Light-Responsive Sugar Surfactants:
Design, Synthesis and Characterization of Photoswitchable and Fluorescent Amphiphiles

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Abstract

The integration of photoswitches into surfactant structures expands the basic properties and thus also the areas of application of amphiphiles. This work deals with the synthesis and investigation of photoswitchable sugar surfactants. Synthesis routes to three different basic structures of surfactants containing a spiropyran unit as photoswitch were developed. A wide variety of indole and chromene building blocks were synthesized, which could be condensed to form the desired target structures. The final compounds were investigated for their physico- and photochemical properties using surface tension and UV-vis measurements.

Furthermore, synthesis routes to novel fluorescent sugar surfactants with siloxane and carbosilane chains were devised. The surfactants obtained were investigated using surface tension measurements as well as absorption and fluorescence spectroscopy.

Kurzzusammenfassung

Die Integration von Photoschaltern in Tensidstrukturen erweitern die Grundeigenschaften und somit auch die Anwendungsbereiche von Amphiphilen. Die vorliegende Arbeit befasst sich mit der Synthese und Untersuchung von photoschaltbaren Zuckertensiden. Syntheserouten wurden entwickelt, um drei verschiedene Grundstrukturen von Tensiden zu erhalten, die eine Spiropyran-Einheit als Photoschalter enthalten. Es wurden verschiedenste Indol- und Chromenbausteine synthetisiert, die zu den gewünschten Zielstrukturen kondensiert werden konnten. Die finalen Verbindungen wurden mittels Oberflächenspannungs- und UV-vis Messungen auf ihre physiko- und photochemischen Eigenschaften hin untersucht.

Des Weiteren wurden Syntheserouten zu neuartigen fluoreszierenden Zuckertensiden mit Siloxan- und Carbosilanketten entwickelt. Die erhaltenen Tenside wurden mittels Oberflächenspannungsmessungen sowie Absorptions- und Fluoreszenz-spektroskopie untersucht.

Table of Contents

1 Introduction

Surfactants are among the most versatile products in the chemical industry. As a result, their areas of application have steadily expanded in recent years.[2] Due to the continuously growing range of applications and increasingly specialized requirements, the development and research of innovative and novel surfactants is of great interest.

A surfactant comprise a hydrophilic and hydrophobic unit and thus has an amphiphilic character.[2] By the combination of surfactants and a photosensitive unit, which can be specifically controlled or made visible by light irradiation, so called high-performance surfactants can be formed (Figure 1).

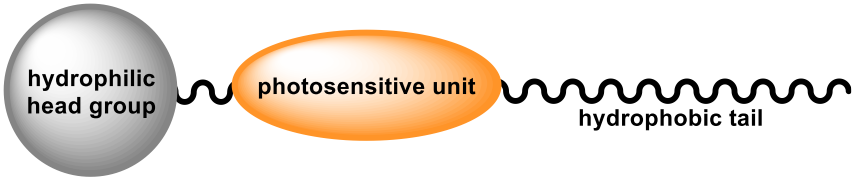


Figure 1: Schematic structure of a photosensitive surfactant.

Due to the properties gained, the range of applications is considerably expanded, making these compounds of great interest today.[3]

Light can be used as an analytical tool for structural elucidation, monitoring, and imaging, as well as for influencing chemical reactions and structural transformations.[4],[5],[6] The use of light radiation has many advantages. Light stimulation can be specifically varied by changing the wavelength, intensity and radiation range, making the use of light quick, easy and precise. Light can be used to start, accelerate, or redirect chemical processes without producing by-products or other waste. For this purpose, light is used as an energy source. Irradiation can excite molecules, enabling them to overcome energy barriers.[6] Therefore, it is a cost-effective initiator and no additional additives or catalysts are necessary.

Light-sensitive surfactants can change their properties by irradiation due to the embedded photosensitive groups in their amphiphilic structure. Structural isomerization[7], polarity changes[8] or photochemical reactions[9] result in changes in their physical and chemical properties such as surface tension, solubility, viscosity and aggregation behavior. Therefore, the emulsification, dispersion and wetting properties of their solutions can be effectively controlled for specific applications.[3] This has shown great potential in areas such as environmental remediation[10], biotechnology[11],

medicine[12] and industrial synthesis[13], among others. Despite the great interest, there are currently only a few publications on photosensitive surfactants. Thus, the synthesis of derivatives and investigations of their physico- and photochemical properties are still incomplete and unexplored in many areas.

2 General theoretical background

2.1 Surfactants

Surfactants (*surface active agents*) are molecules which combine subunits of different lyophilicity and lyophobicity. In water, these properties are referred to as hydrophobicity and hydrophilicity (Figure 2).[2]

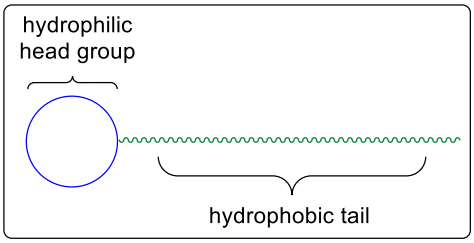


Figure 2: Schematic structure of a surfactant.

The general structure of a surfactant is based on a polar head group linked to an apolar side chain. In addition to this general structure, further architectures are also known, such as bola or gemini surfactants, in which two tails or head groups are connected by spacers.[2] Due to their amphiphilic structure, surfactants can accumulate at surfaces or interfaces of two insoluble liquids. This allows surfactants to reduce the surface or interfacial tension. In addition, they can form spherical clusters, called micelles, and further aggregates of the monomers. Therefore, they are soluble in both organic solvents and water.[14],[15]

Due to their unic structure and physicochemical behavior, surfactants have applications in a wide variety of chemistry. They are used, for example, in pharmaceutical formulations[16], detergents[17], nanotechnology[18] and emulsifier systems[19].

The hydrophobic tail often consists of long carbon chains.[2] Fluorinated carbon chains are also sometimes used to optimize the physicochemical properties and make the surfactants more resistant. However, these surfactants are toxic and not biodegradable. Molecules containing siloxane or carbosilane chains exhibit physicochemical properties comparable to those of fluorinated surfactants and are also non-toxic and biodegradable.[20]

Depending on the structure of the head group, surfactants can be divided into four main classes which are characterized as non-ionic, cationic, anionic or zwitterionic (Figure 3).

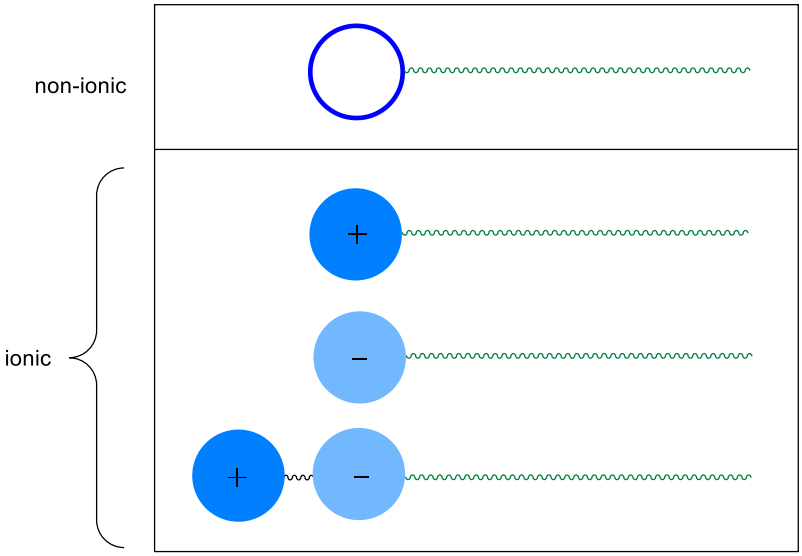


Figure 3: Classification of surfactants into non-ionic and ionic surfactants based on their head groups.

Cationic surfactants are often formed by head groups with quaternary ammonium compounds.[21] Anionic surfactants usually contain carboxylates or sulphates. Examples for the group of zwitterionic surfactants are aminocarboxylates or aminoxides.[22] Non-ionic surfactants are uncharged and their solubility in water is therefore based on the formation of hydrogen bonds. Their hydrophilicity is achieved by polar, non-ionic functional groups. As single hydroxy, amino or carboxyl groups are usually not sufficient, the surfactant head groups carry several of these hydrophilic groups. Good examples of this are polyglycoethers, polyalcohols and sugar derivatives.[23],[24],[25]

2.1.1 Carbohydrate surfactants

Sugar compounds can be utilized as the polar head groups of non-ionic surfactants. Due to the large number of hydroxyl groups with geometrical and structural diversity, carbohydrates easily participate in hydrogen bonding in aqueous environment. Carbohydrates are major building blocks in biological systems and are involved in several important biological processes. In addition, they are utilized in storage of energy and can be obtained from various natural raw materials. Carbohydrate surfactants, known as glycolipids, are therefore considered as natural surfactants, as the starting substances can be obtained from regenerative sources.[26],[27] Glucolipids

are usually hydroxy fatty acids attached to a sugar *via* a glycosidic bond. Sophorolipids and rhamnolipids are well known examples produced in nature by *Candida* and by *Pseudomonas*.[28]

Since the growing environmental awareness, sugar-based surfactants have been commercially utilized and are used in many different areas, such as in food industry, biology, immunology and detergents. Therefore, the interest in synthetic processes to produce surfactants in larger quantities is also growing.[2],[29]

In recent years, there has been a focus on three classes of surfactants with sugar or a polyol derived from sugar as polar head group: alkyl polyglycosides (**A**), alkyl glucamides (**B**) and sugar esters (**C**) (Figure 4).

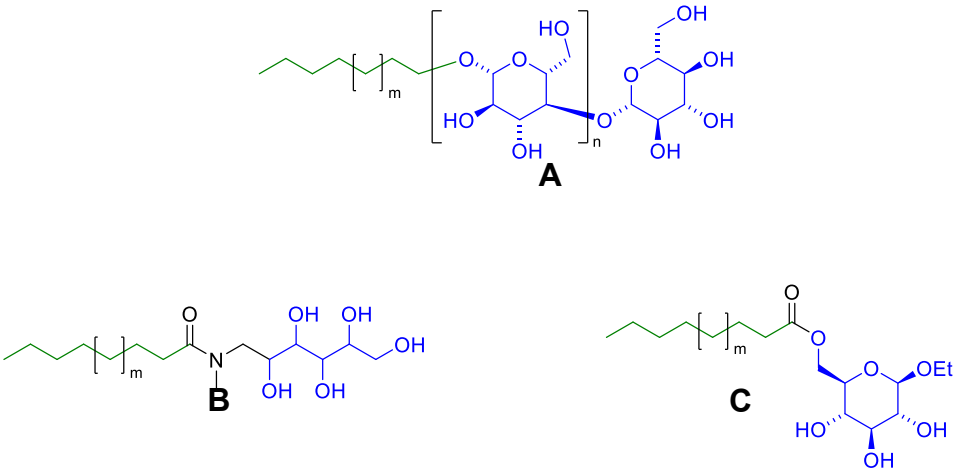


Figure 4: Examples of different sugar surfactants.

Alkyl polyglycosides (APGs) (**A**) are currently attracting the greatest interest. They are synthesized by direct acid-catalyzed reaction of glucose (or polysaccharides) and fatty alcohols. A large excess of alcohol is used to minimize sugar oligomerization. Transacetalizations of short chain alkyl glucosides with long chain alcohols or enzymatic synthesis using glucosidase as a catalyst are also known.[28] APGs are stable at high pH and sensitive at low pH to hydrolysis. They have a high rate of biodegradation and a low aquatic toxicity.[30],[31] In addition to their technical applications, they are also interesting for personal care products and have favorable dermatological properties due to their mildness.[32]

Alkylgucoamides (**B**), *N*-alkanoyl-*N*-methylglucamines, are sold in large quantities for the detergent sector and are predominantly used in hand-dishwashing agents. Besides their low toxicity and minimal environmental impact, they also show synergistic effects when combined with other surfactants. They are mostly synthesized starting with

sucrose, glucose or sorbitol, methyl amine and methyl laurate. As APGs, they can be synthesized from natural inexpensive raw materials.[28],[33]

A third major class of carbohydrate surfactants are sugar esters (**C**). Sucrose esters, or similar polysaccharides, are synthesized primarily by combining the primary hydroxyl group of the nonreducing glucose moiety with a methyl ester of a fatty acid. Also, the condensation of fatty acid chlorides with sucrose in pyridine is known. Monosaccharides can also be esterified enzymatically using a lipase catalyst.[34] To obtain the correct selectivity after esterification, much attention must also be paid to the use of protecting groups, especially acetal and benzyl groups. In addition to compounds that are only esterified *via* the primary oxygen, simple multi-esterified or even gemini surfactants can also be produced, which increases their range of application.[28]

2.1.2 Surface tension and *cmc*

Due to their surface activity, surfactants are used to reduce the surface tension of liquids, among other things. The property of a liquid to oppose an increase in surface area with a force is the surface tension. This force is based on intermolecular interactions between molecules in the phase. If surfactants are added to liquids, they initially accumulate on the surface (or interface). Here they disrupt the intermolecular interactions of the liquid so that the surface tension (σ) is lowered. Figure 5 shows an aqueous solution with different concentrations of surfactants. The logarithmic concentration is shown in dependency on the surface tension.

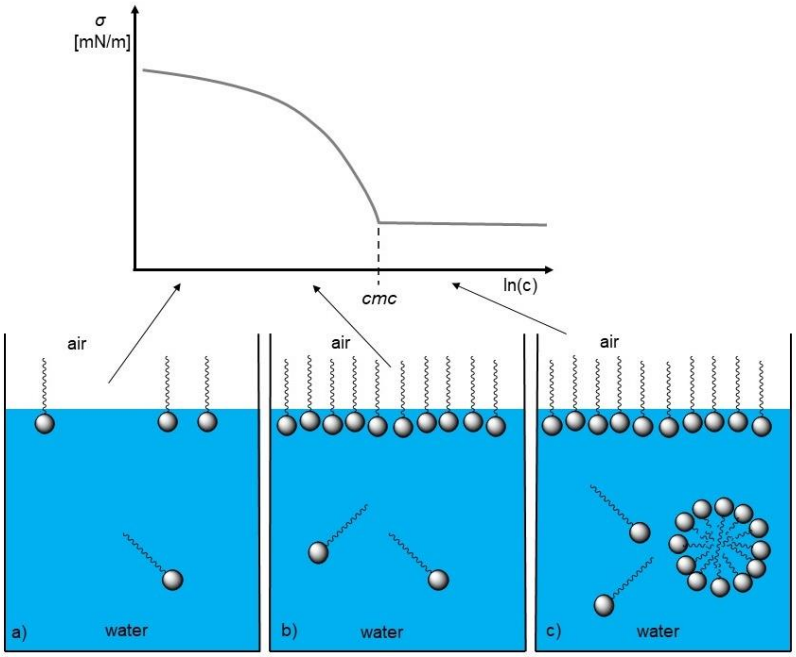


Figure 5: Concentration-dependent representation of the surface tension and illustration of the aggregation behavior of an aqueous surfactant solution. Plotted is the surface tension against the logarithm of the concentration.

In surfactant solutions, there is a constant equilibrium between surfactants on the surface and in the solution. Dissolving a surfactant requires energy to transfer the hydrophobic part of the surfactant into the aqueous polar environment. This can be greater than the energy achieved by dissolving the hydrophilic component. The ability to dissolve a surfactant in water is therefore strongly dependent on the size of the hydrophilic and hydrophobic units and their ratio to each other. Nevertheless, the transfer of the hydrophobic component into the polar environment creates an energy-rich interface between the hydrophobic component and the water molecules (hydrophobic effect).[35] To minimize the energy, the surfactants starts to accumulate at the surface with the polar head groups towards the polar liquid. If the surfactant concentration is increased until the surface is completely wetted by surfactants, micelles start to be formed to continuously minimize the energy. Micelles are spherical aggregations in which the polar head groups point towards the polar solution and the hydrophobic part towards the inside of the sphere. The surfactant concentration at which micelles begin to form in a solution is called the *critical micelle concentration* (*cmc*). Above this value, the surface tension no longer decreases significantly and the minimum surface tension is reached (see Figure 5). If the concentration is increased further above the *cmc*, alternative and more highly ordered structures may form.[36],[37]

Different methods to measure the surface tension of liquid/gas interfaces are known. In this work, the vertical plate method according to *Wilhelmy*[38] is used (Figure 6).

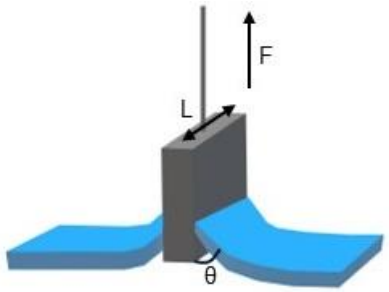


Figure 6: Simplified representation of surface tension measurement using the Wilhelmy[38] plate method.

Here, a roughened platinum plate is dipped into the solution to be examined. The wetting of the plate results in the lamellar tensile force of the liquid when it is pulled up. This is the *Wilhelmy* force *F*, which correlates with the surface tension *σ* of the solution, the wetted length *L* and the contact angle *θ* according to Equation 1:

$$\sigma = \frac{F}{L \cdot \cos\theta} \tag{1}$$

The force *F* required to hold the plate in its original position and thus compensate for the surface force is measured using a scale.[39]

To determine the *cmc*, the surface tension is plotted against the logarithm of the concentration (Figure 7).

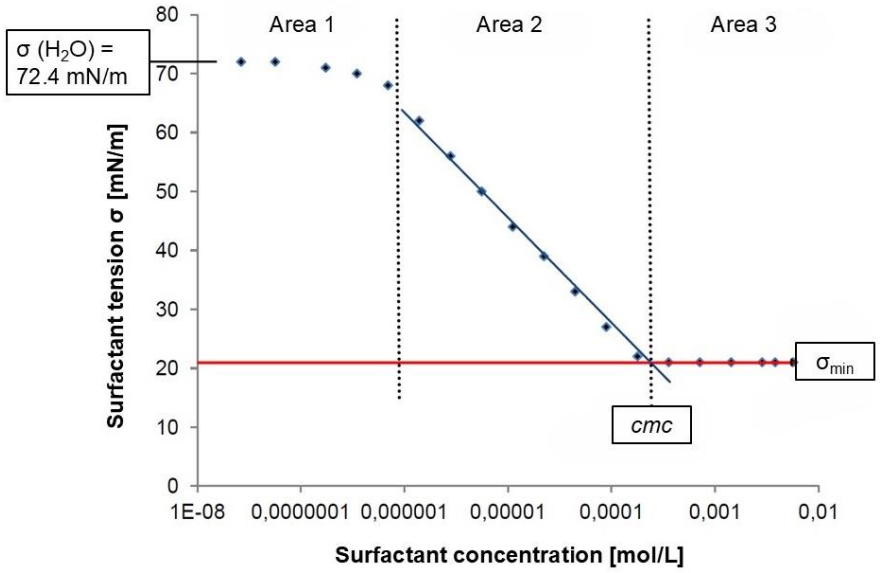


Figure 7: Example plot of surface tension (σ) against the concentration of the aqueous surfactant solution in a semi-logarithmic plot.[40]

The non-linear part is then adjusted using a second-order polynomial (blue). The linear part is described by a linear equation (red). The *cmc* can be determined *via* the intersection of the two functions.

The value of the surface tension depends on the temperature and pressure. Pure water shows a surface tension of 72.8 mN/m at 20 °C. The surface tension decreases linearly with increasing temperature, at 60 °C the value of pure water is only 66.2 mN/m.[41]

Other values that result from plotting surface tension against concentration are the maximum interfacial concentration Γ_∞ and the minimum head group requirement A_{min}. The interfacial concentration can be determined using the *Gibbs* isotherm[42] (Equation 2), where R is the universal gas constant (R = 8.314 J/mol·K) and T is the temperature at which the measurement is taken.

$$\Gamma_\infty = -\frac{1}{RT}\left(\frac{d\sigma}{dln(c)}\right)_{p,T} \tag{2}$$

The minimum head group requirement A_{min} is determined by the ratio of the maximum interfacial concentration Γ_∞ and *Avogadro* number N_A (Equation 3).[43]

$$A_{min} = -\frac{1}{\Gamma_\infty \cdot N_A} \tag{3}$$

The maximum interfacial concentration Γ_∞ and the minimum head group requirement A_{min} are determined to enable further characterization of the surface-active substances. These are described and compared in detail in the respective sections.

Part 1: Novel photoswitchable surfactants

3 Theoretical background

3.1 Photochromism

Research into photochromic molecules has experienced exponential growth in recent years. This is in particular due to the increasing demand for stimuli-responsive molecular switches in organic electronics and smart materials.

Photochromic molecules show several physical phenomena such as optical memories, variable electric current, ion transport and variable wettability. For this purpose, organic photochromic molecules are often incorporated in polymers, liquid crystalline materials or other matrices.[44] They have a wide range of applications, including data storage, optoelectronic switches, biomolecules and biomimicry, detection and imaging, surface functionalization, ion sensing, drug delivery and photopharmacology. The main advantages of using photochromic compounds are the precise directional and wavelength control, as well as the reduced risk of chemical contamination as they are applied in closed systems.[45]

Photochromism is the reversible change of a material between the different states in response to light, a light-induced reversible change of color. The two species of switchable compounds exhibit different absorption spectra (Figure 8).

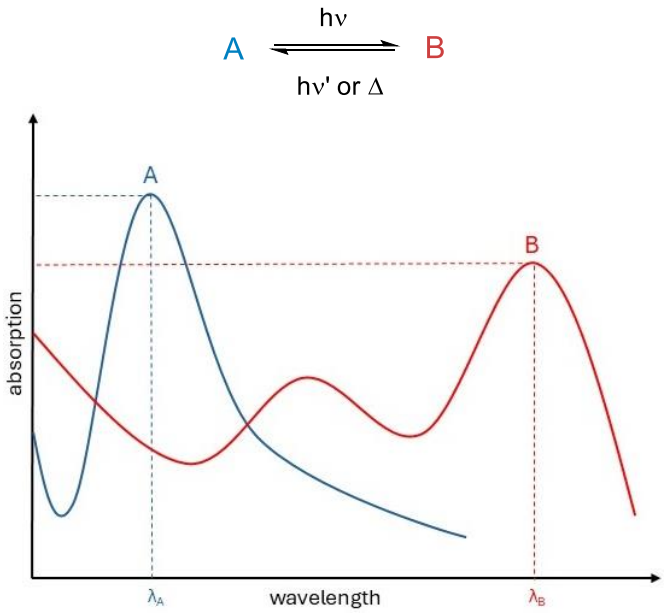
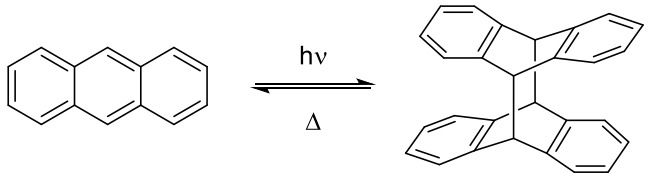


Figure 8: Exemplary illustration of a spectrum of a photochromic system.

In addition to the different absorption spectra, the photochemical change can also lead to various other changes in chemical and electronic properties. It influences the dipole

moment, dielectric field constant, refractive index, energy transfer, redox properties, conductivity, molecular structure and reactivity. These properties are decisive for the wide range of applications.[46]

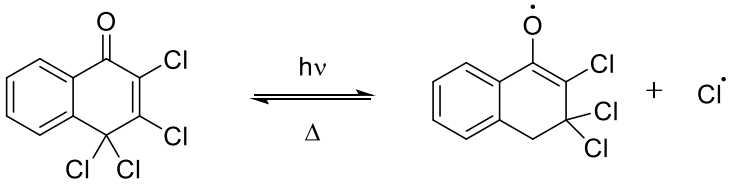
The term *photochromism* is derived from the Greek words “phos” (light) and “chroma” (color). Already in the early 19th century, different compounds were discovered that show coloration or decolorization under the influence of light. In 1876, *Fritzsche* reported the bleaching of an orange-colored solution of anthracene (**1**) in the daylight and the regeneration in the dark by heating (Scheme 1).[47]



1 **2**

*Scheme 1: Photoreaction of anthracene (**1**) and regeneration in the dark.*

Anthracene (**1**) can form dimers, which can regenerate back in the dark. Later *Marckwald* published the reversible color change of 2,3,4,4-tetrachloro-4*H*-naphthalen-1-one (**3**) (Scheme 2).[48]



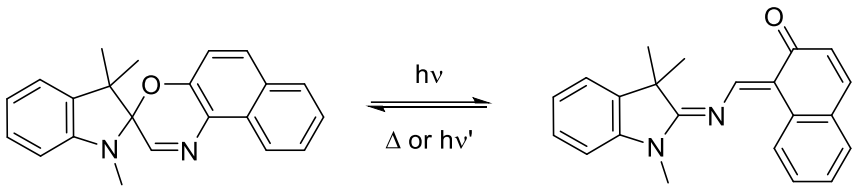
3 **4**

*Scheme 2: Photoreaction of naphthalen-1-one **3**.*

By irradiation, the anhydrous hydrochloride of benzo-1,8-naphthyridine (**4**) is formed, which can thermically revert back to the ketone.

In 1899, this phenomenon was termed *phototropy*, which is now used to describe the growth of organisms towards light.[48] In the early 20th century, the targeted synthesis of photochromic compounds and the exploration of their interaction with radiation, as well as the research into the mechanism started. In addition to the synthesis of fulgides, a few years later, *Stobbe* also reported the ability to use a different wavelength of light to reverse the initial photochromic response.[49],[50] A review in 1929 introduced the concept of fatigue (loss of performance over time).[51] By the mid-20th century, photochromism was generally understood as a chemical transformation to a thermodynamically metastable state. Later, the correlation of chemical constitution and

photochromic mechanism was proposed.[52] *Hirschberg* and *Fischer* made great achievements in research parallel to the development of physical analytical methods. They introduced the term *photochromism*. In the 1980s, fatigue resistant spirooxazine **5** and chromene derivatives were developed (Scheme 3).

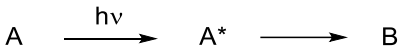


5 **6**

*Scheme 3: Photoreaction of spirooxazine **5**.*

Spirooxazine **5** can isomerize to the open merocyanine **6** by UV light. These compounds triggered the fabrication and commercial application of photochromic ophthalmic lenses. Since then, other commercial systems have been developed.[44] In 1999, *Feringa* achieved a highly acclaimed breakthrough with the development of a light-driven molecular motor, for which he was awarded the Nobel Prize in Chemistry in 2016.[53]

As mentioned above, photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms having different absorption spectra. In most cases, photochromism is a unimolecular photochemical reaction (Scheme 4).



Scheme 4: Unimolecular photochemical reaction.

By absorbing a particular wavelength, thermodynamically stable form A is promoted to the excited state A*. This transformation requires a discrete amount of energy, $E = h \cdot v$, to overcome the potential energy barrier. Afterwards, A* can be transformed into B. In general, the processes involve a one-photon mechanism and can be described using the *Jablonski* diagram (Figure 9).

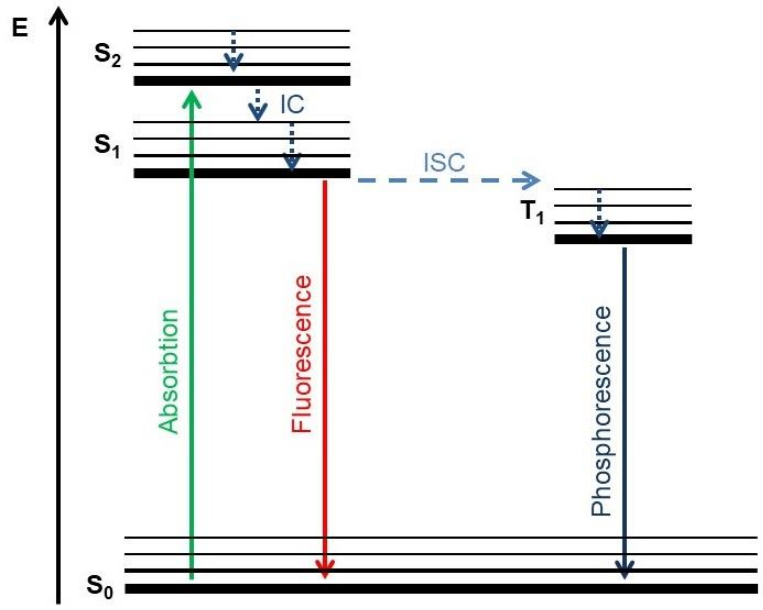


Figure 9: Simplified Jablonski diagram.[54]

By absorbing light, an electron can be promoted to an excited state from the ground state (S_0 → S_n). The nuclear positions of the vertical transition do not change during the excitation, which is explained in the *Franck-Condon* principle[55],[56]. The molecule will adapt a new electronic configuration by molecular motion. The transformation of A* to B can take place by different photophysical and photochemical processes. The excited electrons can relax in different ways: While by internal conversion (IC) a non-radiative transition between the energy levels of the same multiplicity takes place (S_n → S_{n-1}), the intersystem crossing (ISC) is a non-radiative transition between energy levels of different multiplicities (S_n → T_n). These processes are an energy disruption and are irreversible. Fluorescence and phosphorescence involve an emission of a photon by electron transition to lower states.[46]

Potential energy surfaces (PESs) are employed to describe the process from reactant to photoproducts through relevant excited states (Figure 10).

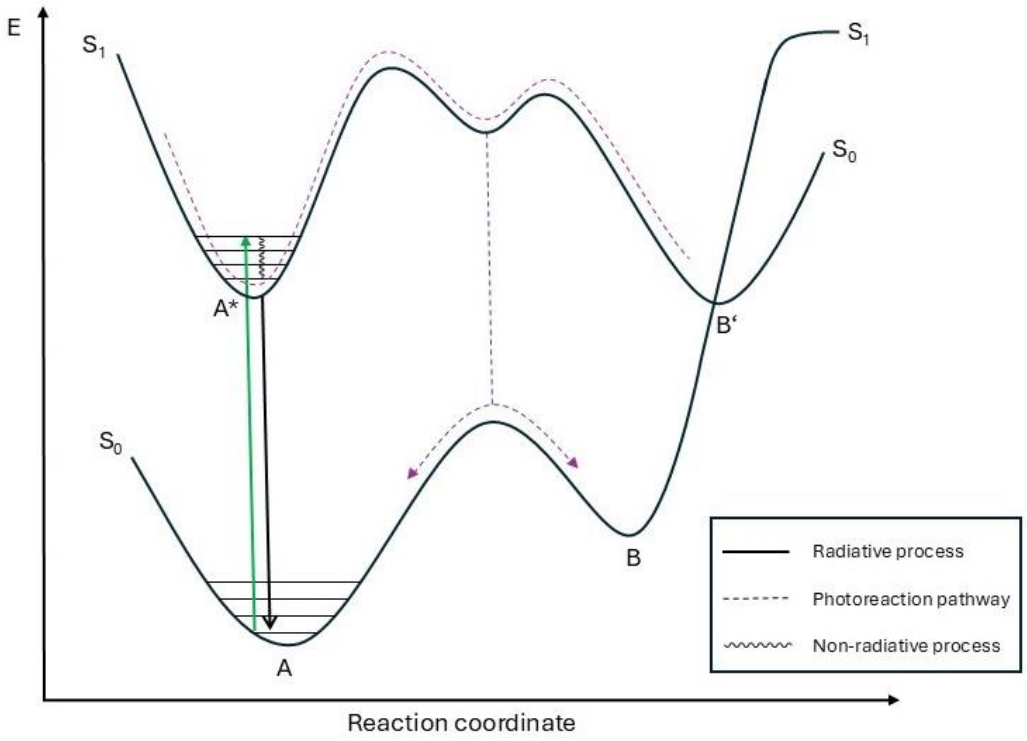


Figure 10: Simplified potential energy surface diagram of a photochemical process.[57]

When compound A absorbs a photon to give the excited state A*, the new electron density gained by the molecule after the photoexcitation coincides with a change in nuclear positions to minimize the energy.[58]

The photoproduct may also be formed from an upper state populated by absorption of two photons (Figure 11).

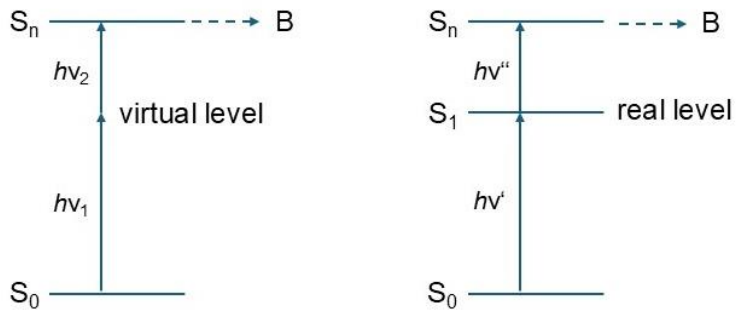


Figure 11: Simultaneous (left) and stepwise (right) two-photon absorption leading to product B.[44]

The absorption of two photos can take place simultaneously *via* a virtual level or proceed stepwise where the second photon absorption takes place from a real level. Another example of two-photochromic reactions is the formation of a metastable intermediate.[44]

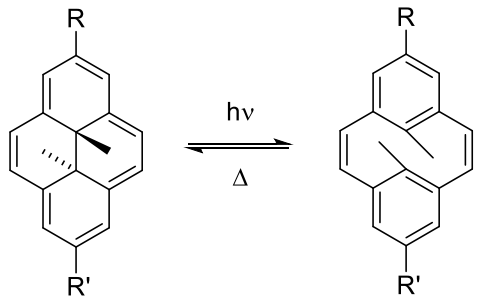
Unwanted side reactions and oxidation can occur during the photochromic reaction. The limit of the number of photochromic cycles is called fatigue. Even extremely

low-yield side reactions lead to a significant loss of photochromic species as the number of staining/decolorization cycles increases. Back reactions of photochromic processes can occur thermally (T-type photochromism) or photochemically (P-type photochromism). T-type photochromes have a lower potential energy barrier between B and A. Thus, state B is metastable and can spontaneously convert to A. Conversion of B to A of photochromic systema of type P can only proceed by irradiation of a specific wavelength.

Another classification of photochromic systems is the division into positive and negative photochromism. The transition of a colorless compound A to a colored state B is called positive photochromism. In negative photochromic systems, molecule A is colored and converts into a colorless state B.[46]

A large number of photochromes can be found in literature, which offer different applications due to their various properties. The largest groups are briefly explained below:

Dihydropyrenes (DHPs) (**7**) were first discovered and synthesized by *Boekelheide* in 1965. DHPs can switch between a more conjugated colored and a colorless form and thus belong to the negative photochromes (Scheme 5).[59]

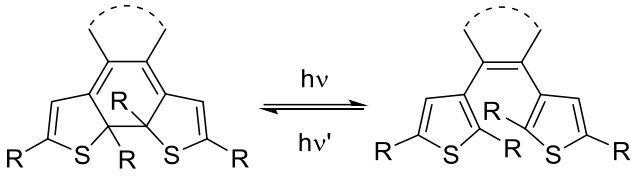


7 **8**

*Scheme 5: Photoisomerization of dihydropyrenes **7**.*

The special feature of the photochromes is that the transformation occurs by cleavage of the central transannular bond. The transformation is induced by visible light. The backreaction of the metastable product to the fully aromatic form occurs thermally (T-type). The introduction of donor or acceptor substituents allows to shift the absorption of the molecules to the NIR region.[59]

Another class of photochromes is the diarylethenes (DAE) (**9**), which also exhibits a transformation through a bond cleavage and can switch from an open to a close form (Scheme 6).

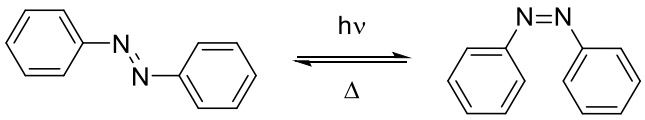


9 **10**

Scheme 6: Photoisomerization of diarylethenes **9**.

They are modified stilbene derivatives and often include thiophenes in place of aryl rings. The closed form is colored due to the extended conjugated system. They belong to the P-type photochromes and are highly thermally stable.[60]

A very well-known class are the azobenzenes (**11**), which were already investigated by *Hartley* as early as 1937.[61] The two phenyl rings of the compounds are linked by an azo bond and belong to the T-type photochromes (Scheme 7).

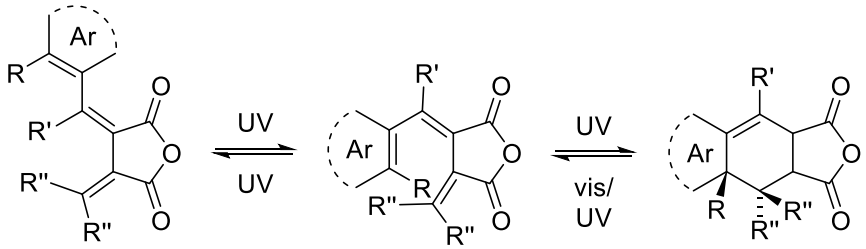


11 **12**

Scheme 7: Light-induced E-/Z-isomerization of azobenzenes ***11***.

By irradiation with UV light, they undergo a *cis-trans* isomerization, with the *trans* isomer as the thermally stable isomer. The stability of the *cis* form can strongly be influenced using substituents and steric modification. Azobenzenes show a high fatigue resistance and a clean and efficient switching process.[62]

As mentioned before, *Stobbe* was the first to describe the synthesis and photochromism of fulgides, which are derivatives of the 1,3-butandiene-2,3-dicarboxylic acid (**13**) (Scheme 8).



13 **14** **15**
Z-Form *E*-Form *C*-Form

Scheme 8: Photoisomerization of dicarboxylic acids ***13***.

These compounds show a transformation between the colorless open form and the closed colored form. The colorless open form can be further divided into two

geometrical isomers regarding the double bonds connecting to the acid anhydride and the aromatic ring.[63]

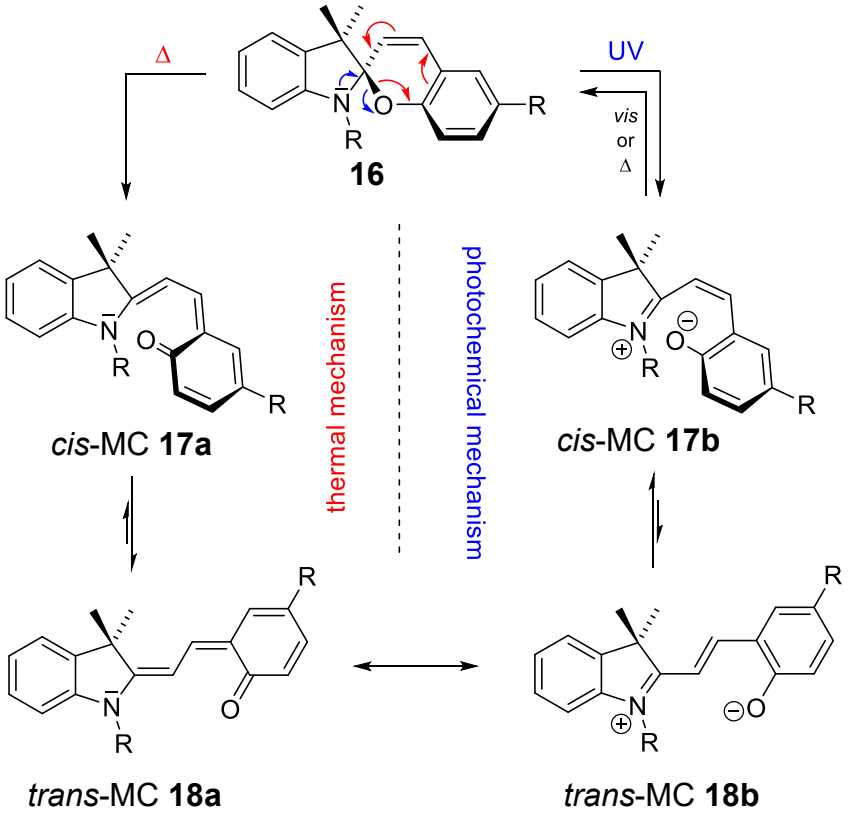
Spiropyrans belong to a class of photochromic compounds that has been the subject of much research in recent years. The synthesis and investigation of these compounds is also part of this work and therefore these photochromes are described in more detail in the following chapter.

3.2 Spiropyrans and merocyanines

Spiropyrans are interesting T-type photoswitches that can undergo reversible structural transformations through isomerization between the closed spiro form (SP) and the open merocyanine form (MC). In 1952, *Fisher* and *Hirshberg* reported for the first time the photochromic behavior of these molecules.[64] The two isomers of this photoswitch have vastly different properties. They can be influenced by many different stimuli, such as different solvents, metal ions, pH-value, temperature, redox potential and mechanical forces, resulting in a wide range of possible applications.[65]

Spiropyrans usually have two heteroatomic rings, an indoline and a benzopyran moiety, which are linked through a sp^3-hybridized spiro C atom. The two rings are oriented perpendicular to each other. The spiro-isomer show two localized transitions attributed to the π-π* electronic transitions in the indoline part (272 – 296 nm) and the chromene moiety (323 - 351 nm). The ring opening to the MC form can be induced by UV light (~365 nm). The open structure is planar and has an extended π-conjugation between the indoline and the chromene moieties. The MC form shows a single electronic transition (550 – 600 nm).[66],[67]

The switching mechanism has been investigated extensively in the last decades. So far, there are two possible mechanisms, the thermal and the photochemical isomerization (Scheme 9).



Scheme 9: Proposed mechanisms for the transformation of SP to MC.[68]

The mechanism starts with the cleavage of the C-O bond resulting in *cis*-MC **17**. The ring opening reaction can proceed either as a 6π electrocyclic ring opening to form the quinoidal form **17a** or by a heterolytic C-O bond cleavage leading to the zwitterionic species **17b**. Rotation about the central C-C bond yield the *trans*-MC **18**. The isomerization from the SP form to the MC form can also be induced by using near-infrared (NIR). This proceeds *via* a two-photon excitation and shows reduced photodegradation.

The reverse isomerization, from the MC form to the SP form, occurs spontaneously and can be accelerated by visible light.[68]

The open and closed isomers have different physical properties. Due to the charge separation, the MC form shows a large electric dipole moment. The dipole moment of SP is calculated to 4 – 6 D and changes to 14 – 18 D in the MC form. The SP is optically transparent, while the MC form absorbs strongly and often appears blue. While the closed isomer shows no strong emission, the open form emits intensely.[68]

All properties of SP and MC are related to the sensitive response to multiple stimuli, which is described in detail in the next section.

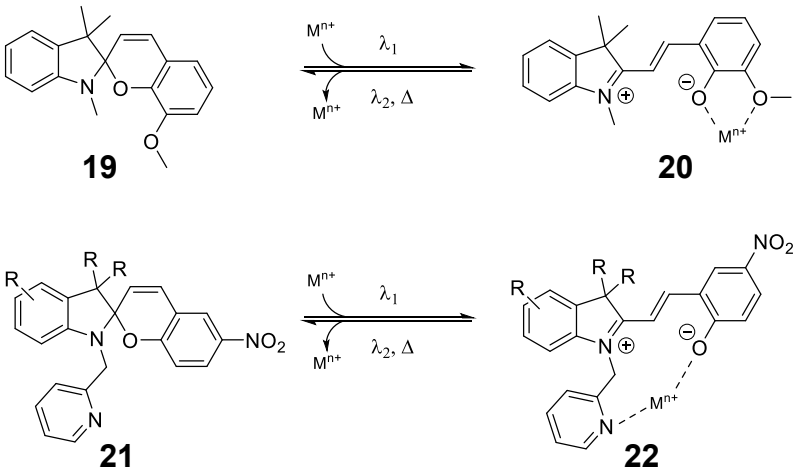
3.2.1 Influence on the photochromic behavior

3.2.1.1 Influence by external factors

Spiropyrans are used as smart materials because they respond to many external stimuli. The above-mentioned isomerization and molecular switching can be triggered not only by light, but also by temperature[69], pH-value[70], redox potential[68], (metal) ions[71], mechanical forces[72] and, in particular, solvent polarity[73]. They are therefore also used as sensors and switches in many areas.[74]

All stimuli depend on the different impact on the stability of the two isomers SP and MC and their excited states. Polar solvents such as methanol or ethanol destabilize the excited state (MC*) and stabilize the ground state (MC) of the zwitterionic form, which is reflected in a blue shift (hypsochromic shift). The energy gap between the two states increases with increasing solvent polarity. This phenomenon occurs primarily through differences in solvation energies and possible H-bonding interactions in the MC form. Additionally, MC* has a lower dipole moment than MC. Non-polar solvents such as *n*-hexane or petroleum stabilize the ground state of the SP form.[75],[8]

The isomerization can also be influenced by ions, both cations, especially metal ions, and anions. Metal ions can coordinate to the phenolate group of the MC form, stabilize the open form and thus prevent isomerization back to the SP form.[76] To improve the complexation or influence the selectivity to different metal ions, spiropyrans can be modified with additional chelating substituents (Scheme 10).



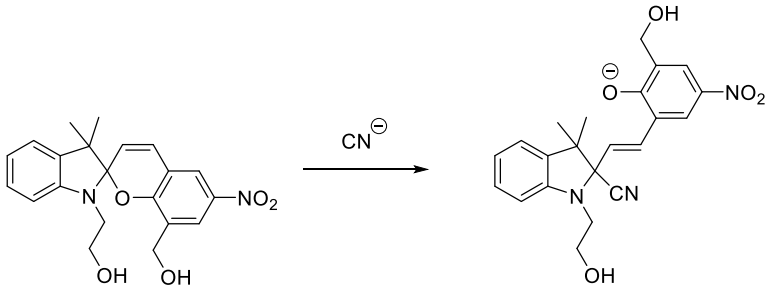
Scheme 10: Spiropyrans with additional coordination centers.[77],[78]

In particular, the addition of divalent or trivalent ions shifts the equilibrium strongly towards the MC form. In addition, a red shift and change in intensity of the MC absorption band can usually be seen. In the case of strong complex formation, the

reverse reaction is often not possible by thermal relaxation alone. In order to return to the initial colorless SP state, irradiation with visible light is used.[77],[78] Therefore, spiropyrans can be used as sensors for selective detection of metal ions with specific optical signals.

There are many examples in literature where spiropyrans are bound to polymers and thus used for colorimetry, including medical applications.[79],[80]

Anions are detected by reaction with the positively charged iminium carbon in MC isomer or electron deficient spiro carbon in SP form. Spiropyrans are mainly used as sensors for halogens and cyanines (Scheme 11), but there are also examples in literature for the detection of sulphates, phosphates and other anions.[81]



23 **24**

*Scheme 11: Nucleophilic addition of CN^- ions to form the open MC-CN **24** form for detection and colorimetric applications.[81]*

In addition, the equilibrium of the two forms can be influenced by bases and acids. The SP form shows a very low basicity, while in the zwitterionic form, which carries a phenoxy group, the basicity is increased. This basicity allows proton attachment to MC and its transformation to MCH^+. In the presence of acids, a fast equilibrium occurs between the SP and the open *cis* isomer. Due to the higher acidity of the twisted *cis* isomer the conversion to the stable trans MCH^+ isomer is preferred. Addition of strong acids results in a bathochromic shift and enhanced electron delocalization. This is also dependent on substituents and concentration. Switching isomerization between *Z*- and *E*-MCH^+ occurs upon irradiation. The open isomers of the protonated MCH^+ are thermally more stable than the deprotonated isomers.[82]

3.2.1.2 Influence of substituents

In addition to all the external influences already listed, substituents play a crucial role in tuning the properties of spiropyrans. In general, substituents are often varied at four specific positions as shown in Figure 12.

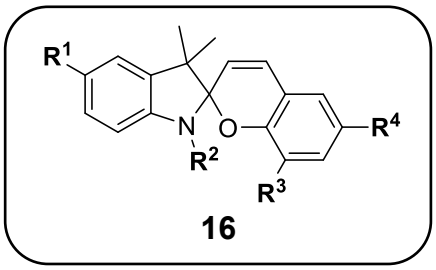


Figure 12: General illustration of a spiropyran with typical positions for substituents.

There is little data on the influence of different substituents (**R¹**) on the indole. *Zaichenko et al*. investigated the inversion of the spiro center of differently substituted spiropyrans. They found that electron-withdrawing substituents, such as CF_3, COOH and NO_2, stabilize the SP form. In contrast, electron-donating groups, such as OMe, destabilize the closed form and support the ring opening to the MC, which is necessary for the inversion of the spiro center. Electron-withdrawing groups reduce the electron density in the indole so that the thermal formation of the MC form is suppressed.[83],[84] In contrast to the other substituents, substituent R^1 probably has the least influence on the equilibrium between open and closed form.[85]

Substitution at the indole nitrogen (**R²**) mainly affects the thermal stability and lifetime of the MC form. *Beves et al.* investigated the pH changes of solutions of merocyanines with different alkyl chains at the indole nitrogen. As mentioned above, the open MC has an alkaline character and can be protonated at the phenolate oxygen. The equilibrium between the open MC and closed SP form can be described by the equilibrium constant K_C (Equation 4).

$$K_c = \frac{[SP\,]}{[MC]} = \frac{k_c}{k_o} \tag{4}$$

k_c is the rate constant for the ring-closing and k_o the rate constant for the ring-opening process. *Breves*' group investigated spiropyrans with alkyl chains of different lengths with terminal sulphonate and ammonium groups and compared the equilibrium constants. Short alkyl chains with sulfonate or ammonium groups showed a high K_C and thus stabilization of SP form. The longer the alkyl group and the larger the distance

of the sulfonate or ammonium group to the indole nitrogen, the more SP form is destabilized and the K_C becomes smaller.[86]

Brügner evaluated DFT studies and compared the influence of *N*-substituents. A trend was observed that electron-donating groups stabilize the merocyanine form. Electron-withdrawing substituents lead to ring closure, and the equilibrium shifts to the spiro form. Since the electron pair of the indole nitrogen is involved in ring closure and ring opening, the electron-withdrawing and electron-donating groups have a major influence here.[87]

Electron-donating and electron-withdrawing substituents on the chromene unit (**R³**, **R⁴**) strongly influence the equilibrium between the SP and MC form by stabilizing and destabilizing the conjugated system. *Thomson* and coworkers were among the first to study the effect of different substituents in the *para* (**R⁴**) and *ortho* (**R³**) position of the phenol oxygen. They investigated the thermal stability of the MC form at 6 °C in ethanol and compared the rate constant for the dark solution by observation of the absorption. The rates were correlated with substituents by applying the *Hammett* constant (σ_H). σ_H establishes a quantitative relationship between the structure of reactants and their reactivity. Substitution with NO_2 in *para* position results in a very low rate constant and high *Hammett* constant. A second substitution with Br or F led to further decrease of *k* and increase of σ_H. Due to the strong electron-withdrawing effect, the open MC form is more stabilized. Electron-donating secondary substituents such as MeO or allyl groups decrease the values and destabilizes the MC form (Table 1).[88]

Table 1: Rate constants (k) for thermal stability and Hammett constants (σ_H) of substituted spiropyrans.[88]

R³	H	Br	F	MeO	NO_2	allyl
R⁴	NO_2	NO_2	NO_2	NO_2	MeO	NO_2
k [s^{-1}]	$4.28 \cdot 10^{-5}$	$3.67 \cdot 10^{-6}$	$6.33 \cdot 10^{-6}$	$5.53 \cdot 10^{-4}$	$1.32 \cdot 10^{-2}$	$2.10 \cdot 10^{-4}$
σ_H	0.79	1.00	1.03	0.37	0.01	0.62

In particular, the combination of NO_2 in *ortho* (**R³**) and MeO in *para* position (**R⁴**) has a strong influence on the equilibrium.[88] *Beves et al*. proved the findings that EWG stabilizes the open MC form and investigated further substituents in the para position and calculated the equilibrium constants. For NO_2-substituted spiropyrans, the constant is comparatively small (K_c = 1.45), which indicates that the ring closure is not as favored as with electron donating substituents. For example, substitution with *t*Bu results in a high value of the constant (K_c = 183). In comparison, the values of

substitution with aldehydes (K_c = 2.38) or nitriles (K_c = 6.25) are quiet low. *Beves* also indicated that the substitution in *para* position has a stronger impact on the equilibrium SP/MC than in other positions.[86]

3.3 Photoswitchable surfactants

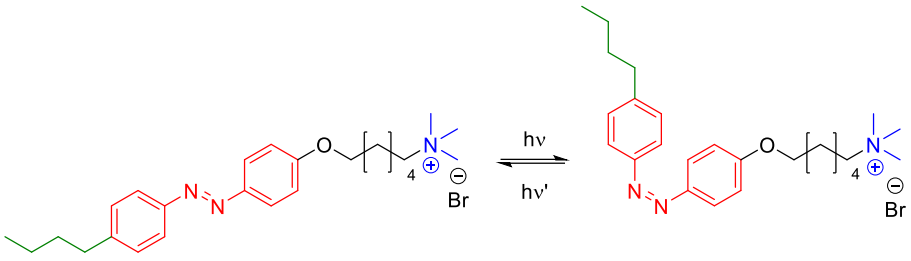
The general fundamentals of surfactants and carbohydrate-based surfactants are presented in *Chapter 2*. In the following, the focus will be on photochromic systems.

Photoswitchable surfactants consist of a hydrophobic tail, a switchable unit and a hydrophilic head group.[89] By integrating a switch into a surfactant framework, the molecular surface activity of the surfactants can be specifically changed from a highly surface-active to a less surface-active form. Depending on their switching state, the surfactants can form different aggregates and the rheological properties can adjust in a controlled manner.[90],[91] Thus, colloidal systems, emulsions, surfaces or foams can be manipulated by light.[92],[93],[94],[95] In addition, the aggregation and transport of particles (e.g. nanoparticles, metal ions) can be influenced by switching. If surfactants accumulate on nanoparticles, superstructures can emerge and be used for photoswitchable magnetic or catalytic activity.[96],[97],[98],[99] There are investigations in which the solubility of structures is changed by the addition of photoswitchable surfactants so that transport from a polar to a non-polar environment (or vice versa) is possible.[100],[101] This is also interesting in a biological context, for example for immigration into cell media. Recently, *Trauner et al*. published a review about photoswitchable phospholipids for the optical control of membrane processes, protein function and drug delivery.[102]

To date, only a few photoswitchable surfactants have been thoroughly researched. Three classes are explained in more detail below.

