 417 (5.24), 515 (3.89), 548 (3.44), 591 (3.13), 649 (3.18) nm.

5,15-Bis(3-acetoxyphenyl)-10,20-diphenylporphyrin (51):

According to the general procedure IV, 5-phenyldipyrromethane **42** (2.25 g, 10.1 mmol), 3-acetoxybenzaldehyde (1.73 g, 10.5 mmol), TFA (0.17 mL, 2.25 mmol), DDQ (5.56 g, 25.0 mmol) and triethylamine (1.37 mL, 9.82 mmol) were reacted in dry dichloromethane (2500 mL). Purification was achieved by column chromatography on silica using dichloromethane/methanol (99:1) as the eluent and subsequent recrystallization from dichloromethane/methanol to obtain the desired product (224 mg, 6%) as a violet solid.



Melting Point: > 300 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.83 (br s, 2 H, NH), 2.39 (s, 6 H, 2 x OAc), 7.52-7.55 (m, 2 H, Ar-H), 7.73-7.80 (m, 8 H, 4 x Ph-H_{meta}, 2 x Ph-H_{para}, 2 x Ar-H), 7.96-7.98 (m, 2 H, Ar-H), 8.08-8.10 (m, 2 H, Ar-H), 8.19-8.22 (m, 4 H, Ph-H_{ortho}), 8.87 (d, J = 4.6 Hz, 4 H, β -H), 8.91 (d, J = 4.6 Hz, 4 H, β -H) ppm.

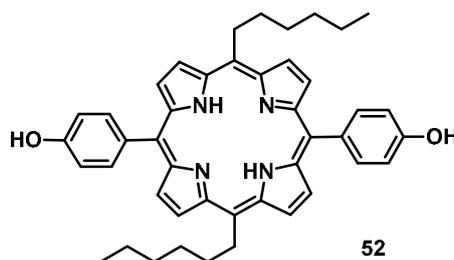
¹³C-NMR (126 MHz, CDCl₃): δ = 21.35 (OCH₃), 118.88 (Ph-C_{meso}), 120.47 (Ar-C_{meso}), 121.07 (Ar-C), 126.80 (Ar-C), 127.67 (Ph-C_{meta}), 127.87 (Ph-C_{para}), 128.05 (Ar-C), 132.31 (Ar-C), 134.65 (Ph-C_{ortho}), 142.11 (Ph-C_{ipso}), 143.54 (Ar-C_{ipso}), 149.33 (Ar-C_{OAc}), 169.74 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₈H₃₅N₄O₄ [M + H]⁺: 731.2658, found: 731.2655.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 416 (5.37), 514 (3.81), 547 (3.45), 590 (3.21), 648 (3.33) nm.

5,15-Bis(4-hydroxyphenyl)-10,20-dihexylporphyrin (52):

According to the general procedure V, acetylated porphyrin **44** (200 mg, 286 μ mol) was dissolved in THF (30 ml) and saturated methanolic KOH solution (50 ml) was added. After full conversion, purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent followed by recrystallization from dichloromethane/methanol to obtain the desired product (184 mg, 97%) as a violet solid.



Melting Point: 112 °C

¹H-NMR (700 MHz, (CD₃)₂CO): δ = -2.67 (br s, 2 H, NH), 0.90 (t, J = 7.4 Hz, 6 H, 2 x CH₃), 1.34-1.41 (m, 4 H, 2 x CH₂), 1.45-1.52 (m, 4 H, 2 x CH₂), 1.78-1.85 (m, 4 H, 2 x CH₂), 2.46-2.54 (m, 4 H, 2 x CH₂), 4.93-4.98 (m, 4 H, 2 x CH₂), 7.27 (d, J = 8.4 Hz, 4 H, Ar-H_{meta}), 8.00 (d, J = 8.4 Hz, 4 H, Ar-H_{ortho}), 8.88 (d, J = 4.8 Hz, 4 H, β -H), 9.54 (d, J = 4.8 Hz, 4 H, β -H) ppm.

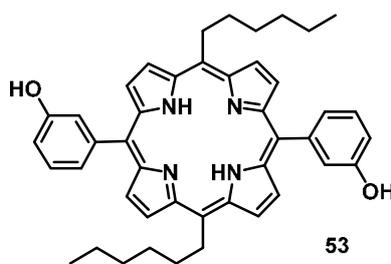
¹³C-NMR (176 MHz, (CD₃)₂CO): δ = 13.47 (CH₃), 22.49 (CH₂), 29.89 (CH₂), 31.76 (CH₂), 34.76 (CH₂), 38.80 (CH₂), 113.60 (Ar-C_{meta}), 118.95 (Ar-C_{meso}), 119.63 (Ar-C_{meso}), 133.60 (Ar-C_{ipso}), 135.40 (Ar-C_{ortho}), 157.39 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₄₇N₄O₂ [M + H]⁺: 663.3699, found: 663.3693.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 418 (5.61), 515 (4.30), 551 (4.13), 596 (3.79), 652 (3.93) nm.

5,15-Bis(3-hydroxyphenyl)-10,20-dihexylporphyrin (53):

According to the general procedure V, acetylated porphyrin **48** (240 mg, 0.32 mmol) was dissolved in THF (30 ml) and saturated methanolic KOH solution (60 ml) was added. After full conversion, purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent followed by recrystallization from dichloromethane/methanol to obtain the desired product (204 mg, 96%) as a violet solid.



Melting Point: 217 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = -2.70 (br s, 2 H, NH), 0.85 (t, J = 7.3 Hz, 6 H, 2 x CH₃), 1.28-1.35 (m, 4 H, 2 x CH₂), 1.40-1.46 (m, 4 H, 2 x CH₂), 1.72-1.78 (m, 4 H, 2 x CH₂), 2.41-2.47 (m, 4 H, 2 x CH₂), 4.91 (t, J = 8.2 Hz, 4 H, 2 x CH₂), 7.31-7.33 (m, 2 H, Ar-H), 7.56-7.60 (m, 2 H, Ar-H), 7.61-7.63 (m, 2 H, Ar-H), 7.67-7.69 (m, 2 H, Ar-H), 8.88 (d, J = 4.8 Hz, 4 H, β -H), 9.16 (br s, 2 H, Ar-OH), 9.53 (d, J = 4.8 Hz, 4 H, β -H) ppm.

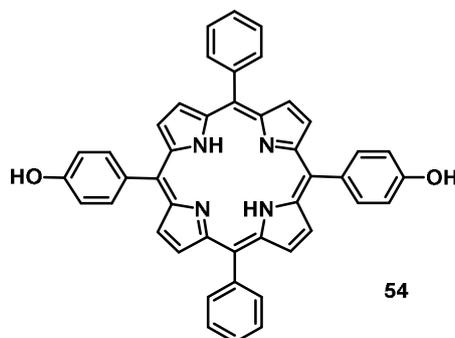
¹³C-NMR (126 MHz, CDCl₃): δ = 13.54 (CH₃), 22.54 (CH₂), 29.92 (CH₂), 31.80 (CH₂), 34.75 (CH₂), 38.86 (CH₂), 114.93 (Ar-C), 117.38 (Ar-C_{meso}), 118.86 (Alkyl-C_{meso}), 119.90 (Alkyl-C_{meso}), 121.94 (Ar-C), 126.20 (Ar-C), 127.60 (Ar-C), 143.83 (Ar-C_{ipso}), 155.95 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for $C_{44}H_{47}N_4O_2$ $[M + H]^+$: 663.3699, found: 663.3714.

UV/Vis ((CH₃)₂CO): λ_{max} (log $\epsilon/dm^3 mol^{-1} cm^{-1}$): 417 (5.39), 515 (4.24), 552 (4.11), 596 (3.83), 653 (3.87) nm.

5,15-Bis(4-hydroxyphenyl)-10,20-diphenylporphyrin (54):

According to the general procedure V, acetylated porphyrin 50 (120 mg, 164 μ mol) was dissolved in THF (20 ml) and saturated methanolic KOH solution (25 ml) was added. After full conversion, purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent followed by recrystallization from dichloromethane/methanol to obtain the desired product (102 mg, 96%) as a violet solid.



Melting Point: > 300 °C

¹H-NMR (700 MHz, (CD₃)₂SO): δ = -2.89 (br s, 2 H, NH), 7.21 (d, J = 7.8 Hz, 4 H, Ar-H_{meta}), 7.81-7.86 (m, 6 H, 4 x Ph-H_{meta}, 2 x Ph-H_{para}), 8.00 (d, J = 7.8 Hz, 2 H, Ar-H_{ortho}), 8.20-8.23 (m, 4 H, Ph-H_{ortho}), 8.80-8.89 (m, 8 H, β -H), 9.96 (br s, 2 H, Ar-OH) ppm.

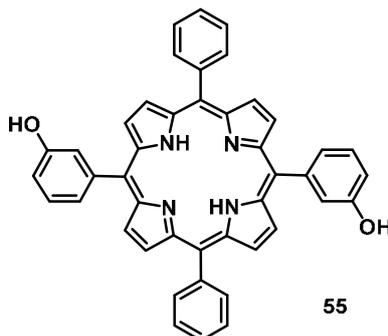
¹³C-NMR (176 MHz, (CD₃)₂SO): δ = 114.41 (Ar-C_{meta}), 120.18 (Ph-C_{meso}), 120.78 (Ar-C_{meso}), 127.44 (Ph-C_{meta}), 128.50 (Ph-C_{para}), 132.22 (Ar-C_{ipso}), 134.68 (Ph-C_{ortho}), 135.97 (Ar-C_{ortho}), 141.82 (Ph-C_{ipso}), 157.90 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for $C_{44}H_{31}N_4O_2$ $[M + H]^+$: 647.2447, found: 647.2452.

UV/Vis ((CH₃)₂SO): λ_{max} (log $\epsilon/dm^3 mol^{-1} cm^{-1}$): 416 (5.19), 513 (3.85), 547 (3.49), 591 (3.04), 650 (3.27) nm.

5,15-Bis(3-hydroxyphenyl)-10,20-diphenylporphyrin (55):

According to the general procedure V, acetylated porphyrin 51 (100 mg, 137 μmol) was dissolved in THF (20 ml) and saturated methanolic KOH solution (25 ml) was added. After full conversion, purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent followed by recrystallization from dichloromethane/methanol to obtain the desired product (88 mg, 99%) as a violet solid.



Melting Point: > 300 °C

$^1\text{H-NMR}$ (500 MHz, $\text{C}_4\text{D}_8\text{O}$): δ = -2.71 (br s, 2 H, NH), 7.18-7.21 (m, 2 H, Ar-H), 7.52-7.55 (m, 2 H, Ar-H), 7.64-7.67 (m, 4 H, Ar-H), 7.74-7.80 (m, 6 H, 4 x Ph- H_{meta} , 2 x Ph- H_{para}), 8.19-8.22 (m, 4 H, Ph- H_{ortho}), 8.73 (br s, 2 H, Ar-OH), 8.80 (d, J = 4.7 Hz, 4 H, β -H), 8.91 (d, J = 4.7 Hz, 4 H, β -H) ppm.

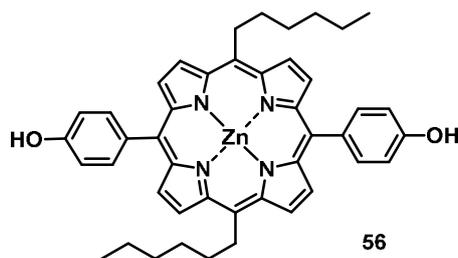
$^{13}\text{C-NMR}$ (126 MHz, $\text{C}_4\text{D}_8\text{O}$): δ = 114.74 (Ar-C), 119.87 (Ph- C_{meso}), 120.15 (Ar- C_{meso}), 122.08 (Ar-C), 126.18 (Ar-C), 126.66 (Ph- C_{meta}), 127.36 (Ar-C), 127.65 (Ph- C_{para}), 134.42 (Ph- C_{ortho}), 142.42 (Ph- C_{ipso}), 143.45 (Ar- C_{ipso}), 156.28 (Ar- C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{44}\text{H}_{31}\text{N}_4\text{O}_2$ [$\text{M} + \text{H}$] $^+$: 647.2447, found: 647.2448.

UV/Vis ($\text{C}_4\text{H}_8\text{O}$): λ_{max} ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 417 (5.18), 513 (3.72), 548 (3.51), 590 (2.99), 649 (3.27) nm.

[5,15-Bis(4-hydroxyphenyl)-10,20-dihexylporphyrinato]zinc(II) (56):

According to the general procedure VI, a mixture of porphyrin 52 (184 mg, 278 μmol) and $\text{Zn}(\text{OAc})_2 \cdot 2 \text{H}_2\text{O}$ (250 mg, 1.14 mmol) was reacted in dichloromethane/methanol (15 ml, 4:1). Purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent and subsequent recrystallization from dichloromethane/methanol to obtain the desired product (199 mg, 98%) as a pink solid.



Melting Point: 273 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = 0.92 (t, J = 7.4 Hz, 6 H, 2 x CH₃), 1.33-1.44 (m, 4 H, 2 x CH₂), 1.47-1.59 (m, 4 H, 2 x CH₂), 1.81-1.93 (m, 4 H, 2 x CH₂), 2.55 (m, 4 H, 2 x CH₂), 5.06 (t, J = 8.2 Hz, 4 H, 2 x CH₂), 7.26 (d, J = 8.2 Hz, 4 H, Ar-H_{meta}), 8.00 (d, J = 8.2 Hz, 4 H, Ar-H_{ortho}), 8.92 (d, J = 4.6 Hz, 4 H, β -H), 9.59 (d, J = 4.6 Hz, 4 H, β -H) ppm.

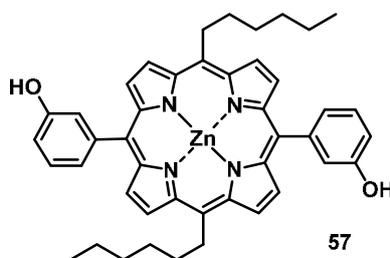
¹³C-NMR (126 MHz, (CD₃)₂CO): δ = 13.59 (CH₃), 22.62 (CH₂), 30.12 (CH₂), 31.92 (CH₂), 35.38 (CH₂), 39.27 (CH₂), 113.41 (Ar-C_{meta}), 119.44 (Ar-C_{meso}), 120.04 (Ar-C_{meso}), 128.51 (β -C), 131.84 (β -C), 134.78 (Ar-C_{ipso}), 135.40 (Ar-C_{ortho}), 149.66 (α -C), 150.18 (α -C), 157.09 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₄₄N₄O₂Zn [M]⁺: 724.2756, found: 724.2743.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 424 (5.52), 552 (4.26), 592 (3.86) nm.

[5,15-Bis(3-hydroxyphenyl)-10,20-dihexylporphyrinato]zinc(II) (57):

According to the general procedure VI, porphyrin 53 (180 mg, 272 μ mol) was dissolved in dichloromethane/methanol (25 ml, 4:1) and Zn(OAc)₂ · 2 H₂O (250 mg, 1.14 mmol) was added. Purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent followed by recrystallization from dichloromethane/methanol to obtain the desired product (207 mg, 97%) as a pink solid.



Melting Point: > 300 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = 0.92 (t, J = 7.3 Hz, 6 H, 2 x CH₃), 1.36-1.43 (m, 4 H, 2 x CH₂), 1.49-1.55 (m, 4 H, 2 x CH₂), 1.84-1.90 (m, 4 H, 2 x CH₂), 2.51-2.58 (m, 4 H, 2 x CH₂), 5.05 (t, J =

8.2 Hz, 4 H, 2 x CH₂), 7.27-7.29 (m, 2 H, Ar-H), 7.56-7.59 (m, 2 H, Ar-H), 7.62-7.64 (m, 2 H, Ar-H), 7.67-7.69 (m, 2 H, Ar-H), 8.91 (d, *J* = 4.6 Hz, 4 H, β-H), 9.03 (br s, 2 H, Ar-OH), 9.58 (d, *J* = 4.6 Hz, 4 H, β-H) ppm.

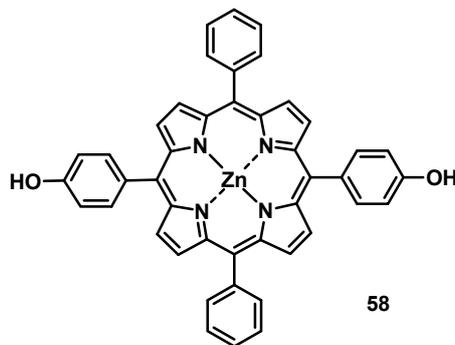
¹³C-NMR (126 MHz, (CD₃)₂CO): δ = 13.60 (CH₃), 22.63 (CH₂), 30.14 (CH₂), 31.93 (CH₂), 35.41 (CH₂), 39.33 (CH₂), 114.34 (Ar-C), 119.24 (Ar-C_{meso}), 120.10 (Ar-C_{meso}), 122.04 (Ar-C), 126.32 (Ar-C), 127.21 (Ar-C), 128.56 (β-C), 131.73 (β-C), 145.09 (Ar-C_{ipso}), 149.06 (α-C), 150.25 (α-C), 155.70 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): *m/z* calcd. for C₄₄H₄₄N₄O₂Zn [M]⁺: 724.2756, found: 724.2815.

UV/Vis ((CH₃)₂CO): λ_{max} (log ε/dm³ mol⁻¹ cm⁻¹): 423 (5.58), 552 (4.39), 594 (3.91) nm.

[5,15-Bis(4-hydroxyphenyl)-10,20-diphenylporphyrinato]zinc(II) (58):

According to the general procedure VI, porphyrin 54 (90 mg, 139 μmol) was dissolved in dichloromethane/methanol (10 ml, 4:1) and Zn(OAc)₂ · 2 H₂O (150 mg, 0.68 mmol) was added. Purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent followed by recrystallization from dichloromethane/methanol to obtain the desired product (97 mg, 98%) as a pink solid.



Melting Point: > 300 °C

¹H-NMR (700 MHz, (CD₃)₂SO): δ = 7.18 (d, *J* = 8.2 Hz, 4 H, Ar-H_{meta}), 7.78-7.82 (m, 6 H, 4 x Ph-H_{meta}, 2 x Ph-H_{para}), 7.96 (d, *J* = 8.2 Hz, 4 H, Ar-H_{ortho}), 8.17-8.20 (m, 4 H, Ph-H_{ortho}), 8.75 (d, *J* = 4.5 Hz, 4 H, β-H), 8.84 (d, *J* = 4.5 Hz, 4 H, β-H), 9.84 (br s, 2 H, Ar-OH) ppm.

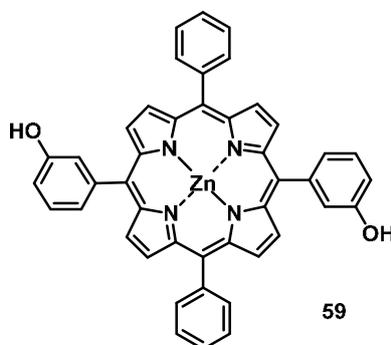
¹³C-NMR (176 MHz, (CD₃)₂SO): δ = 113.98 (Ar-C_{meta}), 120.48 (Ph-C_{meso}), 121.02 (Ar-C_{meso}), 127.03 (Ph-C_{meta}), 127.86 (Ph-C_{para}), 131.75 (β-C), 132.16 (β-C), 133.78 (Ar-C_{ipso}), 134.62, (Ph-C_{ortho}), 135.74 (Ar-C_{ortho}), 143.34 (Ph-C_{ipso}), 149.57 (α-C), 150.23 (α-C), 157.39 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for $C_{44}H_{28}N_4O_2Zn^+ [M]^+$: 708.1504, found: 708.1493.

UV/Vis ($(CH_3)_2SO$): λ_{max} ($\log \epsilon/dm^3 mol^{-1} cm^{-1}$): 424 (5.33), 554 (4.25), 594 (3.64) nm.

[5,15-Bis(3-hydroxyphenyl)-10,20-diphenylporphyrinato]zinc(II) (59):

According to the general procedure VI, porphyrin 55 (50 mg, 77 μ mol) was dissolved in dichloromethane/methanol (5 ml, 4:1) and $Zn(OAc)_2 \cdot 2 H_2O$ (100 mg, 0.45 mmol) was added. Purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent followed by recrystallization from dichloromethane/methanol to obtain the desired product (60 mg, 100%) as a pink solid.



Melting Point: > 300 °C

1H -NMR (500 MHz, C_4D_8O): δ = 7.18-7.20 (m, 2 H, Ar-H), 7.51-7.55 (m, 2 H, Ar-H), 7.65-7.68 (m, 4 H, Ar-H), 7.72-7.76 (m, 6 H, 4 x Ph-H_{meta}, 2 x Ph-H_{para}), 8.20-8.23 (m, 4 H, Ph-H_{ortho}), 8.71 (br s, 2 H, Ar-OH), 8.84 (d, J = 4.6 Hz, 4 H, β -H), 8.95 (d, J = 4.6 Hz, 4 H, β -H) ppm.

^{13}C -NMR (126 MHz, C_4D_8O): δ = 114.23 (Ar-C), 120.38 (Ph-C_{meso}), 120.70 (Ar-C_{meso}), 122.24 (Ar-C), 126.26 (Ph-C_{meta}), 126.90 (Ar-C), 127.14 (Ph-C_{para}), 131.09 (β -C), 131.41 (β -C), 134.46 (Ph-C_{ortho}), 143.75 (Ph-C_{ipso}), 144.78 (Ar-C_{ipso}), 150.01 (α -C), 150.05 (α -C), 156.01 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for $C_{44}H_{29}N_4O_2Zn [M + H]^+$: 709.1582, found: 709.1615.

UV/Vis (C_4H_8O): λ_{max} ($\log \epsilon/dm^3 mol^{-1} cm^{-1}$): 423 (5.40), 556 (4.32), 595 (3.77) nm.

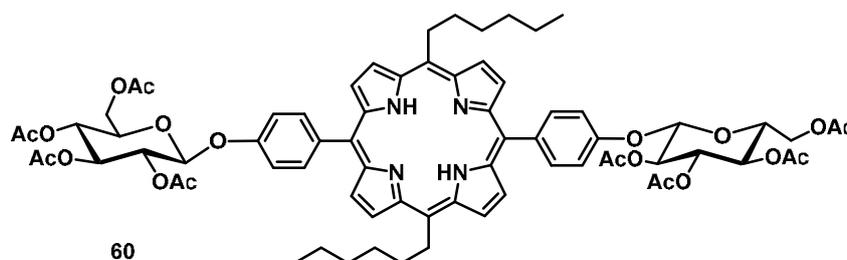
5,15-Bis[4-(2,3,4,6-tetraacetyl- β -D-glucosyl)phenyl]-10,20-dihexylporphyrin (60):

According to the general procedure VII, metallated hydroxyporphyrin 56 (75 mg, 103 μ mol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate 2 (250 mg, 512 μ mol) and $BF_3 \cdot Et_2O$ (5.0 μ l, 40 μ mol) were

reacted in a mixture of dry dichloromethane/acetonitrile (20 ml, 95:5) for 2 h. Demetallation was accomplished with HCl (1.0 ml, 25%) in THF (20 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired product (113 mg, 82%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.

Upscaled Reaction:

According to the general procedure VII, metallated hydroxyporphyrin **56** (170 mg, 234 μmol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate **2** (668 mg, 1.36 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (10.0 μl , 80 μmol) were reacted in a mixture of dry dichloromethane/acetonitrile (30 ml, 29:1) for 2 h. Demetallation was accomplished with HCl (3.0 ml, 25%) in THF (60 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired product (238 mg, 77%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 204 °C

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = -2.70 (br s, 2 H, NH), 0.91 (t, J = 7.5 Hz, 6 H, 2 x CH_3), 1.33-1.41 (m, 4 H, 2 x CH_2), 1.46-1.52 (m, 4 H, 2 x CH_2), 1.75-1.81 (m, 4 H, 2 x CH_2), 2.11 (s, 6 H, 2 x OAc), 2.12 (s, 6 H, 2 x OAc), 2.14 (s, 6 H, 2 x OAc), 2.24 (s, 6 H, 2 x OAc), 2.47-2.53 (m, 4 H, 2 x CH_2), 4.07 (ddd, J = 2.4, 5.5, 10.2 Hz, 2 H, 2 x H-5'ose'), 4.32 (dd, J = 2.4, 12.3 Hz, 2 H, 2 x H-6_A'ose'), 4.44 (dd, J = 5.5, 12.3 Hz, 2 H, 2 x H-6_B'ose'), 4.92-4.97 (m, 4 H, 2 x CH_2), 5.32 (dd, J = 9.4, 10.1 Hz, 2 H, 2 x H-4'ose'), 5.45-5.53 (m, 6 H, 2 x H-1'ose', 2 x H-2'ose', 2 x H-3'ose'), 7.38 (d, J = 8.5 Hz, 4 H, Ar-H_{meta}), 8.11 (d, J = 8.5 Hz, 4 H, Ar-H_{ortho}), 8.85 (d, J = 4.8 Hz, 4 H, β -H), 9.42 (d, J = 4.8 Hz, 4 H, β -H) ppm.

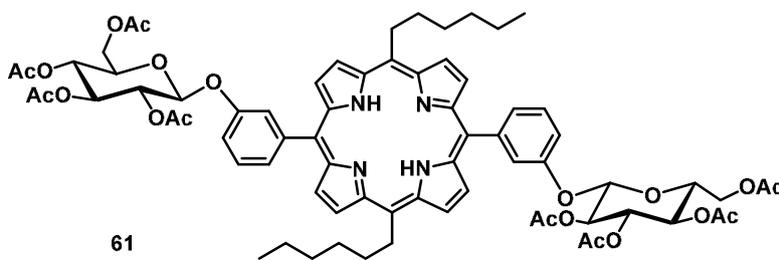
$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ = 14.11 (CH_3), 20.64 (OCH_3), 20.72 (OCH_3), 20.82 (OCH_3), 22.69 (CH_2), 30.32 (CH_2), 31.89 (CH_2), 35.31 (CH_2), 38.68 (CH_2), 62.14 (C-6'ose'), 68.46 (C-4'ose'), 71.38 (C-2'ose'), 72.32 (C-5'ose'), 72.89 (C-3'ose'), 99.30 (C-1'ose'), 114.93 (Ar-C_{meta}), 117.96 (Ar-C_{meso}), 119.93 (Ar-C_{meso}), 135.40 (Ar-C_{ortho}), 137.79 (Ar-C_{ipso}), 156.57 (Ar-C_{OGLc}), 169.48 (C=O), 170.35 (C=O), 170.65 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{72}\text{H}_{82}\text{N}_4\text{O}_{20}^+$ [$\text{M} + \text{H}$]⁺: 1323.5601, found: 1323.5572.

UV/Vis (CH₂Cl₂): λ_{\max} (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 419 (5.59), 518 (4.28), 554 (4.03), 597 (3.71), 653 (3.81) nm.

5,15-Bis[3-(2,3,4,6-tetraacetyl- β -D-glucosyl)phenyl]-10,20-dihexylporphyrin (61):

According to the general procedure VII, metallated hydroxyporphyrin 57 (75 mg, 0.1 mmol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate 2 (250 mg, 507 μmol) and BF₃·Et₂O (5.0 μl , 40 μmol) were reacted in a mixture of dry dichloromethane/acetonitrile (20 ml, 19:1) for 2 h. Demetallation was accomplished with HCl (1.0 ml, 25%) in THF (10 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired product (108 mg, 78%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/aqueous methanol.



¹H-NMR (500 MHz, CDCl₃): δ = -2.75 (m, 2 H, NH), 0.96-1.01 (m, 6 H, 2 x CH₃), 1.31 (s, 3 H, OAc), 1.32 (s, 3 H, OAc), 1.36-1.43 (m, 4 H, 2 x CH₂), 1.48-1.57 (m, 4 H, 2 x CH₂), 1.77-1.84 (m, 4 H, 2 x CH₂), 1.98 (s, 6 H, 2 x OAc), 2.04 (s, 6 H, 2 x OAc), 2.11 (s, 6 H, 2 x OAc), 2.47-2.57 (m, 4 H, 2 x CH₂), 3.76-3.80 (m, 2 H, H-5'ose'), 4.03-4.07 (m, 2 H, H-6_A'ose'), 4.14-4.19 (m, 2 H, H-6_B'ose'), 4.93-5.00 (m, 4 H, 2 x CH₂), 5.18 (dd, J = 9.3, 9.3 Hz, 2 H, H-4'ose'), 5.32 (dd, J = 9.3, 9.3 Hz, 2 H, H-3'ose'), 5.36 (d, J = 7.9 Hz, 2 H, H-1'ose'), 5.41 (dd, J = 7.9, 9.3 Hz, 2 H, H-2'ose'), 7.40-7.44 (m, 2 H, Ar-H), 7.62-7.68 (m, 2 H, Ar-H), 7.80-7.85 (m, 2 H, Ar-H), 7.90-7.93 (m, 2 H, Ar-H), 8.86 (d, J = 4.8 Hz, 4 H, β -H), 9.39-9.45 (m, 4 H, β -H) ppm.

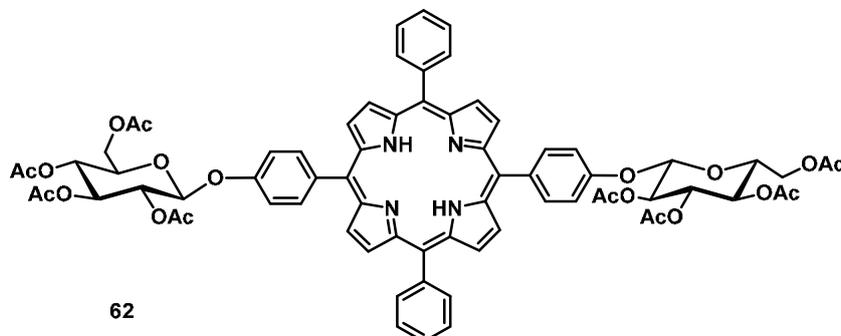
HRMS (ESI-TOF): m/z calcd. for C₇₂H₈₃N₄O₂₀ [M + H]⁺: 1323.5601, found: 1323.5552.

Analytical data are in accordance with published data.^[112]

5,15-Bis[4-(2,3,4,6-tetraacetyl- β -D-glucosyl)phenyl]-10,20-diphenylporphyrin (62):

According to the general procedure VII, metallated hydroxyporphyrin 58 (40 mg, 56 μmol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate 2 (100 mg, 203 μmol) and BF₃·Et₂O (2.0 μl , 16 μmol) were reacted in a mixture of dry dichloromethane/acetonitrile (8 ml, 19:1) for 2 h. Demetallation was accomplished with HCl (0.4 ml, 25%) in THF (8 ml). Purification was achieved by column

chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired product (54 mg, 73%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/aqueous methanol.



Melting Point: > 300 °C

¹H-NMR (700 MHz, CDCl₃): δ = -2.77 (br s, 2 H, NH), 2.13 (s, 6 H, 2 x OAc), 2.14 (s, 6 H, 2 x OAc), 2.15 (s, 6 H, 2 x OAc), 2.25 (s, 6 H, 2 x OAc), 4.09 (ddd, J = 2.4, 5.5, 10.1 Hz, 2 H, 2 x H-5'ose'), 4.33 (dd, J = 2.4, 12.3 Hz, 2 H, 2 x H-6_A'ose'), 4.45 (dd, J = 5.5, 12.3 Hz, 2 H, 2 x H-6_B'ose'), 5.32-5.36 (m, 2 H, H-4'ose'), 5.47-5.53 (m, 6 H, H-1'ose', H-2'ose', H-3'ose'), 7.41 (d, J = 8.5 Hz, 4 H, Ar-H_{meta}), 7.77-7.83 (m, 6 H, 4 x Ph-H_{meta}, 2 x Ph-H_{para}), 8.17 (d, J = 8.5 Hz, 4 H, Ar-H_{ortho}), 8.22-8.25 (m, 4 H, Ph-H_{ortho}), 8.87-8.91 (m, 8 H, β -H) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 20.70 (CH₃), 20.74 (CH₃), 20.82 (CH₃), 20.87 (CH₃), 62.10 (C-6'ose'), 68.37 (C-4'ose'), 71.31 (C-2'ose'), 72.29 (C-5'ose'), 72.85 (C-3'ose'), 99.15 (C-1'ose'), 115.03 (Ar-C_{meta}), 119.24 (Ar-C_{meso}), 120.26 (Ph-C_{meso}), 126.74 (Ph-C_{meta}), 127.80 (Ph-C_{para}), 134.55 (Ph-C_{ortho}), 135.58 (Ar-C_{ortho}), 137.22 (Ar-C_{ipso}), 142.07 (Ph-C_{ipso}), 156.62 (Ar-C_{Oglc}), 169.52 (C=O), 170.37 (C=O), 170.67 (C=O) ppm.

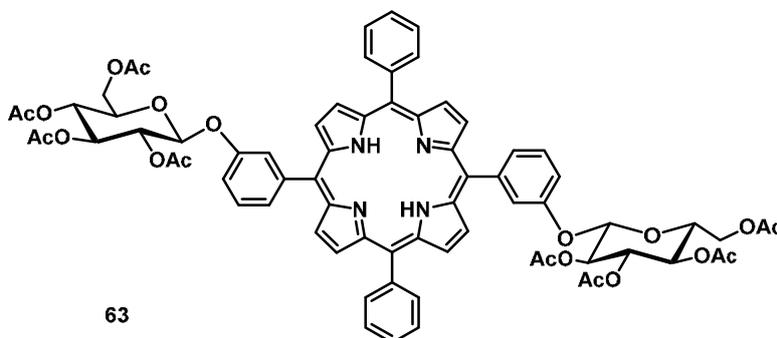
HRMS (ESI-TOF): m/z calcd. for C₇₂H₆₆N₄O₂₀Na [M + Na]⁺: 1329.4120, found: 1329.4182.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 416 (5.38), 513 (3.79), 548 (3.51), 590 (3.23), 648 (3.32) nm.

5,15-Bis[3-(2,3,4,6-tetraacetyl- β -D-glucosyl)phenyl]-10,20-diphenylporphyrin (63):

According to the general procedure VII, metallated hydroxyporphyrin **59** (20 mg, 28 μ mol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate **2** (50 mg, 102 μ mol) and BF₃·Et₂O (1.0 μ l, 8.0 μ mol) were reacted in a mixture of dry dichloromethane/acetonitrile (4 ml, 19:1) for 2 h. Demetallation was accomplished with HCl (0.2 ml, 25%) in THF (4 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired

product (28 mg, 75%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/aqueous methanol.



Melting Point: > 300 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.83 (br s, 2 H, NH), 1.31-1.34 (m, 6 H, 2 x OAc), 1.97-1.98 (m, 6 H, 2 x OAc), 2.03 (m, 6 H, 2 x OAc), 2.09 (s, 6 H, 2 x OAc), 3.76-3.80 (m, 2 H, H-5'ose'), 4.00-4.04 (m, 2 H, H-6_A'ose'), 4.13-4.17 (m, 2 H, H-6_B'ose'), 5.13-5.18 (m, 2 H, H-4'ose'), 5.29-5.40 (m, 6 H, H-1'ose', H-2'ose', H-3'ose'), 7.41-7.44 (m, 2 H, Ar-H), 7.64-7.69 (m, 2 H, Ar-H), 7.75-7.79 (m, 6 H, 4 x Ph-H_{meta}, 2 x Ph-H_{para}), 7.85-7.88 (m, 2 H, Ar-H), 7.93-7.96 (m, 2 H, Ar-H), 8.16-8.23 (m, 4 H, Ph-H_{ortho}), 8.84-8.88 (m, 8 H, β -H) ppm.

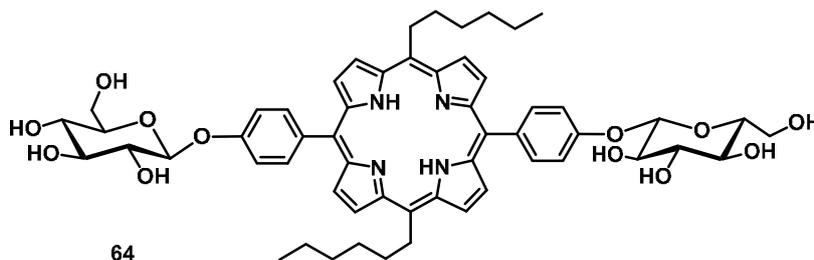
¹³C-NMR (126 MHz, CDCl₃): δ = 19.99 (CH₃), 20.63 (CH₃), 20.70 (CH₃), 20.81 (CH₃), 61.96 (C-6'ose'), 68.30 (C-4'ose'), 71.30 (C-2'ose'), 72.23 (C-5'ose'), 72.81 (C-3'ose'), 99.31 (C-1'ose'), 116.71 (Ar-C), 119.31 (Ph-C_{meso}), 120.50 (Ar-C_{meso}), 122.84 (Ar-C), 126.88 (Ph-C_{meta}), 127.84 (Ar-C), 127.95 (Ph-C_{para}), 129.99 (Ar-C), 134.61 (Ph-C_{ortho}), 142.01 (Ph-C_{ipso}), 143.78 (Ar-C_{ipso}), 155.41 (Ar-C_{O_{Gl}c}), 169.46 (C=O), 170.32 (C=O), 170.48 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for C₇₂H₆₆N₄O₂₀Na [M + Na]⁺: 1329.4120, found: 1329.4168.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 415 (5.41), 513 (3.79), 547 (3.56), 591 (3.26), 648 (3.36) nm.

5,15-Bis(4- β -D-glucosylphenyl)-10,20-dihexylporphyrin (64):

According to the general procedure VIII, acetylated glycoporphyrin **60** (50 mg, 38 μ mol) was dissolved in a mixture of dry THF/methanol (18 ml, 1:1). Then a solution of sodium methanolate in dry methanol (3 ml, 0.02 N) was added. After 4 h, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, using dichloromethane/methanol (8:2) as the eluent. The desired product (36 mg, 97%) was obtained as a violet crystalline solid.



Melting Point: 226 °C

¹H-NMR (500 MHz, (CD₃)₂SO): δ = -2.92 (br s, 2 H, NH), 0.84 (t, J = 7.3 Hz, 6 H, 2 x CH₃), 1.27 (m_c, 4 H, 4 x CH₂), 1.38 (m_c, 4 H, 4 x CH₂), 1.72 (m_c, 4 H, 4 x CH₂), 2.36 (m_c, 4 H, 4 x CH₂), 3.38-3.43 (m, 4 H, H'ose'), 3.48-3.53 (m, 2 H, H'ose'), 3.55-3.61 (m, 2 H, H'ose'), 3.79-3.83 (m, 2 H, H'ose'), 4.69-4.72 (m, 2 H, H'ose'), 4.91-4.98 (m, 4 H, 2 x CH₂), 5.25 (d, J = 7.4 Hz, 2 H, H-1'ose'), 7.46 (d, J = 8.6 Hz, 4 H, Ar-H_{meta}), 8.08 (d, J = 8.6 Hz, 4 H, Ar-H_{ortho}), 8.82 (d, J = 4.8 Hz, 4 H, β -H), 9.64 (d, J = 4.8 Hz, 4 H, β -H) ppm.

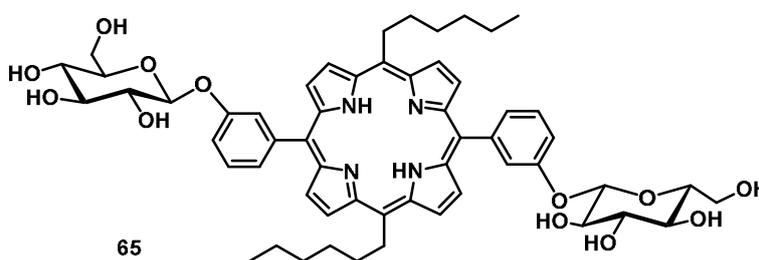
¹³C-NMR (126 MHz, (CD₃)₂SO): δ = 14.53 (CH₃), 22.72 (CH₂), 29.79 (CH₂), 29.94 (CH₂), 31.90 (CH₂), 39.24 (CH₂), 61.35 (C-6'ose'), 70.36 (C'ose'), 74.00 (C'ose'), 77.26 (C'ose'), 77.80 (C'ose'), 101.12 (C-1'ose'), 114.97 (Ar-C_{meta}), 118.78 (Ar-C_{meso}), 120.49 (Alkyl-C_{meso}), 135.68 (Ar-C_{ortho}), 157.90 (Ar-C_{OGlc}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₆H₆₇N₄O₁₂ [M + H]⁺: 987.4750, found: 987.4746.

UV/Vis ((CH₃)₂SO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 420 (5.19), 519 (3.89), 554 (3.73), 597 (3.43), 654 (3.56) nm.

5,15-Bis(3- β -D-glucosylphenyl)-10,20-dihexylporphyrin (65):

According to the general procedure VIII, acetylated glycoporphyrin **61** (20 mg, 15 μ mol) was dissolved in a mixture of dry THF/methanol (5 ml, 1:1). Then a solution of sodium methanolate in dry methanol (1.0 ml, 0.02 N) was added. After 4 h, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, using dichloromethane/methanol (8:2) as the eluent. The desired product (14 mg, 91%) was obtained as a violet crystalline solid.



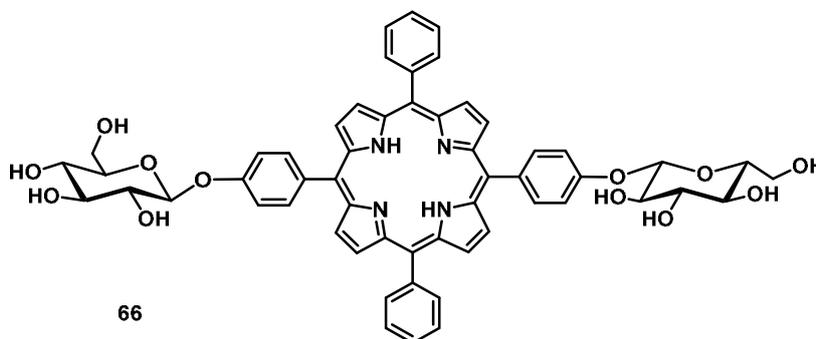
¹H-NMR (500 MHz, CD₃OD): δ = 0.85-0.92 (m, 6 H, 2 x CH₃), 1.29-1.43 (m, 8 H, 4 x CH₂), 1.65-1.73 (m, 4 H, 2 x CH₂), 2.31-2.42 (m, 4 H, 2 x CH₂), 3.38-3.90 (m, 10 H, H'ose'), 4.61-4.66 (m, 2 H, H'ose'), 4.82-4.91 (4 H, 2 x CH₂)*, 5.19-5.25 (m, 2 H, H'ose'), 7.56-7.62 (m, 2 H, Ar-H), 7.65-7.70 (m, 2 H, Ar-H), 7.74-7.81 (m, 2 H, Ar-H), 7.89-7.94 (m, 2 H, Ar-H), 8.79-8.91 (m, 4 H, β -H), 9.34-9.45 (m, 4 H, β -H) ppm.

* = signals of carbohydrate hydrogens are overlapped by the water peak of methanol

Analytical data are in accordance with published data.^[112]

5,15-Bis(4- β -D-glucosylphenyl)-10,20-diphenylporphyrin (66):

According to the general procedure VIII, acetylated glycoporphyrin **62** (40 mg, 31 μ mol) was dissolved in a mixture of dry THF/methanol (10 ml, 1:1). Then a solution of sodium methanolate in dry methanol (1.8 ml, 0.02 N) was added. After 4 h, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, using dichloromethane/methanol (8:2) as the eluent. The desired product (26 mg, 88%) was obtained as a violet crystalline solid.



Melting Point: > 300 °C

¹H-NMR (700 MHz, (CD₃)₂SO): δ = -2.90 (br s, 2 H, NH), 3.30-3.41 (m, 4 H, 2 x H'ose')*, 3.43-3.45 (m, 2 H, H'ose'), 3.50-3.53 (m, 2 H, H'ose'), 3.58-3.63 (m, 2 H, H-6'ose'), 3.79-3.84 (m, 2 H, H-6'ose'), 4.79 (br s, 2 H, OH'ose'), 5.23 (d, J = 7.2 Hz, 2 H, 2 x H-1'ose'), 5.38 (br s, 2 H, OH'ose'), 5.63 (br s, 2 H, OH'ose'), 5.88 (br s, 2 H, OH'ose'), 7.48 (d, J = 8.2 Hz, 4 H, Ar-H_{meta}), 7.83-7.89 (m, 6 H, 4 x Ph-H_{meta}, 2 x Ph-H_{para}), 8.14 (d, J = 8.2 Hz, 4 H, Ar-H_{ortho}), 8.22-8.24 (m, 4 H, Ph-H_{ortho}), 8.83-8.89 (m, 8 H, β -H) ppm.

* = signals of carbohydrate hydrogens are overlapped by the water peak of DMSO

¹³C-NMR (176 MHz, (CD₃)₂SO): δ = 61.27 (C-6'ose'), 66.15 (C'ose'), 70.27 (C'ose'), 73.93 (C'ose'), 77.76 (C'ose'), 101.04 (C-1'ose'), 115.00 (Ar-C_{meta}), 120.21 (Ar-C_{meso}), 120.37 (Ph-C_{meso}),

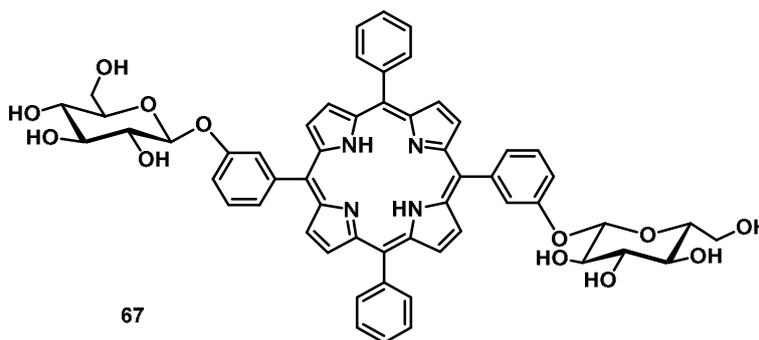
127.47 (Ph-C_{meta}), 128.54(Ph-C_{para}), 134.66 (Ph-C_{ortho}), 135.68 (Ar-C_{ortho}), 141.73 (Ph-C_{ipso}), 157.98 (Ar-C_{Oglc}) ppm.

HRMS (ESI-TOF): *m/z* calcd. for C₅₆H₅₀N₄O₁₂Na [M + Na]⁺: 993.3323, found: 993.3329.

UV/Vis ((CH₃)₂SO): λ_{max} (log ε/dm³ mol⁻¹ cm⁻¹): 415 (5.15), 514 (3.92), 548 (3.75), 590 (3.51), 647 (3.53) nm.

5,15-Bis(3-β-D-glucosylphenyl)-10,20-diphenylporphyrin (67):

According to the general procedure VIII, acetylated glycoporphyrin **63** (20 mg, 16 μmol) was dissolved in a mixture of dry THF/methanol (8 ml, 1:1). Then a solution of sodium methanolate in dry methanol (1.6 ml, 0.02 N) was added. After 4 h, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, using dichloromethane/methanol (8:2) as the eluent. The desired product (13 mg, 89%) was obtained as a violet crystalline solid.



Melting Point: > 300 °C

¹H-NMR (700 MHz, (CD₃)₂SO): δ = -2.92 (br s, 2 H, NH), 3.20-3.24 (m, 2 H, H'ose'), 3.29-3.35 (m, 6 H, H'ose')*, 3.46-3.50 (m, 2 H, H-6A'ose'), 3.66-3.69 (m, 2 H, H-6B'ose'), 4.54-4.56 (m, 2 H, OH'ose'), 4.98-5.00 (m, 2 H, OH'ose'), 5.09 (d, *J* = 4.9 Hz, 1 H, OH'ose'), 5.19-5.21 (m, 2 H, H-1'ose'), 5.42 (d, *J* = 4.8 Hz, 1 H, OH'ose'), 7.52-7.55 (m, 2 H, Ar-H), 7.72-7.75 (m, 2 H, Ar-H), 7.83-7.89 (m, 8 H, 4 x Ph-H_{meta}, 2 x Ph-H_{para}, 2 x Ar-H), 7.89-7.91 (m, 2 H, Ar-H), 8.23-8.25 (m, 4 H, Ph-H_{ortho}), 8.84-8.93 (m, 8 H, β-H) ppm.

* = signals of carbohydrate hydrogens are overlapped by the water peak of DMSO

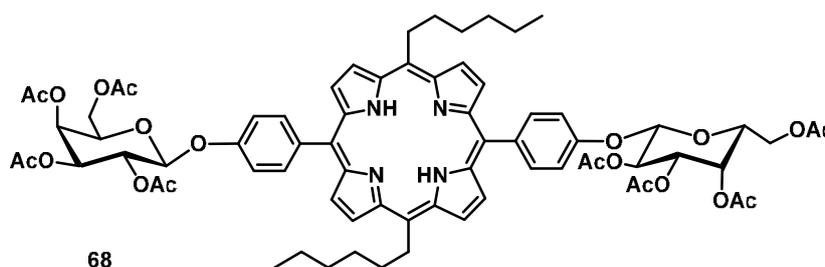
¹³C-NMR (176 MHz, (CD₃)₂SO): δ = 61.11 (C-6'ose'), 70.16 (C'ose'), 73.87 (C'ose'), 77.03 (C'ose'), 77.44 (C'ose'), 100.83-100.85 (C-1'ose'), 116.28 (Ar-C), 120.06 (Ar-C_{meso}), 120.46 (Ph-C_{meso}), 122.88 (Ar-C), 127.50 (Ph-C_{meta}), 128.34 (Ar-C), 128.58 (Ph-C_{para}), 128.93 (Ar-C), 134.66-134.72 (Ph-C_{ortho}), 141.66 (Ph-C_{ipso}), 142.82 (Ar-C_{ipso}), 156.35 (Ar-C_{Oglc}) ppm.