Most literature examples about photoswitchable surfactants focus on azobenzene-based or related systems. Azobenzenes have high fatigue resistance and are easily accessible synthetically. They are also small and hydrophobic, which makes them suitable for many different applications. Azobenzene-based surfactants with two hydrophobic tails are the basis of synthetic switchable membrane structures. Due to their small size, they can be used to mimic different lipids, that are components of cellular membranes. Different transmembrane proteins, such as ion channels and protein coupled receptors, or nuclear hormone receptors and enzymes respond to switchable lipids and can be controlled specifically.[103]

Bekir et al. synthesized azobenzene-based surfactants and investigated the kinetics of the photo-isomerization in aqueous solution. The surfactants consist of a positively charged head group, a hydrophobic spacer to the azobenzene unit and a hydrophobic alkyl tail (Scheme 12).[104]

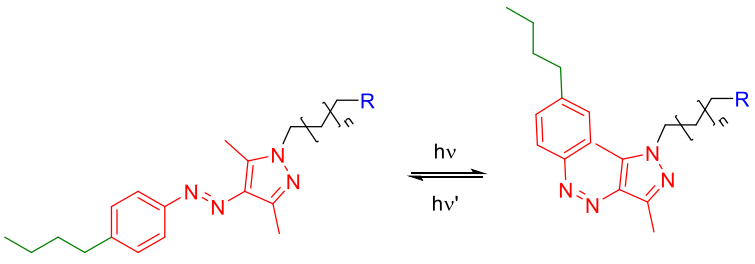


trans-**25** *cis*-**25**

*Scheme 12: Photoisomerization of azobenzene-based surfactants **25** with a cationic head group.*

In an aqueous medium, surfactant **25** switches from the *trans* to the *cis* form at < 400 nm. They determined a slower *trans-cis* switch at concentrations above the *cmc* and explained this observation with steric hindrance in micelles. In addition, they determined strong dependency of the *trans-cis* photoisomerization kinetics on light intensity and wavelength.[105]

A subclass of azobenzenes are the arylazopyrazoles (Scheme 13). They show nearly quantitative isomerization at 520 nm or 365 nm[106], a long-lived metastable state[107] and large change in dipole moment[108]. So far, there are few studies on the use of these azoheteroarenes. *Cabral et al.* investigated the light responsiveness and assembly behavior of arylazopyrazole-based surfactants **26** in neat and mixed micelles.[109]



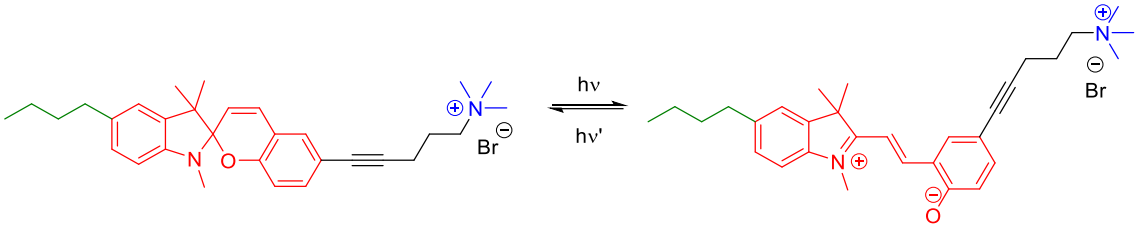
trans-**26** *cis*-**26**

Scheme 13: Photoisomerization of arylazopyrazole-based surfactants.

They modified the arylazopyrazoles with quaternary head groups and hydrophobic alkyl chains. In addition, they tested different substituents, such as fluorine, at the benzole ring. They observed transformation from oblate ellipsoidal micelles into smaller, spherical micelles with larger shell thickness by irradiation and isomerization from *E*- to *Z*-form.[109] *Braunschweig et al*. investigated the dynamic wetting of monolayers of arylazopyrazole phosphonic acids. They used the surfactants to functionalize aluminium oxide surfaces. Monolayers were deposited on Al_2O_3 and *E*/*Z* isomerization caused the contact angle to change by up to 10° upon irradiation. They

found that water can stabilize the *Z*-configuration and even lock the surfactants in this state.[110]

Surfactants with spiropyrans as integrated photoswitches have not been widely explored and represent new potential structures for switchable surfactants. Due to the numerous stimuli (see Chapter 3.2.1.1) and their switch between a non-charged and zwitterionic open form, they represent outstanding switchable surfactants (Scheme 14) and can therefore be used in numerous other areas. *Reifarth et al*. recently synthesized a surfactant **27** with a spiropyran backbone (Scheme 14).[111]



trans-**27** *cis*-**27**

Scheme 14: Photoisomerization of spiropyran-based surfactants ***27*** *synthesized by Reifarth et al.*[111]

They used a butyl chain as hydrophobic tail and connected a quaternary ammonium group as polar head group through a spacer. The surfactant showed good switching behavior with pronounced differences in their surface activity under acidic conditions. The surfactant was dual-responsive due to the pH-dependency.[111] There are also known spiropyran-based surfactants, in which the head group or tail is bridged *via* the indole nitrogen, resulting in a non-linear surfactant structure.[112],[113]

Depending on the application, switchable surfactants must have certain properties. In emulsions, microgels or polymer networks, these surfactants can be used to specifically change the material properties. However, certain properties of switchable surfactants are also crucial for their addition to aqueous solutions or adsorption on surfaces. Only recently, *Reifarth et al.* summarized the most important aspects of good switchable surfactants in a review.[104] Adsorption or desorption on surfaces or particles should be strongly dependent on the isomer. One isomer should adsorb strongly, while the other desorbs slightly and goes into solution. The switching speed between the isomers should be in a similar time frame as the adsorption processes. In addition, the lifetime of the isomers should be long enough to ensure a stable switching effect without continuous irradiation. If the lifetime is too short, the light intensity must be increased, which can lead to decomposition.[74],[104] Other important parameters for determining whether switchable surfactants are suitable for certain applications are

hydrophobicity, polarity and *cmc*. The properties should differ significantly between the two surfactant forms.[104],[114],[115] Geometric change in particular plays a major role in the switching process. *Reifarth et al*. assume that geometric changes (e.g. by kinking the hydrophobic unit) influence the self-organization of surfactants more strongly than changes in polarity. Azobenzene isomerization from *E* to *Z* shows a clear geometrical change (from stretched to bent), resulting in a strong *cmc* difference. In contrast, although the polarity and dipole moment of spiropyran surfactants change (formation of a zwitterion), the molecular geometry remains relatively constant. Both surfactants provide similar Δcmc values. In addition, the length and position of the hydrophobic tail influence the *cmc*, with the tail having a greater influence than the spacer.[104],[116]

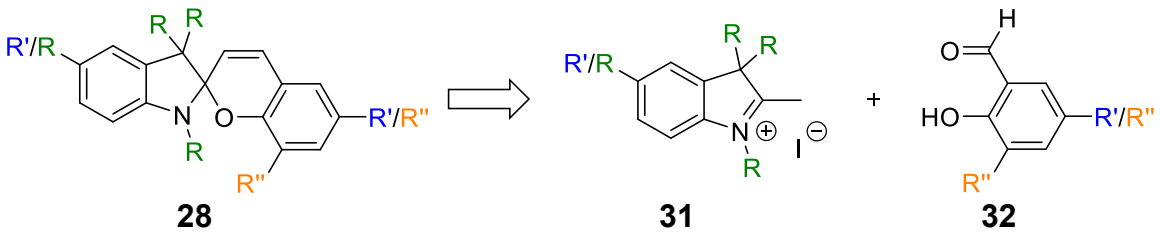
4 Concept and motivation

A central goal in modern surfactant chemistry is the development of systems whose properties can be controlled in a targeted and reversible manner. In addition to classical parameters such as surface tension or aggregation behavior, complexation properties are increasingly gaining importance. Through appropriately designed head groups, surfactants can not only stabilize interfaces but also selectively interact with ions or molecules.[117],[118],[119] In this way, *smart surfactants* are created that can adapt to changing conditions or be specifically activated and deactivated for certain applications.

Photoswitchable surfactants can be specifically controlled by irradiation with certain wavelengths, which influences a number of their properties and enables a wide range of applications. Spiropyrans are known as light switches with many external triggers and are functionalized at various positions. The closed and open forms have very different properties and can be switched in the UV and visible light range. Therefore, the aim of this part of the work was to develop photoswitchable surfactants based on spiropyrans to investigate their structural, physicochemical and spectroscopic properties.

Hydrophobic alkyl chains of various lengths and different hydrophilic head groups should be bound to a spiropyran backbone to obtain a range of switchable surfactants, which can then be investigated and compared. A mono- and a disaccharide should be used as hydrophilic head groups. Previous work has shown that sugar surfactants have good physicochemical properties and can moreover be obtained inexpensively from renewable raw materials.[26],[27]

Spiropyrans were to be synthesized using the known synthesis route *via* the condensation of indole **31** and benzaldehyde **32** (Scheme 15).



Scheme 15: Retrosynthesis of functionalized spiropyrans for the synthesis of photoswitchable surfactants.

In order to obtain different basic structures of linear and branched switchable surfactants, the hydrophobic (R) and hydrophilic (R') units were to be bound to the synthesized indole and benzaldehyde at different positions. In addition, different

auxochromic and anti-auxochromic groups (R'') were to be added to influence the switching behavior. Therefore, new synthesis routes to the two desired building blocks **31** and **32** should be developed.

After synthesizing a substance library of surfactants, the compounds should be examined and compared using UV-vis spectroscopy to analyze their photochemical properties, especially their switching behavior after irradiation with different wavelengths. In addition, surface tension measurements should be carried out to investigate the physicochemical properties. The collected data could then be used to further optimize the switchable sugar surfactants. By further adjusting the head groups, tails, auxochromic and anti-auxochromic groups, as well as the basic structures, the properties of the surfactants could be tailored to specific areas of application.

5 Results and discussion

As part of this work, synthetic strategies for surfactants with a spiropyran backbone were developed. These photoswitchable surfactants can be divided into three main groups based on their basic structure (Figure 13).

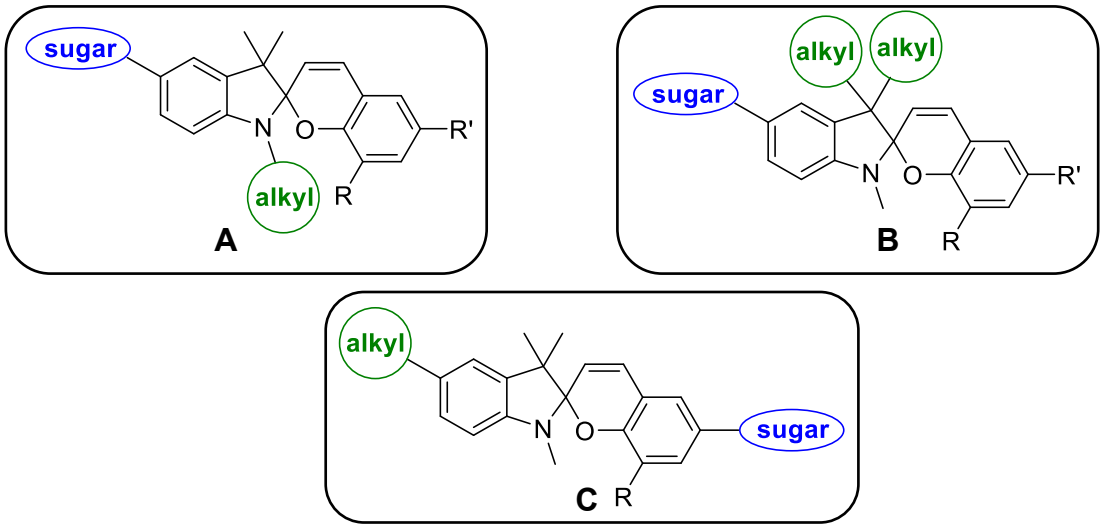
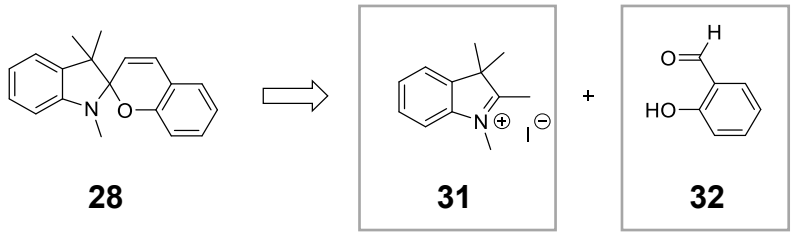


*Figure 13: Simplified illustration of the three main target structures: Spiropyran with glycosylated indoles and N-connected tails (**A**). Spiropyrans with glycosylated indoles and geminal tails (**B**). Linear spiropyrans with alkylated indoles and glycosylated chromene unit (**C**).*

Retrosynthetically seen, spiropyrans can be obtained by the condensation of indoles and benzaldehydes (Scheme 16).[120]

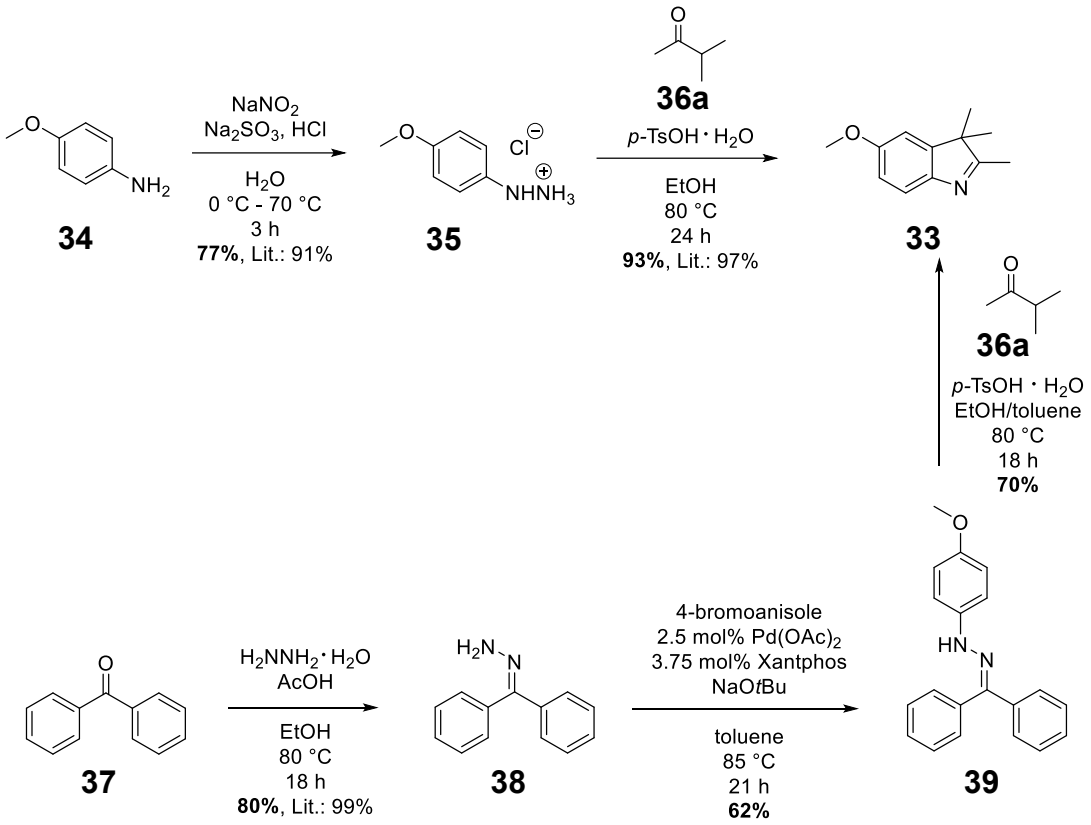


*Scheme 16: General retrosynthesis of spiropyrans **28**.*

Therefore, various derivatives of these two building blocks **31** and **32** were synthesized first. The following chapters explain and discuss the synthesis strategies developed for various indole building blocks.

5.1 Synthesis of glycosylated indoles with *N*-connected tails

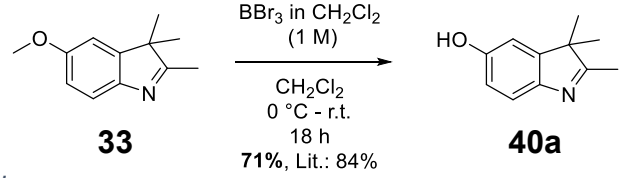
First, indole **33** should be synthesized according to a literature known synthesis route starting from *p*-anisidine (**34**).[121],[122] Even after testing various conditions, the synthesis of the hydrazine salt **35** was challenging due to purification difficulties. Thus, another route was tested parallel starting from benzophenone (**37**) (Scheme 17).



*Scheme 17: Synthesis of indole **33**.[121],[122],[123]*

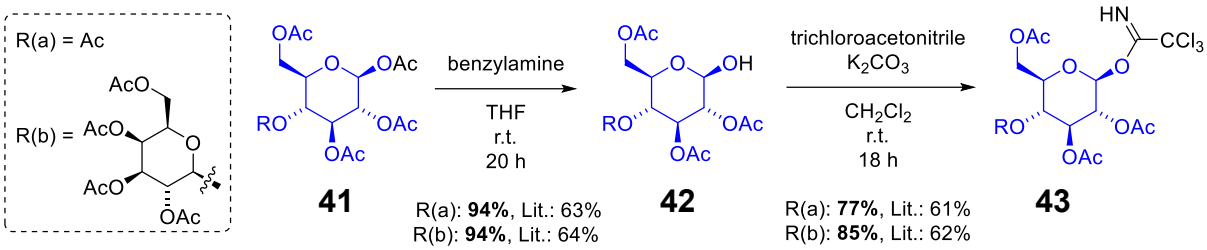
However, for the synthesis of larger quantities of indole **33**, the classical *Fischer* indole synthesis *via* hydrazine salt **35** remained the more cost-effective and efficient one.

The sugar unit, as hydrophilic head group, should be introduced *via* *O*-glycosylation. In order to obtain the free hydroxy group on the indole, demethylation was first carried out with BBr_3 (or HBr) according to a procedure by *Koh et al*.[124] (Scheme 18).



*Scheme 18: Deprotection of indole **33**.*

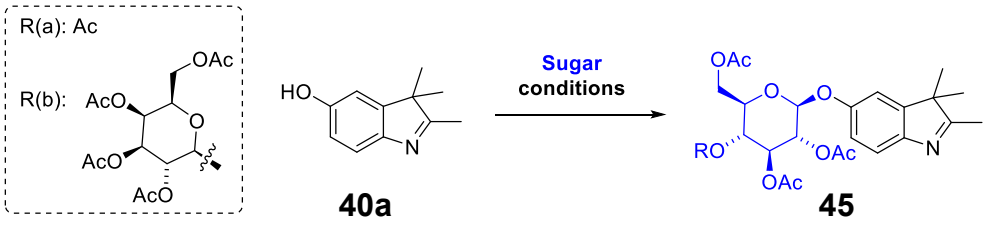
In the previous master's thesis[1] screening experiments showed that the use of glycosyl trichloroacetimidates **43** in combination with BF_3OEt_2 as *Lewis* acid was best suited for glycosylation on aromatic compounds. For this purpose, the suitable sugar building block **43** had to be synthesized first as shown in Scheme 19.

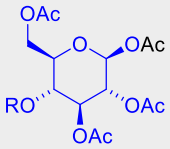
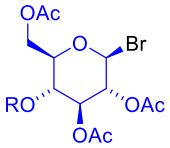
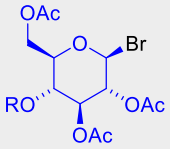
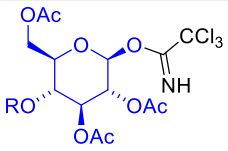


*Scheme 19: Synthesis of glycosyl trichloroacetimidates **43** for glycosylation.*[125],[126]

However, only acetoglucose **41** and trichloroacetimidates **43** and various *Lewis* acids have been tested for *O*-glycosylation so far. Since the use of trichloroacetimidates **43** always required new synthetic efforts, glycosylation was also examined using the *Königs-Knorr* method with the commercially available acetobromoglucose (**44**) and a silver salt (Table 2). In this case, no second stage synthesis of the sugar is necessary and the use of the highly corrosive BF_3OEt_2 can be avoided.

*Table 2: Overview of the conditions and sugar compounds tested for O-glycosylation of indole **40a**.*



Entry	Sugar	Conditions	Isolated yield
1	 **41**	$BF_3 \cdot OEt_2$ CH_2Cl_2 0 °C – r.t. 16 – 24 h	-
2	 **44**	Ag_2CO_3, Na_2SO_4 MeCN r.t. 16 h	-
3	 **44**	AgOTf, Na_2SO_4 CH_2Cl_2 r.t. 15 h	a: **35%**
4	 **43**	$BF_3 \cdot OEt_2$ CH_2Cl_2 0 °C – r.t. 16 – 18 h	a: **82%** b: **99%**

Since the yield of the *Königs-Knorr* method was proved to be significantly lower than using the trichloroacetimidates **43**, the first synthesis route was ultimately retained. *O*-glycosylation with the mono- **43a** and disaccharides **43b** to afford the glycosylated indoles **45a** and **45b** was successful realized in yields of 82% and 99%.

The hydrophobic unit should be introduced by alkylation on the indole nitrogen using primary alkyl iodides of different lengths as shown in Figure 14.

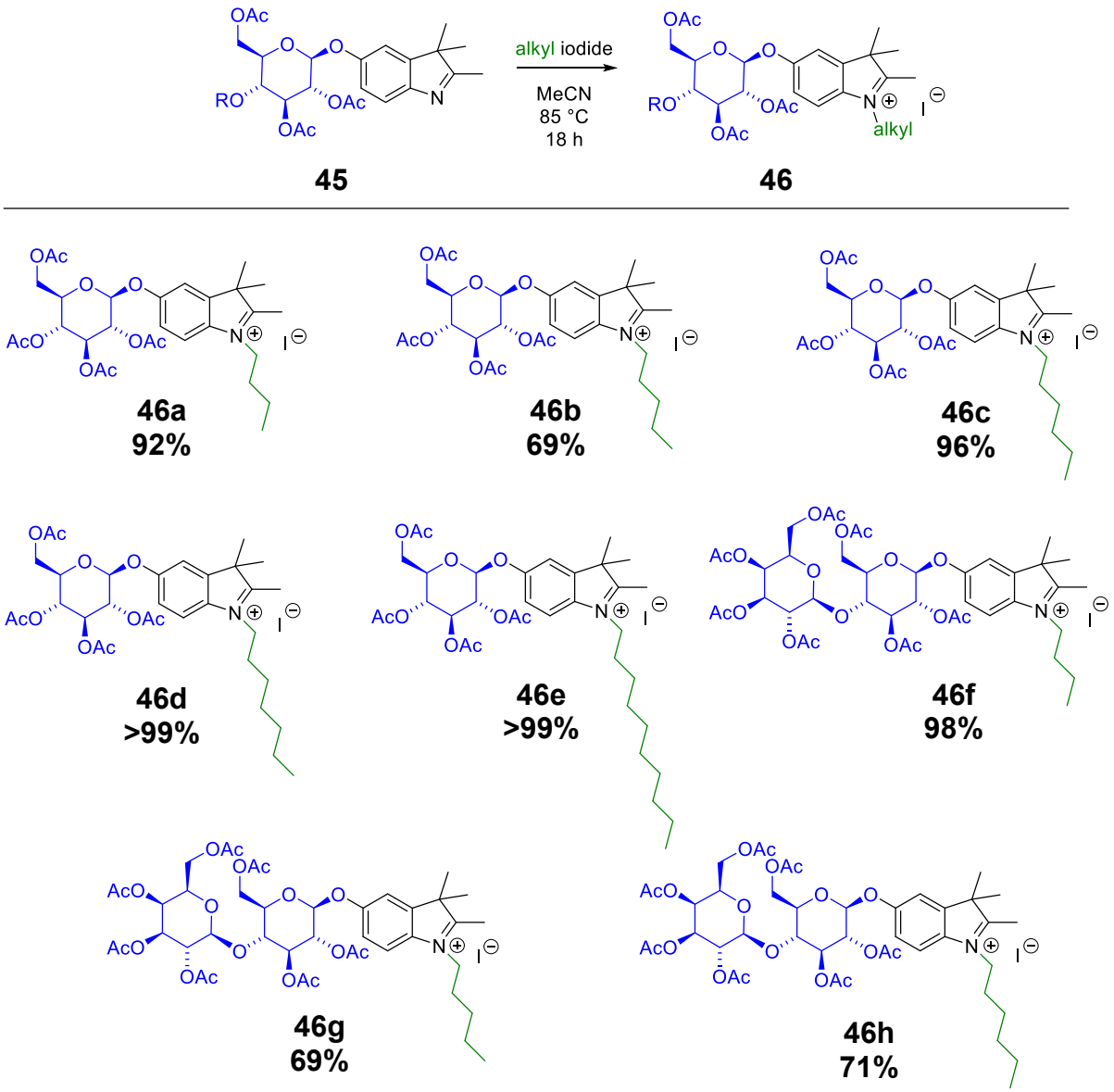


Figure 14: Accomplished alkylation of indoles with alkyl iodides of different lengths.

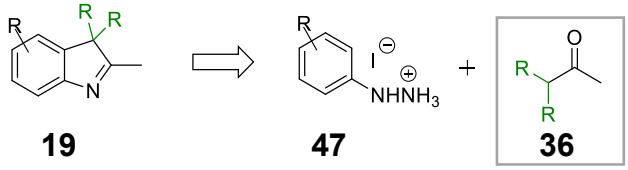
Eight alkylated indoles were obtained in yields ranging from 69% to 99%. The decreased lower yields of the alkylation employing pentyl iodide as alkylation agent might be explained by the reagent's purity. The size of the sugar unit and the length of the alkyl chain do not appear to influence the alkylation. Some of the *N*-alkylated indole

salts showed to be highly hygroscopic. Therefore, they were only washed with MTBE and then stored in a refrigerator in the absence of air.

In summary, the *N*-tail strategy has proven to be synthetically reliable. To increase structural variability, synthetic strategies should be developed to link geminal alkyl chains to the indole unit. This will provide access to a wider range of derivatives.

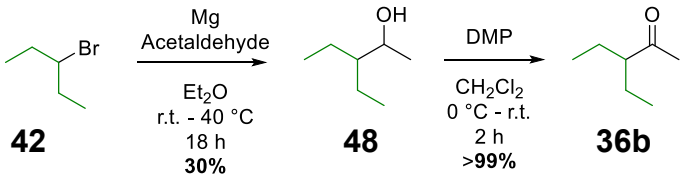
5.2 Synthesis of glycosylated indoles with geminal tails

In order to compare different surfactant structures, the hydrophobic chains and hydrophilic head groups should be linked to the spiropyran at different positions and in different lengths. For this purpose, alkyl chains should be attached at position 3 as geminal side chains (Scheme 20). This allows functional groups, such as ligands for ion coordination, to be linked through the unsubstituted indole nitrogen.



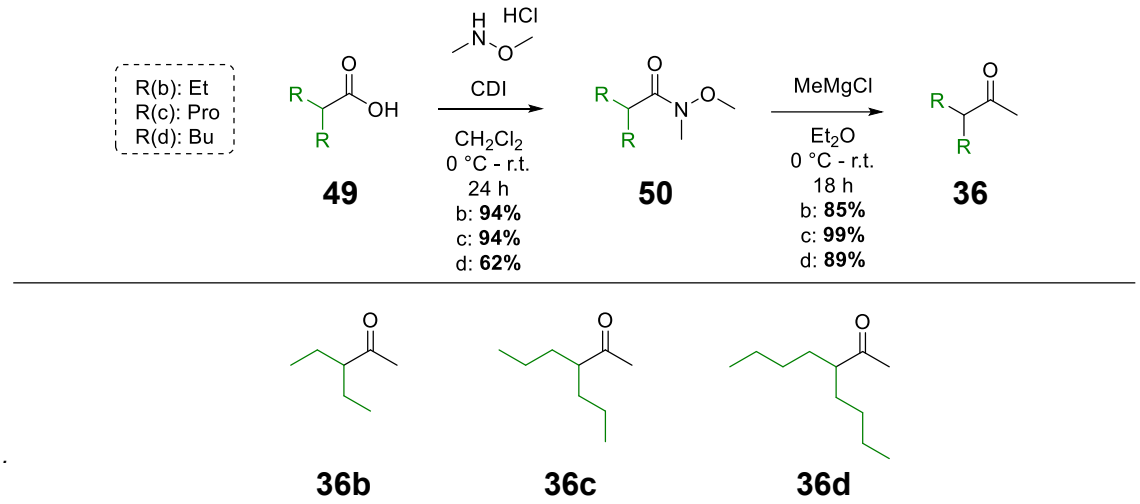
*Scheme 20: Retrosynthesis of indole **19**.*

Since the indole building block **19** should be synthesized by *Fischer* indole[127] synthesis, different ketones **36** must first be prepared for the introduction of different alkyl chains at position 3. Various synthesis routes were investigated for this purpose. First, ketone **36b** was obtained by synthesizing alcohol **48** and subsequent DMP oxidation
Scheme 21).



*Scheme 21: Synthesis of ketone **36b** with symmetrical alkyl chains.*

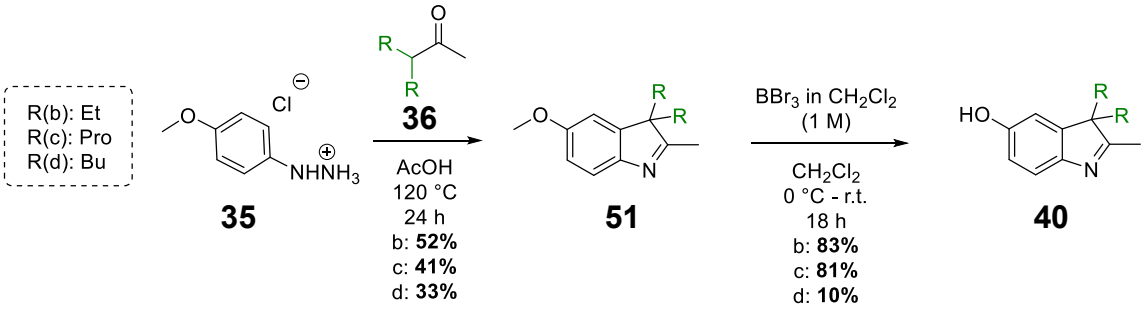
Good yields were achieved, but the bromoalkanes were expensive in large quantities and not commercially available with symmetrical longer chains. Therefore, a change was made to a synthesis route based on the favorable carboxylic acids **49** with alkyl chains of different lengths (Scheme 22).



*Scheme 22: Synthesis of ketone **36** with alkyl chains of different sizes.*

The desired ketones **36** were obtained by reaction with *N*,*O*-dimethylhydroxylamine and subsequent *Grignard* reaction in good yields of 85% to 99%.

After preparing the ketones **36** with different geminal alkyl chains, the indoles **40** were synthesized by reaction with hydrazine **35** (Scheme 23).



*Scheme 23: Synthesis of indoles **40** with geminal alkyl chains.*

In this case, the yield was lower than with butanone **36a**. Subsequently, the indoles had to be demethylated for the *O*-glycosylation again. The deprotection was successful and yield above 80% could be achieved. The poor yield for the conversion of indoles with longer chains can so far only be attributed to the use of an older sample of BBr_3. The deprotection has not yet been repeated, as the amount of indoles obtained was only sufficient for the subsequent investigations and the renewed synthesis of the ketones and indoles was very time-consuming. In principle, however, it should be possible to achieve a better yield using indoles with longer alkyl chains.

After deprotection of the hydroxy moiety, the *O*-glycosylation could be performed using the trichloroacetimidates **43** again (Figure 15).

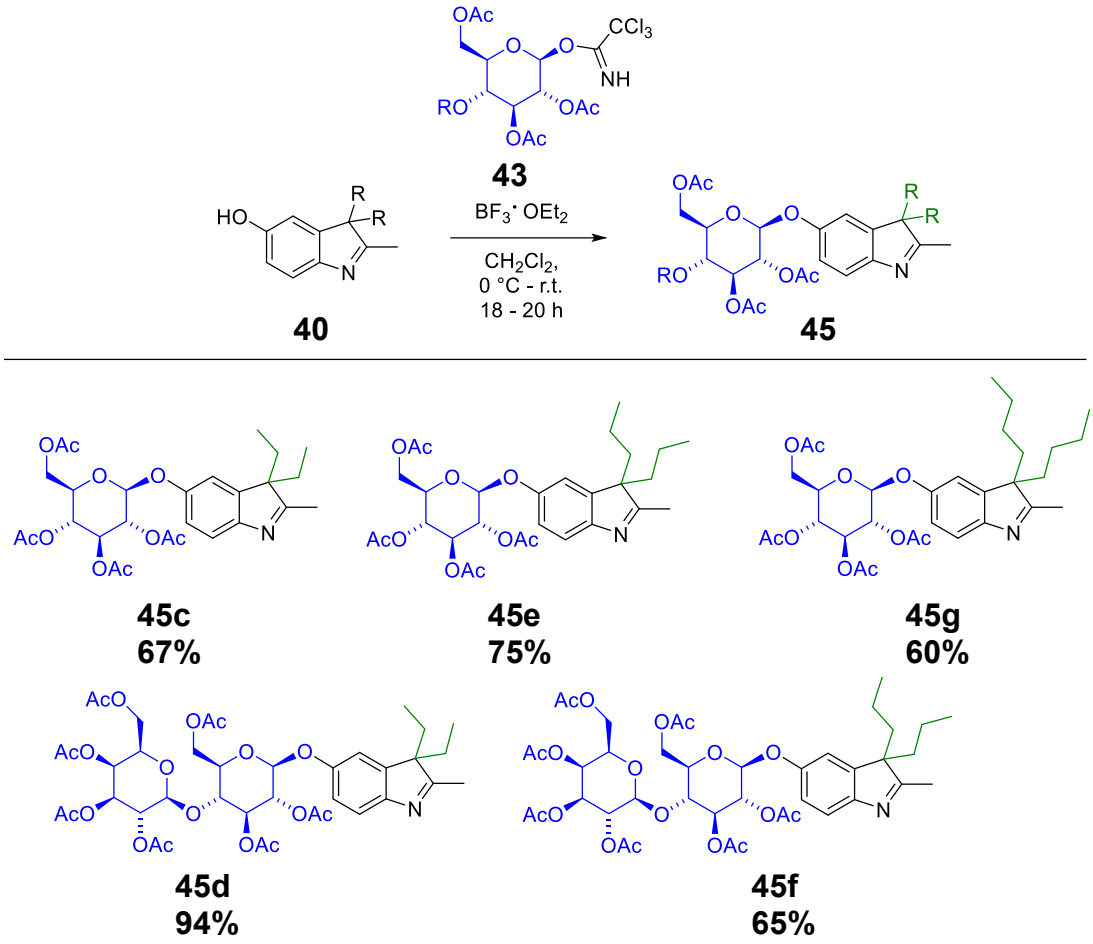
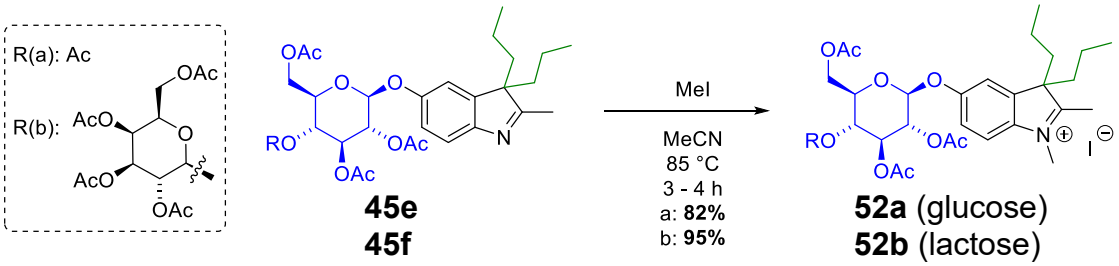


Figure 15: Accomplished O-glycosylation of the new indoles with geminal alkyl chains.

Five new glycosylated indoles **45** with geminal alkyl chains as hydrophobic units were obtained in sufficient yields above 60%.

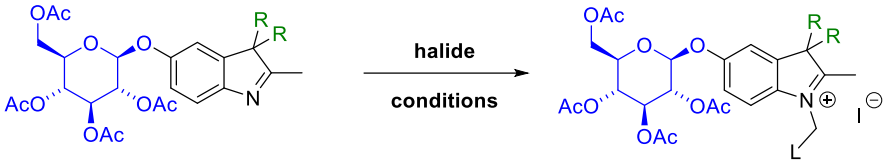
Subsequently, the indole nitrogen was methylated using iodomethane in good yields above 80% (Scheme 24).



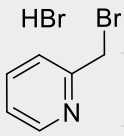
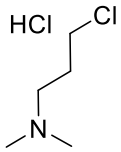
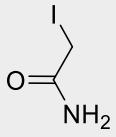
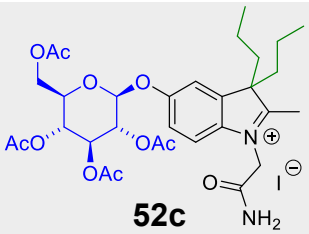
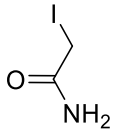
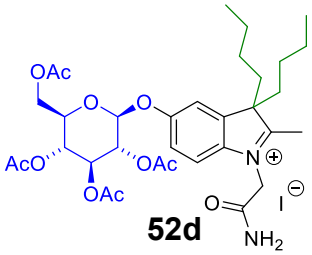
Scheme 24: Accomplished alkylation of indoles with geminal alkyl chains.

In some cases, attempts were also made to bridge different functional groups *via* the indole nitrogen. For example, amine ligands were tried to be linked for a possible application in photoswitchable ion coordination. For this purpose, various halogen compounds with amines, that were readily available and could act as ligands, were tested. A few tested conditions are summarized in Table 3.

Table 3: Tested conditions for alkylation of the indole nitrogen.



45 **52**

Entry	Halide	Conditions	Product	Conversion/ Isol. yield
1	 **53**	K_2CO_3, MeCN, 85 °C	-	-/-
		Na_2CO_3, MeOH, 65 °C		-/-
		1. NaOH aq., MTBE, r.t. 2. Ag-salt[a], toluene or MeCN, 110 or 85 °C		new spots on TLC/-
2	 **54**	1. NaOH aq., MTBE, r.t. 2. NaI, MeCN, 85 °C	-	-/-
		Ag-salt[a], K_2CO_3, toluene or MeCN, 110 °C or 85 °C		new spots on TLC/ -
3	 **55**	MeCN, 85 °C, 3 h	 **52c**	100%/ **99%**
4	 **55**	MeCN, 85 °C, 4 h	 **52d**	100%/ **>99%**

[a] Ag-salts: AgOTf or $AgClO_4$

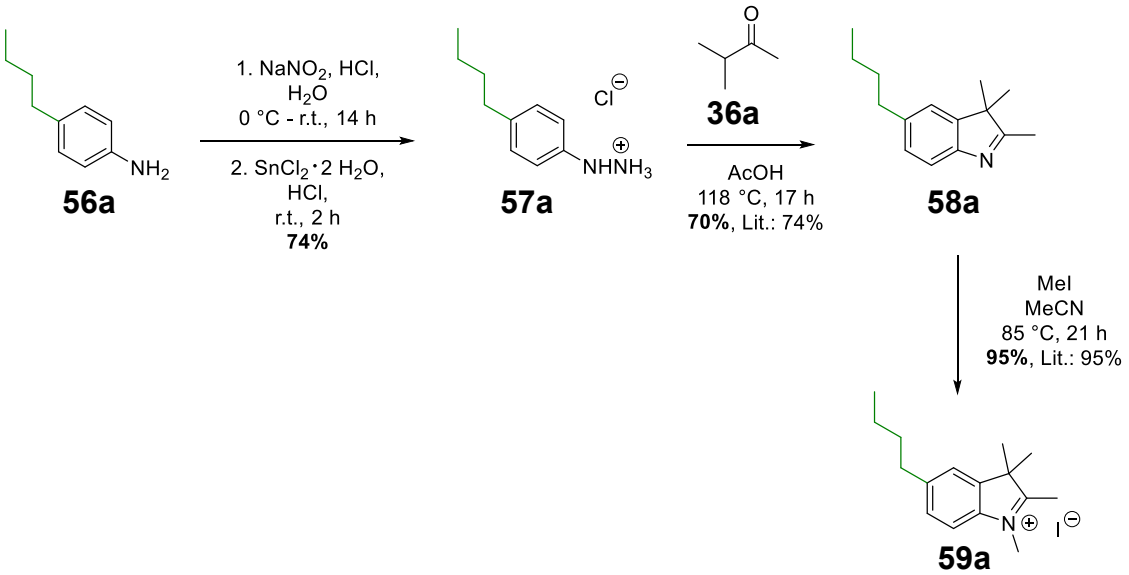
Alkylation appeared to be difficult. In most cases, no conversion was observed and the starting material was re-isolated. Even under *Finkelstein* conditions or the use of various silver salts as promoters the desired product could not be obtained. Although few examples of substitution reactions with bromine or chlorine compounds on indole nitrogen can be found in the literature, this reaction could not be reproduced in this work. When iodine compounds such as iodoalkanes or iodoacetamides **55** were used, full conversion and yields of > 99% were achieved. The screening thus showed that

the choice of halogen reagent in particular plays a decisive role for alkylation on the indole nitrogen.

In summary, the geminal tail approach enabled the introduction of two hydrophobic chains, which significantly increased the amphiphilic character of the molecules. While overall yields were lower than in the *N*-tail route, the broader structural variability and improved surfactant-like properties made this strategy attractive for further development.

5.3 *C*-Alkylation of indoles

In order to synthesize linear surfactants, different alkyl chains should be linked at position 4 of the indole unit. To introduce a butyl chain, it was possible to start with the commercially available 4-butylaniline (**56a**). First, the hydrazine salt **57a** was synthesized by diazotization and subsequent reduction. Then, the literature known *Fischer* indole[127] reaction with butanone **36a** was carried out successfully (Scheme 25).

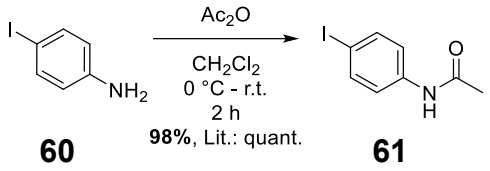


*Scheme 25: Accomplished synthesis of the alkylated indole **59a**.[111]*

After methylation, building block **59a** was obtained over three steps in 49% yield and could then be used for the synthesis of linear surfactants containing spiropyran building blocks.

To compare several linear surfactants with hydrophobic units of different sizes, additional longer alkyl chains should be linked to the indole. The same route as described above was supposed to be used for this purpose. However, as the alkylamines **56** with longer chains were not commercially available, they first had to be

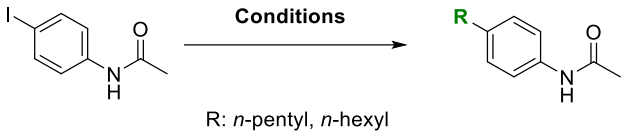
synthesized. Therefore, 4-iodoaniline (**60**) was first protected by acetylation (Scheme 26eme 26).



*Scheme 26: Accomplished protection of 4-iodoaniline (**60**).*

Afterwards the alkyl chain should be introduced. For this purpose, different cross coupling reactions were tested (Table 4).

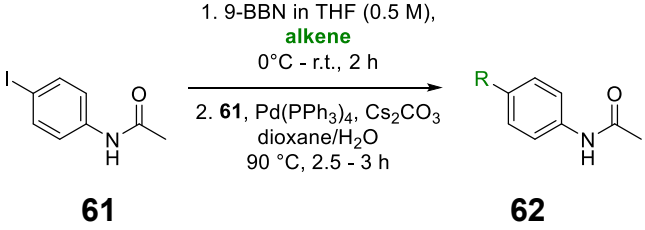
*Table 4: Tested conditions for the alkylation of acetamide **61**.*

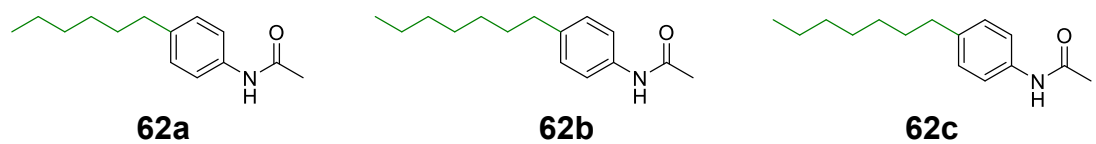


Entry	Conditions	Yield
1	1. 1-bromopentane, Mg, THF, 66 °C, 5 h 2. $PdCl_2$(dppf), THF, 66 °C, 20 h	**29%**
2	1. 1-hexene, 9-BBN in THF, 0 °C - r.t., 2 h 2. $Pd(PPh_3)_4$, Cs_2CO_3, dioxane/H_2O, 90 °C, 5 h	**85%**

Kumada coupling was tested using pentyl bromide and a Pd catalyst. The product was only obtained in low yields, so another route was investigated. After several optimization attempts, it turned out that a *Suzuki* coupling using the conditions shown in Table 4 was best suited to obtain the desired products in good yields.

After the *Suzuki* coupling was successfully performed using 1-hexene, further alkyl chains were linked under the same conditions (Scheme 27).





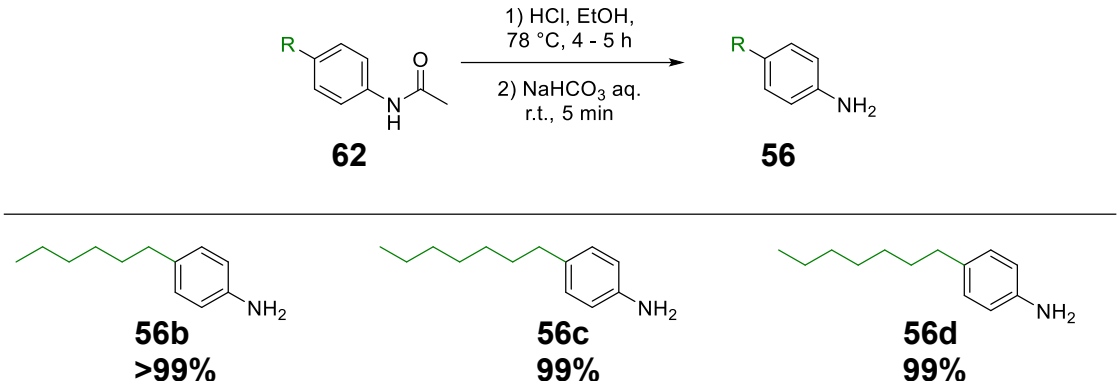
62a 83%

62b 96%

62c 98%

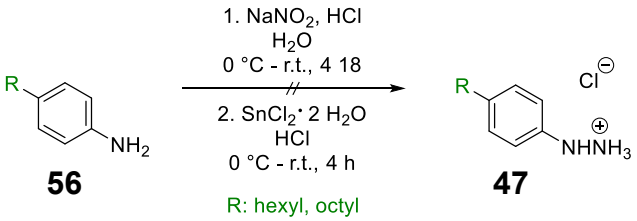
*Scheme 27: Accomplished alkylation of acetamide **61**.*

Coupling with 1-heptene and 1-octene worked just as well with very good yields of 96% and 98%, resulting in the three new amides **62**. These were then deprotected under acidic conditions as shown in Scheme 28.



*Scheme 28: Accomplished deprotection of amides **62**.*

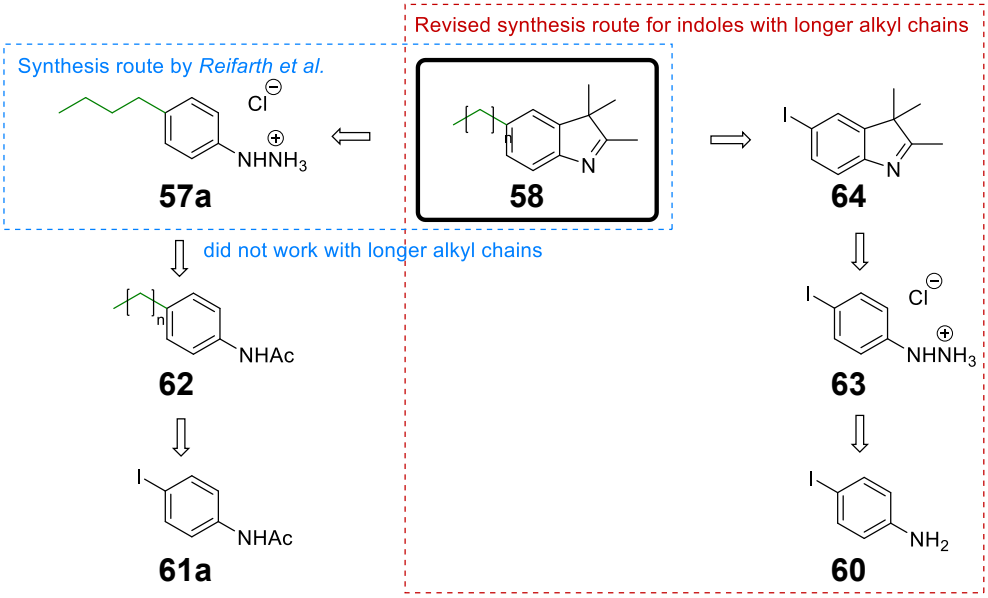
The three amines **56** were obtained in quantitative yields and should subsequently be converted to the corresponding hydrazine salts **47** according to the synthesis procedure that was already used for the successful hydrazine synthesis from butylaniline **56a** (Scheme 29).



Scheme 29: Tested conditions of hydrazine synthesis.

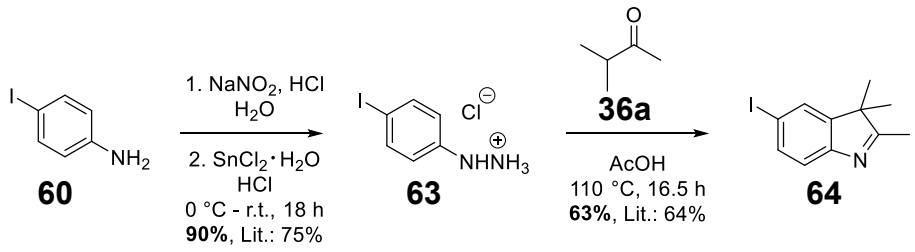
Only a crude product consisting of unidentified species was isolated. A reason for this could be that it was not possible to purify the crude product as it could not be washed with ether, neither a column chromatography could be performed. Nevertheless, the *Fischer* indole synthesis was tested with the crude product. Conversion was observed by TLC, but only the alkylanilines **56** were reisolated. The hydrazine synthesis was then also tested under other conditions, but so far no desired product could be isolated.

The route that was first followed and already partially published by *Reifarth et al.*[111] has so far only been known with 4-butylaniline (**56a**) and, as previously mentioned, has so far not worked with longer alkyl chains. Therefore, a new synthesis route was developed in which the *Suzuki* coupling for alkylation only takes place as the last step. The two tested synthetic routes are shown in Scheme 30.



*Scheme 30: Comparison of the two synthetic approaches towards alkylated indoles **58***

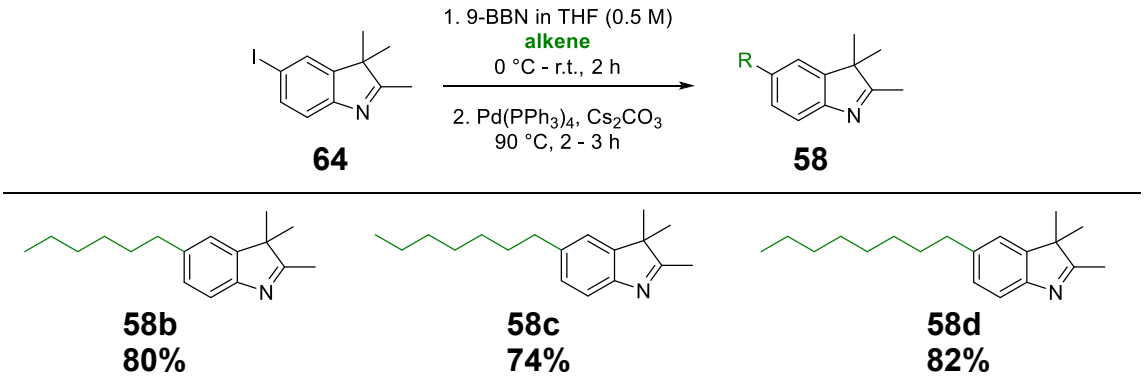
According to the new synthesis route, the first step was to synthesis the hydrazine salt **63** directly from 4-iodoaniline (**60**) (Scheme 31).



*Scheme 31: Accomplished synthesis of the hydrazine salt **63** and subsequent Fischer indole synthesis.[128],[129]*

The hydrazine salt **63** was obtained in very good yields. Subsequently, indole **64** was synthesized using ketone **36a** under the already applied conditions for *Fischer* indole synthesis.

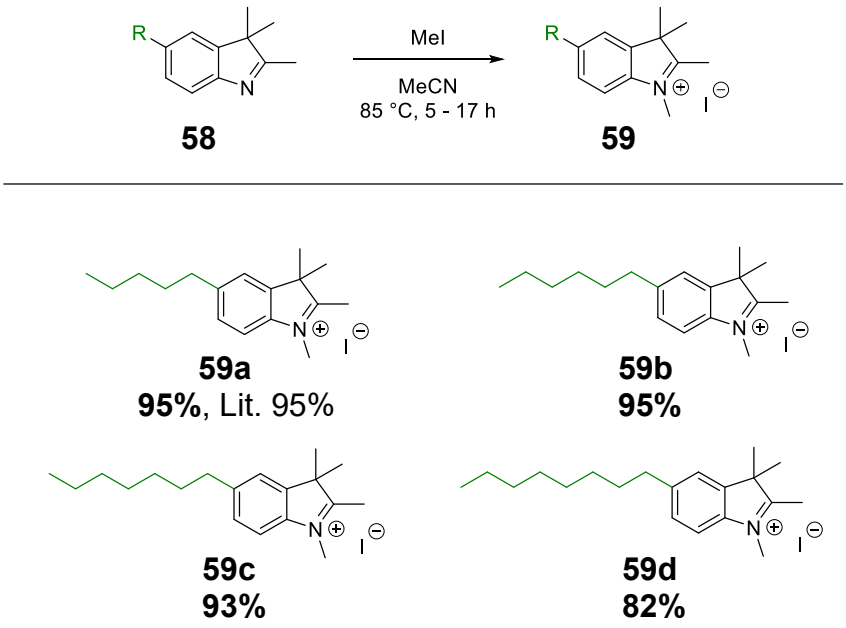
With indole **64** in hand the alkylation under *Suzuki* conditions was investigated. After already 2.5 h full conversion for coupling with hydroborated hexene was detected by GC-MS and 80% yield of the desired product **58b** was obtained (Scheme 32).



*Scheme 32: Accomplished Suzuki coupling of indole **64** with different alkenes (1-hexene, 1-heptene, 1-octene).*

Since the coupling reaction with hexene was successful, the reaction was tested with further alkenes as shown in Scheme 33. The *Suzuki* coupling with longer alkenes was also successfully carried out and yields of up to 82% were achieved.

Subsequently, the alkylated indoles could be methylated under the already known conditions (Scheme 33).



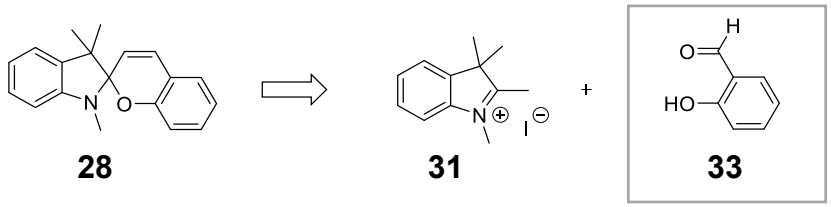
*Scheme 33: Accomplished methylation of indole **58**.*

The methylation was performed successfully and four new indole building blocks **59** with different alkyl chains as hydrophobic side chains for the following spiropyran synthesis were obtained in yields up to 95%.

In summary, a new synthesis route for the synthesis of alkylated indoles for linear surfactants was developed. The yields of the route are predominantly above 80%. The new route is also shorter than the first synthesis approach, as two synthesis steps are eliminated. The protection and deprotection of the amine are no longer necessary.

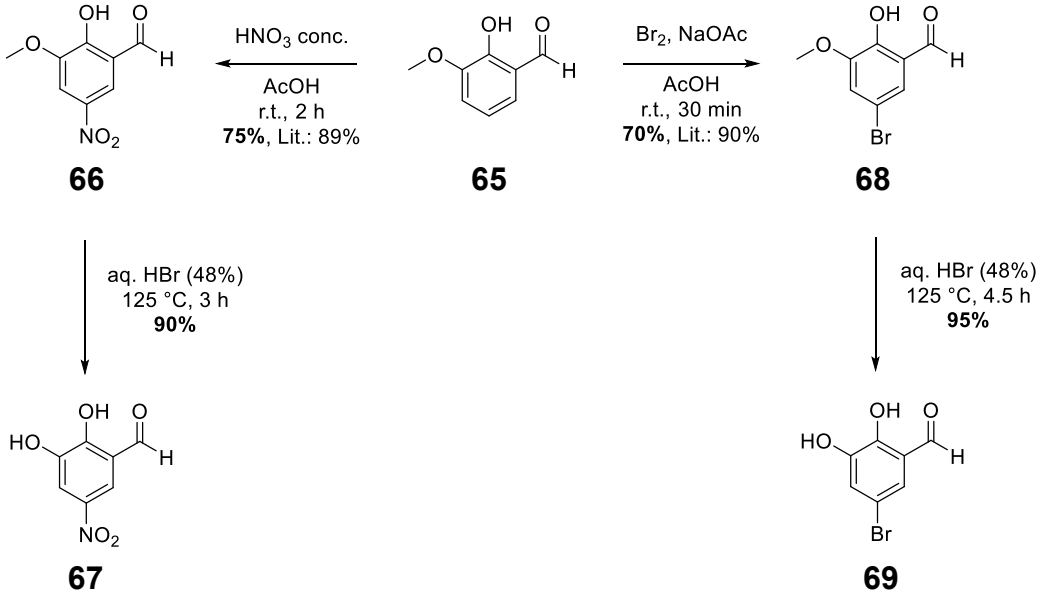
5.4 Synthesis of the eastern building block with different auxochromic groups

For the focused synthesis of spiropyrans, derivatives of salicylaldehyde **33** (described as eastern building block) had to be synthesized in addition to the indole building blocks. As mentioned above, according to the general synthesis of spiropyrans the eastern building block can be converted with the indole building block by condensation to the desired target structures (Scheme 34).



*Scheme 34: General retrosynthesis of spiropyran **28**.*

Initially, various auxochromic or anti-auxochromic groups were introduced on the basis of *o*-vanillin (**65**), which were intended to influence the photoswitch in different ways (Scheme 35).



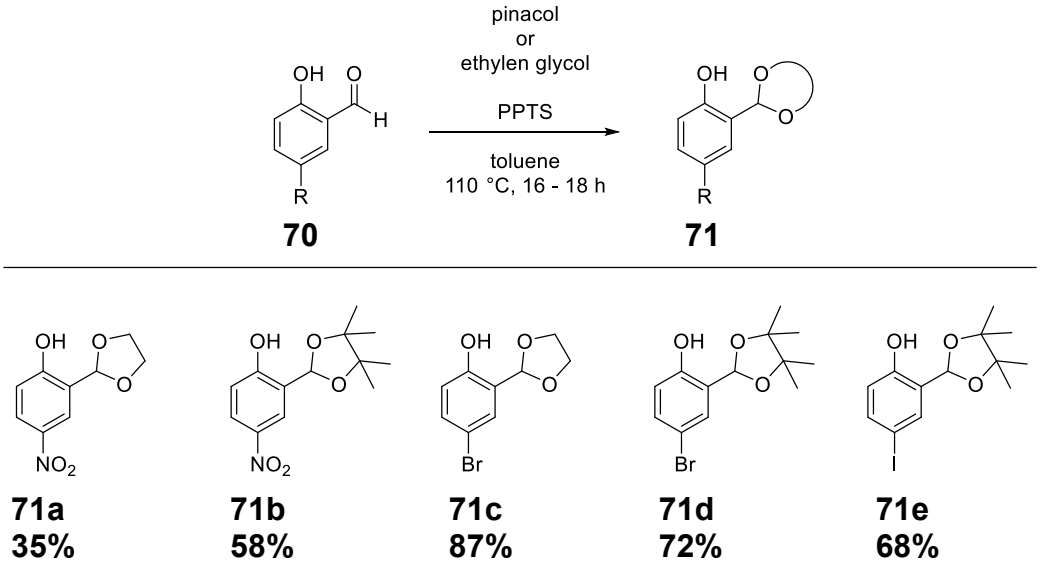
Scheme 35: Accomplished synthesis of different eastern building blocks with different auxochromic and anti-auxochromic groups.[130],[131],[132]

First, a nitro group was added to attach an anti-auxochromic group with -M/-I effect. The methoxy group acts as auxochrome (+M/+I effect) and the electron pushing effect can be amplified by demethylation to obtain the free hydroxy group. In addition, the *OH*-group can be used as a ligand for ion coordination in specific applications. Finally,

bromine was bound to the chromophore, which can act as an auxochrome as well as an anti-auxochrome.

Furthermore, an amino group should be introduced in *ortho* position of the eastern building block. This should be used for investigations on the influence on the electron density of the chromophore, and thus also on the influence on the switching process, but also for applications on ion coordination by acting as additional ligand.

Various routes were tried out to introduce an amine function. Therefore, the aldehyde had to be protected first. Acetal protection using a *Dean-Stark* set up was performed (Scheme 36).

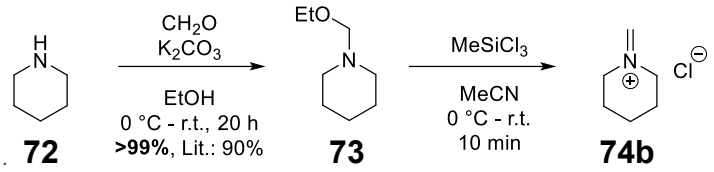


*Scheme 36: Acetal protection of salicylaldehyde **70**.*

It turned out that the acetal protection with *p*-TsOH did not work, so PPTS was used instead. Five different acetals were obtained by reaction with pinacol or ethylene glycol in sufficient yields.

To introduce the amine functions, initially, an attempt was made to obtain the desired product by chloromethylation using MOM-Cl and subsequent substitution of the halogen with the amine. The chloromethylation was successful, but the substitution could not be realized. Thus, a *Mannich*-type aminomethylations using *Eschenmoser* salts were tested as shown in Scheme 38.

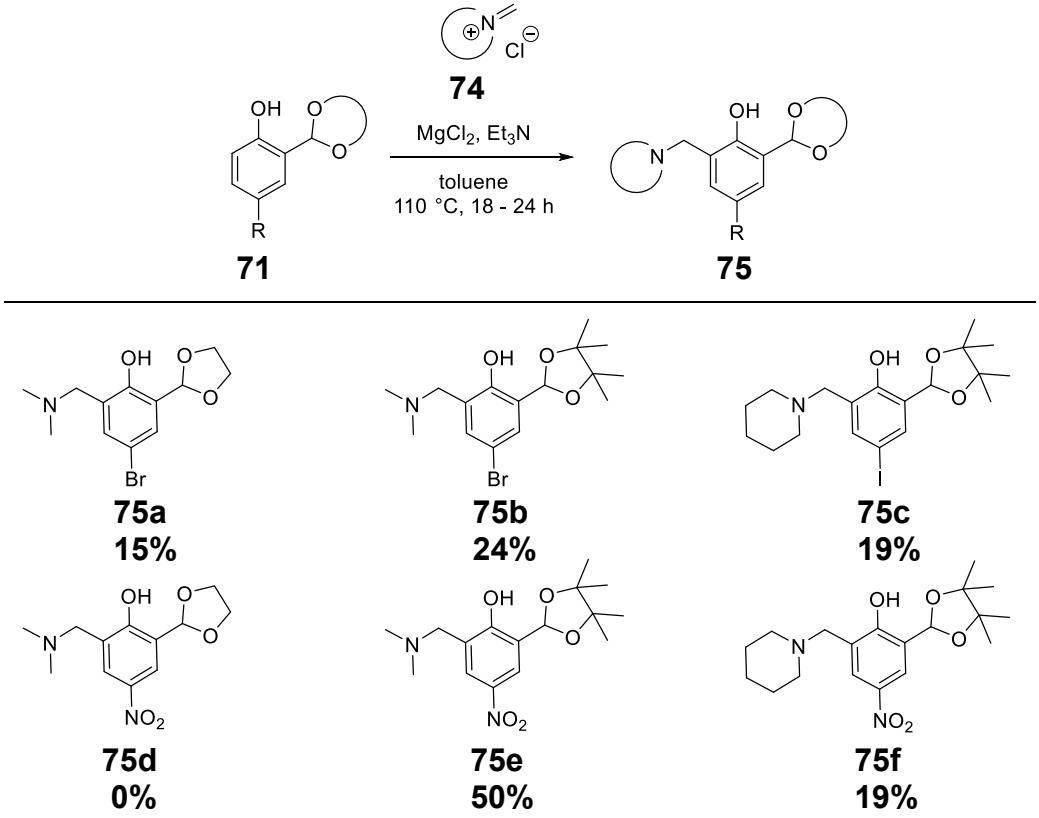
First, the commercially available and stable *N*,*N*-dimethylmethaniminium chloride (**74a**) was used for methylamination. In addition, the iminium salt **74b** was also synthesized from piperidine to improve the solubility of the product (Scheme 37).



*Scheme 37: Synthesis of the literature known iminium salt **74b**.*

The iminium salt **74b** was obtained according to a synthesis procedure by *Quintard et al.*[133]. Due to its instability, the product was converted directly after freeze-drying without further purification.

For the subsequent methylamination various solvents were initially screened. No conversion was observed using CH_2Cl_2 and THF with both iminium salts. The desired conversion could only be achieved by reaction in toluene (Scheme 38).

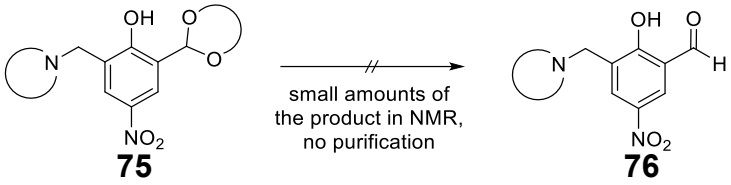


*Scheme 38: Accomplished amine alkylation of acetal **71** with iminium salts **74**.*

It turned out that the alkylamination with the 1,3-dioxalane protected compounds **71a** and **71c** was difficult due to the low solubility of the reactants in toluene. With the brominated compound **71c** only a yield of 15% could be achieved. No conversion at all was observed with the nitrated compounds. To increase the solubility of the reactants in the unpolar solvent toluene, the protecting group was changed and pinacol acetals were used. The conversion was thus slightly increased and up to 50% yield was achieved.

After successful amine methylation, only the acetal should be deprotected to obtain the free aldehyde for subsequent spiropyran synthesis. The acetal was tried to be removed under many different conditions (Table 5).

*Table 5: Tested conditions for the deprotection of acetal **75**.*



75 **76**

Entry	Conditions	Result
1	HCl (aq. 10 - 37%), THF, r.t. – 60 °C	-
2	TfOH, H_2O, 0 °C – r.t.	traces of product in NMR
3	$PPh_3 \cdot HBr$, 1,4-dioxane, 70 °C	mixture of side products
4	I_2, acetone, r.t.	-
5	$ZrCl_4$, MeOH, r.t.	-
6	*p*-TsOH, toluene/H_2O (1:1), 100 °C	-

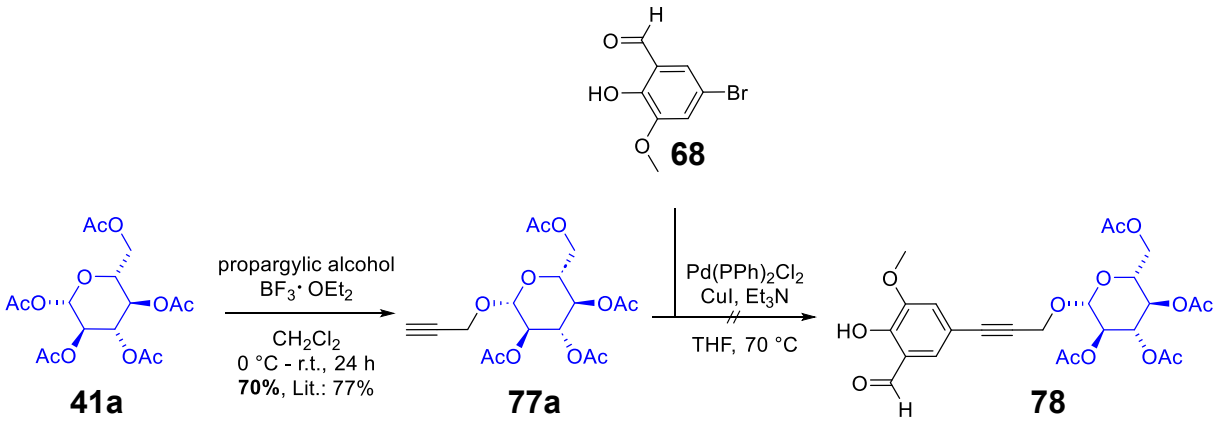
The product was obtained in low yields after deprotection using TfOH, but it has not yet been possible to isolate it. But the aldehyde signal could be clearly assigned in NMR. Due to the strong polarity and the interactions between the functional groups, the product could not be purified. The use of piperidine salts to improve the stability and solubility in organic solvents also did not give the desired results.

Since the synthesis route was very time-consuming and many conditions for the individual steps had already been investigated, the synthesis route was initially rejected. However, since the aminomethylation led to interesting compounds, these should be further investigated for the synthesis of spiropyrans. Perhaps a one-pot synthesis would be possible in which the aldehyde is deprotected and condensed with the indole. This could be investigated in the future.

5.5 Glycosylation of the eastern building block

In order to synthesize the linear surfactants, the hydrophilic sugar unit was to be linked to the eastern building block. Various routes were tested for this purpose.

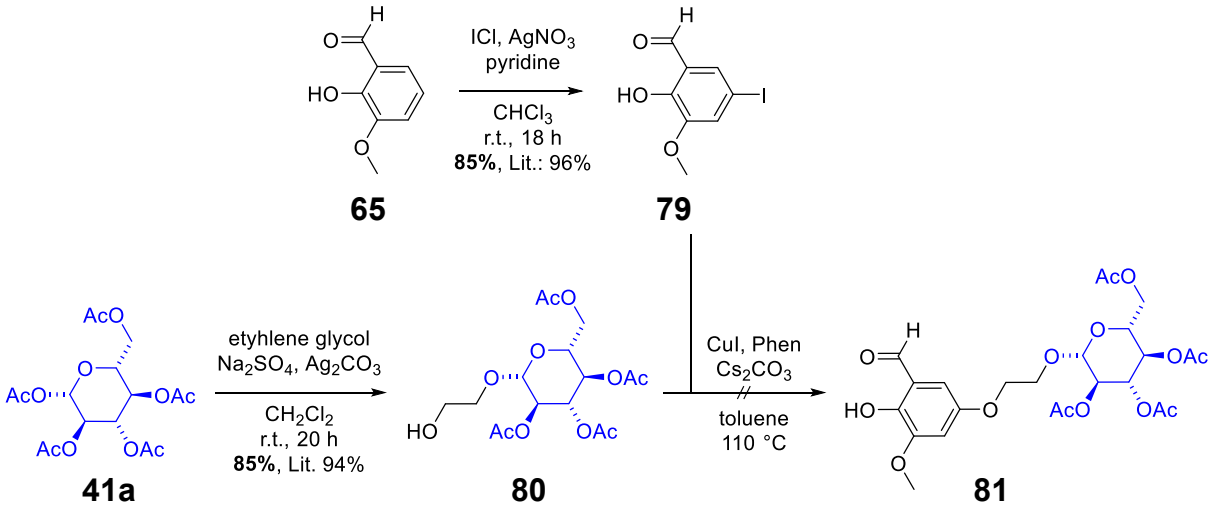
First, a *Sonogashira* coupling was tried, as it had already worked well in previous work on similar systems (see Section 9, Part 2) (Scheme 39).



*Scheme 39: Accomplished synthesis of alkyne **77a**[134] and tested Sonogashira coupling.*

For this purpose, the sugar **41a** was reacted with propargyl alcohol to obtain the corresponding alkyne **77a** in 70% yield. However, the subsequent *Sonogashira* coupling could not be successfully implemented. Various conditions and approaches in the microwave did not lead to the desired conversion.

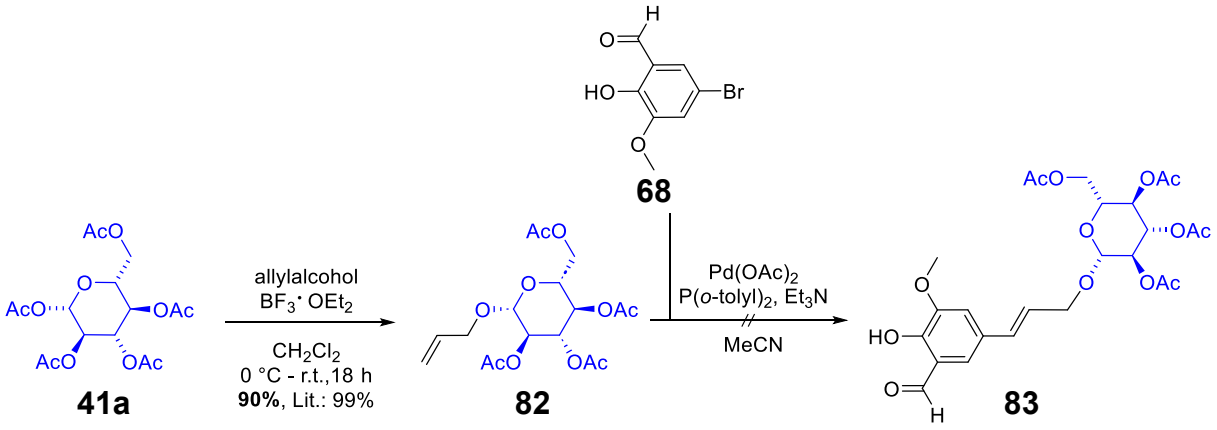
Next, an *Ullmann* coupling was tested as shown in Scheme 40.



*Scheme 40: Accomplished synthesis of sugar **80**[135] and iodine compound **79**[136] as well as the tested Ullmann coupling.*

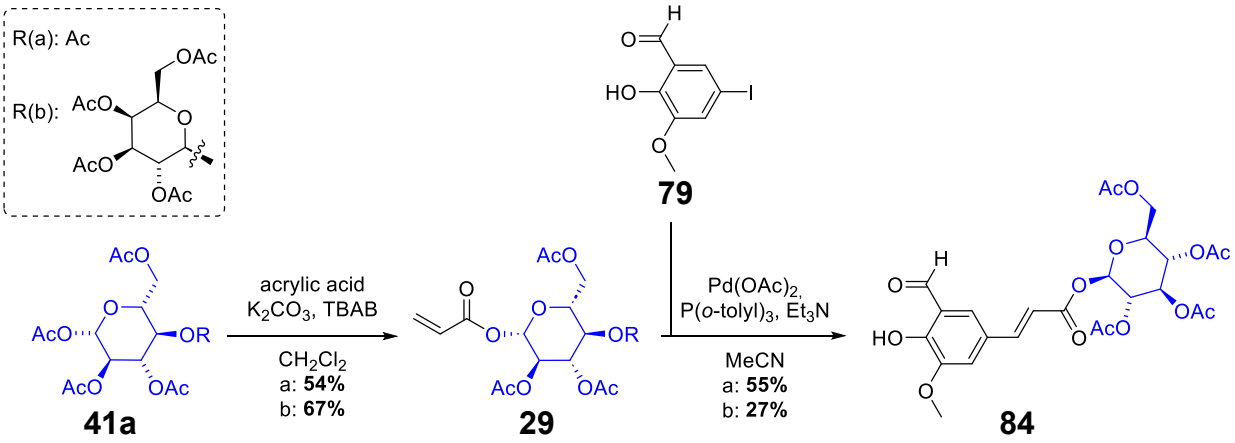
Therefore, sugar compound **41a** was first synthesized with 85% yield. In addition, compound **65** was iodized, which should then be linked to sugar **80**. Even after the investigation of various conditions, the desired product was not obtained.

As a third approach, a *Heck* coupling was tested (Scheme 41).



*Scheme 41: Accomplished synthesis of sugar **82**[137] and tested Heck coupling.*

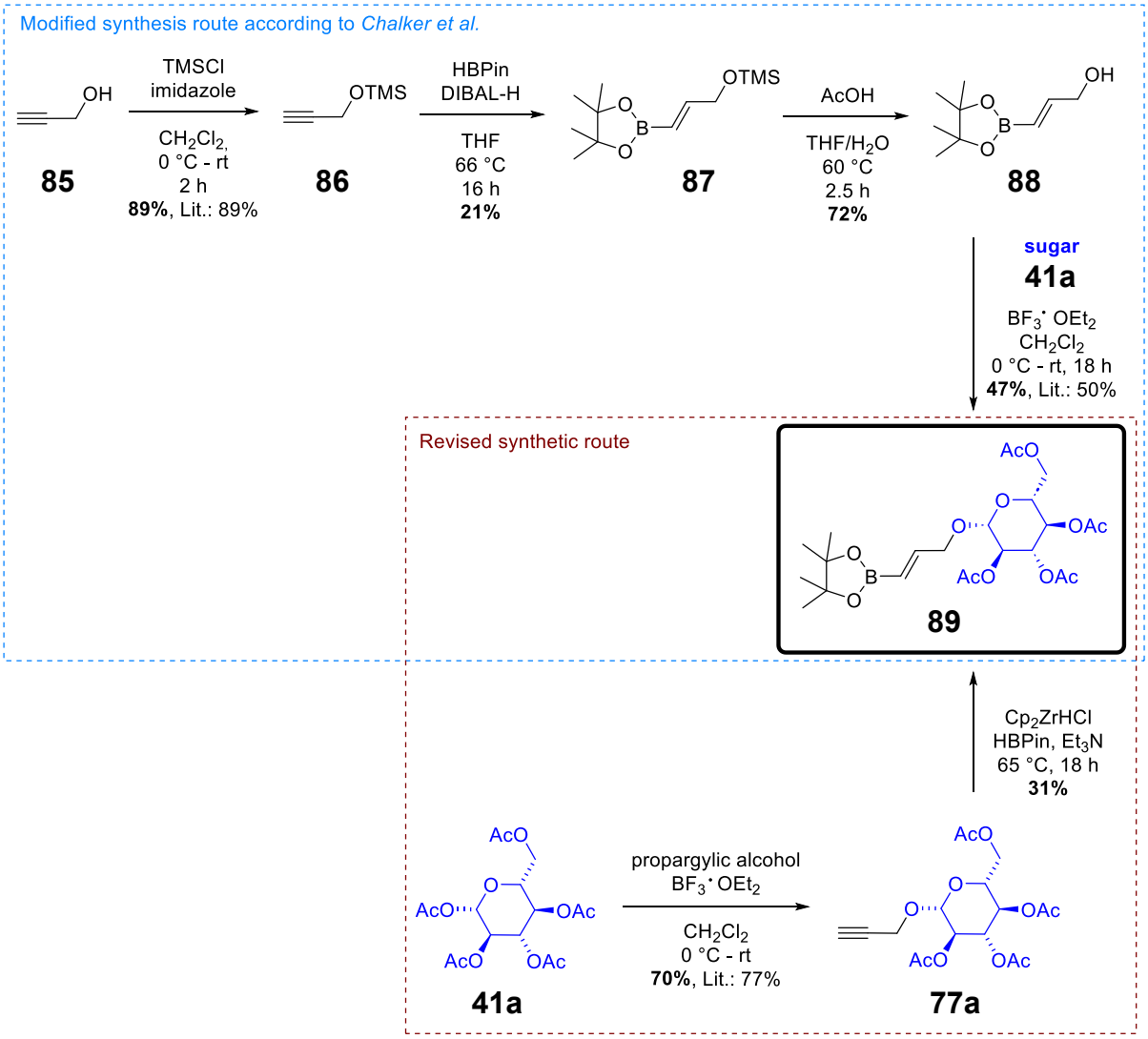
The alkene **82** was synthesized for this purpose. Various conditions were then tried out to link the sugar with the bromine compound **68**. Unfortunately, no conversion was observed here either. However, the *Heck* coupling was also tested with sugar acrylates **29** at the same time (Scheme 42).



*Scheme 42: Synthesis of sugar acrylates **29** and subsequent Heck coupling.*

The coupling was successful, but the product could not be used for further synthesis due to the resulting ester, as the protecting groups cannot be removed without simultaneous cleavage of this ester. However, this coupling reaction could be suitable for linking the two building blocks if other protecting groups on the sugar (such as benzyl groups) are used. However, this was not investigated further in this work, as other coupling reactions were tested in parallel.

Finally, an attempt was made to link the sugar moiety *via* a *Suzuki* cross coupling (Scheme 43).



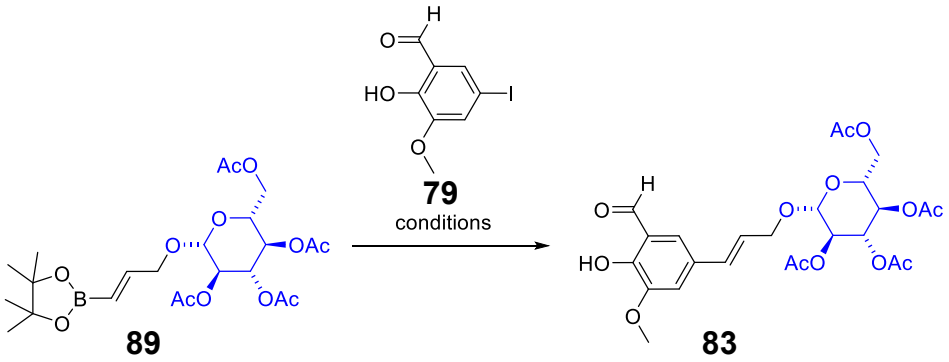
*Scheme 43:Two synthetic routes towards the glycosylated eastern building block **89**.*

For this purpose, a modified route by *Chalker et al.*[138] was followed to synthesize sugar borane **89**. The synthetic route started with the revised hydroboration of the trimethylsiyl ether **88**, which was synthesized from propargylic alcohol **85**. The vinyl boronate **87** was subsequently deprotected under acidic conditions. This yielded the free hydroxyl group, which was used for glycosylation with the sugar moiety **41a**. This gave the desired compound **89** in 6% overall yield over 4 steps.

As the route was very time-consuming and the yields were relatively low after four synthesis steps, an alternative route was developed. For this purpose, the acetylated sugar **41a** was reacted with propargylic alcohol. The resulting alkyne **77a** was subsequently converted to the desired product **89** by borylation under catalysis using the *Schwartz* reagent. This synthesis route was significantly shorter. Although the yield

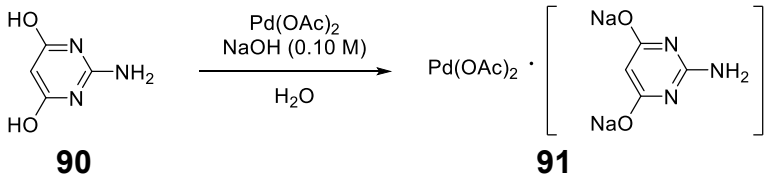
of the last step is low, the total yield after two steps is significantly higher at 21%. Thus, enough product was obtained for the subsequent investigation of the *Suzuki* cross coupling. The tested conditions are summarized in Table 6.

*Table 6: Screening of Suzuki cross coupling conditions to synthesize the glycosylated moiety **83**.*



Entry	Conditions	Yield
1	$PdCl_2$, PPh_3, Na_2CO_3 (2 N) 1,4-dioxane, 101 °C	-
2	$Pd(PPh_3)_4$, K_3PO_4 1,4-dioxane, 101 °C	-
3	$Pd(dppf)Cl_2$, CsOAc THF, 66 °C	-
4	catalyst complex **91** MeCN, 80 °C, 3 h	**45%**

For the *Suzuki* cross coupling of the sugar borane **89** with iodovanillin **79** various Pd catalysts and bases were tested. No yield of the desired product could be achieved with the first approaches. Finally, a catalyst complex **91** was synthesized according to a literature known procedure of *Chalker et al.*[138].



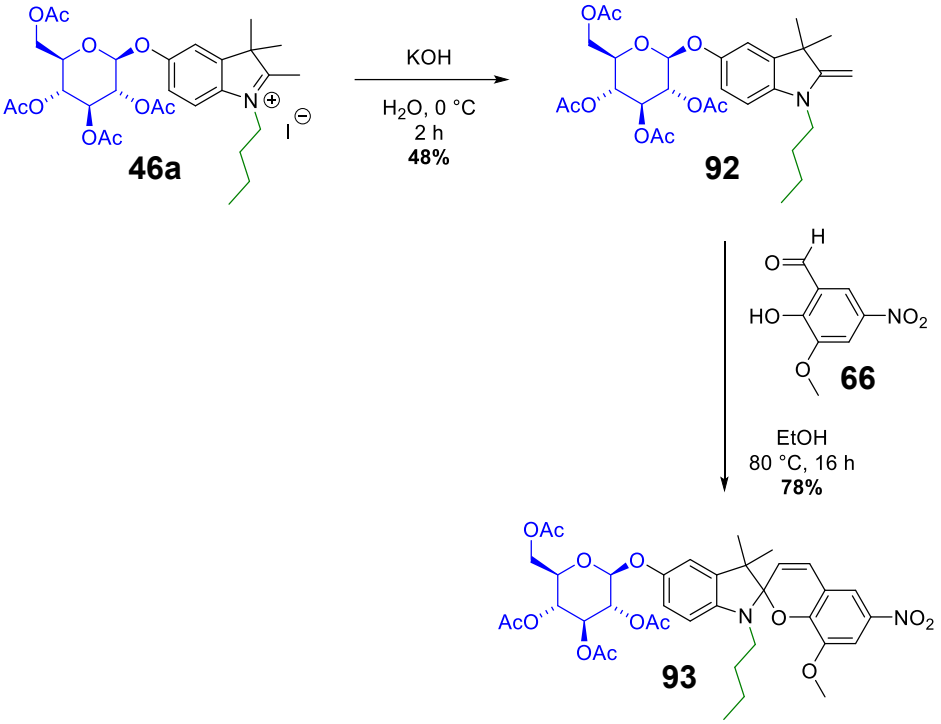
*Scheme 44: Synthesis of the catalyst complex **91**.*

The catalyst complex **91** was prepared by stirring pymiridine **90** in NaOH-solution and subsequent addition of $Pd(OAc)_2$. After dilution to 0.01 M, the stock solution could be stored in the fridge for several weeks. Using this catalyst **91** the desired product **83** could be obtained in 45% yield.

5.6 Condensation of the indoles and hydroxybenzaldehydes

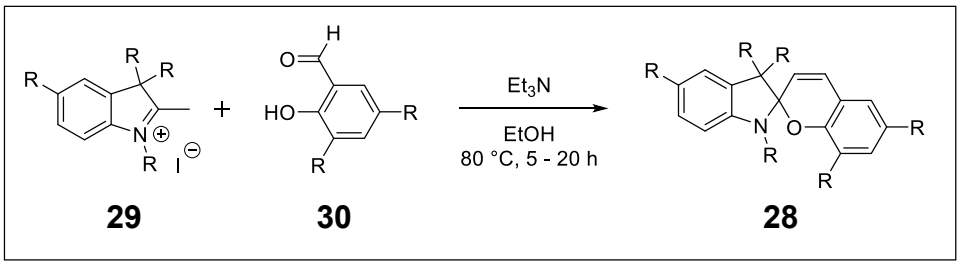
After a total of 16 different indole building blocks (west building block) and 6 different eastern building blocks were successfully synthesized, these could be converted to spiropyrans by base-catalyzed condensation.

The coupling was initially tried out by first deprotonating indole **46a** and then reacting indoline **92** with the aldehyde **66** (Scheme 45).



*Scheme 45: Stepwise synthesis of spiropyran **93**.*

Spiropyran **93** was obtained sufficient yields, but indoline **92** was very viscous and hygroscopic. For easier handling and to save one reaction step, the synthesis was carried out as a one-pot reaction (Scheme 46).



*Scheme 46: Synthetic conditions used for the synthesis of spiropyrans **28**.*

Initially, piperidine was tested as a base. However, it turned out that the workup and conversion was best using Et_3N. Thus, a total of 14 new spiropyrans were synthesized. Purification of the products proved difficult because the compounds were in equilibrium

between the two isomers (SP and MC). The two isomers exhibit different solubilities. For this reason, the crude product was just washed with ether and no further purification was carried out.

According to the general procedure shown in Scheme 46 eight spiropyrans with *N*-alkylated and *O*-glycosylated indole moieties and different chromene units were obtained (Figure 16).

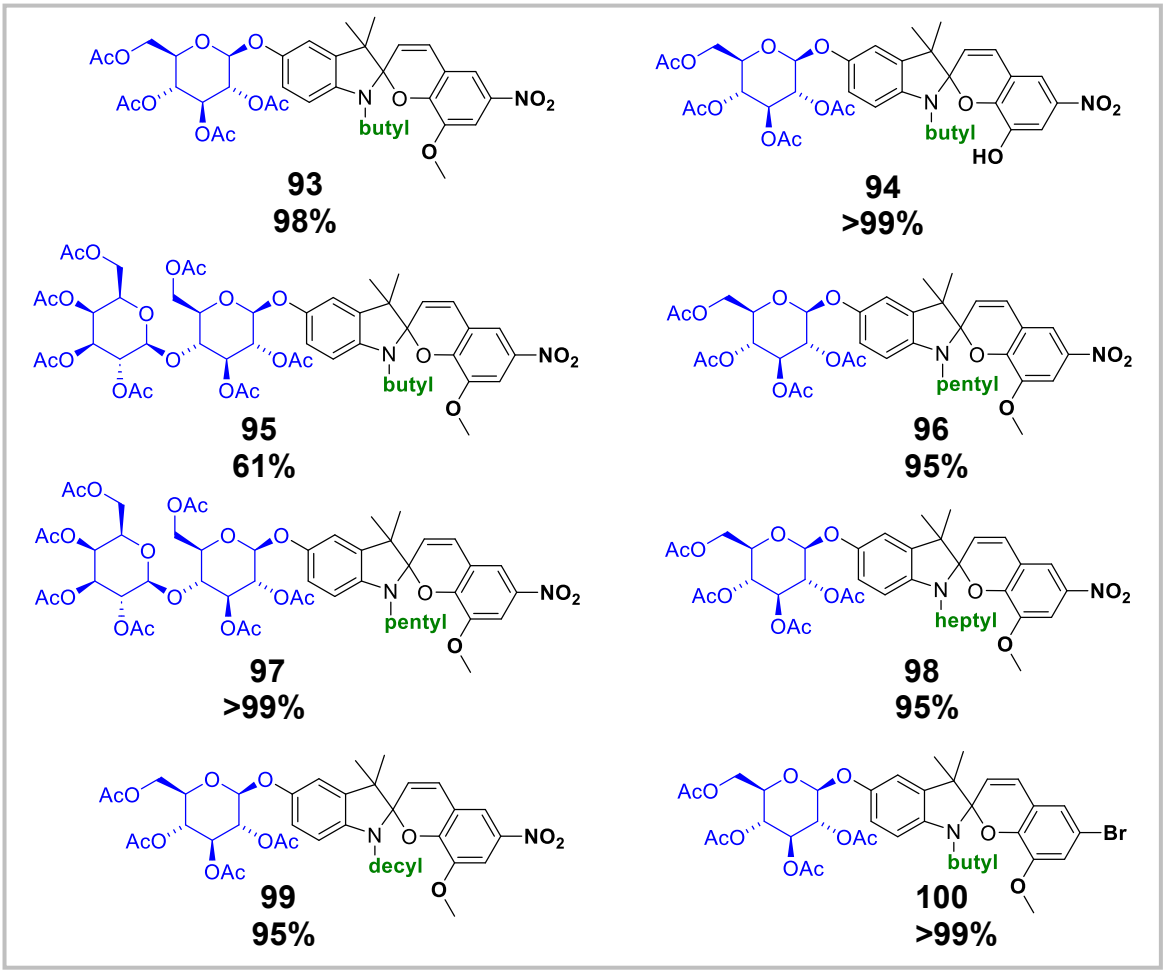


Figure 16: Successfully synthesized spiropyrans with O-glycosylated and N-alkylated indole moieties.

The spiropyrans **93** - **100** were obtained in good yields of 61% to 99%.

Three different linear spiropyrans with alkylated indoles and glycosylated benzopyran were synthesized with 89% yield (Figure 17).

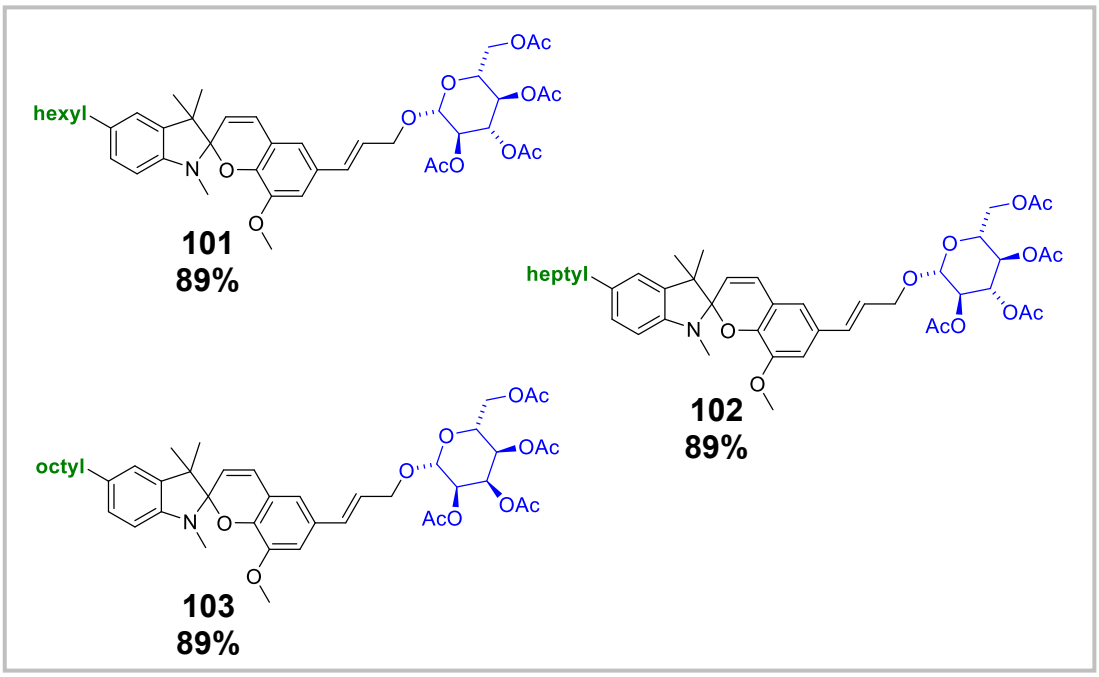


Figure 17. Successfully synthesized spiropyrans with alkylated indole moieties and glycosylated benzopyrans.

In further investigations also disaccharides could be used to compare different head groups.

Four different spiropyrans were synthesized by condensation of the *O*-glycosylated indoles with various geminal alkyl chains and nitrated benzopyrans (Figure 18).

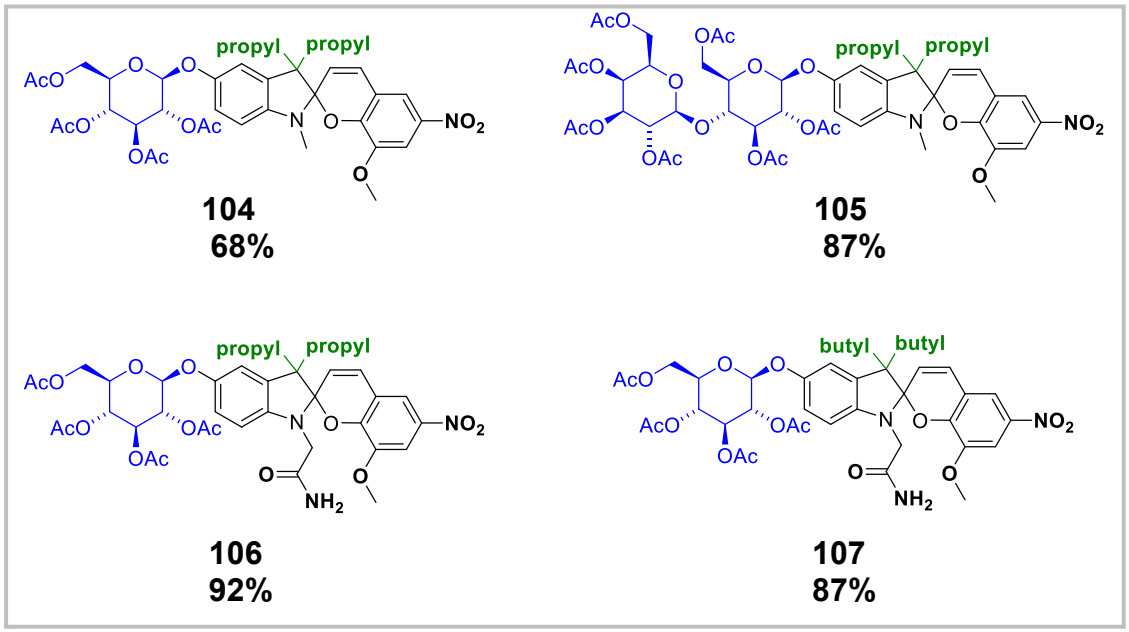
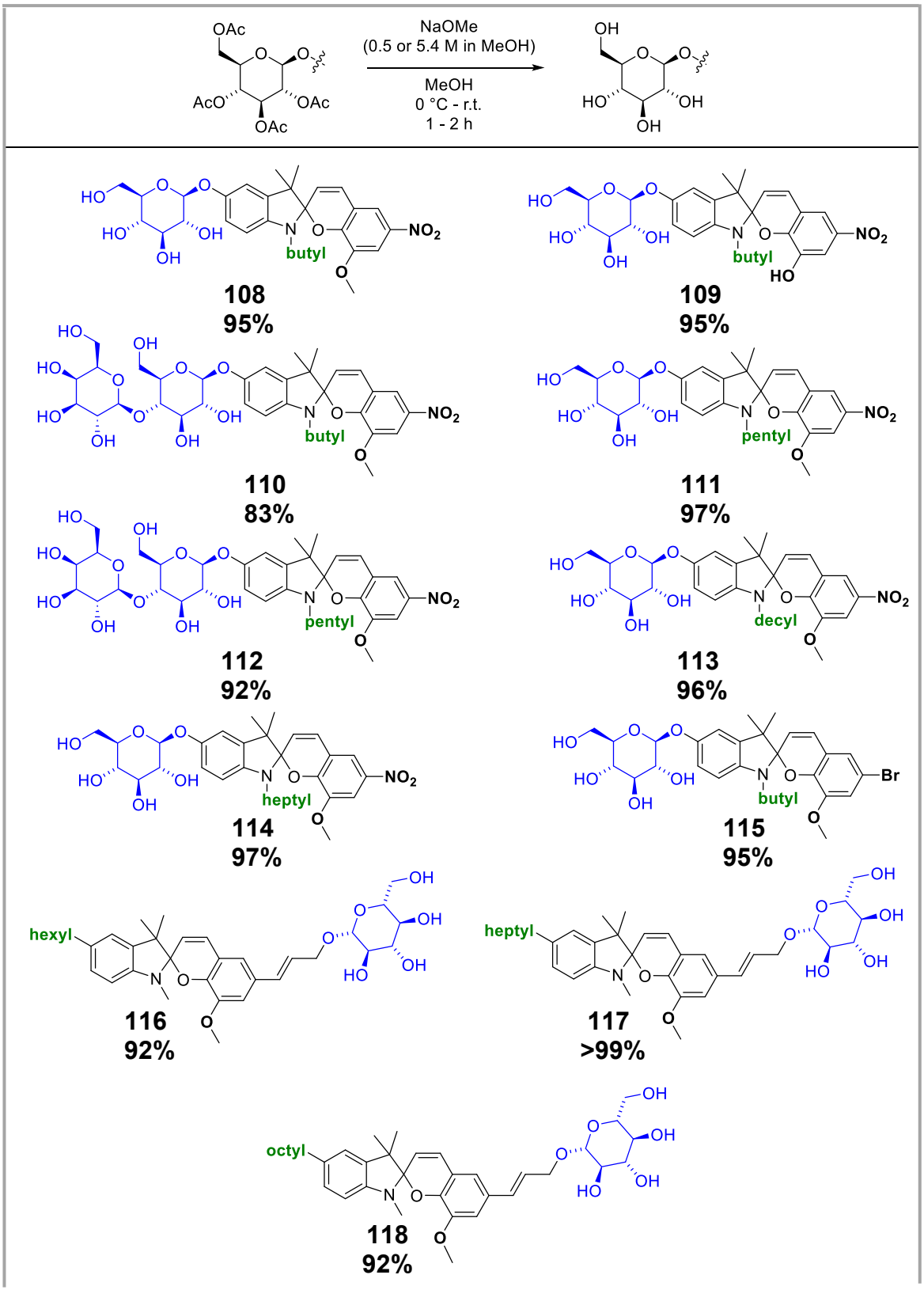


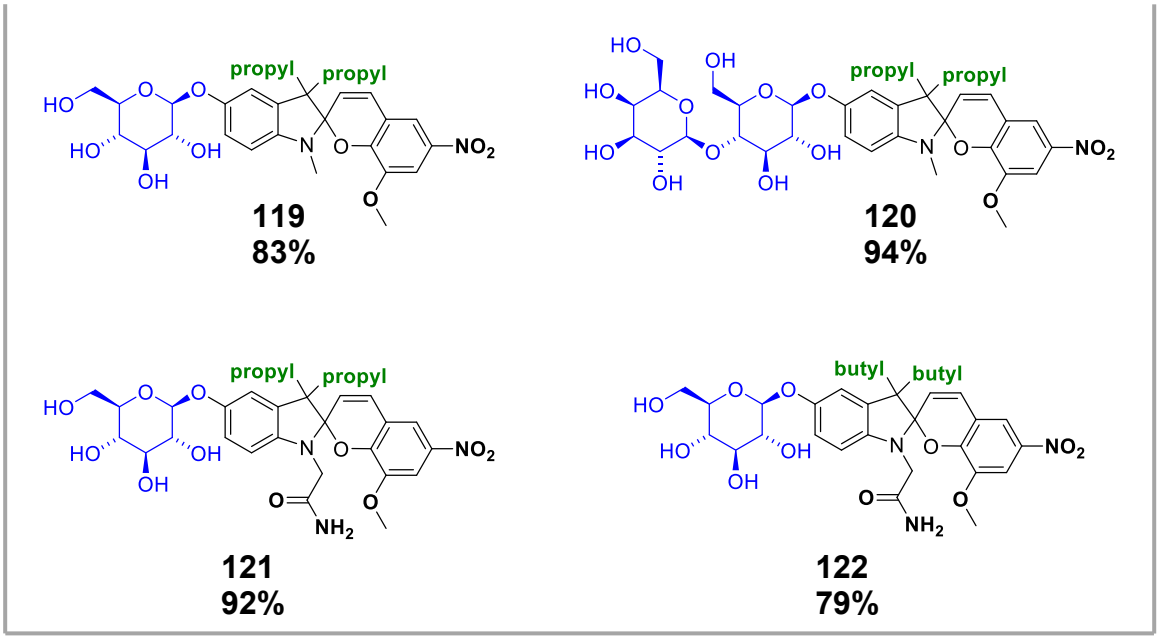
Figure 18: Successfully synthesized spiropyrans with O-glycosylated and geminal alkylated indole moieties.

The desired compounds **104** - **107** were obtained with 68% to 92% yield.

5.7 Deprotection of sugar units and preservation of the final surfactants

Subsequently, the acetyl groups of the sugar units were cleaved to achieve the hydrophilic head groups and thus the final surfactants (Scheme 47).

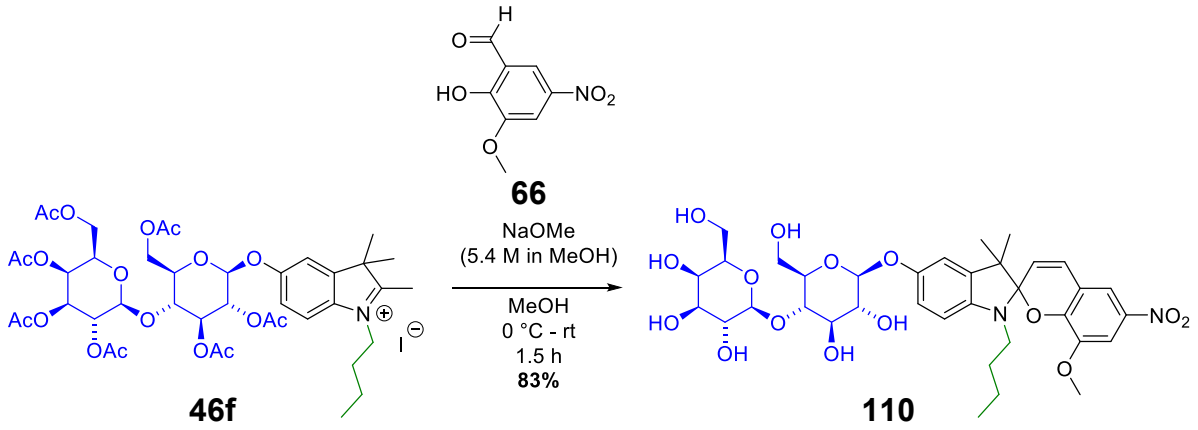




Scheme 47: Accomplished deprotection of the sugar units of the spiropyrans to obtain 15 new surfactants.

The deprotection was carried out using NaOMe in MeOH and yields of 83% to 99% were reached. Depending on the solubility of the products, they were then washed with EtOAc or ether. All 15 spiropyrans could be deprotected successfully and used for further physicochemical and UV-vis investigations.

In addition, a **one-pot synthesis** was tested, in which the condensation and deprotection of the sugar unit take place simultaneously. For this purpose, the deprotection conditions with NaOMe in MeOH were used. Due to the basic conditions, not only the sugar is deprotected, but also the indole is deprotonated, enabling condensation (Scheme 48).



*Scheme 48: Accomplished one-pot synthesis of surfactant **110**.*

The one-pot synthesis worked well and the yield of 83% was comparable to the two-step synthesis. In the future, this could also be tested for the other compounds to simplify the synthesis.

The 15 obtained target compounds showed strong solvatochromism. They were soluble in water and methanol. The linear surfactants, which were mainly present in the SP form, were also soluble in EtOAc and $CHCl_3$. The compounds appeared blue in methanol and water. The linear spiropyrans appeared reddish in color in $CHCl_3$ and green in EtOAc.

The NMR assignment for all target compounds was difficult because they were present in equilibrium of the open and closed form. Measurements after storage in the dark also showed no major shift in equilibrium. The UV-vis measurements also showed that the equilibrium of the two forms was quickly established by irradiation with UV and visible light, especially of the *N*-alkylated spiropyrans. However, all molecular structures could be clearly demonstrated through the combination of NMR, ESI-MS and IR.

5.7 UV-vis analysis of photoswitchable surfactants

In the following, the UV-vis spectra of the synthesized photoswitchable surfactants are compared. All spectra were obtained from 0.025 mM methanolic solutions at 20 °C. Three spectra were recorded for each system. Once at a thermal equilibrium in dark (black), and the other after irradiation with UV (red) or visible light (blue).

In addition to the general absorption spectra after different irradiation, kinetics were also recorded. To observe the ring opening reaction and to determine the rate constant (k_{obs}), the sample was irradiated with UV light to maximize the concentration of merocyanines. The sample was then kept in the dark and the absorption spectrum was measured in regular intervals. Through this, the decrease in absorption could be monitored over time.