HRMS (ESI-TOF): m/z calcd. for $C_{56}H_{51}N_4O_{12}$ $[M + H]^+$: 971.3503, found: 971.3530.

UV/Vis ((CH₃)₂SO): λ_{max} (log $\epsilon/dm^3 mol^{-1} cm^{-1}$): 416 (5.26), 513 (3.84), 547 (3.54), 590 (3.32), 649 (3.30) nm.

5,15-Bis[4-(2,3,4,6-tetraacetyl- β -D-galactosyl)phenyl]-10,20-dihexylporphyrin (68):

According to the general procedure VII, metallated hydroxyporphyrin **56** (50 mg, 69 μ mol), 2,3,4,6-tetraacetyl-D-galactose trichloroacetimidate **4** (165 mg, 335 μ mol) and $BF_3 \cdot Et_2O$ (5.0 μ l, 40 μ mol) were reacted in a mixture of dry dichloromethane/acetonitrile (15 ml, 14:1) for 2 h. Demetallation was accomplished with HCl (0.7 ml, 25%) in THF (10 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired product (73 mg, 80%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/aqueous methanol.



Melting Point: 161 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.70 (br s, 2 H, NH), 0.91 (t, J = 7.4 Hz, 6 H, 2 x CH₃), 1.34-1.41 (m, 4 H, 2 x CH₂), 1.46-1.54 (m, 4 H, 2 x CH₂), 1.76-1.82 (m, 4 H, 2 x CH₂), 2.07 (s, 6 H, 2 x OAc), 2.08 (s, 6 H, 2 x OAc), 2.24 (s, 6 H, 2 x OAc), 2.27 (s, 6 H, 2 x OAc), 2.47-2.53 (m, 4 H, 2 x CH₂), 4.22-4.26 (m, 2 H, 2 x H-5'ose'), 4.29-4.39 (m, 4 H, 2 x H-6'ose'), 4.94-4.96 (m, 4 H, 2 x CH₂), 5.28 (dd, J = 3.6, 10.0 Hz, 2 H, 2 x H-3'ose'), 5.41 (d, J = 8.2 Hz, 2 H, 2 x H-1'ose'), 5.57 (dd, J = 0.9, 3.6 Hz, 2 H, 2 x H-4'ose'), 5.71 (dd, J = 8.2, 10.0 Hz, 2 H, 2 x H-2'ose'), 7.40 (d, J = 8.4 Hz, 4 H, Ar-H_{meta}), 8.12 (d, J = 8.4 Hz, 4 H, Ar-H_{ortho}), 8.86 (d, J = 4.8 Hz, 4 H, β -H), 9.42 (d, J = 4.8 Hz, 4 H, β -H) ppm.

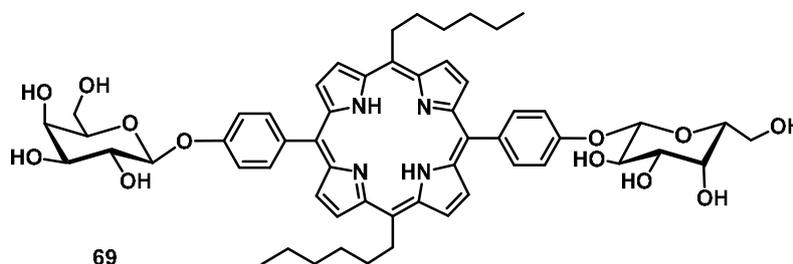
¹³C-NMR (126 MHz, CDCl₃): δ = 14.20 (CH₃), 20.74 (OCH₃), 20.79 (OCH₃), 20.83 (OCH₃), 21.02 (OCH₃), 22.78 (CH₂), 30.29 (CH₂), 31.98 (CH₂), 35.40 (CH₂), 38.78 (CH₂), 61.63 (C-6'ose'), 67.13 (C-4'ose'), 68.96 (C-2'ose'), 71.10 (C-3'ose'), 71.41 (C-5'ose'), 99.94 (C-1'ose'), 115.05 (Ar-C_{meta}), 118.08 (Ar-C_{meso}), 120.01 (Ar-C_{meso}), 135.48 (Ar-C_{ortho}), 137.85 (Ar-C_{ipso}), 156.70 (Ar-C_{OGal}), 169.63 (C=O), 170.30 (C=O), 170.40 (C=O), 170.50 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for $C_{72}H_{83}N_4O_{20}$ $[M + H]^+$: 1323.5601, found: 1323.5558.

UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 419 (5.60), 519 (4.26), 554 (4.02), 597 (3.69), 654 (3.80) nm.

5,15-Bis(4- β -D-galactosylphenyl)-10,20-dihexylporphyrin (69):

According to the general procedure VIII, acetylated glycoporphyrin 68 (30 mg, 23 μmol) was dissolved in a mixture of dry THF/methanol (10 ml, 1:1). Then a solution of sodium methanolate in dry methanol (1.8 ml, 0.02 N) was added. After 4 h, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, using dichloromethane/methanol (8:2) as the eluent. The desired product (21 mg, 93%) was obtained as a violet crystalline solid.



Melting Point: 176 °C

$^1\text{H-NMR}$ (500 MHz, $(\text{CD}_3)_2\text{SO}$): δ = -2.89 (br s, 2 H, NH), 0.86 (t, J = 7.5 Hz, 6 H, 2 x CH_3), 1.31 (m_c , 4 H, 2 x CH_2), 1.43 (m_c , 4 H, 2 x CH_2), 1.74 (m_c , 4 H, 2 x CH_2), 2.39 (m_c , 4 H, 2 x CH_2), 3.56-3.58 (m, 2 H, 2 x H-5'ose'), 3.67-3.71 (m, 4 H, 2 x H-6'ose'), 3.77-3.84 (m, 6 H, 2 x H-2'ose', 2 x H-3'ose', 2 x H-4'ose'), 4.64 (d, J = 4.7 Hz, 2 H, 2 x OH), 4.75-4.78 (m, 2 H, 2 x OH), 4.92-4.98 (m, 4 H, 2 x CH_2), 4.99 (d, J = 5.6 Hz, 2 H, 2 x OH), 5.20 (d, J = 7.8 Hz, 2 H, 2 x H-1'ose'), 5.40 (d, J = 5.2 Hz, 2 H, 2 x OH), 7.48 (d, J = 8.5 Hz, 4 H, Ar-H_{meta}), 8.09 (d, J = 8.5 Hz, 4 H, Ar-H_{ortho}), 8.84 (d, J = 4.4 Hz, 4 H, β -H), 9.65 (d, J = 4.4 Hz, 4 H, β -H) ppm.

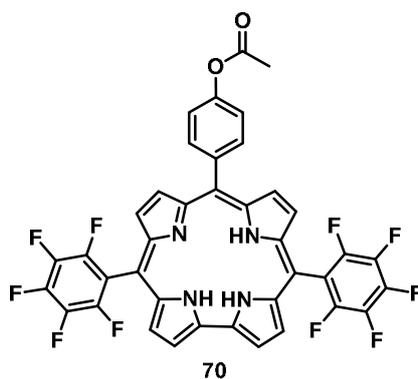
$^{13}\text{C-NMR}$ (126 MHz, $(\text{CD}_3)_2\text{SO}$): δ = 14.52 (CH_3), 22.71 (CH_2), 29.94 (CH_2), 30.98 (CH_2), 31.89 (CH_2), 34.91 (CH_2), 39.22 (CH_2), 61.12 (C-6'ose'), 68.86 (C'ose'), 71.08 (C'ose'), 74.01 (C-5'ose'), 76.31 (C'ose'), 101.83 (C-1'ose'), 115.03 (Ar-C_{meta}), 118.81, 120.47, 135.67 (Ar-C_{ortho}), 158.02 (Ar-C_{OGal}) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{56}\text{H}_{67}\text{N}_4\text{O}_{12}$ [$\text{M} + \text{H}$]⁺: 987.4750, found: 987.4697.

UV/Vis ($(\text{CH}_3)_2\text{SO}$): λ_{max} ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 421 (5.19), 519 (3.92), 555 (3.76), 597 (3.47), 654 (3.56) nm.

10-(4-Acetoxyphenyl)-5,15-bis(pentafluorophenyl)corrole (70) and 5,15-Bis(4-acetoxyphenyl)-10,20-bis(pentafluorophenyl)porphyrin (71):

According to the general procedure **IX**, 4-acetoxybenzaldehyde (0.33 ml, 2.40 mmol), 5-(pentafluorophenyl)dipyrromethane **43** (1.50 g, 4.80 mmol), TFA (0.18 ml, 2.40 mmol), DDQ (1.63 g, 7.14 mmol) and triethylamine (0.48 ml, 3.41 mmol) were reacted in dry dichloromethane (1200 ml). Purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (4:1) as the eluent. The first band gave corrole **70** (188 mg, 10%) in form of violet crystals, and the second gave the porphyrin **71** (100 mg, 5%) in form of violet crystals.



Melting Point: 169 °C

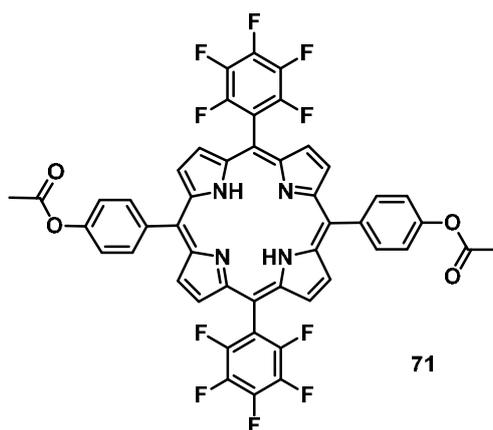
¹H-NMR (700 MHz, CDCl₃): δ = -2.29 (s, 3 H, NH), 2.49 (s, 3 H, OAc), 7.52 (d, J = 7.9 Hz, 2 H, Ar-H_{meta}), 8.21 (d, J = 7.9 Hz, 2 H, Ar-H_{ortho}), 8.60 (d, J = 4.1 Hz, 2 H, β -H), 8.75 (br s, 4 H, β -H), 9.13 (d, J = 4.1 Hz, 2 H, β -H) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 21.35 (OCH₃), 96.75 (Ar_F-C_{meso}), 112.30 (Ar-C_{meso}), 113.92-114.12 (Ar_F-C_{ipso}), 117.60 (β -C), 120.48 (Ar-C_{meta}), 121.69 (β -C), 125.58 (β -C), 127.78 (β -C), 131.39 (α -C), 135.31 (α -C), 135.43 (Ar-C_{ortho}), 137.03-137.26 (Ar_F-C), 138.44-138.69 (Ar_F-C), 138.84 (Ar-C_{ipso}), 140.05 (α -C), 141.16 (α -C), 142.33-142.66 (Ar_F-C), 145.30-145.62 (Ar_F-C), 146.69-146.93 (Ar_F-C), 150.65 (Ar-C_{OAc}), 169.58 (C=O) ppm.

¹⁹F-NMR (471 MHz, CDCl₃): δ = -161.86 – -161.71 (m, 4 F, Ar-F_{meta}), -152.16 – -152.05 (m, 2 F, Ar-F_{para}), -136.77 – -136.68 (m, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₃₉H₁₉F₁₀N₄O₂ [M + H]⁺: 765.1343, found: 765.1375.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 411 (4.92), 561 (4.16), 613 (3.94), 640 (3.77) nm.



Melting Point: > 300 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.86 (s, 2 H, NH), 2.51 (s, 6 H, OAc), 7.54 (d, J = 8.4 Hz, 4 H, Ar-H_{meta}), 8.22 (d, J = 8.4 Hz, 4 H, Ar-H_{ortho}), 8.82 (d, J = 4.6 Hz, 4 H, β -H), 8.98 (d, J = 4.6 Hz, 4 H, β -H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 21.40 (OCH₃), 102.34 (Ar-C_{meso}), 116.21-116.50 (Ar-F-C_{ipso}), 120.13 (Ar-C_{meta}), 120.41 (Ar-C_{meso}), 135.35 (Ar-C_{ortho}), 136.26-136.64 (Ar-F-C), 138.13-138.57 (Ar-F-C), 138.69 (Ar-C_{ipso}), 145.35-145.76 (Ar-F-C), 147.35-147.71 (Ar-F-C), 150.92 (Ar-C_{OAc}), 169.55 (C=O) ppm.

¹⁹F-NMR (471 MHz, CDCl₃): δ = -161.62 (dt, J = 8.3, 23.2 Hz, 4 F, Ar-F_{meta}), -152.66 (t, J = 20.7 Hz, 2 F, Ar-F_{para}), -137.77 (dd, J = 8.2, 24.5 Hz, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₈H₂₅F₁₀N₄O₄ [M + H]⁺: 911.1711, found: 911.1730.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 416 (5.21), 511 (4.23), 544 (3.77), 588 (3.96), 642 (3.43) nm.

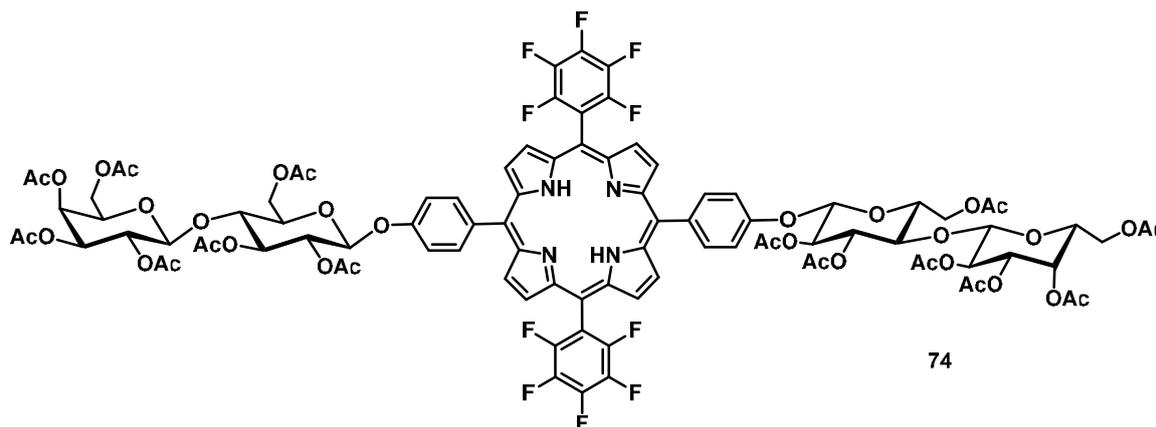
10-(4-Acetoxyphenyl)-5,15-bis(pentafluorophenyl)corrole (70):

According to the general procedure X, 5-(pentafluorophenyl)dipyrromethane **43** (156 mg, 0.50 mmol) and 4-acetoxybenzaldehyde (0.03 ml, 0.25 mmol) were dissolved in methanol (25 ml). Then a mixture of HCl (36%, 1.25 ml) and water (25 ml) was added and it was stirred at room temperature for one hour. Then the mixture was extracted three times with dichloromethane. The combined organic layers were washed three times with water, dried over sodium sulfate and the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (125 ml) and DDQ (169 mg, 0.75 mmol) was added. After 3 hours stirring at room temperature, purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (3:1) and a

subsequent recrystallization from dichloromethane/*n*-pentane to obtain the desired product (94 mg, 49%) as a violet solid.

5,15-Bis[4-(2,3,4,6,2',3',6'-heptaacetyl- β -D-lactosyl)phenyl]-10,20-bis(pentafluorophenyl)porphyrin (74):

According to the general procedure V, acetylated porphyrin 71 (150 mg, 165 μ mol) was dissolved in THF (14 ml). Then a solution of sodium methanolate in dry methanol (2.00 ml, 0.50 N) was added. After 10 min, purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (3:1) as the eluent followed by recrystallization from dichloromethane/aqueous methanol to obtain deprotected porphyrin 72 (127 mg, 93%) as a violet solid. According to the general procedure VI, a mixture of porphyrin 72 (100 mg, 121 μ mol) and Zn(OAc)₂ · 2 H₂O (100 mg, 457 μ mol) was reacted in dichloromethane/methanol (6 ml, 1:1). Purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent and subsequent recrystallization from dichloromethane/aqueous methanol to obtain metallated porphyrin 73 (107 mg, 99%) as a purple solid. According to the general procedure VII, metallated hydroxyporphyrin 73 (20 mg, 23 μ mol), 2,3,4,6,2',3',6'-heptaacetyl- α -D-lactose trichloroacetimidate 8 (200 mg, 256 μ mol) and BF₃·Et₂O (4 μ l, 32 μ mol) were reacted in a mixture of dry dichloromethane/THF/acetonitrile (5 ml, 3:1:1) for 2 h. Demetallation was accomplished with HCl (0.2 ml, 25%) in THF (4 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (97:3) as the eluent. The desired product (41 mg, 84%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: > 300 °C

¹H-NMR (700 MHz, (CD₃)₂CO): δ = -2.80 (br s, 2 H, NH), 1.94 (s, 6 H, 2 x OAc), 2.08 (s, 6 H, 2 x OAc), 2.09 (s, 6 H, 2 x OAc), 2.14 (s, 6 H, 2 x OAc), 2.15 (s, 6 H, 2 x OAc), 2.17 (s, 6 H, 2 x OAc), 2.19 (s, 6 H, 2 x OAc), 4.20 (dd, J = 9.0, 9.9 Hz, 2 H, 2 x H-4' 'ose'), 4.22 (dd, J = 7.1, 11.1 Hz, 2 H, 2 x H-6_A' 'ose'), 4.26 (dd, J = 6.3, 11.1 Hz, 2 H, 2 x H-6_B' 'ose'), 4.29-4.34 (m, 4 H, 2 x H-5' 'ose'),

2 x H-5 'ose'), 4.38 (dd, $J = 6.5, 11.7$ Hz, 2 H, 2 x H-6_B 'ose'), 4.70 (dd, $J = 1.9, 11.7$ Hz, 2 H, 2 x H-6_A 'ose'), 4.97 (d, $J = 7.7$ Hz, 2 H, 2 x H-1 'ose'), 5.15 (dd, $J = 7.7, 10.3$ Hz, 2 H, 2 x H-2 'ose'), 5.18 (dd, $J = 3.3, 10.3$ Hz, 2 H, 2 x H-3 'ose'), 5.37 (dd, $J = 8.0, 9.7$ Hz, 2 H, 2 x H-2 'ose'), 5.43 (dd, $J = 1.3, 3.3$ Hz, 2 H, 2 x H-4 'ose'), 5.50 (dd, $J = 9.0, 9.7$ Hz, 2 H, 2 x H-3 'ose'), 5.84 (d, $J = 8.0$ Hz, 2 H, 2 x H-1 'ose'), 7.57 (d, $J = 8.4$ Hz, 4 H, Ar-H_{meta}), 8.28 (d, $J = 8.4$ Hz, 4 H, Ar-H_{ortho}), 9.04-9.07 (m, 4 H, β -H), 9.21-9.24 (m, 4 H, β -H) ppm.

¹³C-NMR (176 MHz, (CD₃)₂CO): $\delta = 19.61$ (OCH₃), 19.69 (OCH₃), 19.77 (OCH₃), 19.80 (OCH₃), 19.89 (OCH₃), 19.96 (OCH₃), 20.10 (OCH₃), 60.99 (C-6'ose'), 62.32 (C-6''ose'), 67.22 (C-4'ose'), 69.17 (C-2'ose'), 70.59 (C-5'ose'), 70.92 (C-3'ose'), 71.57 (C-2''ose'), 72.76 (C-3''ose'), 72.99 (C-5''ose'), 76.52 (C-4''ose'), 98.16 (C-1''ose'), 100.88 (C-1'ose'), 102.37 (Ar_F-C_{meso}), 115.08 (Ar-C_{meta}), 116.01-116.26 (Ar_F-C_{ipso}), 120.95 (Ar-C_{meso}), 135.55 (Ar-C_{ipso}), 135.57 (Ar-C_{ortho}), 137.11-137.40 (Ar_F-C), 138.52-138.83 (Ar_F-C), 141.51-141.77 (Ar_F-C), 142.95-143.22 (Ar_F-C), 145.95-146.14 (Ar_F-C), 147.35-147.56 (Ar_F-C), 157.29 (Ar-C_{OLac}), 168.81 (C=O), 169.15 (C=O), 169.29 (C=O), 169.30 (C=O), 169.71 (C=O), 169.80 (C=O), 170.00 (C=O) ppm.

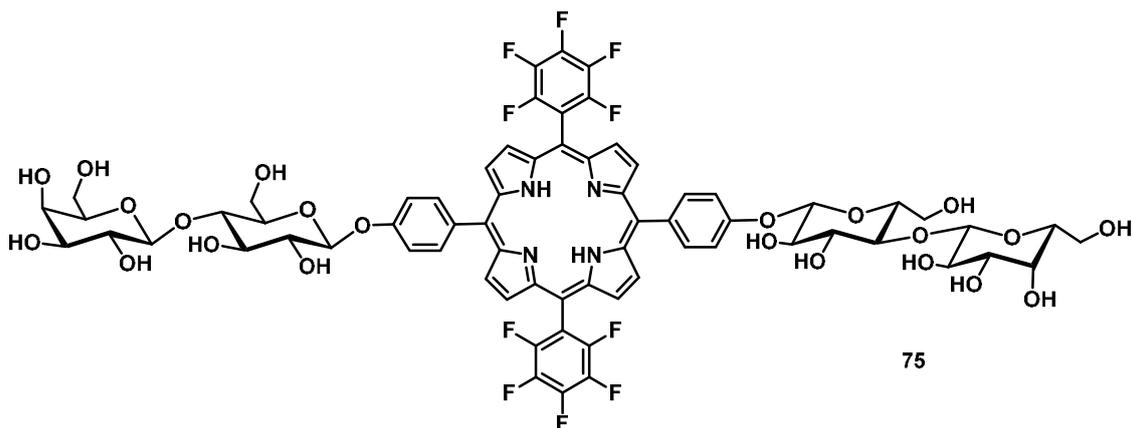
¹⁹F-NMR (471 MHz, (CD₃)₂CO): $\delta = -164.70$ (td, $J = 7.8, 22.8$ Hz, 4 F, Ar-F_{meta}), -155.80 (t, $J = 20.7$ Hz, 2 F, Ar-F_{para}), -140.04 (dd, $J = 7.4, 23.6$ Hz, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₉₆H₈₈F₁₀N₄O₃₆Na [M + Na]⁺: 2085.4916, found: 2085.4887.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 416 (5.52), 511 (4.29), 543 (3.57), 590 (3.80), 644 (3.49) nm.

5,15-Bis(4- β -D-lactosylphenyl)-10,20-bis(pentafluorophenyl)porphyrin (75):

According to the general procedure VIII, acetylated glycoporphyrin **74** (20 mg, 10 μ mol) was dissolved in a mixture of dry THF/methanol (5 ml, 1:1). Then a solution of sodium methanolate in dry methanol (0.80 ml, 0.08 N) was added. After 40 min, the solvent was evaporated under reduced pressure and the crude product was purified by reversed phase column chromatography, using THF/water (3:2). The desired product (14 mg, 96%) was obtained as a violet solid.



Melting Point: > 300 °C

¹H-NMR (500 MHz, (CD₃)₂SO): δ = -3.00 (br s, 2 H, NH), 3.34-3.45 (m, 4 H, 4 x H'ose')*, 3.51-3.63 (m, 12 H, 4 x H-6'ose', 8 x H'ose'), 3.66-3.70 (m, 2 H, 2 x H'ose'), 3.75-3.83 (m, 4 H, 2 x H-6'ose', 2 x H'ose'), 3.89-3.93 (m, 2 H, 2 x H-6'ose'), 4.33 (d, J = 7.4 Hz, 2 H, 2 x H-1'ose'), 4.68 (br s, 2 H, OH'ose'), 4.78 (br s, 2 H, OH'ose'), 4.97 (br s, 2 H, OH'ose'), 5.37 (d, J = 7.6 Hz, 2 H, 2 x H-1''ose'), 5.72 (br s, 2 H, OH'ose'), 7.52 (d, J = 8.4 Hz, 4 H, Ar-H_{meta}), 8.21 (d, J = 8.4 Hz, 4 H, Ar-H_{ortho}), 8.99 (d, J = 5.0 Hz, 4 H, β -H), 9.25 (d, J = 5.0 Hz, 4 H, β -H) ppm.

* = signals of carbohydrate hydrogens are overlapped by the water peak of DMSO

¹³C-NMR (126 MHz, (CD₃)₂SO): δ = 60.73 (C'ose'), 60.93 (C'ose'), 68.70 (C'ose'), 71.09 (C'ose'), 73.71 (C'ose'), 73.79 (C'ose'), 75.42 (C'ose'), 75.63 (C'ose'), 76.11 (C'ose'), 80.62 (C'ose'), 100.43 (C-1''ose'), 102.39 (Ar_F-C_{meso}), 104.35 (C-1'ose'), 115.14 (Ar-C_{meta}), 115.61-116.24 (Ar_F-C_{ipso}), 121.42 (Ar-C_{meso}), 131.03-131.69 (Ar_F-C), 132.72-133.46 (Ar_F-C), 134.31 (Ar-C_{ipso}), 135.92 (Ar-C_{ortho}), 136.63-137.05 (Ar_F-C), 138.57-139.18 (Ar_F-C), 145.31-146.16 (Ar_F-C), 147.08-147.73 (Ar_F-C), 157.98 (Ar-C_{OLac}) ppm.

¹⁹F-NMR (471 MHz, (CD₃)₂SO): δ = -162.84 – -162.68 (m, 4 F, Ar-F_{meta}), -154.00 – -153.82 (m, 2 F, Ar-F_{para}), -139.43 – -139.31 (m, 4 F, Ar-F_{ortho}) ppm.

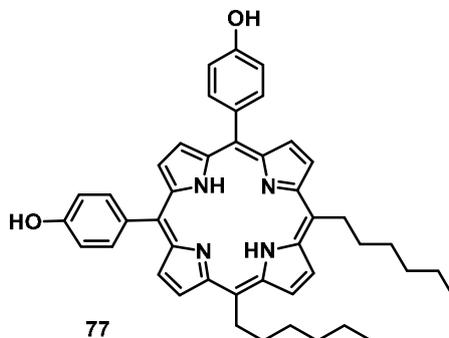
HRMS (ESI-TOF): m/z calcd. for C₆₈H₆₀F₁₀N₄O₂₂Na [M + Na]⁺: 1497.3437, found: 1497.3472.

UV/Vis ((CH₃)₂SO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 417 (5.74), 510 (4.33), 543 (3.78), 590 (3.98), 645 (3.70) nm.

5,10-Bis(4-hydroxyphenyl)-15,20-dihexylporphyrin (76):

According to the general procedure V, acetylated porphyrin 45 (40 mg, 55 μ mol) was dissolved in THF (8 ml) and saturated methanolic KOH solution (12 ml) was added. After full conversion,

purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent followed by recrystallization from dichloromethane/methanol to obtain the desired product (36 mg, 99%) as a violet solid.



Melting Point: 104 °C

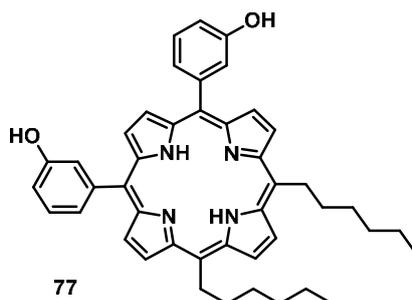
¹H-NMR (500 MHz, (CD₃)₂CO): δ = -2.72 (br s, 2 H, NH), 0.90 (t, J = 7.4 Hz, 6 H, 2 x CH₃), 1.33-1.44 (m, 4 H, 2 x CH₂), 1.47-1.54 (m, 4 H, 2 x CH₂), 1.79-1.87 (m, 4 H, 2 x CH₂), 2.47-2.55 (m, 4 H, 2 x CH₂), 4.95-4.99 (m, 4 H, 2 x CH₂), 7.27 (d, J = 8.4 Hz, 4 H, Ar-H_{meta}), 7.99 (d, J = 8.4 Hz, 4 H, Ar-H_{ortho}), 8.69-8.89 (m, 4 H, β -H), 8.45-8.68 (m, 4 H, β -H) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₄₇N₄O₂ [M + H]⁺: 663.3699, found: 663.3778.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 417 (5.54), 515 (4.21), 550 (4.33), 596 (3.72), 653 (3.91) nm.

5,10-Bis(3-hydroxyphenyl)-15,20-dihexylporphyrin (77):

According to the general procedure V, acetylated porphyrin 49 (45 mg, 60 μ mol) was dissolved in THF (8 ml) and saturated methanolic KOH solution (12 ml) was added. After full conversion, purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent followed by recrystallization from dichloromethane/methanol to obtain the desired product (39 mg, 98%) as a violet solid.



Melting Point: 224 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = -2.78 (br s, 2 H, NH), 0.81 (t, J = 7.2 Hz, 6 H, 2 x CH₃), 1.19-1.26 (m, 4 H, 2 x CH₂), 1.28-1.34 (m, 4 H, 2 x CH₂), 1.55-1.61 (m, 4 H, 2 x CH₂), 2.25-2.32 (m, 4 H, 2 x CH₂), 4.60-4.64 (m, 4 H, 2 x CH₂), 7.28-7.33 (m, 2 H, Ar-H), 7.53-7.56 (m, 2 H, Ar-H), 7.58-7.62 (m, 2 H, Ar-H), 7.69-7.72 (m, 2 H, Ar-H), 8.83 (br s, 2 H, 2 x OH), 8.84 (d, J = 4.6 Hz, 2 H, β -H), 8.94 (s, 2 H, β -H), 9.32 (s, 2 H, β -H), 9.35 (d, J = 4.6 Hz, 2 H, β -H) ppm.

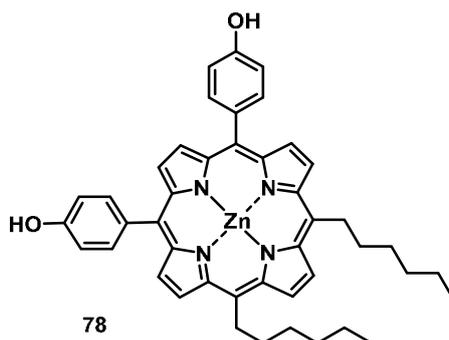
¹³C-NMR (126 MHz, (CD₃)₂CO): δ = 13.56 (CH₃), 22.55 (CH₂), 29.92 (CH₂), 31.77 (CH₂), 35.05 (CH₂), 38.96 (CH₂), 114.89 (Ar-C), 118.56 (Ar-C_{meso}), 120.12 (Alkyl-C_{meso}), 121.96 (Ar-C), 126.27 (Ar-C), 127.72 (Ar-C), 143.55 (Ar-C_{ipso}), 155.97 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₄₇N₄O₂ [M + H]⁺: 663.3699, found: 663.3703.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 416 (5.42), 515 (4.16), 551 (4.10), 596 (3.74), 654 (3.88) nm.

[5,10-Bis(4-hydroxyphenyl)-15,20-dihexylporphyrinato]zinc(II) (78):

According to the general procedure VI, a mixture of porphyrin **76** (30 mg, 46 μ mol) and Zn(OAc)₂ · 2 H₂O (50 mg, 0.2 mmol) was reacted in dichloromethane/methanol (5 ml, 4:1). Purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent and subsequent recrystallization from dichloromethane/methanol to obtain the desired product (33 mg, 95%) as a pink solid.



Melting Point: 176 °C

¹H-NMR (700 MHz, (CD₃)₂CO): δ = 0.94 (t, J = 7.4 Hz, 6 H, 2 x CH₃), 1.42-1.47 (m, 4 H, 2 x CH₂), 1.55-1.60 (m, 4 H, 2 x CH₂), 1.89-1.94 (m, 4 H, 2 x CH₂), 2.58-2.62 (m, 4 H, 2 x CH₂), 5.08-5.11 (m, 4 H, 2 x CH₂), 7.27 (d, J = 8.2 Hz, 4 H, Ar-H_{meta}), 8.00 (d, J = 8.2 Hz, 4 H, Ar-H_{ortho}), 8.83 (s, 2 H, β -H), 8.86 (br s, 2 H, 2 x OH), 8.93 (d, J = 4.5 Hz, 2 H, β -H), 9.61 (d, J = 4.5 Hz, 2 H, β -H), 9.70 (s, 2 H, β -H) ppm.

¹³C-NMR (176 MHz, (CD₃)₂CO): δ = 13.54 (CH₃), 22.58 (CH₂), 30.09 (CH₂), 31.87 (CH₂), 35.43 (CH₂), 39.32 (CH₂), 113.34 (Ar-C_{meta}), 119.25 (Ar-C_{meso}), 120.03 (Ar-C_{meso}), 128.49 (β -C),

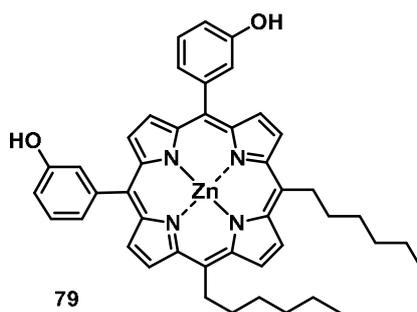
128.97 (β -C), 131.10 (β -C), 131.56 (β -C), 134.63 (Ar-C_{ipso}), 135.29 (Ar-C_{ortho}), 149.51 (α -C), 149.65 (α -C), 149.96 (α -C), 150.10 (α -C), 157.00 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₄₄N₄O₂Zn [M]⁺: 724.2756, found: 724.2818.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 423 (5.15), 560 (3.97), 601 (3.76) nm.

[5,10-Bis(3-hydroxyphenyl)-15,20-dihexylporphyrinato]zinc(II) (79):

According to the general procedure VI, porphyrin 77 (30 mg, 46 μ mol) was dissolved in dichloromethane/methanol (5 ml, 4:1) and Zn(OAc)₂ · 2 H₂O (50 mg, 0.2 mmol) was added. Purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent followed by recrystallization from dichloromethane/methanol to obtain the desired product (35 mg, 96%) as a pink solid.



Melting Point: > 300 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = 0.94 (t, J = 7.4 Hz, 6 H, 2 x CH₃), 1.38-1.46 (m, 4 H, 2 x CH₂), 1.52-1.58 (m, 4 H, 2 x CH₂), 1.86-1.92 (m, 4 H, 2 x CH₂), 2.54-2.60 (m, 4 H, 2 x CH₂), 5.06-5.10 (m, 4 H, 2 x CH₂), 7.24-7.27 (m, 2 H, Ar-H), 7.53-7.57 (m, 2 H, Ar-H), 7.61-7.65 (m, 2 H, Ar-H), 7.65-7.67 (m, 2 H, Ar-H), 8.81 (s, 2 H, β -H), 8.84 (br s, 2 H, 2 x OH), 8.91 (d, J = 4.7 Hz, 2 H, β -H), 9.60 (d, J = 4.7 Hz, 2 H, β -H), 9.69 (s, 2 H, β -H) ppm.

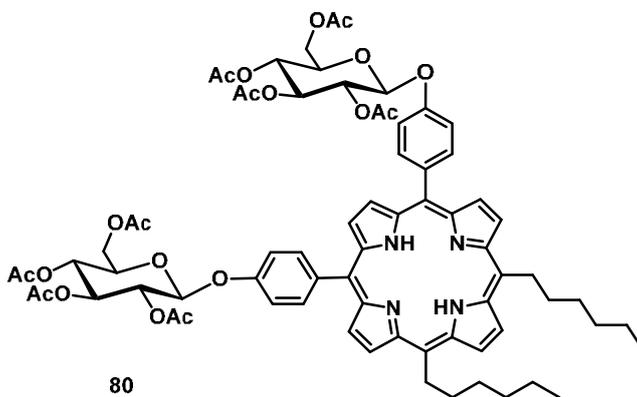
¹³C-NMR (176 MHz, (CD₃)₂CO): δ = 13.62 (CH₃), 22.66 (CH₂), 30.17 (CH₂), 31.94 (CH₂), 35.53 (CH₂), 39.45 (CH₂), 114.32 (Ar-C), 119.02 (Ar-C_{meso}), 120.47 ((Alkyl-C_{meso})), 121.99 (Ar-C), 126.30 (Ar-C), 127.28 (Ar-C), 128.76 (β -C), 129.13 (β -C), 131.17 (β -C), 131.53 (β -C), 144.98 (Ar-C_{ipso}), 149.56 (α -C), 149.63 (α -C), 149.65 (α -C), 149.73 (α -C), 155.71 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₄₅N₄O₂Zn [M + H]⁺: 725.2834, found: 725.2798.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 423 (5.42), 558 (4.01), 599 (3.83) nm.

5,10-Bis[4-(2,3,4,6-tetraacetyl- β -D-glucosyl)phenyl]-15,20-dihexylporphyrin (80):

According to the general procedure VII, metallated hydroxyporphyrin **78** (20 mg, 29 μ mol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate **2** (50 mg, 102 μ mol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.0 μ l, 8.0 μ mol) were reacted in a mixture of dry dichloromethane/acetonitrile (4 ml, 19:1) for 2 h. Demetallation was accomplished with HCl (0.2 ml, 25%) in THF (4 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired product (25 mg, 64%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 213 °C

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = -2.72 (br s, 2 H, NH), 0.94 (t, J = 7.3 Hz, 6 H, 2 x CH_3), 1.37-1.44 (m, 4 H, 2 x CH_2), 1.49-1.54 (m, 4 H, 2 x CH_2), 1.80-1.86 (m, 4 H, 2 x CH_2), 2.10 (s, 6 H, 2 x OAc), 2.11 (s, 6 H, 2 x OAc), 2.12 (s, 6 H, 2 x OAc), 2.22 (s, 6 H, 2 x OAc), 2.52-2.58 (m, 4 H, 2 x CH_2), 4.05 (ddd, J = 2.4, 5.5, 10.1 Hz, 2 H, 2 x H-5'ose'), 4.30 (dd, J = 2.4, 12.3 Hz, 2 H, 2 x H-6 $_{\text{A}}$ 'ose'), 4.42 (dd, J = 5.4, 12.3 Hz, 2 H, 2 x H-6 $_{\text{B}}$ 'ose'), 4.98-5.02 (m, 4 H, 2 x CH_2), 5.31 (dd, J = 9.2, 9.8 Hz, 2 H, 2 x H-4'ose'), 5.43-5.51 (m, 6 H, 2 x H-1'ose', 2 x H-2'ose', 2 x H-3'ose'), 7.36 (d, J = 8.4 Hz, 4 H, Ar-H $_{\text{meta}}$), 8.08 (d, J = 8.4 Hz, 4 H, Ar-H $_{\text{ortho}}$), 8.73 (s, 2 H, β -H), 8.85 (d, J = 4.8 Hz, 2 H, β -H), 9.45 (d, J = 4.8 Hz, 2 H, β -H), 9.57 (s, 2 H, β -H) ppm.

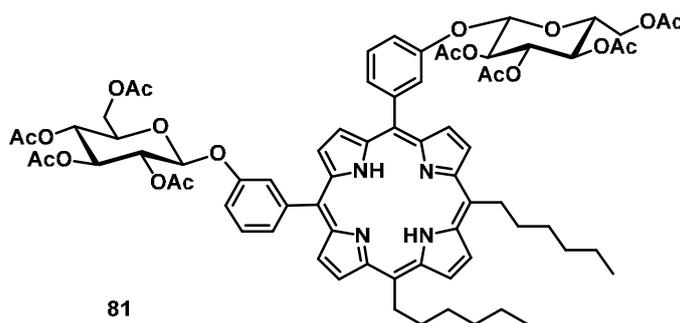
$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ = 14.24 (CH_3), 20.74 (OCH_3), 20.78 (OCH_3), 20.87 (OCH_3), 20.91 (OCH_3), 22.83 (CH_2), 30.38 (CH_2), 32.01 (CH_2), 35.80 (CH_2), 38.99 (CH_2), 62.18 (C-6'ose'), 68.49 (C-4'ose'), 71.42 (C-2'ose'), 72.37 (C-5'ose'), 72.95 (C-3'ose'), 99.30 (C-1'ose'), 115.04 (Ar-C $_{\text{meta}}$), 117.82, 120.35, 135.52 (Ar-C $_{\text{ortho}}$), 137.51, 156.62 (Ar-C $_{\text{Oglc}}$), 169.57 (C=O), 170.43 (C=O), 170.74 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{72}\text{H}_{83}\text{N}_4\text{O}_{20}$ [$\text{M} + \text{H}$] $^+$: 1323.5601, found: 1323.5628

UV/Vis (CH_2Cl_2): λ_{max} (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 419 (5.41), 519 (4.11), 554 (3.90), 595 (3.66), 652 (3.72) nm.

5,10-Bis[3-(2,3,4,6-tetraacetyl- β -D-glucosyl)phenyl]-15,20-dihexylporphyrin (81):

According to the general procedure VII, metallated hydroxyporphyrin **79** (30 mg, 41 μ mol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate **2** (70 mg, 144 μ mol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.4 μ l, 11 μ mol) were reacted in a mixture of dry dichloromethane (5 ml) for 2 h. Demetallation was accomplished with HCl (0.4 ml, 25%) in THF (6 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. The desired product (37 mg, 68%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



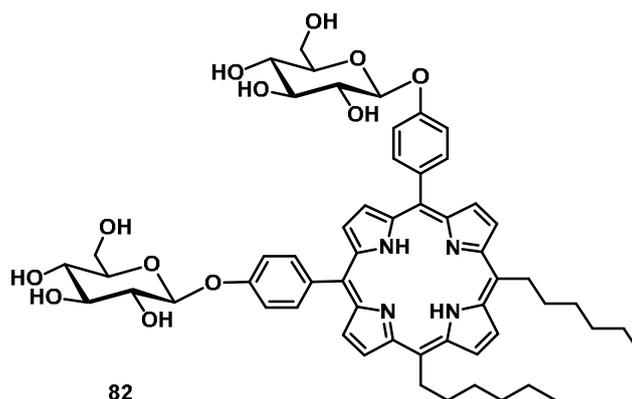
$^1\text{H-NMR}$ (700 MHz, CDCl_3): δ = -2.70 (m, 2 H, NH), 0.96-0.99 (m, 6 H, 2 x CH_3), 1.28-1.39 (m, 6 H, 2 x OAc), 1.41-1.47 (m, 4 H, 2 x CH_2), 1.54-1.59 (m, 4 H, 2 x CH_2), 1.85-1.89 (m, 4 H, 2 x CH_2), 1.99-2.02 (m, 6 H, 2 x OAc), 2.05-2.07 (m, 6 H, 2 x OAc), 2.10-2.13 (m, 6 H, 2 x OAc), 2.56-2.62 (m, 4 H, 2 x CH_2), 3.77-3.85 (m, 2 H, H-5'ose'), 4.03-4.08 (m, 2 H, H-6_A'ose'), 4.15-4.21 (m, 2 H, H-6_B'ose'), 5.02-5.08 (m, 4 H, 2 x CH_2), 5.17-5.22 (m, 2 H, H-4'ose'), 5.31-5.42 (m, 6 H, H-1'ose', H-2'ose', H-3'ose'), 7.43-7.45 (m, 2 H, Ar-H), 7.65-7.71 (m, 2 H, Ar-H), 7.83-7.96 (m, 4 H, Ar-H), 8.77-8.79 (m, 2 H, β -H), 8.88-8.91 (m, 2 H, β -H), 9.48-9.51 (m, 2 H, β -H), 9.59-9.61 (m, 2 H, β -H) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{72}\text{H}_{83}\text{N}_4\text{O}_{20}$ [$\text{M} + \text{H}$] $^+$: 1323.5601, found: 1323.5557.

Analytical data are in accordance with published data.^[112]

5,10-Bis(4- β -D-glucosylphenyl)-15,20-dihexylporphyrin (82):

According to the general procedure VIII, acetylated glycoporphyrin **80** (20 mg, 15 μ mol) was dissolved in a mixture of dry THF/methanol (5 ml, 1:1). Then a solution of sodium methanolate in dry methanol (1.0 ml, 0.02 N) was added. After 2 h, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, using dichloromethane/methanol (8:2) as the eluent. The desired product (13 mg, 86%) was obtained as a violet crystalline solid.



Melting Point: 234 °C

¹H-NMR (500 MHz, (CD₃)₂SO): δ = -2.92 (br s, 2 H, NH), 0.87 (t, J = 7.3 Hz, 6 H, 2 x CH₃), 1.29-1.35 (m, 4 H, 2 x CH₂), 1.42-1.48 (m, 4 H, 2 x CH₂), 1.75-1.83 (m, 4 H, 2 x CH₂), 2.39-2.46 (m, 4 H, 2 x CH₂), 3.28-3.32 (m, 2 H, H'ose'), 3.41-3.46 (m, 2 H, H'ose'), 3.49-3.83 (m, 8 H, 2 x H-6_A'ose', 2 x H-6_B'ose', 4 x H'ose')*, 5.00-5.06 (m, 4 H, 2 x CH₂), 5.22 (d, J = 7.3 Hz, 2 H, 2 x H-1'ose'), 7.45 (d, J = 8.2 Hz, 4 H, Ar-H_{meta}), 8.07 (d, J = 8.2 Hz, 4 H, Ar-H_{ortho}), 8.75 (s, 2 H, β -H), 8.82-8.85 (m, 2 H, β -H), 9.66-9.70 (m, 2 H, β -H), 9.78 (s, 2 H, β -H) ppm.

* = signals of carbohydrate hydrogens are overlapped by the water peak of DMSO

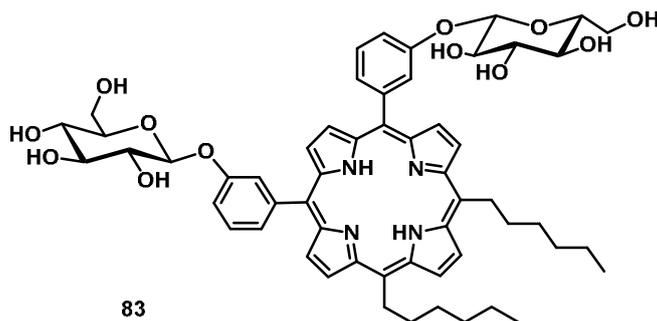
¹³C-NMR (126 MHz, (CD₃)₂SO): δ = 14.39 (CH₃), 22.56 (CH₂), 29.83 (CH₂), 31.81 (CH₂), 35.11 (CH₂), 39.21 (CH₂), 61.27 (C-6'ose'), 70.34 (C'ose'), 73.91 (C'ose'), 77.15 (C'ose'), 77.73 (C'ose'), 101.08 (C-1'ose'), 115.02 (Ar-C_{meta}), 118.52 (Ar-C_{meso}), 120.60 (Alkyl-C_{meso}), 135.59 (Ar-C_{ortho}), 157.80 (Ar-C_{Oglc}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₆H₆₇N₄O₁₂ [M + H]⁺: 987.4755, found: 987.4773.

UV/Vis ((CH₃)₂SO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 419 (5.35), 517 (4.29), 551 (4.04), 589 (3.76), 651 (3.73) nm.

5,10-Bis(3- β -D-glucosylphenyl)-15,20-dihexylporphyrin (83):

According to the general procedure VIII, acetylated glycoporphyrin **81** (20 mg, 15 μ mol) was dissolved in a mixture of dry THF/methanol (5 ml, 1:1). Then a solution of sodium methanolate in dry methanol (1.0 ml, 0.02 N) was added. After 4 h, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography, using dichloromethane/methanol (8:2) as the eluent. The desired product (12 mg, 83%) was obtained as a violet crystalline solid.



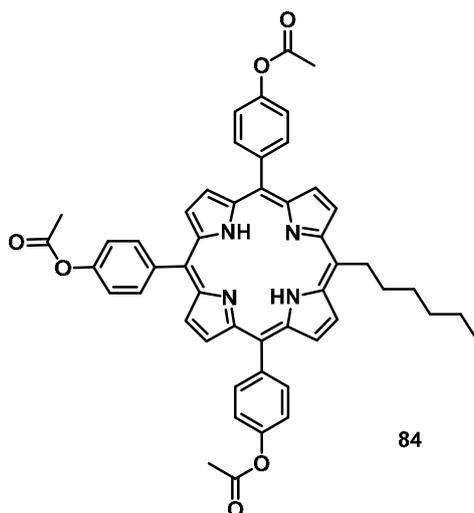
$^1\text{H-NMR}$ (500 MHz, $(\text{CD}_3)_2\text{SO}$): δ = -2.90 (br s, 2 H, NH), 0.86 (t, J = 7.2 Hz, 6 H, 2 x CH_3), 1.29-1.37 (m, 4 H, 2 x CH_2), 1.42-1.45 (m, 4 H, 2 x CH_2), 1.72-1.82 (m, 4 H, 2 x CH_2), 2.40-2.46 (m, 4 H, 2 x CH_2), 3.19-3.26 (m, 2 H, H'ose'), 3.32-3.37 (6 H, H'ose')*, 3.45-3.50 (m, 2 H, H'ose'), 3.64-3.71 (m, 2 H, H'ose'), 4.52-4.58 (m, 2 H, H'ose'), 4.96-5.04 (m, 6 H, 2 x H'ose', 2 x CH_2), 5.14 (d, J = 4.1 Hz, 2 H, OH'ose'), 5.20 (d, J = 7.2 Hz, 2 H, 2 x H-1'ose'), 5.41-5.44 (m, 2 H, H'ose'), 7.50-7.55 (m, 2 H, Ar-H), 7.69-7.75 (m, 2 H, Ar-H), 7.76-7.80 (m, 2 H, Ar-H), 7.82-7.86 (m, 2 H, Ar-H), 8.76-8.87 (m, 4 H, β -H), 9.66 (s, 2 H, β -H), 9.76 (s, 2 H, β -H) ppm.