The rate constants for the SP/MC systems were determined using the following equations:

$$SP \underset{k_{MC\text{-}SP}}{\overset{k_{SP\text{-}MC}}{\rightleftharpoons}} MC$$

The observed rate constant can be described by the sum of the rate constants of the ring-opening reaction ($k_{SP\text{-}MC}$) and the cyclisation ($k_{MC\text{-}SP}$) (Equation 5).[139]

$$k_{obs} = k_{SP-MC} + k_{MC-SP} \tag{5}$$

The cyclisation of the merocyanine and the ring opening reaction of the spiropyran are first order reactions. Therefore, both reactions can be described by Equation 6, with [X] being the concentration of species X (SP or MC) at a given time and $[X]_0$ being the concentration of the same species at the beginning of the reaction.

$$[X] = [X]_0 e^{-kt} \tag{6}$$

Equation 6 can be rearranged to Equation 7:

$$k = -\frac{1}{t} ln\left(\frac{[X]}{[X]_0}\right) \tag{7}$$

Utilizing the relaxation method this can be written as follows:

$$k_{obs} = -\frac{1}{t} ln\left(\frac{[X]_t - [X]_e}{[X]_i - [X]_e}\right) \tag{8}$$

Based on the *Lambert-Beer* law[140], concentration is proportional to absorption. Thus, Equation 9 can be obtained.

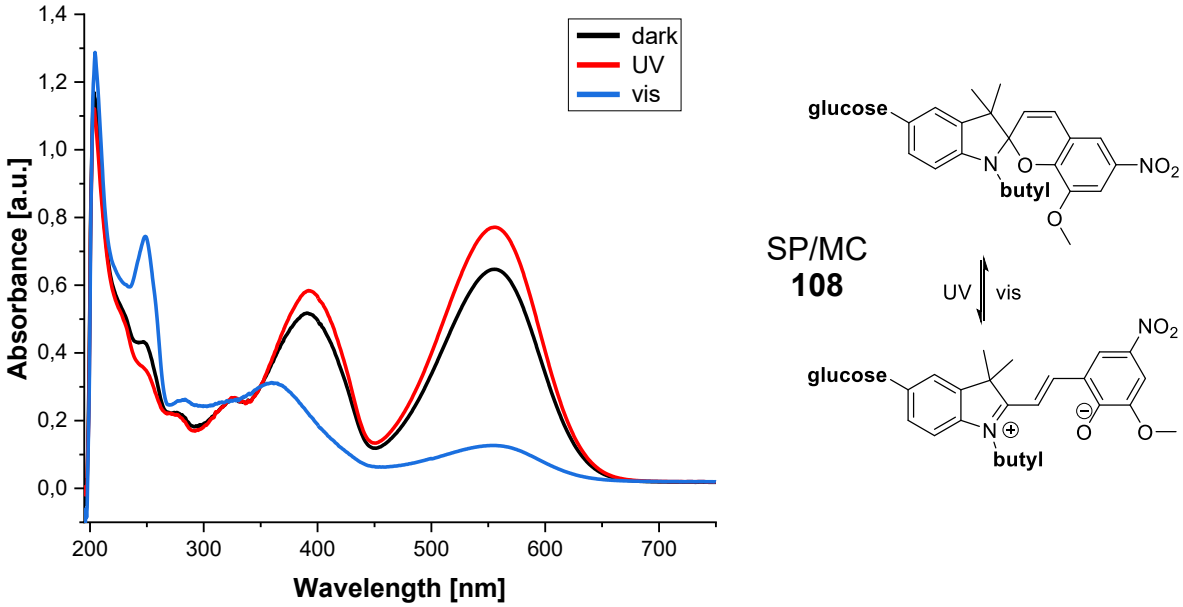
$$k_{obs} = -\frac{1}{t} ln\left(\frac{A_t - A_e}{A_i - A_e}\right) \leftrightarrow -k_{obs}t = ln\left(\frac{A_t - A_e}{A_i - A_e}\right) \quad (9)$$

A_e is defined as the absorption at the equilibrium and A_i is the initial absorption directly after the equilibrium is shifted by an external trigger. In case of the cyclisation, A_i is measured directly after irradiation with visible light. A_t is the absorption at a given time t after the initial irradiation. Utilizing Equation 9, the rate constant -k_{obs} (simplified as k in following section) can be determined as the slope of the linear regression of the time plotted against the logarithmic absorption ratios.[139],[141]

Since the absorption spectra of the surfactants of the same general structure are similar and the different lengths of the chains did not have a major influence, the further spectra of the derivatives of the photoswitches can be found in *Appendix 13.2*. For a better overview, only the surfactants with the most structural differences, for example with the shortest and longest alkyl chains, are discussed in detail in the following sections.

5.7.1 UV-vis analysis of photoswitchable surfactants with *N*-connected tails

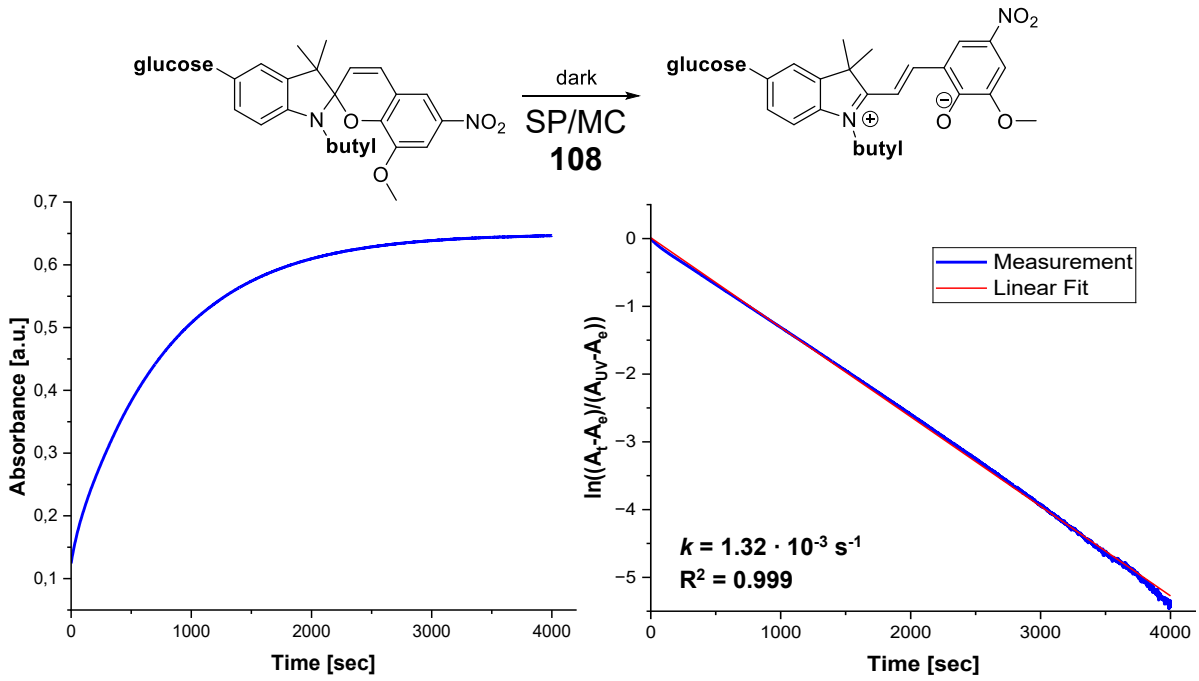
The UV-vis spectra of the SP/MC system **108** are shown in Scheme 49.



*Scheme 49: UV-vis spectra of SP/MC **108** (0.025 mM in MeOH) at the thermal equilibrium in the dark (black) and after irradiation with UV (red) and visible (blue) light. By irradiating with UV or visible light, the equilibrium between SP and MC forms can be shifted in a targeted manner and the intensity of the maxima can be varied.*

The conjugated MC form can be indicated by the absorption maxima at λ = 392 and 530 nm. After irradiation with UV light the intensity of absorption band of the MC form increases (hyperchromic shift) and the maxima are shifted to higher wavelengths (bathochromic shift). The observed bathochromic shift of the absorption maxima indicates enhanced conjugation in the MC form. After irradiation with visible light the intensity of the absorptions bands of the MC form drops sharply (hypochromic shift) and the absorption maxima at λ = 204, 250 and 282 nm of the SP isomer increases. In the dark, there is an equilibrium between the two forms. However, due to the strong -M effect of the nitro group, the equilibrium could be shifted slightly toward the open MC form, which could be explained by the strong intensity of the maxima in the longer wavelength range in the dark.

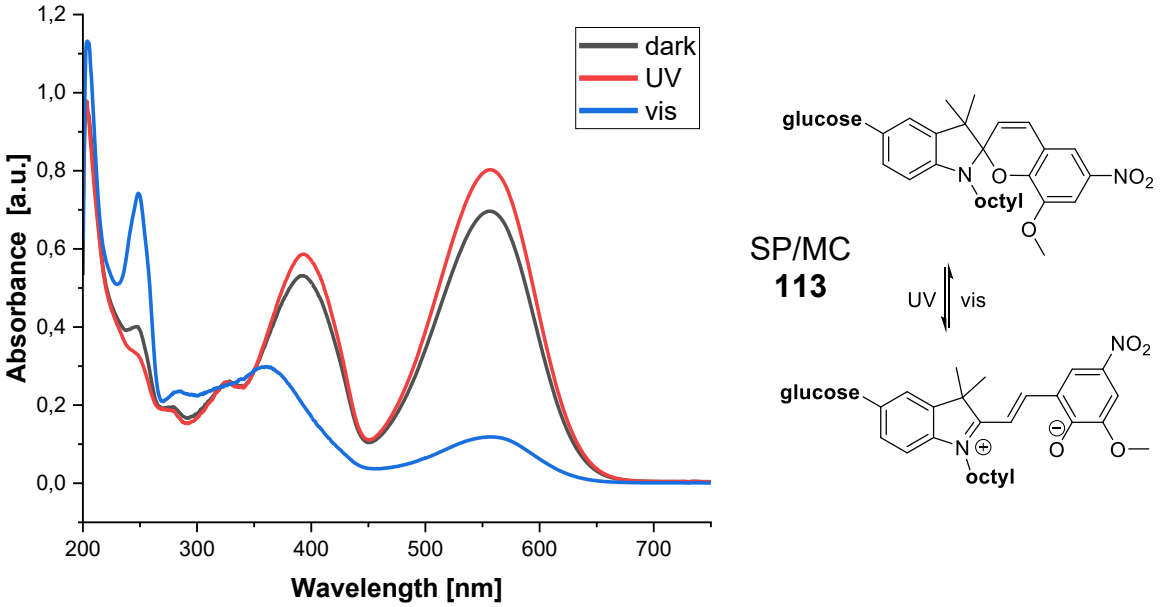
In Scheme 50, the kinetic measurements of the ring opening of spiropyran **108** to the merocyanine form are shown.



*Scheme 50: Kinetics for the ring opening reaction of spiropyran **108** to the corresponding merocyanine. Plot of the absorbance at the absorption maximum of the merocyanine against time (left) and the logarithmic plot of the conversion to determine the rate constant k (right).*

After irradiation with visible light, the sample was kept in the dark while the absorbance of the merocyanine (530 nm) was measured until the equilibrium was reached. An equilibrium was reached at an absorbance of 0.65 after 50 minutes. By Equation 9 a rate constant of $k = 1.32 \cdot 10^{-3}$ s^{-1} was determined.

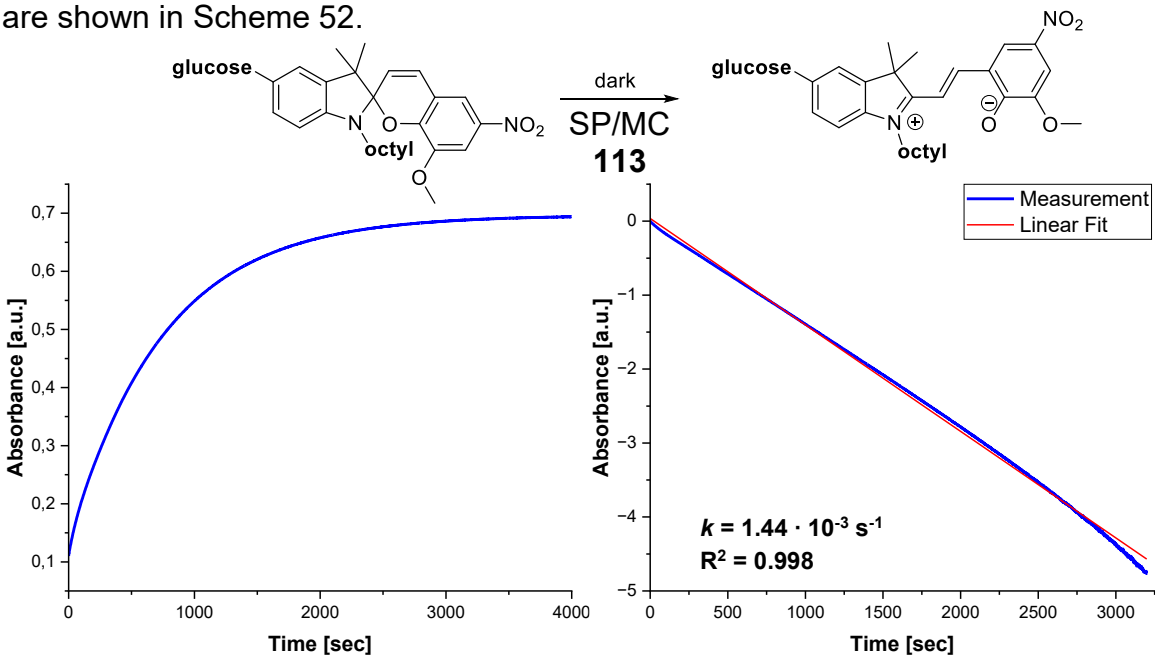
In Scheme 51 the UV-vis spectra of system **113** are shown.



*Scheme 51: UV-vis spectra of SP/MC **113** (0.025 mM in MeOH) at the thermal equilibrium in the dark (black) and after irradiation with UV (red) and visible (blue) light. By irradiating with UV or visible light, the equilibrium between SP and MC forms can be shifted in a targeted manner and the intensity of the maxima can be varied.*

The hydrophobic alkyl chains of the surfactants do not appear to have a major influence on the spectroscopic properties. The maxima and shifts are found at comparable wavelengths as in the spectrum of the previous compound **108**. The intensities of the bands for the MC form are equally strong. The SP form shows slightly stronger intensity of the absorption maximum at λ = 234 nm.

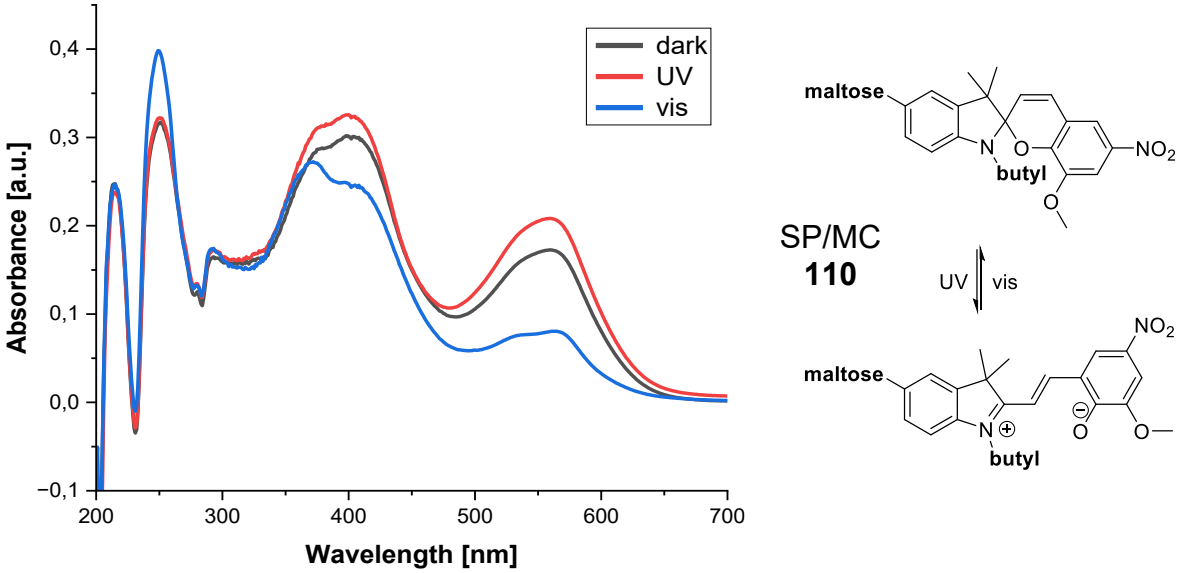
The kinetic measurements of the system **113** with the longest *N*-connected alkyl chains are shown in Scheme 52.



*Scheme 52: Kinetics for the ring opening reaction of spiropyran **113** to the corresponding merocyanine. Plot of the absorbance at the absorption maximum of the merocyanine against time (left) and the logarithmic plot of the conversion to determine the rate constant k.*

The maximum absorbance of 0.70 was reached after 50 minutes. The reaction rate (k = 1.44 · 10^{-3} s^{-1}) is only slightly higher and the equilibrium is reached a little faster.

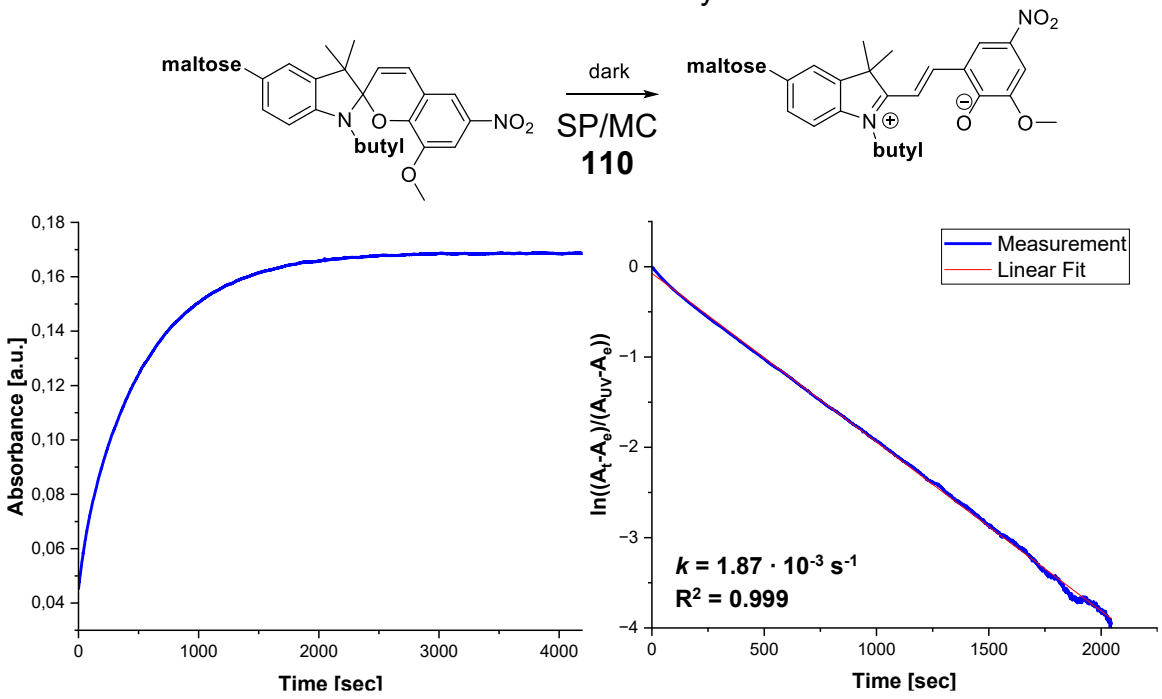
In Scheme 53 the UV-vis spectra of the system **110** are shown.



*Scheme 53: UV-vis spectrum of SP/MC **110** (0.025 mM in MeOH) at the thermal equilibrium in the dark (black) and after irradiation with UV (red) and visible (blue) light. Irradiation with UV or visible light can only slightly influence the equilibrium between SP and MC form.*

Compound **110** contains the same substituents as the systems described above, but the head group consists of a disaccharide (lactose). The polar group appears to have a strong influence on the spectroscopic and switching properties. The absorption maxima are all slightly shifted towards the longer wavelength range (λ(dark) = 213, 243, 292, 399 and 560 nm). There is also an additional maximum at 370 nm, which is more intense after irradiation with visible light. The overall absorption intensity is only half that of the compounds with the monosaccharide glucose.

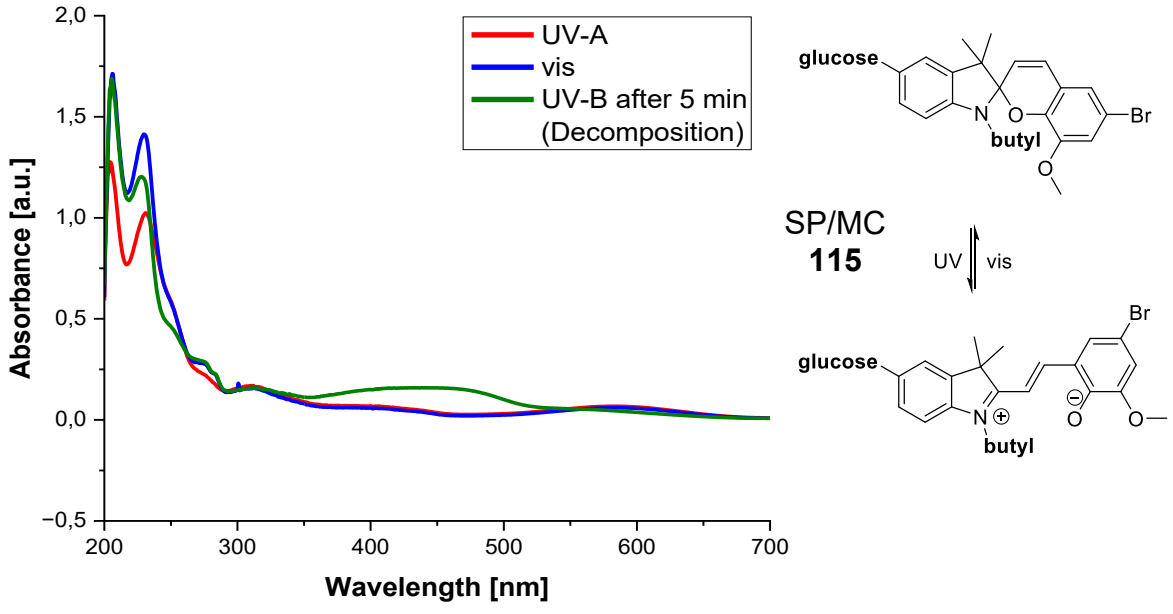
Scheme 54 shows the kinetic measurements of system **110**.



*Scheme 54: Kinetics for the ring opening reaction of spiropyran **110** to the corresponding merocyanine. Plot of the absorbance at the absorption maximum of the merocyanine against time (left) and the logarithmic plot of the conversion to determine the rate constant k (right).*

The equilibrium in the dark after irradiation with visible light is established more quickly than the compounds connected to monosaccharides. A maximum absorption intensity of 0.16 is reached after 34 minutes. The reaction constant is slightly higher with a value of $k = 1.87 \cdot 10^{-3}\ s^{-1}$.

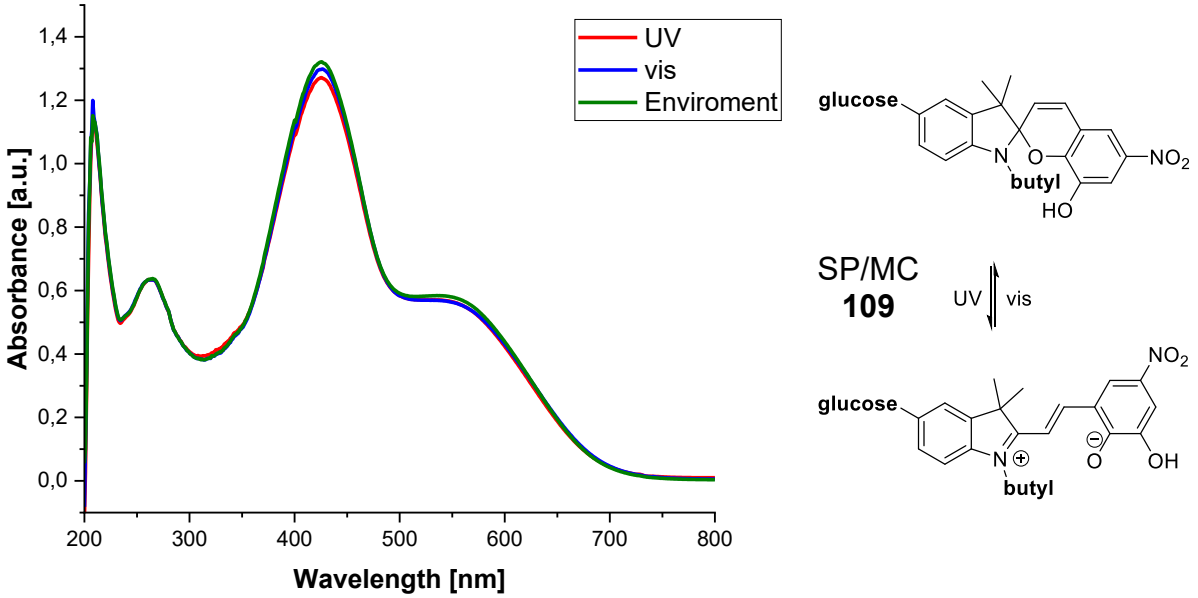
The UV-vis spectra of the system **115** are shown in Scheme 55.



*Scheme 55: UV-vis spectra of SP/MC **115** (0.025 mM in MeOH) after irradiation with UV (red), UV-A (green) and visible (blue) light. Irradiation with UV or visible light does not affect the equilibrium between SP and MC forms. No maxima are visible that can be assigned to the MC form.*

Instead of the anti-auxochromic nitro group, the compound is substituted with bromine. The spectrum differs greatly from the systems discussed so far. The bands for the MC form are barely visible. There are two maxima of the SP form at λ = 206 and 231 nm. Since UV-B radiation hardly showed any spectroscopic change, the compound was irradiated with UV-A light. This reduced the intensity of the maxima (hypochromic shift) and led to a slight bathochromic shift, but no new maxima were visible in the longer wavelength range. Presumably, the closed SP form is present. This could be explained by the auxochromic methoxy group, which donates electron density into the π-system and neutralizes the -I effect of the bromine. This increases the electron density at the phenolic oxygen, which nucleophilically attacks the spiro center during ring closure. The nitro group in the previous systems is strongly electron-withdrawing that it promotes ring opening. As no switching process was visible, no kinetic measurement was carried out. After exposure to UV-B radiation for a longer period of time (over 5 min), the sample turned yellow and new absorption bands appeared. Decomposition of the compound is suspected.

In Scheme 56 the UV-vis spectra of **109** are shown.

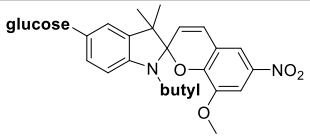
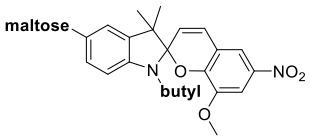
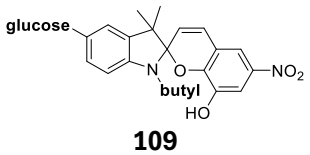
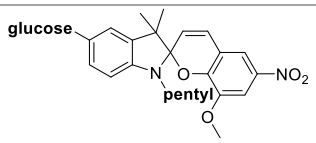
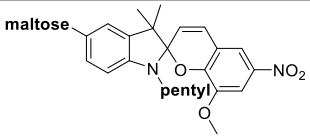
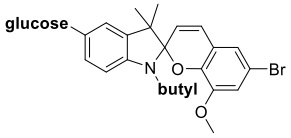
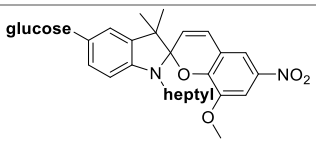
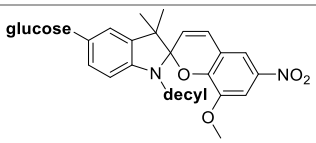


*Scheme 56: UV-vis spectrum of SP/MC **109** (0.025 mM in MeOH) after irradiation with UV (red), environment (green) and visible (blue) light. Irradiation with UV or visible light does not affect the equilibrium between SP and MC forms.*

The chromene unit of compound **109** contains a hydroxy group instead of the methoxy function. Thus, another auxochromic group is introduced with a +M effect. A strong absorption band occurs at 425 nm. The equilibrium of the system **109** is established very quickly, so that no switching behavior could be measured.

In Table 7 the received values of the absorption spectra of the *N*-alkylated surfactants are summarized.

*Table 7: Overview of the received values of the absorption spectra of the measured SP/MC systems **108** – **115** in the dark.*

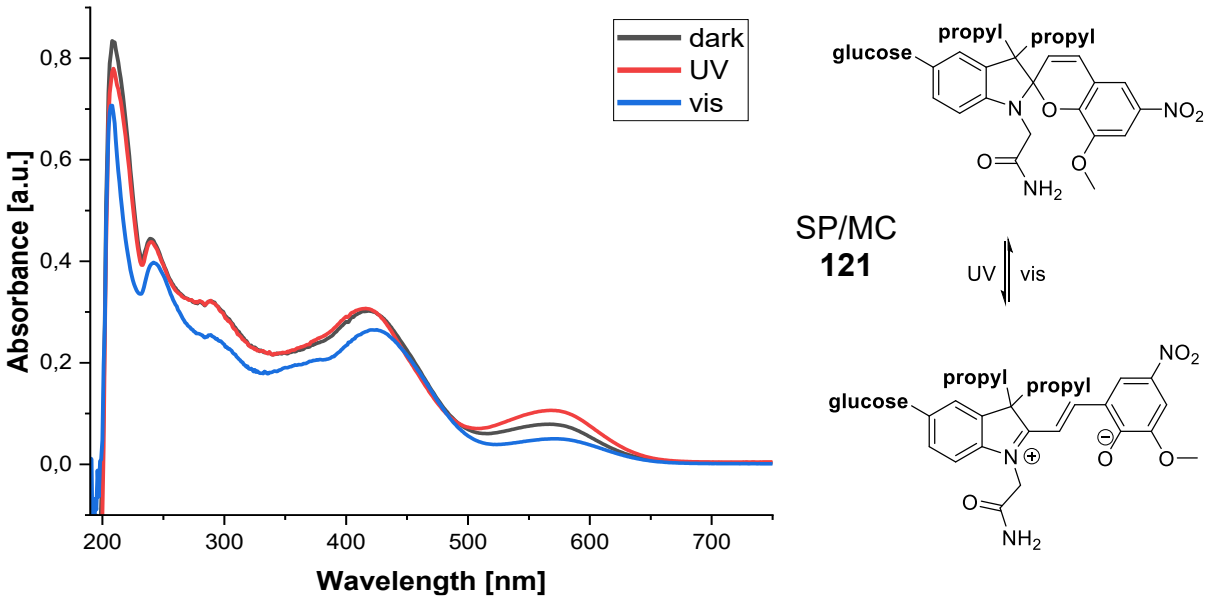
Surfactant	λ_{max} [nm]	Absorbance [a.u.]	$k_{SP\text{-}MC}$ [s^{-1}]
 **108**	204	1.28	$1.32 \cdot 10^{-3}$
	248	0.43	
	390	0.51	
	554	0.65	
 **110**	216	0.24	$1.44 \cdot 10^{-3}$
	253	0.31	
	295	0.16	
	376	0.28	
	405	0.30	
	556	0.17	
 **109**	208	1.19	-
	262	0.63	
	425	1.29	
	550	0.57	
 **111**	201	0.87	$1.42 \cdot 10^{-3}$
	246	0.36	
	392	0.46	
	556	0.61	
 **112**	207	0.87	2.02 · 10-3
	268	0.65	
	399	0.39	
	558	0.23	
 **115**	206	1.67	-
	229	1.19	
 **114**	202	1.02	$1.51 \cdot 10^{-3}$
	248	0.50	
	391	0.51	
	556	0.67	
 **113**	201	0.94	$1.44 \cdot 10^{-3}$
	248	0.39	
	392	0.53	
	557	0.69	

In summary, the influence of the *N*-connected alkyl groups on the switching behavior of the surfactants was negligible. The size of the sugar unit sometimes led to additional

shoulders in the absorption bands. The auxochromes and anti-auxochromic groups on the chromene unit had the greatest influence. Replacing the methoxy or nitro group partially suppressed the switching between the two isomers or the equilibrium was established so quickly that it was no longer measurable after transfer to the spectrometer. Overall, the observed bathochromic shift of the absorption maxima measured for all compounds substituted with a nitro group underlines the enhanced conjugation in the open MC form.

5.7.2 UV-vis analysis of photoswitchable surfactants with geminal alkyl chains

Scheme 57 shows the UV-vis spectra of system **121** with geminal alkyl chains.

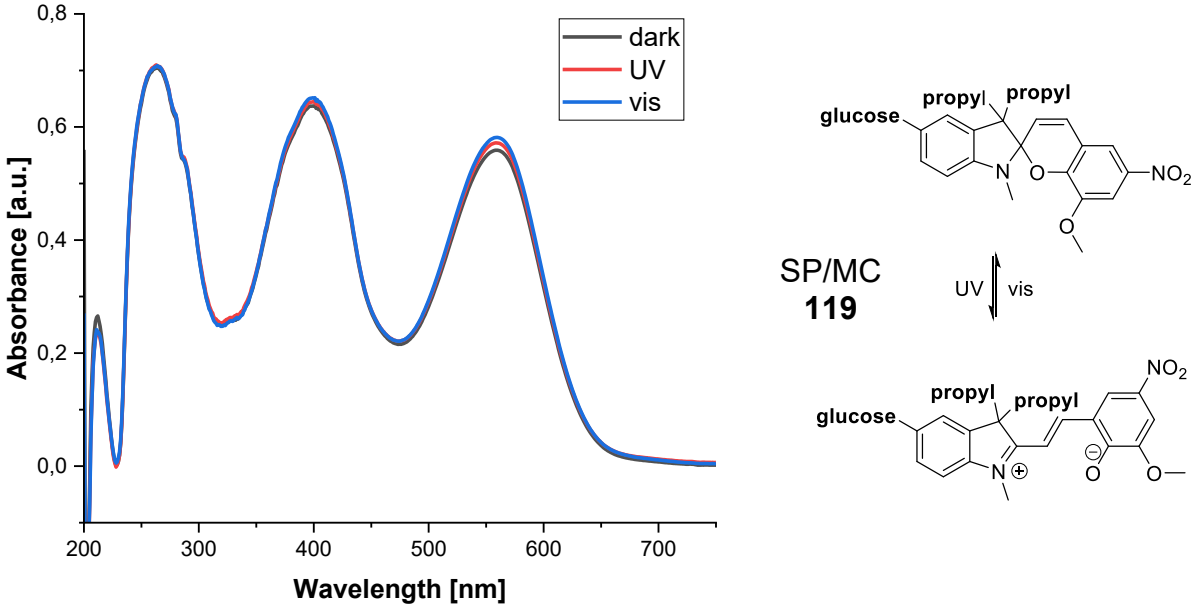


*Scheme 57: UV-vis spectra of SP/MC **121** (0.025 mM in MeOH) at the thermal equilibrium in the dark (black) and after irradiation with UV (red) and visible (blue) light. No strong switching process can be measured.*

The absorption bands for the MC form of compound **121** after irradiation with UV light are at 416 and 573 nm, which are thus shifted to the longer wavelength range compared to the *N*-alkylated surfactants. Further absorption maxima are visible at λ = 208, 243 and 290 nm. No strong switching process was measurable. The amide substituent and the geminal alkyl chains seem to strongly influence the equilibrium between the two isomers. The amine and methoxy groups can form hydrogen bonds to the solvent, possibly stabilizing the structure and preventing further switching.

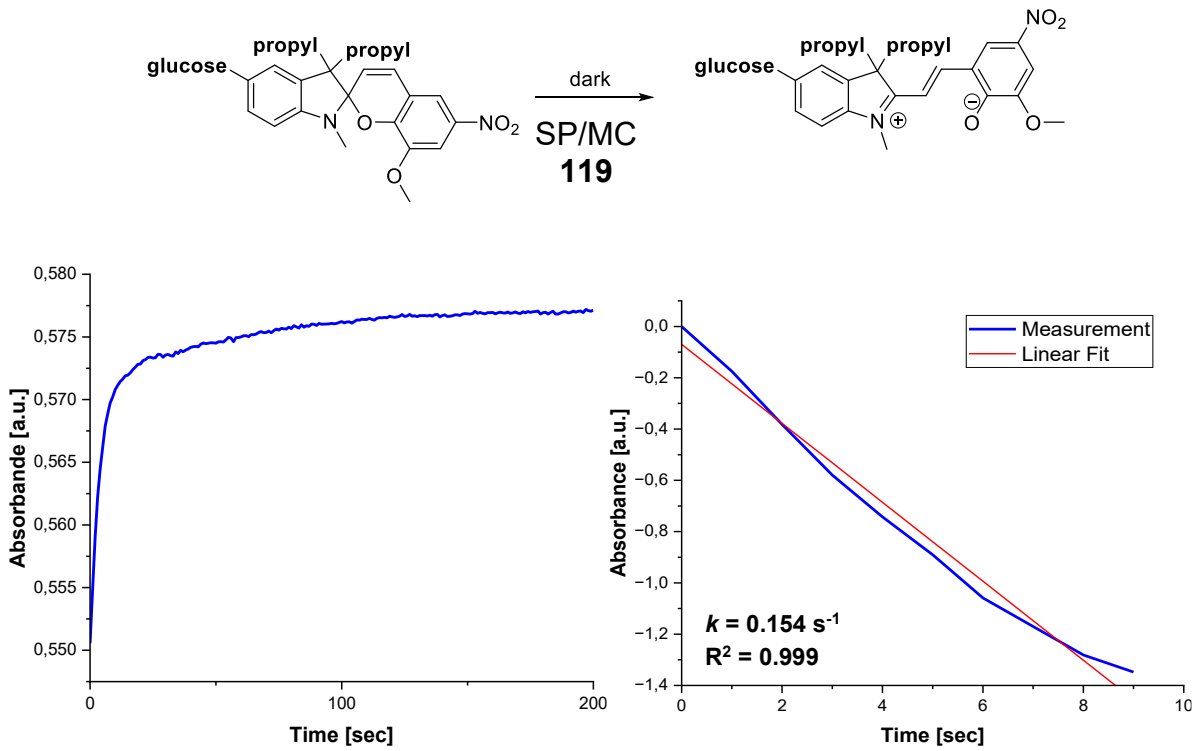
As no clear switching process was measurable, no kinetic measurement was recorded.

Scheme 58 shows the UV-vis spectra of system **119**.



*Scheme 58: UV-vis spectra of SP/MC **119** (0.025 mM in MeOH) at the thermal equilibrium in the dark (black) and after irradiation with UV (red) and visible (blue) light. No strong switching process can be measured.*

Four absorption maxima at λ = 210, 265, 402 and 558 nm were measured of compound **119**. The two maxima in the longer wavelength range are in the same range as the *N*-alkylated photoswitches. The maxima in the shorter wavelength range are much broader and more intense. The absorption bands do not show any significant changes after irradiation. Presumably, the equilibrium between the isomers was already established after conversion in the measuring device, or it could not be switched properly. Nevertheless, an attempt was made to record a kinetic measurement shown in Scheme 59.

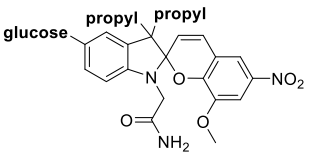
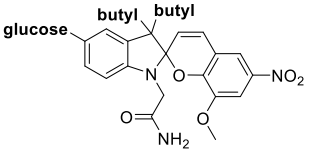


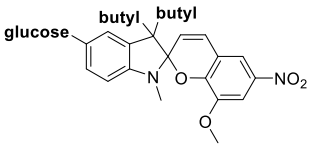
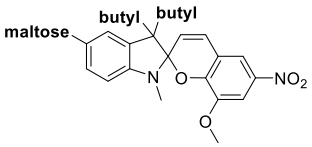
*Scheme 59: Kinetics for the ring opening reaction of spiropyran **119** to the corresponding merocyanine. Plot of the absorbance at the absorption maximum of the merocyanine against time (left) and the logarithmic plot of the conversion to determine the rate constant k.*

The equilibrium between the two isomers was re-established so quickly after UV irradiation that an absorption maximum of 0.57 was reached after only 50 seconds. After that, no change in the absorption maximum was detected in the dark. The reaction constant with a value of k = 0.154 s^{-1} is also much higher than in the previous systems. Overall, it was still possible to achieve a slight influence on the absorption maximum through irradiation.

In Table 8 received data of the absorption measurements of the SP/MC systems after storing in the dark are summarized.

*Table 8: Overview of the received values of the absorption spectra of the measured SP/MC systems **119** - **121** in the dark.*

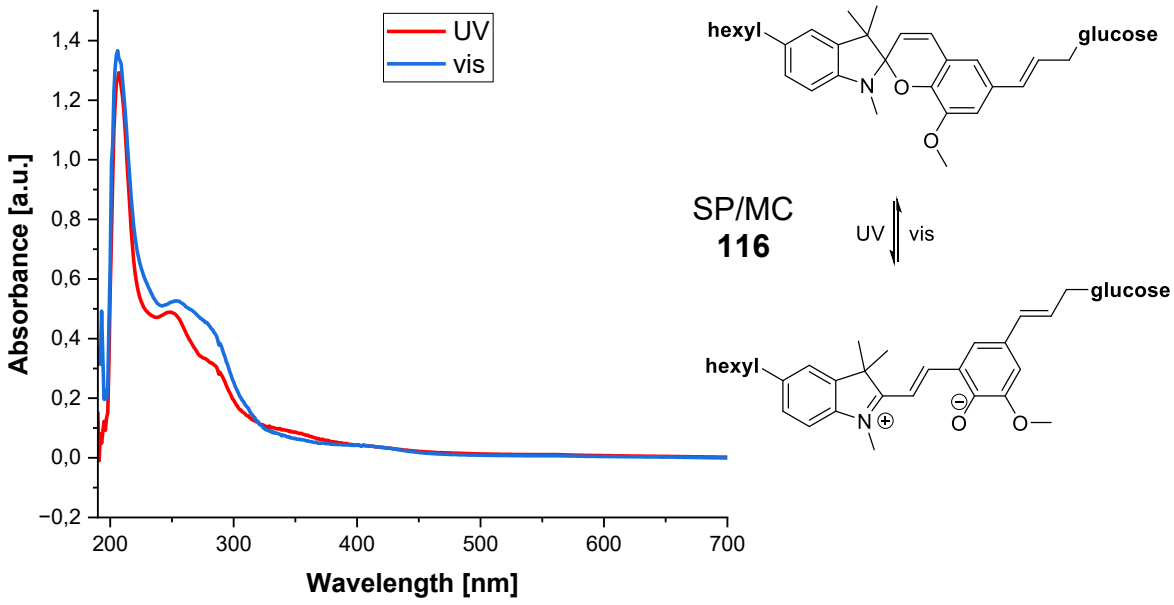
Surfactant	λ_{max} [nm]	Absorbance [a.u.]	k_{SP-MC} [s^{-1}]
 **121**	208	0.83	-
	238	0.43	
	421	0.30	
	572	0.07	
 **122**	210	0.67	-
	247	0.38	
	426	0.26	
	576	0.05	

 **119**	214	0.24	0.154
	266	0.70	
	404	0.63	
	554	0.55	
 **120**	208	0.31	0.215
	247	0.26	
	401	0.40	
	559	0.42	

In summary, the surfactants with geminal alkyl chains showed significantly altered absorption spectra. The substituents on the indole nitrogen had a major influence on the switching behavior between the two isomers. The equilibrium was established so quickly that it was sometimes no longer measurable due to the transfer into the spectrometer after irradiation.

5.7.3 UV-vis analysis of photoswitchable linear surfactants

The UV-vis spectra of system **116** are shown in Scheme 60.



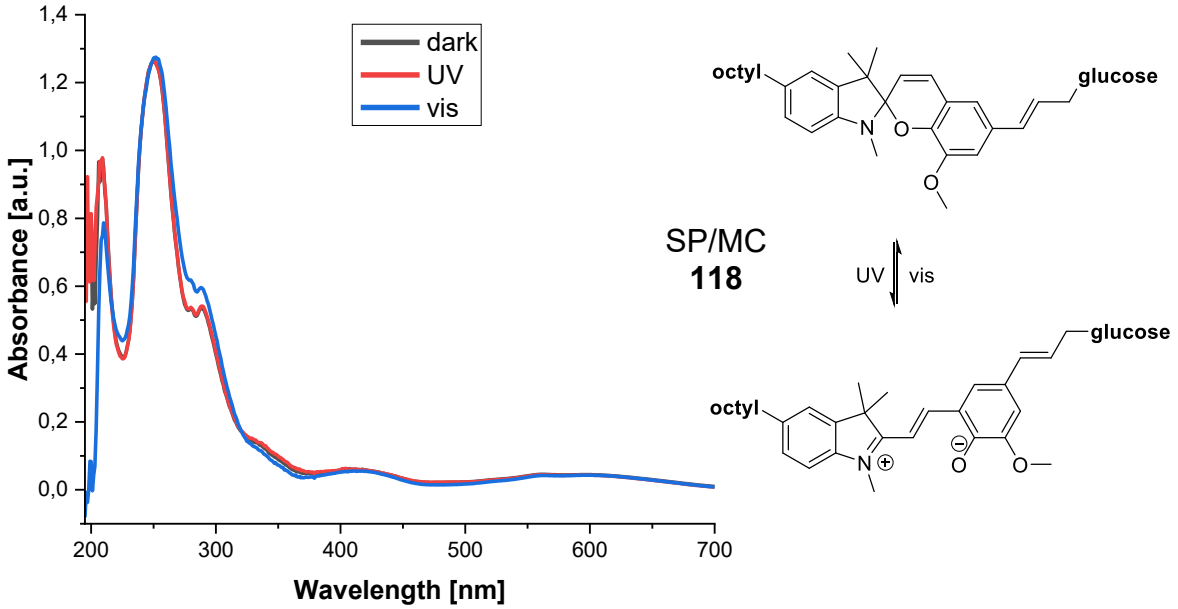
*Scheme 60: UV-vis spectra of SP/MC **116** (0.025 mM in MeOH) after irradiation with UV (red) and visible (blue) light. Absorption maxima in the longer wavelength range are not visible.*

The linear surfactant **116** is alkylated at the indole and the sugar is bridged *via* the benzopyran unit and a methoxy group is substituted. Therefore, the photoswitch contains only auxochromes and no electron-withdrawing groups. In the spectrum no absorption bands of the MC form in the longer wavelength range are visible. A sharp

band appears at 205 nm and another band is detected at 252 nm as well as a slight shoulder at 281 nm. A hypsochromic shift of these bands can be seen by irradiation with visible light. However, no bands of the merocyanine form are visible by irradiation with UV light. The compounds would have to be substituted with anti-auxochromic groups to allow ring opening.

Since the equilibrium is almost completely on the side of the spiropyran form even when irradiated with UV light, no kinetic measurement was recorded.

The UV-vis spectra of system **118** are shown in Scheme 61.

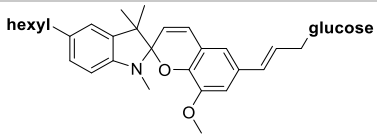
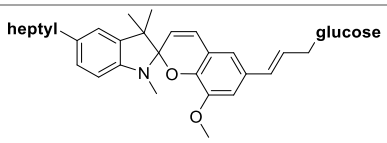
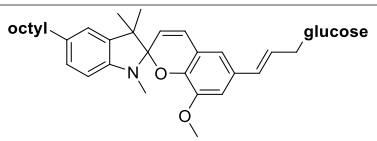


*Scheme 61: UV-vis spectra of SP/MC **118** (0.025 mM in MeOH) at the thermal equilibrium in the dark (black) and after irradiation with UV (red) and visible (blue) light. Strong absorption maxima in the longer wavelength range are not visible.*

Surfactant **118** has a longer alkyl chain than compound **116**. However, it also has no anti-auxochromic groups. There is a band at 208 nm, which shows a hyperchromic shift by UV irradiation. A very broad band can be seen at 250 nm. In addition, there are two small maxima at 279 and 289 nm, which show a hypochromic shift when irradiated with visible light. However, no bands of the merocyanine form are visible here either when irradiated with UV light. Two very slight increases can be seen at 420 nm and 580 nm. As the equilibrium was already completely on the side of the spiroform after irradiation with UV light and transfer of the sample to the measuring device, no kinetics measurement could be recorded.

In Table 9 the data of the absorption spectra measured in the dark are summarized.

*Table 9: Overview of the received values of the absorption spectra of the measured SP/MC systems **116** - **118** in the dark.*

Surfactant	λ_{max} [nm]	Absorbance [a.u.]	k_{SP-MC} [s^{-1}]
 **116**	205	1.34	-
	255	0.53	
 **117**	208	0.97	-
	248	0.64	
 **118**	211	0.92	-
	249	0.26	

In summary, the absorption spectra of the linear surfactants mainly exhibit maxima in the shorter wavelength range, which can be assigned to the closed SP form. Due to the absence of auxochromic and anti-auxochromic groups, it was not possible to switch between the two isomers. However, by introducing anti-auxochromes such as a nitro group, it might also be possible to switch the linear surfactants to the open MC form.

5.8 Surface tension measurements

In this chapter, the surface tension measurements of the synthesized surfactants are described and compared with each other. The theoretical background to the measurement using the *Wilhelmy* plate method and the detailed calculation of the substance-specific values is described in *Chapter 2.1.2*. Since there is an equilibrium of the open and closed form during most measurements, the results may vary. The values for minimum surface tension (σ_{min}) were additionally measured under irradiation with UV and visible light. The following graphs show the measured concentration curves of the surface tensions of the switchable surfactants under ambient light.

In Figure 19 the measured surface tension in dependency of the surfactant concentration of the *N*-alkylated surfactants with chains of varying lengths is shown.

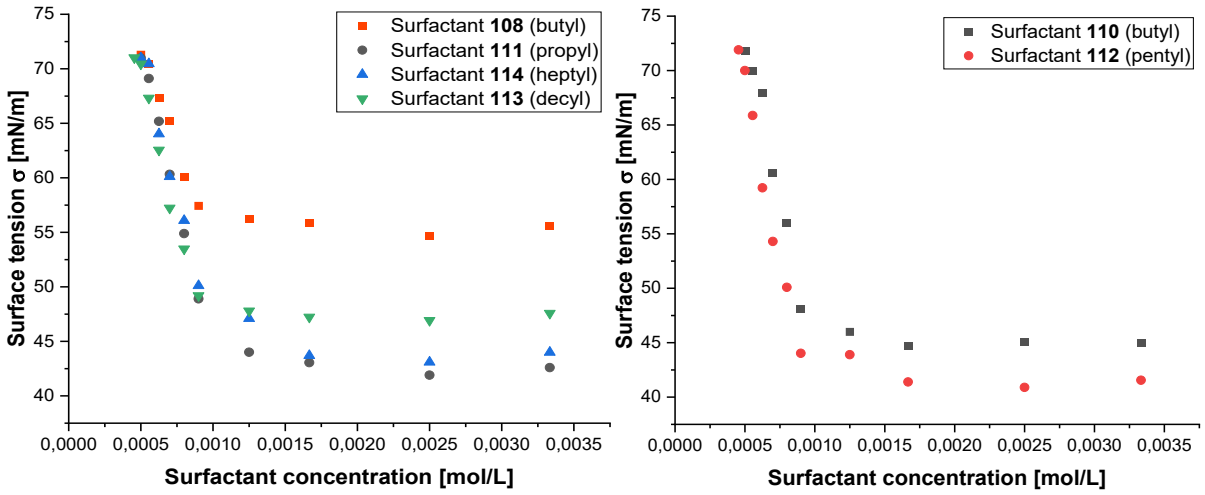
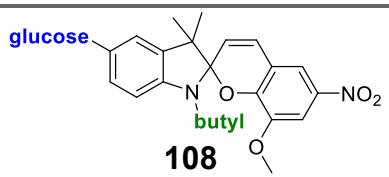
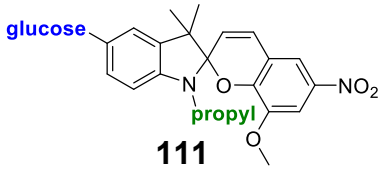
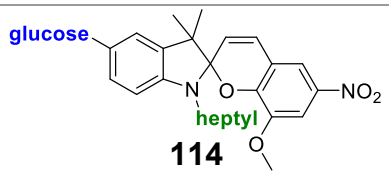
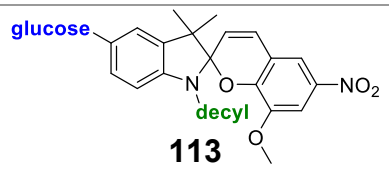
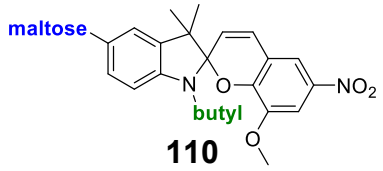
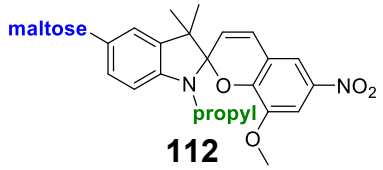


Figure 19: Measured surface tension against the concentration of surfactants with N-connected tails. Left: surfactants with glucose as head group, right: surfactants with lactose as head group.

The graph shows that for all *N*-alkylated surfactants, a steep decrease in surface tension occurs at similar concentrations. This leads to the conclusion that the solubility of the surfactants must be in a similar range. The surfactants accumulate at the surface at a similar rate and thus reduce the tension there. This can also be seen from the *cmc* values. They are all in a range between 0.92 mmol/L and 1.11 mmol/L. Thus, the concentration for micelle formation is in a similar region

The values of *cmc*, maximum interfacial concentration Γ_{∞}, and minimum head group requirement A_{min}, which were determined by adjusting the fitted lines, are summarized in Table 10.

Table 10: Summary of the substance-specific values of surfactants with N-connected alkyl chains obtained by plotting the surface tension against the logarithmic values of the concentrations, which were calculated using linear regression.

surfactant	σ_{min} [mN/m]	*cmc* [mmol/L]	Γ_{∞} [µmol/m²]	A_{min} [nm²]
 **108**	55.62 53.32 (UV) 55.89 (vis)	0.92	1.26	0.13
 **111**	42.59 41.06 (UV) 43.04 (vis)	1.00	2.16	0.07
 **114**	44.00 42.09 (UV) 44.03 (vis)	1.11	1.32	0.12
 **113**	47.58 46.02 (UV) 47.89 (vis)	0.94	1.36	0.12
 **110**	44.98 43.98 (UV) 43.63 (vis)	0.94	2.22	0.07
 **112**	41.55 41.20 (UV) 42.50 (vis)	0.91	1.57	0.10

The calculation of the head group requirement also yielded similar values between 0.07 nm² and 0.13 nm². The value is determined not only by the type and shape of the head group, but also by the side chain used. The highest value is obtained for compound **110** with 0.13 nm². Due to the higher head group requirement, a small maximum interfacial concentration results, as described in formula (3) in *Chapter 2.1.2*, since these are proportional to each other.

The values for the measured minimum surface tension are relatively high, ranging between 41.55 mN/m and 55.62 mN/m. Irradiation with UV light reduced the values by 1 – 3 mN/m for all compounds except surfactant **110**. This shows that surfactants in the merocyanine form can reduce surface tension more effectively than surfactants in the spiro form.

Figure 20 shows the graph of the surface tension measurement of the surfactants with different auxochromic and anti-auxochromic groups. The chromene unit of compound **109** is substituted with a nitro and a hydroxy group, while compound **115** is substituted with a methoxy group and bromine. The different groups influence the equilibrium between the spiropyran and merocyanine forms.

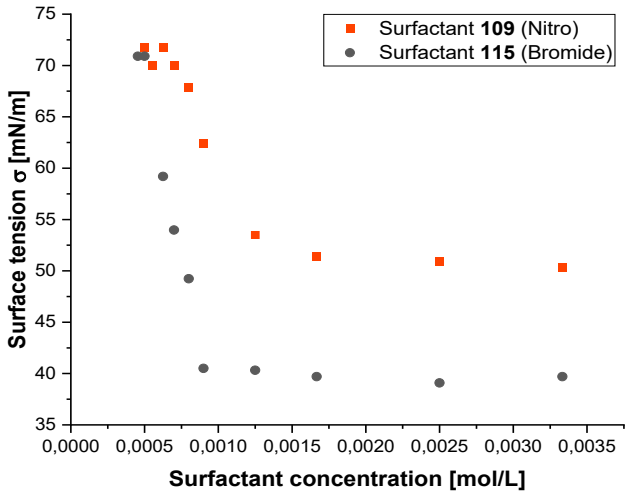
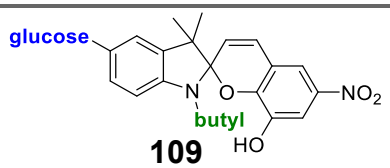
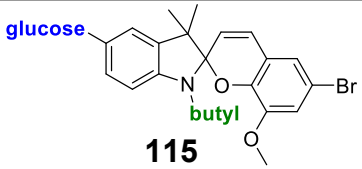


Figure 20: Measured surface tension against the concentration of surfactants with N-connected tails and different auxochromic and anti-auxochromic substituents.

The measurement curve for the nitro-substituted compound **109** begins to decline at a slightly higher concentration than the bromine-substituted compound **115**. This suggests that surfactant **109** has better solubility, as the molecules accumulate only at higher concentration on the surface and reduce the tension there.

In the Table 11 physicochemical data of the two surfactants with different auxochromic and anti-auxochromic groups are summarized.

Table 11: Summary of the substance-specific values of surfactants with N-connected alkyl chains and different auxochromic and anti-auxochromic substituents obtained by plotting the surface tension against the logarithmic values of the concentrations, which were calculated using linear regression.

surfactant	σ_{min} [mN/m]	*cmc* [mmol/L]	Γ_{∞} [µmol/m²]	A_{min} [nm²]
 **109**	50.34 49.80 (UV) 49.50 (vis)	1.29	0.39	0.41
 **115**	39.70 40.64 (UV) 40.08 (vis)	0.91	2.15	0.07

The head group requirement is significantly higher of surfactant **109**, which is also reflected in the lower maximum interfacial concentration.

Figure 21 shows the graph of the surface tension measurement of the surfactants with geminal alkyl chains and different substituents on the indole nitrogen.

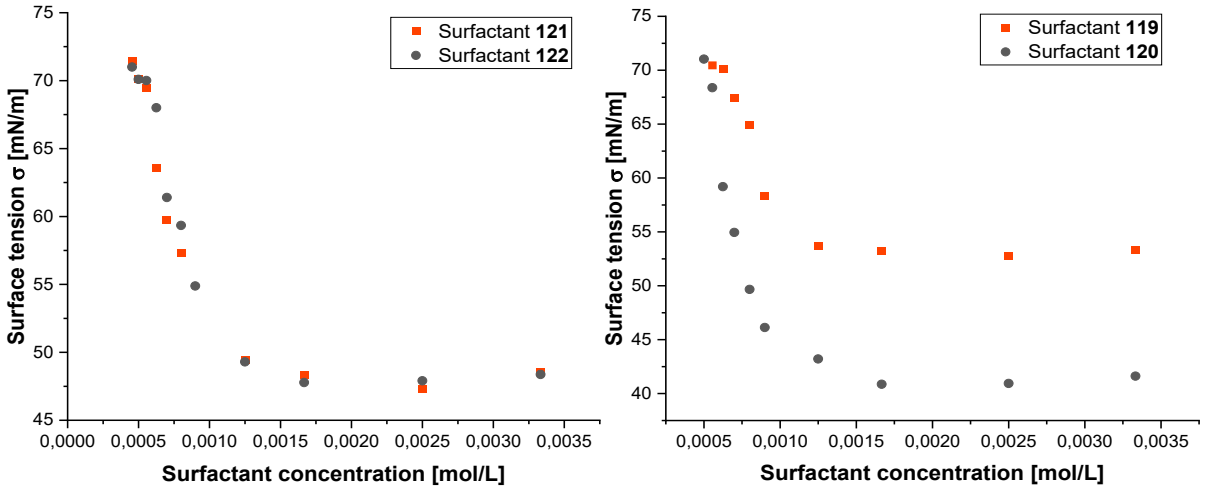
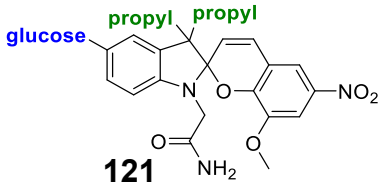
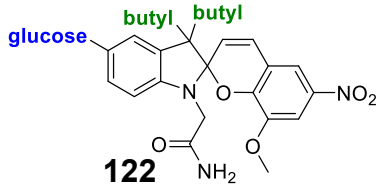
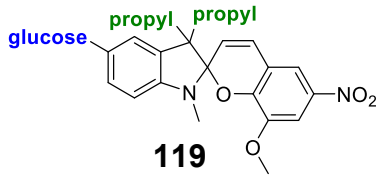


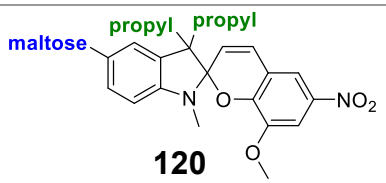
Figure 21: Measured surface tension against the concentration of surfactants with geminal alkyl chains. Left: surfactants with amide ligands, right: N-methylated surfactants.

The surface tension drops sharply again at similar concentrations. Only with surfactant **119** does it drop somewhat more gradually, indicating that it dissolves slightly better than the other three surfactants.

In Table 12 the physicochemical data of the surfactants with geminal alkyl chains are summarized.

Table 12: Summary of the substance-specific values of surfactants with geminal alkyl chains obtained by plotting the surface tension against the logarithmic values of the concentrations, which were calculated using linear regression.

surfactant	σ_{min} [mN/m]	*cmc* [mmol/L]	Γ_{∞} [µmol/m²]	A_{min} [nm²]
 **121**	48.37 48.09 (UV) 47.78 (vis)	0.86	0.89	0.18
 **122**	48.52 46.09 (UV) 48.50 (vis)	1.28	0.16	0.98
 **119**	53.30 52.87 (UV) 53.93 (vis)	0.97	2.64	0.12

 **120**	41.62 41.78 (UV) 40.98 (vis)	0.79	0.94	0.17

The minimum surface tension and the maximum limiting concentration differ for surfactant **119**. The minimum surface tension is 53.30 mN/m, while surfactant **120** with **lactose** as the head group has the lowest value of 41.62 mN/m. Irradiation with UV light and, especially, visible light reduces the minimum surface tension. The choice of the head group appears to have a great influence on the physicochemical properties.

Figure 22 shows the graph for the surface tension measurement of the linear surfactants.

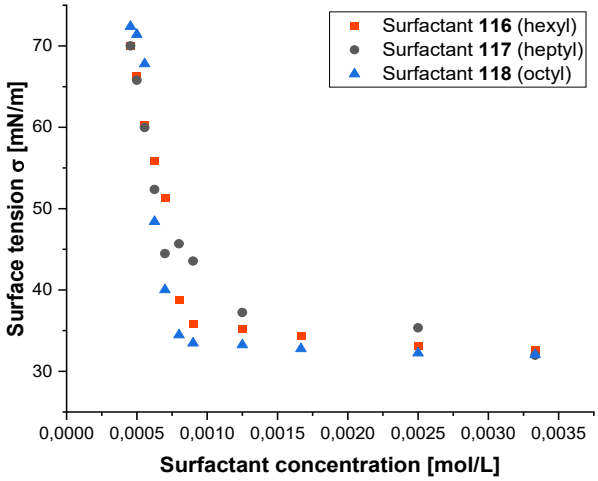
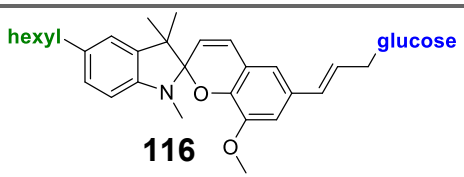
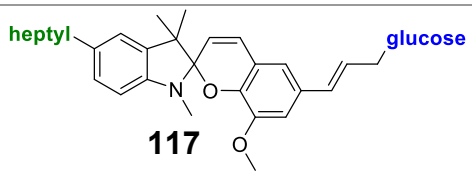
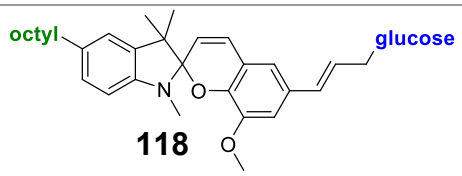


Figure 22: Measured surface tension against the concentration of the linear surfactants.

The three surfactants **116**, **117** and **118** all show very similar values, which are summarized in Table 13. The surface tension decreases sharply at the same concentration. In Table 13 received physicochemical data of the linear surfactants are summarized.

Table 13: Summary of the substance-specific values of the linear surfactants by plotting the surface tension against the logarithmic values of the concentrations, which were calculated using linear regression.

surfactant	σ_{min} [mN/m]	*cmc* [mmol/L]	Γ_{∞} [µmol/m²]	A_{min} [nm²]
 **116**	32.62 32.09 (UV) 31.88 (vis)	0.83	3.49	0.04

 **117**	31.97 43.98 (UV) 43.63 (vis)	0.94	2.22	0.07
 **118**	32.03 32.05 (UV) 31.01 (vis)	0.79	1.96	0.08

The values for the minimum surface tension are low, at 31.97 – 32.62 mN/m. Exposure to UV and visible light further reduced the values, with only compound **117** showing an increase. The maximum interfacial concentration decreases and the minimum head group requirement increases with increasing chain length.

The minimum surface tension values of aqueous solutions with common sugar surfactants are in the range of 27 to 44 mN/m.[142] For the synthesized photoswitchable surfactants with geminal or *N*-substituted alkyl chains, higher values were measured in some cases, ranging from 39.70 to 55.62 mN/m. The synthesized linear photoswitchable surfactants show quite low values in the range of 31.97 to 32.62 mN/m. Overall, physicochemical values in the range of normal sugar surfactants were measured for many of the synthesized photoswitchable surfactants. However, some of the values deviate. The linear surfactants showed values most similar to those of normal sugar surfactants. This may also be due to the fact that the equilibrium between the SP and MC forms in linear surfactants lies primarily on the closed SP form side. This was also demonstrated in the UV-vis and NMR measurements. The other surfactants are in equilibrium between the open and closed structures in ambient light. In some cases, the MC form is more prevalent. The two isomers present in aqueous solution can have a strong influence on the physicochemical properties. The minimum surface tension was also measured specifically under UV and visible light, and deviations were observed. However, not all dilution measurements were taken at specific wavelengths. Further errors in the measured values are due to weighing and dilution errors, as well as the quality of the fit. In particular, the accuracy of the fitting curve had a major impact on the calculated values of the maximum interfacial concentration and the minimum head group requirement.

6 Summary and outlook

The working group led by *PD Dr. Dirk Blunk* has already synthesized high-performance surfactants with sugar head groups. Based on this, the aim of this work was to synthesize photoswitchable sugar surfactants and the subsequent photo- and physicochemical investigation of these compounds. The light-sensitive surfactants were to be synthesized by integrating a spiropyran basic framework into the structures of sugar surfactants.

Since it is known that spiropyrans can be synthesized by the condensation of an indole and benzaldehyde, the focus was placed on the synthesis of these building blocks. Various synthesis routes were developed to successfully link sugar units as hydrophilic head groups and alkyl chains as hydrophobic tails to the indole and chromene building blocks. A total of **15 new indole building blocks** were obtained (Figure 23).

New glycosylated and alkylated indole building blocks

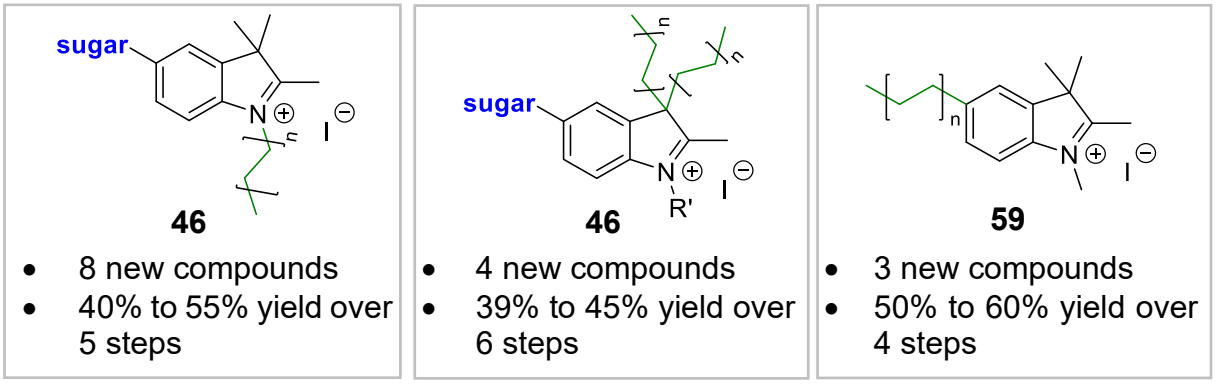


Figure 23: General structures of the synthesized novel indole building blocks. R = Me, acetamide; sugar = glucose, lactose.

Mono- and disaccharides were bound to the indole by *O*-glycosylation. Alkyl chains were introduced as hydrophobic units by substitution at the indole nitrogen (Figure 23, left). In addition, various ketones with geminal alkyl chains were synthesized to integrate them into the indole building block and obtain branched surfactants (Figure 23, center). Moreover, a synthesis route was developed to obtain alkylated indoles by *Suzuki* coupling (Figure 23, right). A previously known synthesis route was thus improved and shortened.

Six new chromene building blocks were synthesized (Figure 24).

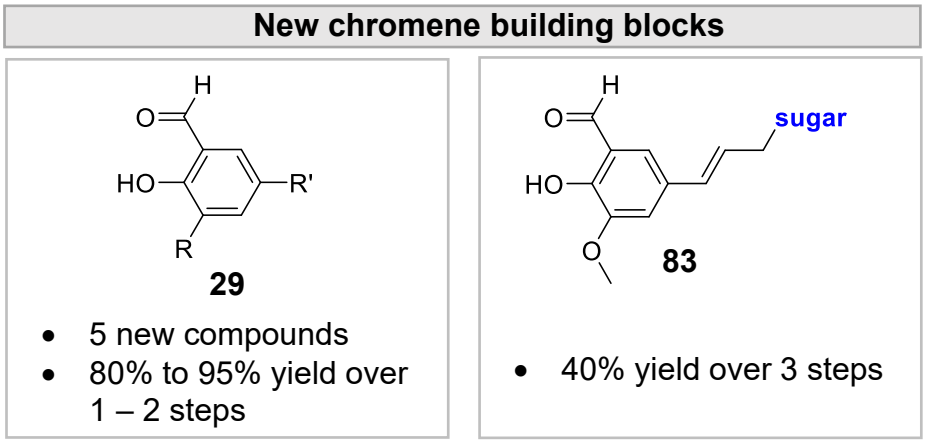


Figure 24: General structures of the novel synthesized chromene building blocks. R = OH, OMe, R' = NO_2, Br.

Various auxochrome and anti-auxochrome groups (R) were substituted to the chromene unit to obtain different switching properties of the surfactants (Figure 24, left). In addition, a synthesis route was developed to successfully bind sugar units to the chromene building block (Figure 24, right).

Through condensation and subsequent deprotection of the sugar units, **15 new switchable surfactants** were obtained, which can be divided into three basic structures as shown in Figure 25.

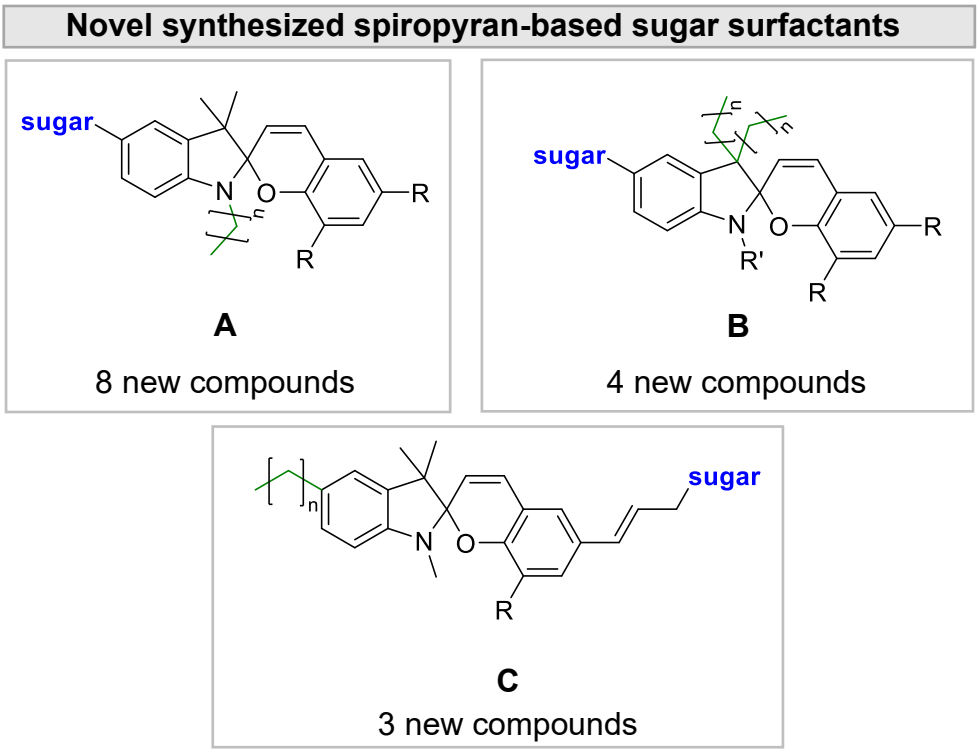


*Figure 25: Successfully synthesized surfactants with switchable spiropyran basic structures, which can be divided into three main classes: branched surfactants with N-alkylated indoles (**A**), branched surfactants with geminal alkyl chains (**B**), linear surfactants (**C**). R = NO_2, Br, OMe, OH; R' = Me, acetamide, n = 1 – 10.*

Various derivatives of these three basic structures **A**, **B** and **C** were synthesized to create a database and compare the photo- and physicochemical properties of the different photoswitchable sugar surfactants.

Surface tension measurements were performed to obtain various values relating to the physicochemical properties of the surfactants (Table 14).

Table 14: Received value ranges of surface tension measurements and subsequent graphical calculation.

Surfactant	σ_{min} [mN/m]	*cmc* [mmol/L]	Γ_{∞} [µmol/m^2]	A_{min} [nm^2]
A	39.7 – 55.6	0.91 – 1.92	0.39 – 2.16	0.07 – 0.41
B	40.9 – 53.3	0.79 – 1.28	0.16 – 2.64	0.12 – 0.98
C	31.0 – 32.6	0.79 – 0.94	1.96 – 3.49	0.04 – 0.08

Values such as the critical micelle concentration (*cmc*) and minimum surface tension (σ_{min}) of the surfactant solutions were obtained by dilution series and linear fits. The minimum surface tension was also measured under UV or visible light. As shown in Table 14, a few compounds are in the range of common sugar surfactants.

For some surfactants, the minimum surface tension was increased so the alkyl chain length or the size of the head group could still be varied to optimize the physicochemical properties. Furthermore, additional data of the already measured surfactants should be collected to obtain average values, as the measurements and evaluation are very prone to error. In particular, the equilibrium of the two isomers influences the surfactant's properties in solution. This should be investigated in more detail under the specific irradiation.

UV-vis measurements were performed with the synthesized surfactants in methanolic solutions to investigate the switching behavior of the molecules. Absorption spectra were recorded both after excitation with UV or visible light and after storage in the dark. In addition, kinetic measurements were performed to detect the equilibrium between the open and closed forms. The received value ranges of the measurements of the SP/MC equilibrium after storing in the dark are summarized in Table 15.

*Table 15: Received value ranges of the UV-vis measurements of the SP/MC systems **A** - **C** in thermal equilibrium.*

Surfactant	λ_{max} [nm]	Absorbance [a.u.]	$k_{SP\text{-}MC}$ [s^{-1}]
A	201 – 216 (SP) 248 – 268 (SP) 390 – 425 (MC) 550 – 558 (MC)	0.24 – 1.67 0.31 – 1.19 0.39 – 1.29 0.23 – 0.69	$1.32 \cdot 10^{-3}$ – $2.02 \cdot 10^{-3}$
B	208 – 214 (SP) 238 – 266 (SP) 401 – 426 (MC) 554 – 576 (MC)	0.24 – 0.83 0.26 – 0.70 0.26 – 0.63 0.05 – 0.55	0.15 – 0.21
C	205 – 211 (SP) 248 – 255 (SP)	0.92 – 1.34 0.26 – 0.64	-

The absorption spectra of surfactant **A** and **B** show four significant absorption bands of the SP and MC forms. The branched surfactants **A** exhibited good switching behavior. By irradiating them with the appropriate wavelengths, the equilibrium could be shifted to one side in a targeted manner so that mainly one isomer was present in the solution. The equilibrium was partially established after 20 minutes. The equilibrium of the two isomers of the surfactants **B** is established very quickly. The linear surfactants **C** mainly showed the closed SP form. After irradiation, the closed form was reformed so quickly that the open form could not be detected. Thus, no switching behavior was observed for linear surfactants **C** after irradiation with UV light or visible light.

Since the switching behavior of a few of the surfactants obtained still need improvement, further derivatives were to be synthesized. In particular, the linear surfactants should be complemented with anti-auxochrome groups, as these molecules were mainly present in closed form. In addition, the switching behavior of the surfactants could also be measured under the influence of further triggers, such as changes in pH and solvent.

Overall, the present results point to two specific directions for future research: (i) how the stability of the respective isomers can be further optimized by suitable substituents and thus the switching behavior can be further improved in a targeted manner, and (ii)

in which areas such reactive surfactants could be used, for example, whether the surfactants could be used in micellar drug delivery or in sensor technologies.

Furthermore, the idea of using siloxane chains instead of alkyl chains was also considered. The siloxane surfactants have already been synthesized and investigated by *Blunk et al.*.[143] These compounds show outstanding physicochemical properties. In addition, siloxanes are extremely stable, even when exposed to UV radiation.[144] The synthesis of switchable siloxane surfactants could be an interesting topic for future research projects.

Overall, the objective of synthesizing and conducting initial physico- and photochemical investigations of switchable sugar surfactants was successfully achieved. The compounds obtained exhibit promising properties and can be tested for a wide range of applications in the future.

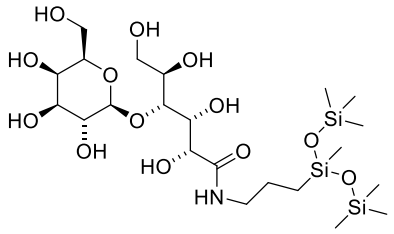
Part 2: Novel fluorescent silicon-based surfactants

7 Theoretical background

The general fundamentals of surfactants and carbohydrate-based surfactants are presented in *Chapter 2*. The following sections focus on silicon-based and fluorescent surfactants.

7.1 Silicon-based surfactants

In addition to the classic alkyl surfactants, there are also siloxane and carbosilane surfactants. The hydrophobic chains of these surfactants consist of Si-O or Si-C bonds and are summarized in the literature as silane surfactants.[145],[146] In these surfactants, the hydrophobic silane building block is linked to the polar head group *via* an alkyl linker. The special thing about silane surfactants is that the side chain is not only hydrophobic, but also amphiphobic due to its lipophobic properties.[147] Similar properties are observed for fluorosurfactants.[148] However, certain fluorosurfactants (PFOS) have been banned in the EU since 2011, as they accumulate in nature, are not degraded and are believed to be carcinogenic.[149],[150] The focus was therefore placed on silane surfactants, which have similar physicochemical properties. They achieve a minimum surface tension value of 20 - 25 mN/m. This value is significantly lower than the value for many alkyl surfactants (30 - 35 mN/m) and comes close to the values of perfluorinated surfactants (16 - 20 mN/m).[151],[40] In addition, their ability to wet hydrophobic surfaces with aqueous silane surfactant solutions is significantly greater than that of conventional surfactants. Due to their high surface activity and unique association behavior, they are now used in numerous areas. Silane surfactants are often employed as stabilizers in polyurethane foams, fuels and heavy oils, for example.[152] They are used in watery and non-watery coatings and have also proven to be effective wetting agents in aqueous formulations.[20] *Y. Shute* synthesized the sugar surfactant **123** with a siloxane chain as part of his doctoral thesis[143] in the *Blunk* research group (Figure 26).

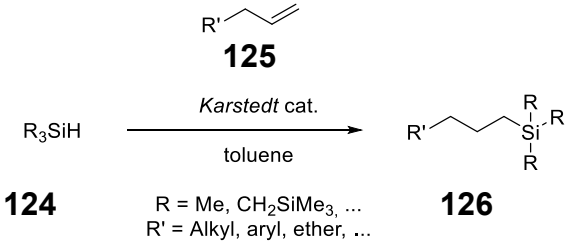


123

Figure 26: Sugar surfactant with a siloxane-based chain synthesized by Y. Shute.[143]

Due to the outstanding physicochemical properties such as spreading ability on hydrophobic liquids and foaming, the surfactant **123** is a promising candidate for the use in fire-extinguishing foams.[143]

There are two options to synthesize silicon-containing surfactants: First, etherification with silicon halides is possible, resulting in a Si-O-C bond, which is, however, relatively unstable in aqueous media. Secondly, there is the possibility of producing the surfactants by hydrosilylation. These are more stable against hydrolysis, as a direct bond is formed between silicon and carbon. The second method is therefore more suitable for the application of surfactants in aqueous media.[153] In this mechanism, silicon hydride **124** is hydrosilylated with alkyl unit **125** via a transition metal-catalyzed reaction (Scheme 62). In the mechanism postulated by *Chalk* and *Harrod*, a platinum catalyst is usually used. Rhodium, iridium or ruthenium are now also used.[154]



Scheme 62: Hydrosilylation of alkenes.

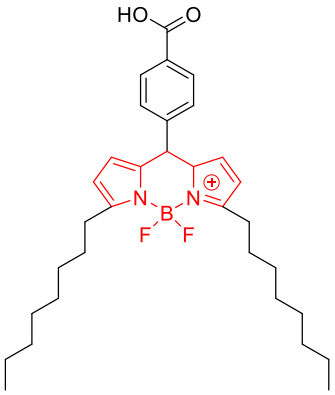
In industry, hydrosilylation is one of the most important reactions for the production of organosilicon compounds such as silicone oil. The *Karstedt* catalyst, which is also used in this work, consists of an organoplatinum compound with divinylsiloxane ligands and is often utilized for hydrosilylation.[154]

7.2 Fluorescent surfactants

Fluorescent surfactants are molecules that combine the properties of a surfactant with a fluorescent dye. This combination makes it possible to visualize the behavior and interactions of surfactants, particularly in complex systems such as cell membranes and in drug delivery. This combination provides the hydrophobic dyes with hydrophilicity and at the same time enables the fluorescence intensity and sensitivity to be adjusted by different aggregates. Various external influences can change the aggregation behavior and thus also the fluorescence.[155],[156]

Luminescence is a physical phenomenon in which a substance absorbs light of a certain wavelength and then emits light of another, usually longer, wavelength. It is described as spontaneous emission of radiation from an electronically excited species or from a vibrationally excited species.[157] Depending on the mode of deexcitation it can be classified in various types. Phosphorescence and fluorescence can be described as photoluminescence. Here, the excitation is induced by absorption of photons. The photoluminescence takes place as spontaneous or stimulated emission by deexcitation, which can be described by the *Jablonski* diagram (see Figure 9, *Chapter 3.1 of Part 1*). After absorption from the singlet ground state to the excited states, the electrons can fall back in nonradiative fashion to lower vibrational states by relaxation. Radiant transitions can occur from the lowest excited singlet state (S_1), which can then be visible as fluorescence. The emission process is slow enough to determine different interactions with the environment. The emission can be influenced, for example, by pH-value, polarity, pressure, temperature or hydrogen bonds. Thus, fluorescent surfactants have a wide range of applications and can be used as indicators, for labeling or as tracers. In addition, the emission can provide information about the surfactants themselves and their aggregation behavior.[158]

Wang et al. synthesized the fluorescent surfactant **127** with a BODIPY (4,4-difluoro-4-bora-3,4-diaza-indacene) as dye (Figure 27), a well-known dye with sharp emissions, high quantum yields and a high photostability.[156],[159]

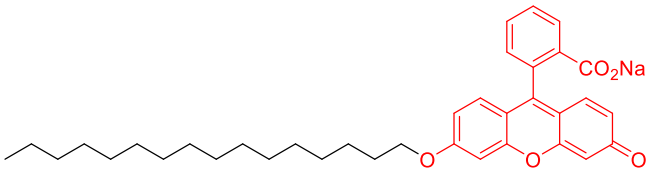


127

*Figure 27: Fluorescent surfactant **127** with a BODIPY dye synthesized by Wang et al.[156]*

They studied the self-assembly behavior of the surfactant and its properties for cell imaging and phototherapy. The surfactant efficiently binds on living cells and stains the cell membrane with long retention time at low concentrations. They observed that the fluorescence intensity increases with aggregation into vesicles. In addition, they found that the surfactant can destroy cancer cell membranes under irradiation and therefore could be a promising candidate for photodynamic therapy.[156]

Another common fluorescent dye to implement in surfactants is sodium fluorescein, as demonstrated by *Kong et al*. (Figure 28).



128

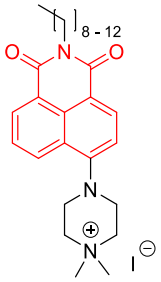
Figure 28: Synthesized fluorescent surfactant by Meng et al.[160]

They synthesized the fluorescent surfactant **128** (F-C16) by esterification of dye with palmitoyl chloride under catalysis of pyridine. F-C16 showed good emulsification properties and wettability.[160] *Kong* and his coworkers explored the penetration of surfactants contained in cosmetics into skin. The synthesized surfactant showed low cytotoxicity and dependency on pH-value and solvent polarity. By staining with F-C16, they found that the surfactants can penetrate well into skin and cells. They can even reach the dermal layer of skin.[160]

In this work, naphthalimide and naphthalene units are inserted into surfactant structure. Naphthalene and its derivatives are already known fluorescent probes for detecting and imaging purposes. Naphthalene dyes have a rigid planar and large conjugated

π-system and show high quantum yields and excellent photostability. Due to the high fluorescent lifetime, naphthalene derivatives are suitable fluorescent sensors. They can be easily modified to act as donor or acceptor.[161],[162],[163],[164]

Zhao et al. synthesized three different cationic surfactants containing naphthalimides as fluorescent units (Figure 29).[165]

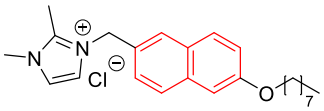


129

Figure 29: Naphthalimide fluorescent surfactants synthesized by Zhao et al.[165]

The surfactants show low *cmc* and the values of the minimal surface tension (σ = ~38 mN/m) are in the range of other cationic alkyl surfactants. They assumed that the incorporation of naphthalimide groups facilitates micelle formation due to π-π-interactions of the dye. The absorption and fluorescence spectra are in the visible light region, which make direct monitoring of the surfactant´s aggregation behavior in solution possible.[165]

Yenupuri et al. synthesized the fluorescent naphthalene-based surfactant **130** with a cationic imidazolium head group (Figure 30).



130

Figure 30: Naphthalene fluorescent surfactant synthesized by Yenupuri et al.[166]

They used steady state and time-resolved fluorescence techniques to examine the binding properties and interactions of the fluorescent surfactant to three other common surfactants (e.g. sodium dodecyl sulfate (SDS)) within micelles. They used fluorescence spectroscopy as a tool to determine different values of the micelles, for example micropolarity, binding constant, fluorescence lifetime and probable location of the probe.[166] With their experiments, *Yenupuri*'s group showed how versatile the application of fluorescence spectroscopy can be. In combination with computer calculations and measurements of surfactant properties, it is possible to precisely

determine and track surfactants, their aggregation and binding behavior as well as their photochemical properties such as changes of the dipole moment and conformation. Overall, research into fluorescent surfactants for the use as sensors in a wide variety of areas remains interesting and promising.

8 Concept and motivation

Sugar surfactants with siloxane and carbosilane chains as hydrophobic side chains have already been a major research topic in the *Blunk* group and were strongly investigated.[143] Due to their outstanding physicochemical properties, these surfactants find application in firefighting foams.

Fluorescent markers are indispensable tools in many areas of chemistry[167], biology[168], and materials science[169]. They make it possible to visualize molecules and their behavior in complex environments and to follow their dynamics in real time.[167] For surfactants, which play a central role in numerous technical and biological processes through their self-assembly at interfaces or in solution, only few specifically designed fluorescent analogues are available so far. The synthesis of fluorescent surfactants opens the possibility of specifically tracing their distribution in different systems. Using methods such as fluorescence microscopy, assembly processes, transport mechanisms, or the stability of interfaces can thus be directly visualized.

The aim of this part of the work was therefore to synthesize novel fluorescent, silicon-containing surfactants, to characterize their photophysical properties, and to demonstrate their suitability as molecular markers for the investigation of dynamic systems. For this purpose, chromophore units should be integrated into the basic structures of sugar surfactants as shown in Figure 31:

Figure 31: Conceptual representation of fluorescent surfactants.

The head groups should consist of carbohydrates, the side chains of siloxanes. Naphthalene derivatives were used as fluorophores. Figure 32 shows the targeted siloxane surfactants.

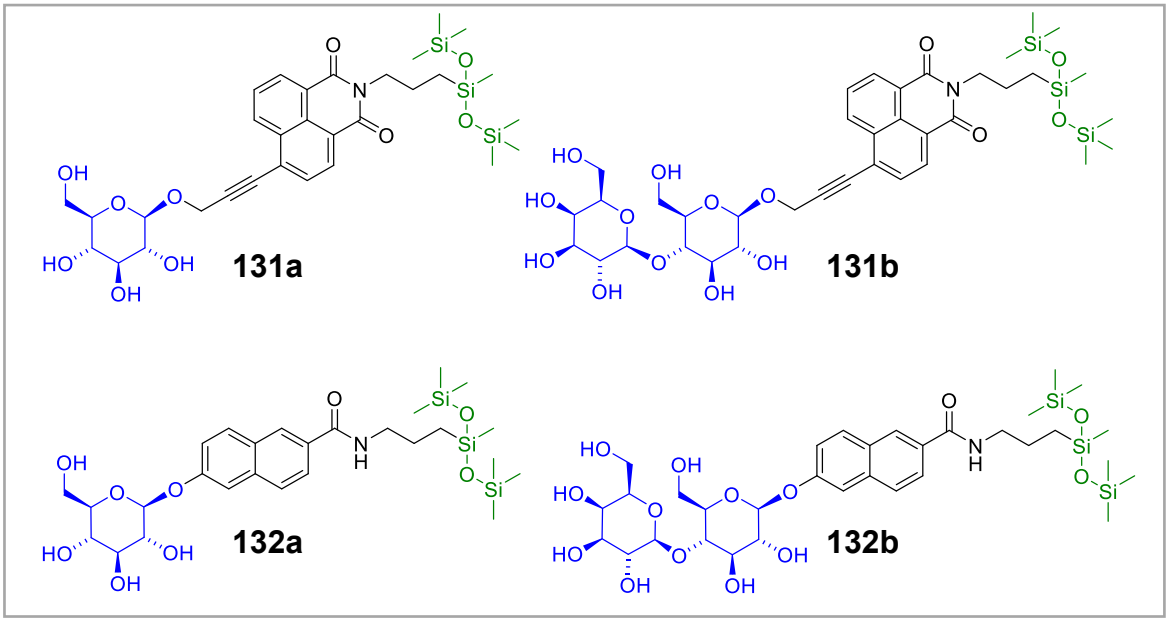


Figure 32: The desired fluorescent sugar surfactants with siloxane chains. The deacetylated sugar units could not be obtained due to difficulties in the final deprotection process during the master's thesis.[1]

As part of the master's thesis[1], various acetyl-protected mono- and disaccharides as well as siloxane chains were successfully linked to two different fluorophores. Unfortunately, the final surfactants could not be obtained and thus could not be investigated, as the last step of deprotection could not be carried out successfully.

At the beginning of this work, the final step to obtain the deprotected surfactants **131 - 134** should therefore be realized.

In addition, carbosilane side chains of different size and shape were to be synthesized and linked to the fluorophores to obtain an expanded database of silicon-based surfactants and compare them with each other. Therefore, new synthesis strategies should be developed. All newly obtained surfactants were then to be investigated for their physicochemical and photochemical properties using surface tension measurements and absorption and fluorescence spectroscopy.

9 Results and discussion

The synthesis of fluorescent sugar surfactants with siloxane chains had already been started as part of the master's thesis[1]. The general target structures **A** and **B** of the two desired compounds are shown in Figure 33.

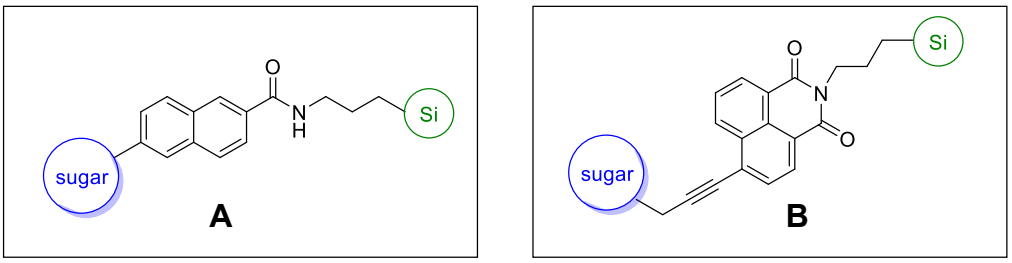


Figure 33: General structures of the fluorescent surfactants with sugar head groups and siloxane or carbosilane chains.

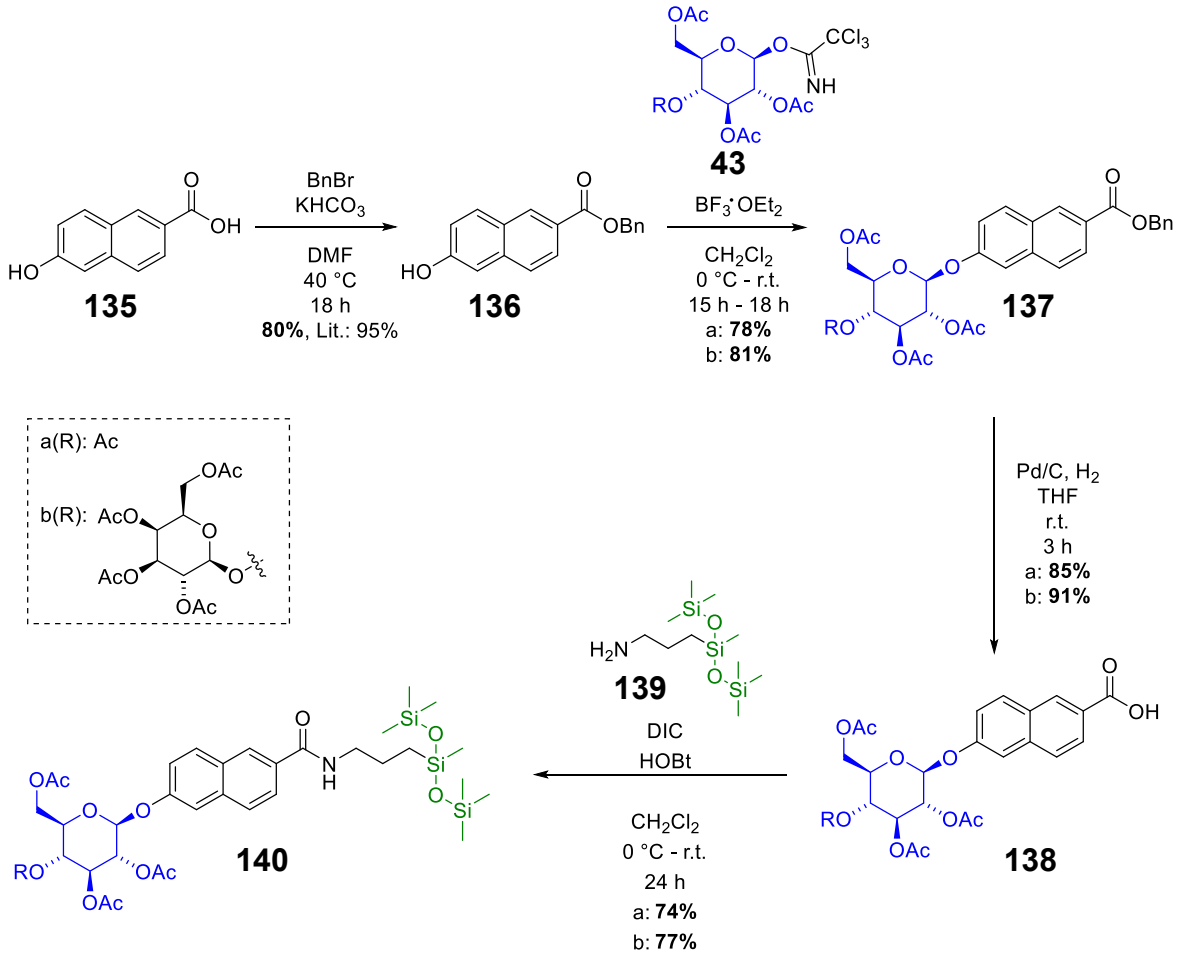
Besides the sugar units as hydrophilic head moieties and the siloxanes as hydrophobic side chains, naphthalene and napthalimide should be integrated as chromophoric units.

The final deprotection step could not be carried out successfully, the desired surfactants could not be obtained and therefore the physicochemical and spectrochemical investigations were still outstanding. Thus, the final siloxane surfactants were to be synthesized as part of this work by optimization of the deprotection step.

In addition, the idea arose to develop a synthetic strategy for fluorescent sugar surfactants with carbosilane chains for comparison to siloxane surfactants.

The following section provides a brief overview of the synthesis route for the compounds synthesized as part of the master's thesis[1]. These compounds were reproduced during the doctoral thesis to optimize the final synthesis step and investigate the linkage with new carbosilane chains.

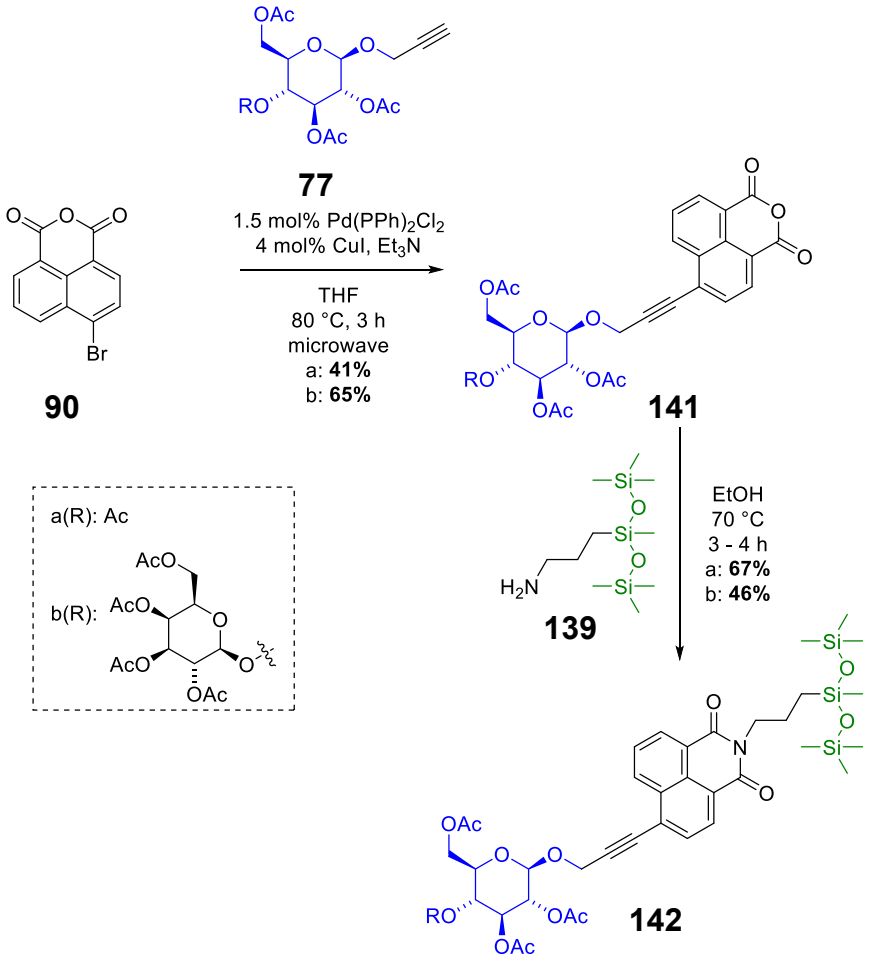
Scheme 63 shows the integration of chromophore **135**.



*Scheme 63: Synthesis route towards the glycosylated naphthoic acid **138** and subsequent amide coupling with the siloxane chain **139** developed during the Master's thesis[1].*

The synthetic route starts the protection of chromophore **135** to obtain the bezylester **136** according to a literature known procedure of *Chakraborty et al.*[170]. Siubsequently, the *O*-glycosylation of chromophore **136** with the trichloroacetimidates **43** was carried out. After deprotection of the benzyl ester **137**, the commercially available aminosiloxane **139** chain was linked to the chromophore by amide coupling.

Scheme 64 shows the functionalization of chromophore **135**.



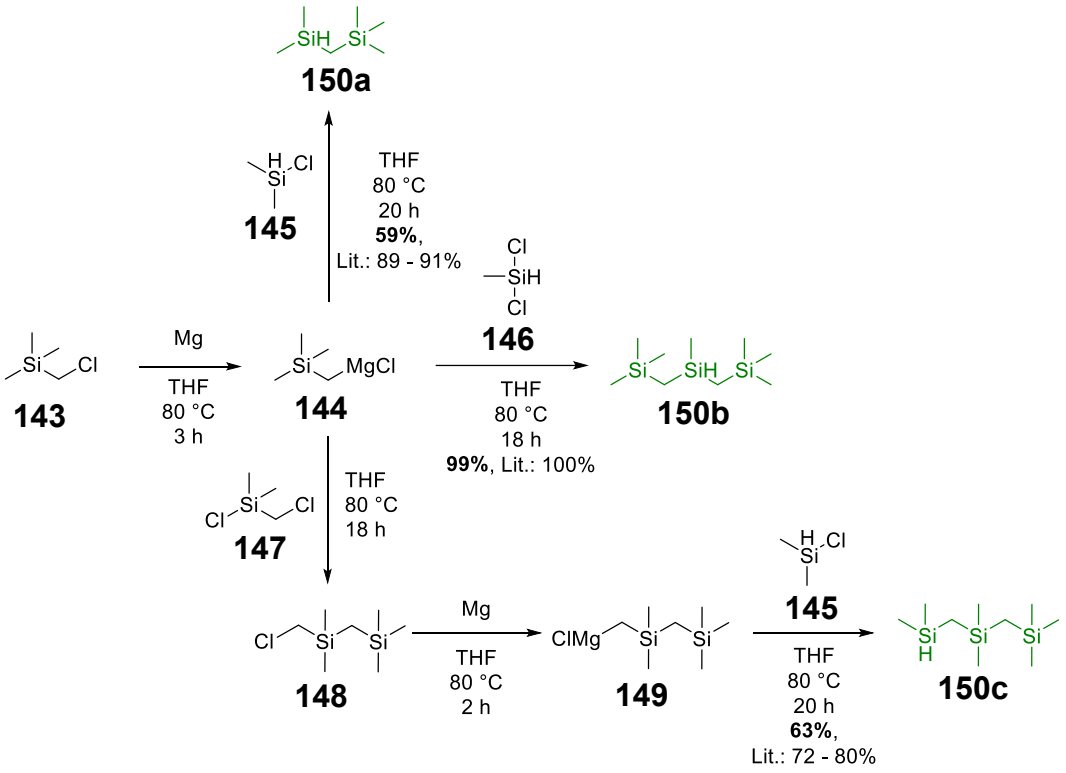
*Scheme 64: Synthesis of glycosylated naphthoic anhydride **141** and subsequent addition of the siloxane chain **139** developed during the Master's thesis[1].*

To link the sugar units with naphthoic anhydride **90** a *Sonogashira* coupling was carried out. The aminosiloxane **139** was subsequently reacted with the anhydride **141** to get the imides **142**.

The four re-synthesized compounds **140** and **142** were used to investigate the deprotection step. Additionally, the preliminary stage (the glycosylated naphthalene compounds **138** and **141**) was applied for the investigation of the introduction of carbosilane chains.

9.1 Synthesis of surfactants with carbosilane chains

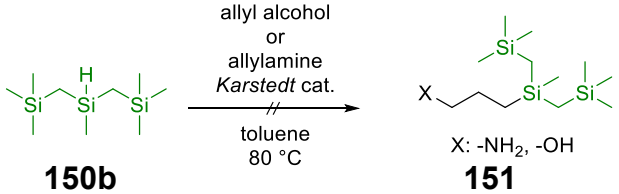
Carbosilane units can be connected to carbon chains by hydrosilylation and thus linked to form surfactant structures. For this purpose, the corresponding carbosilane units had to be synthesized first as shown in Scheme 65.



Scheme 65: Synthesis route towards different carbosilane chains as hydrophobic tails.[171],[172],[173],[37]

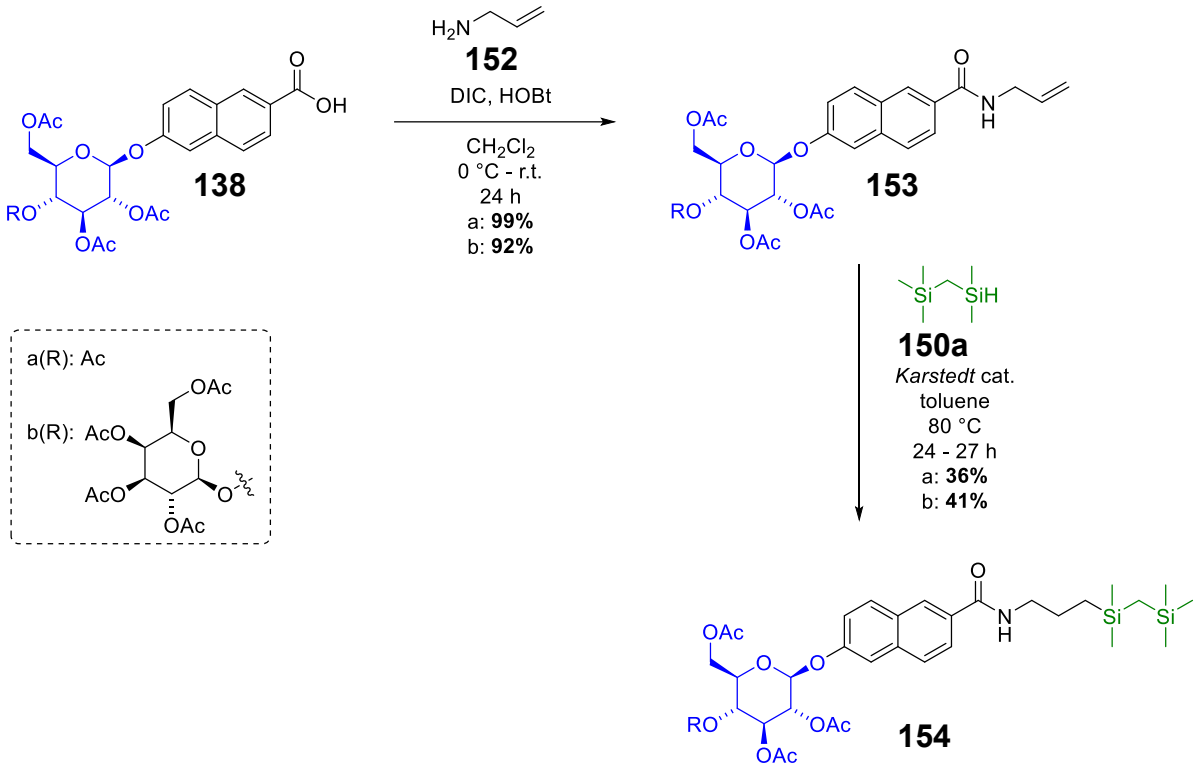
By *Grignard* reaction the individual carbosilane chlorides were linked to form differently branched and long chains. Sufficient total yields of 63% to 99% of the individual chains were obtained to use them for subsequent hydrosilylation.