* = signals of carbohydrate hydrogens are overlapped by the water peak of DMSO

Analytical data are in accordance with published data.^[112]

5,10,15-Tris(4-acetoxyphe-nyl)-20-hexylporphyrin (84):

According to the general procedure III, 4-acetoxyphe-nylaldehyde (2.08 ml, 14.8 mmol), heptanal (0.70 ml, 5.02 mmol), pyrrole (1.39 ml, 20.1 mmol), TFA (1.55 ml, 20.2 mmol), DDQ (4.00 g, 17.6 mmol) and triethylamine (4.00 ml, 28.8 mmol) were reacted in dry dichloromethane (2000 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (98:2) as the eluent and subsequent recrystallization from dichloromethane/methanol. The first band gave the desired product (444 mg, 11%) in form of violet crystals, and the second gave 5,10,15,20-tetrakis(4-acetoxyphe-nyl)porphyrin (402 mg, 9%) in form of violet crystals.



Melting Point: 270 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.76 (s, 2 H, NH), 0.94 (t, J = 7.3 Hz, 3 H, CH₃), 1.36-1.44 (m, 2 H, CH₂), 1.48-1.53 (m, 2 H, CH₂), 1.77-1.84 (m, 2 H, CH₂), 2.50 (s, 3 H, OAc), 2.52 (s, 6 H, OAc), 2.53-2.58 (m, 2 H, CH₂), 4.99-5.02 (m, 2 H, CH₂), 7.50 (m, 6 H, Ar-H_{meta}), 8.20 (m, 6 H, Ar-H_{ortho}), 8.83 (s, 4 H, β -H), 8.94 (d, J = 4.7 Hz, 2 H, β -H), 9.50 (d, J = 4.7 Hz, 2 H, β -H) ppm.

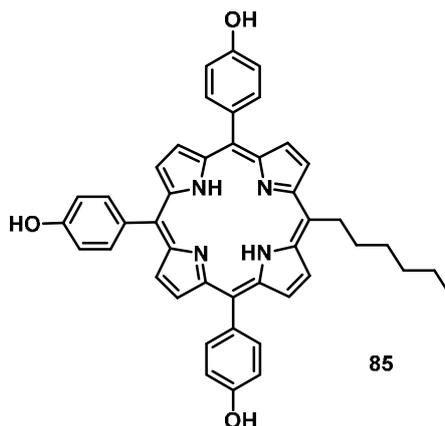
¹³C-NMR (126 MHz, CDCl₃): δ = 14.05 (CH₃), 21.30 (OCH₃), 21.32 (OCH₃), 22.61 (CH₂), 30.14 (CH₂), 31.79 (CH₂), 35.47 (CH₂), 38.80 (CH₂), 118.16 (Ar-C_{meso}), 118.42 (Ar-C_{meso}), 119.68 (Ar-C_{meta}), 119.78 (Ar-C_{meta}), 121.00 (Alkyl-C_{meso}), 135.14 (Ar-C_{ortho}), 135.20 (Ar-C_{ortho}), 139.40 (Ar-C_{ipso}), 139.76 (Ar-C_{ipso}), 150.43 (Ar-C_{OH}), 150.45 (Ar-C_{OH}), 169.49 (C=O), 169.51 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₀H₄₅N₄O₆ [M + H]⁺: 797.3339, found: 797.3348.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 418 (5.15), 516 (4.04), 551 (3.80), 593 (3.66), 650 (3.63) nm.

5,10,15-Tris(4-hydroxyphenyl)-20-hexylporphyrin (85):

According to the general procedure V, acetylated porphyrin **84** (317 mg, 398 μ mol) was dissolved in THF (40 ml) and saturated methanolic KOH solution (100 ml) was added. After full conversion, purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent followed by recrystallization from dichloromethane/methanol to obtain the desired product (251 mg, 94%) as a violet solid.



Melting Point: 192 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = -2.70 (s, 2 H, NH), 0.89 (t, J = 7.3 Hz, 3 H, CH₃), 1.32-1.40 (m, 2 H, CH₂), 1.44-1.51 (m, 2 H, CH₂), 1.76-1.82 (m, 2 H, CH₂), 2.45-2.52 (m, 2 H, CH₂), 4.91-4.95 (m, 2 H, CH₂), 7.27-7.30 (m, 6 H, Ar-H_{meta}), 8.01-8.04 (m, 6 H, Ar-H_{ortho}), 8.87 (br s, 3 H, Ar-OH), 8.90 (br s, 4 H, β -H), 8.94 (d, J = 4.6 Hz, 2 H, β -H), 9.57 (d, J = 4.6 Hz, 2 H, β -H) ppm.

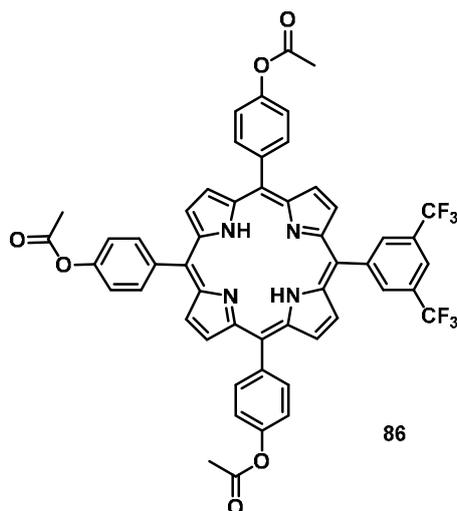
¹³C-NMR (126 MHz, (CD₃)₂CO): δ = 14.36 (CH₃), 23.36 (CH₂), 30.76 (CH₂), 32.61 (CH₂), 35.78 (CH₂), 39.80 (CH₂), 114.54 (Ar-C_{meta}), 114.65 (Ar-C_{meta}), 120.31 (Ar-C_{meso}), 120.37 (Ar-C_{meso}), 121.17 (Alkyl-C_{meso}), 133.94 (Ar-C_{ipso}), 134.25 (Ar-C_{ipso}), 136.35 (Ar-C_{ortho}), 136.38 (Ar-C_{ortho}), 158.28 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₃₉N₄O₃ [M + H]⁺: 671.3022, found: 671.3063.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 420 (5.15), 520 (4.21), 554 (4.07), 595 (3.91), 652 (3.93) nm.

5,10,15-Tris(4-acetoxyphenyl)-20-[3,5-bis(trifluoromethyl)phenyl]porphyrin (86):

According to the general procedure III, 4-acetoxybenzaldehyde (1.57 ml, 11.2 mmol), 3,5-bis(trifluoromethyl)benzaldehyde (0.62 ml, 3.81 mmol), pyrrole (1.04 ml, 15.0 mmol), TFA (1.16 ml, 15.1 mmol), DDQ (2.55 g, 11.3 mmol) and triethylamine (2.10 ml, 15.0 mmol) were reacted in dry dichloromethane (1500 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (98:2) as the eluent and subsequent recrystallization from dichloromethane/methanol. The first band gave the desired product (520 mg, 15%) in form of violet crystals, and the second gave 5,10,15,20-tetrakis(4-acetoxyphenyl)porphyrin (443 mg, 14%) in form of violet crystals.



Melting Point: > 300 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.82 (br s, 2 H, NH), 2.50 (s, 6 H, 2 x OAc), 2.51 (s, 3 H, 2 x OAc), 7.52 (d, J = 8.4 Hz, 6 H, 6 x Ar-H_{meta}), 8.22 (d, J = 8.4 Hz, 6 H, 6 x Ar-H_{ortho}), 8.36 (br s, 1 H, Ar_F-H_{para}), 8.69-8.72 (m, 4 H, 2 x Ar_F-H_{ortho}, 2 x β -H), 8.91 (br s, 4 H, β -H), 8.95 (d, J = 4.8 Hz, 2 H, β -H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 21.57 (OCH₃), 115.90 (Ar_F-C_{meso}), 119.92 (Ar-C_{meso}), 120.14 (Ar-C_{meta}), 120.29 (Ar-C_{meso}), 122.03 (Ar_F-C_{para}), 122.61 (Ar_F-C_{para}), 124.78, 130.43 (CF₃), 133.90 (Ar_F-C_{ortho}), 135.49 (Ar-C_{ortho}), 139.38 (Ar-C_{ipso}), 144.43 (Ar_F-C_{ipso}), 150.87 (Ar-C_{OH}), 169.75 (C=O) ppm.

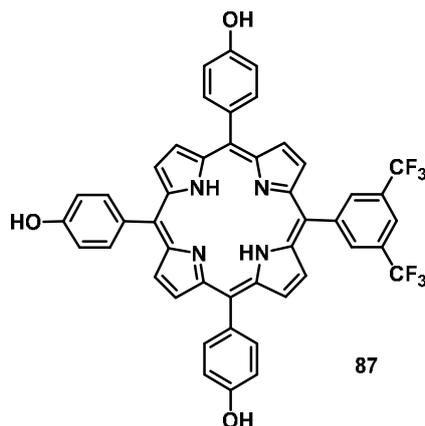
¹⁹F-NMR (471 MHz, CDCl₃): δ = -62.20 (s, 6 F, 2 x CF₃) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₂H₃₅F₆N₄O₆ [M + H]⁺: 925.2461, found: 925.2451.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 418 (5.22), 514 (4.20), 550 (4.00), 590 (3.91), 646 (3.80) nm.

5,10,15-Tris(4-hydroxyphenyl)-20-[3,5-bis(trifluoromethyl)phenyl]porphyrin (87):

According to the general procedure V, acetylated porphyrin **86** (250 mg, 270 μ mol) was dissolved in THF (30 ml) and saturated methanolic KOH solution (50 ml) was added. After full conversion, purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent followed by recrystallization from dichloromethane/aqueous methanol to obtain the desired product (207 mg, 96%) as a violet solid.



Melting Point: > 300 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = -2.69 (br s, 2 H, NH), 7.29-7.31 (m, 6 H, 6 x Ar-H_{meta}), 8.06-8.08 (m, 6 H, 6 x Ar-H_{ortho}), 8.57 (br s, 1 H, Ar_F-H_{para}), 8.83 (br s, 2 H, 2 x Ar-OH), 8.93 (br s, 2 H, 2 x Ar_F-H_{ortho}), 8.96 (br s, 6 H, β -H), 9.00 (d, J = 4.4 Hz, 2 H, β -H) ppm.

¹³C-NMR (126 MHz, (CD₃)₂CO): δ = 113.92 (Ar-C_{meta}), 113.96 (Ar-C_{meta}), 115.32 (Ar_F-C_{meso}), 120.85 (Ar-C_{meso}), 121.46 (Ar-C_{meso}), 121.93 (Ar_F-C_{para}), 125.10, 129.99 (CF₃), 132.92 (Ar-C_{ipso}), 133.02 (Ar-C_{ipso}), 133.90 (Ar_F-C_{ortho}), 135.68 (Ar-C_{ortho}), 144.89 (Ar_F-C_{ipso}), 157.72 (Ar-C_{OH}) ppm.

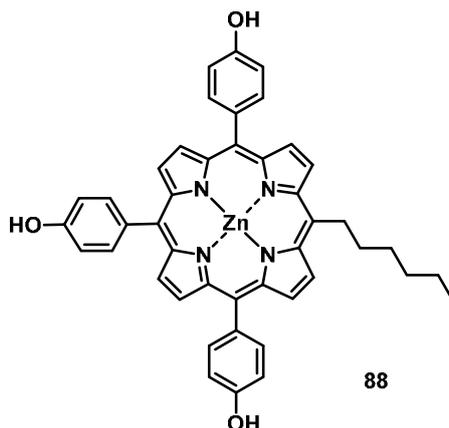
¹⁹F-NMR (471 MHz, (CD₃)₂CO): δ = -62.68 (s, 6 F, 2 x CF₃) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₆H₂₉F₆N₄O₃ [M + H]⁺: 799.2144, found: 799.2131.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 418 (5.13), 517 (3.92), 554 (3.64), 593 (3.43), 649 (3.33) nm.

[5,10,15-Tris(4-hydroxyphenyl)-20-hexylporphyrinato]zinc(II) (88):

According to the general procedure VI, a mixture of porphyrin 85 (240 mg, 0.35 mmol) and Zn(OAc)₂ · 2 H₂O (310 mg, 1.40 mmol) was reacted in methanol (15 ml). Purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent and subsequent recrystallization from dichloromethane/aqueous methanol to obtain the desired product (259 mg, 100%) as a pink solid.



Melting Point: > 300 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = 0.94 (t, J = 7.3 Hz, 3 H, CH₃), 1.39-1.45 (m, 2 H, CH₂), 1.51-1.59 (m, 2 H, CH₂), 1.86-1.94 (m, 2 H, CH₂), 2.54-2.64 (m, 2 H, CH₂), 5.09-5.17 (m, 2 H, CH₂), 7.25-7.28 (m, 6 H, Ar-H_{meta}), 7.99-8.03 (m, 6 H, Ar-H_{ortho}), 8.78 (br s, 2 H, Ar-OH), 8.79 (br s, 4 H, β -H), 8.98 (d, J = 4.7 Hz, 2 H, β -H), 9.67 (d, J = 4.7 Hz, 2 H, β -H) ppm.

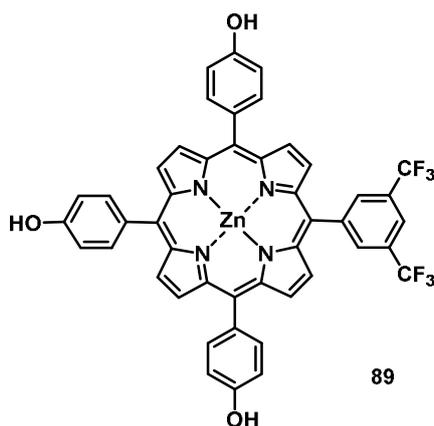
¹³C-NMR (126 MHz, (CD₃)₂CO): δ = 13.67 (CH₃), 22.65 (CH₂), 30.47 (CH₂), 31.88 (CH₂), 35.28 (CH₂), 38.29 (CH₂), 113.49 (Ar-C_{meta}), 113.52 (Ar-C_{meta}), 119.95 (Ar-C_{meso}), 120.02 (Ar-C_{meso}), 128.67 (β -C), 131.31 (β -C), 131.46 (β -C), 131.90 (β -C), 134.68 (Ar-C_{ipso}), 134.75 (Ar-C_{ipso}), 135.48 (Ar-C_{ortho}), 135.51 (Ar-C_{ortho}), 149.98 (α -C), 150.06 (α -C), 150.13 (α -C), 150.52 (α -C), 157.08 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₃₇N₄O₃Zn [M + H]⁺: 733.2152, found: 733.2134.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 421 (4.87), 551 (3.81) nm.

[5,10,15-Tris(4-hydroxyphenyl)-20-[3,5-bis(trifluoromethyl)phenyl]porphyrinato]zinc(II) (89):

According to the general procedure VI, a mixture of porphyrin **87** (200 mg, 250 μ mol) and Zn(OAc)₂ · 2 H₂O (250 mg, 1.15 mmol) was reacted in methanol (10 ml). Purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent and subsequent recrystallization from dichloromethane/aqueous methanol to obtain the desired product (211 mg, 98%) as a pink solid.



Melting Point: 276 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = 7.25-7.28 (m, 6 H, 6 x Ar-H_{meta}), 8.06-8.08 (m, 6 H, 6 x Ar-H_{ortho}), 8.57 (br s, 1 H, Ar_F-H_{para}), 8.82 (br s, 2 H, 2 x Ar-OH), 8.83 (d, J = 4.5 Hz, 2 H, β -H), 8.84 (br s, 1 H, Ar-OH), 8.89 (br s, 2 H, 2 x Ar_F-H_{ortho}), 8.98-9.01 (m, 4 H, β -H), 9.04 (d, J = 4.5 Hz, 2 H, β -H) ppm.

¹³C-NMR (126 MHz, (CD₃)₂CO): δ = 113.58 (Ar-C_{meta}), 113.60 (Ar-C_{meta}), 115.65 (Ar_F-C_{meso}), 121.26 (Ar-C_{meso}), 121.39 (Ar_F-C_{para}), 121.82 (Ar-C_{meso}), 123.07, 125.23, 127.40, 129.59 (CF₃), 130.51 (β -C), 131.82 (β -C), 132.01 (β -C), 132.59 (β -C), 133.79 (Ar_F-C_{ortho}), 134.37 (Ar-C_{ipso}), 134.42 (Ar-C_{ipso}), 135.58 (Ar-C_{ortho}), 146.37 (Ar_F-C_{ipso}), 149.30 (α -C), 150.57 (α -C), 150.64 (α -C), 150.96 (α -C), 157.24 (Ar-C_{OH}) ppm.

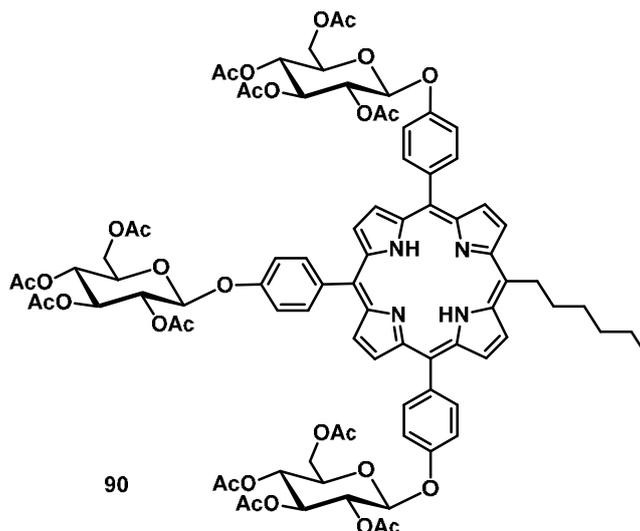
¹⁹F-NMR (471 MHz, (CD₃)₂CO): δ = -62.57 (s, 6 F, 2 x CF₃) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₆H₂₇F₆N₄O₃Zn [M + H]⁺: 861.1279, found: 861.1260.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 421 (5.54), 548 (4.39) nm.

5,10,15-Tris[4-(2,3,4,6-tetraacetyl- β -D-glucosyl)phenyl]-20-hexylporphyrin (90):

According to the general procedure VII, metallated hydroxyporphyrin **88** (100 mg, 0.13 mmol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate **2** (300 mg, 609 μ mol) and BF₃·Et₂O (5.0 μ l, 40 μ mol) were reacted in a mixture of dry dichloromethane/THF/acetonitrile (20 ml, 8:1:1) for 2 h. Demetallation was accomplished with HCl (1.4 ml, 25%) in THF (14 ml). Purification was achieved by column chromatography on silica using dichloromethane/methanol (99:1) as the eluent. The desired product (92 mg, 43%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 251 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.77 (s, 2 H, NH), 0.92 (t, J = 7.3 Hz, 3 H, CH₃), 1.34-1.42 (m, 2 H, CH₂), 1.48-1.53 (m, 2 H, CH₂), 1.78-1.85 (m, 2 H, CH₂), 2.10-2.13 (m, 27 H, OAc), 2.21 (s, 3 H, OAc), 2.23 (s, 6 H, OAc), 2.51-2.57 (m, 2 H, CH₂), 4.00-4.10 (m, 3 H, H-5'ose'), 4.26-4.33 (m, 3 H, H-6_A'ose') 4.39-4.45 (m, 3 H, H-6_B'ose'), 4.99-5.03 (m, 2 H, CH₂), 5.28-5.35 (m, 3 H, H-4'ose'), 5.40-5.52 (m, 9 H, H-1'ose', H-2'ose', H-3'ose'), 7.35-7.39 (m, 6 H, Ar-H_{meta}), 8.08-8.13 (m, 6 H, Ar-H_{ortho}), 8.79 (br s, 4 H, β -H), 8.91 (d, J = 4.8 Hz, 2 H, β -H), 9.49 (d, J = 4.8 Hz, 2 H, β -H) ppm.

¹³C-NMR (126 MHz, CDCl₃) δ = 14.24 (CH₃), 20.75 (OCH₃), 20.79 (OCH₃), 20.89 (OCH₃), 20.93 (OCH₃), 22.80 (CH₂), 30.35 (CH₂), 31.99 (CH₂), 35.68 (CH₂), 39.01 (CH₂), 62.18 (C-6'ose'), 68.47 (C-4'ose'), 71.41 (C-2'ose'), 72.38 (C-5'ose'), 72.93 (C-3'ose'), 99.23 (C-1'ose'), 99.28 (C-1'ose'), 115.00 (Ar-C_{meta}), 115.15 (Ar-C_{meta}), 118.53 (Ar-C_{meso}), 118.76 (Ar-C_{meso}), 121.06 (Alkyl-C_{meso}), 135.56 (Ar-C_{ortho}), 137.17 (Ar-C_{ipso}), 137.52 (Ar-C_{ipso}), 156.68 (Ar-C_OGlc), 169.58 (C=O), 170.45 (C=O), 170.75 (C=O) ppm.

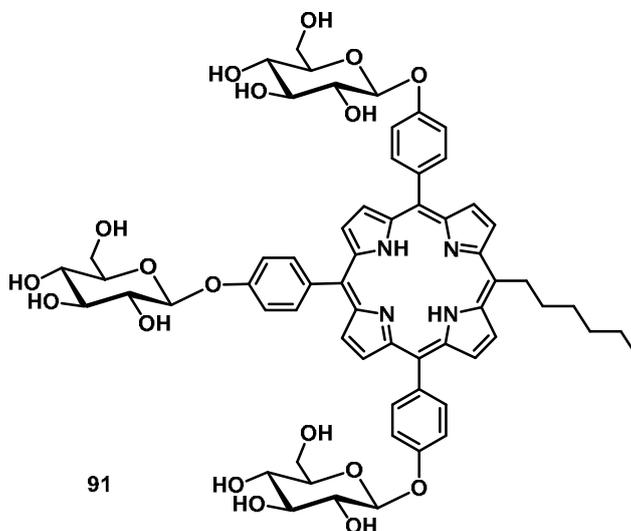
HRMS (ESI-TOF): m/z calcd. for C₈₆H₉₃N₄O₃₀ [M + H]⁺: 1661.5874, found: 1661.5868.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 418 (5.27), 517 (4.18), 551 (4.04), 595 (3.92), 650 (3.89) nm.

5,10,15-Tris(4- β -D-glucosylphenyl)-20-hexylporphyrin (91):

According to the general procedure VIII, acetylated glycoporphyrin 90 (50 mg, 30 μ mol) was dissolved in a mixture of dry THF/methanol (10 ml, 1:1). Then a solution of sodium methanolate in dry methanol (1.9 ml, 0.08 N) was added. After 3 h, the solvent was evaporated under reduced pressure

and the crude product was purified by reversed phase column chromatography, using methanol/water (9:1) as the eluent. The desired product (30 mg, 81%) was obtained as a violet crystalline solid.



Melting Point: 237 °C

¹H-NMR (700 MHz, (CD₃)₂SO): δ = -2.90 (br s, 2 H, NH), 0.87 (t, J = 7.4 Hz, 3 H, CH₃), 1.30-1.35 (m, 2 H, CH₂), 1.42-1.47 (m, 2 H, CH₂), 1.75-1.80 (m, 2 H, CH₂), 2.39-2.46 (m, 2 H, CH₂), 3.27-3.33 (m, 3 H, H'ose'), 3.41-3.54 (m, 9 H, H-6'ose', 2 x H'ose'), 3.57-3.63 (m, 3 H, H-6'ose'), 3.81-3.83 (m, 3 H, H'ose'), 4.76 (br s, 3 H, OH'ose'), 5.00-5.04 (m, 2 H, CH₂), 5.16 (br s, 3 H, OH'ose'), 5.22 (d, J = 7.3 Hz, 1 H, H-1'ose'), 5.24 (d, J = 7.3 Hz, 2 H, H-1'ose'), 5.57 (br s, 3 H, OH'ose'), 7.46-7.49 (m, 6 H, Ar-H_{meta}), 8.09-8.12 (m, 6 H, Ar-H_{ortho}), 8.81 (br s, 4 H, β -H), 8.88-8.91 (m, 2 H, β -H), 9.70-9.74 (m, 2 H, β -H) ppm.

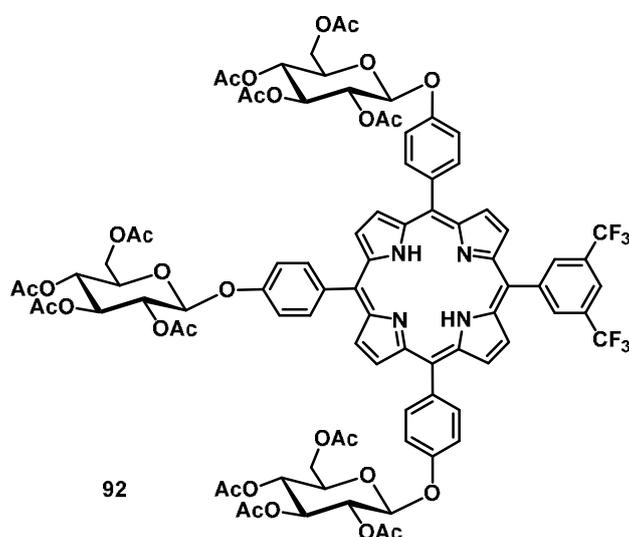
¹³C-NMR (176 MHz, (CD₃)₂SO): δ = 14.43 (CH₃), 22.62 (CH₂), 29.87 (CH₂), 31.80 (CH₂), 35.05 (CH₂), 39.31 (CH₂), 61.29 (C-6'ose'), 70.30 (C'ose'), 73.92 (C'ose'), 77.16 (C'ose'), 77.67 (C'ose'), 101.03 (C-1'ose'), 114.99 (Ar-C_{meta}), 115.06 (Ar-C_{meta}), 119.24 (Ar-C_{meso}), 119.40 (Ar-C_{meso}), 121.40 (Alkyl-C_{meso}), 135.04 (Ar-C_{ipso}), 135.35 (Ar-C_{ipso}), 135.64 (Ar-C_{ortho}), 157.87 (Ar-C_{Oglc}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₆₂H₆₉N₄O₁₈ [M + H]⁺: 1157.4607, found: 1157.4601.

UV/Vis ((CH₃)₂SO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 422 (5.42), 518 (4.41), 554 (4.24), 595 (3.97), 651 (3.99) nm.

5,10,15-Tris[4-(2,3,4,6-tetraacetyl- β -D-glucosyl)phenyl]-20-[3,5-bis(trifluoromethyl)phenyl]porphyrin (92):

According to the general procedure VII, metallated hydroxyporphyrin **89** (50 mg, 58 μ mol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate **2** (250 mg, 507 μ mol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (5.0 μ l, 40 μ mol) were reacted in a mixture of dry dichloromethane/THF/acetonitrile (10 ml, 8:1:1) for 1 h. Demetallation was accomplished with HCl (0.7 ml, 25%) in THF (7 ml). Purification was achieved by column chromatography on silica using dichloromethane/methanol (99:1) as the eluent. The desired product (88 mg, 85%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 160 °C

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = -2.83 (br s, 2 H, NH), 2.10 (s, 9 H, 3 x OAc), 2.11 (s, 9 H, 3 x OAc), 2.12 (s, 9 H, 3 x OAc), 2.21 (s, 6 H, 2 x OAc), 2.22 (s, 3 H, OAc), 4.06 (ddd, J = 2.4, 5.3, 10.0 Hz, 3 H, 3 x H-5'ose'), 4.31 (dd, J = 2.3, 12.4 Hz, 3 H, 3 x H-6_A'ose'), 4.42 (dd, J = 5.3, 12.4 Hz, 3 H, 3 x H-6_B'ose'), 5.29-5.34 (m, 3 H, 3 x H-4'ose'), 5.44-5.51 (m, 9 H, 3 x H-3'ose', 3 x H-1'ose', 3 x H-2'ose'), 7.40 (d, J = 8.4 Hz, 6 H, 6 x Ar-H_{meta}), 8.13 (d, J = 8.4 Hz, 6 H, 6 x Ar-H_{ortho}), 8.34 (br s, 1 H, Ar_F-H_{para}), 8.66-8.69 (m, 4 H, 2 x Ar_F-H_{ortho}, 2 x β -H), 8.88 (s, 4 H, β -H), 8.92 (d, J = 4.7 Hz, 2 H, β -H) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ = 20.72 (OCH₃), 20.76 (OCH₃), 20.85 (OCH₃), 20.90 (OCH₃), 62.18 (C-6'ose'), 68.48 (C-4'ose'), 71.42 (C-2'ose'), 72.41 (C-5'ose'), 72.91 (C-3'ose'), 99.24 (C-1'ose'), 115.23 (Ar-C_{meta}), 115.69 (Ar_F-C_{meso}), 120.03 (Ar-C_{meso}), 120.45 (Ar-C_{meso}), 121.91 (Ar_F-C_{para}), 122.55, 124.72, 130.40 (CF₃), 133.84 (Ar_F-C_{ortho}), 135.66 (Ar-C_{ortho}), 136.91 (Ar-C_{ipso}), 136.97 (Ar-C_{ipso}), 144.41 (Ar_F-C_{ipso}), 156.85 (Ar-C_{Oglc}), 169.53 (C=O), 169.55 (C=O), 170.40 (C=O), 170.68 (C=O) ppm.

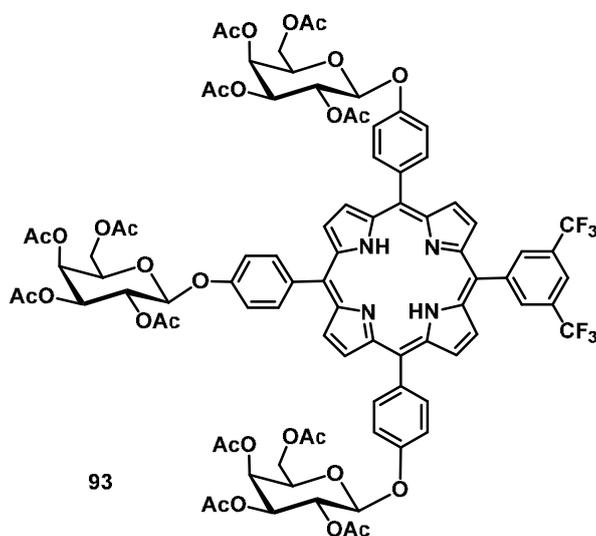
^{19}F -NMR (471 MHz, CDCl_3): $\delta = -62.24$ (s, 6 F, 2 x CF_3) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{88}\text{H}_{83}\text{F}_6\text{N}_4\text{O}_{30}$ $[\text{M} + \text{H}]^+$: 1789.4996, found: 1789.4974.

UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 420 (5.41), 515 (4.09), 553 (3.71), 591 (3.59), 648 (3.43) nm.

5,10,15-Tris[4-(2,3,4,6-tetraacetyl- β -D-galactosyl)phenyl]-20-[3,5-bis(trifluoromethyl)-phenyl]porphyrin (93):

According to the general procedure VII, metallated hydroxyporphyrin **89** (50 mg, 58 μmol), 2,3,4,6-tetraacetyl-D-galactose trichloroacetimidate **4** (500 mg, 1.02 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (5.0 μl , 40 μmol) were reacted in a mixture of dry dichloromethane/THF/acetonitrile (10 ml, 8:1:1) for 2 h. Demetallation was accomplished with HCl (0.7 ml, 25%) in THF (7 ml). Purification was achieved by column chromatography on silica using dichloromethane/methanol (99:1) as the eluent. The desired product (76 mg, 73%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 156 $^{\circ}\text{C}$

^1H -NMR (500 MHz, CDCl_3): $\delta = -2.81$ (br s, 2 H, NH), 2.08 (s, 9 H, 3 x OAc), 2.09 (s, 9 H, 3 x OAc), 2.24 (s, 6 H, 2 x OAc), 2.25 (s, 3 H, OAc), 2.27 (s, 6 H, 2 x OAc), 2.28 (s, 3 H, OAc), 4.25-4.31 (m, 6 H, 3 x H-6 $'_A$ 'ose', 3 x H-5'ose'), 4.37-4.42 (m, 3 H, 3 x H-6 $'_B$ 'ose'), 5.28 (dd, $J = 3.4, 10.5$ Hz, 3 H, 3 x H-3'ose'), 5.44 (d, $J = 8.0$ Hz, 3 H, 3 x H-1'ose'), 5.56-5.58 (m, 3 H, 3 x H-4'ose'), 5.71 (dd, $J = 7.9, 10.5$ Hz, 3 H, 3 x H-2'ose'), 7.42 (d, $J = 8.4$ Hz, 6 H, 6 x Ar-H $_{\text{meta}}$), 8.15 (d, $J = 8.4$ Hz, 6 H, 6 x Ar-H $_{\text{ortho}}$), 8.35 (br s, 1 H, Ar $_{\text{F}}$ -H $_{\text{para}}$), 8.67-8.69 (m, 4 H, 2 x Ar $_{\text{F}}$ -H $_{\text{ortho}}$, 2 x β -H), 8.89 (s, 4 H, β -H), 8.93 (d, $J = 4.7$ Hz, 2 H, β -H) ppm.

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ = 20.76 (OCH_3), 20.81 (OCH_3), 20.84 (OCH_3), 21.03 (OCH_3), 61.58 (C-6'ose'), 67.06 (C-4'ose'), 68.89 (C-2'ose'), 71.05 (C-3'ose'), 71.39 (C-5'ose'), 99.75 (C-1'ose'), 115.24 (Ar-C_{meta}), 115.70 ($\text{Ar}_F\text{-C}_{meso}$), 120.07 (Ar-C_{meso}), 120.48 (Ar-C_{meso}), 121.92 ($\text{Ar}_F\text{-C}_{para}$), 122.56, 124.73, 130.39 (CF_3), 133.86 ($\text{Ar}_F\text{-C}_{ortho}$), 135.67 (Ar-C_{ortho}), 136.87 (Ar-C_{ipso}), 136.94 (Ar-C_{ipso}), 144.42 ($\text{Ar}_F\text{-C}_{ipso}$), 156.87 (Ar-C_{OGal}), 169.66 (C=O), 170.33 (C=O), 170.42 (C=O), 170.52 (C=O) ppm.

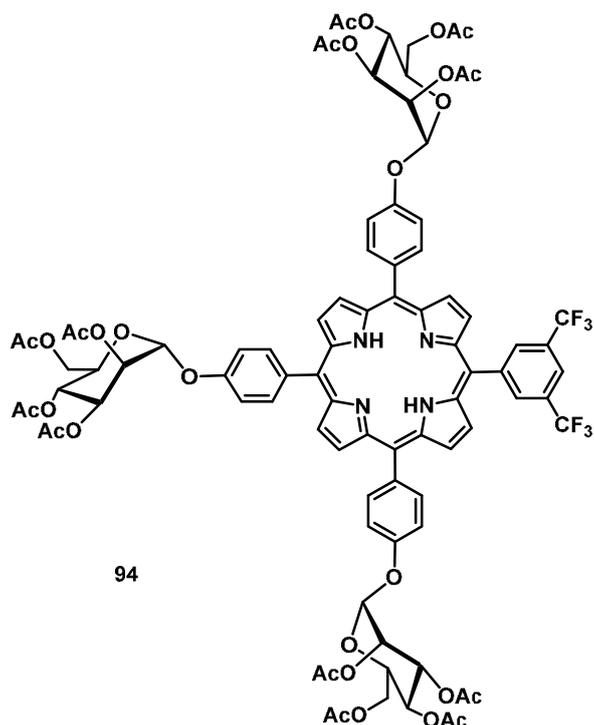
$^{19}\text{F-NMR}$ (471 MHz, CDCl_3): δ = -62.21 (s, 6 F, 2 x CF_3) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{88}\text{H}_{83}\text{F}_6\text{N}_4\text{O}_{30}$ [$\text{M} + \text{H}$] $^+$: 1789.4996, found: 1789.5021.

UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 420 (5.58), 517 (4.29), 553 (4.01), 591 (3.87), 649 (3.75) nm.

5,10,15-Tris[4-(2,3,4,6-tetraacetyl- α -D-mannosyl)phenyl]-20-[3,5-bis(trifluoromethyl)-phenyl]porphyrin (94):

According to the general procedure VII, metallated hydroxyporphyrin **89** (150 mg, 174 μmol), 2,3,4,6-tetraacetyl- α -D-mannose trichloroacetimidate **6** (710 mg, 1.44 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (10 μl , 80 μmol) were reacted in a mixture of dry dichloromethane/THF/acetonitrile (20 ml, 8:1:1) for 4 h. Demetallation was accomplished with HCl (0.7 ml, 25%) in THF (7 ml). Purification was achieved by column chromatography on silica using dichloromethane/methanol (99:1) as the eluent. The desired product (112 mg, 36%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 155 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.81 (br s, 2 H, NH), 2.11 (br s, 9 H, 3 x OAc), 2.12 (br s, 9 H, 3 x OAc), 2.13 (br s, 9 H, 3 x OAc), 2.29 (s, 9 H, 3 x OAc), 4.25-4.30 (m, 3 H, 3 x H-6_A'ose'), 4.38-4.46 (m, 6 H, 3 x H-6_B'ose', 3 x H-5'ose'), 5.49-5.53 (m, 3 H, 3 x H-4'ose'), 5.64-5.66 (m, 3 H, 3 x H-2'ose'), 5.73-5.77 (m, 3 H, 3 x H-3'ose'), 5.85-5.88 (m, 3 H, 3 x H-1'ose'), 7.51 (d, J = 8.3 Hz, 6 H, 6 x Ar-H_{meta}), 8.15 (d, J = 8.3 Hz, 6 H, 6 x Ar-H_{ortho}), 8.34 (br s, 1 H, Ar-F-H_{para}), 8.67-8.69 (m, 4 H, 2 x Ar-F-H_{ortho}, 2 x β -H), 8.86 (s, 4 H, β -H), 8.90 (d, J = 4.6 Hz, 2 H, β -H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 20.84 (OCH₃), 20.87 (OCH₃), 20.88 (OCH₃), 20.90 (OCH₃), 21.07 (OCH₃), 62.37 (C-6'ose'), 66.15 (C-4'ose'), 69.05 (C-3'ose'), 69.51 (C-5'ose'), 69.68 (C-2'ose'), 96.28 (C-1'ose'), 114.91 (Ar-C_{meta}), 115.61 (Ar-F-C_{meso}), 120.04 (Ar-C_{meso}), 121.87 (Ar-F-C_{para}), 130.42 (CF₃), 133.81 (Ar-F-C_{ortho}), 135.73 (Ar-C_{ortho}), 136.65 (Ar-C_{ipso}), 136.72 (Ar-C_{ipso}), 155.98 (Ar-C_{OMan}), 169.89 (C=O), 170.16 (C=O), 170.25 (C=O), 170.71 (C=O) ppm.

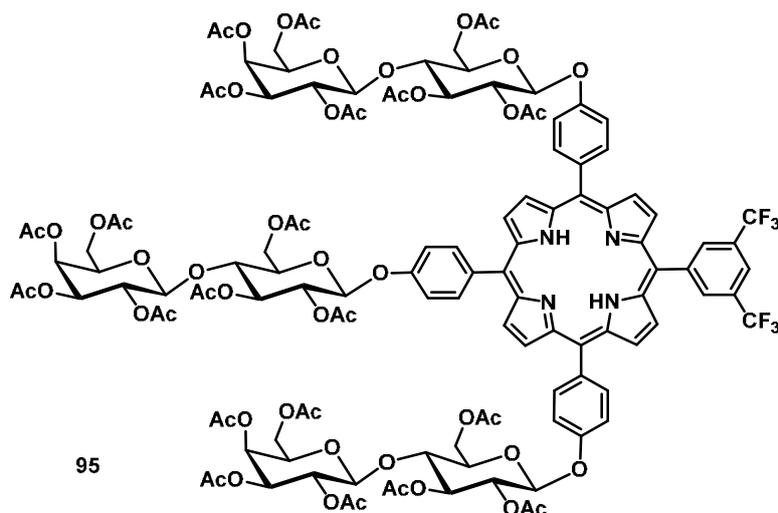
¹⁹F-NMR (471 MHz, CDCl₃): δ = -62.78 (s, 6 F, 2 x CF₃) ppm.

HRMS (ESI-TOF): m/z calcd. for C₈₈H₈₃F₆N₄O₃₀ [M + H]⁺: 1789.4996, found: 1789.4976.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 420 (5.24), 516 (4.00), 552 (3.75), 592 (3.56), 650 (3.40) nm.

5,10,15-Tris[4-(2,3,4,6,2',3',6'-heptaacetyl- β -D-lactosyl)phenyl]-20-[3,5-bis(trifluoromethyl)phenyl]porphyrin (95):

According to the general procedure VII, metallated hydroxyporphyrin **89** (25 mg, 29 μ mol), 2,3,4,6,2',3',6'-heptaacetyl- α -D-lactose trichloroacetimidate **8** (250 mg, 320 μ mol) and BF₃·Et₂O (5.0 μ l, 40 μ mol) were reacted in a mixture of dry dichloromethane/THF/acetonitrile (5 ml, 8:1:1) for 2 h. Demetallation was accomplished with HCl (0.7 ml, 25%) in THF (7 ml). Purification was achieved by column chromatography on silica using dichloromethane/methanol (99:1) as the eluent. The desired product (39 mg, 51%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 176 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.83 (br s, 2 H, NH), 1.99 (s, 9 H, 3 x OAc), 2.08 (s, 6 H, 2 x OAc), 2.09 (s, 3 H, OAc), 2.11 (s, 9 H, 3 x OAc), 2.13 (s, 6 H, 2 x OAc), 2.14 (s, 3 H, OAc), 2.15 (s, 6 H, 2 x OAc), 2.16 (s, 3 H, OAc), 2.19 (s, 9 H, 3 x OAc), 2.21 (s, 6 H, 2 x OAc), 2.22 (s, 3 H, OAc), 3.94-4.06 (m, 9 H, 3 x H-5'ose', 3 x H-4'ose', 3 x H-5'ose'), 4.14 (dd, J = 7.4, 11.2 Hz, 3 H, 3 x H-6_A'ose'), 4.21 (dd, J = 6.3, 11.2 Hz, 3 H, 3 x H-6_B'ose'), 4.27 (dd, J = 5.8, 11.9 Hz, 3 H, 3 x H-6_B'ose'), 4.59 (d, J = 7.9 Hz, 3 H, 3 x H-1'ose'), 4.64 (dd, J = 2.1, 11.9 Hz, 3 H, 3 x H-6_A'ose'), 5.01 (dd, J = 3.4, 10.4 Hz, 3 H, 3 x H-3'ose'), 5.18 (dd, J = 7.9, 10.4 Hz, 3 H, 3 x H-2'ose'), 5.37-5.46 (m, 12 H, 3 x H-4'ose', 3 x H-1'ose', 3 x H-2'ose', 3 x H-3'ose'), 7.38 (d, J = 8.3 Hz, 6 H, 6 x Ar-H_{meta}), 8.12 (d, J = 8.3 Hz, 6 H, 6 x Ar-H_{ortho}), 8.34 (br s, 1 H, Ar_F-H_{para}), 8.65-8.69 (m, 4 H, 2 x Ar_F-H_{ortho}, 2 x β -H), 8.87 (s, 4 H, β -H), 8.91 (d, J = 4.8 Hz, 2 H, β -H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 20.63 (CH₃), 20.77 (CH₃), 20.78 (CH₃), 20.79 (CH₃), 20.95 (CH₃), 20.96 (CH₃), 20.98 (CH₃), 60.93 (C-6'ose'), 62.28 (C-6''ose'), 66.70 (C'ose'), 69.21 (C-2'ose'), 70.89 (C'ose'), 71.06 (C-3'ose'), 71.71 (C'ose'), 73.00 (C'ose'), 73.17 (C'ose'), 76.45 (C'ose'), 98.95 (C-1'ose'), 101.34 (C-1'ose'), 115.18 (Ar-C_{meta}), 115.21 (Ar-C_{meta}), 115.69 (Ar_F-C_{meso}), 120.04 (Ar-C_{meso}), 120.45 (Ar-C_{meso}), 121.93 (Ar_F-C_{para}), 122.55, 124.72, 130.39 (CF₃), 133.85 (Ar_F-C_{ortho}), 135.66 (Ar-C_{ortho}), 136.83 (Ar-C_{ipso}), 136.90 (Ar-C_{ipso}), 144.40 (Ar_F-C_{ipso}), 156.86 (Ar-C_{OLac}), 169.23 (C=O), 169.87 (C=O), 169.92 (C=O), 170.18 (C=O), 170.26 (C=O), 170.43 (C=O), 170.50 (C=O) ppm.

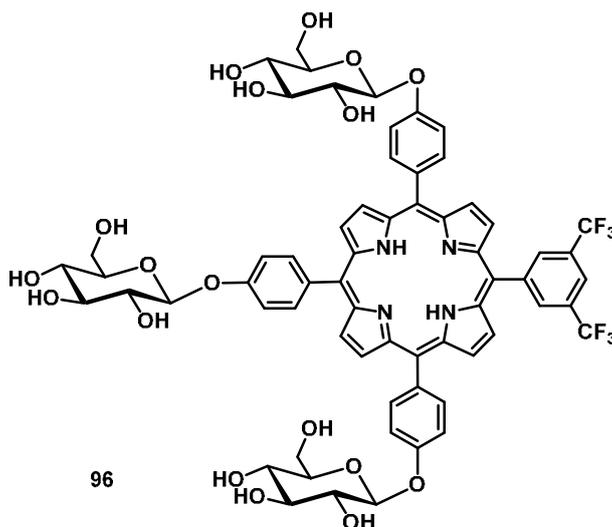
¹⁹F-NMR (471 MHz, CDCl₃): δ = -62.23 (s, 6 F, 2 x CF₃) ppm.

HRMS (ESI-TOF): m/z calcd. for C₁₂₄H₁₃₀F₆N₄NaO₅₄ [M + Na]⁺: 2676.7385, found: 2676.7347.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 420 (5.53), 518 (4.23), 553 (3.94), 590 (3.79), 649 (3.67) nm.

5,10,15-Tris(4- β -D-glucosylphenyl)-20-[3,5-bis(trifluoromethyl)phenyl]porphyrin (96):

According to the general procedure VIII, acetylated glycoporphyrin **92** (25 mg, 14 μ mol) was dissolved in a mixture of dry THF/methanol (8 ml, 1:1). Then a solution of sodium methanolate in dry methanol (0.63 ml, 0.12 N) was added. After 3 h, the solvent was evaporated under reduced pressure and the crude product was purified by reversed phase column chromatography, using methanol/water (95:5). The desired product (17 mg, 96%) was obtained as a violet crystalline solid.



Melting Point: 182 °C

$^1\text{H-NMR}$ (700 MHz, $(\text{CD}_3)_2\text{SO}$): δ = -2.91 (br s, 2 H, NH), 3.29-3.32 (m, 3 H, 3 x H'ose')*, 3.42-3.45 (m, 6 H, 6 x H'ose')*, 3.50-3.53 (m, 3 H, 3 x H'ose'), 3.57-3.61 (m, 3 H, 3 x H-6'ose'), 3.79-3.81 (m, 3 H, 3 x H-6'ose'), 5.21-5.23 (m, 3 H, 3 x H-1'ose'), 7.46-7.49 (m, 6 H, 6 x Ar-H_{meta}), 8.12-8.14 (m, 6 H, 6 x Ar-H_{ortho}), 8.61 (br s, 1 H, Ar_F-H_{para}), 8.74-8.79 (m, 2 H, β -H), 8.85-8.92 (m, 6 H, β -H), 8.93 (br s, 2 H, 2 x Ar_F-H_{ortho}) ppm.

* = signals of carbohydrate hydrogens are overlapped by the water peak of DMSO

$^{13}\text{C-NMR}$ (176 MHz, $(\text{CD}_3)_2\text{SO}$): δ = 61.22 (C-6'ose'), 70.23 (C'ose'), 73.91 (C'ose'), 77.17 (C'ose'), 77.69 (C'ose'), 101.01 (C-1'ose'), 115.05 (Ar-C_{meta}), 116.09 (Ar_F-C_{meso}), 120.53 (Ar-C_{meso}), 121.01 (Ar-C_{meso}), 122.61 (Ar_F-C_{para}), 123.29, 124.84, 129.53 (CF₃), 134.25 (Ar_F-C_{ortho}), 134.87 (Ar-C_{ipso}), 134.96 (Ar-C_{ipso}), 135.70 (Ar-C_{ortho}), 144.35 (Ar_F-C_{ipso}), 158.00 (Ar-C_{Oglc}) ppm.

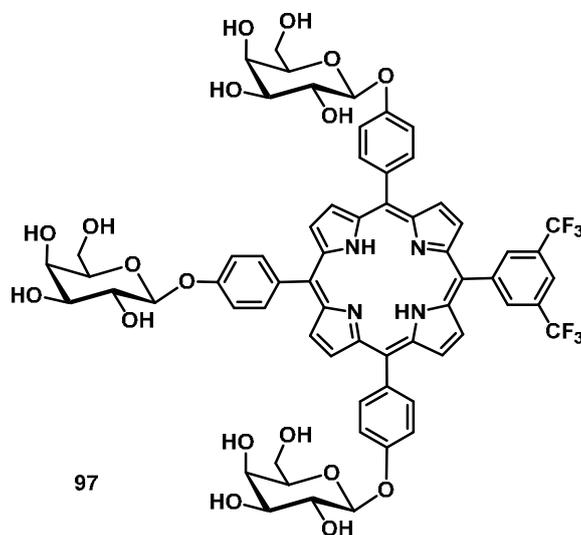
$^{19}\text{F-NMR}$ (471 MHz, $(\text{CD}_3)_2\text{SO}$): δ = -62.23 (s, 6 F, 2 x CF₃) ppm.

HRMS (ESI-TOF): m/z calcd. for C₆₄H₅₈F₆N₄O₁₈Na [M + Na]⁺: 1307.3548, found: 1307.3598.

UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 422 (5.34), 518 (4.31), 554 (4.15), 591 (4.01), 649 (3.98) nm.

5,10,15-Tris(4- β -D-galactosylphenyl)-20-[3,5-bis(trifluoromethyl)phenyl]porphyrin (97):

According to the general procedure VIII, acetylated glycoporphyrin **93** (33 mg, 18 μmol) was dissolved in a mixture of dry THF/methanol (10 ml, 1:1). Then a solution of sodium methanolate in dry methanol (1.50 ml, 0.08 N) was added. After 3 h, the solvent was evaporated under reduced pressure and the crude product was purified by reversed phase column chromatography, using methanol/water (95:5). The desired product (23 mg, 97%) was obtained as a violet crystalline solid.



Melting Point: 142 °C

$^1\text{H-NMR}$ (700 MHz, $(\text{CD}_3)_2\text{SO}$): δ = -2.92 (br s, 2 H, NH), 3.50-3.56 (m, 3 H, 3 x H'ose')*, 3.60-3.69 (m, 6 H, 6 x H-6'ose'), 3.74-3.78 (m, 6 H, 6 x H'ose'), 3.79-3.84 (m, 3 H, 3 x H'ose'), 4.26 (t, J = 7.1 Hz, 3 H, 3 x OH'ose'), 5.17-5.19 (m, 3 H, 3 x H-1'ose'), 7.45-7.49 (m, 6 H, 6 x Ar-H_{meta}), 8.12-8.14 (m, 6 H, 6 x Ar-H_{ortho}), 8.61 (br s, 1 H, Ar_F-H_{para}), 8.75-8.79 (m, 2 H, β -H), 8.84-8.93 (m, 6 H, β -H), 8.94 (br s, 2 H, 2 x Ar_F-H_{ortho}) ppm.

* = signals of carbohydrate hydrogens are overlapped by the water peak of DMSO

$^{13}\text{C-NMR}$ (176 MHz, $(\text{CD}_3)_2\text{SO}$): δ = 60.99 (C-6'ose'), 68.67 (C'ose'), 71.08 (C'ose'), 74.01 (C'ose'), 76.30 (C'ose'), 101.80 (C-1'ose'), 115.18 (Ar-C_{meta}), 116.19 (Ar_F-C_{meso}), 120.57 (Ar-C_{meso}), 121.06 (Ar-C_{meso}), 122.61 (Ar_F-C_{para}), 123.29, 124.85, 126.40, 129.53 (CF₃), 134.26 (Ar_F-C_{ortho}), 134.77 (Ar-C_{ipso}), 134.83 (Ar-C_{ipso}), 135.85 (Ar-C_{ortho}), 144.35 (Ar_F-C_{ipso}), 158.22 (Ar-C_{OGal}) ppm.

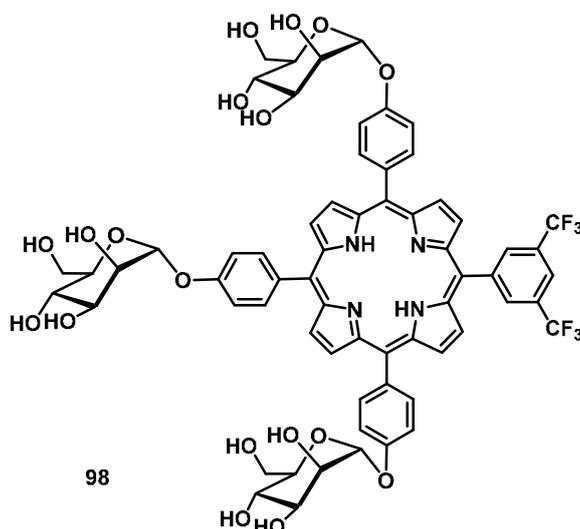
$^{19}\text{F-NMR}$ (471 MHz, $(\text{CD}_3)_2\text{SO}$): δ = -60.57 (s, 6 F, 2 x CF₃) ppm.

HRMS (ESI-TOF): m/z calcd. for $C_{64}H_{58}F_6N_4O_{18}Na [M + Na]^+$: 1307.3548, found: 1307.3505.

UV/Vis ((CH₃)₂SO): λ_{max} (log $\epsilon/dm^3 mol^{-1} cm^{-1}$): 423 (5.30), 518 (4.24), 554 (4.13), 591 (4.03), 649 (4.00) nm.

5,10,15-Tris(4- α -D-mannosylphenyl)-20-[3,5-bis(trifluoromethyl)phenyl]porphyrin (98):

According to the general procedure VIII, acetylated glycoporphyrin 94 (50 mg, 28 μ mol) was dissolved in a mixture of dry THF/methanol (10 ml, 1:1). Then a solution of sodium methanolate in dry methanol (1.25 ml, 0.08 N) was added. After 3 h, the solvent was evaporated under reduced pressure and the crude product was purified by reversed phase column chromatography, using methanol/water (95:5). The desired product (28 mg, 78%) was obtained as a violet crystalline solid.



Melting Point: > 300 °C

¹H-NMR (700 MHz, (CD₃)₂SO): δ = -2.91 (br s, 2 H, NH), 3.60-3.66 (m, 6 H, 3 x H-4'ose', 3 x H-6_A'ose'), 3.68-3.71 (m, 3 H, 3 x H-5'ose'), 3.76-3.80 (m, 3 H, 3 x 6_B'ose'), 3.87-3.90 (m, 3 H, 3 x H-3'ose'), 4.04-4.06 (m, 3 H, 3 x H-2'ose'), 4.67 (br s, 3 H, 3 x OH'ose'), 4.91 (br s, 3 H, 3 x OH'ose'), 5.01 (br s, 3 H, 3 x OH'ose'), 5.23 (br s, 3 H, 3 x OH'ose'), 5.72-5.74 (m, 3 H, 3 x H-1'ose'), 7.54-7.57 (m, 6 H, 6 x Ar-H_{meta}), 8.12-8.15 (m, 6 H, 6 x Ar-H_{ortho}), 8.62 (br s, 1 H, Ar_F-H_{para}), 8.76-8.80 (m, 2 H, β -H), 8.88-8.92 (m, 6 H, β -H), 8.93 (br s, 2 H, 2 x Ar_F-H_{ortho}) ppm.

¹³C-NMR (176 MHz, (CD₃)₂SO): δ = 61.64 (C-6'ose'), 67.32 (C-4'ose'), 70.72 (C-2'ose'), 71.30 (C-3'ose'), 75.73 (C-5'ose'), 99.82 (C-1'ose'), 115.85 (Ar-C_{meta}), 115.87 (Ar-C_{meta}), 116.10 (Ar_F-C_{meso}), 120.55 (Ar-C_{meso}), 122.60 (Ar_F-C_{para}), 129.53 (CF₃), 134.31 (Ar_F-C_{ortho}), 135.05 (Ar-C_{ipso}), 135.15 (Ar-C_{ipso}), 135.89 (Ar-C_{ortho}), 144.31 (Ar_F-C_{ipso}), 157.03 (Ar-C_{OMan}), 157.06 (Ar-C_{OMan}) ppm.

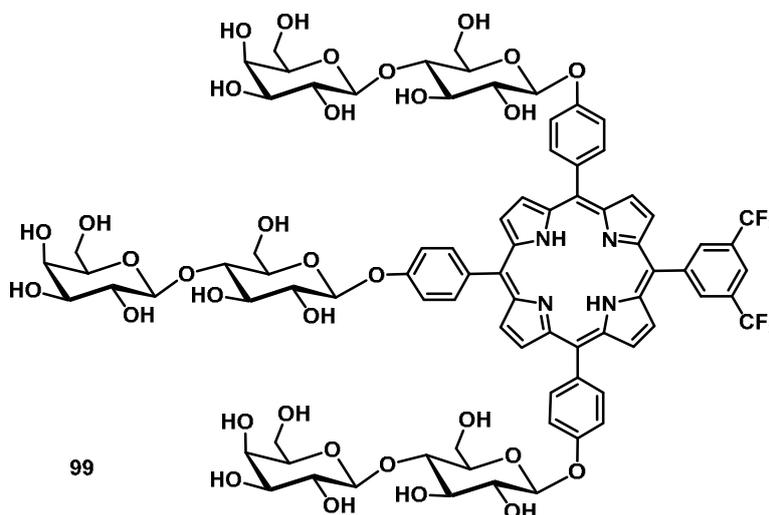
¹⁹F-NMR (471 MHz, (CD₃)₂SO): δ = -60.58 (s, 6 F, 2 x CF₃) ppm.

HRMS (ESI-TOF): m/z calcd. for $C_{64}H_{58}F_6N_4O_{18}Na [M + Na]^+$: 1307.3548, found: 1307.3558.

UV/Vis ((CH₃)₂SO): λ_{max} (log $\epsilon/dm^3 mol^{-1} cm^{-1}$): 421 (5.43), 518 (4.39), 554 (4.17), 593 (3.96), 649 (3.92) nm.

5,10,15-Tris(4- β -D-lactosylphenyl)-20-[3,5-bis(trifluoromethyl)phenyl]porphyrin (99):

According to the general procedure VIII, acetylated glycoporphyrin 95 (25 mg, 10 μ mol) was dissolved in a mixture of dry THF/methanol (6 ml, 1:1). Then a solution of sodium methanolate in dry methanol (1.25 ml, 0.10 N) was added. After 5 h, the solvent was evaporated under reduced pressure and the crude product was purified by reversed phase column chromatography, using methanol/water (9:1). The desired product (15 mg, 91%) was obtained as a violet crystalline solid.



Melting Point: 259 °C

¹H-NMR (700 MHz, (CD₃)₂SO): δ = -2.91 (br s, 2 H, NH), 3.29-3.43 (m, 6 H, 2 x 'ose')*, 3.48-3.64 (m, 18 H, 6 x H'ose'), 3.65-3.68 (m, 3 H, H'ose'), 3.72-3.79 (m, 6 H, 2 x H'ose'), 3.88-3.92 (m, 3 H, H'ose'), 4.32 (d, J = 7.5 Hz, 3 H, H-1'ose'), 4.56 (d, J = 4.6 Hz, 3 H, OH'ose'), 4.70-4.73 (m, 3 H, OH'ose'), 4.74-4.78 (m, 3 H, OH'ose'), 4.82 (d, J = 5.7 Hz, 3 H, OH'ose'), 4.88-4.91 (m, 3 H, OH'ose'), 5.14 (d, J = 4.7 Hz, 3 H, OH'ose'), 5.34 (d, J = 7.7 Hz, 3 H, H-1''ose'), 5.67 (d, J = 5.3 Hz, 3 H, OH'ose'), 7.48-7.51 (m, 6 H, 6 x Ar-H_{meta}), 8.14-8.16 (m, 6 H, 6 x Ar-H_{ortho}), 8.62 (br s, 1 H, Ar_F-H_{para}), 8.76-8.81 (m, 2 H, β -H), 8.88-8.93 (m, 6 H, β -H), 8.94 (br s, 2 H, 2 x Ar_F-H_{ortho}) ppm.

* = signals of carbohydrate hydrogens are overlapped by the water peak of DMSO

¹³C-NMR (176 MHz, (CD₃)₂SO): δ = 60.65 (C'ose'), 60.95 (C'ose'), 68.67 (C'ose'), 71.06 (C'ose'), 73.67 (C'ose'), 73.76 (C'ose'), 75.38 (C'ose'), 75.59 (C'ose'), 76.07 (C'ose'), 80.61 (C'ose'), 100.50 (C'ose'), 104.31 (C'ose'), 115.05 (Ar-C_{meta}), 116.14 (Ar_F-C_{meso}), 120.50 (Ar-C_{meso}),

120.97 (Ar-C_{meso}), 122.64 (Ar_F-C_{para}), 123.30, 124.85, 129.54 (CF₃), 134.26 (Ar_F-C_{ortho}), 134.97 (Ar-C_{ipso}), 135.06 (Ar-C_{ipso}), 135.71 (Ar-C_{ortho}), 144.33 (Ar_F-C_{ipso}), 157.87 (Ar-C_{OLac}) ppm.

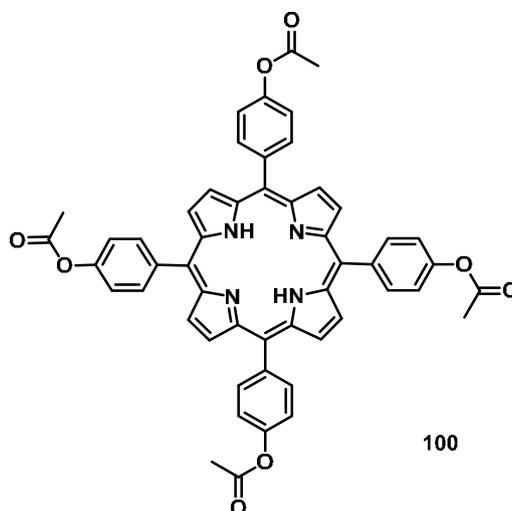
¹⁹F-NMR (471 MHz, (CH₃)₂SO): δ = -60.58 (s, 6 F, 2 x CF₃) ppm.

HRMS (ESI-TOF): *m/z* calcd. for C₈₂H₈₈F₆N₄O₃₃Na [M + Na]⁺: 1793.5133, found: 1793.5196.

UV/Vis ((CH₃)₂SO): λ_{max} (log ε/dm³ mol⁻¹ cm⁻¹): 420 (5.57), 518 (4.51), 554 (4.24), 595 (4.09), 650 (3.94) nm.

5,10,15,20-Tetrakis(4-acetoxyphenyl)porphyrin (100):

According to the general procedure III, 4-acetoxybenzaldehyde (2.10 ml, 15.0 mmol), pyrrole (1.04 ml, 15.0 mmol), TFA (1.16 ml, 15.1 mmol), DDQ (2.55 g, 11.3 mmol) and triethylamine (3.00 ml, 21.5 mmol) were reacted in dry dichloromethane (1500 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (9:1) as the eluent and subsequent recrystallization from dichloromethane/methanol to obtain the desired product (1.33 g, 43%) in form of violet crystals.



Melting Point: > 300 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.84 (br s, 2 H, NH), 2.50 (s, 12 H, 4 x OCH₃), 7.50 (d, *J* = 8.4 Hz, 8 H, Ar-H_{meta}), 8.21 (d, *J* = 8.4 Hz, 8 H, Ar-H_{ortho}), 8.88 (s, 8 H, β-H) ppm.

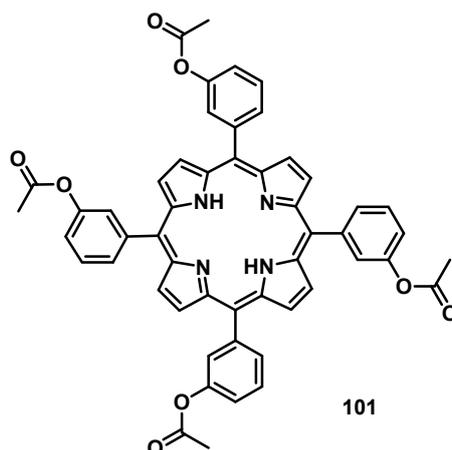
¹³C-NMR (126 MHz, CDCl₃): δ = 21.52 (OCH₃), 119.32 (Ar-C_{meso}), 119.98 (Ar-C_{meta}), 135.43 (Ar-C_{ortho}), 139.63 (Ar-C_{ipso}), 150.71 (Ar-C_{OH}), 169.70 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for $C_{52}H_{39}N_4O_8$ $[M + H]^+$: 847.2768, found: 847.2738.

UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/dm^3 mol^{-1} cm^{-1}$): 418 (5.59), 515 (4.36), 550 (4.05), 591 (3.91), 647 (3.78) nm.

5,10,15,20-Tetrakis(3-acetoxyphenyl)porphyrin (101):

According to the general procedure **III**, 3-acetoxybenzaldehyde (2.47 g, 15.0 mmol), pyrrole (1.04 ml, 15.0 mmol), TFA (1.16 ml, 15.1 mmol), DDQ (2.55 g, 11.3 mmol) and triethylamine (3.00 ml, 21.5 mmol) were reacted in dry dichloromethane (1500 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (9:1) as the eluent and subsequent recrystallization from dichloromethane/methanol to obtain the desired product (1.21 g, 39%) in form of violet crystals.

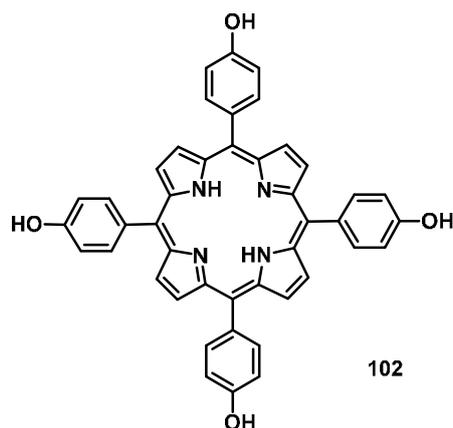


1H -NMR (500 MHz, $CDCl_3$): δ = -2.88 (br s, 2 H, NH), 2.39 (s, 12 H, 4 x OAc), 7.53-7.56 (m, 4 H, Ar-H), 7.74-7.77 (m, 4 H, Ar-H), 7.95-7.98 (m, 4 H, Ar-H), 8.06-8.09 (m, 4 H, Ar-H), 8.93 (br s, 8 H, β -H) ppm.

HRMS (ESI-TOF): m/z calcd. for $C_{52}H_{39}N_4O_8$ $[M + H]^+$: 847.2768, found: 847.2735.

5,10,15,20-Tetrakis(4-hydroxyphenyl)porphyrin (102):

According to the general procedure **V**, acetylated porphyrin **100** (100 mg, 118 μ mol) was dissolved in THF (25 ml) and saturated methanolic KOH solution (20 ml) was added. After full conversion, purification was achieved by column chromatography on silica using dichloromethane/methanol (9:1) as the eluent followed by washing with dichloromethane to obtain the desired product (80 mg, 100%) as a purple solid.



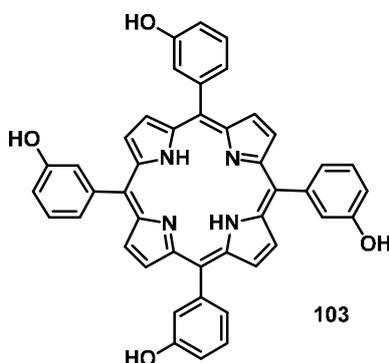
Melting Point: > 300 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = -2.69 (br s, 2 H, NH), 7.30 (d, J = 8.6 Hz, 8 H, Ar-H_{meta}), 8.07 (d, J = 8.6 Hz, 8 H, Ar-H_{ortho}), 8.89 (br s, 4 H, OH), 8.93 (s, 8 H, β -H) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₃₁N₄O₄ [M + H]⁺: 679.2340, found: 679.2337.

5,10,15,20-Tetrakis(3-hydroxyphenyl)porphyrin (103):

According to the general procedure V, acetylated porphyrin **101** (50 mg, 59 μ mol) was dissolved in THF (12 ml) and saturated methanolic KOH solution (10 ml) was added. After full conversion, purification was achieved by column chromatography on silica using dichloromethane/methanol (9:1) as the eluent followed by washing with dichloromethane to obtain the desired product (39 mg, 98%) as a purple solid.



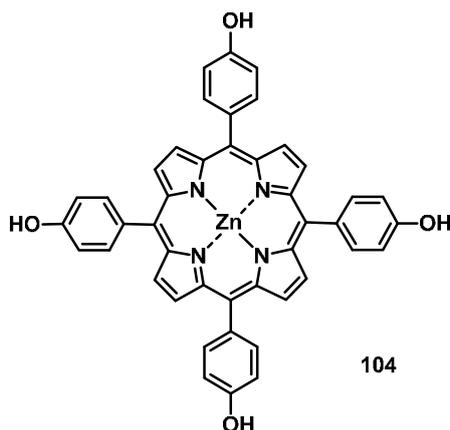
¹H-NMR (500 MHz, (CD₃)₂CO): δ = -2.79 (br s, 2 H, NH), 7.29-7.33 (m, 4 H, Ar-H), 7.60-7.63 (m, 4 H, Ar-H), 7.69-7.74 (m, 8 H, Ar-H), 8.92 (br s, 4 H, OH), 8.96 (s, 8 H, β -H) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₃₁N₄O₄ [M + H]⁺: 679.2345, found: 679.2339.

Analytical data are in accordance with published data.^[113]

[5,10,15,20-Tetrakis(4-hydroxyphenyl)porphyrinato]zinc(II) (104):

According to the general procedure VI, a mixture of porphyrin **102** (156 mg, 230 μmol) and $\text{Zn}(\text{OAc})_2 \cdot 2 \text{H}_2\text{O}$ (200 mg, 912 μmol) was reacted in dichloromethane/methanol (16 ml, 1:1). Purification was achieved by column chromatography on silica using dichloromethane/methanol (9:1) as the eluent and subsequent recrystallization from dichloromethane/aqueous methanol to obtain the desired product (163 mg, 96%) as a purple solid.



Melting Point: > 300 °C

$^1\text{H-NMR}$ (500 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 7.26 (d, J = 8.3 Hz, 8 H, Ar-H_{meta}), 8.04 (d, J = 8.3 Hz, 8 H, Ar-H_{ortho}), 8.91 (br s, 4 H, OH), 8.92 (s, 8 H, β -H) ppm.

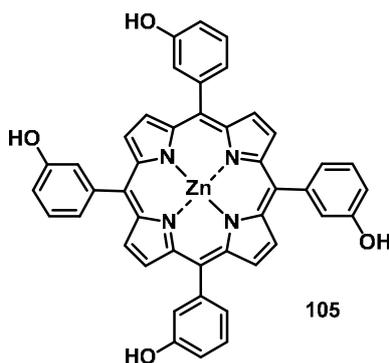
$^{13}\text{C-NMR}$ (126 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 113.49 (Ar-C_{meta}), 120.51 (Ar-C_{meso}), 131.44 (β -C), 134.65 (Ar-C_{ipso}), 135.49 (Ar-C_{ortho}), 150.41 (α -C), 157.16 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{44}\text{H}_{28}\text{N}_4\text{O}_4\text{ZnNa}$ [$\text{M} + \text{Na}$]⁺: 763.1300, found: 763.1285.

UV/Vis ($(\text{CH}_3)_2\text{CO}$): λ_{max} (log $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 424 (5.56), 557 (4.32), 599 (4.08) nm.

[5,10,15,20-Tetrakis(3-hydroxyphenyl)porphyrinato]zinc(II) (105):

According to the general procedure VI, a mixture of porphyrin **103** (200 mg, 295 μmol) and $\text{Zn}(\text{OAc})_2 \cdot 2 \text{H}_2\text{O}$ (250 mg, 1.14 mmol) was reacted in dichloromethane/methanol (18 ml, 1:1). Purification was achieved by column chromatography on silica using dichloromethane/methanol (9:1) as the eluent and subsequent recrystallization from dichloromethane/aqueous methanol to obtain the desired product (220 mg, 94%) as a purple solid.



Melting Point: > 300 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = 7.28-7.30 (m, 4 H, Ar-H), 7.57-7.61 (m, 4 H, Ar-H), 7.69-7.72 (m, 8 H, Ar-H), 8.76 (br s, 4 H, OH), 8.94 (br s, 8 H, β -H) ppm.

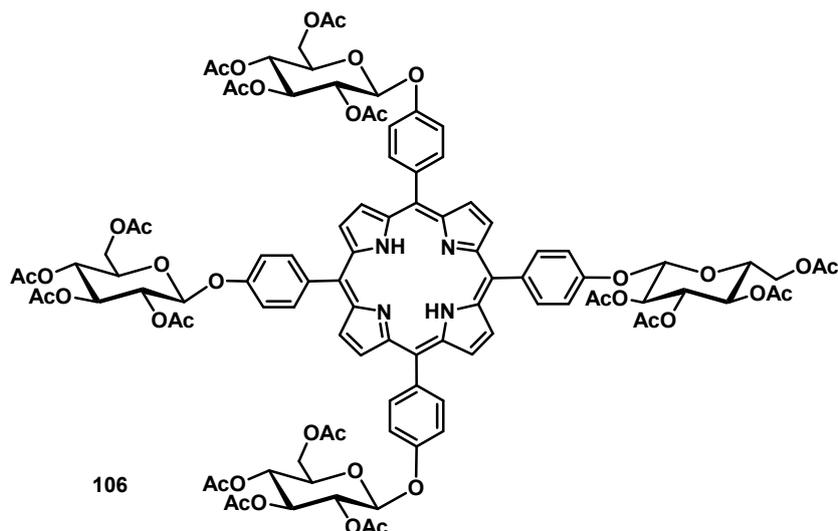
¹³C-NMR (126 MHz, (CD₃)₂CO): δ = 114.47 (Ar-C), 120.47 (Ar-C_{meso}), 122.06 (Ar-C), 126.41 (Ar-C), 127.36 (Ar-C), 131.47 (β -C), 144.78 (Ar-C_{ipso}), 149.91 (α -C), 155.71 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₂₉N₄O₄Zn [M + H]⁺: 741.1475, found: 741.1488.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 422 (5.21), 554 (4.24), 593 (3.76) nm.

5,10,15,20-[4-(2,3,4,6-Tetraacetyl- β -D-glucosyl)phenyl]porphyrin (106):

According to the general procedure VII, metallated hydroxyporphyrin **104** (50 mg, 62 μ mol), 2,3,4,6-tetraacetyl-D-glucose trichloroacetimidate **2** (0.8 g, 1.5 mmol) and BF₃·Et₂O (4.0 μ l, 32 μ mol) were reacted in a mixture of dry dichloromethane/THF/acetonitrile (10 ml, 8:1:1) for 3 h. Demetallation was accomplished with HCl (1.0 ml, 25%) in THF (10 ml). Purification was achieved by column chromatography on silica using dichloromethane/methanol (98:2) as the eluent. The desired product (93 mg, 69%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/aqueous methanol.



Melting Point: 287 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.83 (br s, 2 H, NH), 2.10 (s, 12 H, 4 x OAc), 2.11 (s, 12 H, 4 x OAc), 2.12 (s, 12 H, 4 x OAc), 2.21 (s, 12 H, 4 x OAc), 4.06 (ddd, J = 2.5, 5.4, 10.1 Hz, 4 H, H-5'ose'), 4.30 (dd, J = 2.5, 12.3 Hz, 4 H, H-6_A'ose'), 4.42 (dd, J = 5.4, 12.3 Hz, 4 H, H-6_B'ose'), 5.31 (dd, J = 9.6, 10.1 Hz, 4 H, H-4'ose'), 5.45 (dd, J = 9.6, 9.6 Hz, 4 H, H-3'ose'), 5.47 (d, J = 7.6 Hz, 4 H, H-1'ose'), 5.49 (dd, J = 7.6, 9.6 Hz, 4 H, H-2'ose'), 7.38 (d, J = 8.5 Hz, 8 H, 8 x Ar-H_{meta}), 8.12 (d, J = 8.5 Hz, 8 H, 8 x Ar-H_{ortho}), 8.85 (s, 8 H, β -H) ppm.

¹³C-NMR (126 MHz, CDCl₃): δ = 20.73 (CH₃), 20.77 (CH₃), 20.86 (CH₃), 20.90 (CH₃), 62.18 (C-6'ose'), 68.48 (C-4'ose'), 71.43 (C-2'ose'), 72.39 (C-5'ose'), 72.93 (C-3'ose'), 99.25 (C-1'ose'), 115.17 (Ar-C_{meta}), 119.43 (Ar-C_{meso}), 135.62 (Ar-C_{ortho}), 137.21 (Ar-C_{ipso}), 156.74 (Ar-C_{OGLic}), 169.55 (C=O), 170.41 (C=O), 170.70 (C=O) ppm.

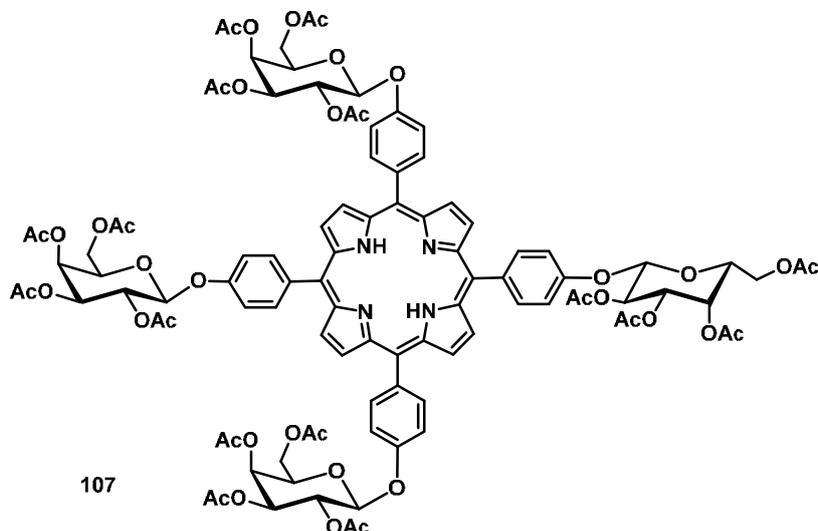
HRMS (ESI-TOF): m/z calcd. for C₁₀₀H₁₀₃N₄O₄₀ [M + H]⁺: 1999.6149, found: 1999.6105.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 420 (5.20), 515 (3.89), 551 (3.66), 594 (3.46), 649 (3.39) nm.

5,10,15,20-Tetrakis[4-(2,3,4,6-tetraacetyl- β -D-galactosyl)phenyl]porphyrin (107):

According to the general procedure VII, metallated hydroxyporphyrin **104** (100 mg, 125 μ mol), 2,3,4,6-tetraacetyl-D-galactose trichloroacetimidate **4** (1.5 g, 3.1 mmol) and BF₃·Et₂O (7.5 μ l, 60 μ mol) were reacted in a mixture of dry dichloromethane/THF/acetonitrile (20 ml, 8:1:1) for 3 h. Demetallation was accomplished with HCl (1.5 ml, 25%) in THF (20 ml). Purification was achieved by column chromatography on silica using dichloromethane/methanol (98:2) as the eluent. The

desired product (200 mg, 74%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/aqueous methanol.



Melting Point: 276 °C

¹H-NMR (700 MHz, (CD₃)₂SO): δ = -2.92 (br s, 2 H, NH), 2.02 (s, 12 H, 4 x OAc), 2.05 (s, 12 H, 4 x OAc), 2.20 (s, 12 H, 4 x OAc), 2.23 (s, 12 H, 4 x OAc), 4.21 (dd, J = 5.1, 11.2 Hz, 4 H, 4 x H-6_A'ose'), 4.24 (dd, J = 7.4, 11.2 Hz, 4 H, 4 x H-6_B'ose'), 4.60-4.63 (m, 4 H, 4 x H-5'ose'), 5.40-5.48 (m, 12 H, 4 x H-2'ose', 4 x H-3'ose', 4 x H-4'ose'), 5.85-5.88 (m, 4 H, 4 x H-1'ose'), 7.46 (d, J = 8.5 Hz, 8 H, 8 x Ar-H_{meta}), 8.19 (d, J = 8.5 Hz, 8 H, 8 x Ar-H_{ortho}), 8.87 (s, 8 H, β -H) ppm.

¹³C-NMR (176 MHz, (CD₃)₂SO): δ = 20.89 (CH₃), 20.95 (CH₃), 21.01 (CH₃), 21.11 (CH₃), 61.92 (C-6'ose'), 67.82 (C-4'ose'), 69.01 (C-2'ose'), 70.80 (C-3'ose'), 71.08 (C-5'ose'), 98.25 (C-1'ose'), 115.36 (Ar-C_{meta}), 119.86 (Ar-C_{meso}), 135.86 (Ar-C_{ortho}), 136.15 (Ar-C_{ipso}), 156.86 (Ar-C_{OGal}), 169.89 (C=O), 170.12 (C=O), 170.42 (C=O), 170.53 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for C₁₀₀H₁₀₃N₄O₄₀ [M + H]⁺: 1999.6149, found: 1999.6183.

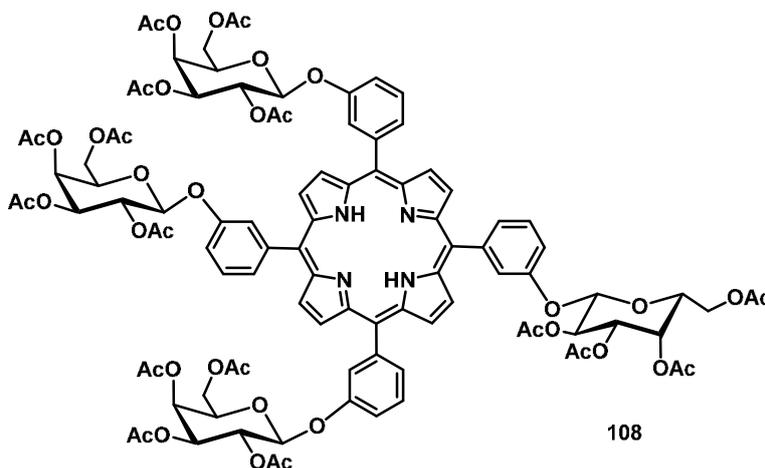
UV/Vis ((CH₃)₂SO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 420 (5.63), 516 (4.26), 551 (4.03), 592 (3.83), 648 (3.76) nm.

5,10,15,20-[3-(2,3,4,6-Tetraacetyl- β -D-galactosyl)phenyl]porphyrin (108):

According to the general procedure VII, metallated hydroxyporphyrin **105** (50 mg, 62 μ mol), 2,3,4,6-tetraacetyl-D-galactose trichloroacetimidate **4** (0.8 g, 1.5 mmol) and BF₃·Et₂O (3.5 μ l, 28 μ mol) were reacted in a mixture of dry dichloromethane/THF/acetonitrile (10 ml, 8:1:1) for 3 h. Demetallation was accomplished with HCl (1.0 ml, 25%) in THF (10 ml). Purification was achieved by column

chromatography on silica using dichloromethane/methanol (98:2) as the eluent. The desired product (97 mg, 78%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/aqueous methanol.

This porphyrin is obtained as a mixture of atropisomers.



Melting Point: 225 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = -2.84 (br s, 2 H, NH), 0.97-1.04 (m, 12 H, 4 x OAc), 1.90-1.93 (m, 12 H, 4 x OAc), 2.06-2.09 (m, 12 H, 4 x OAc), 2.12 (s, 12 H, 4 x OAc), 4.00-4.09 (m, 8 H, H-6'ose'), 4.32-4.37 (m, 4 H, H-5'ose'), 5.24-5.28 (m, 4 H, H-3'ose'), 5.37-5.40 (m, 4 H, H-4'ose'), 5.50-5.55 (m, 4 H, H-2'ose'), 5.71-5.75 (m, 4 H, H-1'ose'), 7.53-7.57 (m, 4 H, Ar-H), 7.75-7.80 (m, 4 H, Ar-H), 7.92-8.06 (m, 8 H, Ar-H), 8.93-8.97 (m, 8 H, β -H) ppm.

¹³C-NMR (126 MHz, (CD₃)₂CO): δ = 18.83 (CH₃), 19.71 (CH₃), 19.92 (CH₃), 19.94 (CH₃), 61.63-61.68 (C-6'ose'), 67.51 (C-4'ose'), 68.75 (C-2'ose'), 70.76 (C-3'ose'), 71.13-71.20 (C-5'ose'), 99.05-99.24 (C-1'ose'), 116.82 (Ar-C), 119.81 (Ar-C_{meso}), 122.41-122.73 (Ar-C), 128.04 (Ar-C), 129.26-129.37 (Ar-C), 143.32-143.37 (Ar-C_{ipso}), 155.79-155.88 (Ar-C_{OGal}), 169.12 (C=O), 169.38-169.47 (C=O), 169.95 (C=O) ppm.

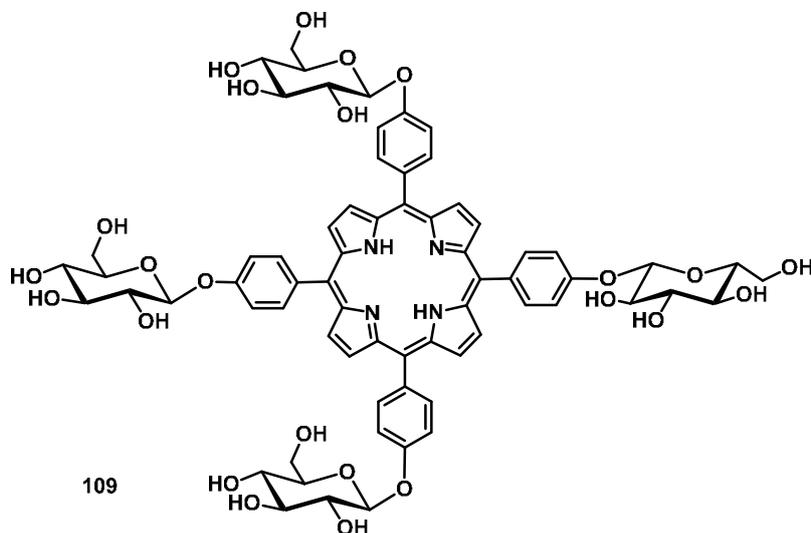
HRMS (ESI-TOF): m/z calcd. for C₁₀₀H₁₀₃N₄O₄₀ [M + H]⁺: 1999.6149, found: 1999.6140.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 418 (5.54), 513 (4.22), 548 (3.74), 589 (3.69), 645 (3.38) nm.

5,10,15,20-Tetrakis(4- β -D-glucosylphenyl)porphyrin (109):

According to the general procedure VIII, acetylated glycoporphyrin **106** (30 mg, 15 μ mol) was dissolved in a mixture of dry THF/methanol (12 ml, 1:1). Then a solution of sodium methanolate in

dry methanol (0.55 ml, 0.12 N) was added. After 4 h, the solvent was evaporated under reduced pressure and the crude product was purified by reversed phase column chromatography, using methanol/water(9:1). The desired product (17 mg, 84%) was obtained as a violet crystalline solid.



Melting Point: > 300 °C

¹H-NMR (500 MHz, (CD₃)₂SO): δ = -2.91 (br s, 2 H, NH), 3.27-3.31 (m, 4 H, H'ose'), 3.40-3.45 (m, 8 H, H'ose'), 3.49-3.54 (ddd, J = 1.9, 5.7, 9.5 Hz, 4 H, H-5'ose'), 3.56-3.62 (dd, J = 5.7, 11.8 Hz, 4 H, H-6_B'ose'), 3.79-3.83 (m, 4 H, H-6_A'ose'), 4.73 (t, J = 5.8 Hz, 4 H, OH'ose'), 5.12 (d, J = 5.4 Hz, 4 H, OH'ose'), 5.21 (d, J = 4.2 Hz, 4 H, OH'ose'), 5.23 (d, J = 7.2 Hz, 4 H, H-1'ose'), 5.52 (d, J = 4.7 Hz, 4 H, OH'ose'), 7.48 (d, J = 8.5 Hz, 8 H, 8 x Ar-H_{meta}), 8.13 (d, J = 8.5 Hz, 8 H, 8 x Ar-H_{ortho}), 9.87 (s, 8 H, β -H) ppm.

¹³C-NMR (126 MHz, (CD₃)₂SO): δ = 61.36 (C-6'ose'), 70.35 (C'ose'), 74.01 (C'ose'), 77.26 (C'ose'), 77.79 (C'ose'), 101.13 (C-1'ose'), 115.11 (Ar-C_{meta}), 120.18 (Ar-C_{meso}), 135.21 (Ar-C_{ipso}), 135.78 (Ar-C_{ortho}), 158.06 (Ar-C_{Oglc}) ppm.

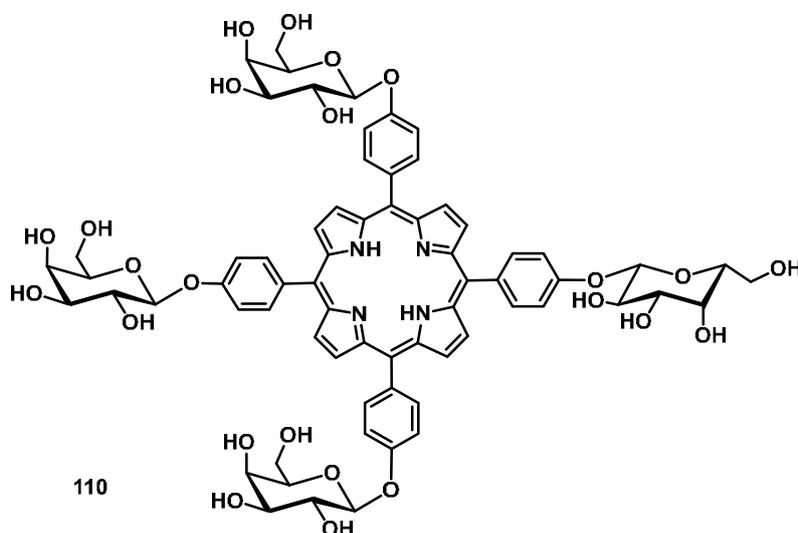
HRMS (ESI-TOF): m/z calcd. for C₆₈H₇₁N₄O₂₄ [M + H]⁺: 1327.4458, found: 1327.4490.

UV/Vis ((CH₃)₂SO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 423 (5.67), 518 (4.62), 555 (4.51), 594 (4.33), 650 (4.31) nm.

5,10,15,20-Tetrakis(4- β -D-galactosylphenyl)porphyrin (110):

According to the general procedure VIII, acetylated glycoporphyrin 107 (30 mg, 15 μ mol) was dissolved in a mixture of dry THF/methanol (12 ml, 1:1). Then a solution of sodium methanolate in dry methanol (0.55 ml, 0.12 N) was added. After 4 h, the solvent was evaporated under reduced

pressure and the crude product was purified by reversed phase column chromatography, using methanol/water (9:1). The desired product (14 mg, 69%) was obtained as a violet crystalline solid.



Melting Point: > 300 °C

¹H-NMR (700 MHz, (CD₃)₂SO): δ = -2.95 (br s, 2 H, NH), 3.54-3.58 (m, 4 H, H-5'ose'), 3.65-3.71 (m, 8 H, H-6'ose'), 3.75-3.80 (m, 8 H, H'ose'), 3.82-3.85 (m, 4 H, H'ose'), 4.63 (br s, 4 H, OH'ose'), 4.77 (br s, 4 H, OH'ose'), 4.99 (br s, 4 H, OH'ose'), 5.15 (d, J = 7.7 Hz, 4 H, H-1'ose'), 5.36 (br s, 4 H, OH'ose'), 7.44 (d, J = 8.6 Hz, 8 H, 8 x Ar-H_{meta}), 8.10 (d, J = 8.6 Hz, 8 H, 8 x Ar-H_{ortho}), 8.84 (s, 8 H, β -H) ppm.

¹³C-NMR (176 MHz, (CD₃)₂SO): δ = 61.04 (C-6'ose'), 68.76 (C'ose'), 71.06 (C'ose'), 73.99 (C-5'ose'), 76.11 (C'ose'), 101.94 (C-1'ose'), 114.29 (Ar-C_{meta}), 120.84 (Ar-C_{meso}), 135.72 (Ar-C_{ortho}), 156.99 (Ar-C_{OGal}) ppm.

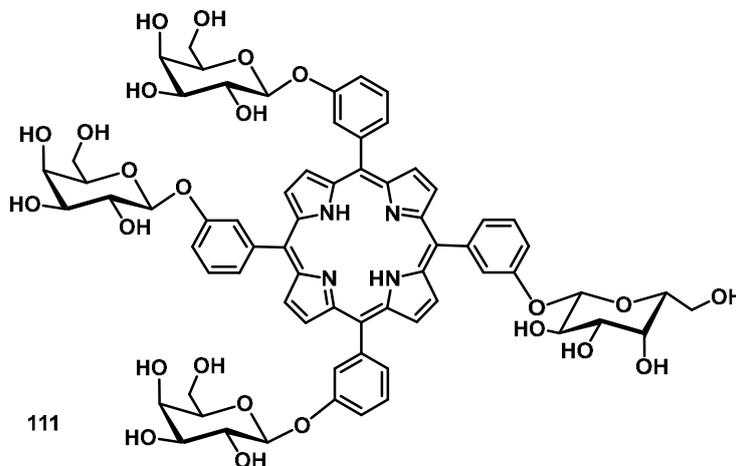
HRMS (ESI-TOF): m/z calcd. for C₆₈H₇₀N₄O₂₄Na [M + Na]⁺: 1349.4278, found: 1349.4250.

UV/Vis ((CH₃)₂SO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 422 (5.65), 517 (4.60), 555 (4.48), 595 (4.32), 651 (4.30) nm.

5,10,15,20-Tetrakis(3- β -D-galactosylphenyl)porphyrin (111):

According to the general procedure VIII, acetylated glycoporphyrin **108** (55 mg, 28 μ mol) was dissolved in dry THF (10 ml). Then a solution of sodium methanolate in dry methanol (1.00 ml, 0.12 N) was added. After 4 h, the solvent was evaporated under reduced pressure and the crude product was purified by reversed phase column chromatography, using methanol/water (9:1). The desired product (30 mg, 82%) was obtained as a violet crystalline solid.

This porphyrin is obtained as a mixture of atropisomers.



Melting Point: 253 °C

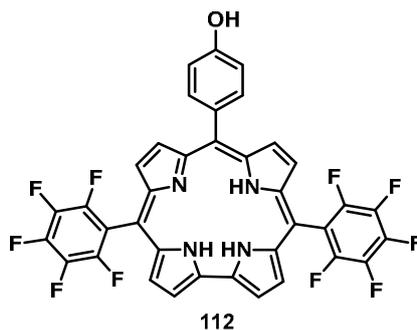
¹H-NMR (700 MHz, (CH₃)₂SO): δ = -2.95 (br s, 2 H, NH), 3.42-3.45 (m, 4 H, H'ose'), 3.48-3.52 (m, 4 H, H'ose'), 3.55-3.59 (m, 8 H, H'ose'), 3.66-3.70 (m, 8 H, H'ose'), 4.59 (br s, 8 H, OH-'ose'), 4.92 (br s, 4 H, OH-'ose'), 5.12-5.18 (m, 4 H, H-1'ose'), 5.30 (br s, 4 H, OH-'ose'), 7.50-7.53 (m, 4 H, Ar-H), 7.71-7.75 (m, 4 H, Ar-H), 7.79-7.84 (m, 4 H, Ar-H), 7.87-7.90 (m, 4 H, Ar-H), 8.87-8.93 (m, 8 H, β -H) ppm.

HRMS (ESI-TOF): m/z calcd. for C₆₈H₇₀N₄O₂₄Na [M + Na]⁺: 1349.4297, found: 1349.4278.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 416 (5.09), 513 (3.67), 546 (3.45), 589 (3.36), 644 (3.30) nm.

10-(4-Hydroxyphenyl)-5,15-bis(pentafluorophenyl)corrole (112):

According to the general procedure V, acetylated corrole **70** (60 mg, 78.474 μ mol) was dissolved in THF (7 ml). Then a solution of sodium methanolate in dry methanol (1.00 ml, 0.50 N) was added. After 10 min, purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (3:1) as the eluent followed by recrystallization from dichloromethane/aqueous methanol to obtain the desired product (55 mg, 97%) as a solid.



Melting Point: 271 °C

¹H-NMR (700 MHz, CDCl₃): δ = -0.72 (br s, 3 H, NH), 6.90 (d, J = 8.3 Hz, 2 H, Ar-H_{meta}), 7.97 (d, J = 8.3 Hz, 2 H, Ar-H_{ortho}), 8.61 (d, J = 4.2 Hz, 2 H, β -H), 8.72 (d, J = 4.6 Hz, 2 H, β -H), 8.76 (d, J = 4.6 Hz, 2 H, β -H), 9.10 (d, J = 4.2 Hz, 2 H, β -H) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 96.52 (Ar_F-C_{meso}), 112.98 (Ar-C_{meso}), 114.06 (Ar-C_{meta}), 114.06-114.24 (Ar_F-C_{ipso}), 117.65 (β -C), 121.71 (β -C), 125.30 (β -C), 127.78 (β -C), 131.52 (α -C), 133.77 (Ar-C_{ipso}), 135.43 (α -C), 135.69 (Ar-C_{ortho}), 137.12-137.31 (Ar_F-C), 138.55-138.74 (Ar_F-C), 139.90 (α -C), 140.97-141.15 (Ar_F-C), 141.28 (α -C), 142.43-142.58 (Ar_F-C), 145.43-145.50 (Ar_F-C), 146.80-146.91 (Ar_F-C), 155.01 (Ar-C_{OH}) ppm.

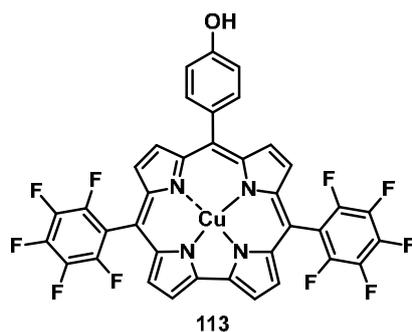
¹⁹F-NMR (471 MHz, CDCl₃): δ = -161.62 (dt, J = 8.2, 23.1 Hz, 4 F, Ar-F_{meta}), -152.70 (t, J = 20.9 Hz, 2 F, Ar-F_{para}), -137.74 (dd, J = 7.8, 24.0 Hz, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₃₇H₁₇F₁₀N₄O [M + H]⁺: 723.1243, found: 723.1211.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 410 (4.74), 561 (4.26), 612 (3.77), 640 (3.42) nm.

[10-(4-Hydroxyphenyl)-5,15-bis(pentafluorophenyl)corrolinato]copper(III) (113):

Corrole **112** (30 mg, 42 μ mol) and Cu(OAc)₂ (30 mg, 188 μ mol) was reacted in THF (8 ml) for 10 min. Purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (3:1) as the eluent and subsequent recrystallization from dichloromethane/aqueous methanol to obtain the desired product (32 mg, 97%) as a violet-green solid.



Melting Point: > 300 °C

¹H-NMR (700 MHz, CDCl₃): δ = 5.05 (s, 1 H, OH), 6.97 (d, J = 8.4 Hz, 2 H, Ar-H_{meta}), 7.24 (d, J = 4.2 Hz, 2 H, β -H), 7.29 (d, J = 4.6 Hz, 2 H, β -H), 7.45 (d, J = 4.2 Hz, 2 H, β -H), 7.51 (d, J = 8.4 Hz, 2 H, Ar-H_{ortho}), 7.96-7.98 (m, 2 H, β -H) ppm.