As explained in the previous section, the siloxanes were bound to the chromophore by amide coupling with the commercially available aminosiloxane chain during the master's thesis[1]. For the synthesis of the carbosilane surfactants, a hydrosilylation of allylamine and allyl alcohol was therefore first attempted (Scheme 66) to investigate subsequent amide coupling or esterification.



Scheme 66: Attempted hydrosilylation of allyl alcohol and allylamine.

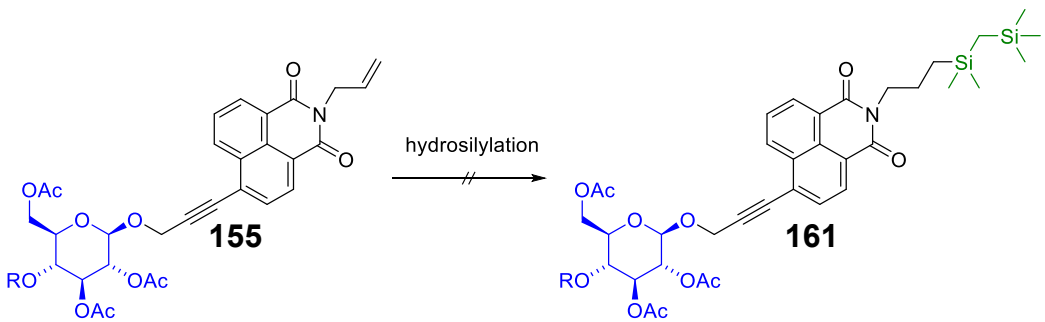
Under hydrosilylation conditions, no conversion could be achieved with either allyl alcohol or allylamine **152**. It was assumed that this was due to the free hydroxy or amine group, as it is close to the reaction center. Therefore, allylamine **152** should first be linked with naphthalene **138** and the carbosilane chain should be added subsequently (Scheme 67).



*Scheme 67: Accomplished amide coupling and hydrosilylation of carbosilane chain **150a** to naphthalene **153**.*

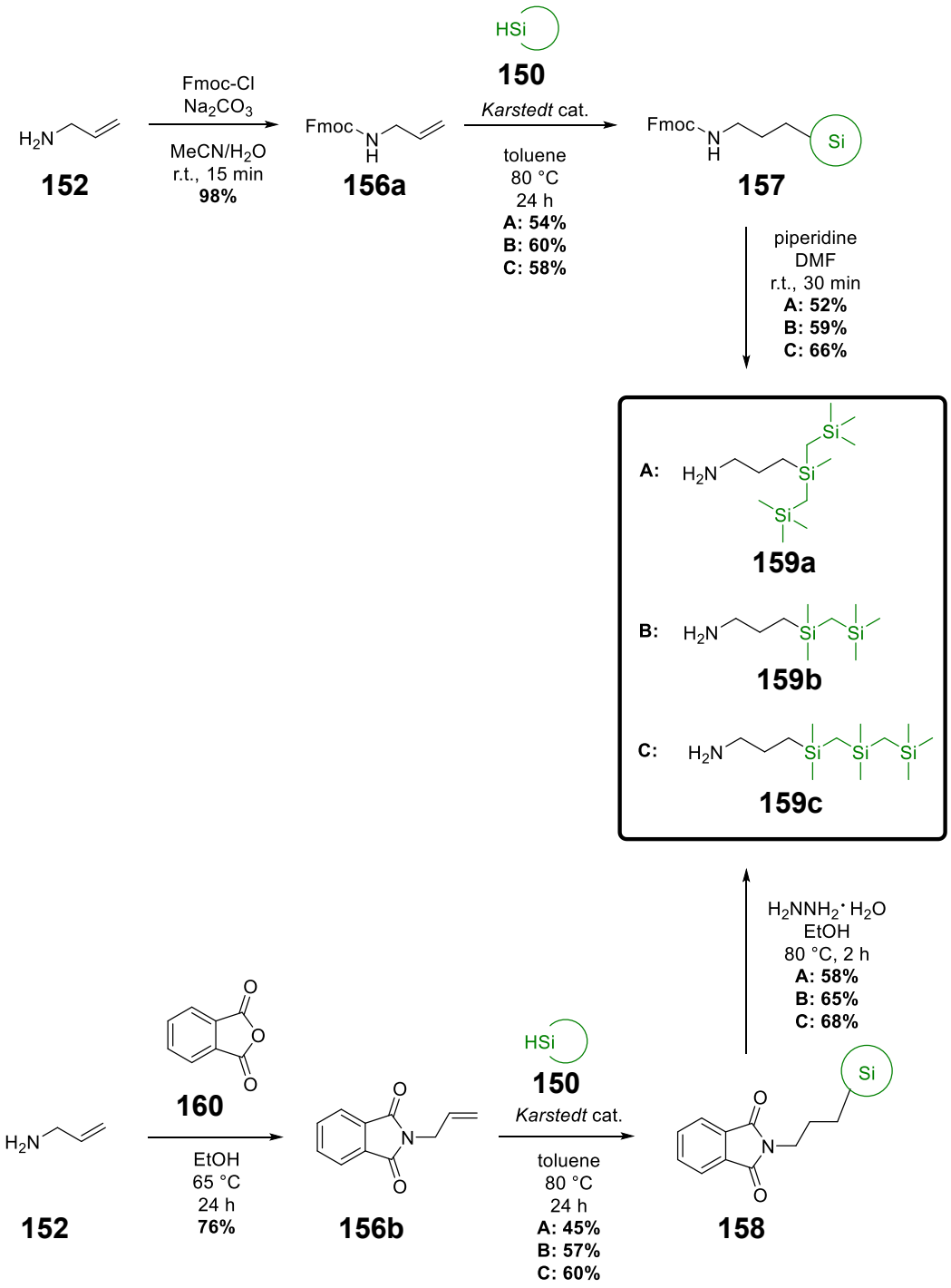
By amide coupling with allylamine **152** amides **153** were obtained. Subsequent hydrosilylation with carbosilane **150a** provided the desired compounds **154** in total yields of 35% and 37%.

However, this route could not be used for the integration of the carbosilane chain on chromophore **155** due to the alkine present (Scheme 68).



*Scheme 68: Representation of hydrosilylation, which would not lead to the desired product **161** due to the triple bond present.*

Therefore, two synthetic routes were developed to synthesize aminocarbosilane chains (Scheme 69).



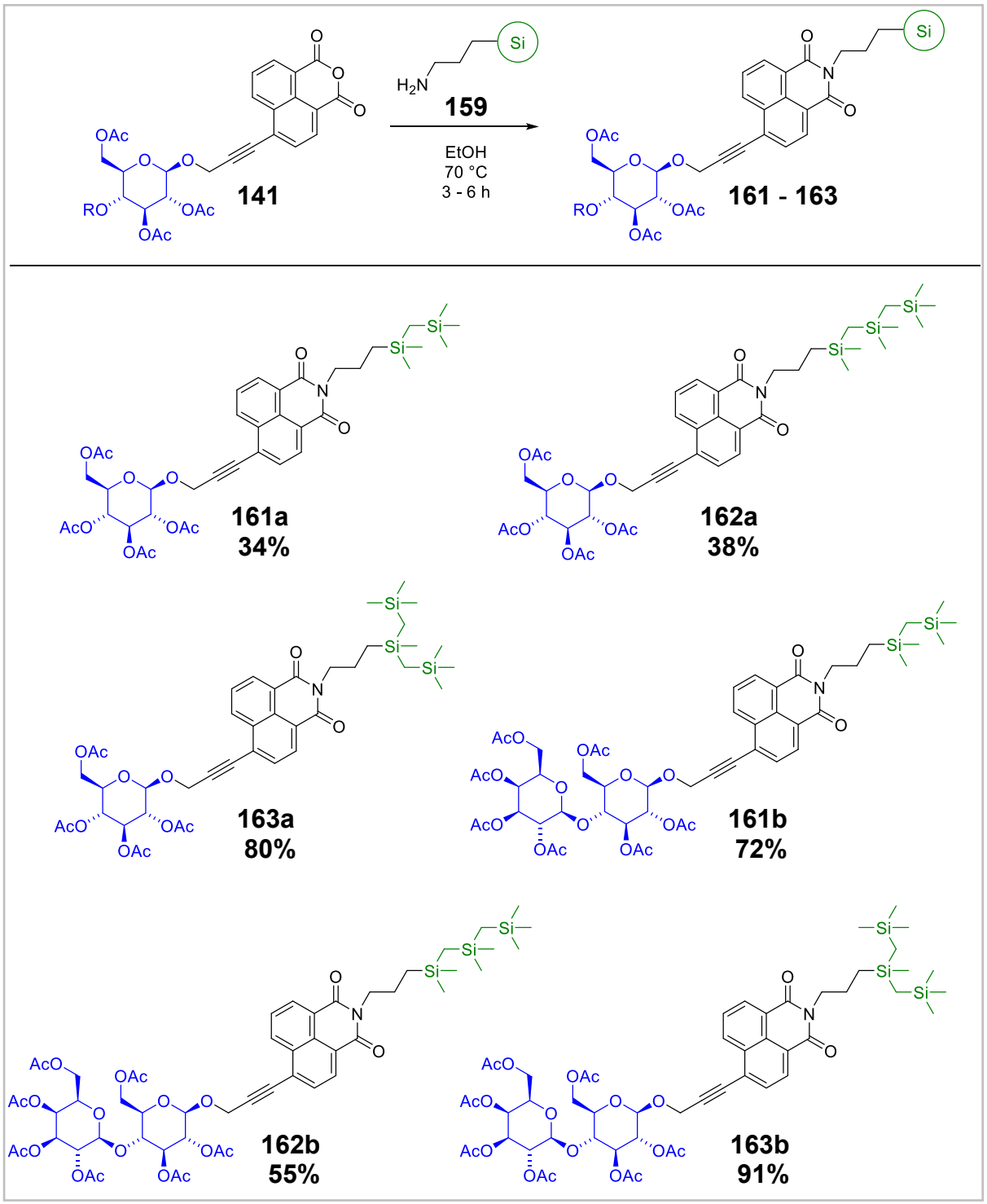
*Scheme 69: Accomplished synthesis of the aminocarbosilane chains **159**.*

First, allylamine (**152**) was protected by Fmoc, and in parallel a synthesis route *via* the phthalimide **156b** was tested which was similar to the *Gabriel* synthesis. The effective protection of the amine function led to successful conversion to the carbosilane chains by hydrosilylation using the *Karstedt* catalyst. After final deprotection, three new aminocarbosilane chains **159** were obtained. The synthesis route using Fmoc as a

protective group yielded total yields of 28% (**A**), 35% (**B**), and 38% (**C**). The use of phthalimides resulted yields of 20% (**A**), 28% (**B**), and 31% (**C**).

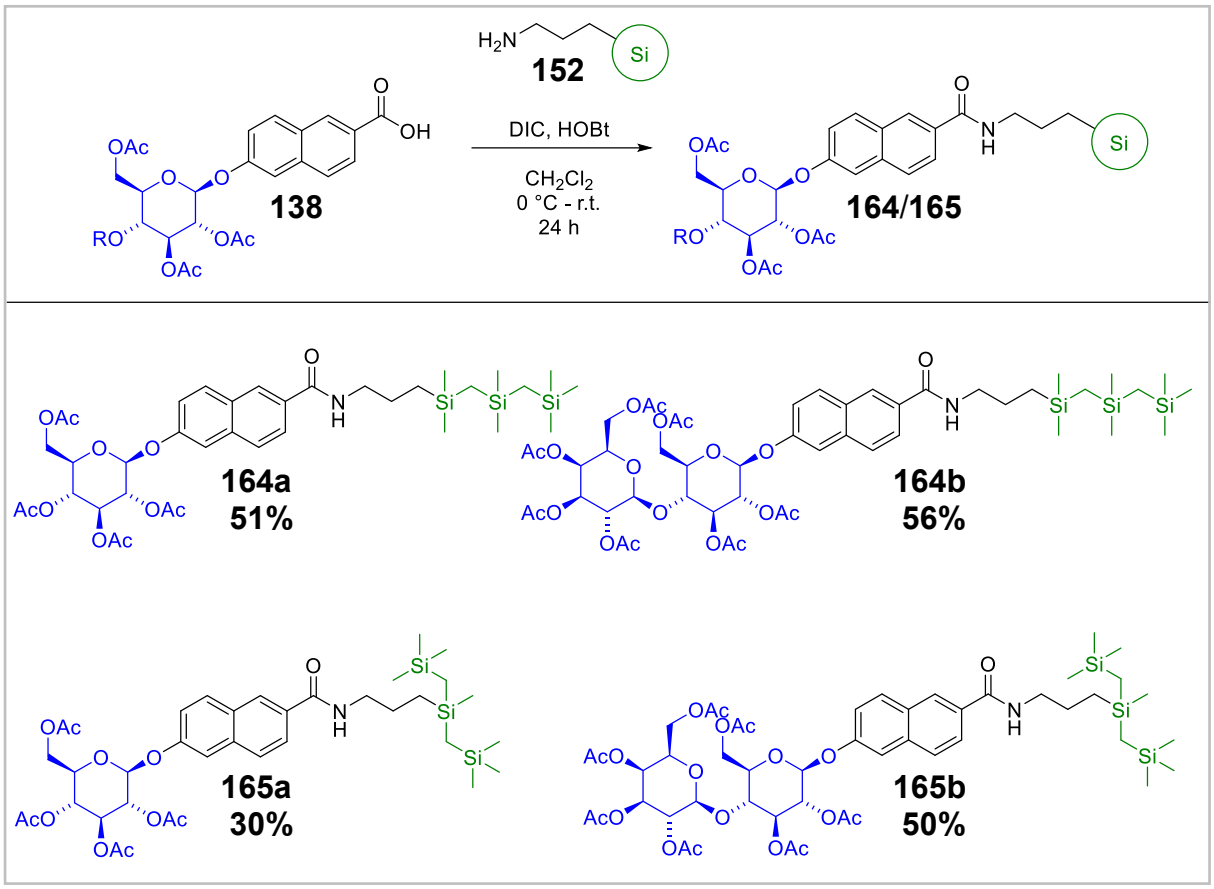
Since the phthalic anhydride **160** is less expensive than Fmoc-Cl and the workup during the *Gabriel*-like synthesis was easier to handle, this route should be used for the synthesis of carbosilaneamines in future, despite the slightly lower yield.

Subsequently the amines could be used to link the chains to the glycosylated chromophores **141** as shown in Scheme 70:



*Scheme 70: Accomplished synthesis of the imides **161**, **162** and **163**.*

The aminocarbosilane chains **159** were successfully added to the chromophore **141**. Thus, six new compounds with differently shaped carbosilane chains and two different sugar moieties were synthesized. The yields with the T-shaped chains **159a** were significantly better (80 and 91%) than with the linear chains **159b** and **159c** (34% to 70%). Additionally, the T-formed and linear chains **159c** and **159a** were also linked to the glycosylated chromophore **138** by amide coupling (Scheme 71).



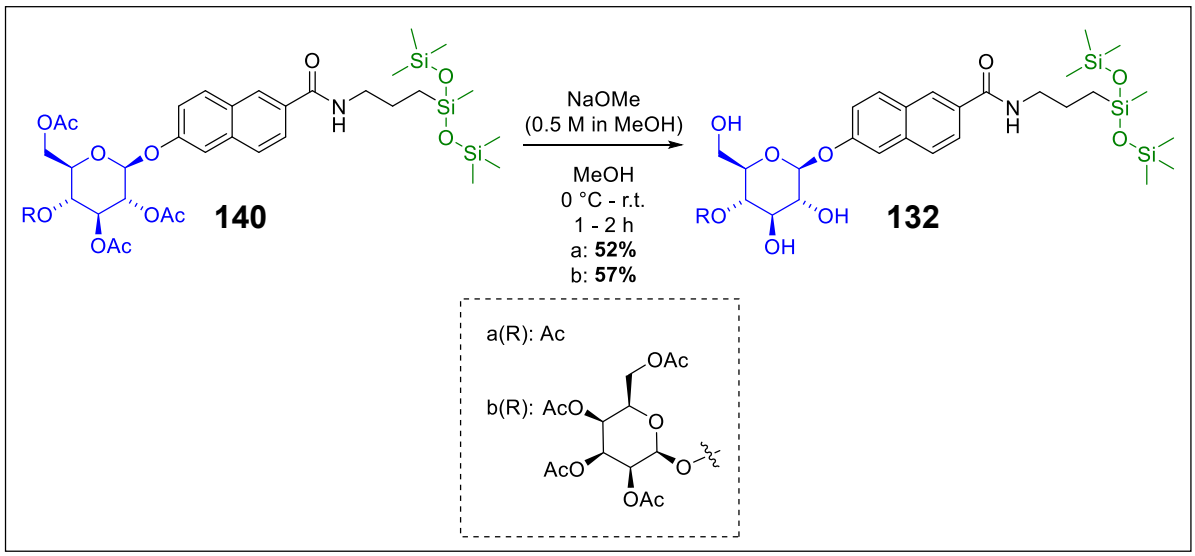
*Scheme 71: Accomplished amide coupling of chromophore **138** with different carbosilane chains.*

Four further carbosilane compounds with the linear and T-shaped chains could thus be synthesized by amide coupling. Yields up to 56% were achieved.

9.2 Deacetylation of the sugar moieties and preservation of the final carbosilane and siloxane surfactants

The final step in the targeted synthesis route to the surfactants was the deacetylation of the sugar units to obtain the polar head groups. During the Master's thesis[1], this step could not be realized for the siloxane surfactants due to purification issues. Thus, within the scope of this work conditions were tested to improve the work up after deprotection of the newly synthesized carbosilane structures and the already existing siloxane compounds.

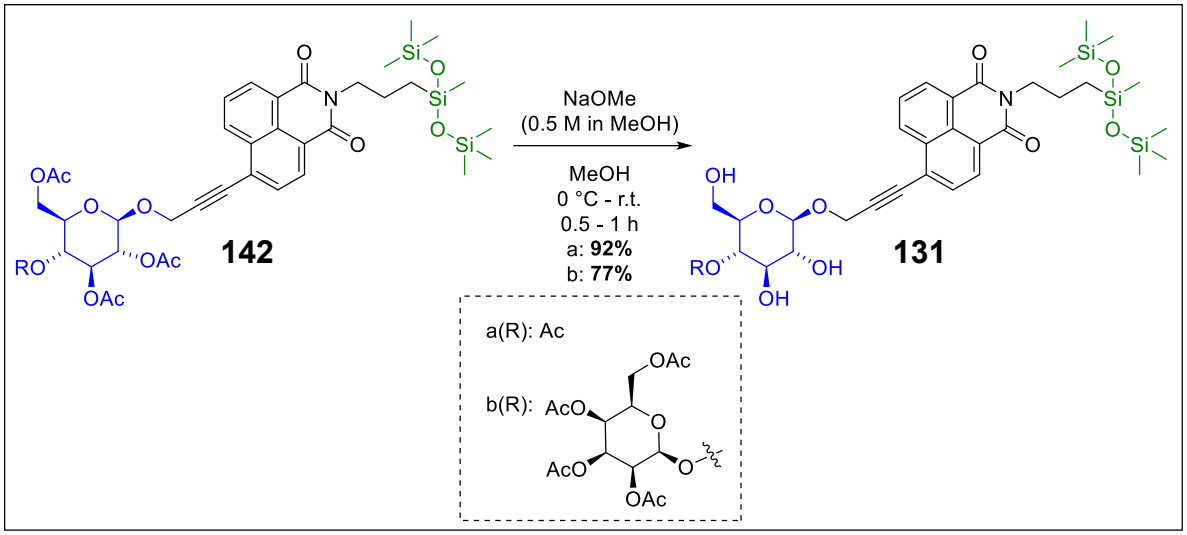
In Scheme 72 the deprotections of the **siloxane** compounds **140** are shown.



*Scheme 72: Accomplished deprotection and preservation of the final surfactants **132**.*

The acetylated sugar compounds were deprotected under basic conditions using NaOMe. In initial attempts, the products were first dried after complete conversion and should then be washed. However, the compounds decomposed during drying and became partially black. Therefore, the next attempt was to neutralize using different acids and subsequently extract the products. However, the extraction turned out to be difficult. Due to the strong polarity of the product, a lot of substance was lost in the aqueous phase. Finally, the product was neutralized with an acidic ion exchanger and then filtered off. After the crude product was dried, it could be purified by column chromatography. Thus, two new siloxane surfactants **132** were obtained in yields of 51% and 57%.

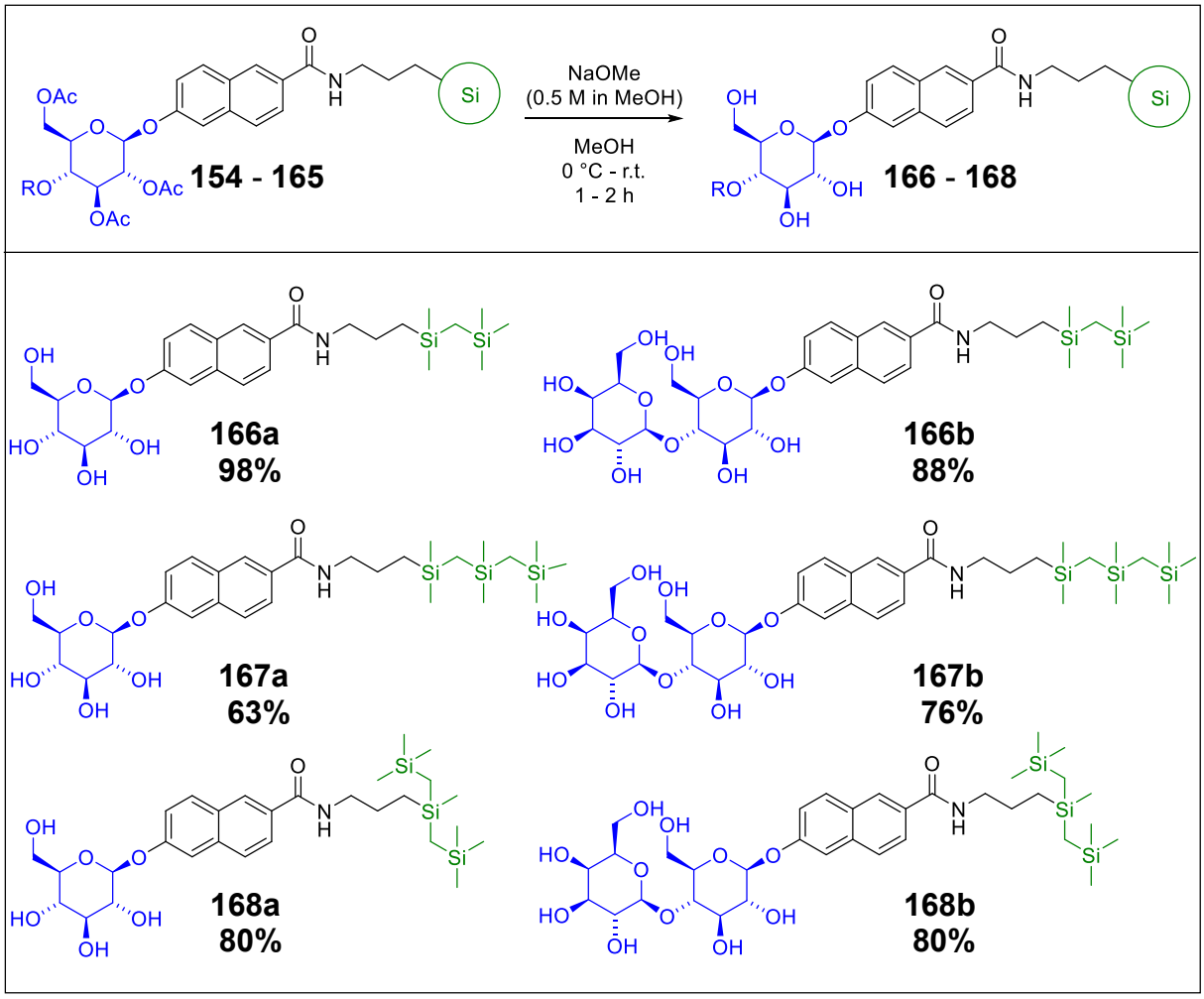
The optimized conditions for the work up and purification were then also applied to the synthesis of the other surfactants. The deprotections of the naphthalimide-based compounds **142** are shown in Scheme 73.



*Scheme 73: Accomplished deprotection and preservation of the final surfactants **131**.*

The desired novel surfactants **131** were obtained in good yields of 92% and 77%. The lower yield of the disaccharide **131b** can be derived from the fact that the column was run with a methanolic solvent due to the strong product polarity. Silica gel was partially rinsed down and the product had to be washed out several times afterwards.

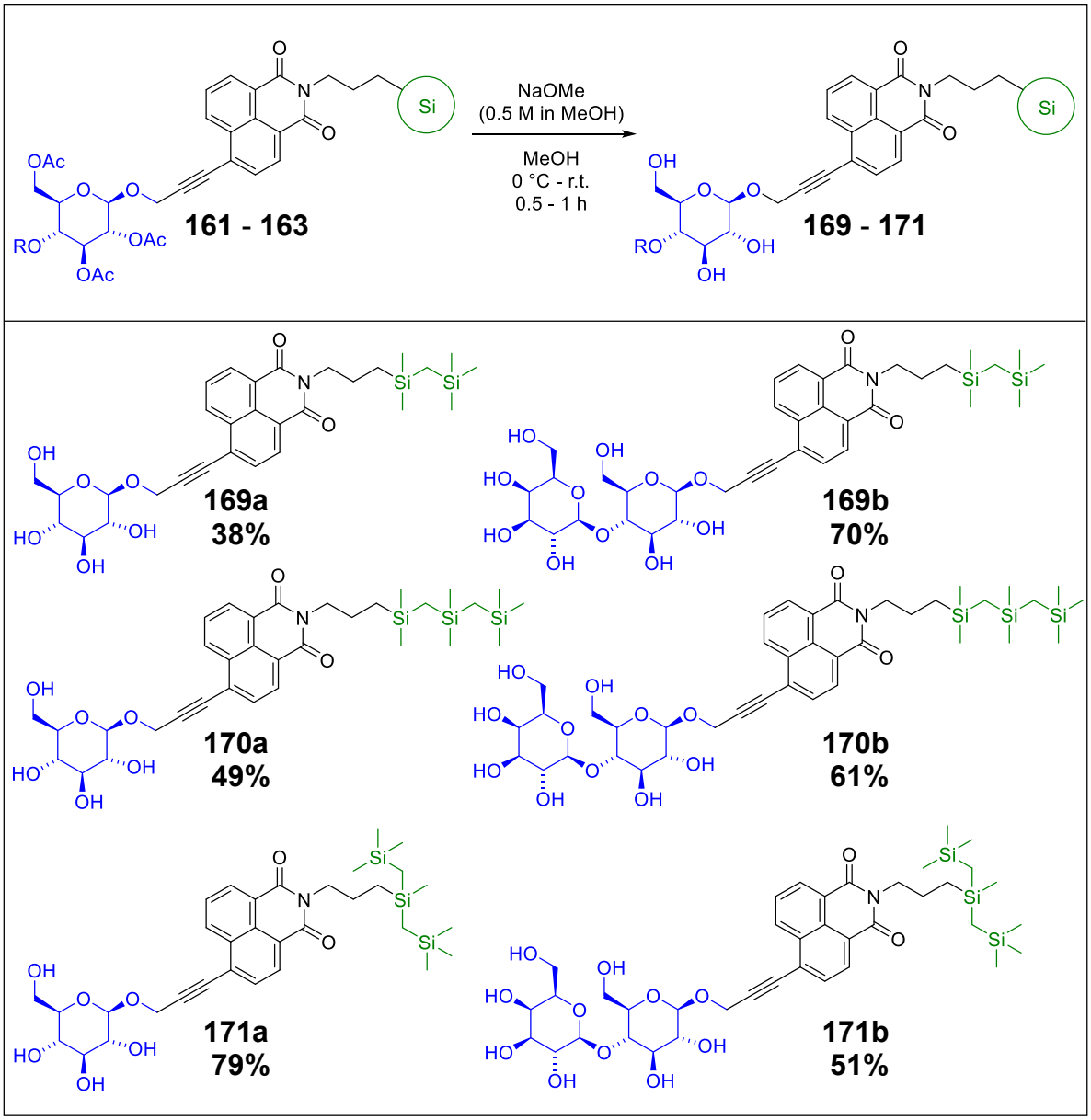
Finally, the new **carbosilane** structures **154**, **164** and **165** were deprotected under the same conditions as the siloxane compounds (Scheme 74).



*Scheme 74: Accomplished deprotection and preservation of the final surfactants **166**, **167** and **168**.*

Yields of 63% to 98% of the desired naphthylamides **166** - **168** were achieved. Thus, six new carbosilane surfactants could be obtained. The poorer yield of surfactant **167a** can certainly be improved by repeating the synthesis.

Scheme 75 provides an overview of the final products after deacetylation of the naphthylimides **161** - **163**.



*Scheme 75: Accomplished deprotection and preservation of the final surfactants **169**, **170** and **171**.*

By deprotection of the carbosilane compounds **161**, **162** and **163** yields of 38% to 79% were achieved. Here, the last synthesis step should also be repeated to improve some yields.

Overall, sufficient yields of all final surfactants were achieved to carry out further UV-vis and physicochemical measurements. In total **16** new sugar surfactants with carbosilane and siloxane chains were obtained. Two new synthesis routes have been developed, which include the synthesis of three new aminocarbosilane chains and the optimization of the final deprotection step. The two naphthalene chromophores could thus be successfully integrated into the surfactant structures.

9.3 Absorption and fluorescence measurements

Absorption- and fluorescence spectra of the 16 synthesized silicon-based surfactants were recorded. Solutions (MeCN and H_2O) of each compound with a concentration of 10^{-6} mol/L were measured in 1 cm cuvettes. The spectra show the normalized absorption or emission intensity against the wavelength of the UV-vis range. The extinction coefficients ε were calculated by the *Lambert-Beer* Law[140] (Equation 10) with the absorbance E, the substance concentration c and the cuvette thickness d:

$$E = \varepsilon \cdot c \cdot d \tag{10}$$

The compounds were excited with the wavelengths of the measured absorption maxima. These can be found in the legend in the related emission spectrum.

Since the absorption and emission spectra of compounds with the same chromophore unit are very similar, only a few spectra are shown below for a better overview. Two carbosilane and siloxane surfactants with different head groups are compared. The remaining spectra can be found in *Appendix 13.3*.

9.3.1 Absorption and fluorescence measurements of the carbamoyl naphthalene derivatives

The absorption and emission spectra of surfactant **168a** are shown in Figure 34.

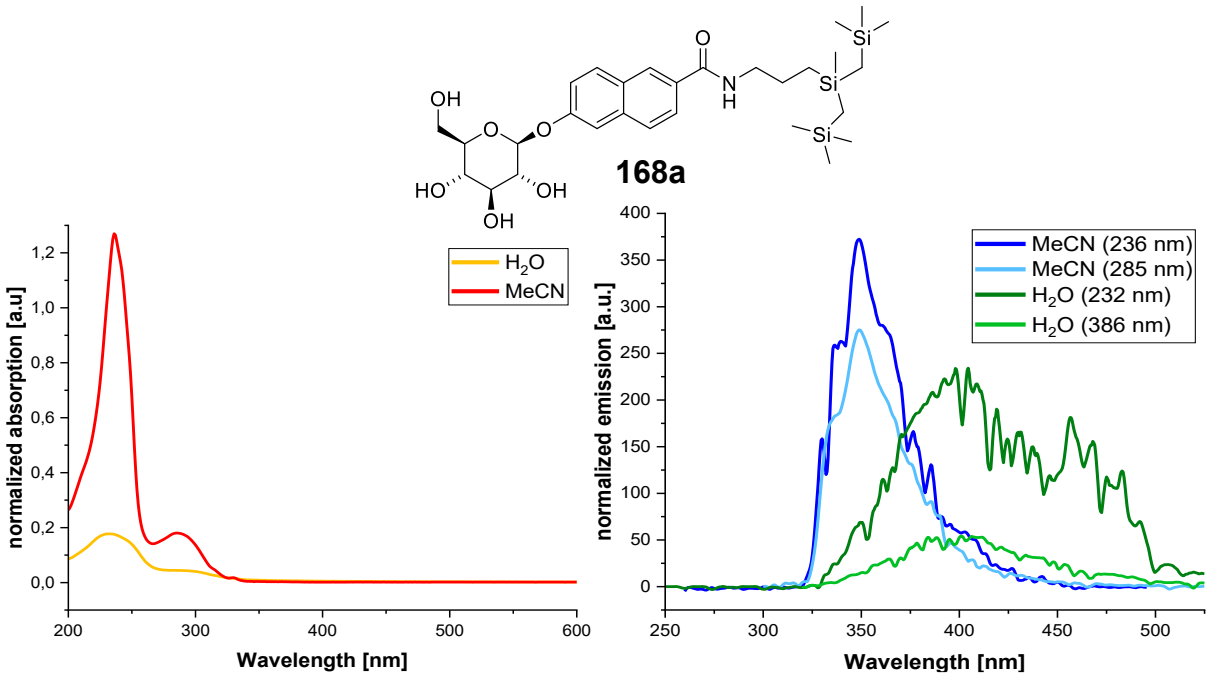


*Figure 34: Absorption (left) and emission (right) spectra of solutions of surfactant **168a** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

A sharp absorption maximum at 236 nm can be seen in MeCN. A second maximum with a lower intensity occurs at 285 nm. In water, a hypochromic shift can be seen and at the same time the maxima are slightly shifted to the longer wavelength range (bathochromic shift). The second maximum at 290 nm is barely recognizable.

The emission spectrum of surfactant **168a** clearly shows a *Stoke* shift to the longer wavelength range. In MeCN the maxima are at 350 nm. In water, the intensity decreases and a red shift is visible. The strong interactions with the polar solvent appear to have a major influence on the emission behavior of the compounds. The emission lines also show many deviations. The maxima in water are at 400 nm.

The absorption and emission spectra of surfactant **168b** with a disaccharide as head group are shown in Figure 35.

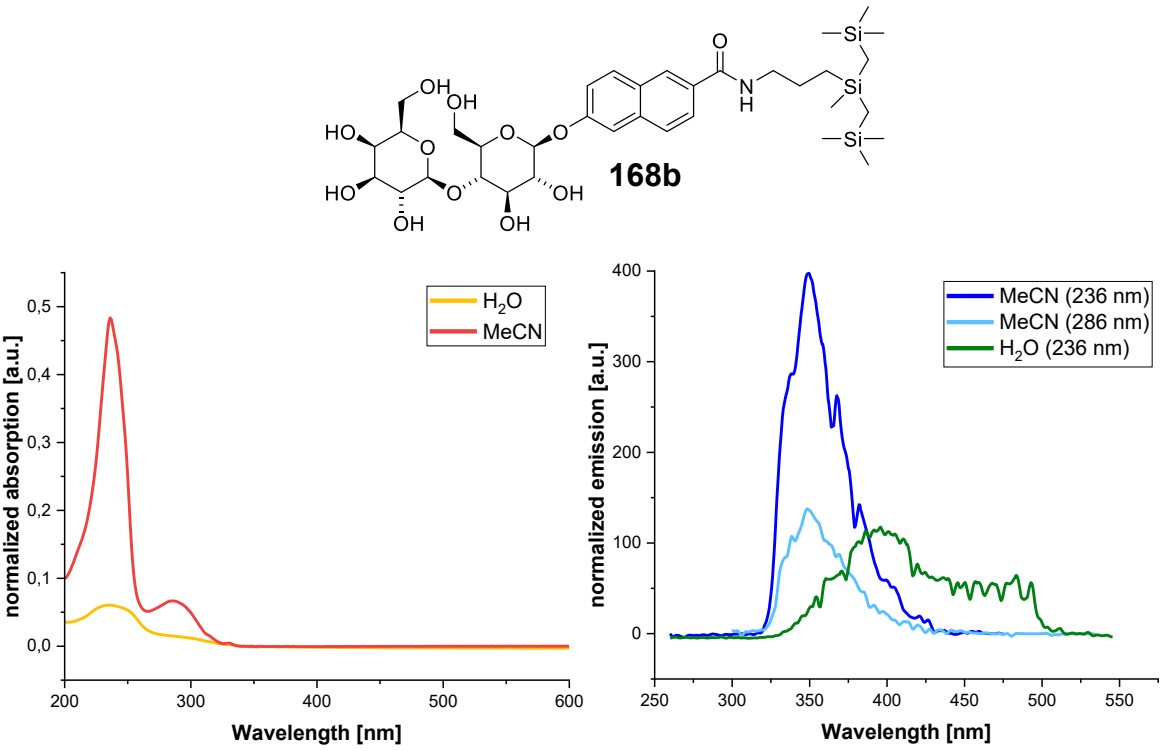


*Figure 35: Absorption (left) and emission (right) spectra of solutions of surfactant **168b** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The maxima in both spectra are in the same range as the previous compound with the monosaccharide as head group. However, the absorption band of the aqueous solution is very low in intensity. The associated maximum of the emission spectrum is broad and flat. It could be assumed that the lower intensity of the maxima measured in aqueous solution depends on the strong interaction (hydrogen bonds) of the hydroxy groups with the polar solvent.

In Figure 36 the absorption and emission spectra of siloxane surfactant **132a** are shown.

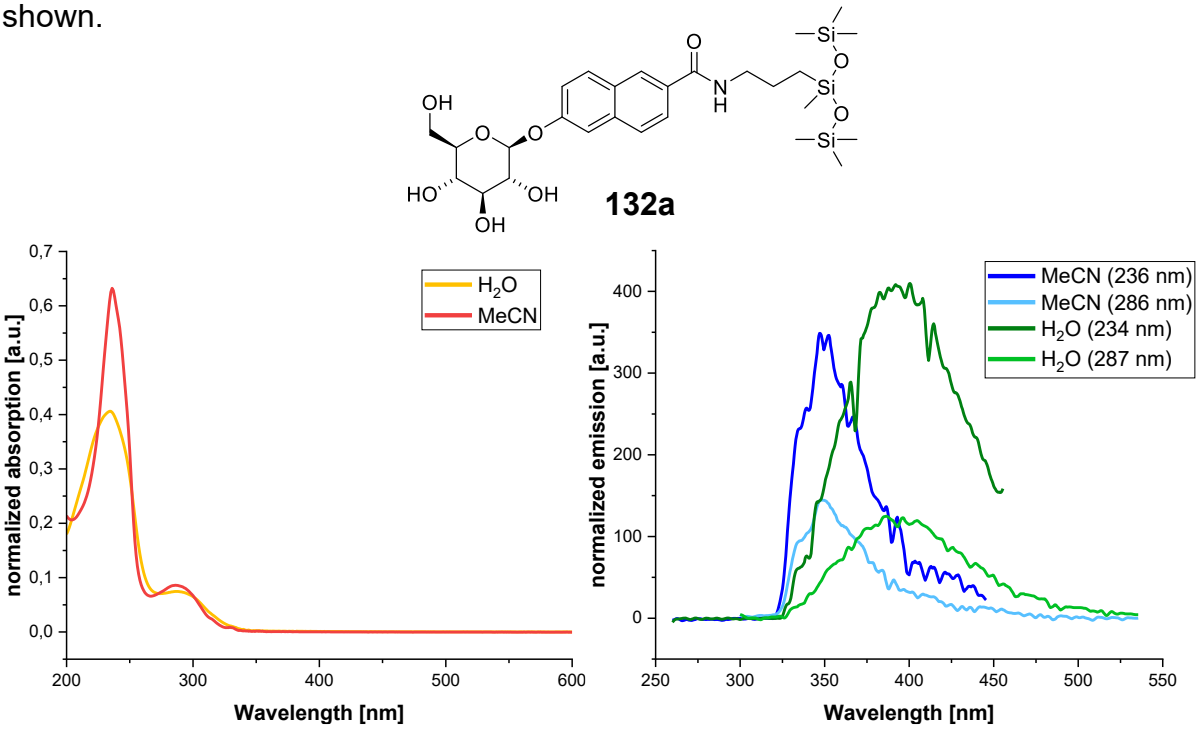
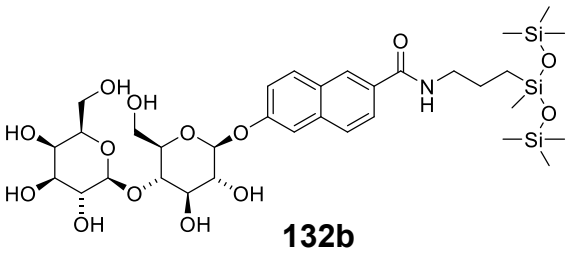


*Figure 36: Absorption (left) and emission (right) spectra of solutions of surfactant **132a** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The spectra look almost identical to the spectra of the previous carbosilane surfactants. But the maxima of the absorption and emission measured of the aqueous solution are more intense.

In Figure 37 the absorption and emission spectra of surfactant **132b** are shown.



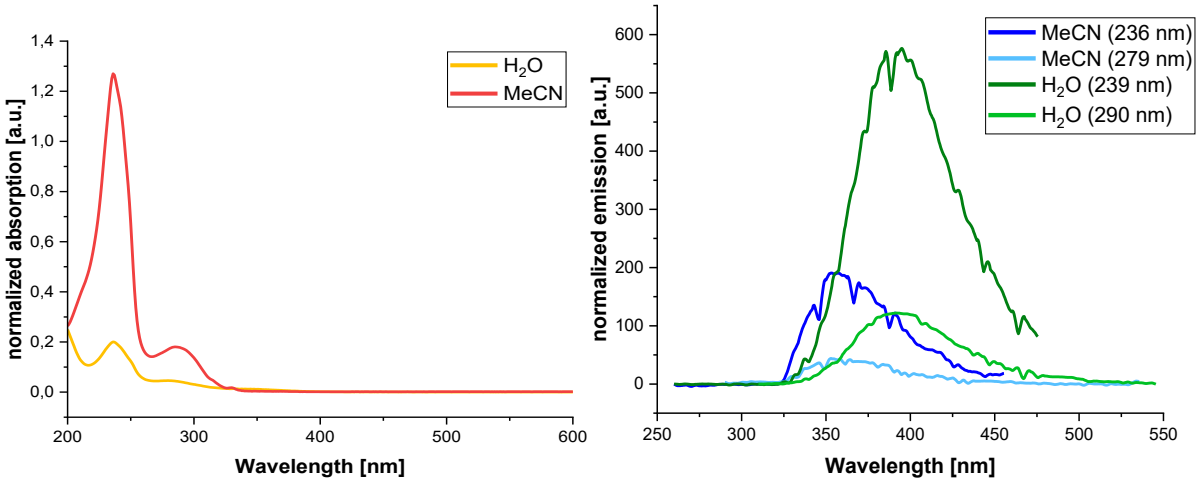


*Figure 37: Absorption (left) and emission (right) spectra of solutions of surfactant **132b** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The absorption maxima are slightly shifted to maxima at 236 nm and 279 nm in MeCN and 239 nm and 290 nm in H_2O. A major difference to the previous compounds can be seen in the emission spectrum. The intensity of the maxima of the MeCN solution is much lower than those of the aqueous solution. The siloxane surfactant with the disaccharide as head group appears to have increased fluorescence in water.

In Table 16 the absorption and emission maxima and the extinction coefficients of all synthesized naphthalene derivatives are summarized.

*Table 16: Photophysical data of the naphthalene-based surfactants **166** - **132**.*

Surfactant	λ_{Abs}	ε	λ_{em}	Solvent	Chain	Sugar
168a	236	1270000	350	MeCN	Carbosilane	Glucose
	232	177000	410	H_2O		
166a	236	770000	355	MeCN		
	232	250000	-	H_2O		
167a	236	750000	355	MeCN		
	234	400000	410	H_2O		
168b	236	470000	350	MeCN		Lactose
	234	60000	404	H_2O		
166b	236	780000	348	MeCN		
	237	210000	376	H_2O		
167b	236	790000	349	MeCN		
	236	80000	394	H_2O		
132a	237	620000	350	MeCN	Siloxane	Glucose
	234	400000	395	H_2O		
132b	236	1240000	358	MeCN		Lactose
	239	190000	293	H_2O		

It is noticeable that the compounds with disaccharide as head group in particular have a lower value for the extinction coefficient in H_2O. In addition, a slight hypsochromic shift can be seen in the emission spectra for these compounds in both solvents. The extinction coefficients calculated for solutions in MeCN are in a similar range for both head groups. The interactions of the surfactants with water as a polar solvent seem to influence the absorption and emission. Especially the hydroxyl groups of the sugar units create strong interactions such as hydrogen bonds. But for some naphthalene derivatives, the emission is even stronger than in MeCN. Especially for the siloxane surfactant **132b.** Although the intensities of the maxima vary greatly, no significant shift in the wavelength range is recognizable in the absorption spectra. Thus, no positive or negative solvatochromism can be concluded. However, a clear shift is visible in all emission spectra. The aqueous solutions almost all emit in the longer wavelength range compared to MeCN solutions, which can be attributed to a smaller energy gap between the excited and ground state.

Overall, all compounds show absorption and fluorescence in the UV range in both tested solvents.

9.3.2 Absorption and fluorescence measurements of the naphthalimide derivatives

In Figure 38 the absorption and emission spectra of surfactant **171a** are shown.

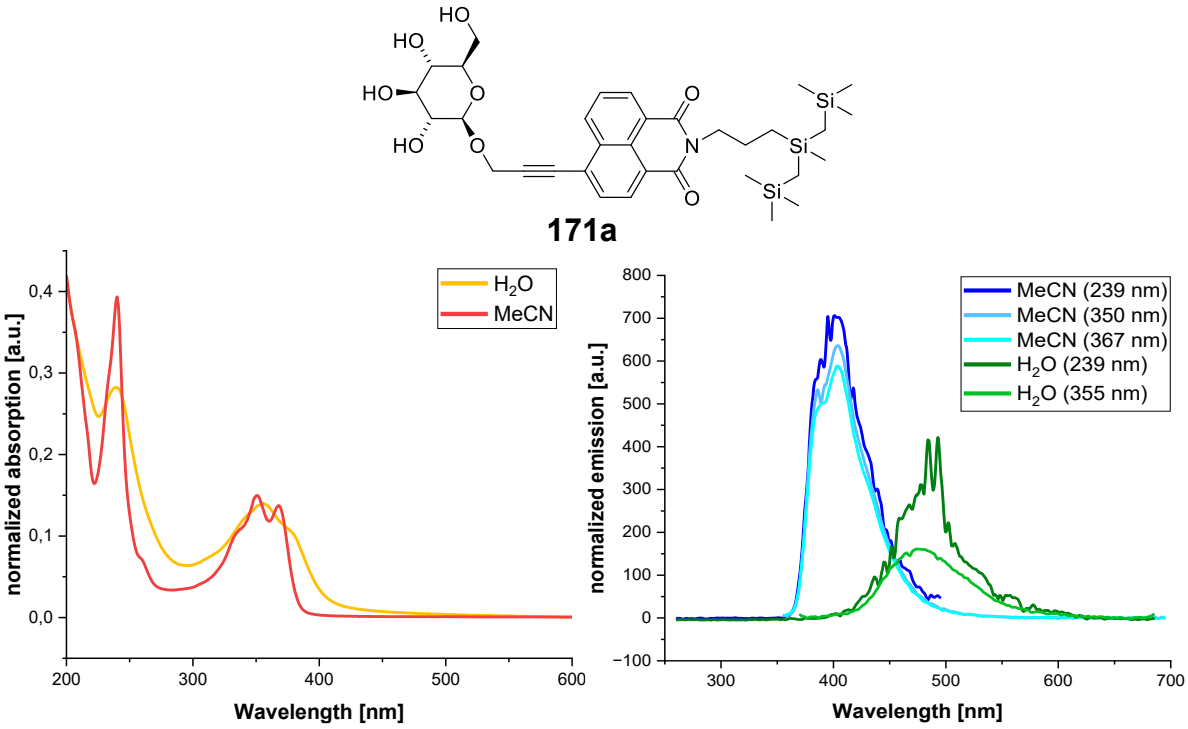


*Figure 38: Absorption (left) and emission (right) spectra of solutions of surfactant **169a** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The absorption spectra of naphthalimide **171a** shows three maxima. In MeCN, a sharp band is visible at 239 nm and two smaller bands at 350 nm and 355 nm. A slight red shift can be seen in H_2O. In addition, the smaller maxima have merged to form a broad band.

The emission spectrum of the solution in MeCN shows a maximum at 406 nm. The measurement of the aqueous solution results in a spectrum with a weak band at 490 nm with many irregularities.

In Figure 39 the absorption and emission spectra of surfactant **171b** with a disaccharide as head group are shown.

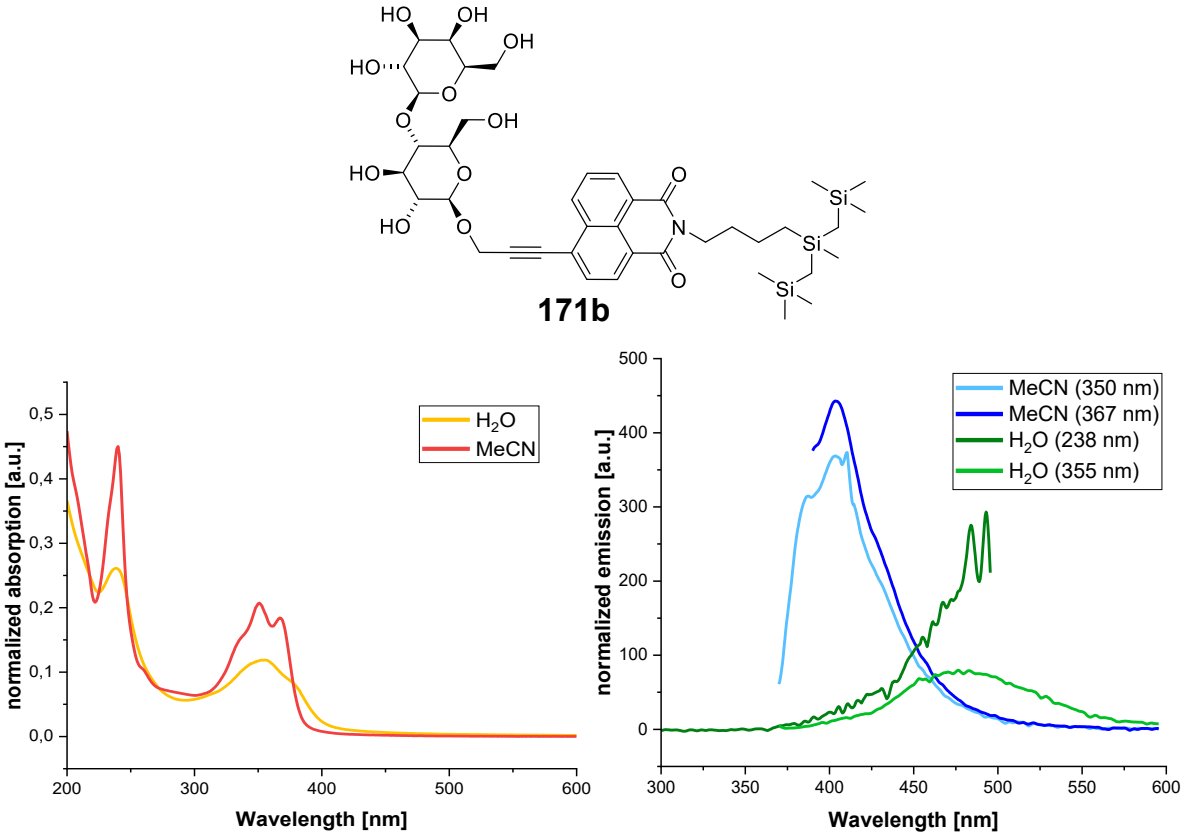
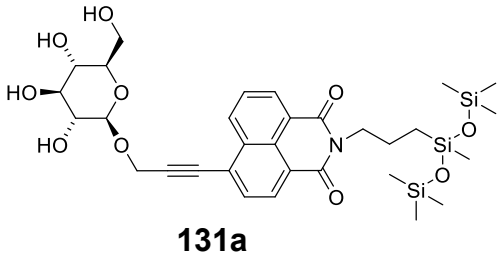


*Figure 39: Absorption (left) and emission (right) spectra of solutions of surfactant **171b** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The spectra also show similar absorption and emission lines as the previous compound with a monosaccharide as head group, but the intensities of the lines of the aqueous solution are lower in intensity. The sugar unit seems to influence the absorption and emission behavior. This could be due to strong interactions of the hydroxy groups with the polar solvent.

In Figure 40 the absorption and emission spectra of surfactant **131a** are shown.



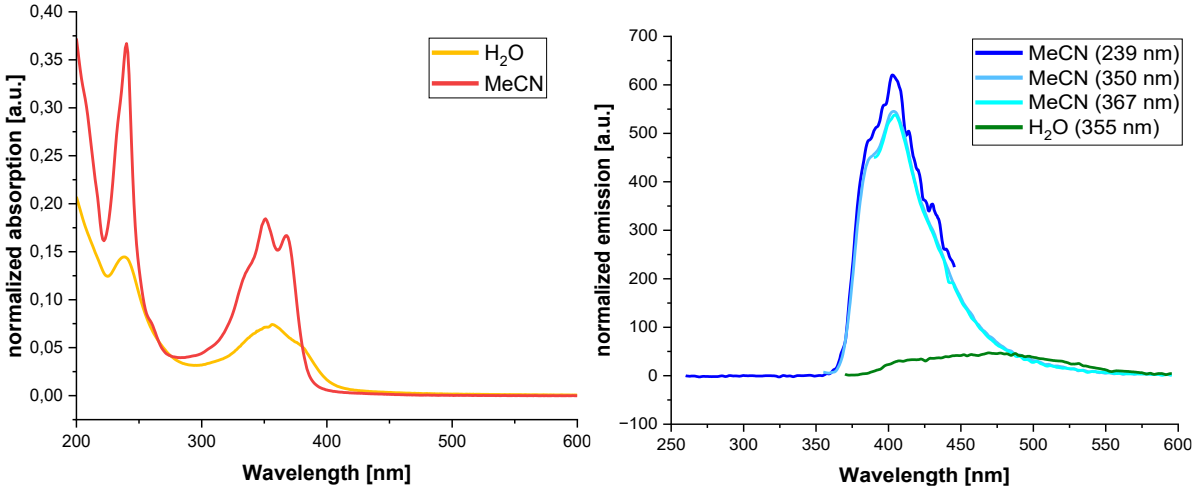


*Figure 40: Absorption (left) and emission (right) spectra of solutions of surfactant **131a** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The intensity of the absorption bands of the aqueous solution is less intense. No emission band could be obtained by excitation at 239 nm. The emission line after excitation at 355 nm is also very flat. In MeCN, the intensity is comparable to the previous spectra.