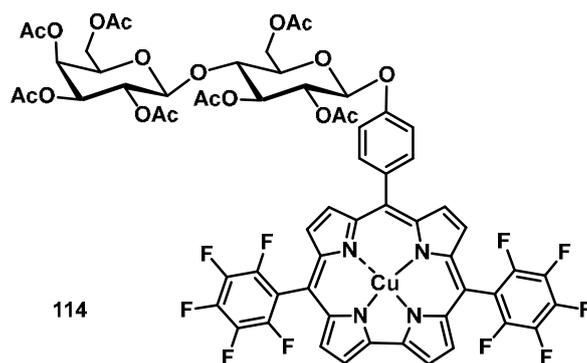
¹³C-NMR (176 MHz, CDCl₃): δ = 111.88-112.24 (Ar_F-C), 115.21 (Ar-C_{meta}), 122.81 (β -C), 126.31 (β -C), 129.78 (β -C), 132.29 (Ar-C_{ortho}), 132.52 (β -C), 136.92-137.20 (Ar_F-C), 138.34-138.65 (Ar_F-C), 140.61-140.98 (Ar_F-C), 142.09-142.47 (Ar_F-C), 143.96 (α -C), 144.15-144.42 (Ar_F-C), 144.99 (α -C), 145.63-145.91 (Ar_F-C), 149.63 (α -C), 150.43 (α -C), 156.44 (Ar-C_{OH}) ppm.

¹⁹F-NMR (471 MHz, CDCl₃): δ = -160.78 (td, J = 8.1, 22.9 Hz, 4 F, Ar-F_{meta}), -152.30 (t, J = 20.8 Hz, 2 F, Ar-F_{para}), -136.94 (dd, J = 7.8, 23.9 Hz, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₃₇H₁₄CuF₁₀N₄O [M + H]⁺: 783.0304, found: 783.0283.

[10-{4-(2,3,4,6,2',3',6'-Heptaacetyl- β -D-lactosyl)phenyl}-5,15-bis(pentafluorophenyl)-corrolinato]copper(III) (114):

According to the general procedure VII, metallated hydroxycorrole **113** (10 mg, 13 μ mol), 2,3,4,6,2',3',6'-heptaacetyl- α -D-lactose trichloroacetimidate **8** (60 mg, 77 μ mol) and BF₃·Et₂O (0.7 μ l, 5.7 μ mol) were reacted in dry dichloromethane (3 ml) for 5 min. Purification was achieved by column chromatography on silica using dichloromethane/methanol (98:2) as the eluent. The desired product (15 mg, 85%) was obtained as a violet-green crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 254 °C

¹H-NMR (700 MHz, CDCl₃): δ = 1.98 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 2.08 (s, 3 H, OAc), 2.09 (s, 3 H, OAc), 2.10 (s, 3 H, OAc), 2.11 (s, 3 H, OAc), 2.17 (s, 3 H, OAc), 3.86 (ddd, J = 2.2, 6.0, 9.8 Hz, 1 H, H-5'ose'), 3.89-3.93 (m, 1 H, H-5'ose'), 3.93 (dd, J = 8.7, 9.8 Hz, 1 H, H-4''ose'), 4.10 (dd, J = 7.4, 11.2 Hz, 1 H, H-6_A'ose'), 4.15-4.20 (m, 2 H, H-6_B'ose', H-6_B''ose'), 4.53 (d, J = 7.9 Hz, 1 H, H-1'ose'), 4.53-4.56 (m, 1 H, H-6_A''ose'), 4.98 (dd, J = 3.4, 10.4 Hz, 1 H, H-3'ose'), 5.14 (dd, J = 7.9, 10.4 Hz, 1 H, H-2'ose'), 5.20 (d, J = 7.7 Hz, 1 H, H-1''ose'), 5.24 (dd, J = 7.7, 9.1 Hz, 1 H, H-2''ose'), 5.34 (dd, J = 8.7, 9.1 Hz, 1 H, H-3''ose'), 5.37 (dd, J = 1.2, 3.4 Hz, 1 H, H-4'ose'), 7.08 (d, J = 8.4 Hz, 2 H, Ar-H_{meta}), 7.19-7.23 (m, 4 H, β -H), 7.42 (d, J = 4.2 Hz, 2 H, β -H), 7.52 (d, J = 8.4 Hz, 2 H, Ar-H_{ortho}), 7.94-7.96 (m, 2 H, β -H) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 20.51 (OCH₃), 20.64 (OCH₃), 20.65 (2 x OCH₃), 20.73 (OCH₃), 20.81 (OCH₃), 20.83 (OCH₃), 60.82 (C-6'ose'), 62.10 (C-6''ose'), 66.61 (C-4'ose'), 69.11 (C-2'ose'), 70.79 (C-5'ose'), 70.94 (C-3'ose'), 71.46 (C-2''ose'), 72.80 (C-3''ose'), 73.00 (C-5''ose'), 76.25 (C-4''ose'), 98.39 (C-1'ose'), 101.19 (C-1'ose'), 111.74-112.10 (Ar_F-C), 116.41 (Ar-C_{meta}), 122.90 (β -C), 126.53 (β -C), 130.00 (β -C), 132.11 (Ar-C_{ortho}), 132.26 (β -C), 136.90-137.27 (Ar_F-C), 138.38-138.61 (Ar_F-C), 140.58-141.01 (Ar_F-C), 142.07-142.41 (Ar_F-C), 144.15 (α -C), 144.23-144.46 (Ar_F-C), 144.97 (α -C), 145.66-145.87 (Ar_F-C), 149.57 (α -C), 150.31 (α -C), 157.33 (Ar-C_{OAc}), 169.09 (C=O), 169.60 (C=O), 169.72 (C=O), 170.04 (C=O), 170.11 (C=O), 170.23 (C=O), 170.35 (C=O) ppm.

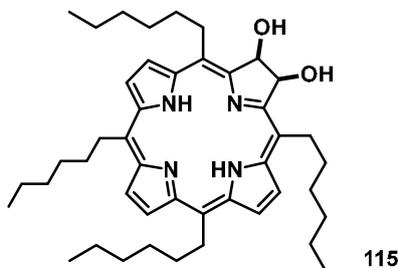
¹⁹F-NMR (471 MHz, CDCl₃): δ = -160.77 – -160.65 (m, 4 F, Ar-F_{meta}), -152.17 (t, J = 21.1 Hz, 2 F, Ar-F_{para}), -137.02 – -136.91 (m, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₆₃H₄₇F₁₀N₄O₁₈CuNa [M + Na]⁺: 1423.1919, found: 1423.1931.

5,10,15,20-Tetrahexyl-7,8-dihydroxy-7,8-chlorin (115):

Starting material 5,10,15,20-tetrahexylporphyrin **11** (2.5 g, 3.9 mmol) and osmium tetroxide (1.0 g, 3.9 mmol) were reacted in dichloromethane/pyridine (195 ml, 2:1) at 0 °C for 6 h. Then a saturated

solution of sodium bisulfite (150 ml) was added and the mixture was stirred for 15 h. Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (95:5) as the eluent. After recrystallization from dichloromethane/methanol, the first band gave starting material (548 mg, 21%) in form of violet crystals, the second gave the desired product (1.71 g, 61%) in form of violet crystals.



Melting Point: 111 °C

¹H-NMR (700 MHz, CDCl₃): δ = -2.14 (s, 2 H, NH), 0.96 (t, J = 7.2 Hz, 6 H, 2 x CH₃), 1.00 (t, J = 7.2 Hz, 6 H, 2 x CH₃), 1.36-1.47 (m, 12 H, 6 x CH₂), 1.49-1.53 (m, 4 H, 2 x CH₂), 1.57-1.67 (m, 4 H, 2 x CH₂), 1.71-1.80 (m, 4 H, 2 x CH₂), 1.90-1.97 (m, 2 H, CH₂), 1.98-2.05 (m, 2 H, CH₂), 2.30-2.42 (m, 4 H, 2 x CH₂), 3.93-4.01 (m, 4 H, 2 x CH₂), 4.32-4.36 (m, 2 H, CH₂), 4.44-4.48 (m, 2 H, CH₂), 5.94 (s, 2 H, β -H), 8.64 (d, J = 4.8 Hz, 2 H, β -H), 8.82-8.85 (m, 2 H, β -H), 9.10 (s, 2 H, β -H) ppm.

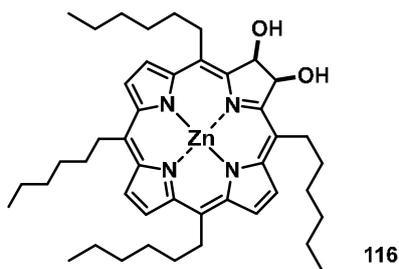
¹³C-NMR (176 MHz, CDCl₃): δ = 14.17 (CH₃), 14.20 (CH₃), 22.78 (CH₂), 22.80 (CH₂), 30.15 (CH₂), 30.30 (CH₂), 31.89 (CH₂), 32.96 (CH₂), 35.01 (CH₂), 36.25 (CH₂), 37.99 (CH₂), 73.19 (β -C), 110.86 (Alkyl-C_{meso}), 121.32 (Alkyl-C_{meso}), 121.42 (β -C), 124.75 (β -C), 129.64 (β -C), 134.02 (α -C), 139.57 (α -C), 152.06 (α -C), 159.68 (α -C) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₆₅N₄O₂ [M + H]⁺: 681.5108, found: 681.5113.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 409 (5.34), 431 (5.21), 532 (4.33), 559 (4.46), 597 (4.11), 651 (4.34) nm.

[5,10,15,20-Tetrahexyl-7,8-dihydroxy-7,8-chlorinato]zinc(II) (116):

According to the general procedure VI, a mixture of 5,10,15,20-tetrahexyl-7,8-dihydroxy-7,8-chlorin 115 (140 mg, 206 μ mol) and Zn(OAc)₂ · 2 H₂O (250 mg, 1.14 mmol) was reacted in dichloromethane/methanol (16 ml, 1:1). Purification was achieved by column chromatography on silica using dichloromethane/methanol (99:1) as the eluent and subsequent recrystallization from dichloromethane/aqueous methanol to obtain the desired product (144 mg, 94%) as a purple solid.



Melting Point: 132 °C

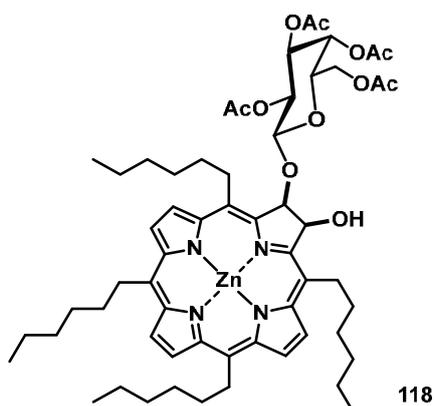
¹H-NMR (700 MHz, (CD₃)₂CO): δ = 0.95 (t, J = 7.4 Hz, 6 H, 2 x CH₃), 0.98 (t, J = 7.4 Hz, 6 H, 2 x CH₃), 1.40-1.48 (m, 8 H, 4 x CH₂), 1.51-1.56 (m, 8 H, 4 x CH₂), 1.76-1.84 (m, 8 H, 4 x CH₂), 2.17-2.24 (m, 2 H, CH₂), 2.30-2.36 (m, 2 H, CH₂), 2.40-4.44 (m, 4 H, 2 x CH₂), 4.23-4.27 (m, 2 H, CH₂), 4.42-4.45 (m, 2 H, CH₂), 4.64-4.71 (m, 4 H, 2 x CH₂), 6.39-6.41 (m, 2 H, β -H), 8.93 (d, J = 4.6 Hz, 2 H, β -H), 9.09 (s, 2 H, β -H), 9.29 (d, J = 4.6 Hz, 2 H, β -H) ppm.

¹³C-NMR (176 MHz, (CD₃)₂CO): δ = 13.51 (CH₃), 13.57 (CH₃), 22.56 (CH₂), 22.66 (CH₂), 30.01 (CH₂), 30.17 (CH₂), 31.81 (CH₂), 31.90 (CH₂), 33.24 (CH₂), 34.96 (CH₂), 36.91 (CH₂), 38.06 (CH₂), 72.86 (β -C), 110.57 (Alkyl-C_{meso}), 122.81 (Alkyl-C_{meso}), 124.84 (β -C), 125.62 (β -C), 129.18 (β -C), 145.12 (α -C), 146.89 (α -C), 153.58 (α -C), 157.24 (α -C) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₆₃N₄O₂Zn [M + H]⁺: 743.4242, found: 743.4231.

[5,10,15,20-Tetrahexyl-7-hydroxy-8-(2,3,4,6-tetraacetyl- β -D-galactosyl)-7,8-chlorinato]-zinc(II) (118):

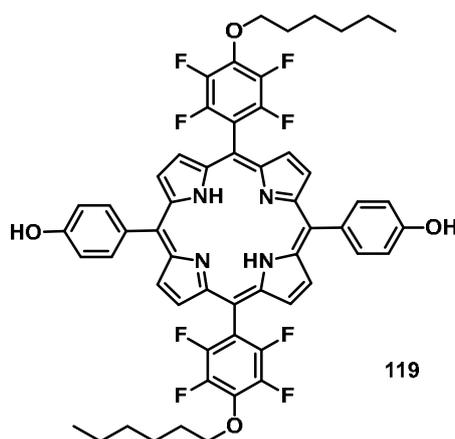
According to the general procedure VII, metallated chlorin 116 (30 mg, 40 μ mol), 2,3,4,6-tetraacetyl-D-galactose trichloroacetimidate 4 (3 x 60 mg, 367 μ mol) and BF₃·Et₂O (2.5 μ l, 20 μ mol) were reacted in a mixture of dry dichloromethane/acetonitrile (4 ml, 19:1) for 6 h. Only traces of the desired product could be detected.



HRMS (ESI-TOF): m/z calcd. for $C_{58}H_{81}N_4O_{11}Zn [M + H]^+$: 1073.5192, found: 1073.5181.

5,15-Bis(hydroxyphenyl)-10,20-bis(4-hexyloxytetrafluorophenyl)porphyrin (119):

Under an argon atmosphere, porphyrin **70** (85 mg, 93 μ mol) was dissolved in dry DMSO (4 ml) to add KOH (72 mg, 1.3 mol) and *n*-hexanol (1.18 ml, 9.49 mmol). The reaction mixture was stirred at room temperature for 30 min. Water (100 ml) was added and the aqueous layer was extracted with ethyl acetate (3 x 100 ml). The combined organic layers were washed with water (3 x 100 ml), dried over sodium sulfate and the solvent was evaporated under reduced pressure. Further purification was achieved by column chromatography on silica using dichloromethane/methanol (97:3) as the eluent. The desired product (76 mg, 82%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 223 °C

1H -NMR (700 MHz, $(CD_3)_2CO$): δ = -2.73 (br s, 2 H, NH), 0.99 (t, J = 7.2 Hz, 6 H, 2 x CH_3), 1.43-1.51 (m, 8 H, 4 x CH_2), 1.66-1.71 (m, 4 H, 2 x CH_2), 1.99-2.04 (m, 4 H, 2 x CH_2), 4.63 (t, J = 6.5 Hz, 4 H, 2 x CH_2), 7.35 (d, J = 8.3 Hz, 4 H, Ar-H_{meta}), 8.14 (d, J = 8.3 Hz, 4 H, Ar-H_{ortho}), 8.97 (br s, 2 H, Ar-OH), 9.06 (d, J = 4.6 Hz, 4 H, β -H), 9.16 (d, J = 4.6 Hz, 4 H, β -H) ppm.

^{13}C -NMR (176 MHz, $(CD_3)_2CO$): δ = 13.43 (CH_3), 22.42 (CH_2), 25.24 (CH_2), 29.93 (CH_2), 31.37 (CH_2), 75.67 (CH_2), 103.12 (Ar-F-C_{meso}), 113.95 (Ar-C_{meta}), 114.23-114.46 (Ar-F-C_{ipso}), 121.46 (Ar-C_{meso}), 132.30 (Ar-C_{ipso}), 135.74 (Ar-C_{ortho}), 138.77-139.01 (Ar-F-C), 140.56-140.84 (Ar-F-C), 142.04-142.26 (Ar-F-C), 146.07-146.30 (Ar-F-C), 147.48-147.66 (Ar-F-C), 157.75 (Ar-C_{OH}) ppm.

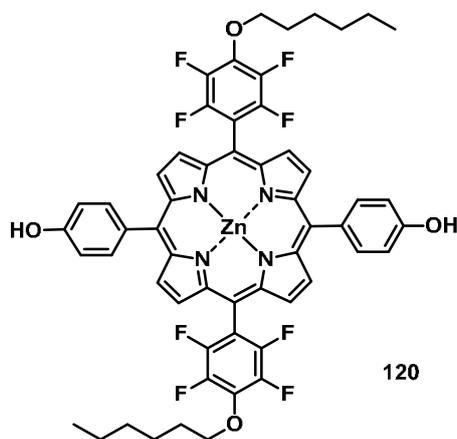
^{19}F -NMR (471 MHz, $(CD_3)_2CO$): δ = -159.13 (dd, J = 8.5, 23.1 Hz, 4 F, Ar-F_{meta}), -141.84 (dd, J = 8.1, 23.2 Hz, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for $C_{56}H_{47}F_8N_4O_4 [M + H]^+$: 991.3470, found: 991.3458.

UV/Vis ((CH₃)₂CO): λ_{\max} (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 418 (5.38), 513 (4.32), 545 (3.78), 590 (3.78), 643 (3.40) nm.

[5,15-Bis(hydroxyphenyl)-10,20-bis(4-hexyloxytetrafluorophenyl)porphyrinato]zinc(II)
(120):

According to the general procedure VI, a mixture of porphyrin 119 (40 mg, 40 μmol) and Zn(OAc)₂ · 2 H₂O (50 mg, 229 μmol) was reacted in dichloromethane/methanol (6 ml, 1:1). Purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent and subsequent recrystallization from dichloromethane/aqueous methanol to obtain the desired product (41 mg, 97%) as a purple solid.



Melting Point: 273 °C

¹H-NMR (700 MHz, (CD₃)₂CO): δ = 0.98 (t, J = 7.0 Hz, 6 H, 2 x CH₃), 1.40-1.51 (m, 8 H, 4 x CH₂), 1.64-1.71 (m, 4 H, 2 x CH₂), 1.98-2.04 (m, 4 H, 2 x CH₂), 4.61 (t, J = 6.5 Hz, 4 H, 2 x CH₂), 7.28 (d, J = 8.4 Hz, 4 H, Ar-H_{meta}), 8.06 (d, J = 8.4 Hz, 4 H, Ar-H_{ortho}), 8.90 (br s, 2 H, Ar-OH), 9.01 (d, J = 4.6 Hz, 4 H, β -H), 9.05 (d, J = 4.6 Hz, 4 H, β -H) ppm.

¹³C-NMR (176 MHz, (CD₃)₂CO): δ = 13.44 (CH₃), 22.43 (CH₂), 25.26 (CH₂), 29.95 (CH₂), 31.39 (CH₂), 75.64 (CH₂), 103.16 (Ar_F-C_{meso}), 113.52 (Ar-C_{meta}), 115.68-115.91 (Ar_F-C_{ipso}), 121.64 (Ar-C_{meso}), 130.25 (β -C), 132.93 (β -C), 133.80 (Ar-C_{ipso}), 135.52 (Ar-C_{ortho}), 138.28-138.42 (Ar_F-C), 140.53-140.67 (Ar_F-C), 141.95-142.03 (Ar_F-C), 146.11-146.22 (Ar_F-C), 147.48-147.58 (Ar_F-C), 149.52 (α -C), 151.12 (α -C), 157.40 (Ar-C_{OH}) ppm.

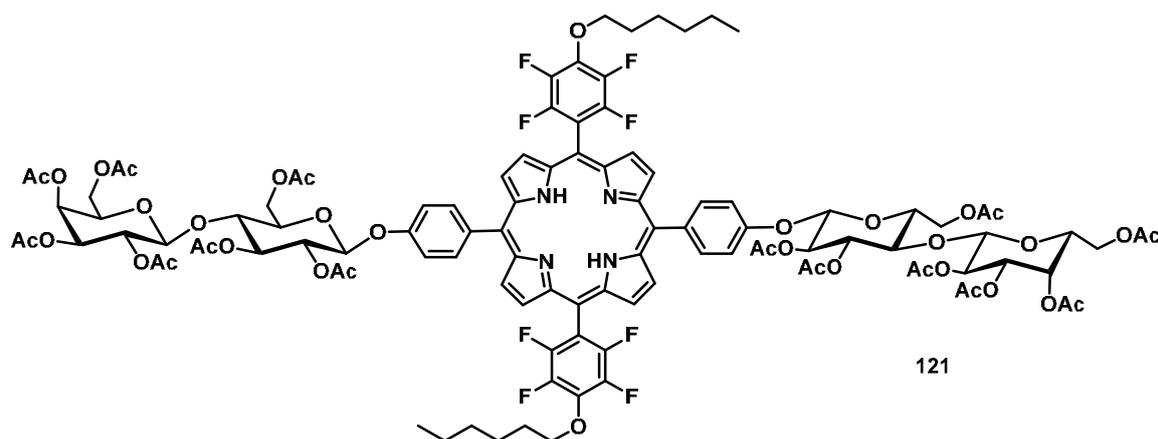
¹⁹F-NMR (471 MHz, (CD₃)₂CO): δ = -159.70 (dd, J = 8.4, 23.5 Hz, 4 F, Ar-F_{meta}), -141.55 (dd, J = 8.6, 23.3 Hz, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₆H₄₅F₈N₄O₄Zn [M + H]⁺: 1053.2605, found: 1053.2589.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 416 (5.48), 547 (4.42) nm.

5,15-Bis[4-(2,3,4,6,2',3',6'-heptaacetyl- β -D-lactosyl)phenyl]-10,20-bis(4-hexyloxytetrafluoro-phenyl)porphyrin (121):

According to the general procedure VII, metallated hydroxyporphyrin **120** (12 mg, 11 μ mol), 2,3,4,6,2',3',6'-heptaacetyl- α -D-lactose trichloroacetimidate **8** (100 mg, 128 μ mol) and BF₃·Et₂O (3 μ l, 24 μ mol) were reacted in a mixture of dry dichloromethane/THF/acetonitrile (4 ml, 2:1:1) for 2 h. Demetallation was accomplished with HCl (0.2 ml, 25%) in THF (4 ml). Purification was achieved by column chromatography on silica using dichloromethane/ethyl acetate (97:3) as the eluent. The desired product (19 mg, 78%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 263 °C

¹H-NMR (700 MHz, CDCl₃): δ = -2.81 (br s, 2 H, NH), 1.02 (t, J = 7.1 Hz, 6 H, 2 x CH₃), 1.44-1.53 (m, 8 H, 4 x CH₂), 1.66-1.72 (m, 4 H, 2 x CH₂), 2.01 (s, 6 H, 2 x OAc), 2.02-2.08 (m, 4 H, 2 x CH₂), 2.12 (s, 6 H, 2 x OAc), 2.14 (s, 6 H, 2 x OAc), 2.17 (s, 6 H, 2 x OAc), 2.18 (s, 6 H, 2 x OAc), 2.21 (s, 6 H, 2 x OAc), 2.24 (s, 6 H, 2 x OAc), 3.98 (ddd, J = 1.3, 6.3, 7.3 Hz, 2 H, 2 x H-5'ose'), 4.02 (ddd, J = 2.1, 5.8, 9.8 Hz, 2 H, 2 x H-5''ose'), 4.06 (dd, J = 8.4, 9.8 Hz, 2 H, 2 x H-4'ose'), 4.17 (dd, J = 7.3, 11.1 Hz, 2 H, 2 x H-6_A'ose'), 4.24 (dd, J = 6.3, 11.1 Hz, 2 H, 2 x H-6_B'ose'), 4.31 (dd, J = 5.8, 11.8 Hz, 2 H, 2 x H-6_B''ose'), 4.59-4.62 (m, 4 H, 2 x CH₂), 4.62 (d, J = 7.8 Hz, 2 H, 2 x H-1'ose'), 4.66 (dd, J = 2.1, 11.8 Hz, 2 H, 2 x H-6_A''ose'), 5.04 (dd, J = 3.4, 10.4 Hz, 2 H, 2 x H-3'ose'), 5.21 (dd, J = 7.8, 10.4 Hz, 2 H, 2 x H-2'ose'), 5.42 (dd, J = 7.6, 9.2 Hz, 2 H, 2 x H-2''ose'), 5.43 (dd, J = 1.3, 3.4 Hz, 2 H, 2 x H-4'ose'), 5.47 (d, J = 7.6 Hz, 2 H, 2 x H-1''ose'), 5.48 (dd, J = 8.4, 9.2 Hz, 2 H, 2 x H-3''ose'), 7.41 (d, J = 8.4 Hz, 4 H, Ar-H_{meta}), 8.16 (d, J = 8.4 Hz, 4 H, Ar-H_{ortho}), 8.87 (d, J = 4.6 Hz, 4 H, β -H), 8.95 (d, J = 4.6 Hz, 4 H, β -H) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 14.08 (CH₃), 20.53 (OCH₃), 20.67 (OCH₃), 20.68 (OCH₃), 20.69 (OCH₃), 20.86 (OCH₃), 20.88 (OCH₃), 20.90 (OCH₃), 22.65 (CH₂), 25.39 (CH₂), 30.14

(CH₂), 31.56 (CH₂), 60.88 (C-6'ose'), 62.26 (C-6''ose'), 66.66 (C-4'ose'), 69.16 (C-2'ose'), 70.84 (C-5'ose'), 70.99 (C-3'ose'), 71.66 (C-2''ose'), 72.94 (C-3''ose'), 73.14 (C-5''ose'), 75.73 (CH₂), 76.42 (C-4''ose'), 98.87 (C-1'ose'), 101.25 (C-1'ose'), 103.38 (Ar_F-C_{meso}), 114.19-114.41 (Ar_F-C_{ipso}), 115.15 (Ar-C_{meta}), 120.23 (Ar-C_{meso}), 135.60 (Ar-C_{ortho}), 136.40 (Ar-C_{ipso}), 138.61-138.84 (Ar_F-C), 140.14-140.35 (Ar_F-C), 141.56-141.72 (Ar_F-C), 145.91-146.12 (Ar_F-C), 147.28-147.49 (Ar_F-C), 156.83 (Ar-C_{OLac}), 169.13 (C=O), 169.75 (C=O), 169.81 (C=O), 170.06 (C=O), 170.14 (C=O), 170.34 (C=O), 170.39 (C=O) ppm.

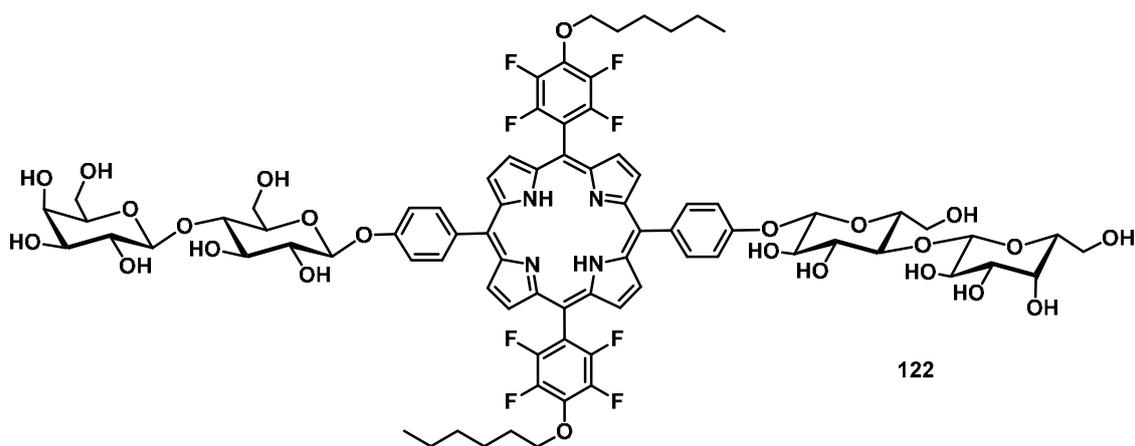
¹⁹F-NMR (471 MHz, CDCl₃): δ = -157.50 (dd, *J* = 8.8, 24.0 Hz, 4 F, Ar-F_{meta}), -139.17 (dd, *J* = 8.8, 23.7 Hz, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): *m/z* calcd. for C₁₀₈H₁₁₄F₈N₄O₃₈K [M + K]⁺: 2265.6620, found: 2265.6588.

UV/Vis (CH₂Cl₂): λ_{max} (log ε/dm³ mol⁻¹ cm⁻¹): 417 (5.47), 514 (4.29), 545 (3.81), 590 (3.51), 642 (3.51) nm.

5,15-Bis(4-β-D-lactosylphenyl)-10,20-bis(4-hexyloxytetrafluorophenyl)porphyrin (122):

According to the general procedure VIII, acetylated glycoporphyrin 121 (16 mg, 7 μmol) was dissolved in a mixture of dry THF/methanol (4 ml, 1:1). Then a solution of sodium methanolate in dry methanol (0.70 ml, 0.08 N) was added. After 2 h, the solvent was evaporated under reduced pressure and the crude product was purified by washing with dichloromethane and THF. The desired product (11 mg, 91%) was obtained as a violet solid.



Melting Point: > 300 °C

¹H-NMR (700 MHz, (CD₃)₂SO): δ = -2.99 (br s, 2 H, NH), 0.96 (t, *J* = 7.0 Hz, 6 H, 2 x CH₃), 1.39-1.48 (m, 8 H, 4 x CH₂), 1.59-1.64 (m, 4 H, 2 x CH₂), 1.94-1.99 (m, 4 H, 2 x CH₂), 3.34-3.45 (m, 4 H, 4 x H'ose')*, 3.49-3.63 (m, 12 H, 4 x H-6'ose', 8 x H'ose'), 3.64-3.71 (m, 2 H, 2 x H'ose'), 3.73-3.83

(m, 4 H, 2 x H-6'ose', 2 x H'ose'), 3.87-3.96 (m, 2 H, 2 x H-6'ose'), 4.33 (d, $J = 7.6$ Hz, 2 H, 2 x H-1'ose'), 4.58-4.62 (m, 4 H, 2 x CH₂), 4.80 (br s, 3 H, OH'ose'), 4.84 (br s, 3 H, OH'ose'), 5.00 (br s, 6 H, OH'ose'), 5.36 (d, $J = 7.8$ Hz, 2 H, 2 x H-1''ose'), 7.51 (d, $J = 8.0$ Hz, 4 H, Ar-H_{meta}), 8.20 (d, $J = 8.0$ Hz, 4 H, Ar-H_{ortho}), 8.94-9.00 (m, 4 H, β -H), 9.17-9.24 (m, 4 H, β -H) ppm.

* = signals of carbohydrate hydrogens are overlapped by the water peak of DMSO

¹³C-NMR (176 MHz, (CD₃)₂SO): $\delta = 14.41$ (CH₃), 22.58 (CH₂), 25.33 (CH₂), 29.70 (CH₂), 30.02 (CH₂), 31.40 (CH₂), 60.69 (C'ose'), 60.90 (C'ose'), 68.59 (C'ose'), 71.11 (C'ose'), 73.69 (C'ose'), 73.81 (C'ose'), 75.40 (C'ose'), 75.61 (C'ose'), 75.89 (CH₂), 76.12 (C'ose'), 80.56 (C'ose'), 100.40 (C-1''ose'), 103.33 (Ar_F-C_{meso}), 104.35 (C-1'ose'), 113.70-113.92 (Ar_F-C_{ipso}), 115.10 (Ar-C_{meta}), 121.21 (Ar-C_{meso}), 134.40 (Ar-C_{ipso}), 135.91 (Ar-C_{ortho}), 138.75-138.99 (Ar_F-C), 140.58-140.77 (Ar_F-C), 141.95-142.15 (Ar_F-C), 143.16 (Ar_F-C), 145.94-146.10 (Ar_F-C), 147.29-147.51 (Ar_F-C), 157.94 (Ar-C_{OLac}) ppm.

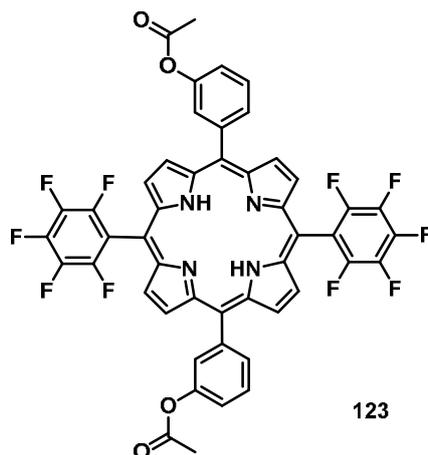
¹⁹F-NMR (471 MHz, (CD₃)₂SO): $\delta = -157.82$ – -157.55 (m, 4 F, Ar-F_{meta}), -141.16 – -140.93 (m, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₈₀H₈₆F₈N₄O₂₄Na [M + Na]⁺: 1661.5402, found: 1661.5427.

UV/Vis ((CH₃)₂SO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 418 (5.56), 514 (4.33), 544 (3.82), 590 (3.62), 642 (3.56) nm.

5,15-Bis(3-acetoxyphenyl)-10,20-bis(pentafluorophenyl)porphyrin (123):

According to the general procedure IV, 5-(pentafluorophenyl)dipyrromethane **43** (625 mg, 2.00 mmol), 3-acetoxybenzaldehyde (326 mg, 1.99 mmol), TFA (154 μ l, 2.06 mmol), DDQ (700 mg, 3.07 mmol) and triethylamine (0.21 ml, 1.46 mmol) were reacted in dry dichloromethane (500 ml). Purification was achieved by column chromatography on silica using pure dichloromethane as the eluent followed by recrystallization from dichloromethane/methanol to obtain the desired product (227 mg, 25%) as a violet solid.



Melting Point: > 300 °C

¹H-NMR (700 MHz, CDCl₃): δ = -2.87 (s, 2 H, NH), 2.40 (s, 6 H, OAc), 7.56-7.60 (m, 2 H, Ar-H), 7.77-7.81 (m, 2 H, Ar-H), 7.97-8.00 (m, 2 H, 2 x Ar-H), 8.08-8.11 (m, 2 H, 2 x Ar-H), 8.83 (d, J = 4.6 Hz, 4 H, β -H), 9.02 (d, J = 4.7 Hz, 4 H, β -H) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 21.25 (OCH₃), 102.39 (Ar_F-C_{meso}), 116.23-116.45 (Ar_F-C_{ipso}), 120.13 (Ar-C_{meso}), 121.45 (Ar-C), 126.54 (Ar-C), 127.99 (Ar-C), 132.19 (Ar-C), 136.58-136.85 (Ar_F-C), 138.14-138.28 (Ar_F-C), 141.07-141.52 (Ar_F-C), 142.45 (Ar-C_{ipso}), 142.60-142.97 (Ar_F-C), 145.67-145.98 (Ar_F-C), 147.07-147.41 (Ar_F-C), 149.39 (Ar-C_{OAc}), 169.62 (C=O) ppm.

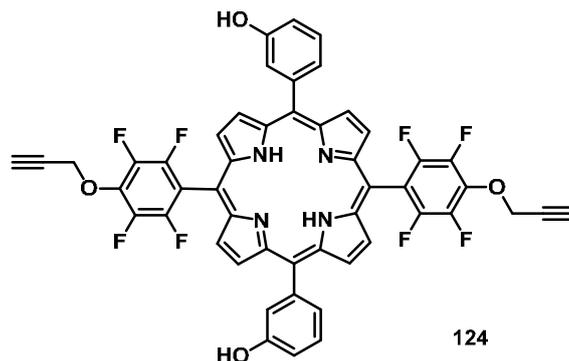
¹⁹F-NMR (471 MHz, (CD₃)₂CO): δ = -161.87 – -161.76 (m, 6 F, Ar-F_{meta}), -152.12 – -152.03 (m, 3 F, Ar-F_{para}), -136.74 – -136.67 (m, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₈H₂₅F₁₀N₄O₄ [M + H]⁺: 911.1716, found: 911.1734.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 416 (5.41), 512 (4.32), 542 (3.74), 586 (3.80), 643 (3.32) nm.

5,15-Bis(3-hydroxyphenyl)-10,20-bis[4-(2-propyn-1-oxy)tetrafluorophenyl]porphyrin (124):

Under an argon atmosphere, porphyrin **123** (130 mg, 144 μ mol) was dissolved in dry DMSO (5 ml) to add KOH (110 mg, 1.70 mol) and propargyl alcohol (820 mg, 14.6 mmol). The reaction mixture was stirred at room temperature for 30 min. Water (100 ml) was added and the aqueous layer was extracted with ethyl acetate (3 x 100 ml). The combined organic layers were washed with water (3 x 100 ml), dried over sodium sulfate and the solvent was evaporated under reduced pressure. Further purification was achieved by column chromatography on silica using dichloromethane/methanol (9:1) as the eluent. The desired product (106 mg, 82%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 241 °C

¹H-NMR (500 MHz, (CD₃)₂CO): δ = -2.83 (br s, 2 H, NH), 3.48 (t, J = 2.5 Hz, 2 H, -C \equiv C-H), 5.31 (d, J = 2.5 Hz, 4 H, -CH₂-C \equiv C-), 7.33-7.37 (m, 2 H, Ar-H), 7.63-7.66 (m, 2 H, Ar-H), 7.74-7.79 (m, 4 H, 2 x Ar-H), 8.93 (br s, 2 H, Ar-OH), 9.05-9.14 (m, 8 H, β -H) ppm.

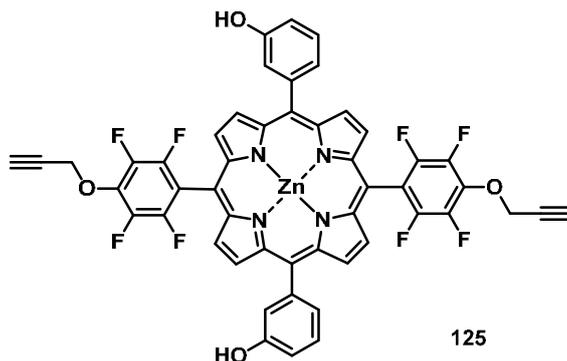
¹³C-NMR (126 MHz, (CD₃)₂CO): δ = 62.41 (CH₂), 77.65 (\equiv CH), 78.59 (-C \equiv), 103.13 (Ar_F-C_{meso}), 115.38 (Ar-C), 115.60-115.78 (Ar_F-C_{ipso}), 121.36 (Ar-C_{ipso}), 122.12 (Ar-C), 126.54 (Ar-C), 127.99 (Ar-C), 137.24-137.42 (Ar_F-C), 140.59-140.92 (Ar_F-C), 142.52 (Ar-C_{ipso}), 156.08 (Ar-C_{OH}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₀H₂₇F₈N₄O₄ [M + H]⁺: 899.1905, found: 899.1943.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 416 (5.43), 512 (4.42), 543 (3.66), 587 (3.91), 644 (3.22) nm.

[5,15-Bis(3-hydroxyphenyl)-10,20-bis{4-(2-propyn-1-oxy)tetrafluorophenyl}porphyrinato]-zinc(II) (125):

According to the general procedure **VI**, a mixture of porphyrin **124** (50 mg, 55 μ mol) and Zn(OAc)₂ · 2 H₂O (50 mg, 229 μ mol) was reacted in dichloromethane/methanol (6 ml, 1:1). Purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent and subsequent recrystallization from dichloromethane/aqueous methanol to obtain the desired product (49 mg, 93%) as a purple solid.



Melting Point: > 300 °C

¹H-NMR (700 MHz, (CD₃)₂CO): δ = 3.50 (t, J = 2.5 Hz, 2 H, -C \equiv C-H), 5.35 (d, J = 2.5 Hz, 4 H, -CH₂-C \equiv C-), 7.33-7.36 (m, 2 H, Ar-H), 7.64-7.67 (m, 2 H, Ar-H), 7.75-7.79 (m, 4 H, 2 x Ar-H), 8.80 (br s, 2 H, Ar-OH), 9.08 (d, J = 4.5 Hz, 4 H, β -H), 9.10 (d, J = 4.5 Hz, 4 H, β -H) ppm.

¹³C-NMR (176 MHz, (CD₃)₂CO): δ = 62.27 (CH₂), 77.63 (\equiv CH), 78.45 (-C \equiv), 103.22 (Ar_F-C_{meso}), 114.76 (Ar-C), 116.86-117.10 (Ar_F-C_{ipso}), 121.61 (Ar-C_{ipso}), 122.11 (Ar-C), 126.50 (Ar-C), 127.50 (Ar-C), 130.39 (β -C), 133.07 (β -C), 136.61-136.79 (Ar_F-C), 140.92-141.05 (Ar_F-C), 142.32-142.46 (Ar_F-C), 143.97 (Ar-C_{ipso}), 146.03-146.16 (Ar_F-C), 147.43-147.52 (Ar_F-C), 149.59 (α -C), 150.64 (α -C), 155.71 (Ar-C_{OH}) ppm.

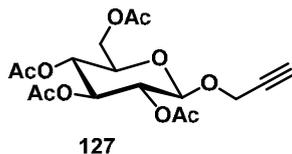
¹⁹F-NMR (471 MHz, (CD₃)₂CO): δ = -158.20 – -158.13 (m, 4 F, Ar-F_{meta}), -141.19 – -141.08 (m, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₀H₂₅F₈N₄O₄Zn [M + H]⁺: 961.1040, found: 961.1018.

UV/Vis ((CH₃)₂CO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 417 (5.32), 547 (4.18) nm.

2-Propynyl-tetra-*O*-acetyl- β -D-glucopyranoside (127):

Under an argon atmosphere, β -D-glucose pentaacetate (10.0 g, 25.6 mmol) was dissolved in dichloromethane (200 ml) and propargyl alcohol (1.80 ml, 30.7 mmol) and BF₃·OEt₂ (4.80 ml, 38.4 mmol) were added at 0 °C. The reaction mixture was stirred for 2 d at room temperature and then K₂CO₃ (4.80 g, 34.7 mmol) was added. After another 30 min stirring the mixture was filtrated using dichloromethane. The filtrate was washed with water (3 x 150 ml) and the aqueous layer was extracted with dichloromethane (3 x 50 ml). The combined organic layers were dried over sodium sulfate, filtered and evaporated under reduced pressure to afford the desired product (9.23 g, 93%) as a colorless solid.



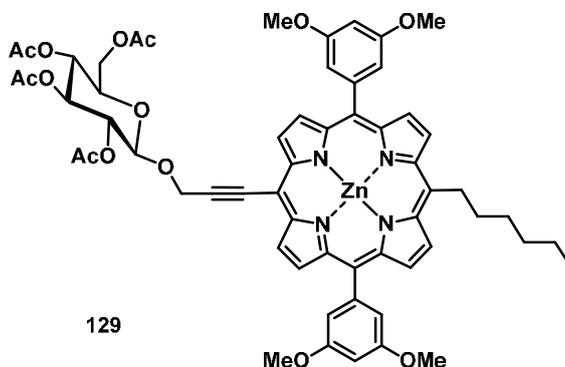
$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 2.00 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 2.08 (s, 3 H, OAc), 2.46 (t, J = 2.3 Hz, 1 H, $\equiv\text{C-H}$), 3.72 (ddd, J = 2.3, 4.6, 10.0 Hz, 1 H, H-5'ose'), 4.14 (dd, J = 2.3, 12.3 Hz, 1 H, H-6_A'ose'), 4.27 (dd, J = 4.6, 12.5 Hz, 1 H, H-6_B'ose'), 4.36 (d, J = 2.3 Hz, 2 H, $-\text{CH}_2-\text{C}\equiv$), 4.77 (d, J = 8.1 Hz, 1 H, H-1'ose'), 4.99-5.03 (m, 1 H, H-4'ose'), 5.07-5.12 (m, 1 H, H-3'ose'), 5.21-5.29 (m, 1 H, H-2'ose') ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_{10}\text{Na}$ $[\text{M} + \text{Na}]^+$: 409.1111, found: 409.1112.

Analytical data are in accordance with published data.^[83]

[5,15-Bis(3,5-dimethoxyphenyl)-10-hexyl-20-(2-propynyl-2,3,4,6-tetraacetyl- β -D-glucopyranosyl)porphyrinato]zinc(II) (129):

Under an argon atmosphere, mono-iodinated porphyrin **128** (100 mg, 117 μmol) was dissolved in dry THF (30 ml) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (22 mg, 31.2 μmol), copper(I) iodide (22 mg, 116 μmol) and triethylamine (0.29 ml, 2.09 mmol) were added. Then 2-propynyl-tetra-*O*-acetyl- β -D-glucopyranoside **127** (451 mg, 1.17 mmol) and the reaction mixture was stirred for 2 h at room temperature under an argon atmosphere. After full conversion the solvent was evaporated under reduced pressure. Purification was achieved by column chromatography on silica using dichloromethane/methanol (99:1) as the eluent. The desired product (115 mg, 88%) was obtained as a green-violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 128 °C

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 0.93 (t, J = 7.3 Hz, 3 H, CH_3), 1.37-1.43 (m, 2 H, CH_2), 1.49-1.55 (m, 2 H, CH_2), 1.80-1.88 (m, 2 H, CH_2), 1.99 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 2.08 (s, 6 H, 2 x OAc),

2.50-2.58 (m, 2 H, CH₂), 3.96 (s, 12 H, 4 x OCH₃), 4.25 (dd, $J = 2.2, 12.2$ Hz, 1 H, H-6_A'ose'), 4.37 (dd, $J = 4.2, 12.2$ Hz, 1 H, H-6_B'ose'), 4.97-5.01 (m, 2 H, H'ose'), 5.18-5.21 (m, 3 H, H'ose'), 5.22-5.27 (m, 2 H, H'ose'), 5.30 (d, $J = 9.0$ Hz, 1 H, H'ose'), 5.34-5.37 (m, 1 H, H'ose'), 6.89 (t, $J = 2.2$ Hz, 2 H, Ar), 7.35-7.36 (m, 4 H, Ar), 9.02 (d, $J = 4.6$ Hz, 2 H, β -H), 9.04 (d, $J = 4.6$ Hz, 2 H, β -H), 9.52 (d, $J = 4.6$ Hz, 2 H, β -H), 9.61 (d, $J = 4.6$ Hz, 2 H, β -H) ppm.

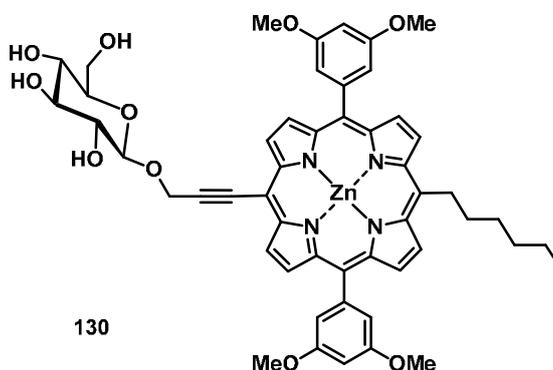
¹³C-NMR (126 MHz, CDCl₃): $\delta = 14.22$ (CH₃), 20.62 (CH₃), 20.64 (CH₃), 20.74 (CH₃), 20.78 (CH₃), 22.79 (CH₂), 55.70 (OCH₃), 56.00 (OCH₃), 61.82 (C-6'ose'), 68.36 (C'ose'), 71.02 (C'ose'), 71.97 (C'ose'), 72.82 (C'ose'), 75.56, 78.17, 98.18 (C-1'ose'), 144.42 (Ph), 158.85 (Ar), 169.46 (C=O), 169.51 (C=O), 170.31 (C=O), 170.73 (C=O) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₉H₆₀N₄O₁₄ZnNa [M + Na]⁺: 1135.3290, found: 1135.3356.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 428 (5.54), 560 (4.31), 598 (4.04).

[5,15-Bis(3,5-dimethoxyphenyl)-10-hexyl-20-(2-propynyl- β -D-glucopyranosyl)-porphyrinato]zinc(II) (130):

According to the general procedure VIII, acetylated glycoporphyrin 129 (29 mg, 26 μ mol) was dissolved in a mixture of dry THF/methanol (6 ml, 1:1). Then a solution of sodium methanolate in dry methanol (0.8 ml, 0.02 N) was added. After 4 h, the solvent was evaporated under reduced pressure and the crude product was tried to purify by repeated column chromatography, using dichloromethane/methanol (95:5) as the eluent. Unfortunately, the desired product (23 mg, 93%) contained impurities making a full spectroscopic characterization impossible, albeit the existence of the desired product could be verified through HRMS-analysis.



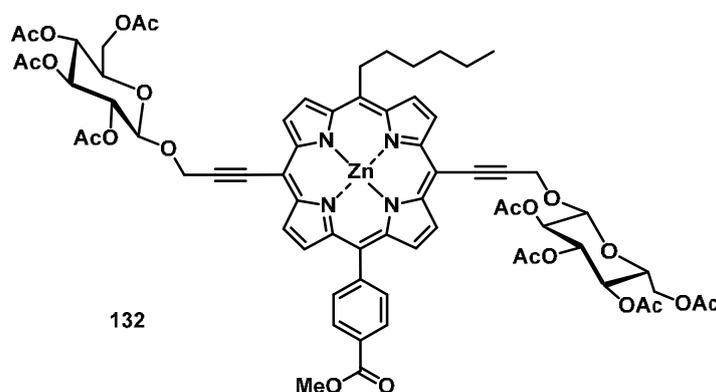
Melting Point: 266 °C

HRMS (ESI-TOF): m/z calcd. for C₅₁H₅₂N₄O₁₀ZnNa [M + Na]⁺: 967.2873, found: 967.2885.

UV/Vis ((CD₃)₂SO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 430 (5.44), 567 (4.14), 608 (3.98).

5-(3,5-Dimethoxyphenyl)-10-hexyl-20-bis(2-propynyl-2,3,4,6-tetraacetyl- β -D-glucopyranosyl)porphyrin (132):

Under an argon atmosphere di-iodinated porphyrin **131** (50 mg, 59 μ mol) was dissolved in dry THF (15 ml) and Pd(PPh₃)₂Cl₂ (12 mg, 17 μ mol), copper(I) iodide (12 mg, 63 μ mol) and triethylamine (0.2 ml, 1.1 mmol) were added. Then 2-propynyl-tetra-*O*-acetyl- β -D-glucopyranoside **127** (0.2 g, 0.6 mmol) and the reaction mixture was stirred for 3 h at room temperature under an argon atmosphere. After full conversion the solvent was evaporated under reduced pressure. Purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent. Unfortunately, the green product (33 mg, 59%) contained impurities making a full spectroscopic characterization impossible, albeit the existence of the desired product could be verified through HRMS-analysis.



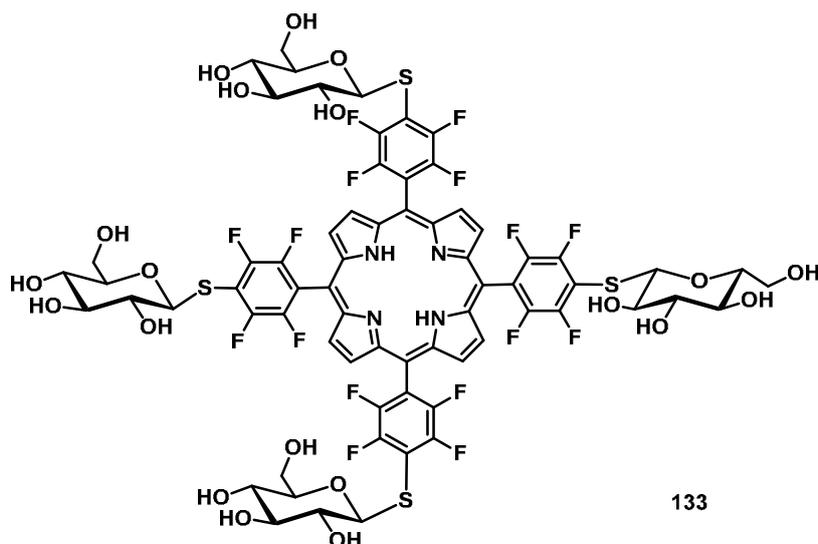
Melting Point: 80 °C

HRMS (ESI-TOF): m/z calcd. for C₆₈H₇₀N₄O₂₂ZnNa [M + Na]⁺: 967.2873, found: 967.2885.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 435 (5.07), 580 (3.81), 632 (4.09).

5,10,15,20-Tetrakis(4-1'-thio- β -D-glucosyl-2,3,5,6-tetrafluorophenyl)porphyrin (133):

According to the general procedure **XIII**, porphyrin **16** (30 mg, 31 μ mol) and 1-thio- β -D-glucose sodium salt (27 mg, 123 μ mol) were reacted under an argon atmosphere in dry DMF (5 ml) overnight at room temperature. Purification was achieved by column chromatography on silica using ethyl acetate/methanol (17:3) as the eluent. The desired product (43 mg, 82%) was obtained as a crystalline violet solid.



¹H-NMR (500 MHz, CD₃OD): δ = -3.02 (s, 2 H, NH), 3.43-3.55 (m, 16 H, 4 x H-2'ose', 4 x H-3'ose', 4 x H-4'ose', 4 x H-5'ose'), 3.78 (dd, J = 6.3, 12.0 Hz, 4 H, 4 x H-6_B'ose'), 4.02 (dd, J = 2.0, 12.0 Hz, 4 H, 4 x H-6_A'ose'), 5.20 (d, J = 9.0 Hz, 4 H, 4 x H-1'ose'), 9.02-9.36 (m, 8 H, β -H) ppm.

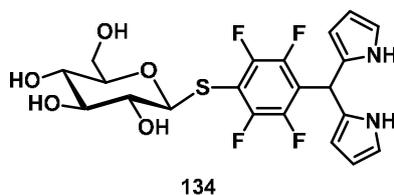
¹⁹F-NMR (471 MHz, CD₃OD): δ = -140.44 (dd, J = 11.7, 24.6 Hz, 8 F, Ar-F_{meta}), -135.01 (dd, J = 11.6, 24.7 Hz, 8 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₆₈H₅₄F₁₆N₄NaO₂₀S₄ [M + Na]⁺: 1701.1851, found: 1701.1839.

Analytical data are in accordance with published data.^[114]

5-[4-(1'-Thio- β -D-glucosyl)-2,3,5,6-tetrafluorophenyl]dipyrromethane (134):

According to the general procedure **XIII**, 5-(pentafluorophenyl)dipyrromethane **43** (50 mg, 160 μ mol) and 1-thio- β -D-glucose sodium salt (42 mg, 192 μ mol) were reacted under an argon atmosphere in dry DMF (5 ml) for 30 min at room temperature. Purification was achieved by column chromatography on silica using dichloromethane/methanol (8:2) as the eluent. The desired product (56 mg, 72%) was obtained as a colorless crystalline solid.



Melting Point: 114 °C

¹H-NMR (700 MHz, CD₃OD): δ = 3.23 (ddd, J = 2.3, 5.6, 9.6 Hz, 1 H, H-5'ose'), 3.27 (dd, J = 8.7, 9.6 Hz, 1 H, H-2'ose'), 3.30-3.33 (m, 1 H, H-4'ose'), 3.37 (t, J = 8.7 Hz, 1 H, H-3'ose'), 3.61 (dd, J = 5.5, 12.0 Hz, 1 H, H-6_B'ose'), 3.76 (dd, J = 2.3, 12.0 Hz, 1 H, H-6_A'ose'), 4.77 (d, J = 9.6 Hz, 1 H, H-1'ose'), 5.90- 5.92 (m, 3 H, Ar-H_{pyrrole}, Ar-H_{meso}), 6.02-6.05 (m, 2 H, Ar-H_{pyrrole}), 6.67-6.69 (m, 2 H, Ar-H_{pyrrole}) ppm.

¹³C-NMR (176 MHz, (CD₃OD): δ = 33.55 (Ar-C_{meso}), 61.25 (C-6'ose'), 69.84 (C-4'ose'), 73.99 (C-2'ose'), 78.12 (C-3'ose'), 80.87 (C-5'ose'), 86.01 (C-1'ose'), 106.41 (Ar-C_{pyrrole}), 107.08 (Ar-C_{pyrrole}), 109.46-109.70 (Ar_F-C_{Sglu}), 117.05 (Ar-C_{pyrrole}), 122.55-122.73 (Ar_F-C_{ipso}), 128.66 (Ar-C_{pyrrole}), 128.68 (Ar-C_{pyrrole}), 143.91-144.06 (Ar_F-C), 145.32-145.47 (Ar_F-C), 146.51-146.63 (Ar_F-C), 147.92-148.01 (Ar_F-C) ppm.

¹⁹F-NMR (471 MHz, CD₃OD): δ = -143.95 (dd, J = 11.5, 23.8 Hz, 2 F, Ar-F_{meta}), -135.31 (dd, J = 11.5, 22.9 Hz, 2 F, Ar-F_{ortho}) ppm.

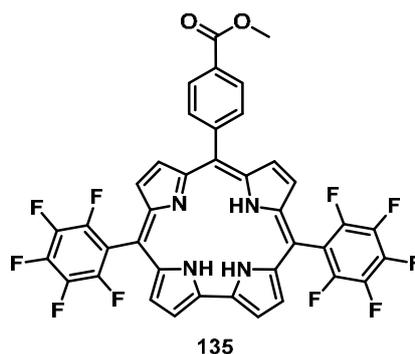
EA: C₂₁H₂₀F₄N₂O₅S (488.1): calcd. C 51.64, H 4.13, N 5.74; found C 51.50 H 4.34; N 5.79.

HRMS (ESI-TOF): m/z calcd. for C₂₁H₂₀F₄N₂NaO₅S [M + Na]⁺: 511.0927, found: 511.0946.

$[\alpha]_D^{25} = -21.7^\circ$ ($c = 0.15$, CH₃OH).

10-(4-Methoxycarbonylphenyl)-5,15-bis(pentafluorophenyl)corrole (135) and 5,15-Bis(4-methoxycarbonylphenyl)-10,20-bis(pentafluorophenyl)porphyrin (136):

According to the general procedure **IX**, 5-(pentafluorophenyl)dipyrromethane **43** (1.28 g, 4.10 mmol), 4-(methoxycarbonyl)benzaldehyde (609 mg, 3.71 mmol), TFA (0.07 mL, 909 μ mol), DDQ (1.40 g, 6.17 mmol) and triethylamine (0.50 ml, 3.61 mmol) were reacted in dry dichloromethane (1000 ml). Purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (2:1) as the eluent. Two fractions could be isolated and were recrystallized from dichloromethane/methanol. The first fraction gave corrole **135** (174 mg, 11%) as a green-violet solid and the second fraction gave the corresponding *trans*-A₂B₂-porphyrin **136** (96 mg, 5%) as a side-product.



Melting Point: > 300 °C

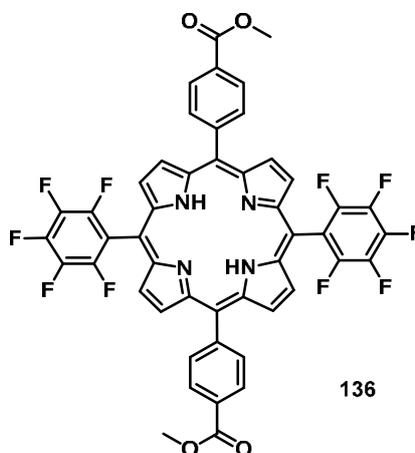
¹H-NMR (700 MHz, CDCl₃): δ = 4.09 (s, 3 H, CH₃), 8.28 (d, J = 7.6 Hz, 2 H, Ar-H_{ortho}), 8.44 (d, J = 7.6 Hz, 2 H, Ar-H_{meta}), 8.60 (br s, 2 H, β -H), 8.68 (br s, 2 H, β -H), 8.75 (br s, 2 H, β -H), 9.15 (br s, 2 H, β -H) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 52.39 (OCH₃), 112.22 (Ar-C_{meso}), 113.83-114.02 (Ar_F-C_{ipso}), 117.61 (β -C), 125.91 (β -C), 127.54 (β -C), 128.50 (Ar-C_{meta}), 129.53 (Ar-C_{ipso}), 134.69 (Ar-C_{ortho}), 137.06-137.37 (Ar_F-C), 138.51-138.82 (Ar_F-C), 140.97-141.25 (Ar_F-C), 142.42-142.67 (Ar_F-C), 145.42 (Ar_F-C), 146.13 (Ar-C_{para}), 146.83 (Ar_F-C), 167.24 (C=O) ppm.

¹⁹F-NMR (471 MHz, CDCl₃): δ = -161.52 (dd, J = 8.3, 23.3 Hz, 4 F, Ar-F_{meta}), -152.50 (t, J = 20.4 Hz, 2 F, Ar-F_{para}), -137.77 (dd, J = 8.3, 23.3 Hz, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₃₉H₁₉F₁₀N₄O₂ [M + H]⁺: 765.1348, found: 765.1353.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 411 (5.15), 563 (4.35), 612 (4.10) nm.



Melting Point: > 300 °C

¹H-NMR (500 MHz, CDCl₃): δ = -2.85 (br s, 2 H, NH), 4.10 (s, 6 H, 2 x CH₃), 8.27 (d, J = 7.8 Hz, 4 H, Ar-H_{ortho}), 8.45 (d, J = 7.8 Hz, 4 H, Ar-H_{meta}), 8.78 (d, J = 4.4 Hz, 4 H, β -H), 8.88 (d, J = 4.4 Hz, 4 H, β -H) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₈H₂₅F₁₀N₄O₄ [M + H]⁺: 911.1711, found: 911.1729.

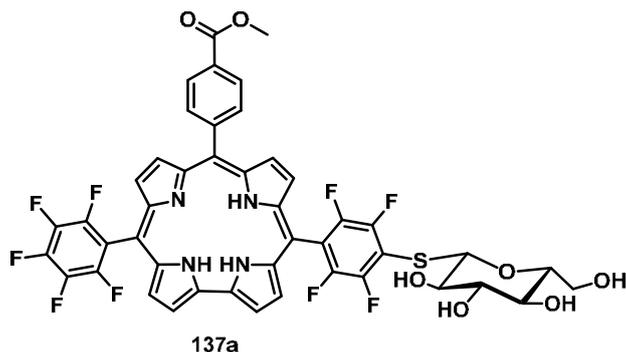
UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 416 (5.48), 510 (4.26), 543 (3.42), 585 (3.74), 643 (3.29) nm.

10-(4-Methoxycarbonylphenyl)-5,15-bis(pentafluorophenyl)corrole (135):

According to the general procedure **X**, 5-(pentafluorophenyl)dipyrromethane **43** (156 mg, 0.50 mmol) and 4-(methoxycarbonyl)benzaldehyde (41,1 mg, 0.25 mmol) were dissolved in methanol (25 ml). Then a mixture of HCl (36%, 1.25 ml) and water (25 ml) was added and it was stirred at room temperature for one hour. Then the mixture was extracted three times with dichloromethane. The combined organic layers were washed three times with water, dried over sodium sulfate and the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (125 ml) and DDQ (169 mg, 0.75 mmol) was added. After 3 hours stirring at room temperature, purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (3:1) and a subsequent recrystallization from dichloromethane/*n*-pentane to obtain the desired product (88 mg, 46%) as a violet solid.

10-(4-Methoxycarbonylphenyl)-5-(pentafluorophenyl)-15-[4-(1'-thio- β -D-glucosyl)-2,3,5,6-tetrafluorophenyl]corrole (137a) and 10-(4-Methoxycarbonylphenyl)-5,15-bis[4-(1'-thio- β -D-glucosyl)-2,3,5,6-tetrafluorophenyl]corrole (137b):

According to the general procedure **XIII**, corrole **135** (30 mg, 39 μ mol) and 1-thio- β -D-glucose sodium salt (27 mg, 125 μ mol) were reacted under an argon atmosphere in dry DMF (5 ml) overnight at room temperature. Purification was achieved by column chromatography on silica using dichloromethane/methanol (8:2) as the eluent. The first band gave the monoglycosylated corrole **137a** (5 mg, 14%) in form of green-violet crystals, and the second gave diglycosylated corrole **137b** (32 mg, 73%) in form of green-violet crystals.



Melting Point: 211 °C

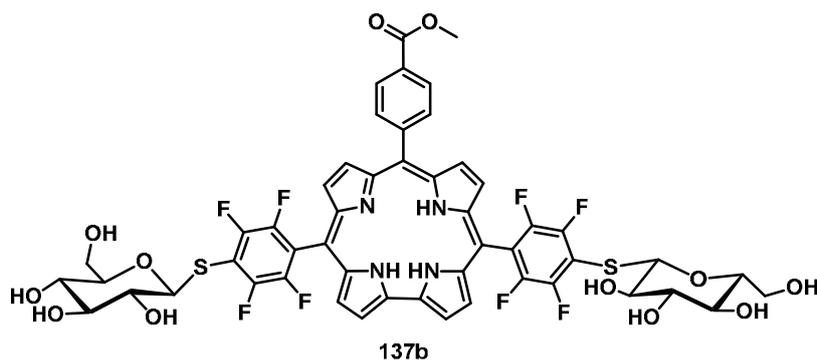
¹H-NMR (700 MHz, CD₃OD): δ = 3.43-3.53 (m, 4 H, H-2'ose', H-3'ose', H-4'ose', H-5'ose'), 3.75 (dd, J = 5.5, 11.9 Hz, 1 H, H-6_B'ose'), 3.96 (dd, J = 1.7, 11.9 Hz, 1 H, H-6_A'ose'), 4.04 (s, 3 H, OCH₃), 5.12 (d, J = 8.8 Hz, 1 H, H-1'ose'), 8.25 (br s, 2 H, Ar-H_{ortho}), 8.37 (br s, 2 H, Ar-H_{meta}), 8.57 (br s, 4 H, β -H), 8.79 (br s, 2 H, β -H), 9.08 (br s, 2 H, β -H) ppm.

¹³C-NMR (176 MHz, CH₃OD): δ = 51.49 (OCH₃), 61.52 (C-6'ose'), 70.14 (C-4'ose'), 74.39 (C-2'ose'), 78.29 (C-3'ose'), 81.19 (C-5'ose'), 85.75 (C-1'ose'), 96.53 (Ar_F-C_{meso}), 97.63 (Ar_F-C_{meso}), 111.30-111.49 (Ar-C_{meso}), 112.26-112.55 (Ar_F-C_{SGLu}), 114.21-114.55 (Ar_F-C_{ipso}), 116.17-116.45 (β -C), 119.26-119.52 (Ar_F-C_{ipso}), 120.48 (β -C), 125.62-126.07 (β -C), 126.61-126.98 (β -C), 127.89 (Ar-C_{meta}), 128.90-129.11 (Ar-C_{ipso}), 130.90-131.39 (α -C), 134.55 (Ar-C_{ortho}), 134.97-135.32 (α -C), 137.05-137.26 (Ar_F-C), 138.44-138.69 (Ar_F-C), 140.80-141.07 (Ar_F-C), 142.29-142.54 (Ar_F-C), 144.94-145.16 (Ar_F-C), 145.41-145.59 (Ar_F-C), 146.36-146.52 (Ar_F-C), 146.69-146.97 (Ar_F-C), 148.09-148.16 (Ar_F-C), 167.35 (C=O) ppm.

¹⁹F-NMR (471 MHz, CH₃OD): δ = -165.46 – -165.23 (m, 2 F, Ar-F_{meta}), -156.86 – -156.65 (m, 1 F, Ar-F_{para}), -141.23 – -141.03 (m, 2 F, Ar-F_{meta}), -140.90 – -140.73 (m, 2 F, Ar-F_{ortho}), -135.42 – -135.21 (m, 2 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₅H₃₀F₉N₄O₇S [M + H]⁺: 941.1691, found: 941.1675.

UV/Vis (CH₃OH): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 413.0 (4.83), 571.5 (4.09), 611.5 (4.03) nm.



Melting Point: 193 °C

¹H-NMR (700 MHz, CD₃OD): δ = 3.46-3.51 (m, 8 H, 2 x H-2'ose', 2 x H-3'ose', 2 x H-4'ose', 2 x H-5'ose'), 3.78 (dd, J = 5.5, 11.9 Hz, 2 H, 2 x H-6_B'ose'), 3.98 (dd, J = 1.5, 11.9 Hz, 2 H, 2 x H-6_A'ose'), 4.05 (s, 3 H, OCH₃), 5.15 (d, J = 9.0 Hz, 2 H, 2 x H-1'ose'), 8.25-8.28 (m, 2 H, Ar-H_{ortho}), 8.37-8.40 (m, 2 H, Ar-H_{meta}), 8.55-8.62 (m, 4 H, 2 x β -H), 8.78-8.82 (m, 2 H, β -H), 9.06-9.11 (m, 2 H, β -H) ppm.

¹³C-NMR (176 MHz, CH₃OD): δ = 51.43 (OCH₃), 61.54 (C-6'ose'), 70.17 (C-4'ose'), 74.42 (C-2'ose'), 78.32 (C-3'ose'), 81.21 (C-5'ose'), 85.75 (C-1'ose'), 97.66 (Ar-F-C_{meso}), 111.41 (Ar-C_{meso}), 112.26-112.50 (Ar-F-C_{Sglu}), 116.27 (β -C), 119.33-119.52 (Ar-F-C_{ipso}), 120.44 (β -C), 125.93 (β -C), 126.69 (β -C), 127.89 (Ar-C_{meta}), 128.95 (Ar-C_{ipso}), 131.15 (α -C), 134.56 (Ar-C_{ortho}), 135.03 (α -C), 145.02-145.13 (Ar-F-C), 146.39-146.52 (Ar-F-C), 146.66-146.78 (Ar-F-C), 147.01 (Ar-C_{para}), 148.08-148.17 (Ar-F-C), 167.36 (C=O) ppm.

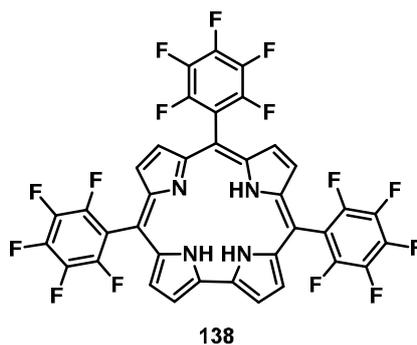
¹⁹F-NMR (471 MHz, CH₃OD): δ = -141.15 – -141.09 (m, 4 F, Ar-F_{meta}), -135.36 – -135.30 (m, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₁H₄₁F₈N₄O₁₂S₂ [M + H]⁺: 1117.2029, found: 1117.2015.

UV/Vis (CH₃OH): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 413.5 (4.88), 572.0 (4.19), 612.5 (3.99) nm.

5,10,15-Tris(pentafluorophenyl)corrole (138):

According to the general procedure **X**, 2,3,4,5,6-pentafluorobenzaldehyde (0.30 ml, 2.50 mmol) and pyrrole (0.35 ml, 5.00 mmol) were dissolved in methanol (100 ml). Then a mixture of HCl (36%, 2.10 ml) and water (100 ml) was added and it was stirred at room temperature for one hour. Then the mixture was extracted three times with dichloromethane. The combined organic layers were washed three times with water, dried over sodium sulfate and the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (160 ml) and DDQ (566 mg, 2.50 mmol) was added. After 1 hour stirring at 50 °C, purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (1:1) and a subsequent recrystallization from dichloromethane/*n*-pentane to obtain the desired product (84 mg, 21%) as a violet solid.



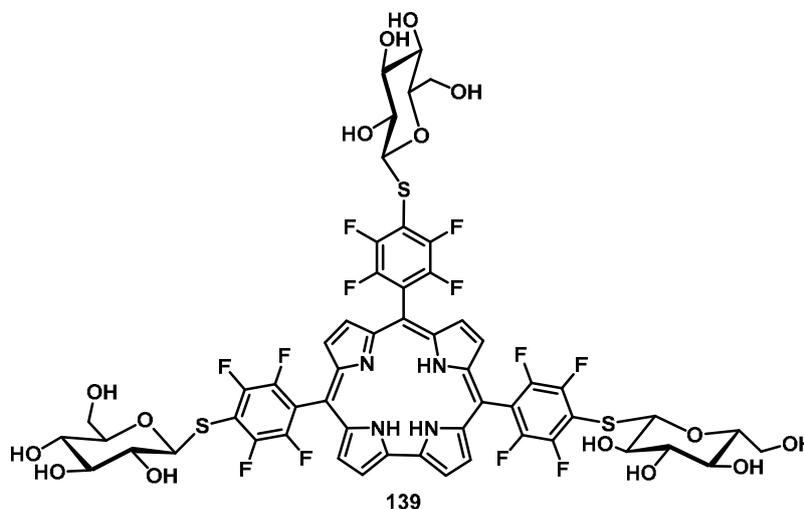
$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 8.57 (br s, 2 H, $\beta\text{-H}$), 8.59 (d, J = 4.6 Hz, 2 H, $\beta\text{-H}$), 8.77 (d, J = 4.4 Hz, 2 H, $\beta\text{-H}$), 9.11 (d, J = 4.1 Hz, 2 H, $\beta\text{-H}$) ppm.

$^{19}\text{F-NMR}$ (471 MHz, CDCl_3): δ = -137.08 (td, J = 7.8, 23.6 Hz, 2 F, Ar-F_{meta}) -161.40 – -161.20 (m, 4 F, Ar-F_{meta}), -152.62 (t, J = 20.8 Hz, 1 F, Ar-F_{para}), -152.15 – -151.93 (m, 2 F, Ar-F_{para}), -137.67 – -137.59 (m, 4 F, Ar-F_{ortho}), -137.08 (dd, J = 8.0, 24.1 Hz, 2 F, Ar-F_{ortho}) ppm.

Analytical data are in accordance with published data.^[19a]

5,10,15-Tris[4-(1'-thio- β -D-glucosyl)-2,3,5,6-tetrafluorophenyl]corrole (139):

According to the general procedure XIII, corrole 138 (40 mg, 50 μmol) and 1-thio- β -D-glucose sodium salt (40 mg, 181 μmol) were reacted under an argon atmosphere in dry DMF (3 ml) overnight at room temperature. Purification was achieved by reverse phase column chromatography on silica using methanol/water (8:2) as the eluent. The first band gave the desired product (46 mg, 69%) as a green-violet solid, and the second gave an inseparable mixture of two bis-thioglycosylated corroles (3 mg, 6%) as a green-violet solid.



¹H-NMR (700 MHz, CD₃OD): δ = 3.45-3.56 (m, 12 H, 2 x H-2'ose', H-2''ose', 2 x H-3'ose', H-3''ose', 2 x H-4'ose', H-4''ose', 2 x H-5'ose', H-5''ose'), 3.77-3.81 (m, 3 H, 2 x H-6_B'ose', H-6_B''ose'), 3.97-4.02 (m, 3 H, 2 x H-6_A'ose', H-6_A''ose'), 5.15 (d, J = 9.1 Hz, 1 H, H-1'ose'), 5.16 (d, J = 9.0 Hz, 2 H, 2 x H-1'ose'), 8.61 (br s, 2 H, β -H), 8.67 (d, J = 4.5 Hz, 2 H, β -H), 8.87 (br s, 2 H, β -H), 9.11 (br s, 2 H, β -H) ppm.

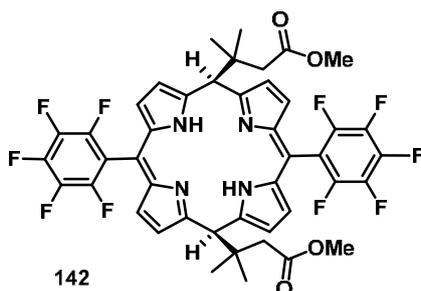
¹³C-NMR (176 MHz, CH₃OD): δ = 61.56 (C-6'ose'), 61.59 (C-6''ose'), 70.19 (C-4'ose'), 70.22 (C-4''ose'), 74.44 (C-2'ose'), 74.47 (C-2''ose'), 78.33 (C-3'ose', C-3''ose'), 81.24 (C-5'ose', C-5''ose'), 85.64 (C-1'ose'), 85.69 (C-1''ose'), 94.38-94.46 (Ar_F-C_{meso}, Ar_F-C'_{meso}), 112.16 (t, J = 20.4 Hz, Ar_F-C'_{Sglu}), 112.42-112.68 (Ar_F-C_{Sglu}), 115.87 (β -C), 119.05-119.42 (β -C), 121.59-121.80 (Ar_F-C_{ipso}, Ar_F-C'_{ipso}), 125.86 (β -C), 127.38 (β -C), 130.73 (α -C), 134.60 (α -C), 144.99-145.14 (Ar_F-C), 145.56-145.72 (Ar_F-C), 146.38-146.58 (Ar_F-C), 146.64-146.80 (Ar_F-C), 146.95-147.10 (Ar_F-C), 147.83-147.97 (Ar_F-C), 148.05-148.19 (Ar_F-C) ppm.

¹⁹F-NMR (471 MHz, CH₃OD): δ = -141.16 – -140.75 (m, 4 F, Ar-F_{meta}), -140.49 – -140.24 (m, 2 F, Ar-F'_{meta}), -135.79 – -135.55 (m, 2 F, Ar-F'_{ortho}), -135.36 – -135.13 (m, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₅H₄₄F₁₂N₄NaO₁₅S₃ [M + Na]⁺: 1347.1671, found: 1347.1671.

5,15-Bis(3-methoxy-1,1-dimethyl-3-oxopropyl)-10,20-bis(pentafluorophenyl)calix[4]-pyrין(1.1.1.1) (142), 5-(3-methoxy-1,1-dimethyl-3-oxopropyl)-15-(5-[4,4-dimethyldihydrofuran-2(3*H*)-one]-yl)-10,20-bis(pentafluorophenyl)calix[4]pyrין(1.1.1.1) (143) and α,α,α -5,15,25-tris(3-methoxy-1,1-dimethyl-3-oxopropyl)-10,20,30-tris(pentafluorophenyl)calix[6]-pyrין(1.1.1.1.1.1) (144):

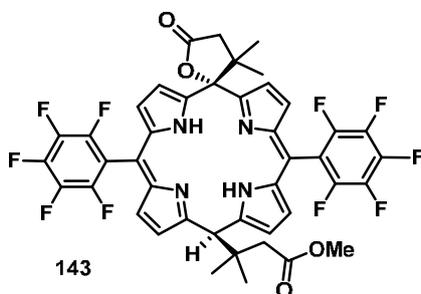
According to the general procedure **XI**, pentafluorobenzaldehyde (123 μ l, 1.00 mmol), 5-(3-methoxy-1,1-dimethyl-3-oxopropyl)dipyrrromethane **141** (260 mg, 1.00 mmol), TFA (75 μ l, 1.00 mmol), DDQ (345 mg, 1.50 mmol) and triethylamine (1.25 ml, 9.02 mmol) were reacted in dry dichloromethane (250 ml). Purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (1:1 to 9:1) as the eluent and subsequent recrystallization from dichloromethane/*n*-pentane. The first band gave calix[4]pyrין **142** (89 mg, 19%) in form of orange crystals, the second band gave *meso*-spirolactone calix[4]pyrין **143** (72 mg, 17%) in form of orange crystals and the third band gave calix[6]pyrין **144** (88 mg, 20%) in form of orange-red crystals.



¹H-NMR (700 MHz, CDCl₃): δ = 1.27 (s, 12 H, 4 x CH₃), 2.44 (s, 4 H, 2 x CH₂), 3.71 (s, 6 H, 2 x OCH₃), 4.49 (s, 2 H, Ar-H_{meso}), 6.32 (d, J = 4.2 Hz, 4 H, β -H), 6.34 (d, J = 4.3 Hz, 4 H, β -H), 12.92 (br s, 2 H, 2 x NH) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 25.76 (CH₃), 38.97 (C(CH₃)₂), 44.63 (CH₂), 49.75 (Ar-C_{meso}), 51.33 (OCH₃), 111.77-111.99 (Ar_F-C_{ipso}), 121.13-121.81 (β -C), 122.33 (Ar_F-C_{meso}), 126.21-126.92 (β -C), 136.54-136.74 (Ar_F-C), 137.97-138.18 (Ar_F-C), 140.59-140.82 (Ar_F-C), 142.06-142.27 (Ar_F-C), 144.19-144.25 (Ar_F-C), 145.55-145.72 (Ar_F-C), 172.47 (C=O) ppm.

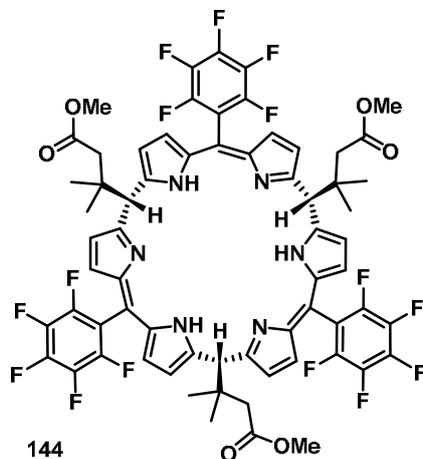
¹⁹F-NMR (471 MHz, CDCl₃): δ = -160.79 (td, J = 8.3, 22.3 Hz, 2 F, Ar-F_{meta}), -160.79 (td, J = 8.0, 21.9 Hz, 2 F, Ar-F_{meta}), -152.59 (t, J = 20.9 Hz, 2 F, Ar-F_{para}), -138.12 – -138.07 (m, 2 F, Ar-F_{ortho}), -137.73 – -137.67 (m, 2 F, Ar-F_{ortho}) ppm.



¹H-NMR (700 MHz, CDCl₃): δ = 1.25 (s, 6 H, 2 x CH₃ lactone), 1.28 (s, 6 H, 2 x CH₃), 2.43 (s, 2 H, CH₂), 2.53 (s, 2 H, CH₂ lactone), 3.70 (s, 3 H, OCH₃), 4.54 (s, 1 H, Ar-H_{meso}), 6.35 (d, J = 4.1 Hz, 2 H, β -H), 6.37 (d, J = 3.9 Hz, 2 H, β -H), 6.38 (d, J = 3.8 Hz, 2 H, β -H), 6.52 (d, J = 4.0 Hz, 2 H, β -H), 12.79 (br s, 2 H, 2 x NH) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 24.15 (CH₃ lactone), 25.85 (CH₃), 39.65 (C(CH₃)₂), 42.85 (CH₂ lactone), 44.68 (CH₂), 46.14 (C(CH₃)₂ lactone), 49.60 (Ar-C_{meso}), 51.44 (OCH₃), 89.04 (Ar-C_{meso} lactone), 111.39-111.60 (Ar_F-C_{ipso}), 116.80-117.62 (β -C), 121.60-122.53 (β -C), 123.27 (Ar_F-C_{meso}), 126.59-127.72 (β -C), 136.59-136.81 (Ar_F-C), 138.02-138.24 (Ar_F-C), 140.75-140.99 (Ar_F-C), 142.24-142.44 (Ar_F-C), 144.07-144.23 (Ar_F-C), 145.47-145.64 (Ar_F-C), 172.29 (C=O), 175.23 (C=O) ppm.

^{19}F -NMR (471 MHz, CDCl_3): $\delta = -160.87$ (td, $J = 8.3, 22.2$ Hz, 2 F, Ar-F_{meta}), -160.36 (td, $J = 8.3, 22.2$ Hz, 2 F, Ar-F_{meta}), -151.94 (t, $J = 20.8$ Hz, 2 F, Ar-F_{para}), -138.48 (dt, $J = 5.6, 22.8$ Hz, 2 F, Ar-F_{ortho}), -137.66 (dt, $J = 5.6, 22.8$ Hz, 2 F, Ar-F_{ortho}) ppm.



^1H -NMR (700 MHz, CDCl_3): $\delta = 1.28$ (s, 18 H, 6 x CH_3), 2.51 (s, 6 H, 3 x CH_2), 3.77 (s, 9 H, 3 x OCH_3), 4.86 (s, 3 H, Ar-H_{meso}), 6.38 (d, $J = 4.3$ Hz, 6 H, β -H), 6.44 (d, $J = 4.3$ Hz, 6 H, β -H), 13.34 (br s, 3 H, 3 x NH) ppm.

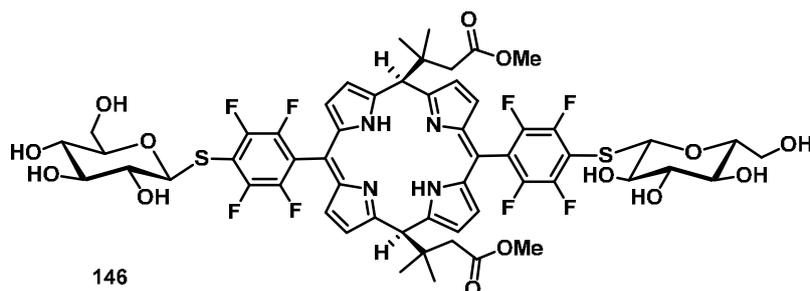
^{13}C -NMR (176 MHz, CDCl_3): $\delta = 25.54$ (CH_3), 38.22 ($\text{C}(\text{CH}_3)_2$), 45.38 (CH_2), 51.33 (OCH_3), 55.06 (Ar-C_{meso}), 111.02-111.27 (Ar_F-C_{ipso}), 118.49 (β -C), 121.77 (Ar_F-C_{meso}), 127.20 (β -C), 136.46-136.76 (Ar_F-C), 137.92-138.19 (Ar_F-C), 138.62 (α -C), 140.54-140.82 (Ar_F-C), 141.99-142.18 (Ar_F-C), 143.95-144.17 (Ar_F-C), 145.33-145.56 (Ar_F-C), 156.58 (α -C), 172.43 (C=O) ppm.

^{19}F -NMR (471 MHz, CDCl_3): $\delta = -161.26$ (td, $J = 8.3, 22.4$ Hz, 3 F, Ar-F_{meta}), -160.89 (td, $J = 8.0, 22.2$ Hz, 3 F, Ar-F_{meta}), -152.53 (t, $J = 20.8$ Hz, 3 F, Ar-F_{para}), $-138.45 - -138.36$ (m, 3 F, Ar-F_{ortho}), $-137.69 - -137.51$ (m, 3 F, Ar-F_{ortho}) ppm.

Analytical data are in accordance with published data.^[27a]

5,15-Bis(3-methoxy-1,1-dimethyl-3-oxopropyl)-10,20-bis[4-(1'-thio- β -D-glucosyl)-2,3,5,6-tetrafluorophenyl]calix[4]phyrin(1.1.1.1) (146):

According to the general procedure XIII, calix[4]phyrin **142** (20 mg, 23 μmol) and 1-thio- β -D-glucose sodium salt (12 mg, 55 μmol) were reacted under an argon atmosphere in dry DMF (3 ml) for 1 h at room temperature. Purification was achieved by column chromatography on silica using dichloromethane/methanol (9:1) as the eluent. The desired product (24 mg, 85%) was obtained as an orange crystalline solid.



Melting Point: 182 °C

¹H-NMR (700 MHz, CD₃OD): δ = 1.25 (s, 12 H, 4 x CH₃), 2.49 (s, 4 H, 2 x CH₂), 3.30 (ddd, J = 2.2, 5.8, 9.8 Hz, 2 H, H-5'ose'), 3.33-3.38 (m, 4 H, H-2'ose', H-4'ose'), 3.42 (t, J = 8.7 Hz, 2 H, H-3'ose'), 3.63 (dd, J = 5.8, 12.0 Hz, 2 H, H-6_B'ose'), 3.67 (s, 6 H, 2 x OCH₃), 3.83 (dd, J = 2.2, 12.0 Hz, 2 H, H-6_A'ose'), 4.50 (s, 2 H, Ar-H_{meso}), 4.95 (d, J = 9.5 Hz, 2 H, H-1'ose'), 6.38 (br s, 4 H, β -H), 6.47 (br s, 4 H, β -H), 12.93 (br s, 2 H, 2 x NH) ppm.

¹³C-NMR (176 MHz, (CD₃OD): δ = 24.95 (CH₃), 38.50 (C(CH₃)₂), 44.03 (CH₂), 49.89 (Ar-C_{meso}), 50.45 (OCH₃), 61.38 (C-6'ose'), 70.07 (C-4'ose'), 74.33 (C-2'ose'), 78.20 (C-3'ose'), 81.07 (C-5'ose'), 85.28 (C-1'ose'), 112.66-112.89 (Ar_F-C_{S_{glu}}), 116.54-116.76 (Ar_F-C_{ipso}), 123.18 (Ar_F-C_{meso}), 143.67-143.82 (Ar_F-C), 145.14-145.23 (Ar_F-C), 146.17-146.25 (Ar_F-C), 147.57-147.65 (Ar_F-C), 172.69 (C=O) ppm.

¹⁹F-NMR (471 MHz, CD₃OD): δ = -142.23 (dd, J = 11.5, 24.4 Hz, 2 F, Ar-F_{meta}), -141.22 (dd, J = 11.5, 24.4 Hz, 2 F, Ar-F_{meta}), -134.52 (dd, J = 11.8, 24.6 Hz, 2 F, Ar-F_{ortho}), -134.45 (dd, J = 12.1, 24.5 Hz, 2 F, Ar-F_{ortho}) ppm.

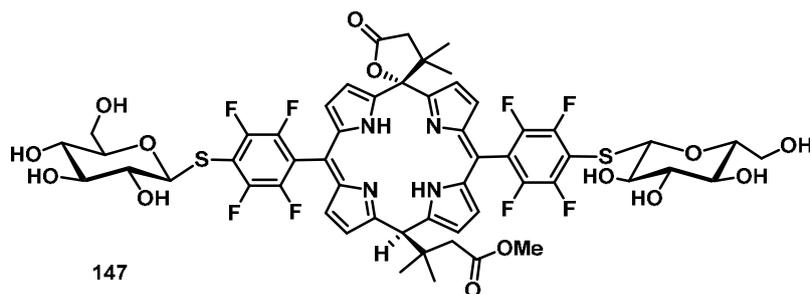
HRMS (ESI-TOF): m/z calcd. for C₅₆H₅₆F₈N₄NaO₁₄S₂ [M + Na]⁺: 1247.3004, found: 1247.3058.

UV/Vis (CH₃OH): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 417.0 (4.59) nm.

$[\alpha]_D^{25}$ = +16.9° (c = 0.05, CH₃OH).

S-(3-Methoxy-1,1-dimethyl-3-oxopropyl)-15-(S-[4,4-dimethyldihydrofuran-2(3H)-one]-yl)-10,20-bis[4-(1'-thio-β-D-glucosyl)-2,3,5,6-tetrafluorophenyl]calix[4]phyrin(1.1.1.1) (147):

According to the general procedure **XIII**, mono-*meso*-spirolactone calix[4]phyrin **143** (20 mg, 23 μ mol) and 1-thio- β -D-glucose sodium salt (13 mg, 61 μ mol) were reacted under an argon atmosphere in dry DMF (3 ml) for 1 h at room temperature. Purification was achieved by column chromatography on silica using dichloromethane/methanol (9:1) as the eluent. The desired product (23 mg, 83%) was obtained as an orange crystalline solid.



Melting Point: 203 °C (decomp.)

¹H-NMR (700 MHz, CD₃OD): δ = 1.28 (s, 6 H, 2 x CH₃ lactone), 1.30 (s, 6 H, 2 x CH₃), 2.49 (s, 2 H, CH₂), 2.61 (s, 2 H, CH₂ lactone), 3.30 (ddd, J = 2.1, 5.8, 9.8 Hz, 2 H, H-5'ose'), 3.32-3.37 (m, 4 H, H-2'ose', H-4'ose'), 3.42 (t, J = 8.6 Hz, 2 H, H-3'ose'), 3.62 (dd, J = 5.8, 12.0 Hz, 2 H, H-6_B'ose'), 3.69 (s, 3 H, OCH₃), 3.82 (dd, J = 2.1, 12.0 Hz, 2 H, H-6_A'ose'), 4.61 (s, 1 H, Ar-H_{meso}), 4.94 (d, J = 9.5 Hz, 2 H, H-1'ose'), 6.46 (br s, 4 H, β -H), 6.57 (br s, 4 H, β -H) ppm.

¹³C-NMR (176 MHz, (CD₃OD): δ = 24.93 (CH₃ lactone), 29.33 (CH₃), 39.18 (C(CH₃)₂), 42.06 (CH₂ lactone), 44.13 (CH₂), 45.74 (C(CH₃)₂ lactone), 49.64 (Ar-C_{meso}), 50.49 (OCH₃), 61.40 (C-6'ose'), 70.10 (C-4'ose'), 74.36 (C-2'ose'), 78.20 (C-3'ose'), 81.12 (C-5'ose'), 85.20 (C-1'ose'), 89.09 (Ar-C_{meso}lactone), 113.03-113.25 (Ar_F-C_SGlu), 116.11-116.32 (Ar_F-C_{ipso}), 122.89 (Ar_F-C_{meso}), 143.60-143.82 (Ar_F-C), 145.03-145.24 (Ar_F-C), 146.19-146.36 (Ar_F-C), 147.61-147.73 (Ar_F-C), 172.44 (C=O), 175.59 (C=O) ppm.

¹⁹F-NMR (471 MHz, CD₃OD): δ = -142.57 (dd, J = 11.5, 24.4 Hz, 2 F, Ar-F_{meta}), -141.32 (dd, J = 11.5, 24.0 Hz, 2 F, Ar-F_{meta}), -134.33 (dd, J = 11.6, 24.2 Hz, 4 F, Ar-F_{ortho}) ppm.

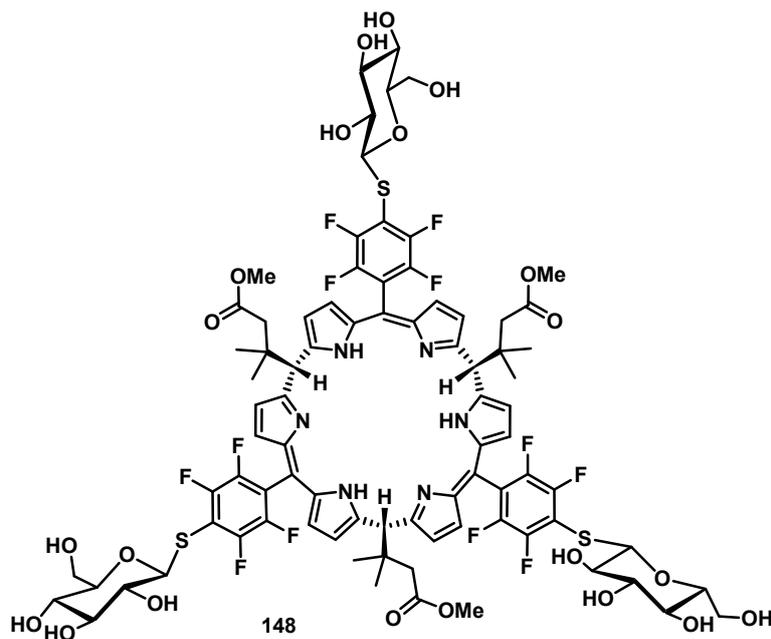
HRMS (ESI-TOF): m/z calcd. for C₅₅H₅₂F₈N₄NaO₁₄S₂ [M + Na]⁺: 1231.2691, found: 1231.2688.

UV/Vis (CH₃OH): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 415.5 (4.65) nm.

$[\alpha]_D^{25}$ = +75.9° (c = 0.05, CH₃OH).

***α,α,α*-5,15,25-Tris(3-methoxy-1,1-dimethyl-3-oxopropyl)-10,20,30-tris[4-(1'-thio-β-D-glucosyl)-2,3,5,6-tetrafluorophenyl]calix[6]phyrin(1.1.1.1.1) (148):**

According to the general procedure **XIII**, calix[6]phyrin **144** (15 mg, 12 μmol) and 1-thio-β-D-glucose sodium salt (9 mg, 41 μmol) were reacted under an argon atmosphere in dry DMF (3 ml) for 1 h at room temperature. Purification was achieved by column chromatography on silica using dichloromethane/methanol (85:15) as the eluent. The desired product (16 mg, 76%) was obtained as an orange-red crystalline solid.



Melting Point: 291 °C (decomp.)

¹H-NMR (700 MHz, CD₃OD): δ = 1.27 (s, 18 H, 6 x CH₃), 2.48 (s, 6 H, 3 x CH₂), 3.29 (ddd, J = 2.2, 5.8, 9.7 Hz, 3 H, H-5'ose'), 3.34-3.37 (m, 6 H, H-2'ose', H-4'ose'), 3.41 (t, J = 8.7 Hz, 3 H, H-3'ose'), 3.62 (dd, J = 5.8, 12.0 Hz, 3 H, H-6_A'ose'), 3.75 (s, 9 H, 3 x OCH₃), 3.80 (dd, J = 2.2, 12.0 Hz, 3 H, H-6_A'ose'), 4.91 (d, J = 9.7 Hz, 3 H, H-1'ose'), 5.00 (s, 3 H, Ar-H_{meso}), 6.47 (d, J = 4.3 Hz, 6 H, β -H), 6.54 (d, J = 4.3 Hz, 6 H, β -H) ppm.

¹³C-NMR (176 MHz, CD₃OD): δ = 24.73 (CH₃), 37.81 (C(CH₃)₂), 44.91 (CH₂), 50.65 (OCH₃), 54.34 (Ar-C_{meso}), 61.34 (C-6'ose'), 70.03 (C-4'ose'), 74.29 (C-2'ose'), 78.16 (C-3'ose'), 81.02 (C-5'ose'), 85.32 (C-1'ose'), 112.58-112.81 (Ar_F-C_{SGLu}), 116.05-116.26 (Ar_F-C_{ipso}), 118.42 (β -C), 122.62 (Ar_F-C_{meso}), 127.32 (β -C), 138.29 (α -C), 143.56-143.71 (Ar_F-C), 144.98-145.17 (Ar_F-C), 146.13-146.25 (Ar_F-C), 147.52-147.71 (Ar_F-C), 156.83 (α -C), 172.70 (C=O) ppm.

¹⁹F-NMR (471 MHz, CD₃OD): δ = -141.91 (dd, J = 11.7, 24.2 Hz, 3 F, Ar-F_{meta}), -140.94 (dd, J = 11.7, 24.2 Hz, 3 F, Ar-F_{meta}), -134.66 (dd, J = 11.7, 24.2 Hz, 3 F, Ar-F_{ortho}), -134.30 (dd, J = 11.7, 24.4 Hz, 3 F, Ar-F_{ortho}) ppm.

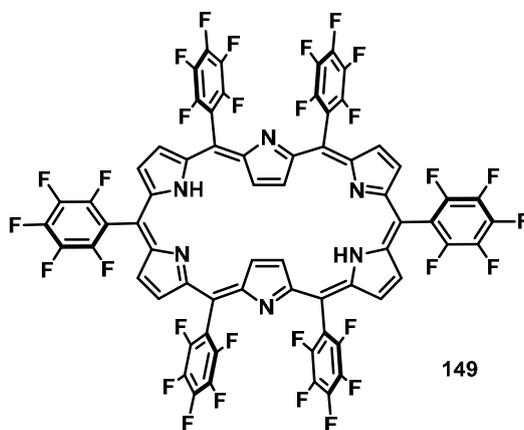
HRMS (ESI-TOF): m/z calcd. for C₈₄H₈₄F₁₂N₆NaO₂₁S₃ [M + Na]⁺: 1859.4558, found: 1859.4697.

UV/Vis (CH₃OH): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 445.5 (4.78) nm.

$[\alpha]_D^{25}$ = +29.6° (c = 0.03, CH₃OH).

meso-5,10,15,20,25,30-Hexakis(pentafluorophenyl)-[26]hexaphyrin (149) and meso-5,10,15,20,25-Pentakis(pentafluorophenyl)-substituted *N*-fused [22]pentaphyrin (150):

According to the general procedure XII, pentafluorobenzaldehyde (494 μl , 4.00 mmol), pyrrole (278 μl , 4.02 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (100 μl , 2.5 N), and DDQ (2.27 g, 10.0 mmol) were reacted in dry dichloromethane (60 ml). Purification was achieved by repeated column chromatography on silica using dichloromethane/*n*-hexane (1:4 to 1:0) as the eluent. The first band gave 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin **16** (71 mg, 7%) in form of violet crystals after recrystallization from dichloromethane/methanol, the second deep purple band gave [26]hexaphyrin **149** (101 mg, 10%) in form of shiny crystals after recrystallization from dichloromethane/*n*-pentane and the third red band gave *N*-fused [22]pentaphyrin **150** (107 mg, 11%) in form of shiny crystals after recrystallization from dichloromethane/*n*-pentane.