The absorption and emission spectra of **131b** look similar to the spectra of the siloxane surfactant **131a** with a monosaccharide as head group (Figure 41).

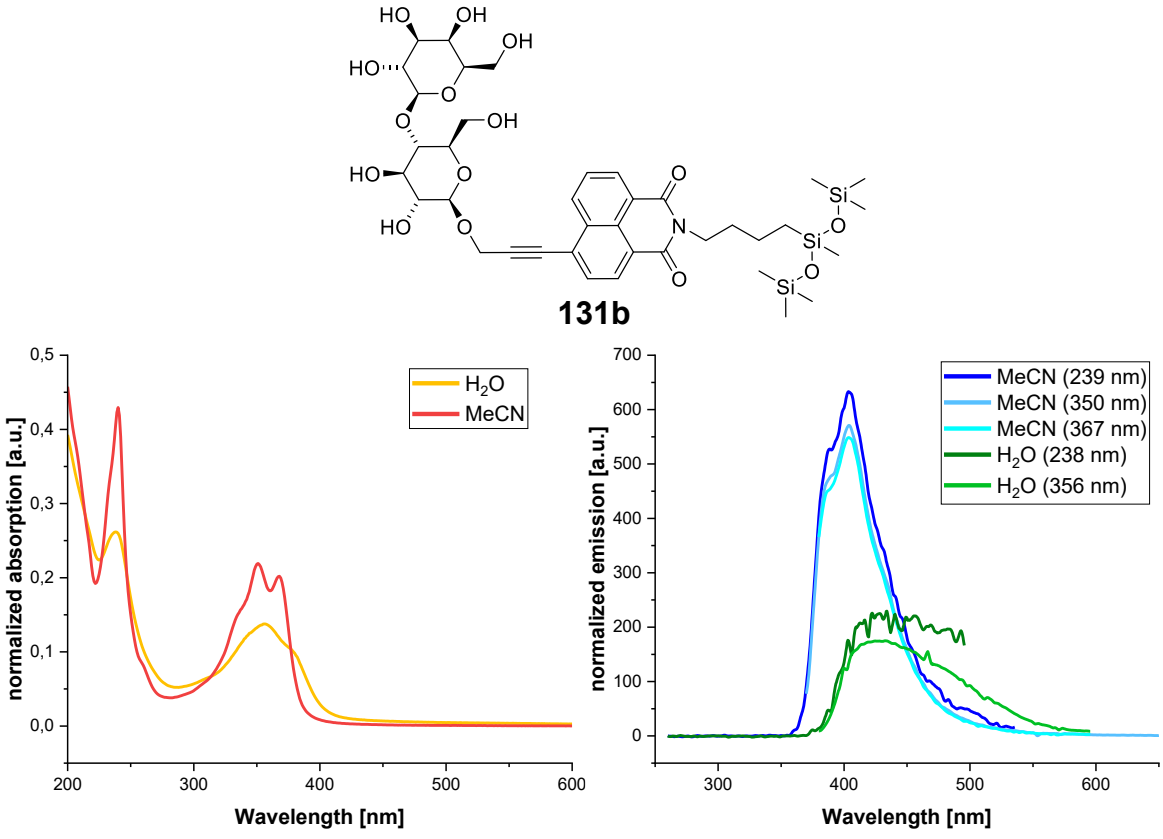


*Figure 41: Absorption (left) and emission (right) spectra of solutions of surfactant **131b** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The maxima of the emission spectrum of the aqueous solution are slightly shifted to the shorter wavelength range compared to the spectrum of the siloxane surfactant above.

In Table 7 the absorption and emission maxima and the extinction coefficients of the naphthalimide derivatives are summarized.

*Table 17: Photophysical data of the naphthalimide derivatives **131**, **169 -171**.*

Surfactant	λ_{Abs}	ε	λ_{em}	solvent	tail	head group
169a	239	470000	406	MeCN	Carbosilane	Glucose
	239	260000	493	H_2O		
170a	239	490000	402	MeCN		
	240	270000	492	H_2O		
171a	239	390000	402	MeCN		
	239	280000	477	H_2O		
169b	239	390000	403	MeCN		Lactose
	240	190000	475	H_2O		
170b	239	480000	406	MeCN		
	240	220000	485	H_2O		
171b	239	440000	404	MeCN		
	238	260000	484	H_2O		
131a	239	360000	403	MeCN	Siloxane	Glucose
	240	140000	475	H_2O		
131b	239	420000	406	MeCN		Lactose
	238	260000	432	H_2O		

The naphthalimides show absorption and emission in the longer wavelength range than the naphthalene derivatives. The values for the extinction coefficient are also much higher. The intensity of the absorbance maxima is somewhat lower in water than in MeCN. However, no shift in the wavelength range is recognizable and therefore no strong solvatochromic influence is visible. In the emission spectra, a bathochromic shift is visible in the aqueous solution compared to the MeCN solution. Overall, the naphthalimides show absorption and emission in the UV and visible light range.

Among the two fluorophores tested, the naphthalimide derivatives provided the most intense and stable emission, while the carboxamide-based systems exhibited weaker but more environmentally sensitive fluorescence. This was demonstrated by the use of solvents with different polarities. This comparison underscores the tunability of the surfactant platform.

9.4 Surface tension measurements

In this chapter, the surface tension measurements of the synthesized carbosilane and siloxane surfactants are described and compared with each other. The theoretical background to the measurement using the *Wilhelmy* plate method and the detailed calculation of the substance-specific values is described in *Chapter 2.1.2*. The following graphs show the obtained concentration curves of the surface tensions of the switchable surfactants under ambient light at 21 °C.

In Figure 42 the measured surface tension in dependency of the surfactant concentration of the surfactants **166** - **168** with different carbosilane chains are shown.

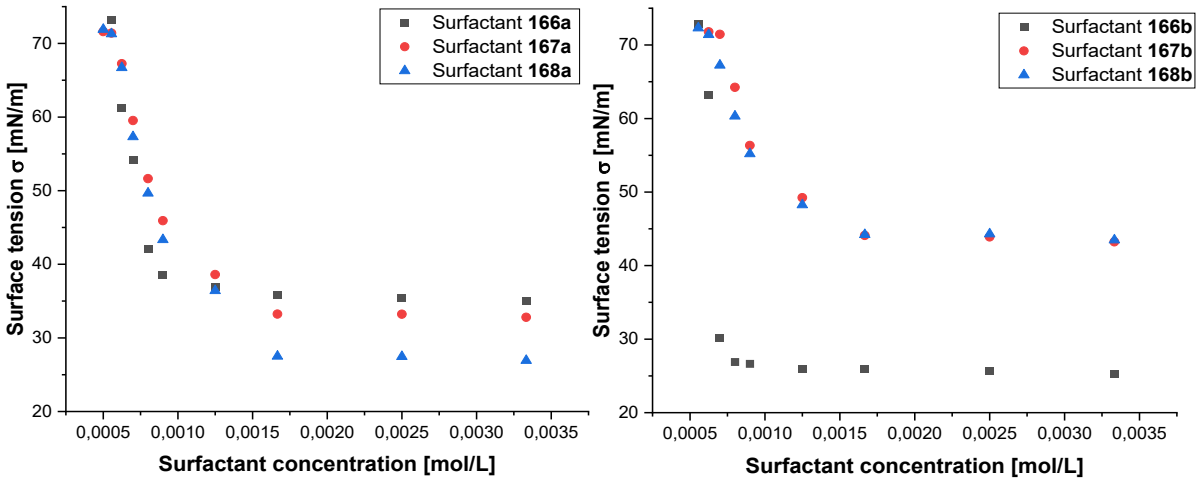
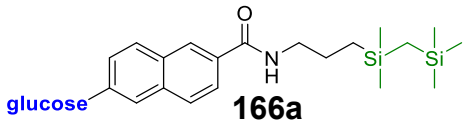
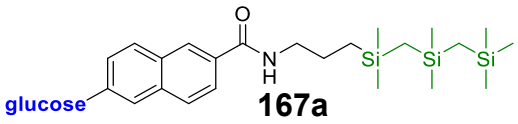
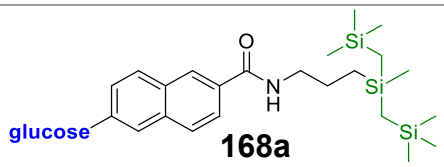
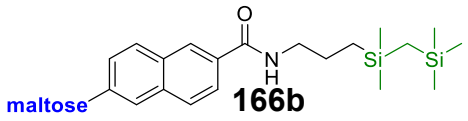
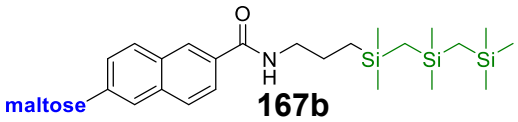
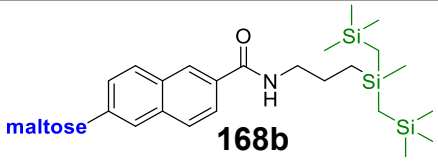


Figure 42: Measured surface tension in dependency of the concentration of surfactants with carbosilane chains. Left: surfactants with glucose as head group, right: surfactants with lactose as head group.

The graph (Figure 42, left) with the measured values for the surfactants with glucose as head group shows that the surface tension drops sharply with all three surfactants at the same concentration. This indicates that the solubility must be very similar and that the carbosilane chain has no significant influence on this. The minimum surface tension for the compound **168a** with the T-shaped carbosilane chain is 26.92 mN/m, which is lower than that of the linear chains **166a** and **168a** (35.06 and 32.79 mN/m). For surfactants with lactose as the head group (Figure 42, right), the surface tension decreases more steeply at lower concentrations with surfactant **166b** containing the dicarbosilane chain. The minimum surface tension is also lower at 25.28 mN/m. The minimum surface tension measured with tricarbosilane **167b** and T-shaped carbosilane **168b** is relatively high at 43.32 and 43.48 mN/m.

The values of *cmc*, maximum interfacial concentration Γ_∞, and minimum head group requirement A_{min}, which were determined by adjusting the fitted lines, are summarized in Table 18.

Table 18: Summary of the substance-specific values of surfactants with carbosilane chains obtained by plotting the surface tension against the logarithmic values of the concentrations, which were calculated using linear regression.

Surfactant	σ_{min} [mN/m]	*cmc* [mmol/L]	Γ_∞ [µmol/m²]	A_{min} [nm²]
 **166a**	35.06	0.86	2.96	0.05
 **167a**	32.79	1.39	0.38	0.43
 **168a**	26.92	0.92	1.55	0.10
 **166b**	25.28	1.03	1.46	0.11
 **167b**	43.32	1.03	3.51	0.07
 **168b**	43.48	1.09	2.22	0.07

The *cmc* is similar for all surfactants. The highest value was calculated for tricarbosilane **167a** with glucose as the head group. The lowest values were obtained with the dicarbosilane **166a** and the T-shaped carbosilane **168a**. The highest values for the maximum interfacial concentration were calculated for the carbosilanes **167b** and **168b** with **lactose** as the hydrophilic unit. This also resulted in the low value for the head group requirement of 0.07 nm². For the surfactant **166a** with glucose, an even lower value of 0.05 nm² and a high interfacial concentration of 2.96 µmol/m² were calculated.

Overall, no general conclusion could be drawn about the individual influence of the shape and size of the head group or side chain. The decisive factor is rather the combination of hydrophilic and hydrophobic units.

In Figure 43 the surface tension measurements of the two siloxane surfactants **140a** and **140b** are compared.

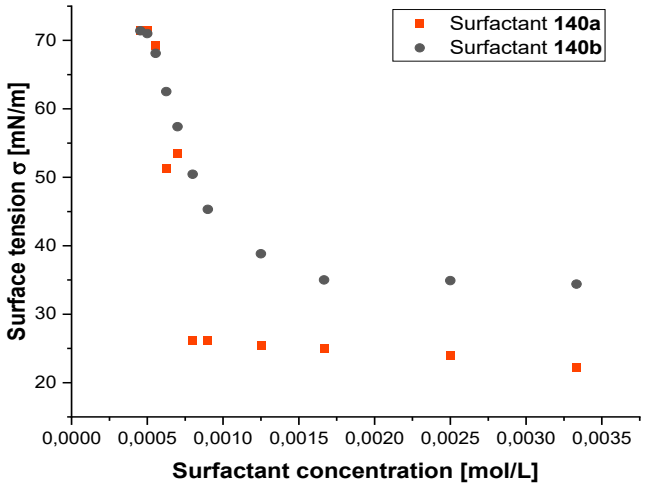
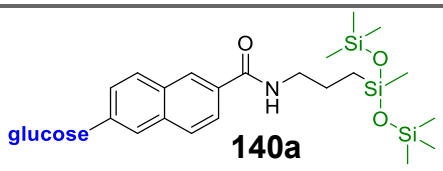
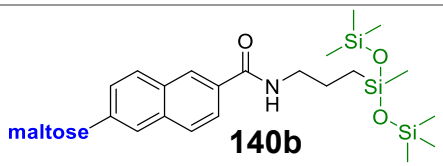


Figure 43: Measured surface tension in dependency of the concentration of surfactants with siloxane chains.

With both surfactants, the surface tension decreases significantly at the same concentration, which indicates that the two compounds have a similar solubility.

In Table 19 the obtained physicochemical values are summarized.

Table 19: Summary of the substance-specific values of surfactants with siloxane chains obtained by plotting the surface tension against the logarithmic values of the concentrations, which were calculated using linear regression.

Surfactant	σ_{min} [mN/m]	*cmc* [mmol/L]	Γ_{∞} [µmol/m²]	A_{min} [nm²]
 **140a**	22.28	0.80	8.46	0.02
 **140b**	34.39	1.10	1.91	0.08

With the siloxane surfactant **140a**, which has glucose as its head group, a lower value for the minimum surface tension of 22.29 mN/m was obtained. Lower values were also calculated for the *cmc* and the head group requirement, which resulted in a higher value for the maximum interfacial concentration.

Figure 44 shows the graphs for naphthalimides **169** - **171** with carbosilane chains.

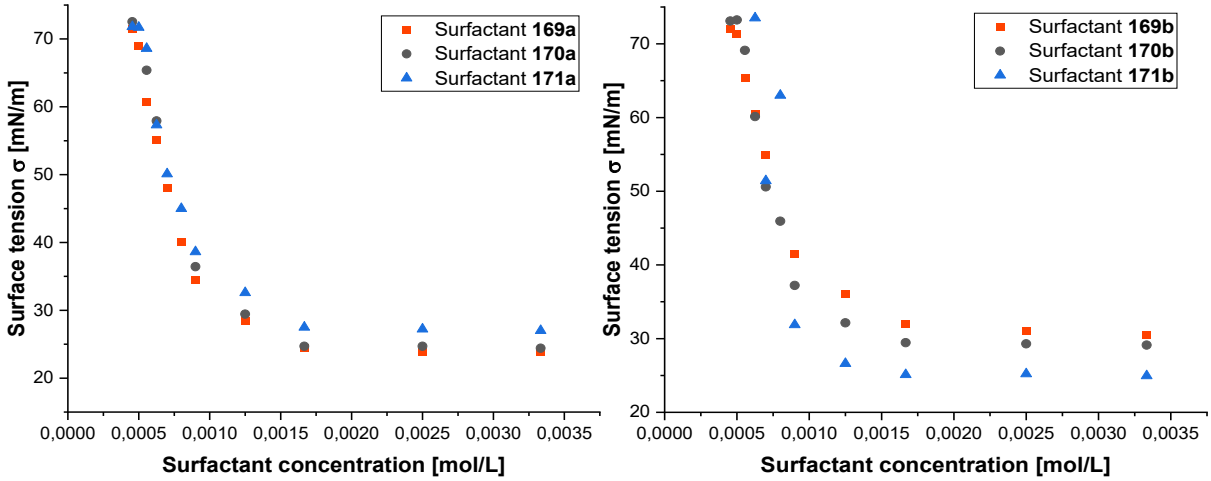
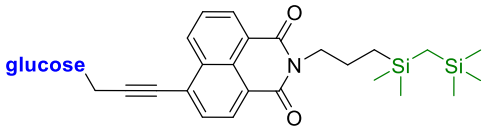
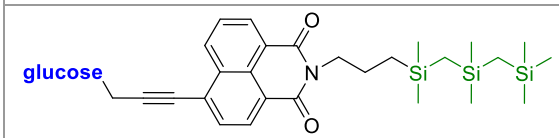


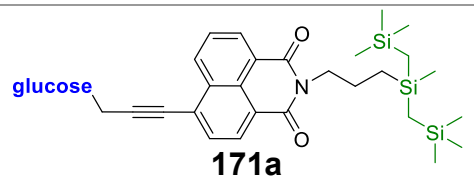
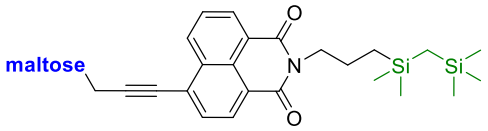
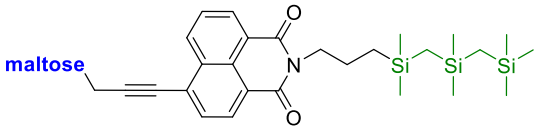
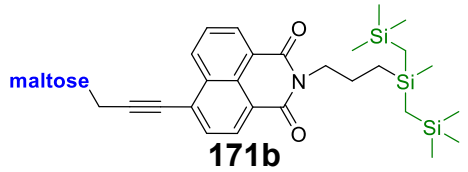
Figure 44: Measured surface tension in dependency of the concentration of surfactants with carbosilane chains. Left: surfactants with glucose as head group, right: surfactants with lactose as head group.

The measurement curves for surfactants **169** - **171** with glucose as head groups show a very similar pattern. The solubility of the surfactants is comparably good.

Values for the minimum surface tension between 23.80 and 27.00 mN/m were obtained, which are in the lower range compared to already known sugar surfactants. The values for the minimum surface tension of naphthalimides with lactose as the hydrophilic unit are also quite low, ranging between 24.95 and 30.45 mN/m. The measurement curves of these lactose compounds also initially show a similar decrease in surface tension, but the linear fit results in different values for the maximum interfacial concentration and the minimum head group requirement as shown in Table 20.

Table 20: Summary of the substance-specific values of surfactants with carbosilane chains obtained by plotting the surface tension against the logarithmic values of the concentrations, which were calculated using linear regression.

Surfactant	σ_{min} [mN/m]	*cmc* [mmol/L]	Γ_{∞} [µmol/m²]	A_{min} [nm²]
 **169a**	23.80	1.06	2.18	0.07
 **170a**	24.40	1.03	2.11	0.06

 **171a**	27.00	0.06	18.3	0.01
 **169b**	30.45	1.03	2.54	0.06
 **170b**	29.13	1.10	1.38	0.11
 **171b**	24.95	0.93	7.18	0.02

The *cmc* values are all in a similar range. The highest value for the interfacial concentration (18.3 and 7.18 µmol/m^2) and thus also the lowest values for the minimum head group requirement (0.01 and 0.02 nm^2) were obtained with the T-shaped carbosilanes **171a** and **171b**. In addition, the values of the *cmc* of these two compounds with 0.06 and 0.93 mmol/L is very low.

Overall, naphthalimides **171** with T-shaped chains differ the most from linear carbosilanes. However, all values for minimum surface tension and *cmc* are in a similar range.

In Figure 45 the surface tension measurements of the siloxane surfactants with naphthalimide chromophores **131** and **131** are plotted.

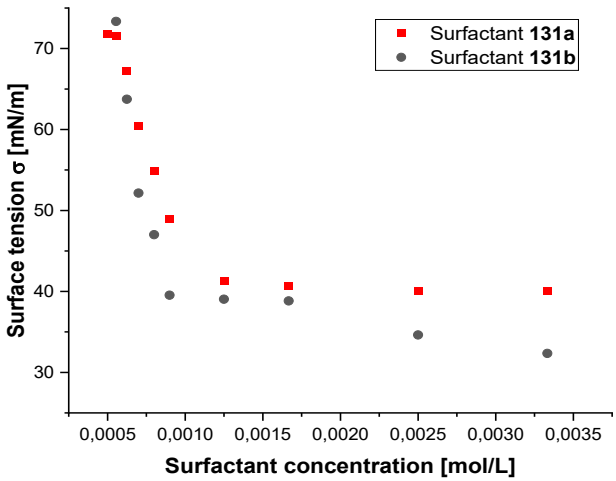
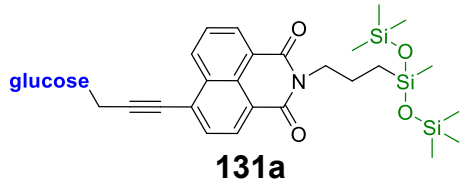
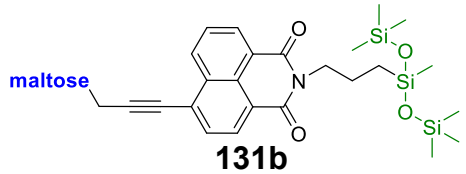


*Figure 45: Measured surface tension in dependency of the concentration of surfactants **131** with siloxane chains.*

The curve is similar, but the surface tension decreases somewhat more steeply and reaches a lower value for the minimum surface tension at 32.35 mN/m. However, the values are slightly higher than the measured values for T-shaped carbosilane surfactants **171**.

Table 21 summarizes the calculated values of the linear fit.

Table 21: Summary of the substance-specific values of surfactants with siloxane chains obtained by plotting the surface tension against the logarithmic values of the concentrations, which were calculated using linear regression

Surfactant	σ_{min} [mN/m]	*cmc* [mmol/L]	Γ_{∞} [µmol/m²]	A_{min} [nm²]
 **131a**	40.00	1.10	1.34	0.12
 **131b**	32.35	0.89	3.45	0.05

The *cmc* for siloxane compound **131b** with lactose as the head group is lower than with glucose as the hydrophilic unit. The minimum head group requirement is also lower, and thus the value of the maximum interfacial concentration is higher. The values of both siloxane surfactants **131** are in a similar range to those of the naphthalimide-based carbosilane surfactants **169** - **171**.

The minimum surface tension values of aqueous solutions with common sugar surfactants are in the range of 27 to 44 mN/m.[142] In addition, previous studies have shown that the surface tension of an aqueous solution can be reduced to values between 20 and 23 mN/m by siloxane surfactants and to values between 23 and 26 mN/m by surfactants with carbosilane chains.[174],[175],[176]

In conclusion, the measurements discussed within this chapter showed that all fluorescent surfactants synthesized in this thesis show surface tension-reducing effects in the range of known sugar surfactants. Some of them also fall within the range of known siloxane and carbosilane surfactants. However, the integration of chromophores has a significant impact on the physicochemical properties and thus, many the fluorescent surfactants deviate from the literature known values of sugar or silicon-based surfactants. The lowest values were achieved with the smaller head

group, glucose. A general trend for siloxane or carbosilane chains and the influence of the chromophore unit could not be determined. It was also found that the physicochemical properties are further influenced by the specific combination of hydrophobic and hydrophilic units. In order to make more accurate statements, additional measurements should be conducted and the previous measurements repeated. All measurements performed are susceptible to certain factors reducing the accuracy of obtained results. These factors include weighing and dilution errors and, especially, the adjustment of the frit line.

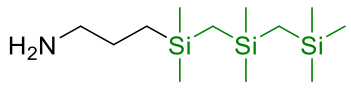
10 Summary and outlook

The aim of this work was the synthesis of fluorescent surfactants and the subsequent photo- and physicochemical investigation of these compounds. The surfactants were to be synthesized by integrating naphthalene frameworks into structures of sugar surfactants with siloxane and carbosilane chains.

Glucose and lactose were chosen as the hydrophilic sugar units, which were bound to the chromophore by *O*-glycosylation or by *Sonogashira* coupling.

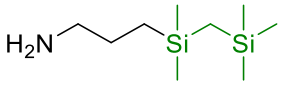
Two synthesis routes were developed to synthesize the carbosilane chains (Figure 46) and link them to the chromophore.

New aminocarbosilane chains



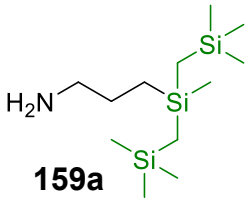
159b

- 20% yield over 3 steps



159c

- 35% yield over 3 steps



159a

- 39% yield over 3 steps

Figure 46: Successfully synthesized aminocarbosilane chains for the synthesis of fluorescent surfactants.

In order to link the carbosilane chains to the glycosylated naphthoic anhydride **138**, the carbosilane units first had to be connected to a primary amine. For this purpose, the amine function was first protected by various protective groups to subsequently obtain the final chains by hydrosilylation. After deprotection, the carbosilane chains could be successfully linked to the naphthoic anhydride.

The chains were linked to the *O*-glycosylated naphthoic acid **141** by amide coupling with allylamine and subsequent hydrosilylation with the corresponding synthesized carbosilane fragments.

As a final step, following difficulties encountered in the previous master's thesis[1], the deacetylation of the sugar unit was successfully carried out in this work. By using ion exchangers, the final surfactants could be obtained in good yields.

Twelve different **carbosilane** surfactants were synthesized (Figure 47).

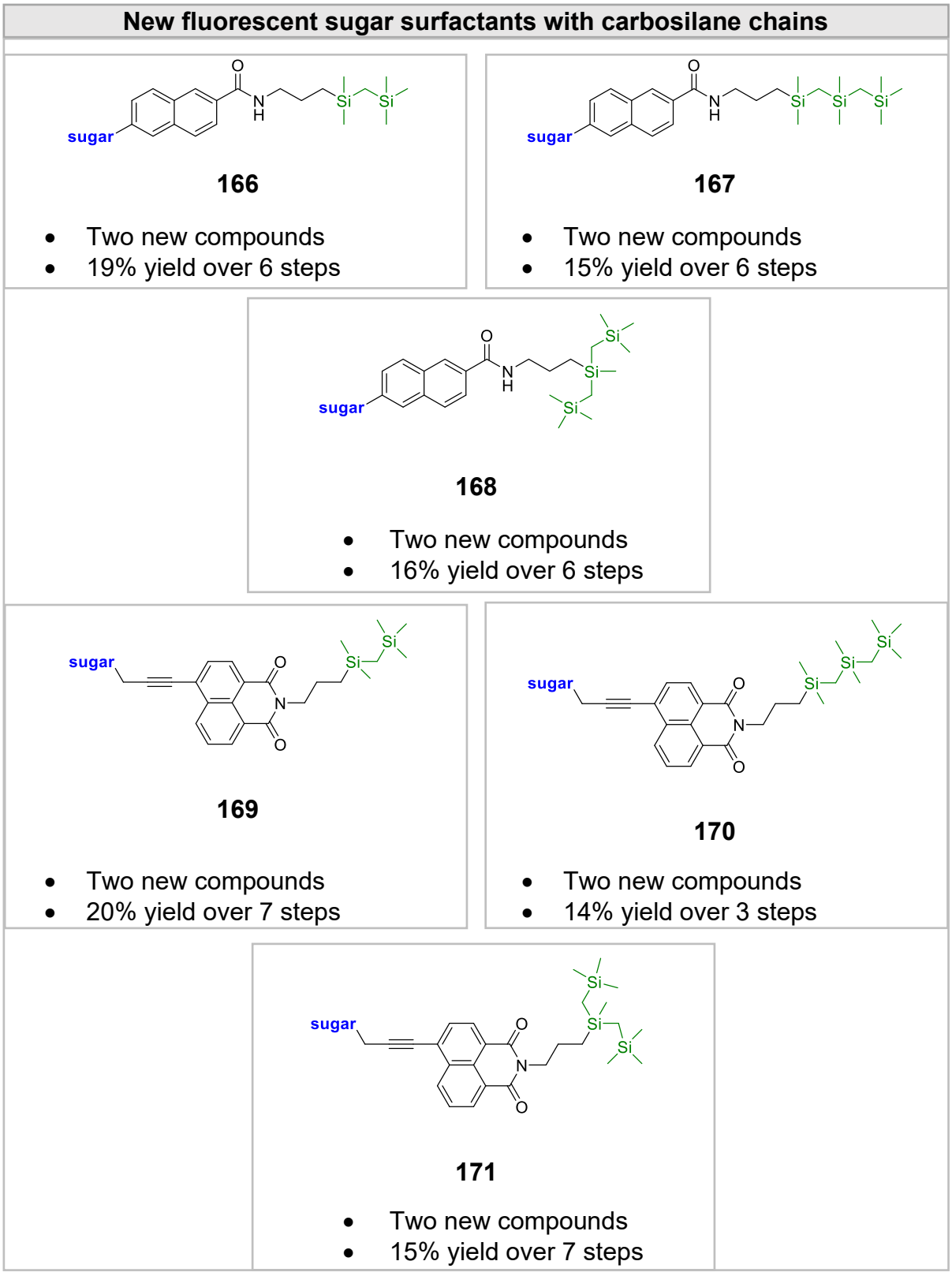


Figure 47: Successfully synthesized fluorescent surfactants with siloxane chains. All compounds were obtained with glucose and lactose as hydrophilic head groups.

The carbosilane surfactants were obtained with glucose and lactose as head groups in sufficient yields over 6 – 7 steps for subsequent investigations.

Their **physicochemical properties** were investigated by measuring the surface tension of dilution series. The data summarized in Table 22 were collected by linear fit.

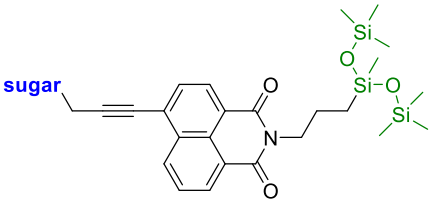
Table 22: Summarized data of the surface tension measurements and subsequent linear fit of the carbosilane surfactants.

Surfactant	σ_{min} [mN/m]	*cmc* [mmol/L]	Γ_{∞} [µmol/m^2]	A_{min} [nm^2]
Amides	25.3 – 43.4	0.86 – 1.39	0.38 – 3.51	0.05 – 0.43
Imides	23.8 – 30.4	0.06 – 1.10	1.38 – 18.3	0.01 – 0.11

Overall, the values were in the range of known sugar and carbosilane surfactants.

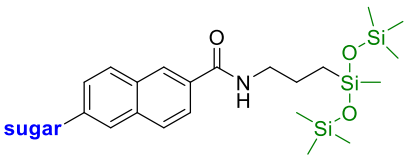
Four new fluorescent sugar surfactants with **siloxane** chains were obtained (Figure 48).

New fluorescent sugar surfactants with siloxane chains



131

- 2 new compounds
- 24% to 30% yield over 4 steps



132

- 2 new compounds
- 20% to 23% yield over 7 steps

Figure 48: Successfully synthesized fluorescent surfactants with siloxane chains. All compounds were obtained with glucose and lactose as hydrophilic head groups.

The compounds were obtained in sufficient yields over 4 – 7 steps and could be used for subsequent investigations.

Their **physicochemical properties** were also investigated by measuring the surface tension of dilution series and subsequent linear fit. The data are summarized in Table 23.

Table 23: Summarized data of the surface tension measurements and subsequent linear fit of the siloxane surfactants.

Surfactant	σ_{min} [mN/m]	*cmc* [mmol/L]	Γ_{∞} [µmol/m^2]	A_{min} [nm^2]
Amides	22.5 – 34.4	0.80 – 1.10	1.91 – 8.46	0.02 – 0.08
Imides	32.4 – 40.0	0.89 – 1.10	1.34 – 3.45	0.05 – 0.12

The values were sometimes lower but also higher than those for fluorescent surfactants with carbosilane chains. But overall, the results of the measurements were within the range of known sugar and siloxane surfactants without chromophores.

To investigate the photochemical properties of the surfactants, **absorption-** and **fluorescence spectra** were detected. The detected maxima are summarized in Table 24.

Table 24: Summarized emission and absorption maxima of the carbosilane and siloxane surfactants.

Surfactant	λ_{abs}	λ_{em}
Amides	236 – 237 (MeCN) 232 – 239 (H_2O)	348 – 358 (MeCN) 376 – 410 (H_2O)
Imides	239 (MeCN) 238 – 240 (H_2O)	402 – 406 (MeCN) 432 – 493 (H_2O)

All surfactants showed strong absorption. The intensity and extinction coefficients were lower for almost all aqueous solutions than for compounds in MeCN. In the emission spectra, large *Stoke* shifts to longer wavelengths are shown. The sugar, carbosilane and siloxane units have no significant impact on the absorption and fluorescence behavior of the surfactants. The two different naphthalene-based structures and the selected solvent had the greatest influence on the photochemical behavior.

Some of the surfactants were difficult to dissolve in water. To improve solubility, disaccharides should primarily be used as head groups, or auxochrome and anti-auxochrome groups should be bound to the chromophore. These could not only improve solubility but also enhance the ability to fluoresce. This would also allow for expansion of the library of fluorescent surfactants and the database of physical and photochemical data.

The enhanced fluorescence properties could be used to study the aggregation behavior of surfactants by monitoring using fluorescence microscopy. Furthermore, the surfactants could be investigated for applications such as imaging or fluorescence sensing in different environments.

In summary, **16 new silicon-based sugar surfactants** were synthesized and two fluorescent chromophores were successfully integrated. Initial physical- and photochemical investigations were conducted and promising results were obtained.

11 Experimental part

11.1 General methods

General conditions

If not stated different, reactions were performed under an argon atmosphere with *Linde*® Argon 4.6 (99.996%, <1 ppm H_2O, <1 ppm O_2) using the *Schlenk* technique. The glass equipment was heated under vacuum with a propane-butane blowtorch gun and flushed with argon before usage. Solids were transferred under an argon counter current *via* a funnel.

Liquids were added *via* a septum using syringes, which were rendered inert by flushing with argon three times. Solvents were removed under reduced pressure using a *Büchi* rotary evaporator at 40 °C water bath temperature. Residual solvents were dried under vacuum pressure with an oil pump.

Reagents and solvents

Commercially available reagents were obtained from common commercial sources, e.g. *Sigma Aldrich*, *Alfa Aesar*, *Acros Organics*, *TCI*, *BLDpharm* and *Carbolution*, and were used without further purification. In case of air- and moisture-sensitive reactions, solvents were distilled before usage. Dichloromethane was freshly distilled over calcium hydride under an argon atmosphere. Tetrahydrofuran and diethyl ether were distilled over sodium and benzophenone under an argon atmosphere. Other absolute solvents like DMF, toluene and MeOH were directly used from commercially available sources.

Chromatography

For TLC analysis, silica gel 60 F254 plates with a thickness of 0.25 mm by *Merck* were used. The corresponding analytes were detected under UV-light or by potassium permanganate stain (3.00 g $KMnO_4$, 20.0 g K_2CO_3, 5.00 mL 5% NaOH-solution in 300 mL H_2O). Purification by column chromatography was carried out with silica gel 60 Å (35-70 µm) by the company *Acros*. The solvents used and the corresponding mixing ratios of the mobile phase are given in fractions of volume for each experiment.

NMR-spectroscopy

NMR-spectra were recorded on a *Bruker* Avance II 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz), Avance III 499 (^{1}H: 500 MHz; ^{13}C: 126 MHz), Avance III 500 (1H: 500 MHz, ^{13}C: 126 MHz) or Avance II+ 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{31}P: 202 MHz). All spectra were measured at room temperature in common deuterated solvents, e.g. $CDCl_3$, DMSO-d_6, MeOD-d_4 and D_2O, and referenced to the internal standard TMS (0 ppm) in case of proton spectra or to the solvent signal for carbon spectra. The chemical shifts are reported in parts per million (ppm) and the coupling constants *J* are given in Hertz (Hz). The multiplicities are given by s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet.

Gas chromatography with mass detector (GC-MS)

GC-MS measurements were conducted on an *Agilent HP6890* system combined with a mass detector (MSD) *5937N*. Hydrogen was used as the carrier gas with a flow rate of 1.7 mL/min and a pressure of 0.3 bar. As the capillary tube, an *Agilent 19091S-4335 HP-5 MS* (30 m · 0.25 mm · 0.25 µm) was used. The intensities were reported relative to the peak with the highest intensity (100%). For measurements the temperature program 50300M (50 °C for 2 min, 25 °C /min to 300 °C, 320 °C for 2 min) was used.

High resolution mass spectroscopy (HR-MS)

High resolution mass spectra were recorded on a *THERMO Scientific LTQ Orbitrap XL* using the electrospray ionisation method (ESI). For the spray voltage a value of 3.4 kV was applied. The capillary voltage and the tube lens voltage had a value of 3.0 V.

Fourier-transformed infrared spectroscopy (FT-IR)

Infrared (IR) spectra were measured on a *PerkinElmer* Spectrum Two FT-IR spectrometer with the aid of the attenuated total reflectance (ATR) technique. The wave numbers v are reported in cm^{-1}. The intensities are defined as w = weak, m = medium, s = strong and br = broad.

Melting point

Melting points of obtained solids were measured in an open glass capillary using a *Büchi B545* with a heat rate of 2 °C/min. The measured melting points are uncorrected.

UV-vis spectroscopy

UV/vis analysis was performed using a Jasco V-730 spectrometer with an ETCS-761 Peltier thermostatic single position cell holder. All measurements were performed in 0.025 mM solutions at 20 °C using HPLC or LCMS grade solvents. Suprasil 110-QS cuvettes by the company *Hellma* were used.

Irradiation of the samples

UV-irradiation was done using a Konrad Benda UV-C lamp with 15 W and a wavelength of 254 nm. For irradiation with visible light a 100 W LED construction spotlight was used.

Surface tension measurements

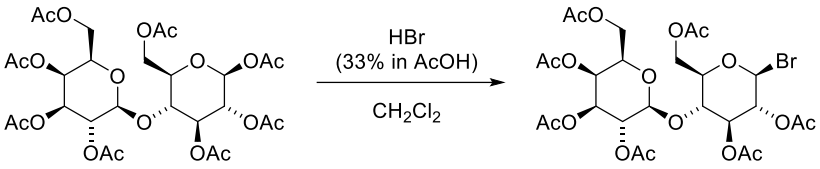
Surface tension measurements were performed at 20 – 23 °C using a tensiometer of the *Krüss* company, model K-11. The measurements were carried out in ultra-pure deionized water. Average values were determined from 300 measured values (measured every 3 seconds).

11.2 Synthetic procedures

Part 1: Novel photoswitchable surfactants

11.2.1 Synthesis of different sugar building blocks

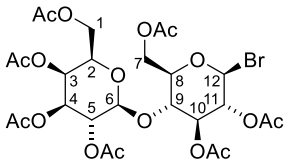
11.2.1.1 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-bromotetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (44b)



41a **44b**

Following a procedure of *Gulati et al.*[177] 5.00 g (7.37 mmol, 1.00 eq.) of sugar **41a** were dissolved in 6 mL CH_2Cl_2. At 0 °C 1.50 mL (8.34 mmol, 1.13 eq.) HBr (33% in AcOH) was added dropwise. The reaction mixture was allowed to warm to rt and stirred for 6 h. The mixture was quenched by pouring the solution into ice water. The aq. phase was extracted with CH_2Cl_2. The layers were separated and the org. layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. 5.14 g (7.35 mmol, >99%, Lit.[177]: >99%) of the desired product **44b** was obtained as a colorless foam.

The crude product was used without further purification due to the sensitivity of the product.



M($C_{26}H_{35}BrO_{17}$) 699.45 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:2) = 0.55.

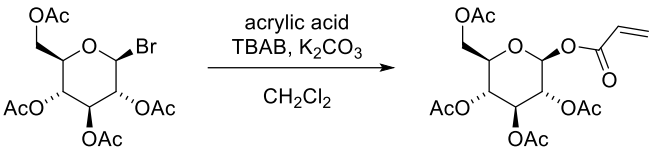
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 6.52 (d, $^3J_{HH}$ = 4.0 Hz, 1H, H-12), 5.63 (dd, $^3J_{HH}$ = 9.9, 8.9 Hz, 1H, H-10), 5.44 (d, $^3J_{HH}$ = 3.9 Hz, 1H, H-6), 5.40 (dd, $^3J_{HH}$ = 10.6, 9.5 Hz, 1H, H-4), 5.10 (t, $^3J_{HH}$ = 9.9 Hz, 1H, H-3), 4.89 (dd, $^3J_{HH}$ = 10.6, 4.0 Hz, 1H, H-5), 4.74 (dd, $^3J_{HH}$ = 9.8, 4.0 Hz, 1H, H-11), 4.58 – 4.52 (m, 1H, H-1), 4.38 – 4.24 (m, 3H, H-1‘, H-7, H-9), 4.12 – 4.06 (m, 2H, H-8, H-7), 3.97 (dt, $^3J_{HH}$ = 10.2, 3.1 Hz, 1H, H-2), 2.17 (s, 3H,

OAc), 2.12 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.03 (s, 3H, OAc).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.7 (OAc), 170.5 (OAc), 170.3 (OAc), 169.9 (2x OAc), 169.5 (OAc), 169.4 (OAc), 95.7 (C-6), 86.0 (C-12), 72.5 (C-9), 72.3 (C-10), 71.5 (C-8), 71.0 (C-11), 70.0 (C-5), 69.6 (C-4), 68.6 (C-2), 67.9 (C-3), 61.8 (C-1), 61.3 (C-7), 20.8 (OAc), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (3x OAc).

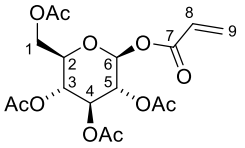
FT-IR ATR, v [cm^{-1}] = 3660 (w), 3475 (w), 2971 (w), 2902 (w), 2123 (w), 1931 (w), 1745 (s), 1650 (w), 1432 (w), 1369 (m), 1325 (w), 1218 (s), 1159 (w), 1109 (m), 1073 (m), 1036 (s), 956 (w), 939 (w), 899 (w), 783 (w), 747 (w), 646 (w), 635 (w), 602 (w), 560 (w), 518 (w).

11.2.1.2 Synthesis of (*2R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(acryloyloxy) tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (29a)



44a **29a**

10.0 g (24.3 mmol, 1.00 eq.) of sugar **44a** were dissolved in 95 mL CH_2Cl_2. 0.78 g (2.43 mmol, 0.10 eq.) of TBAB and 6.72 g (48.6 mmol, 2.00 eq.) of K_2CO_3 were added. 3.40 mL (48.6 mmol, 2.00 eq.) of acrylic acid was added dropwise and the reaction mixture was stirred at rt for 18 h. Remaining K_2CO_3 was filtered off, 50 mL H_2O was added and the aq. phase was extracted with 100 mL CH_2Cl_2. The combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) to afford 5.41g (13.5 mmol, 55%) of the desired product **29a** as a colorless foam.



M($C_{17}H_{22}O_{11}$) 402.35 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:1) = 0.50.

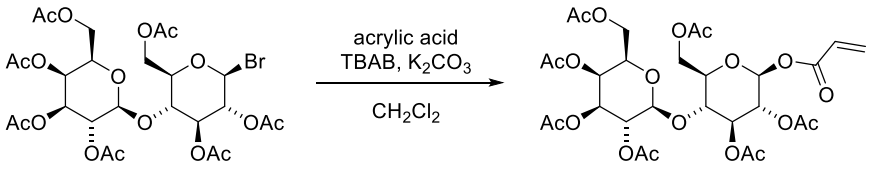
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 6.50 (dd, $^{2,3}J_{HH}$ = 17.3, 1.2 Hz, 1H, H-9), 6.12 (dd, $^{3}J_{HH}$ = 17.3, 10.5 Hz, 1H, H-8), 5.97 (dd, $^{2,3}J_{HH}$ =

10.5, 1.2 Hz, 1H, H-9), 5.79 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, H-6), 5.29 (t, $^{3}J_{HH}$ = 9.4 Hz, 1H, H-4), 5.23 – 5.12 (m, 2H, H-3, H-5), 4.31 (dd, $^{2,3}J_{HH}$ = 12.5, 4.5 Hz, 1H, H-1), 4.12 (dd, $^{2,3}J_{HH}$ = 12.5, 2.2 Hz, 1H, H-1‘), 3.88 (m, 1H, H-2), 2.09 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.02 (s, 3H, OAc).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.6 (OAc), 170.1 (OAc), 169.4 (OAc), 169.2 (OAc), 163.8 (C-7), 133.5 (C-9), 127.0 (C-8), 91.9 (C-6), 72.7 (C-2), 72.6 (C-4), 70.1 (C-3), 67.7 (C-5), 61.4 (C-1), 20.7 (OAc), 20.5 (OAc), 20.5 (OAc), 20.5 (OAc).

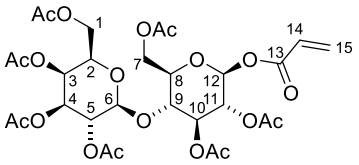
FT-IR ATR, v [cm^{-1}] = 3639 (w), 3484 (w), 2964 (w), 2259 (w), 2106 (w), 1983 (w), 1740 (s), 1636 (w), 1433 (w), 1411 (w), 1367 (m), 1295 (w), 1211 (s), 1172 (m), 1112 (m), 1069 (s), 1034 (s), 983 (m), 908 (m), 808 (w), 733 (w), 705 (w), 647 (w), 600 (m), 562 (w), 536 (w).

11.2.1.3 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-(acryloyloxy)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (29b)



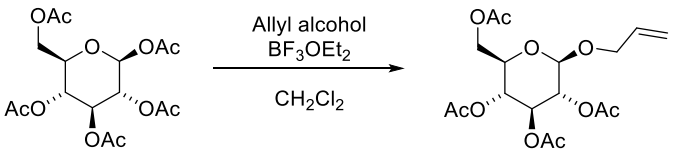
44b **29b**

5.10 g (7.29 mmol, 1.00 eq.) of sugar **44b** were dissolved in 21 mL CH_2Cl_2. 0.24 g (0.73 mmol, 0.10 eq.) of TBAB and 2.02 g (14.6 mmol, 2.00 eq.) of K_2CO_3 were added. 1.00 mL (14.6 mmol, 2.00 eq.) of acrylic acid was added dropwise and the reaction mixture was stirred at rt for 19 h. Remaining K_2CO_3 was filtered off, 10 mL H_2O was added to the solution and the aq. phase was extracted with 20 mL CH_2Cl_2. The combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) to afford 3.38 g (4.90 mmol, 67%) of the desired product **29b** as a colorless foam.



M($C_{29}H_{38}O_{19}$)	690.60 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:1) = 0.38.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 6.48 (dd, $^{2,3}J_{HH}$ = 17.3, 1.0 Hz, 1H, H-15), 6.11 (dd, $^3J_{HH}$ = 17.3, 10.5 Hz, 1H, H-14), 5.96 (dd, $^{2,3}J_{HH}$ = 11.6, 1.0 Hz, 1H, H-15), 5.82 (d, $^3J_{HH}$ = 8.1 Hz, 1H, H-12), 5.46 – 5.27 (m, 3H, H-6, H-3, H-10), 5.11 – 5.01 (m, 2H, H-11, H-5), 4.87 (m, 1H, H-4), 4.46 (dd, $^{2,3}J_{HH}$ = 12.3, 2.6 Hz, 1H, H-7), 4.28 – 4.20 (m, 2H, H-7‘, H-1), 4.09 – 4.01 (m, 2H, H-1‘, H-9), 3.95 (m, 1H, H-8), 3.90 – 3.82 (m, 1H, H-2), 2.14 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.01 (s, 3H, OAc), 2.00 (s, 3H, OAc).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 170.5 (OAc), 170.5 (OAc), 170.4 (OAc), 170.0 (OAc), 169.9 (OAc), 169.6 (OAc), 169.4 (OAc), 163.7 (C-13), 133.4 (C-15), 127.1 (C-14), 95.7 (C-6), 91.5 (C-12), 75.1 (C-3), 73.0 (C-2), 72.4 (C-9), 70.9 (C-5), 70.0 (C-4), 69.3 (C-10), 68.6 (C-8), 67.9 (C-11), 62.5 (C-7), 61.4 (C-1), 20.8 (OAc), 20.8 (OAc), 20.7 (OAc), 20.6 (OAc), 20.5 (OAc).
FT-IR	ATR, v [cm^{-1}] = 3307 (m), 2928 (w), 2123 (w), 1715 (m), 1664 (w), 1411 (w), 1368 (m), 1334 (w), 1252 (m), 1145 (m), 1104 (m), 1072 (s), 1017 (s), 919 (m), 834 (m), 783 (m), 756 (m), 677 (m), 603 (m), 552 (s), 515 (m).
HR-MS (ESI)	Calcd. $[M]^{\cdot+}$: 713.1899498, found: 713.19046.

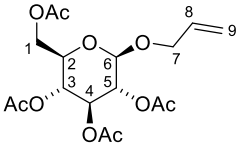
11.2.1.4 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(allyloxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (82)



41a **82**

According to a literature procedure of *Bordes et al*.[137] 2.00 g (5.12 mmol, 1.00 eq.) of sugar **41a** were dissolved in CH_2Cl_2 and 0.53 mL (7.69 mmol, 1.50 eq.) of allyl alcohol

was added. At 0 °C 0.98 mL (7.69 mmol, 1.50 eq.) of BF_3OEt_2 were added dropwise. The reaction mixture was allowed to warm to rt and stirred for 15 h. The reaction mixture was quenched with 5 mL H_2O and the aq. phase was extracted with 10 mL CH_2Cl_2. The combined org. layers were dried over $MgSO_4$. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) to afford 1.79 g (4.61 mmol, 90%, Lit.[137]: 99%) of the desired product **82** as colorless solid.



M($C_{17}H_{24}O_{10}$) 388.37 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:1) = 0.53.

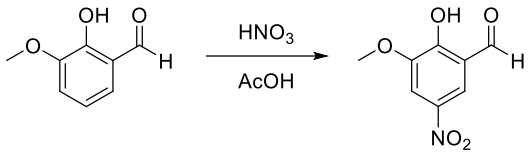
^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 5.92 – 5.82 (m, 1H, H-8), 5.33 – 5.20 (m, 3H, H-7, H-3), 5.15 – 5.01 (m, 2H, H-4, H5), 4.58 (d, $^3J_{HH}$ = 7.9 Hz, 1H, H-6), 4.39 – 4.34 (m, 1H, H-9), 4.28 (dd, $^{2,3}J_{HH}$ = 12.2, 4.7 Hz, 1H, H-1), 4.19 – 4.09 (m, 2H, H-1‘, H-9‘), 3.73 – 3.69 (m, 1H, H-2), 2.11 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.03 (s, 3H, OAc).

^{13}C-NMR (101 MHz, $CDCl_3$) δ [ppm] = 170.7 (OAc), 170.3 (OAc), 169.4 (OAc), 169.3 (OAc), 133.3 (C-8), 117.7 (C-7), 99.5 (C-6), 72.8 (C-3), 71.7 (C-2), 71.2 (C-5), 70.0 (C-9), 68.4 (C-4), 61.9 (C-1), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc).

FT-IR ATR, v [cm^{-1}] = 2983 (w), 2971 (w), 2941 (w), 2879 (w), 2603 (w), 2353 (w), 1690 (w), 1597 (m), 1562 (w), 1504 (w), 1477 (m), 1437 (w), 1419 (w), 1387 (w), 1367 (w), 1338 (w), 1314 (w), 1252 (s), 1221 (s), 1211 (s), 1178 (m), 1154 (s), 1132 (m), 1102 (s), 1084 (s), 991 (m), 972 (m), 954 (w), 936 (w), 928 (m), 911 (m), 869 (w), 845 (w), 824 (w), 816 (w), 785 (w), 774 (w), 761 (w), 754 (m), 733 (w), 680 (w), 667 (w), 646 (w), 632 (w), 620 (w), 602 (w), 589 (w), 545 (w), 531 (w), 509 (w).

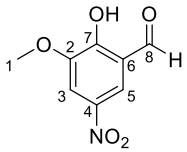
11.2.2 Synthesis of the eastern building block

11.2.2.1 Synthesis of 2-hydroxy-3-methoxy-5-nitrobenzaldehyde (66)



65 **66**

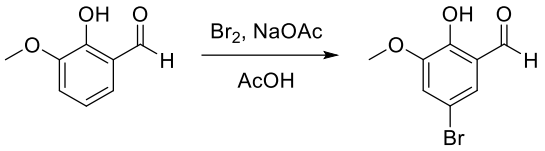
Following a procedure of *Zhang et al*.[131] 1.00 g (6.60 mmol, 1.00 eq.) of *o*-vanillin (**65**) was dissolved in 4 mL glacial acetic acid and 0.46 mL (7.20 mmol, 1.10 eq.) of conc. HNO_3 were added dropwise. The reaction mixture was stirred for 2 h at rt. The suspension was poured onto ice water. The solid was filtered off and washed with cold water. 0.97 g (4.90 mmol, 75%, Lit.[131]: 89%) of the desired product **66** was obtained as a pale brown solid.



M($C_8H_7NO_5$)	197.15 g/mol.
R_f	(SiO_2, CH_2Cl_2/MeOH 10:1) = 0.58.
m.p.	136 °C, Lit.[131]: 140 °C.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 11.72 (s, 1, OH), 10.0 (s, 1H, H-8), 8.23 (1H, d, $^4J_{HH}$ = 2.5 Hz, H-5), 7.94 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-3), 4.03 (s, 3H, H-1).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 195.6 (C-8), 157.0 (C-6), 149.2 (C-2), 140.38 (C-4), 120.6 (C-5), 119.0 (C-7), 111.5 (C-3), 57.0 (C-1).
FT-IR	ATR, v [cm^{-1}] = 3091 (w), 2879 (w), 1666 (m), 1621 (w), 1582 (w), 1520 (m), 1479 (m), 1446 (m), 1339 (m), 1267 (s), 1182 (m), 1199 (m), 1091 (s), 953 (s), 885 (s), 721 (s), 580 (m), 529 (m).