Melting Point: > 300 °C

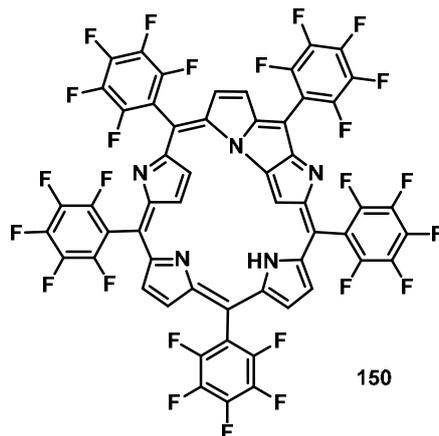
$^1\text{H-NMR}$ (700 MHz, CDCl_3): δ = -2.41 (br s, 4 H, inner $\beta\text{-H}$), -2.00 (br s, 2 H, NH), 9.11 (d, J = 4.6 Hz, 4 H, outer $\beta\text{-H}$), 9.45 (d, J = 4.6 Hz, 4 H, outer $\beta\text{-H}$) ppm.

$^{13}\text{C-NMR}$ (176 MHz, CDCl_3): δ = 106.43 ($\text{Ar}_\text{F}\text{-C}_{\text{meso}}$), 114.39-114.60 ($\text{Ar}_\text{F}\text{-C}_{\text{ipso}}$), 117.55 ($\text{Ar}_\text{F}\text{-C}_{\text{meso}}$), 117.75-117.95 ($\text{Ar}_\text{F}\text{-C}_{\text{ipso}}$), 123.10 (inner $\beta\text{-C}$), 132.67 (outer $\beta\text{-C}$), 135.14 (outer $\beta\text{-C}$), 137.00-137.40 ($\text{Ar}_\text{F}\text{-C}$), 138.43-138.76 ($\text{Ar}_\text{F}\text{-C}$), 141.61-141.84 ($\text{Ar}_\text{F}\text{-C}$), 142.07-142.27 ($\text{Ar}_\text{F}\text{-C}$), 143.10-143.31 ($\text{Ar}_\text{F}\text{-C}$), 143.54-143.77 ($\text{Ar}_\text{F}\text{-C}$), 145.54-145.69 ($\text{Ar}_\text{F}\text{-C}$), 145.89-146.05 ($\text{Ar}_\text{F}\text{-C}$), 146.96-147.11 ($\text{Ar}_\text{F}\text{-C}$), 147.31-147.48 ($\text{Ar}_\text{F}\text{-C}$), 149.75 (outer $\alpha\text{-C}$), 149.91 (outer $\alpha\text{-C}$), 156.40 (inner $\alpha\text{-C}$) ppm.

$^{19}\text{F-NMR}$ (471 MHz, CDCl_3): δ = -162.85 (t, J = 20.4 Hz, 4 F, $\text{Ar-F}_{\text{meta}}$), -160.24 (td, J = 8.4, 22.9 Hz, 2 F, $\text{Ar-F}_{\text{meta}}$), -152.57 (t, J = 20.1 Hz, 2 F, $\text{Ar-F}_{\text{para}}$), -149.72 (t, J = 20.8 Hz, 1 F, $\text{Ar-F}_{\text{para}}$), -136.80 (d, J = 21.2 Hz, 4 F, $\text{Ar-F}_{\text{ortho}}$), -136.25 (dd, J = 7.9, 23.5 Hz, 2 F, $\text{Ar-F}_{\text{ortho}}$) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{66}\text{H}_{15}\text{F}_{30}\text{N}_6$ $[\text{M} + \text{H}]^+$: 1461.0879, found: 1461.0897.

Analytical data are in accordance with published data.^[35]



Melting Point: > 300 °C (decomp.)

¹H-NMR (700 MHz, CDCl₃): δ = -2.22 (s, 1 H, inner β -H), 1.27 (br s, 1 H, NH), 1.74 (d, J = 4.4 Hz, 1 H, inner β -H), 2.23 (d, J = 4.4 Hz, 1 H, inner β -H), 8.37 (d, J = 4.6 Hz, 1 H, outer β -H), 8.41 (d, J = 4.6 Hz, 1 H, outer β -H), 8.44 (d, J = 4.6 Hz, 1 H, outer β -H), 8.63 (d, J = 4.6 Hz, 1 H, outer β -H), 9.16-9.19 (m, 2 H, outer β -H) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 99.08 (Ar_F-C), 99.10 (inner β -C), 100.74 (Ar_F-C_{meso}), 107.73-107.94 (Ar_F-C_{ipso}), 109.61 (Ar_F-C), 112.69 (Ar_F-C), 113.29-113.52 (Ar_F-C_{ipso}), 114.05 (Ar_F-C), 114.08-114.26 (Ar_F-C_{ipso}), 115.04-115.21 (Ar_F-C_{ipso}), 118.17-118.40 (Ar_F-C_{ipso}), 120.47 (Ar_F-C), 122.36 (Ar_F-C), 123.22 (outer β -C), 129.31 (outer β -C), 131.29 (outer β -C), 131.50 (outer β -C), 132.33 (Ar_F-C), 132.35 (Ar_F-C), 132.79 (inner β -C), 133.30 (inner β -C), 133.76 (outer β -C), 136.55 (Ar_F-C), 136.71-137.11 (Ar_F-C), 137.57-137.79 (Ar_F-C), 137.87-138.05 (Ar_F-C), 138.13-138.53 (Ar_F-C), 138.95-139.23 (Ar_F-C), 139.29-139.46 (Ar_F-C), 140.94-141.21 (Ar_F-C), 141.37-141.58 (Ar_F-C), 141.68-141.93 (Ar_F-C), 142.12-142.36 (Ar_F-C), 142.44-142.62 (Ar_F-C), 142.84-143.04 (Ar_F-C), 143.17-143.43 (Ar_F-C), 143.60-143.81 (Ar_F-C), 144.44-144.59 (Ar_F-C), 144.68-145.04 (Ar_F-C), 145.17-145.49 (Ar_F-C), 145.87-146.05 (Ar_F-C), 146.13-146.47 (Ar_F-C), 146.57-146.78 (Ar_F-C), 146.79 (outer α -C), 148.03 (outer α -C), 150.83 (outer α -C), 152.11 (outer α -C), 153.35 (outer α -C), 159.66 (inner α -C), 160.40 (inner α -C), 160.86 (inner α -C), 160.95 (inner α -C) ppm.

¹⁹F-NMR (471 MHz, CDCl₃): δ = -162.97 – -162.81 (m, 2 F, Ar-F_{meta}), -162.31 – -162.18 (m, 1 F, Ar-F_{meta}), -161.99 – -161.86 (m, 1 F, Ar-F_{meta}), -161.28 – -161.17 (m, 2 F, Ar-F_{meta}), -160.33 – -160.05 (m, 4 F, Ar-F_{meta}), -153.71 (t, J = 20.9 Hz, 1 F, Ar-F_{para}), -150.98 (t, J = 20.8 Hz, 1 F, Ar-F_{para}), -150.22 (t, J = 20.8 Hz, 1 F, Ar-F_{para}), -149.92 (t, J = 20.8 Hz, 1 F, Ar-F_{para}), -148.98 (t, J = 20.9 Hz, 1 F, Ar-F_{para}), -140.21 – -140.14 (m, 1 F, Ar-F_{ortho}), -139.52 – -139.46 (m, 1 F, Ar-F_{ortho}), -138.40 – -138.32 (m, 1 F, Ar-F_{ortho}), -137.99 – -137.91 (m, 1 F, Ar-F_{ortho}), -137.33 – -137.27 (m, 2 F, Ar-F_{ortho}), -136.88 – -136.81 (m, 1 F, Ar-F_{ortho}), -136.39 – -136.30 (m, 1 F, Ar-F_{ortho}), -135.70 – -135.65 (m, 1 F, Ar-F_{ortho}), -134.68 – -134.64 (m, 1 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for $C_{55}H_{11}F_{25}N_5$ $[M + H]^+$: 1216.0615, found: 1216.0628.

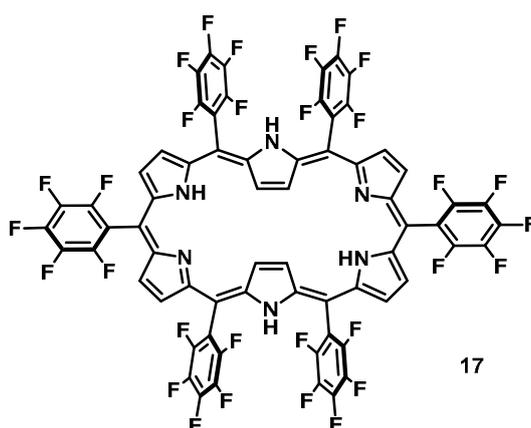
Analytical data are in accordance with published data.^[106]

meso-5,10,15,20,25,30-Hexakis(pentafluorophenyl)-[26]hexaphyrin (149):

According to the general procedure **XII**, pentafluorobenzaldehyde (0.37 ml, 3.00 mmol), 5-(pentafluorophenyl)dipyrromethane **43** (937 mg, 3.00 mmol), methane sulfonic acid (120 μ l, 2.5 N), DDQ (1.36 g, 6.00 mmol) and triethylamine (40 μ l, 0.3 mmol) were reacted in dry dichloromethane (30 ml). Purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (1:4 to 1:0) as the eluent. The first band gave 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (14 mg, 1%) in form of violet crystals after recrystallization from dichloromethane/methanol, the second band gave [26]hexaphyrin (119 mg, 8%) in form of shiny crystals after recrystallization from dichloromethane/*n*-pentane.

meso-5,10,15,20,25,30-Hexakis(pentafluorophenyl)-[28]hexaphyrin (17):

Under an argon atmosphere, $NaBH_4$ (30 mg, 793 μ mol) was added to a solution of *meso*-5,10,15,20,25,30-hexakis-(pentafluorophenyl)-[26]hexaphyrin **149** (50 mg, 34 μ mol) in dry methanol (10 ml). After stirring for 20 min, the solvent was evaporated and the residues were dissolved in dichloromethane. Purification was achieved by a short column chromatography on silica using dichloromethane as the eluent. The first blue band gave the desired product (49 mg, 98%) in form of shiny crystals after recrystallization from dichloromethane/*n*-pentane.



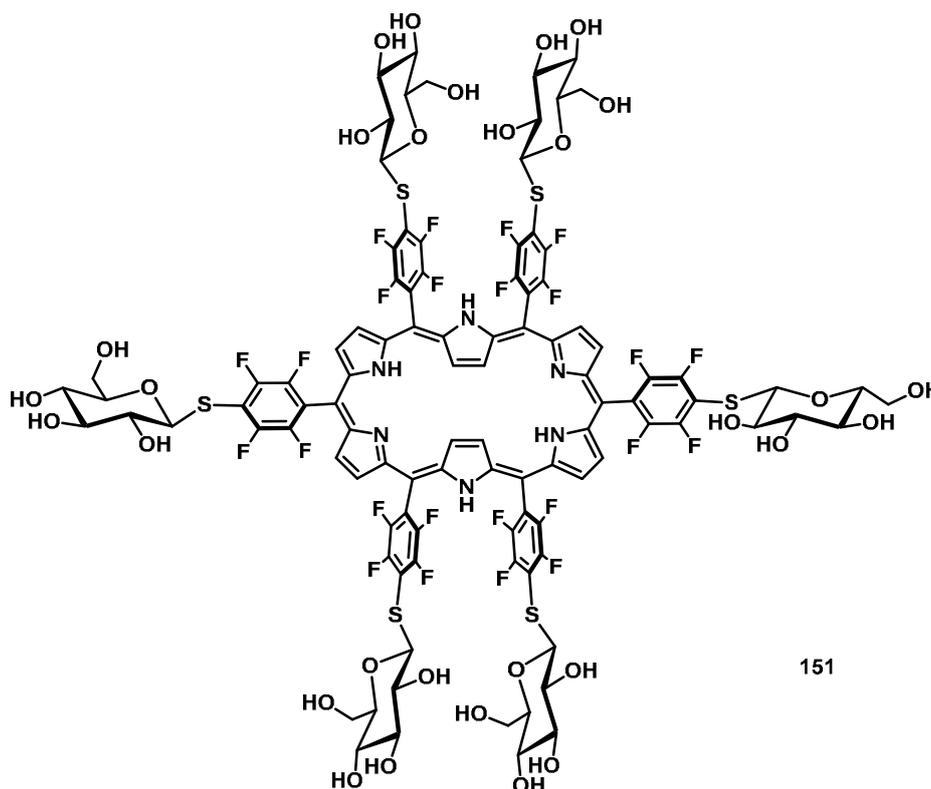
Melting Point: > 300 °C

¹H-NMR (500 MHz, CDCl₃): δ = 2.63 (s, 4 H, inner β -H), 4.57 (br s, 4 H, NH), 7.61 (d, J = 4.9 Hz, 4 H, outer β -H), 7.70 (d, J = 4.9 Hz, 4 H, outer β -H) ppm.

Analytical data are in accordance with published data.^[35]

meso-5,10,15,20,25,30-Hexakis[4-(1'-thio- β -D-glucosyl)-2,3,5,6-tetrafluorophenyl]-[28]hexaphyrin (151):

According to the general procedure XIII, [28]hexaphyrin 17 (20 mg, 14 μ mol) and 1-thio- β -D-glucose sodium salt (22 mg, 98 μ mol) were reacted under an argon atmosphere in dry DMF (1 ml) overnight at room temperature. Purification was achieved by repeated reversed phase column chromatography on silica using methanol/water (50:50 to 65:35) as the eluent. The desired product (27 mg, 78%) was obtained as a shiny solid.



Melting Point: > 300 °C

$^1\text{H-NMR}$ (700 MHz, CD_3OD): δ = 3.22-3.24 (m, 4 H, H-5'ose'), 3.29-3.33 (m, 8 H, 4 x H-2'ose', 4 x H-4'ose'), 3.37-3.43 (m, 8 H, 4 x H-3'ose', 2 x H-4''ose', 2 x H-5''ose'), 3.44-3.47 (m, 2 H, H-2''ose'), 3.48-3.51 (m, 2 H, H-3''ose'), 3.56 (dd, J = 5.8, 12.1 Hz, 4 H, H-6_B'ose'), 3.70-3.74 (m, 6 H, 4 x H-6_A'ose', 2 x H-6_B''ose'), 3.92 (dd, J = 1.6, 11.9 Hz, 2 H, H-6_A''ose'), 4.84 (d, J = 9.8 Hz, 4 H, H-1'ose'), 5.06 (d, J = 9.4 Hz, 2 H, H-1''ose'), 7.74 (d, J = 3.9 Hz, 4 H, outer β -H), 7.86 (d, J = 3.9 Hz, 4 H, outer β -H) ppm.

$^{13}\text{C-NMR}$ (176 MHz, CD_3OD): δ = 61.26 (C-6'ose'), 61.48 (C-6''ose'), 69.96 (C-4'ose'), 70.14 (C-4''ose'), 74.20 (C-2'ose'), 74.37 (C-2''ose'), 78.09 (C-3'ose'), 78.28 (C-3''ose'), 80.92 (C-5'ose'), 81.15 (C-5''ose'), 85.61 (C-1'ose'), 85.64 (C-1''ose'), 95.90 (Ar_F -C_{meso}), 95.94 (Ar_F -C_{meso}), 102.10-102.49 (Ar_F -C_{meso}), 111.76-112.17 (Ar_F -C'_{SGLu}, Ar_F -C_{SGLu}), 118.83-119.20 (Ar_F -C_{meso}), 127.71-127.97 (outer β -C), 129.19-129.41 (outer β -C), 138.25-138.49 (Ar_F -C_{meso}), 144.54-144.62

(Ar_F-C), 145.00-145.12 (Ar_F-C), 145.94-146.06 (Ar_F-C), 146.18-146.30 (Ar_F-C), 146.41-146.51 (Ar_F-C), 146.65-146.74 (Ar_F-C), 147.57-147.69 (outer α -C), 148.01-148.21 (outer α -C), 160.06 (inner α -C) ppm.

¹⁹F-NMR (471 MHz, CD₃OD): δ = -141.47 – -141.19 (m, 8 F, Ar-F_{meta}), -140.21 (dd, J = 11.3, 24.9 Hz, 4 F, Ar-F'_{meta}), -136.01 – -135.74 (m, 8 F, Ar-F_{ortho}), -135.02 (dd, J = 11.3, 24.9 Hz, 4 F, Ar-F'_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₁₀₂H₈₃F₂₄N₆O₃₀S₆ [M + H]⁺: 2519.3095, found: 2519.2778.

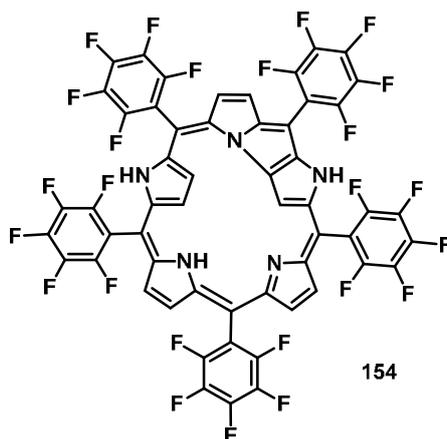
UV/Vis (CH₃OH): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 591.5 (5.29), 765.0 (4.22) nm.

meso-5,10,15,20,25,30-Hexakis[4-(1'-thio- β -D-glucosyl)-2,3,5,6-tetrafluorophenyl]-[26]hexaphyrin (152):

A solution of glycosylated [28]hexaphyrin **151** (10 mg, 4.0 μ mol) in methanol (10 ml) was vigorously stirred for 1 week at room temperature to aerate the solution and hence to oxidize the starting material under mild conditions. A complete oxidation, however, was not achieved and purification attempts failed due to their very similar properties.

meso-5,10,15,20,25-Pentakis(pentafluorophenyl)-substituted *N*-fused[24]pentaphyrin (154):

Under an argon atmosphere, NaBH₄ (15 mg, 397 μ mol) was added to a solution of *meso*-5,10,15,20,25-pentakis-(pentafluorophenyl)-substituted *N*-fused [22]pentaphyrin **150** (24 mg, 20 μ mol) in dry methanol (5 ml). After stirring for 20 min, the solvent was evaporated and the residues were dissolved in dichloromethane. Purification was achieved by a short column chromatography on silica using dichloromethane as the eluent. The first orange-red band gave the desired product (24 mg, 98%) in form of shiny crystals after recrystallization from dichloromethane/*n*-pentane.



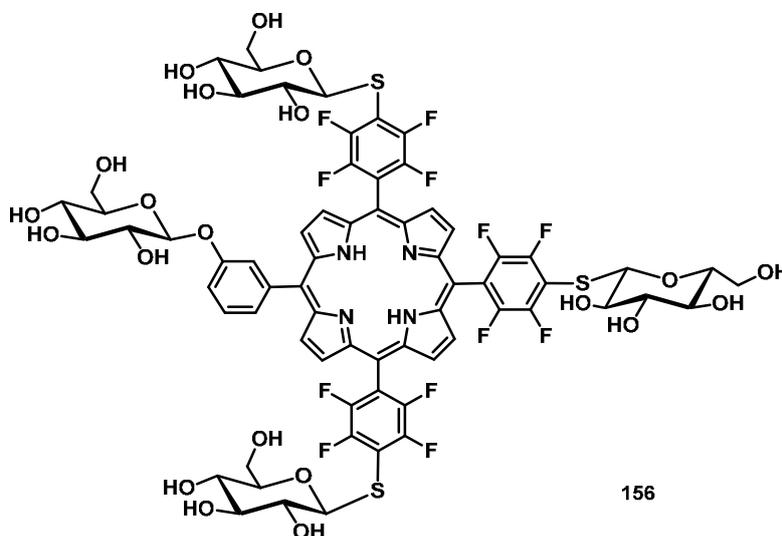
Melting Point: > 300 °C (decomp.)

¹H-NMR (700 MHz, CDCl₃): δ = 5.60 (d, J = 5.9 Hz, 1 H, β -H), 5.87 (d, J = 4.9 Hz, 1 H, β -H), 6.02 (d, J = 4.9 Hz, 1 H, β -H), 6.05 (d, J = 5.4 Hz, 1 H, β -H), 6.18 (d, J = 5.9 Hz, 1 H, β -H), 6.21 (d, J = 5.3 Hz, 1 H, β -H), 6.62 (br s, 1H, outer NH), 6.76 (br s, 1H, outer NH), 7.88 (d, J = 1.9 Hz, 1H, inner β -H), 8.12 (dd, J = 2.2, 3.9 Hz, 1H, β -H), 8.19 (dd, J = 2.2, 3.9 Hz, 1H, β -H), 13.76 (br s, 1H, inner NH) ppm.

Analytical data are in accordance with published data.^[106]

5-(3- β -D-Glucosylphenyl)-10,15,20-tris[4-(1'-thio- β -D-glucosyl)-2,3,5,6-tetrafluorophenyl]-porphyrin (156):

According to the general procedure **XIII**, monoglycosylated porphyrin **40** (30 mg, 28 μ mol) and 1-thio- β -D-glucose sodium salt (20 mg, 93 μ mol) were reacted under an argon atmosphere in dry DMF (4 ml) overnight at room temperature. Purification was achieved by column chromatography on silica using ethyl acetate/methanol (17:3) as the eluent. The desired product (40 mg, 89%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 243 °C

¹H-NMR (700 MHz, CD₃OD): δ = -2.89 (s, 2 H, NH), 3.45-3.60 (m, 15 H, H-2''ose', H-3''ose', H-3'ose', H-4''ose', H-4'ose', H-5''ose', H-5'ose'), 3.62 (dd, J = 7.7, 9.1 Hz, 1 H, H-2'ose'), 3.72 (dd, J = 4.8, 12.0 Hz, 1 H, H-6_B'ose'), 3.82 (dd, J = 6.2, 12.0 Hz, 2 H, H-6_B''ose'), 3.83 (dd, J = 6.2, 12.0 Hz, 1 H, H-6_B''ose'), 3.88 (dd, J = 1.9, 12.0 Hz, 1 H, H-6_A'ose'), 4.05 (dd, J = 2.2, 12.0 Hz, 2 H, H-6_A''ose'), 4.06 (dd, J = 2.2, 12.0 Hz, 1 H, H-6_A''ose'), 5.22 (d, J = 8.8 Hz, 3 H, H-1''ose'), 5.27 (d, J = 7.7 Hz,

1 H, H-1'ose'), 7.59-7.63 (m, 1 H, Ar-H), 7.64-7.68 (m, 1 H, Ar-H), 7.81-7.84 (m, 1 H, Ar-H), 8.02-8.05 (m, 1 H, Ar-H), 8.98-9.30 (m, 8 H, β -H) ppm.

$^{13}\text{C-NMR}$ (176 MHz, CD_3OD): δ = 61.04 (C-6'ose'), 61.70 (C-6''ose'), 69.96 (C-4'ose'), 70.32 (C-4''ose'), 73.63 (C-2'ose'), 74.59 (C-2''ose'), 76.56 (C-3'ose'), 76.68 (C-5'ose'), 78.37 (C-3''ose'), 81.37 (C-5''ose'), 85.41 (C-1''ose'), 100.75 (C-1'ose'), 102.86 ($\text{Ar}_\text{F}\text{-C}_{\text{meso}}$), 103.92 ($\text{Ar}_\text{F}\text{-C}_{\text{meso}}$), 113.41-113.64 ($\text{Ar}_\text{F}\text{-C}_{\text{SGLu}}$), 116.31 (Ar-C), 120.53-120.93 ($\text{Ar}_\text{F}\text{-C}_{\text{ipso}}$), 122.41 (Ar-C_{meso}), 122.83 (Ar-C), 127.59 (Ar-C), 128.78 (Ar-C), 142.15 (Ar-C_{ipso}), 145.58-145.67 (Ar_F-C), 146.43-146.56 (Ar_F-C), 146.98-147.07 (Ar_F-C), 147.87-147.95 (Ar_F-C), 156.20 (Ar-C_{OGLc}) ppm.

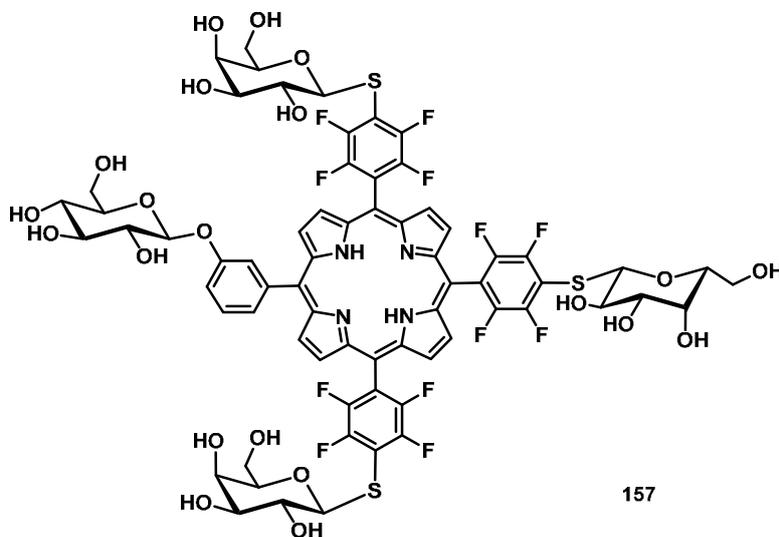
$^{19}\text{F-NMR}$ (471 MHz, CD_3OD): δ = -140.47 – -140.28 (m, 6 F, Ar-F_{meta}), -135.11 – -134.98 (m, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{68}\text{H}_{58}\text{F}_{12}\text{N}_4\text{NaO}_{21}\text{S}_3$ [$\text{M} + \text{Na}$]⁺: 1613.2462, found: 1613.2351.

UV/Vis (CH_3OH): λ_{max} ($\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 411 (5.53), 506 (4.42), 580 (3.77), 636 (3.11) nm.

5-(3- β -D-Glucosylphenyl)-10,15,20-tris[4-(1'-thio- β -D-galactosyl)-2,3,5,6-tetrafluorophenyl]porphyrin (157):

According to the general procedure XIII, monoglycosylated porphyrin 40 (30 mg, 28 μmol) and 1-thio- β -D-galactose sodium salt (20 mg, 93 μmol) were reacted under an argon atmosphere in dry DMF (4 ml) overnight at room temperature. Purification was achieved by column chromatography on silica using methanol/water (8:2) as the eluent. The desired product (36 mg, 81%) was obtained as a violet crystalline solid after recrystallization from dichloromethane/methanol.



Melting Point: 267 °C

¹H-NMR (700 MHz, CD₃OD): δ = -2.92 (s, 2 H, NH), 3.44-3.47 (m, 1 H, H-5'ose'), 3.48 (dd, J = 8.4, 9.8 Hz, 1 H, H-4'ose'), 3.54 (dd, J = 8.4, 9.0 Hz, 1 H, H-3'ose'), 3.61 (dd, J = 7.8, 9.0 Hz, 1 H, H-2'ose'), 3.69 (dd, J = 3.3, 9.3 Hz, 3 H, H-3''ose'), 3.72 (dd, J = 4.9, 12.0 Hz, 1 H, H-6_B'ose'), 3.75-3.78 (m, 3 H, H-5''ose'), 3.85-3.93 (m, 10 H, 1 x H-6_A'ose', 3 x H-2''ose', 3 x H-6_A''ose', 3 x H-6_B''ose'), 4.03-4.05 (m, 3 H, H-4''ose'), 5.12 (d, J = 9.5 Hz, 3 H, H-1''ose'), 5.26 (d, J = 7.8 Hz, 1 H, H-1'ose'), 7.58-7.62 (m, 1 H, Ar-H), 7.64-7.68 (m, 1 H, Ar-H), 7.78-7.81 (m, 1 H, Ar-H), 8.00-8.03 (m, 1 H, Ar-H), 8.93-9.32 (m, 8 H, β -H) ppm.

¹³C-NMR (176 MHz, CD₃OD): δ = 61.00 (C-6'ose'), 61.33 (C-6''ose'), 69.22 (C-4''ose'), 69.93 (C-4'ose'), 71.43 (C-2''ose'), 73.60 (C-2'ose'), 74.94 (C-3''ose'), 76.52 (C-3'ose'), 76.63 (C-5'ose'), 79.91 (C-5''ose'), 86.28 (C-1''ose'), 100.70 (C-1'ose'), 102.86 (Ar_F-C_{meso}), 103.92 (Ar_F-C_{meso}), 113.28-113.52 (Ar_F-C_{SGal}), 116.31 (Ar-C), 120.65-121.05 (Ar_F-C_{ipso}), 122.39 (Ar-C_{meso}), 122.82 (Ar-C), 127.62 (Ar-C), 128.80 (Ar-C), 142.11 (Ar-C_{ipso}), 145.56-145.66 (Ar_F-C), 146.63-146.71 (Ar_F-C), 146.96-147.05 (Ar_F-C), 148.01-148.10 (Ar_F-C), 156.14 (Ar-C_{OGlc}) ppm.

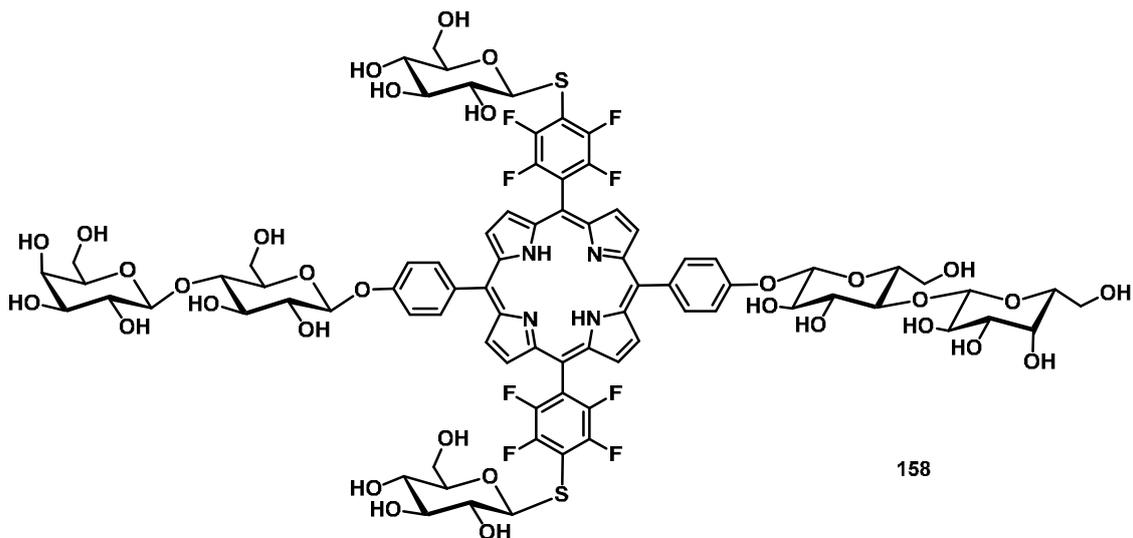
¹⁹F-NMR (471 MHz, CD₃OD): δ = -140.52 – -140.32 (m, 6 F, Ar-F_{meta}), -134.34 – -134.70 (m, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₆₈H₅₈F₁₂N₄NaO₂₁S₃ [M + Na]⁺: 1613.2462, found: 1613.2384.

UV/Vis (CH₃OH): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 412 (5.57), 506 (4.29), 581 (3.81), 636 (2.98) nm.

5,15-Bis(4- β -D-lactosylphenyl)-10,20-bis[4-(1'-thio- β -D-glucosyl)-2,3,5,6-tetrafluorophenyl]porphyrin (158):

According to the general procedure XIII, diglycosylated porphyrin **75** (10 mg, 6.8 μ mol) and 1-thio- β -D-glucose sodium salt (3.6 mg, 16.3 μ mol) were reacted under an argon atmosphere in dry DMF (1 ml) overnight at room temperature. Purification was achieved by reversed phase column chromatography on silica using methanol/water (75:25) as the eluent. The desired product (11 mg, 78%) was obtained as a violet solid.



Melting Point: > 300 °C

¹H-NMR (700 MHz, (CD₃)₂SO): δ = -3.00 (br s, 2 H, NH), 3.16-3.21 (m, 2 H, 2 x H-4'glucose'), 3.31-3.43 (m, 10 H, 2 x H-2'ose', 2 x H-3'ose', 2 x H-5'ose', 4 x H'lactose')*, 3.49-3.63 (m, 14 H, 4 x H-6''lactose', 2 x H-6'glucose', 8 x H'lactose'), 3.64-3.68 (m, 2 H, 2 x H'lactose'), 3.74-3.79 (m, 4 H, 2 x H-6'lactose', 2 x H'lactose'), 3.80-3.83 (m, 2 H, 2 x H-6'glucose'), 3.90 (dd, J = 5.0, 9.8 Hz, 2 H, 2 x H-6'lactose'), 4.05 (br s, 1 H, OH'ose'), 4.33 (d, J = 7.6 Hz, 2 H, 2 x H-1'lactose'), 4.56 (d, J = 4.6 Hz, 2 H, OH'ose'), 4.72-4.78 (m, 6 H, OH'ose'), 4.82 (d, J = 5.7 Hz, 2 H, OH'ose'), 4.89 (br s, 2 H, OH'ose'), 5.06 (d, J = 8.5 Hz, 2 H, H-1'glucose'), 5.12 (d, J = 5.7 Hz, 2 H, OH'ose'), 5.15 (d, J = 4.6 Hz, 2 H, OH'ose'), 5.28 (d, J = 4.3 Hz, 2 H, OH'ose'), 5.35 (d, J = 7.8 Hz, 2 H, 2 x H-1'lactose'), 5.68 (d, J = 5.2 Hz, 2 H, OH'ose'), 5.76 (d, J = 5.9 Hz, 2 H, OH'ose'), 7.51 (d, J = 8.4 Hz, 4 H, Ar-H_{meta}), 8.20 (d, J = 8.4 Hz, 4 H, Ar-H_{ortho}), 8.96-8.99 (m, 4 H, β -H), 9.16-9.18 (m, 4 H, β -H) ppm.

* = signals of carbohydrate hydrogens are overlapped by the water peak of DMSO

¹³C-NMR (176 MHz, (CD₃)₂SO): δ = 60.65 (C-6'lactose'), 60.94 (C-6''lactose'), 61.89 (C-6'glucose'), 68.66 (C'lactose'), 70.87 (C-4'glucose'), 71.05 (C'lactose'), 73.66 (C'lactose'), 73.75 (C'lactose'), 75.24 (C-2'glucose'), 75.36 (C'lactose'), 75.57 (C'lactose'), 76.06 (C'lactose'), 78.57 (C-3'glucose'), 80.59 (C'lactose'), 82.37 (C-5'glucose'), 85.08 (C-1'glucose'), 100.40 (C-1''lactose'), 103.33 (Ar_F-C_{meso}), 104.29 (C-1'lactose'), 113.64-113.88 (Ar_F-C_{SGLu}), 115.11 (Ar-C_{meta}), 120.35-120.67 (Ar_F-C_{ipso}), 121.33 (Ar-C_{meso}), 134.36 (Ar-C_{ipso}), 135.90 (Ar-C_{ortho}), 145.37-145.47 (Ar_F-C), 146.44-146.52 (Ar_F-C), 146.75-146.84 (Ar_F-C), 147.83-147.91 (Ar_F-C), 157.96 (Ar-C_{OLac}) ppm.

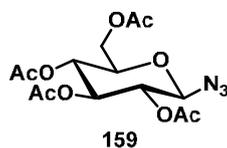
¹⁹F-NMR (471 MHz, (CD₃)₂SO): δ = -139.68 – -139.53 (m, 4 F, Ar-F_{meta}), -133.92 – -133.75 (m, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₈₀H₈₂F₈N₄NaO₃₂S₂ [M + Na]⁺: 1849.4124, found: 1849.4053.

UV/Vis ((CH₃)₂SO): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 414 (5.72), 508 (4.39), 586 (3.92), 639 (3.17) nm.

2,3,4,6-Tetra-*O*-acetyl- β -D-glucopyranosyl azide (159):

To a solution of α -glucosyl bromide (2.00 g, 4.86 mmol), TBAHS (1.65 g, 4.86 mmol) and sodium azide (1.58 g, 24.3 mmol) in dichloromethane (20 ml) was added saturated aqueous NaHCO₃ (20 ml). This two phase mixture was vigorously stirred at room temperature for 2 h. Ethyl acetate (100 ml) was added, the organic layer separated and successively washed with saturated NaHCO₃ (1 x 150 ml), water (2 x 150 ml) and brine (1 x 150 ml). The combined organic layers were dried over sodium sulfate, filtered and evaporated under reduced pressure to afford the desired product (1.67 g, 92%) as a colorless solid.

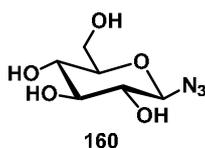


¹H-NMR (500 MHz, CDCl₃): δ = 1.99 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 2.08 (s, 3 H, OAc), 3.78 (ddd, J = 2.3, 4.8, 10.1 Hz, 1 H, H-5'ose'), 4.14 (dd, J = 2.3, 12.5 Hz, 1 H, H-6_A'ose'), 4.25 (dd, J = 4.8, 12.5 Hz, 1 H, H-6_B'ose'), 4.63 (d, J = 8.8 Hz, 1 H, H-1'ose'), 4.93 (m, 1 H, H-2'ose'), 5.08 (m, 1 H, H-4'ose'), 5.20 (m, 1 H, H-3'ose') ppm.

Analytical data are in accordance with published data.^[88]

β -D-Glucosyl azide (160):

The peracetylated glucosyl azide **159** (250 mg, 670 μ mol) was dissolved in dry methanol (10 ml). Then a solution of sodium methanolate in dry methanol (50 μ l, 0.5 N) was added. After stirring at room temperature under argon atmosphere for 24 h, the solvent was evaporated under reduced pressure and the crude product was purified by a short reversed phase column chromatography, using methanol/water (9:1). The desired product (133 mg, 97%) was obtained as a slightly yellow oil.



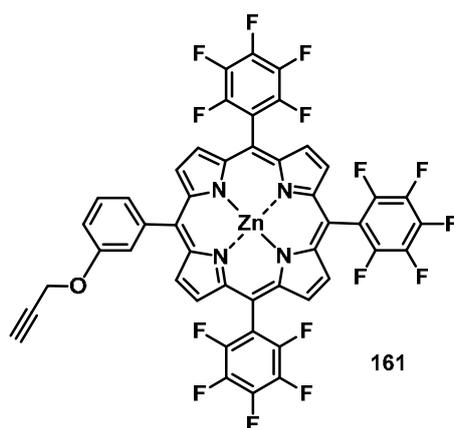
¹H-NMR (500 MHz, CD₃OD): δ = 3.13 (t, J = 8.7 Hz, 1 H, H-2'ose'), 3.27-3.38 (m, 3 H, H-4'ose', H-3'ose', H-5'ose'), 3.67 (dd, J = 5.7, 12.1 Hz, 1 H, H-6_B'ose'), 3.87 (dd, J = 2.2, 12.1 Hz, 1 H, H-6_A'ose'), 4.48 (d, J = 8.7 Hz, 1 H, H-1'ose') ppm.

$^{13}\text{C-NMR}$ (126 MHz, CD_3OD): δ = 61.21 (C-6'ose'), 69.78 (C-4'ose'), 73.44 (C-2'ose'), 76.77 (C-3'ose'), 78.86 (C-5'ose'), 90.77 (C-1'ose') ppm.

Analytical data are in accordance with published data.^[88]

[5-(3-(2-Propyn-1-yloxy)phenyl)-10,15,20-tris(pentafluorophenyl)porphyrinato]zinc(II)
(161):

Under an argon atmosphere, porphyrin **24** (40 mg, 40 μmol) was dissolved in dry DMF (2 ml) to add K_2CO_3 (20 mg, 144 μmol) and propargyl bromid (10.0 μl , 132 μmol). The reaction mixture was stirred at room temperature for 12 h. Water (50 ml) was added and the aqueous layer was extracted with ethyl acetate (3 x 50 ml). The combined organic layers were washed with water (3 x 50 ml), dried over sodium sulfate and the solvent was evaporated under reduced pressure. Further purification was achieved by column chromatography on silica using dichloromethane as the eluent. The desired product (38 mg, 94%) was obtained as a pink crystalline solid.



Melting Point: > 300 °C

$^1\text{H-NMR}$ (700 MHz, CDCl_3): δ = 2.59 (t, J = 2.4 Hz, 2 H, $-\text{C}\equiv\text{C-H}$), 4.79 (d, J = 2.4 Hz, 2 H, $-\text{CH}_2-\text{C}\equiv\text{C}-$), 7.37-7.39 (m, 1 H, Ar-H), 7.68-7.70 (m, 1 H, Ar-H), 7.80-7.82 (m, 1 H, Ar-H), 7.85-7.87 (m, 1 H, Ar-H), 8.93 (d, J = 4.6 Hz, 2 H, $\beta\text{-H}$), 9.01-9.04 (m, 4 H, $\beta\text{-H}$), 9.13 (d, J = 4.6 Hz, 2 H, $\beta\text{-H}$) ppm.

$^{13}\text{C-NMR}$ (176 MHz, CDCl_3): δ = 56.13 (CH_2), 75.89 ($\equiv\text{CH}$), 78.39 ($-\text{C}\equiv$), 102.72 ($\text{Ar}_\text{F}-\text{C}_{\text{meso}}$), 103.71 ($\text{Ar}_\text{F}-\text{C}_{\text{meso}}$), 114.96 (Ar-C), 116.46-116.78 ($\text{Ar}_\text{F}-\text{C}_{\text{ipso}}$), 121.46 (Ar-C), 123.33 ($\text{Ar}-\text{C}_{\text{meso}}$), 127.62 (Ar-C), 128.54 (Ar-C), 130.53 ($\beta\text{-C}$), 131.54 ($\beta\text{-C}$), 131.84 ($\beta\text{-C}$), 134.32 ($\beta\text{-C}$), 136.65-136.92 ($\text{Ar}_\text{F}-\text{C}$), 138.13-138.30 ($\text{Ar}_\text{F}-\text{C}$), 141.17-141.34 ($\text{Ar}_\text{F}-\text{C}$), 142.49-142.80 ($\text{Ar}_\text{F}-\text{C}$), 142.98 ($\text{Ar}-\text{C}_{\text{ipso}}$), 145.79-145.87 ($\text{Ar}_\text{F}-\text{C}$), 147.17-147.31 ($\text{Ar}_\text{F}-\text{C}$), 149.70 ($\alpha\text{-C}$), 149.97 ($\alpha\text{-C}$), 150.19 ($\alpha\text{-C}$), 150.92 ($\alpha\text{-C}$), 155.81 ($\text{Ar}-\text{C}_{\text{Opropargyl}}$) ppm.

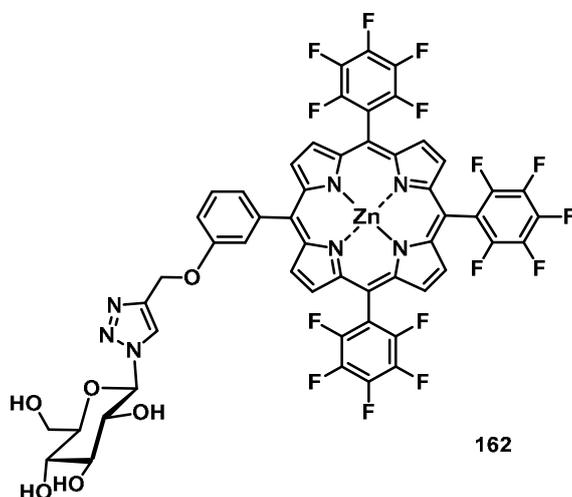
^{19}F -NMR (471 MHz, CDCl_3): $\delta = -161.90 - -161.72$ (m, 6 F, Ar-F_{meta}), -152.24 (t, $J = 20.8$ Hz, 2 F, Ar-F_{para}), -152.17 (t, $J = 20.8$ Hz, 1 F, Ar-F_{para}), $-136.84 - -136.68$ (m, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{47}\text{H}_{16}\text{F}_{15}\text{N}_4\text{OZn}$ $[\text{M} + \text{H}]^+$: 1001.0376, found: 1001.0373.

UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 414 (5.62), 543 (4.26) nm.

[5-{3-((2,3,4,6-Tetraacetyl- β -D-glucopyranosyl)-1H-[1,2,3]-triazol-4-yl)methoxyphenyl}-10,15,20-tris(pentafluorophenyl)porphyrinato]zinc(II) (162):

In a pressure tube, porphyrin **161** (23 mg, 23 μmol) and β -D-glucosyl azide **160** (10 mg, 48 μmol) were dissolved in a mixture of *tert*-butanol/water (10 ml, 1:1). Then $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ (2 mg, 8 μmol) and sodium ascorbate (3 mg, 15 μmol) were added and the reaction mixture was stirred at 70 °C for 24 h. Water (50 ml) was added and the aqueous layer was extracted with ethyl acetate (3 x 50 ml). The combined organic layers were washed with water (3 x 50 ml), dried over sodium sulfate and the solvent was evaporated under reduced pressure. Further purification was achieved by column chromatography on silica using dichloromethane/methanol (95:5) as the eluent. The desired product (25 mg, 91%) was obtained as a pink crystalline solid.



Melting Point: > 300 °C

^1H -NMR (700 MHz, CD_3OD): $\delta = 3.50$ -3.53 (m, 1 H, H-4'ose'), 3.57-3.61 (m, 2 H, H-3'ose', H-5'ose'), 3.72 (dd, $J = 5.5, 12.2$ Hz, 1 H, H-6_B'ose'), 3.88 (dd, $J = 2.2, 12.2$ Hz, 1 H, H-6_A'ose'), 3.94 (t, $J = 9.1$ Hz, 1 H, H-2'ose'), 5.42 (s, 2 H, CH_2), 5.65 (d, $J = 9.1$ Hz, 1 H, H-1'ose'), 7.51-7.53 (m, 1 H, Ar-H), 7.71-7.73 (m, 1 H, Ar-H), 7.87-7.89 (m, 1 H, Ar-H), 7.93-7.95 (m, 1 H, Ar-H), 8.39 (s, 1 H, Ar-H_{triazole}), 8.97-9.00 (m, 2 H, β -H), 9.02 (d, $J = 4.6$ Hz, 1 H, β -H), 9.03 (d, $J = 4.6$ Hz, 1 H, β -H), 9.05 (d, $J = 4.6$ Hz, 2 H, β -H) ppm.

$^{13}\text{C-NMR}$ (176 MHz, CD_3OD): δ = 60.96 (C-6'ose'), 61.14 (CH_2), 69.48 (C-4'ose'), 72.63 (C-2'ose'), 77.09 (C-3'ose'), 79.79 (C-5'ose'), 88.29 (C-1'ose'), 101.69 ($\text{Ar}_F\text{-C}_{\text{meso}}$), 102.81 ($\text{Ar}_F\text{-C}_{\text{meso}}$), 113.92 (Ar-C), 117.02-117.35 ($\text{Ar}_F\text{-C}_{\text{ipso}}$), 121.24 (Ar-C), 122.81 ($\text{Ar-C}_{\text{meso}}$), 123.40 ($\text{Ar-C}_{\text{triazole}}$), 127.21 (Ar-C), 127.84 (Ar-C), 130.05 ($\beta\text{-C}$), 131.04 ($\beta\text{-C}$), 131.34 ($\beta\text{-C}$), 133.32 ($\beta\text{-C}$), 136.67-136.96 ($\text{Ar}_F\text{-C}$), 138.11-138.40 ($\text{Ar}_F\text{-C}$), 141.02-141.30 ($\text{Ar}_F\text{-C}$), 142.45-142.77 ($\text{Ar}_F\text{-C}$), 143.66 ($\text{Ar-C}_{\text{triazole}}$), 143.92 ($\text{Ar-C}_{\text{ipso}}$), 145.81-145.97 ($\text{Ar}_F\text{-C}$), 147.22-147.38 ($\text{Ar}_F\text{-C}$), 149.77 ($\alpha\text{-C}$), 149.96 ($\alpha\text{-C}$), 150.31 ($\alpha\text{-C}$), 150.70 ($\alpha\text{-C}$), 156.66 ($\text{Ar-C}_{\text{OGlc}}$) ppm.

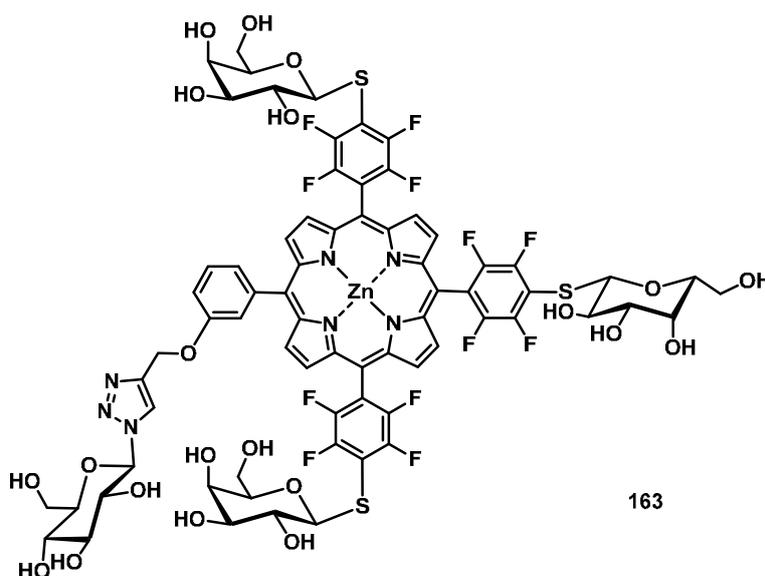
$^{19}\text{F-NMR}$ (471 MHz, CD_3OD): δ = -165.84 – -165.72 (m, 6 F, $\text{Ar-F}_{\text{meta}}$), -156.80 (t, J = 20.8 Hz, 1 F, $\text{Ar-F}_{\text{para}}$), -156.75 (t, J = 20.8 Hz, 2 F, $\text{Ar-F}_{\text{para}}$), -140.13 – -139.98 (m, 6 F, $\text{Ar-F}_{\text{ortho}}$) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{53}\text{H}_{26}\text{F}_{15}\text{N}_7\text{NaO}_6\text{Zn}$ [$\text{M} + \text{Na}$] $^+$: 1228.0894, found: 1228.0886.

UV/Vis (CH_3OH): λ_{max} ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 416 (5.79), 543 (4.32) nm.

[5-{3-(($\beta\text{-D-glucopyranosyl}$)-1*H*-[1,2,3]-triazol-4-yl)methoxyphenyl}-10,15,20-tris{4-(1'-thio- $\beta\text{-D-galactosyl}$)-2,3,5,6-tetrafluorophenyl}porphyrinato]zinc(II) (163):

According to the general procedure XIII, monoglycosylated porphyrin **162** (10 mg, 8.3 μmol) and 1-thio- $\beta\text{-D-galactose}$ sodium salt (6.5 mg, 30 μmol) were reacted under an argon atmosphere in dry DMF (0.5 ml) overnight at room temperature. Purification was achieved by reversed phase column chromatography on silica using methanol/water (75:25) as the eluent. The desired product (11 mg, 77%) was obtained as a violet solid.



163

Melting Point: > 300 °C

¹H-NMR (700 MHz, CD₃OD): δ = 3.50-3.53 (m, 1 H, H-4'ose'), 3.57-3.61 (m, 2 H, H-3'ose', H-5'ose'), 3.66 (dd, J = 3.3, 9.3 Hz, 3 H, H-3''ose'), 3.72 (dd, J = 5.5, 12.2 Hz, 1 H, H-6_B'ose'), 3.73-3.76 (m, 3 H, H-5''ose'), 3.84-3.91 (m, 10 H, 1 x H-6_A'ose', 3 x H-2''ose', 3 x H-6_A''ose', 3 x H-6_B''ose'), 3.94 (t, J = 9.1 Hz, 1 H, H-2'ose'), 4.01-4.03 (m, 3 H, H-4''ose'), 5.10 (d, J = 9.6 Hz, 3 H, H-1''ose'), 5.43 (s, 2 H, CH₂), 5.66 (d, J = 9.1 Hz, 1 H, H-1'ose'), 7.51-7.53 (m, 1 H, Ar-H), 7.70-7.73 (m, 1 H, Ar-H), 7.87-7.89 (m, 1 H, Ar-H), 7.93-7.95 (m, 1 H, Ar-H), 8.39 (s, 1 H, Ar-H_{triazole}), 8.99-9.00 (m, 2 H, β -H), 9.01-9.03 (m, 2 H, β -H), 9.03-9.05 (m, 4 H, β -H) ppm.

¹³C-NMR (176 MHz, CD₃OD): δ = 60.97 (C-6'ose'), 61.13 (CH₂), 61.25 (C-6'ose'), 61.27 (C-6''ose'), 69.18 (C-4''ose'), 69.48 (C-4'ose'), 71.44 (C-2''ose'), 72.63 (C-2'ose'), 74.96 (C-3''ose'), 77.09 (C-3'ose'), 79.77 (C-5'ose'), 79.85 (C-5''ose'), 86.29 (C-1''ose'), 86.34 (C-1'ose'), 88.28 (C-1'ose'), 102.77 (Ar_F-C_{meso}), 103.84 (Ar_F-C_{meso}), 112.32-112.59 (Ar_F-C_{SGal}), 113.90 (Ar-C), 121.26 (Ar-C), 122.51-122.78 (Ar_F-C_{ipso}), 123.40 (Ar-C_{triazole}), 127.19 (Ar-C), 127.85 (Ar-C), 130.13 (β -C), 131.11 (β -C), 131.39 (β -C), 133.20 (β -C), 143.70 (Ar-C_{triazole}), 144.03 (Ar-C_{ipso}), 145.59-145.70 (Ar_F-C), 146.47-146.60 (Ar_F-C), 146.99-147.09 (Ar_F-C), 147.87-147.97 (Ar_F-C), 149.50 (α -C), 149.68 (α -C), 150.02 (α -C), 150.60 (α -C), 156.64 (Ar-C_{OGlc}) ppm.

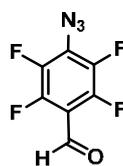
¹⁹F-NMR (471 MHz, CD₃OD): δ = -140.41 – -140.26 (m, 6 F, Ar-F_{meta}), -135.55 – -135.41 (m, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₇₁H₅₉F₁₂N₇NaO₂₁S₃Zn [M + Na]⁺ 1756.1924, found: 1756.1924.

UV/Vis (CH₃OH): λ_{\max} ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 417 (5.88), 544 (4.51) nm.

4-Azido-2,3,5,6-tetrafluorobenzaldehyde (164):

Under argon atmosphere pentafluorobenzaldehyde (1.96 g, 10.0 mmol) and sodium azide (0.72 g, 11.1 mmol) were dissolved in acetone (15 ml) and water (15 ml). Then the mixture was warmed to reflux for 12 h. Water (50 ml) was added and the aqueous layer was extracted with diethyl ether (3 x 50 ml). The combined organic layers were washed with water (3 x 50 ml), dried over sodium sulfate and the solvent was evaporated under reduced pressure. Further purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (1:1) as the eluent. The desired product (1.12 g, 51%) was obtained as a colorless crystalline solid.



164

Melting Point: 45 °C

¹H-NMR (500 MHz, CDCl₃): δ = 10.26 (br s, 1 H, COH) ppm.

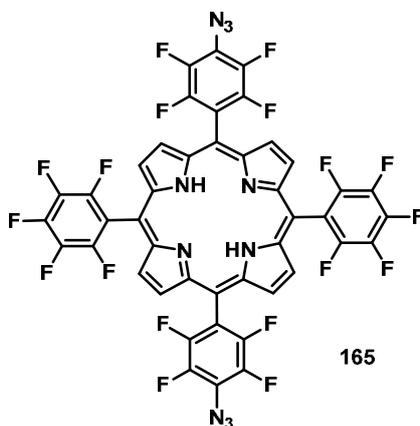
¹³C-NMR (126 MHz, CDCl₃): δ = 110.68 (t, J = 9.81 Hz, Ar-C_{ipso}), 126.21-126.38 (m, Ar_F-C_{para}), 139.46-139.59 (m, Ar_F-C_{meta}), 140.90-141.03 (m, Ar_F-C_{meta}), 146.28-146.41 (m, Ar_F-C_{ortho}), 147.77-147.90 (m, Ar_F-C_{ortho}), 181.60-181.69 (m, COH) ppm.

¹⁹F-NMR (471 MHz, CDCl₃): δ = -150.93 – -150.84 (m, 2 F, Ar-F_{meta}), -144.89 – -144.79 (m, 2 F, Ar-F_{ortho}) ppm.

Analytical data are in accordance with published data.^[89b]

5,15-Bis(4-azido-2,3,5,6-tetrafluorophenyl)-10,20-bis(pentafluorophenyl)porphyrin (165):

According to the general procedure IV, 4-azido-2,3,5,6-tetrafluorobenzaldehyde **164** (219 mg, 1.00 mmol), 5-(pentafluorophenyl)dipyromethane **43** (312 mg, 1.00 mmol), BF₃·Et₂O (0.13 ml, 1.00 mmol) and DDQ (350 mg, 1.54 mmol) were reacted in dry dichloromethane (250 ml). Purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (1:4) as the eluent to obtain the desired product (71 mg, 14%) as a violet solid.



Melting Point: 212 °C

¹H-NMR (700 MHz, CDCl₃): δ = -2.88 (br s, 2 H, NH), 8.94 (br s, 4 H, β -H), 8.97 (br s, 4 H, β -H) ppm.

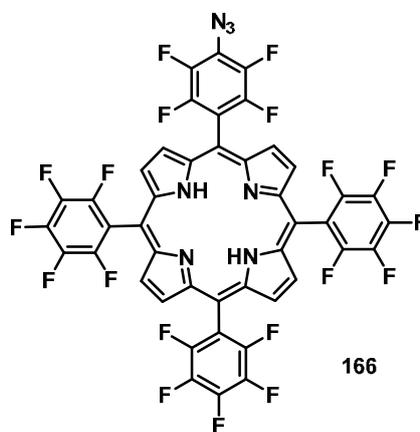
¹³C-NMR (176 MHz, CDCl₃): δ = 103.55 (Ar_F-C_{meso}), 104.12 (Ar_F-C'_{meso}), 115.59 (t, J = 19.1 Hz, Ar_F-C_{ipso}), 115.78 (t, J = 19.0 Hz, Ar_F-C'_{ipso}), 121.55 (t, J = 11.8 Hz, Ar_F-C'_{para}), 130.51-131.73 (β -C), 136.73-137.03 (Ar_F-C), 138.18-138.43 (Ar_F-C), 139.67-139.90 (Ar_F-C), 141.09-141.33 (Ar_F-C), 141.44-141.69 (Ar_F-C), 142.92-143.13 (Ar_F-C), 145.65-145.91 (Ar_F-C), 147.06-147.35 (Ar_F-C) ppm.

^{19}F -NMR (471 MHz, CDCl_3): $\delta = -161.23$ (td, $J = 7.2, 22.9$ Hz, 4 F, Ar-F_{meta}), 151.46 (dd, $J = 10.0, 22.6$ Hz, 4 F, Ar-F_{meta}), -151.18 (t, $J = 20.7$ Hz, 2 F, Ar-F_{para}), -137.05 (dd, $J = 10.0, 22.6$ Hz, 4 F, Ar-F_{ortho}), -136.39 (dd, $J = 7.2, 24.2$ Hz, 4 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{44}\text{H}_{11}\text{F}_{18}\text{N}_{10}$ $[\text{M} + \text{H}]^+$: 1021.0881, found: 1021.0872.

5-(4-Azido-2,3,5,6-tetrafluorophenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (166), 5,15-Bis(4-azido-2,3,5,6-tetrafluorophenyl)-10,20-bis(pentafluorophenyl)porphyrin (165), 5,10,15-Tris(4-azido-2,3,5,6-tetrafluorophenyl)-20-(pentafluorophenyl)porphyrin (167) and 5,10,15,20-Tetrakis(4-azido-2,3,5,6-tetrafluorophenyl)porphyrin (168):

According to the general procedure IV, 4-azido-2,3,5,6-tetrafluorobenzaldehyde **164** (219 mg, 1.00 mmol), 5-(pentafluorophenyl)dipyrromethane **43** (312 mg, 1.00 mmol), TFA (77 μl , 1.00 mmol) and DDQ (350 mg, 1.54 mmol) were reacted in dry dichloromethane (250 ml). Purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (1:4) as the eluent. The first band gave the monoazidated porphyrin **166** (10 mg, 2%) in form of violet crystals, the second band gave diazidated *trans*-porphyrin **165** (26 mg, 5%) in form of violet crystals, the third band gave triazidated porphyrin **167** (11 mg, 2%) in form of violet crystals and the fourth band gave tetraazidated porphyrin **168** (5 mg, 1%) in form of violet crystals.



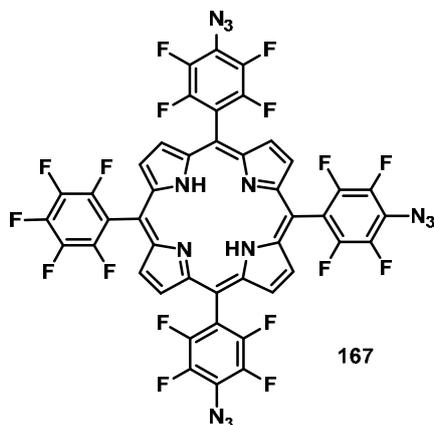
Melting Point: 237 °C

^1H -NMR (700 MHz, CDCl_3): $\delta = -2.87$ (br s, 2 H, NH), 8.96 (br s, 6 H, β -H), 8.97-8.99 (m, 2 H, β -H) ppm.

^{13}C -NMR (176 MHz, CDCl_3): $\delta = 103.61$ (Ar_F-C_{meso}), 104.20 (Ar_F-C'_{meso}), 115.46-115.87 (Ar_F-C_{ipso}, Ar_F-C'_{ipso}), 121.55-121.69 (Ar_F-C'_{para}), 130.49-132.07 (β -C), 136.74-137.04 (Ar_F-C), 138.15-138.46 (Ar_F-C), 139.73-139.82 (Ar_F-C), 141.16-141.25 (Ar_F-C), 141.46-141.68 (Ar_F-C), 142.87-143.21 (Ar_F-C), 145.67-145.93 (Ar_F-C), 147.07-147.37 (Ar_F-C) ppm.

^{19}F -NMR (471 MHz, CDCl_3): $\delta = -161.20$ (td, $J = 7.3, 23.0$ Hz, 6 F, Ar-F_{meta}), 151.44 (dd, $J = 10.0, 22.5$ Hz, 2 F, Ar-F_{meta}), -151.12 (t, $J = 20.8$ Hz, 2 F, Ar-F_{para}), -151.11 (t, $J = 20.8$ Hz, 1 F, Ar-F_{para}), -137.05 (dd, $J = 10.0, 22.5$ Hz, 2 F, Ar-F_{ortho}), -136.39 (dd, $J = 7.3, 23.9$ Hz, 6 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{44}\text{H}_{11}\text{F}_{19}\text{N}_7$ $[\text{M} + \text{H}]^+$: 998.0773, found: 998.0739.



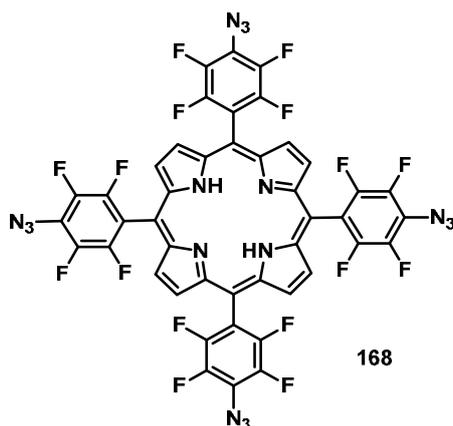
Melting Point: 187 °C

^1H -NMR (700 MHz, CDCl_3): $\delta = -2.86$ (br s, 2 H, NH), 8.93-8.95 (m, 2 H, β -H), 8.97 (br s, 6 H, β -H) ppm.

^{13}C -NMR (176 MHz, CDCl_3): $\delta = 103.50$ (Ar_F-C_{meso}), 104.08 (Ar_F-C'_{meso}), 115.51-115.94 (Ar_F-C_{ipso}, Ar_F-C'_{ipso}), 121.47-121.65 (Ar_F-C'_{para}), 130.72-132.14 (β -C), 136.80-136.94 (Ar_F-C), 138.09-138.39 (Ar_F-C), 139.73-139.82 (Ar_F-C), 141.16-141.25 (Ar_F-C), 141.45-141.80 (Ar_F-C), 142.84-143.20 (Ar_F-C), 145.62-145.95 (Ar_F-C), 147.06-147.35 (Ar_F-C) ppm.

^{19}F -NMR (471 MHz, CDCl_3): $\delta = -161.26$ (td, $J = 7.6, 23.1$ Hz, 2 F, Ar-F_{meta}), 151.48 (dd, $J = 9.8, 22.6$ Hz, 6 F, Ar-F_{meta}), -151.21 (t, $J = 20.8$ Hz, 1 F, Ar-F_{para}), -137.04 (dd, $J = 9.8, 22.6$ Hz, 6 F, Ar-F_{ortho}), -136.38 (dd, $J = 7.6, 23.1$ Hz, 2 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{44}\text{H}_{11}\text{F}_{17}\text{N}_{13}$ $[\text{M} + \text{H}]^+$: 1044.0989, found: 1044.0957.



Melting Point: > 300 °C

¹H-NMR (700 MHz, CDCl₃): δ = -2.88 (br s, 2 H, NH), 8.95 (s, 8 H, β -H) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 104.02 (Ar_F-C_{meso}), 115.85 (t, J = 19.4 Hz, Ar_F-C_{ipso}), 121.53 (t, J = 12.0 Hz, Ar_F-C_{para}), 131.33 (β -C), 139.66-139.86 (Ar_F-C), 141.09-141.27 (Ar_F-C), 145.66-145.81 (Ar_F-C), 147.07-147.22 (Ar_F-C) ppm.

¹⁹F-NMR (471 MHz, CDCl₃): δ = -151.50 (dd, J = 10.0, 22.7 Hz, 8 F, Ar-F_{meta}), -137.03 (dd, J = 10.0, 22.7 Hz, 8 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₁₁F₁₆N₁₆ [M + H]⁺: 1067.1097, found: 1067.1070.

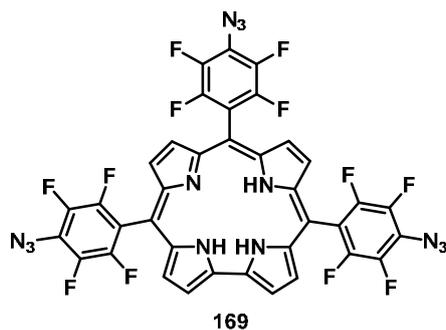
UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 414 (5.11), 509 (3.99), 584 (3.54), 639 (2.71) nm.

5,10,15,20-Tetrakis(4-azido-2,3,5,6-tetrafluorophenyl)porphyrin (168):

According to the general procedure **III**, 4-azido-2,3,5,6-tetrafluorobenzaldehyde **164** (110 mg, 0.50 mmol), pyrrole (35 μ l, 0.50 mmol), BF₃·Et₂O (0.65 μ l, 0.50 mmol), and DDQ (285 mg, 1.25 mmol) were reacted in dry dichloromethane (125 ml). Purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (1:1) as the eluent to obtain the desired product (128 mg, 24%) in form of violet crystals.

5,10,15-Tris(4-azido-2,3,5,6-tetrafluorophenyl)corrole (169):

According to the general procedure **X**, 4-azido-2,3,5,6-tetrafluorobenzaldehyde **164** (274 mg, 1.25 mmol) and pyrrole (0.17 ml, 2.50 mmol) were dissolved in methanol (50 ml). Then a mixture of HCl (36%, 1.05 ml) and water (50 ml) was added and it was stirred at room temperature for one hour. Then the mixture was extracted three times with dichloromethane. The combined organic layers were washed three times with water, dried over sodium sulfate and the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (80 ml) and DDQ (283 mg, 1.25 mmol) was added. After 1 hour stirring at 50 °C, purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (1:1) and a subsequent recrystallization from dichloromethane/*n*-pentane to obtain the desired product (26 mg, 12%) as a violet solid.



Melting Point: 89 °C

¹H-NMR (700 MHz, CDCl₃): δ = 8.60 (br s, 2 H, β -H), 8.62 (d, J = 4.3 Hz, 2 H, β -H), 8.80 (d, J = 4.3 Hz, 2 H, β -H), 9.12 (d, J = 3.9 Hz, 2 H, β -H) ppm.

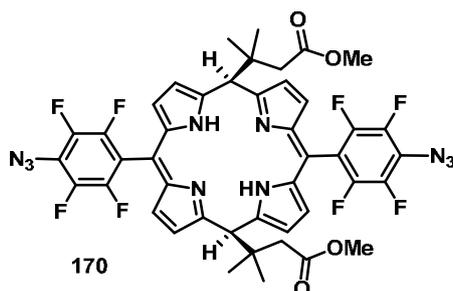
¹³C-NMR (176 MHz, CDCl₃): δ = 94.86 (Ar_F-C_{meso}), 113.90-114.06 (Ar_F-C_{ipso}), 116.23 (t, J = 19.5 Hz, Ar_F-C_{ipso}), 117.09-117.26 (β -C), 120.68-120.96 (Ar_F-C_{para}), 126.05-126.38 (β -C), 127.44-127.70 (β -C), 139.74-139.94 (Ar_F-C), 140.06-140.20 (Ar_F-C), 141.21-141.36 (Ar_F-C), 141.47-141.64 (Ar_F-C) ppm.

¹⁹F-NMR (471 MHz, CDCl₃): δ = -151.88 (dd, J = 10.0, 22.9 Hz, 2 F, Ar-F_{meta}), -151.51-151.36 (m, 4 F, Ar-F_{meta}), -138.29-138.15 (m, 4 F, Ar-F_{ortho}), -137.58 (dd, J = 10.0, 22.9 Hz, 2 F, Ar-F_{ortho}) ppm.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 412 (5.03), 563 (4.21), 605 (3.98) nm.

5,15-Bis(3-methoxy-1,1-dimethyl-3-oxopropyl)-10,20-bis(4-azido-2,3,5,6-tetrafluorophenyl)-calix[4]phyrin(1.1.1.1) (170), 5-(3-methoxy-1,1-dimethyl-3-oxopropyl)-15-(5-[4,4-dimethyl-dihydrofuran-2(3H)-one]-yl)-10,20-bis(4-azido-2,3,5,6-tetrafluorophenyl)calix[4]-phyrin(1.1.1.1) (171) and α,α,α -5,15,25-tris(3-methoxy-1,1-dimethyl-3-oxopropyl)-10,20,30-tris(4-azido-2,3,5,6-tetrafluorophenyl)calix[6]phyrin(1.1.1.1.1.1) (172):

According to the general procedure XI, 4-azido-2,3,5,6-tetrafluorobenzaldehyde **164** (219 mg, 1.00 mmol), 5-(3-methoxy-1,1-dimethyl-3-oxopropyl)dipyrromethane **141** (260 mg, 1.00 mmol), TFA (75 μ l, 1.00 mmol), DDQ (345 mg, 1.50 mmol) and triethylamine (1.25 ml, 9.02 mmol) were reacted in dry dichloromethane (250 ml). Purification was achieved by column chromatography on silica using dichloromethane/*n*-hexane (1:1 to 9:1) as the eluent and subsequent recrystallization from dichloromethane/*n*-pentane. The first band gave calix[4]phyrin **170** (83 mg, 18%) in form of orange crystals, the second band gave *meso*-spirolactone calix[4]phyrin **171** (68 mg, 15%) in form of orange crystals and the third band gave calix[6]phyrin **172** (82 mg, 18%) in form of orange-red crystals.



Melting Point: 126 °C

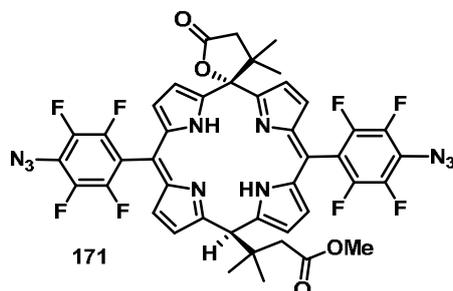
¹H-NMR (700 MHz, CDCl₃): δ = 1.27 (s, 12 H, 4 x CH₃), 2.44 (s, 4 H, 2 x CH₂), 3.71 (s, 6 H, 2 x OCH₃), 4.48 (s, 2 H, Ar-H_{meso}), 6.32 (d, J = 4.2 Hz, 4 H, β -H), 6.36 (d, J = 4.2 Hz, 4 H, β -H), 12.92 (br s, 2 H, 2 x NH) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 25.77 (CH₃), 38.96 (C(CH₃)₂), 44.64 (CH₂), 49.79 (Ar-C_{meso}), 51.32 (OCH₃), 112.13-112.35 (Ar_F-C_{ipso}), 120.43-120.57 (Ar_F-C_{para}), 121.45 (β -C), 122.77 (Ar_F-C_{meso}), 126.59 (β -C), 139.47-139.66 (Ar_F-C), 140.90-141.08 (Ar_F-C), 144.12-144.21 (Ar_F-C), 145.51-145.62 (Ar_F-C), 172.50 (C=O) ppm.

¹⁹F-NMR (471 MHz, CDCl₃): δ = -151.38 (dd, J = 9.8, 22.2 Hz, 2 F, Ar-F_{meta}), -151.01 (dd, J = 9.8, 22.2 Hz, 2 F, Ar-F_{meta}), -138.51 (dd, J = 9.3, 22.0 Hz, 2 F, Ar-F_{ortho}), -138.10 (dd, J = 9.3, 22.0 Hz, 2 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₄H₃₄F₈N₁₀NaO₄ [M + Na]⁺: 941.2534, found: 941.2547.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 441 (4.73) nm.



Melting Point: 119 °C

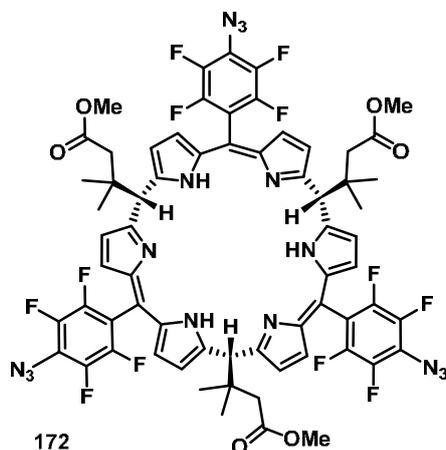
¹H-NMR (700 MHz, CDCl₃): δ = 1.27 (s, 6 H, 2 x CH₃ lactone), 1.30 (s, 6 H, 2 x CH₃), 2.45 (s, 2 H, CH₂), 2.56 (s, 2 H, CH₂ lactone), 3.72 (s, 3 H, OCH₃), 4.55 (s, 1 H, Ar-H_{meso}), 6.37 (d, J = 4.1 Hz, 2 H, β -H), 6.40 (d, J = 3.9 Hz, 2 H, β -H), 6.42 (d, J = 3.7 Hz, 2 H, β -H), 6.53 (d, J = 3.9 Hz, 2 H, β -H), 12.82 (br s, 2 H, 2 x NH) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 24.14 (CH₃ lactone), 25.84 (CH₃), 39.63 (C(CH₃)₂), 42.85 (CH₂ lactone), 44.67 (CH₂), 46.12 (C(CH₃)₂ lactone), 49.65 (Ar-C_{meso}), 51.42 (OCH₃), 89.09 (Ar-C_{meso} lactone), 111.66-111.88 (Ar_F-C_{ipso}), 117.16 (β -C), 120.78-120.92 (Ar_F-C_{para}), 122.30 (β -C), 123.72 (Ar_F-C_{meso}), 126.87 (β -C), 127.53 (β -C), 139.47-139.70 (Ar_F-C), 140.90-141.13 (Ar_F-C), 144.03-144.12 (Ar_F-C), 145.45-145.54 (Ar_F-C), 172.32 (C=O), 175.29 (C=O) ppm.

¹⁹F-NMR (471 MHz, CDCl₃): δ = -151.13 (dd, J = 9.8, 22.2 Hz, 2 F, Ar-F_{meta}), -150.67 (dd, J = 9.8, 22.2 Hz, 2 F, Ar-F_{meta}), -138.91 (dd, J = 9.2, 21.9 Hz, 2 F, Ar-F_{ortho}), -138.10 (dd, J = 9.2, 21.9 Hz, 2 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₄₃H₃₀F₈N₁₀NaO₄ [M + Na]⁺: 925.2221, found: 925.2252.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 438 (4.99) nm.



Melting Point: 142 °C

¹H-NMR (700 MHz, CDCl₃): δ = 1.28 (s, 18 H, 6 x CH₃), 2.51 (s, 6 H, 3 x CH₂), 3.77 (s, 9 H, 3 x OCH₃), 4.85 (s, 3 H, Ar-H_{meso}), 6.40 (d, J = 4.3 Hz, 6 H, β -H), 6.44 (d, J = 4.3 Hz, 6 H, β -H) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 25.53 (CH₃), 38.23 (C(CH₃)₂), 45.38 (CH₂), 51.33 (OCH₃), 55.09 (Ar-C_{meso}), 111.43-111.64 (Ar_F-C_{ipso}), 118.41 (β -C), 120.42-120.54 (Ar_F-C_{para}), 122.23 (Ar_F-C_{meso}), 127.25 (β -C), 138.63 (α -C), 139.46-139.72 (Ar_F-C), 140.84-141.14 (Ar_F-C), 143.91-144.03 (Ar_F-C), 145.32-145.45 (Ar_F-C), 156.48 (α -C), 172.46 (C=O) ppm.

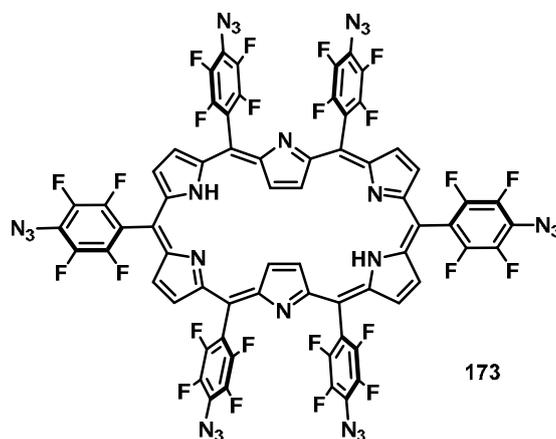
¹⁹F-NMR (471 MHz, CDCl₃): δ = -151.40 (dd, J = 9.8, 22.1 Hz, 3 F, Ar-F_{meta}), -151.07 (dd, J = 9.8, 22.1 Hz, 3 F, Ar-F_{meta}), -138.75 (dd, J = 9.2, 21.9 Hz, 3 F, Ar-F_{ortho}), -137.97 (dd, J = 9.2, 21.9 Hz, 3 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₆₆H₅₁F₁₂N₁₅NaO₆ [M + Na]⁺: 1400.3853, found: 1400.3863.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 408 (5.01), 447 (4.75), 502 (4.11) nm.

meso-5,10,15,20,25,30-hexakis(4-azido-2,3,5,6-tetrafluorophenyl)-[26]hexaphyrin (173) and meso-5,10,15,20,25-Pentakis(4-azido-2,3,5,6-tetrafluorophenyl)-substituted *N*-fused [22]-pentaphyrin (174):

According to the general procedure **XII**, 4-azido-2,3,5,6-tetrafluorobenzaldehyde **164** (438 mg, 2.00 mmol), pyrrole (139 μ l, 2.00 mmol), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (50 μ l, 2.5 N), and DDQ (1.14 g, 5.02 mmol) were reacted in dry dichloromethane (30 ml). Purification was achieved by repeated column chromatography on silica using dichloromethane/*n*-hexane (1:4 to 1:0) as the eluent. The first band gave porphyrin **168** (48 mg, 9%) in form of violet crystals after recrystallization from dichloromethane/methanol, the second deep purple band gave [26]hexaphyrin **173** (64 mg, 12%) in form of shiny crystals after recrystallization from dichloromethane/*n*-pentane and the third red band gave *N*-fused [22]pentaphyrin **174** (69 mg, 13%) in form of shiny crystals after recrystallization from dichloromethane/*n*-pentane.



Melting Point: > 300 °C

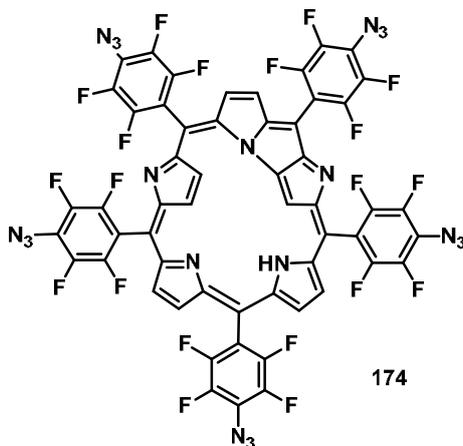
$^1\text{H-NMR}$ (700 MHz, CDCl_3): δ = -2.43 (br s, 4 H, inner β -H), -1.99 (br s, 2 H, NH), 9.14 (d, J = 4.6 Hz, 4 H, outer β -H), 9.48 (d, J = 4.6 Hz, 4 H, outer β -H) ppm.

$^{13}\text{C-NMR}$ (176 MHz, CDCl_3): δ = 106.64 ($\text{Ar}_F\text{-C}$), 117.81 ($\text{Ar}_F\text{-C}$), 118.32-118.50 ($\text{Ar}_F\text{-C}$), 121.01-121.14 ($\text{Ar}_F\text{-C}$), 122.09-122.46 ($\text{Ar}_F\text{-C}$), 122.84 (inner β -C), 125.31-125.39 ($\text{Ar}_F\text{-C}$), 132.43 (outer β -C), 134.86 (outer β -C), 138.85-139.39 ($\text{Ar}_F\text{-C}$), 139.78-140.47 ($\text{Ar}_F\text{-C}$), 141.04-141.57 ($\text{Ar}_F\text{-C}$), 145.38-145.86 ($\text{Ar}_F\text{-C}$), 146.71-147.13 ($\text{Ar}_F\text{-C}$), 147.21-147.64 ($\text{Ar}_F\text{-C}$), 147.78-148.07 ($\text{Ar}_F\text{-C}$), 148.53-148.95 ($\text{Ar}_F\text{-C}$), 149.55 (outer α -C), 149.62 (outer α -C), 156.27 (inner α -C) ppm.

$^{19}\text{F-NMR}$ (471 MHz, CDCl_3): δ = -152.97 – -152.87 (m, 8 F, Ar-F_{meta}), -150.71 – -150.63 (m, 4 F, $\text{Ar-F}'_{meta}$), -137.20 – -137.12 (m, 8 F, Ar-F_{ortho}), -137.02 – -136.94 (m, 4 F, $\text{Ar-F}'_{ortho}$) ppm.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{66}\text{H}_{15}\text{F}_{24}\text{N}_{24}$ [$\text{M} + \text{H}$] $^+$: 1599.1528, found: 1599.1482.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 573 (4.89), 715 (3.92), 769.0 (3.47) nm.



Melting Point: > 300 °C

¹H-NMR (700 MHz, CDCl₃): δ = -2.36 (s, 1 H, inner β -H), 1.26 (br s, 1 H, NH), 1.64 (d, J = 4.3 Hz, 1 H, inner β -H), 2.13 (d, J = 4.3 Hz, 1 H, inner β -H), 8.36 (d, J = 4.6 Hz, 1 H, outer β -H), 8.39 (d, J = 4.6 Hz, 1 H, outer β -H), 8.43 (d, J = 4.6 Hz, 1 H, outer β -H), 8.60-8.62 (m, 1 H, outer β -H), 9.13-9.16 (m, 2 H, outer β -H) ppm.

¹³C-NMR (176 MHz, CDCl₃): δ = 99.00 (Ar_F-C), 101.42 (Ar_F-C), 108.08-108.27 (Ar_F-C), 110.16 (Ar_F-C), 112.86 (Ar_F-C), 113.52-113.73 (Ar_F-C), 114.61-114.77 (Ar_F-C), 115.56-115.74 (Ar_F-C), 118.94-119.16 (Ar_F-C), 120.22-120.36 (Ar_F-C), 120.68 (Ar_F-C), 121.17-121.30 (Ar_F-C), 121.73-122.08 (Ar_F-C), 122.46 (Ar_F-C), 122.61 (Ar_F-C), 123.06 (outer β -C), 129.24 (outer β -C), 131.27 (outer β -C), 131.34 (outer β -C), 132.31 (Ar_F-C), 132.41 (outer β -C), 132.72 (inner β -C), 133.20 (inner β -C), 133.64 (outer β -C), 136.28 (Ar_F-C), 139.65-140.02 (Ar_F-C), 140.45-140.87 (Ar_F-C), 141.10-141.41 (Ar_F-C), 141.91-142.28 (Ar_F-C), 144.29-145.36 (Ar_F-C), 145.73-146.34 (Ar_F-C), 146.57 (outer α -C), 148.27 (outer α -C), 151.00 (outer α -C), 151.69 (outer α -C), 153.08 (outer α -C), 159.60 (inner α -C), 160.17 (inner α -C), 160.61 (inner α -C), 160.96 (inner α -C) ppm.

¹⁹F-NMR (471 MHz, CDCl₃): δ = -152.98 – -152.87 (m, 2 F, Ar-F_{meta}), -152.62 (dd, J = 9.0, 20.4 Hz, 1 F, Ar-F_{meta}), -152.32 (dd, J = 9.0, 20.5 Hz, 1 F, Ar-F_{meta}), -151.68 – -151.57 (m, 2 F, Ar-F_{meta}), -150.73 – -150.56 (m, 4 F, Ar-F_{meta}), -140.80 – -140.74 (m, 1 F, Ar-F_{ortho}), -140.17 – -140.09 (m, 1 F, Ar-F_{ortho}), -138.61 (dd, J = 8.9, 22.7 Hz, 1 F, Ar-F_{ortho}), -138.10 (dd, J = 8.8, 22.6 Hz, 1 F, Ar-F_{ortho}), -137.82 – -137.76 (m, 2 F, Ar-F_{ortho}), -137.52 (dd, J = 9.3, 22.7 Hz, 1 F, Ar-F_{ortho}), -137.01 (dd, J = 9.0, 22.1 Hz, 1 F, Ar-F_{ortho}), -136.24 – -136.15 (m, 1 F, Ar-F_{ortho}), -135.15 – -135.04 (m, 1 F, Ar-F_{ortho}) ppm.

HRMS (ESI-TOF): m/z calcd. for C₅₅H₁₁F₂₀N₂₀ [M + H]⁺: 1331.1156, found: 1331.1099.

UV/Vis (CH₂Cl₂): λ_{\max} (log ϵ /dm³ mol⁻¹ cm⁻¹): 350 (4.59), 461 (4.67), 553 (4.85), 991 (3.27) nm.

5.4 Typical Procedure for *In Vitro* Assays

The photodynamic activity of the synthesized glyco-porphyrinoid was tested by Dr. SUSANNA GRÄFE (biolitec research GmbH) against A431, A253, CAL-27, L929 and HT29 cell lines. The cell lines were grown in DMEM, supplemented with 10% FCS, 1% penicillin and 1% streptomycin and then stored in a humidified incubator (37 °C, 5% CO₂ in air). Then a stock solution of the photosensitizer (2 mmol) was prepared in DMSO or ethanol which was stored in the dark at 4 °C. DMEM (without phenol red) supplemented with 10% FCS was used for further dilution to obtain the desired standardized photosensitizer concentration of 2 µM and 10 µM. In micro plates 2 x 10⁴ cells/well were seeded with fresh medium (DMEM, without phenol red, containing 10% FCS), then they were incubated with the corresponding photosensitizer solutions (no PS as blank test, 2 µM, 10 µM) for 24 h and finally washed with fresh DMEM medium supplemented with 10% FCS (to remove any PS not taken up by the cells). Irradiation was accomplished at room temperature with a diode laser (Ceralas PDT 652, biolitec research GmbH) possessing a radiation energy of 50 J/cm². After irradiation the cells were incubated for another 24 h. The Cell viability was determined by XTT assay. Therefore 0.1 ml of a PMS solution (383 mg PMS in 1 ml PBS buffer) as an activation reagent were added to 5 ml of a XTT solution (500 mg XTT in 500 ml PBS buffer) at a temperature of 37 °C. Then DMEM medium supplemented with 10% FCS and activated XTT solution were added to the cells. The cells were incubated for another 3 h. Finally the absorbance of the samples was measured with a Tecan Infinite 200 microplate reader at a wavelength of 490 nm. For the measurement of the reference absorbance a wavelength of 630-690 nm was used.

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7 APPENDIX

7.1 Abbreviations and Acronyms

The listed abbreviations are used throughout the whole dissertation. For all porphyrinoid systems the letters 'A' or 'B', as in A₃B₃-hexaphyrin or A₃B-porphyrin, are referring to the corresponding substitution patterns in *meso*-position. The mentioned numbers of compounds are written in a bold font.

δ	chemical shift
d	doublet
COSY	correlation spectroscopy
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dd	doublet of doublets
ddd	doublet of doublet of doublets
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DMEM	Dulbecco modified eagle medium
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
DPM	dipyrromethane
EA	elemental analysis
eq	equivalents
ESI-TOF	electrospray ionization time of flight
FCS	fetal calf serum
Gal	galactose
Glc	glucose
GP	general procedure
HMBC	heteronuclear multiple bond correlation
HMQC	heteronuclear multiple quantum correlation
HRMS	high resolution mass spectrometry
Hz	Hertz
IR	infrared
ISC	intersystem crossing
Lac	lactose

m	multiplet
Man	mannose
MSA	methane sulfonic acid
ν	wavenumber
PBS	phosphate buffered saline
$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	Bis(triphenylphosphine)palladium(II) dichloride
PDT	photodynamic therapy
PFP	pentafluorophenyl
PMS	5-methylphenazinium methyl sulfate
PS	photosensitizer
<i>p</i> -TSA	<i>para</i> -toluenesulfonic acid
rt	room temperature
s	singlet
$\text{S}_{\text{N}}\text{Ar}$	nucleophilic aromatic substitution
t	triplet
TBAHS	tetrabutylammonium hydrogen sulfate
THF	tetrahydrofuran
TFA	trifluoroacetic acid
TLC	thin layer chromatography
UV-Vis	ultraviolet-visible
XTT	2,3-bis(2-methoxy-4-nitro-5-sulfophenyl)-5-[(phenylamino)- carbonyl]-2H-tetrazolium salt

7.2 Hazardous Substances Directory

Compound	GHS Code	Hazard and Precautionary Statements
acetic acid (glacial)	GHS02, GHS05	H226-H314, P280-P305+P351+P338-P310
acetone	GHS02, GHS07	H225-H319-H336, P210-P305+P351+P338-P370+P378-P403+P235
acetone-d ₆	GHS02, GHS07	H225-H319-H336, P210-P261-P305+P351+P338
acetonitrile	GHS02, GHS07	H225-H302+H312+H332-H319, P210-P261-P280-P305+P351+P338-P370+P378-P403+P235
3-acetoxybenzaldehyde	GHS07	H315-H319, P264-P280-P302+P352+P332+P313+P362+P364-P305+P351+P338+P337+P313
4-acetoxybenzaldehyde	GHS07	H315-H319-H335, P264-P280-P302+P352+P332+P313+P362+P364-P305+P351+P338+P337+P313
benzaldehyde	GHS07	H302, P264-P270-P301+P312+P330-P501
3,5-bis(tri-fluoromethyl)-benzaldehyde	GHS07	H315-H319-H335, P210-P264-P280-P302+P352+P332+P313+P362+P364-P305+P351+P338+P337+P313
boron trifluoride etherate	GHS02, GHS05, GHS06, GHS08	H226-H302-H314-H330-H372, P260-P280-P284-P305+P351+P338-P310
tert-butanol	GHS02, GHS07	H225-H319-H332-H335-H336, P210-P261-P305+P351+P338-P370+P378-P403+P235
cerium(IV) sulfate	GHS07	H315-H319, P305+P351+P338
chloroform-d ₁	GHS06, GHS08	H302-H315-H319-H331-H351-H361D-H372, P260-P280-P301+P312+P330-P304+P340+P311-P305+P351+P338-P403
copper(II) acetat	GHS05, GHS07, GHS09	H302-H314-H410, P260-P280-P301+P312+P330-P303+P361+P353-P304+P340+P310-P305+P351+P338
copper(I) iodide	GHS05, GHS07, GHS09	H302-H315-H317-H318-H335-H410, P280-P301+P312+P330-P305+P351+P338+P310
copper(II) sulfate	GHS07, GHS09	H302-H315-H319-H410, P273-P305+P351+P338-P501
1,8-diazabicyclo[5.4.0]-undec-7-ene	GHS05, GHS06	H290-H301-H314-H412, P273-P280-P301+P310-P305+P351+P338-P310
2,3-dichloro-5,6-dicyano-1,4-benzoquinone	GHS06	H301+H311+H331-H315-H319, P261-P280-P301+P310+P330-P302+P352+P312+P361+P364-P304+P340+P311-P305+P351+P338+P337+P313

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dichloromethane	GHS07, GHS08	H315-H319-H335-H336-H351-H373, P268-P281-P305+P351+P338
diethyl ether	GHS02, GHS07	H224-H302-H336, P210-P240-P403+P235
<i>N,N</i> -dimethylformamide	GHS02, GHS07, GHS08	H226-H312+H332-H319-H360D, P201-P210-P261-P280-P308+P313-P370+P378
ethanol	GHS02, GHS07	H225-H319, P210-P280-P305+P351+P338-P337+P313-P403+P235
ethyl acetate	GHS02, GHS07	H225-H319-H336, P210-P233-P240-P305+P351+P338-P403+P235
ethylenediamine	GHS02, GHS05, GHS06, GHS08	H226-H302+H332-H311-H314-H317-H334-H412, P210-P260-P303+P361+P353-P305+P351+P338-P370+P378
heptanal	GHS02, GHS07	H226-H315-H319-H412, P210-P241+P242+P243-P280-P302+P352+P332+P313+P362+P364-P305+P351+P338+P337+P313-P370+P378
<i>n</i> -hexane	GHS02, GHS07, GHS08, GHS09	H225-H304-H315-H336-H361F-H373-H411, P210-P261-P273-P281-P301+P310-P331
<i>n</i> -hexanol	GHS02, GHS07	H226-H302+H312-H319, P210-P280-P301+P312+P330-P305+P351+P338-P370+P378
hydrochloric acid (36%)	GHS05, GHS07	H290-H314-H335, P261-P280-P305+P351+P338-P310
3-hydroxybenzaldehyde	GHS07	H315-H319, P264-P280-P302+P352+P332+P313+P362+P364-P305+P351+P338+P337+P313
4-hydroxybenzaldehyde	GHS07	H315-H319-H335, P264-P280-P302+P352+P332+P313+P362+P364-P305+P351+P338+P337+P313
methane sulfonic acid	GHS05, GHS07	H290-H302+H312-H314-H335, P260-P280-P301+P312+P330-P303+P361+P353-P304+P340+P310-P305+P351
methanol	GHS02, GHS06, GHS08	H225-H301-H311-H331-H370, P210-P260-P280-P301+P310-P311
methanol- <i>d</i> ₄	GHS02, GHS06, GHS08	H225-H301+H311+H331-H370, P210-P280-P302+P352+P312-P304+P340+P312-P370+P378-P403+P235
4-methoxybenzaldehyde	GHS07	H302-H315-H319, P264-P270-P280-P301+P312+P330-P302+P352+P332+P313+P362+P364-P305+P351+P338+P337+P313
4-(methoxycarbonyl)-benzaldehyde	GHS07	H315-H319, P264-P280-P302+P352+P332+P313+P362+P364-P305+P351+P338+P337+P313

APPENDIX

osmium tetroxide	GHS06, GHS08	H301-H311-H331-H351, P261-P280-P301+P310-P311
pentafluorobenzaldehyde	GHS06	H301+H311+H331-H315-H319, P261-P280-P301+P310+330-P302+P352+P312+P361+P364-P304+P340+P311-P305+P351+P338+P337+P313
<i>n</i> -pentane	GHS02, GHS07, GHS08, GHS09	H225-H304-H336-H411, P210-P261-P273-P301+P310-P331
potassium carbonate	GHS07	H315-H319-H335, P305+P351+P338
potassium hydroxide	GHS05, GHS07	H290-H302-H314, P280-P301+P312+P330-P303+P361+P353-P304+P340+P310-P305+P351+P338
potassium permanganate	GHS03, GHS07	H272-H315-H319-H335, P220-P261-P305+P351+P338
propargyl alcohol	GHS02, GHS05, GHS06, GHS09	H226-H301-H311-H314-H331-H411, P261-P273-P280-P301+P310-P305+P351+P338-P310
propargyl bromid	GHS02, GHS06, GHS08	H225-H301-H304-H315-H319-H335-H336-H361D-H373, P210-P261-P281-P301+P310-P305+P351+P338-P331
pyridine	GHS02, GHS07	H225-H302+H312+H332-H315-H319, P210-P261-P280-P305+P351+P338-P370+P378-P403+P235
pyrrole	GHS02, GHS05, GHS06	H226-H301-H318-H332, P280-P301+P310-P305+P351+P338
sodium azide	GHS06, GHS08, GHS09	H300+H310-H373-H410, P273-P280-P301+P310+P330-P302+P352+P310-P391-P501
sodium borohydride	GHS02, GHS05, GHS06, GHS08	H260-H301-H314-H360F, P201-P231+P232-P280-P308+P313-P370+P378-P402+P404
sodium hydride	GHS02	H260, P231+P232-P335+P334-P370+P378-P402+P404
sodium hydrogen sulfite	GHS07	H302, P301+P312+P330
sodium hydroxide	GHS05	H290-H314, P280-P303+P361+P353-P304+P340+P310-P305+P351+P338
sodium methanolate	GHS02, GHS05, GHS06, GHS08	H225-H251-H301+H311+H331-H314-H370, P210-P235+P410-P260-P280-P301+P310-P305+P351+P338
tetrabutylammonium hydrogen sulfate	GHS07	H302-H315-H319-H335, P261-P305+P351+P338
tetrahydrofuran	GHS02, GHS07, GHS08	H225-H302-H319-H335-H351, P210-P280-P301+P312+P330-P305+P351+P338-P370+P378-P403+P235
tetrahydrofurane-d ₈	GHS02, GHS07, GHS08	H225-H315-H319-H351, P210-P281-P305+P351+P338

trichloroacetonitrile	GHS06, GHS09	H301+H311+H331-H411, P261-P280-P302+P352+P312-P304+P340+P312-P403+P233
triethylamine	GHS02, GHS05, GHS06	H225-H302-H311+H331-H314-H335, P210-P261-P280-P303+P361+P353-P305+P351+P338-P370+P378
trifluoroacetic acid	GHS05, GHS06	H314-H332-H412, P273-P280-P305+P351+P338-P310
zinc acetate dihydrate	GHS05, GHS07, GHS09	H302-H318-H411, P280-P301+P312+P330-P305+P351+P338+P310

GHS pictograms:



Curriculum Vitae

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