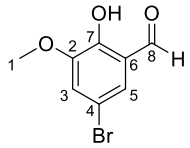
The analytical data are in accordance with the literature.[131]

11.2.2.2 Synthesis of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (68)



65 **68**

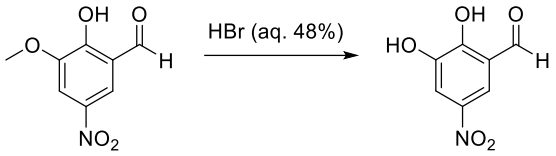
Following a procedure of *Bray et al.*[130] 2.00 g (1.30 mmol, 1.00 eq.) of *o*-vanillin (**65**) were dissolved in glacial acetic acid and 1.68 g (1.45 mmol, 1.10 eq.) of NaOAc was added. 0.75 mL (1.45 mmol, 1.10 eq.) of bromine were added dropwise and the reaction mixture was stirred for 30 min at rt. The reaction mixture was quenched with 5 mL H_2O and extracted with 10 mL CH_2Cl_2. The combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 5:1) to afford 2.10 g (9.09 mmol, 70%, Lit.[130]: 90%) of the desired product **68** as a beige solid.



M($C_8H_4BrO_3$)	231.05 g/mol.
R_f	(SiO_2, cHex/EtOAc 2:1) = 0.59.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 11.01 (s, 1H, H-8), 9.86 (s, 1H, OH), 7.32 (d, $^4J_{HH}$ = 2.1 Hz, 1H, H-5), 7.18 (d, $^4J_{HH}$ = 2.0 Hz, 1H, H-3), 3.92 (s, 3H, H-1).
^{13}C-NMR	(101 MHz, $CDCl_3$) δ [ppm] = 195.4 (C-8), 150.9 (C-2), 149.3 (C-7), 126.1 (C-5), 121.3 (C-6), 120.7 (C-3), 111.0 (C-4), 56.5 (C-1).
FT-IR	ATR, v [cm^{-1}] = 3017 (w), 2984 (w), 2943 (w), 2881 (w), 2036 (w), 1712 (w), 1651 (m), 1580 (w), 1460 (m), 1435 (m), 1426 (m), 1388 (m), 1337 (w), 1309 (m), 1274 (m), 1253 (s), 1202 (s), 1112 (w), 1082 (w), 954 (s), 866 (m), 860 (m), 849 (s), 760 (m), 745 (m), 704 (s), 577 (m), 552 (m).
HR-MS (EI)	Calcd. $[C_8H_7{}^{79}BrO_3]^{\cdot+}$: 229.9573, found: 229.9574. Calcd. $[C_8H_7{}^{81}BrO_3]^{\cdot+}$: 231. 9552, found: 231.9552.

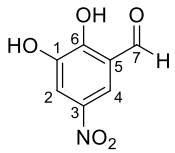
The analytical data are in accordance with the literature.[130]

11.2.2.3 Synthesis of 2,3-dihydroxy-5-nitrobenzaldehyde (67)



66 **67**

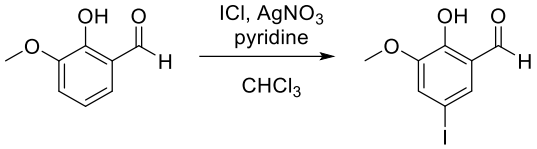
Following a procedure of *Hu et al.*[132] 1.50 g (7.61 mmol, 1.00 eq.) of benzaldehyde **65** was added to 2.16 mL (19.0 mmol, 2.50 eq.) of HBr (48%) and the reaction mixture was heated to 140 °C. After 2.5 h the mixture was cooled to 0 °C and 5 mL H_2O was added. The precipitation was filtered off and washed with H_2O. The crude product was recrystallized in EtOAc to afford 1.30 g (7.10 mmol, 93%, Lit.[132]: 95%) of the desired product **67**.



M($C_7H_5NO_5$)	183.12 g/mol.
R_f	(SiO_2, CH_2Cl_2/MeOH 5:1 = 0.33)
^{1}H-NMR	(500 MHz, DMSO-d_6) δ [ppm] = 11.13 (s, 2H, 2x OH), 10.31 (s, 1H, H-7), 8.00 (s, 1H, H-4), 7.79 (s, 1H, H-2).
^{13}C-NMR	(126 MHz, DMSO-d_6), δ [ppm] = 190.2 (C-7), 156.4 (C-3), 147.6 (C-1), 139.6 (C-6), 122.2 (C-5), 115.0 (C-4), 113.6 (C-2).
FT-IR	ATR, v [cm^{-1}] = 3268 (w), 3088 (w), 1664 (m), 1623 (w), 1519 (s), 1460 (m), 1393 (w), 1341 (s), 1302 (s), 1268 (s), 1200 (m), 1184 (s), 1094 (m), 1046 (m), 951 (s), 903 (m), 885 (w), 876 (w), 824 (w), 756 (m), 743 (s), 721 (s), 679 (m), 630 (m), 597 (m), 564 (m), 543 (m).
HR-MS (EI)	Calcd. $[M]^{\cdot+}$: 183.01622, found: 183.0158.

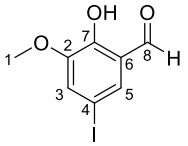
The analytical data are in accordance with the literature.[132]

11.2.2.4 Synthesis of 2,3-dihydroxy-5-iodobenzaldehyde (79)



65 **79**

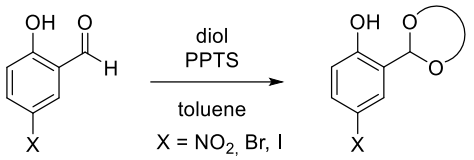
Following a procedure of *Rao et al.*[136] 7.02 g (41.4 mmol, 1.05 eq.) of $AgNO_3$ were suspended in 50 mL $CHCl_3$ and 19.0 mL (245 mmol, 6.00 eq.) of pyridine were added. A solution of 6.75 g (41.4 mmol, 1.05 eq.) of ICl in 12 mL $CHCl_3$ was added dropwise and the reaction mixture was stirred at rt for 2 h. 6.00 g (39.3 mmol, 1.00 eq.) of *o*-vanillin (**65**) in 12 mL $CHCl_3$ was added slowly and the reaction mixture was stirred at rt for further 17 h. After filtration the solvent was removed under reduced pressure. The residue was taken up in EtOAc and washed with 10 mL sat. aq. NH_4Cl. The layers were separated and the aq. phase was extracted with 20 mL EtOAc. The combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 3:1) to afford 9.07 g (32.6 mmol, 82%, Lit.[136]: 96%) of the desired product **79** as a beige solid.



$M(C_8H_7IO_3)$	278.05 g/mol.
R_f	(SiO_2, cHex/EtOAc 3:1) = 0.44.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 11.02 (s, 1H, OH), 9.84 (s, 1H, H-8), 7.49 (d, $^4J_{HH}$ = 1.9 Hz, 1H, H-5), 7.31 (d, $^4J_{HH}$ = 1.7 Hz, 1H, H-3), 3.91 (s, 3H, H-1).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 195.2 (C-8), 151.5 (C-6), 149.2 (C-2), 132.6 (C-5), 126.1 (C-3), 122.2 (C-7), 79.8 (C-4), 56.5 (C-1).
FT-IR	ATR, v [cm^{-1}] = 3087 (w), 3011 (w), 2978 (w), 2940 (w), 2882 (w), 2034 (w), 1708 (w), 1678 (w), 1652 (s), 1575 (w), 1469 (m), 1421 (w), 1387 (w), 1315 (w), 1275 (s), 1260 (m), 1203 (w), 1083 (w), 959 (w), 847 (w), 753 (w), 718 (w), 696 (w), 573 (w), 551 (w).
GC-MS	m/z (%) = 277 (100), 276 (6), 231 (20), 206 (7), 127 (5), 108 (7), 51 (5).

The analytical data are in accordance with the literature.[136]

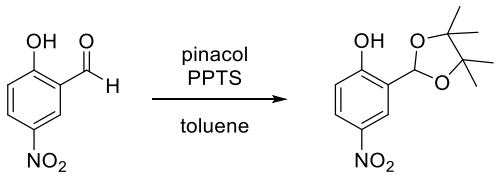
11.2.2.5 Acetal protection of benzaldehydes: General protocol (GP12)



70 **71**

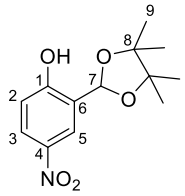
Benzaldehyde **70** (1.00 eq.) was dissolved in toluene. The diol (10.0 eq.) and PPTS (15 mol%) were added and the reaction mixture was heated to 110 °C in a *Dean-Stark* apparatus. The mixture was cooled to rt and sat. aq. $NaHCO_3$ was added and the layers were separated. The aq. phase was extracted with EtOAc, the combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure.

11.2.2.5.1 Synthesis of 4-nitro-2-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenol (71b)



70a **71b**

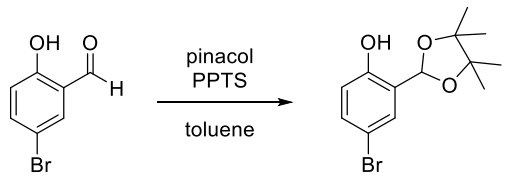
According to **GP12** 0.25 g (1.50 mmol, 1.00 eq.) of benzaldehyde **70a** were reacted with 1.77 g (15.0 mmol, 10.0 eq.) of pinacol and 0.05 g (0.23 mmol, 15 mol%) of PPTS in 2.5 mL toluene for 19 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 3:1) to afford 0.34 g (1.28 mmol, 85%) of the desired product **71b** as a light yellow solid.



M($C_{13}H_{17}NO_5$)	267.28 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:1) = 0.60.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 8.96 (s, 1H, OH), 8.22 (dd, $^{4,5}J_{HH}$ = 2.8, 0.7 Hz, 1H, H-5), 8.11 (dd, $^{3,4}J_{HH}$ = 9.0, 2.9 Hz, 1H, H-3), 6.93 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H, H-2), 6.15 (s, 1H, H-7), 1.35 (s, 6H, H-9), 1.25 (s, 6H, H-9‘).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 160.1 (C-1), 140.9 (C-4), 125.8 (C-3), 124.6 (C-6), 123.9 (C-5), 117.5 (C-2), 98.6 (C-7), 84.1 (C-8), 23.5 (C-9), 22.0 (C-9‘).

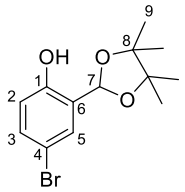
FT-IR ATR, v [cm^{-1}] = 3278 (w), 2891 (w), 1606 (w), 1592 (w), 1488 (m), 1423 (m), 1390 (m), 1329 (m), 1277 (s), 1217 (m), 1142 (m), 1124 (s), 1081 (s), 1062 (s), 968 (s), 943 (s), 906 (m), 881 (m), 864 (m), 842 (m), 830 (s), 814 (m), 753 (m), 723 (m), 699 (m), 675 (m), 612 (s), 589 (m), 564 (m), 518 (m).

11.2.2.5.2 Synthesis of 2-(2-hydroxy-5-bromophenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (71d)



70b **71d**

According to **GP12** 3.00 g (14.9 mmol, 1.00 eq.) of benzaldehyde **70b** were reacted with 17.6 g (149 mmol, 10.0 eq.) of pinacol and 0.50 g (2.24 mmol, 15 mol%) of PPTS in 30 mL toluene for 19 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 3:1) to afford 3.21 g (10.7 mmol, 72%) of the desired product **71d** as a light yellow solid.



M($C_{13}H_{17}BrO_3$) 301.18 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 4:1) = 0.70.

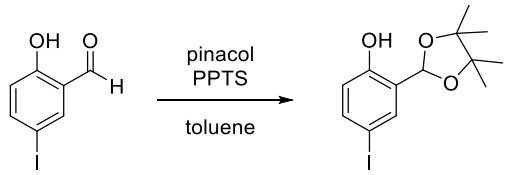
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.10 (s, 1H, OH), 7.36 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-5), 7.29 (dd, $^{3,4}J_{HH}$ = 11.2, 6.2 Hz, 1H, H-3), 6.75 (d, $^3J_{HH}$ = 8.7 Hz, 1H, H-2), 6.08 (s, 1H, H-7), 1.32(s, 6H, H-9), 1.24 (s, 6H, H-9‘).

^{13}C-NMR (126 MHz, $CDCl_3$), δ [ppm] = 153.6 (C-1), 132.5 (C-4), 129.8 (C-3), 126.0 (C-6), 118.8 (C-5), 111.8 (C-2), 98.9 (C-7), 83.6 (C-8), 23.6 (C-9), 22.1 (C-9‘).

FT-IR ATR, v [cm^{-1}] = 3191 (w), 3085 (w), 2999 (w), 2986 (w), 2973 (w), 2910 (w), 1622 (w), 1595 (m), 1532 (m), 1496 (m), 1468 (w), 1442 (w), 1398 (w), 1382 (w), 1371 (w), 1338 (s), 1290 (s), 1232 (m), 1217 (w), 1180 (w), 1157 (w), 1139 (s), 1103 (s), 1059 (s), 970 (m),

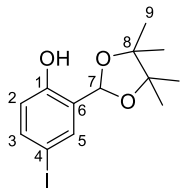
957 (m), 944 (w), 922 (s), 864 (m), 844 (m), 822 (w), 814 (w), 768 (w), 750 (s), 723 (w), 675 (w), 639 (m), 623 (m), 591 (w), 547 (w), 512 (w).

11.2.2.5.3 Synthesis of 4-iodo-2-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenol (71e)



70c **71e**

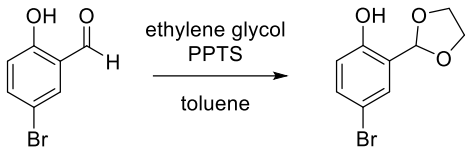
According to **GP12** 1.60 g (6.45 mmol, 1.00 eq.) of benzaldehyde **70c** were reacted with 0.76 g (6.45 mmol, 1.00 eq.) of pinacol and 0.24 g (0.97 mmol, 15 mol%) of PPTS in 13 mL toluene for 20 h. After recrystallisation in EtOAc 1.61 g, (4.63 mmol, 72%) of the desired product **71e** was obtained as a colorless solid.



M($C_{13}H_{17}IO_3$)	348.18 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 3:1) = 0.52.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 8.16 (s, 1H, OH), 7.53 (d, $^4J_{HH}$ = 2.2 Hz, 1H, H-5), 7.46 (dd, $^{3,4}J_{HH}$ = 8.6, 2.3 Hz, 1H, H-3), 6.63 (d, $^3J_{HH}$ = 8.6 Hz, 1H, H-2), 6.07 (s, 1H, H-7), 1.32 (s, 6H, H-9), 1.24 (s, 6H, H-9‘).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 154.3 (C-1), 138.4 (C-3), 135.7 (C-4), 126.4 (C-6), 119.3 (C-2), 98.7 (C-7), 83.5 (C-8), 81.5 (C-5), 23.6 (C-9), 22.1 (C-9‘).
GC-MS	m/z (%) = 348 (43), 248 (100), 218 (9), 163 (5), 129 (6), 121 (22), 101 (34), 92 (15), 83 (52), 65 (28), 57 (49).
FT-IR	ATR, v [cm^{-1}] = 3191 (w), 3085 (w), 2999 (w), 2986 (w), 2973 (w), 2910 (w), 1622 (w), 1595 (m), 1532 (m), 1496 (m), 1468 (w), 1442 (w), 1398 (w), 1382 (w), 1371 (w), 1338 (s), 1290 (s), 1232 (m), 1217 (w), 1180 (w), 1157 (w), 1139 (s), 1103 (s), 1059 (s), 970 (m), 957 (m), 944 (w), 922 (s), 864 (m), 844 (m), 822 (w), 814 (w), 768

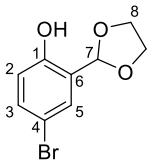
(w), 750 (s), 723 (w), 675 (w), 639 (m), 623 (m), 591 (w), 547 (w), 512 (w).

11.2.2.5.4 Synthesis of 2-(2-hydroxy-5-bromophenyl)-1,3-dioxolane (71c)



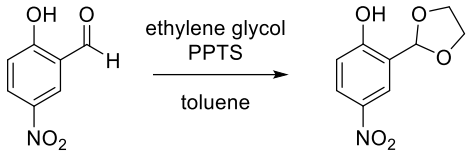
70b **71c**

According to **GP12** 4.00 g (19.9 mmol, 1.00 eq.) of benzaldehyde **70b** were reacted with 10.8 mL (199 mmol, 10.0 eq.) of ethylene glycol and 0.66 g (2.99 mmol, 15 mol%) of PPTS in 40 mL toluene for 24 h. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 40:1) to afford 4.20 g (17.3 mmol, 87%) of the desired product **71c** as a beige solid.



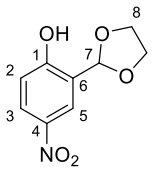
M($C_9H_9BrO_3$)	245.07 g/mol.
R_f	(SiO_2, CH_2Cl_2/MeOH 20:1) = 0.80.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.72 (s, 1H, OH), 7.36 (d, $^4J_{HH}$ = 2.45 Hz, 1H, H-5), 7.35 (d, $^3J_{HH}$ = 8.60 Hz, 1H, H-2), 6.82 (d, $^3J_{HH}$ = 8.60 Hz, 1H, H-3), 5.94 (s, 1H, H-7), 4.13-4.09 (m, 4H, H-8).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 154.6 (C-1), 133.4 (C-4), 130.6 (C-3), 123.0 (C-6), 119.1 (C-5), 111.8 (C-2), 103.2 (C-7), 64.9 (C-8).
FT-IR	ATR, v [cm^{-1}] = 3298 (m), 2954 (w), 2892 (w), 2102 (w), 1672 (w), 1654 (w), 1608 (w), 1593 (w), 1489 (m), 1423 (m), 1401 (m), 1330 (m), 1278 (s), 1255 (m), 1231 (m), 1218 (m), 1172 (m), 1123 (m), 1080 (s), 1060 (s), 982 (m), 937 (s), 890 (s), 815 (s), 767 (w), 728 (m), 696 (m), 665 (m), 635 (m), 608 (s), 557 (m), 539 (w), 517 (m).

11.2.2.5.4 Synthesis of 2-(2-hydroxy-5-nitrophenyl)-1,3-dioxolane (71a)



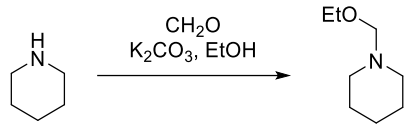
70a **71a**

According to **GP12** 2.00 g (12.0 mmol, 1.00 eq.) of benzaldehyde **70a** were reacted with 6.70 mL (120 mmol, 10.0 eq.) of ethylene glycol and 0.34 g (1.80 mmol, 15 mol%) of PPTS in 20 mL toluene for 23 h. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 9:1) to afford 0.88 g (4.17 mmol, 35%) of the desired product **71a** as a beige solid.



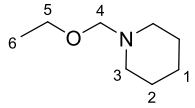
M($C_9H_9NO_5$)	211.20 g/mol.
R_f	(SiO_2, CH_2Cl_2/MeOH 9:1) = 0.44.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 8.59 (s, 1H, OH), 8.21 (d, $^4J_{HH}$ = 2.7 Hz, 1H, H-5), 8.16 (dd, $^{3,4}J_{HH}$ = 9.0, 2.8 Hz, 1H, H-3), 6.97 (d, $^3J_{HH}$ = 9.0 Hz, 1H, H-2), 6.01 (s, 1H, H-7), 4.18 – 4.16 (m, 2H, H-8), 4.16 – 4.13 (m, 2H, H-8‘).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 161.2 (C-1), 141.0 (C-4), 126.5 (C-3), 124.7 (C-5), 121.6 (C-6), 117.8 (C-2), 102.8 (C-7), 64.9 (C-8)
GC-MS	m/z (%) = 211 (69), 194 (14), 181 (46), 165 (49), 151 (27), 137 (100), 123 (30), 121 (19), 93 (17), 73 (35), 65 (18), 53 (16), 45 (44).
FT-IR	ATR, v [cm^{-1}] = 3298 (m), 2954 (w), 2892 (w), 2102 (w), 1672 (w), 1654 (w), 1608 (w), 1593 (w), 1489 (m), 1423 (m), 1401 (m), 1330 (m), 1278 (s), 1255 (m), 1231 (m), 1218 (m), 1172 (m), 1123 (m), 1080 (s), 1060 (s), 982 (m), 937 (s), 890 (s), 815 (s), 767 (w), 728 (m), 696 (m), 665 (m), 635 (m), 608 (s), 557 (m), 539 (w), 517 (m).

11.2.2.6 Synthesis of 1-ethoxypiperidine (73)



72 **73**

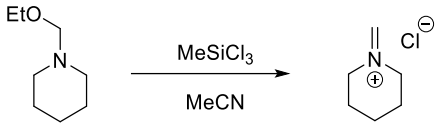
According to a procedure of *Quintard et al.*[133] 4.86 g (35.2 mmol, 1.20 eq.) of K_2CO_3 were suspended in 5.15 mL (88.2 mmol, 3.00 eq.) EtOH and 3.48 mL, (35.2 mmol, 1.20 eq.) of piperidine (**72**) were added. The mixture was cooled to 0 °C and 2.91 mL (29.4 mmol, 1.00 eq.) of formaldehyde (aq. 37%) were added slowly. At rt the reaction mixture was stirred for 15.5 h. The crude product was purified by fractional distillation (80 mbar, 130 °C oil bath temperature) to afford 2.70 g (18.8 mmol, 64%, Lit.[133]: 93%) of the desired product **73** as a colorless liquid.



M($C_8H_{17}NO$)	143.23 g/mol.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 4.06 (s, 2H, H-4), 3.49 (q, $^3J_{HH}$ = 7.02 Hz, 2H, H5), 2.64 (m, 4H, H-3), 1.57 (m, 6H, H-2, H-1) 1.19 (t, $^3J_{HH}$ = 7.02 Hz, 3H, H-6).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 89.2 (C-4), 64.3 (C-5), 50.8 (C-3), 26.1 (C-2), 25.9 (C-1) 15.3 (C-6).
FT-IR	ATR, ν [cm^{-1}] =3314 (w), 2971 (m), 2931 (s), 2854 (s), 2775 (m), 2701 (w), 2669 (w), 2325 (w), 2168 (w), 2089 (w), 2028 (w), 1988 (w), 1666 (w), 1470 (m), 1442 (m), 1413 (m), 1374 (s), 1350 (m), 1315 (m), 1295 (m), 1267 (m), 1261 (m), 1234 (m), 1217 (m), 1189 (m), 1162 (s), 1130 (s), 1098 (s), 1071 (s), 1038 (s), 1023 (s), 1004 (s), 977 (s), 896 (m), 881 (m), 861 (m), 811 (m), 783 (m), 771 (m), 708 (m), 646 (m), 608 (m), 590 (m), 508 (m).

The analytical data are in accordance with the literature.[133]

11.2.2.7 Synthesis of 1-methylenepiperidinium chloride (74b)



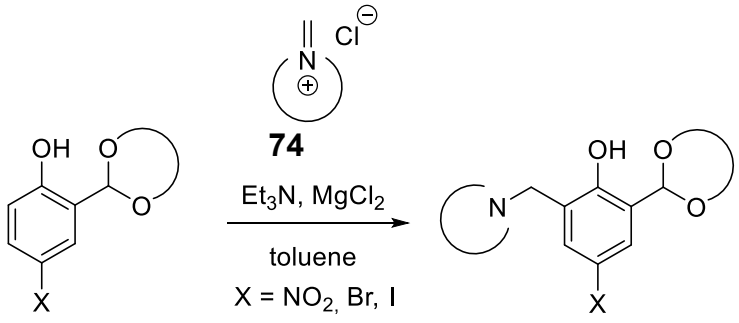
73 **74b**

0.21 mL (1.88 mmol, 1.00 eq.) of trichloromethylsilane were dissolved in 0.80 mL MeCN. At 0 °C 0.27 g (1.88 mmol, 1.00 eq.) ethoxypiperidine **73** were added dropwise, the suspension was stirred for 10 min at rt and then freeze-dried.

The crude product was directly converted without further purification due to the sensitivity.

M($C_{86}H_{12}NCl$) 133.07 g/mol.

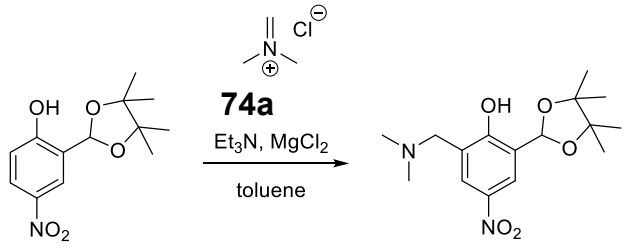
11.2.2.8 Aminomethylation using *Mannich* salts: General protocol (GP11)



71 **75**

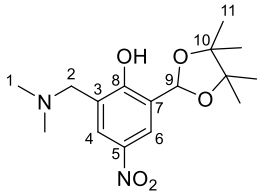
Phenol **71** (1.00 eq.) and $MgCl_2$ (2.00 eq.) were suspended in toluene. Et_3N (1.50 eq.) and *Mannich* salt **74** (2.00 eq.) were added and the reaction mixture were stirred for 18 h at rt. The mixture was filtered over celite and the solvents were removed under reduced pressure. The crude product was purified by column chromatography.

11.2.2.8.1 Synthesis of 2-((dimethylamino)methyl)-4-nitro-6-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenol (75e)



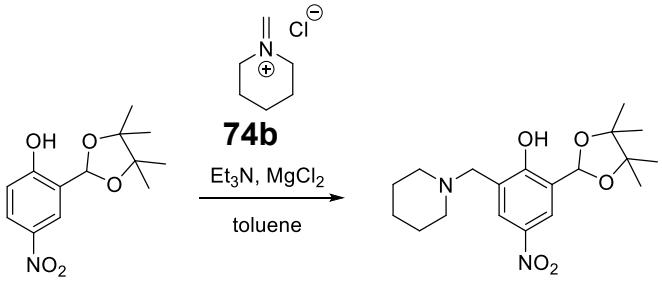
71b **75e**

According to **GP11** 0.15 g (0.56 mmol, 1.00 eq.) of phenol **71b** were reacted with 0.11 g (1.12 mmol, 2.00-2.50 eq.) of *Mannich* salt **74a**, 0.12 mL (0.84 mmol, 1.50 eq.) Et_3N and 0.11 g (1.12 mmol, 2.00 eq.) of $MgCl_2$ in 1.20 mL toluene for 20 h. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 20:1) to afford 0.09 g (0.28 mmol, 50%) of the desired product **75e** as a yellow solid.



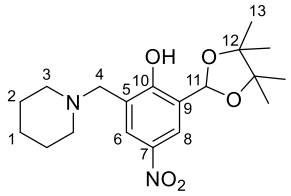
M($C_{16}H_{24}N_2O_5$)	324.38 g/mol.
R_f	(SiO_2, CH_2Cl_2/MeOH 20:1) = 0.32.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 8.44 (d, $^4J_{HH}$ = 2.8 Hz, 1H, H-6), 7.92 (d, $^4J_{HH}$ = 2.8 Hz, 1H, H-4), 6.27 (s, 1H, H-9), 3.79 (s, 2H, H-2), 2.43 – 2.39 (s, 6H, H-1), 1.37 (s, 6H, H-11), 1.32 (s, 6H, H-11').
^{13}C-NMR	(101 MHz, $CDCl_3$), δ [ppm] = 163.6 (C-8), 139.4 (C-3), 127.4 (C-7), 124.3 (C-4), 122.6 (C-6), 121.4 (C-5), 94.9 (C-9), 82.8 (C-10), 62.0 (C-2), 44.2 (C-1), 24.2 (C-11), 22.1 (C-11').
FT-IR	ATR, v [cm^{-1}] = 2983 (w), 2971 (w), 2941 (w), 2879 (w), 2603 (w), 2353 (w), 1690 (w), 1597 (m), 1562 (w), 1504 (w), 1477 (m), 1437 (w), 1419 (w), 1387 (w), 1367 (w), 1338 (w), 1314 (w), 1252 (s), 1221 (s), 1211 (s), 1178 (m), 1154 (s), 1132 (m), 1102 (s), 1084 (s), 991 (m), 972 (m), 954 (w), 936 (w), 928 (m), 911 (m), 869 (w), 845 (w), 824 (w), 816 (w), 785 (w), 774 (w), 761 (w), 754 (m), 733 (w), 680 (w), 667 (w), 646 (w), 632 (w), 620 (w), 602 (w), 589 (w), 545 (w), 531 (w), 509 (w).

11.2.2.8.2 Synthesis of 4-nitro-2-(piperidin-1-ylmethyl)-6-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenol (75f)



71b **75f**

According to **GP11** 0.25 g (0.94 mmol, 1.00 eq.) of phenol **71b** were reacted with 0.25 g (1.41 mmol, 1.50 eq.) of *Mannich* salt **74b**, 0.19 mL (0.41 mmol, 1.50 eq.) Et_3N and 0.18 g (1.88 mmol, 2.00 eq.) of $MgCl_2$ in 3 mL toluene for 48 h. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 30:1) to afford 0.07 g (0.18 mmol, 19%) of the desired product **75f** as a yellow solid.



M($C_{19}H_{28}N_2O_5$) 398.34 g/mol.

R_f (SiO_2, CH_2Cl_2/MeOH 30:1) = 0.10.

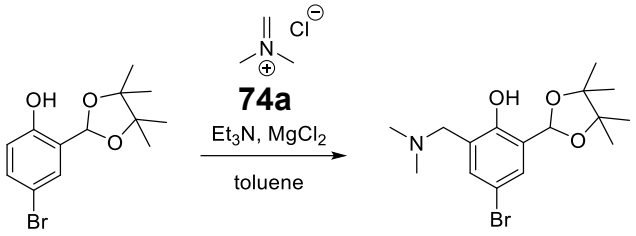
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.42 (d, $^4J_{HH}$ = 2.78 Hz, 1H, H-8), 7.91 (d, $^4J_{HH}$ = 2.78 Hz, 1H, H-6), 6.27 (s, 1H, H-11), 3.80 (s, 2H, H-4), 2.59 (s, 2H, H-2), 2.06 (m, 2H, H-3‘), 1.69-1.57 (m, 6H, H-1, H-2), 1.36 (s, 6H, H-13), 1.31 (s, 6H, H-13‘).

^{13}C-NMR (126 MHz, $CDCl_3$), δ [ppm] = 163.8 (C-10), 139.3 (C-5), 127.4 (C-9), 124.5 (C-6), 122.5 (C-8), 121.1 (C-7), 95.0 (C-11), 82.9 (C-12), 61.3 (C-4), 53.7 (C-3), 25.4 (C-2), 24.2 (C-13), 23.5 (C-1), 22.2 (C-13‘).

FT-IR ATR, v [cm^{-1}] = 3189 (w), 3086 (w), 2999 (w), 2986 (w), 2973 (w), 2910 (w), 1622 (w), 1595 (m), 1533 (m), 1496 (w), 1468 (w), 1442 (w), 1399 (w), 1382 (w), 1371 (w), 1338 (s), 1291 (s), 1232 (m), 1217 (w), 1180 (w), 1157 (w), 1139 (s), 1103 (s), 1058 (s), 971 (m), 957 (m), 944 (w), 923 (s), 864 (m), 844 (m), 822 (w), 814 (w), 768 (w), 750 (s), 723 (w), 675 (w), 639 (m), 623 (m), 591 (w), 548 (w), 513 (w).

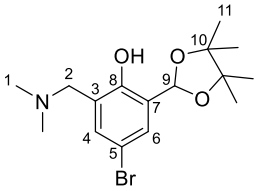
GC-MS m/z (%) = 398 (8), 370 (6), 369 (32), 284 (5), 270 (16), 239 (56), 224 (21), 207 (42), 180 (14), 149 (8), 137 (18), 119 (10), 106 (20), 84 (100), 69 (81), 57 (36), 41 (95).

11.2.2.8.3 Synthesis of 4-bromo-2-((dimethylamino)methyl)-6-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenol (75b)



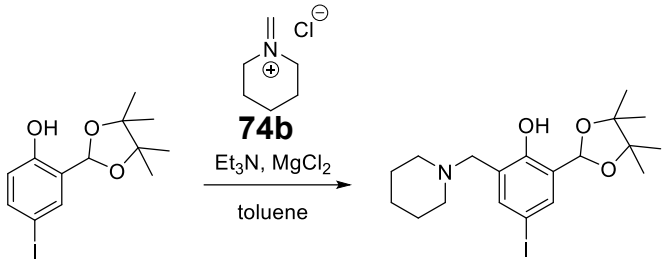
71d **75b**

According to **GP11** 2.20 g (7.30 mmol, 1.00 eq.) of phenol **71d** were reacted with 1.61 g (18.3 mmol, 2.50 eq.) of *Mannich* salt **74a**, 1.53 mL (11.0 mmol, 1.50 eq.) Et_3N and 1.39 g (14.6 mmol, 2.00 eq.) of $MgCl_2$ in 20 mL toluene for 48 h. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 40:1) to afford 0.62 g (1.72 mmol, 24%) of the desired product **75b** as a beige solid.



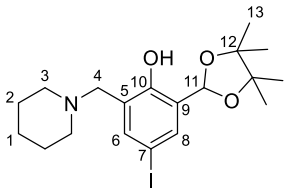
M($C_{16}H_{24}BrNO_3$)	358.28 g/mol.
R_f	(SiO_2, CH_2Cl_2/MeOH 40:1) = 0.55.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.57 (d, $^4J_{HH}$ = 2.44 Hz, 1H, H-6), 7.05 (d, $^4J_{HH}$ = 2.15 Hz, 1H, H-4), 6.24 (s, 1H, H-9), 3.61 (s, 2H, H-2), 2.31 (s, 6H, H-1), 1.33-1.28 (m, 12H, H-11).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 155.8 (C-8), 131.2 (C-4), 128.5 (C-6), 128.3 (C-7), 123.6 (C-3), 110.5 (C-5), 95.3 (C-9), 82.5 (C-10), 62.0 (C-2), 44.4 (C-1), 24.3 (C-11), 22.2 (C-11‘).
FT-IR	ATR, v [cm^{-1}] = 2981 (w), 2963 (w), 2926 (w), 2788 (w), 2595 (w), 2123 (w), 1760 (w), 1667 (w), 1607 (w), 1588 (w), 1455 (m), 1440 (m), 1429 (m), 1389 (s), 1378 (m), 1366 (m), 1355 (m), 1315 (w), 1291 (w), 1256 (m), 1228 (m), 1214 (m), 1186 (m), 1153 (s), 1126 (w), 1098 (s), 1085 (s), 1044 (m), 1020 (m), 1008 (m), 994 (m), 963 (m), 955 (m), 937 (m), 902 (w), 885 (s), 875 (m), 868 (m), 835 (m), 809 (w), 792 (m), 753 (m), 729 (w), 675 (m), 654 (m), 624 (m), 591 (w), 560 (m), 518 (w), 507 (m).

11.2.2.8.4 Synthesis of 4-iodo-2-(piperidin-1-ylmethyl)-6-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenol (75c)



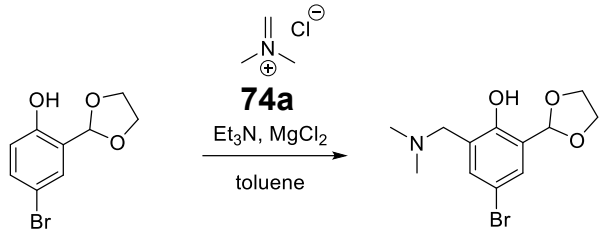
71e **75c**

According to **GP11** 0.20g (0.57 mmol, 1.00 eq.) of phenol **71e** were reacted with 0.08 g (0.57 mmol, 1.00 eq.) of *Mannich* salt **74b**, 0.12 mL (0.86 mmol, 1.50 eq.) Et_3N and 0.11 g (1.14 mmol, 2.00 eq.) of $MgCl_2$ in 1.80 mL toluene for 18 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 3:1) to afford 0.05 g (0.11 mmol, 20%) of the desired product **75b** as a beige solid.



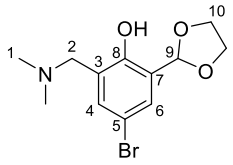
M($C_{19}H_{28}INO_3$)	445.34 g/mol.
R_f	(SiO_2, cHex/EtOAc 3:1) = 0.26.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.72 (d, $^4J_{HH}$ = 2.2 Hz, 1H, H-8), 7.21 (d, $^4J_{HH}$ = 2.2 Hz, 1H, H-6), 6.21 (s, 1H, H-11), 3.61 (s, 2H, H-4), 2.48 (s, 4H, H-3), 1.61 (p, $^3J_{HH}$ = 5.7 Hz, 4H, H-2), 1.48 (br s, 2H, H-1), 1.32 (s, 6H, H-13), 1.27 (s, 6H, H-13‘).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 156.7 (C-10), 136.9 (C-6), 134.1 (C-8), 128.7 (C-9), 124.0 (C-5), 95.0 (C-11), 82.4 (C-12), 80.0 (C-7), 61.3 (C-4), 53.8 (C-3), 25.6 (C-2), 24.3 (C-13), 23.8 (C-1), 22.2 (C-13‘).
FT-IR	ATR, v [cm^{-1}] = 2977 (m), 2935 (m), 2856 (w), 2811 (w), 2755 (w), 2248 (w), 2107 (w), 1714 (w), 1606 (w), 1583 (w), 1453 (s), 1389 (s), 1367 (m), 1340 (m), 1326 (w), 1307 (m), 1287 (m), 1261 (m), 1244 (m), 1219 (m), 1151 (s), 1098 (s), 1038 (m), 1007 (m), 989 (m), 962 (m), 952 (m), 922 (w), 898 (m), 874 (m), 863 (m), 809 (w), 785 (m), 748 (w), 730 (w), 673 (w), 647 (m), 619 (w), 590 (w), 574 (w), 565 (w), 553 (w), 521 (w), 504 (w).
HR-MS (EI)	Calcd. $[M+H]^{\cdot+}$: 445.1108, found: 445.1099.

11.2.2.8.5 Synthesis of 4-bromo-2-((dimethylamino)methyl)-6-(1,3-dioxolan-2-yl)phenol (75a)



71c **75a**

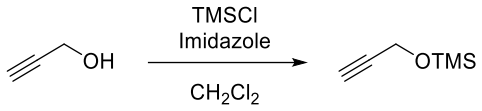
According to **GP11** 0.25 g (1.02 mmol, 1.00 eq.) of phenol **71c** were reacted with 0.19 g (2.04 mmol, 2.00 eq.) of *Mannich* salt **74a**, 0.21 mL (1.53 mmol, 1.50 eq.) Et_3N and 0.19 g (2.04 mmol, 2.00 eq.) of $MgCl_2$ in 3 mL toluene for 18 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 3:1) to afford 0.05 g (0.11 mmol, 20%) of the desired product **75a** as a beige solid.



M($C_{12}H_{16}BrNO_3$)	302.17 g/mol.
R_f	(SiO_2, CH_2Cl_2/MeOH 40:1) = 0.15.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.53 (d, $^4J_{HH}$ = 2.44 Hz, 1H, H-6), 7.10 (d, $^4J_{HH}$ = 2.43 Hz, 1H, H-4), 6.12 (s, 1H, H-9), 4.16-4.05 (m, 4H, H-10), 3.63 (s, 2H, H-2), 2.34 (s, 6H, H-1).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 155.9 (C-8), 131.5 (C-4), 128.8 (C-6), 126.3 (C-7), 123.9 (C-3), 110.5 (C-5), 98.9 (C-9), 65.3 (C-10), 62.1 (C-2), 44.3 (C-1).
FT-IR	ATR, v [cm^{-1}] = 3213 (w), 2957 (m), 2924 (m), 2873 (m), 2857 (m), 1911 (w),1785 (w), 1723 (m), 1670 (m), 1652 (m), 1610 (m), 1563 (m), 1497 (w), 1464 (s), 1425 (m), 1409 (w), 1374 (m), 1303 (w), 1268 (s), 1222 (m), 1153 (s), 1114 (s), 1070 (m), 1017 (m), 957 (m), 892 (s), 839 (m), 828 (s), 765 (s), 747 (m), 730 (m), 694 (s), 626 (s), 538 (s).

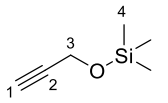
11.2.3 Glycosylation of the eastern building block

11.2.3.1 Synthesis of trimethyl(prop-2-yn-1-yloxy)silane (86)



85 **86**

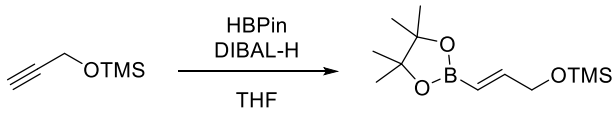
Following a procedure of *Chalker et al.*[178] 10.0 mL (169 mmol, 1.00 eq.) of propargylic alcohol (**85**) and 15.0 g (220 mmol, 1.30 eq.) of imidazole were dissolved in 100 mL CH_2Cl_2. At 0 °C 23.7 mL (1.86 mmol, 1.10 eq.) of TMSCl were added dropwise. The reaction mixture was stirred for 2 h at rt. Subsequently, the reaction mixture was cooled to 0 °C and quenched with 10 mL sat. aq. $NaHCO_3$. The aq. phase was extracted with 20 mL CH_2Cl_2. The combined org. layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by fractional distillation (650 mbar, 30 °C head temperature, 80 °C oil bath temperature) to afford 19.2 g (150 mmol, 89%, Lit.[178]: 89%) of the desired product **86** as a colorless liquid.



M($C_6H_{12}OSi$)	128.25 g/mol.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 4.29 (d, $^4J_{HH}$ = 2.4 Hz, 2H, H-3), 2.40 (t, $^4J_{HH}$ = 2.4 Hz, 1H, H-1), 0.18 (s, 9H, H-4).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 82.1 (C-2), 73.0 (C-1), 50.8 (C-3), -0.3 (C-4).

The analytical data are in accordance with the literature.[178]

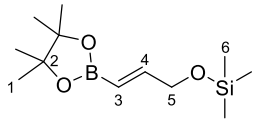
11.2.3.2 Synthesis of (*E*)-trimethyl((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)oxy)silane (88)



86 **87**

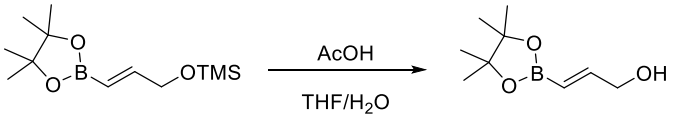
10.0 g (78.0 mmol, 1.00 eq.) of silylether **86** were dissolved in 150 mL THF. 7.80 mL (7.80 mmol, 0.10 eq.) of DIBAL-H (1 M in THF) and 13.6 mL (93.6 mmol, 1.20 eq.) of HBPin were added. The reaction mixture was heated to reflux und stirred for 16 h. At rt SiO_2 was added portion wise and stirred for 10 min. The suspension was filtered over a pad of SiO_2 and the solvent was removed by reduced pressure. The crude product

was purified by column chromatography (SiO_2, *c*Hex/EtOAc 30:1) to afford 4.14 g (16.1 mmol, 21%) of the desired product **87** as a colorless oil.



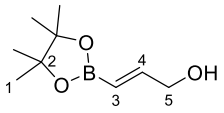
M($C_{12}H_{25}BO_3Si$)	256.22 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 15:1) = 0.47.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 6.68 (dt, $^{3,4}J_{HH}$ = 18.0, 3.9 Hz, 1H, H-4), 5.73 (dt, $^{3,4}J_{HH}$ = 17.9, 2.0 Hz, 1H, H-3), 4.21 (dd, $^{3,4}J_{HH}$ = 3.9, 2.0 Hz, 2H, H-5), 1.27 (s, 12H, H-1), 0.12 (s, 9H, H-6).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 151.7 (C-4), 117.3 (C-3), 83.1 (C-2), 64.1 (C-5) 24.7 (C-1), -0.5 (C-6).
FT-IR	ATR, v [cm^{-1}] = 3676 (w), 3423 (w), 2979 (s), 2928 (m), 2206 (w), 2164 (w), 1645 (m), 1449 (w), 1362 (s), 1323 (s), 1272 (m), 1145 (s), 1085 (m), 1007 (m), 972 (m), 924 (w), 892 (w), 850 (m), 693 (w), 669 (w), 663 (w), 645 (w), 625 (w), 604 (w), 586 (w), 568 (w).
GC-MS	m/z (%) = 256 ($M^{+\cdot}$,22), 241 (23), 199 (5), 156 (14), 141 (100), 117 (40), 99 (52), 83 (38), 73 (63), 57 (33).

11.2.3.3 Synthesis of ((*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-ol (88)



87 **88**

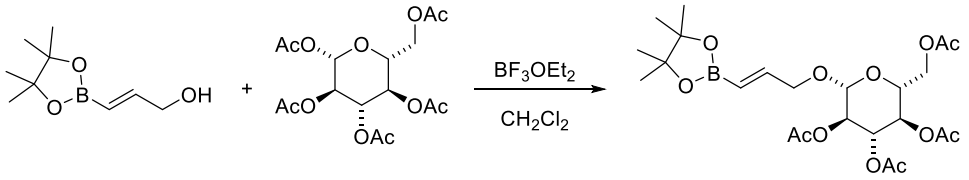
4.33 g (16.9 mmol, 1.00 eq.) of silylether **87** were dissolved in 240 mL THF and 25 mL H_2O. 75 mL of glacial acetic acid were added and the reaction mixture was stirred at 60 °C for 2.5 h. At rt the reaction mixture was neutralized with 100 mL sat. aq. $NaHCO_3$. THF was removed under reduced pressure and the remaining aq. phase was extracted with 150 mL EtOAc. The combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) to afford 2.23 g (12.1 mmol, 72%) of the desired product **88** as a colorless solid.



M($C_9H_{17}BO_3$)	184.04 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 2:1) = 0.30.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 6.74 (dt, $^{3,4}J_{HH}$ = 18.2, 4.2 Hz, 1H, H-4), 5.71 (dt, $^{3,4}J_{HH}$ = 18.2, 1.9 Hz, 1H, H-3), 4.24 (dd, $^{3,4}J_{HH}$ = 4.1, 2.0 Hz, 2H, H-5), 1.27 (s, 12H, H-1).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 151.6 (C-4), 117.3 (C-3), 83.3 (C-2), 64.5 (C-5), 24.7 (C-1).
FT-IR	ATR, v [cm^{-1}] = 3429 (m), 2979 (m), 2932 (m), 2157 (w), 2072 (w), 1988 (w), 1738 (w), 1645 (s), 1447 (m), 1390 (m), 1362 (s), 1336 (s), 1322 (s), 1273 (m), 1241 (m), 1215 (m), 1166 (m), 1145 (s), 1111 (m), 1089 (m), 1005 (m), 972 (m), 923 (m), 892 (m), 850 (m), 830 (m), 774 (w), 669 (m), 627 (m), 598 (w), 578 (w), 548 (w), 527 (w).

11.2.3.4 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(((*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (89)

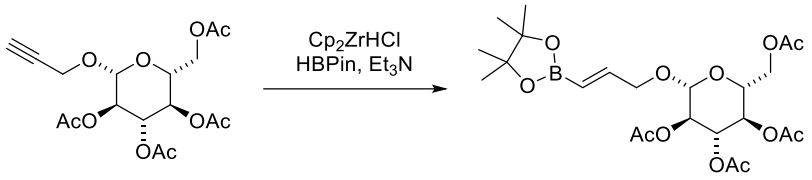
Route 1:



88 **41a** **89**

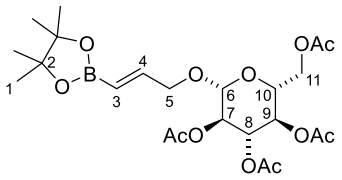
0.86 g (2.20 mmol, 1.00 eq.) of sugar **41a** and 0.49 g (2.65 mmol, 1.20 eq.) of vinyl alcohol **88** were dissolved in 11 mL CH_2Cl_2. At 0 °C 0.42 mL (3.30 mmol, 1.50 eq.) of BF_2OEt_2 were added dropwise. The reaction mixture was stirred at rt and quenched after 18 h with 5 mL sat. aq. $NaHCO_3$. The aq. phase was extracted with 15 mL CH_2Cl_2. The combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) to afford 0.53 g (1.03 mmol, 47%) of the desired product **89** as a colorless solid.

Route 2:



77a **89**

To a mixture of 9.00 mL (62.1 mmol, 3.00 eq.) of HBPin and 8.00 g (20.7 mmol, 1.00 eq.) of sugar **77a** 1.43 mL (10.4 mmol, 0.10 eq.) Et_3N and 0.53 g (2.07 mmol, 0.10 eq.) of *Schwartz* reagent were added. After stirring at 65 °C for 18 h the reaction was terminated upon addition of 10 mL H_2O. The aq. phase was extracted with 20 mL CH_2Cl_2, the combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) to afford 3.30 g (6.41 mmol, 31%) of the pinacolboronate **89** as a colorless solid.

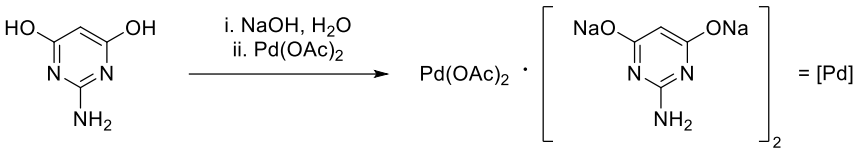


M($C_{23}H_{35}BO_{12}$)	514.33 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:1) = 0.55.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 6.57 (dt, $^{3,4}J_{HH}$ = 18.2, 4.6 Hz, 1H, H-4), 5.69 (dt, $^{3,4}J_{HH}$ = 18.2, 1.8 Hz, 1H, H-3), 5.22 (t, $^{3,4}J_{HH}$ = 9.4 Hz, 1H, H-7), 5.15 – 5.02 (m, 2H, H-8, H-9), 4.57 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, H-6), 4.43 (ddd, $^{2,3,4}J_{HH}$ = 14.7, 4.2, 1.9 Hz, 1H, H-5), 4.28 (dd, $^{2,3}J_{HH}$ = 12.3, 4.7 Hz, 1H, H-11), 4.20 (ddd, $^{2,3,4}J_{HH}$ = 14.7, 5.1, 1.7 Hz, 1H, H-5), 4.15 (dd, $^{2,3}J_{HH}$ = 12.3, 2.4 Hz, 1H, H-11‘), 3.69 (m, 1H, H-10), 2.11 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.29 (s, 12H, H-1).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 170.7 (OAc), 170.3 (OAc), 169.4 (OAc), 169.3 (OAc), 147.2 (C-4), 99.7 (C-6), 83.3 (C-2), 72.9 (C-7), 71.8 (C-10), 71.3 (C-9), 70.6 (C-5), 70.4 (C.3), 68.4 (C-8), 61.9 (C-11), 24.8 (C-1), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc).
FT-IR	ATR, v [cm^{-1}] = 3489 (w), 2979 (w), 2943 (w), 2256 (w), 2187 (w), 2116 (w), 1926 (w), 1755 (s), 1646 (w), 1433 (w), 1367 (m), 1343 (m), 1326 (m), 1220 (s), 1167 (w), 1144 (m), 1040 (s),

973 (w), 907 (w), 849 (w), 781 (w), 734 (w), 695 (w), 679 (w), 627 (w), 600 (w), 562 (w), 541 (w).

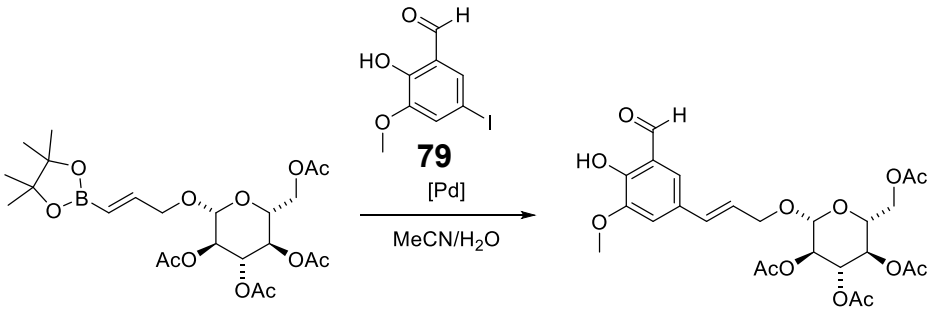
11.2.3.5 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(((*E*)-3-(3-formyl-4-hydroxy-5-methoxyphenyl)allyl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (83)

Preparation of the catalyst solution:



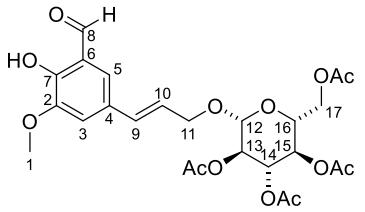
90 **91**

According to a procedure of *Chalker et al.*[138] 30.0 mg (0.20 mmol, 1.00 eq.) of pyrimidine **90** were added to 4 mL NaOH (0.1 M). The suspension was heated to 65 °C and stirred for 5 min. 20.0 mg (0.10 mmol, 0.50 eq.) of $Pd(OAc)_2$ were added and stirred for further 30 min. The reaction mixture was cooled to rt and diluted with H_2O to a volume of 10 mL to obtain a 0.01 M catalyst solution. The solution was stored at 2 °C for several weeks.



89 **83**

0.50 g (1.81 mmol, 1.00 eq.) of iodovanillin **79** and 1.40 g (2.72 mmol, 1.50 mmol) pinacolboronate **89** were dissolved in 13 mL MeCN. 36 mL (0.39 mmol, 30 mol%) of catalyst **91** were added and the reaction mixture was heated to 80 °C for 3.5 h. The reaction mixture was cooled to rt and washed with 15 mL sat. aq. NaCl. The aq. phase was extracted with 30 mL EtOAc, the combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1 → 3:2) to afford 0.44 g (0.82 mmol, 45%) of the desired product **83** as a pale yellow solid.



M($C_{25}H_{30}O_{13}$) 538.50 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:1) = 0.27.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 11.09 (s, 1H, OH), 9.92 (s, 1H, H-8), 7.17 (d, $^4J_{HH}$= 1.9 Hz, 1H, H-5), 7.15 (d, $^4J_{HH}$ = 2.0 Hz, 1H, H-3), 6.55 (d, $^3J_{HH}$ = 16.0 Hz, 1H, H-9), 6.15 (dt, $^{2,3}J_{HH}$ = 15.9, 6.0 Hz, 1H, H-10), 5.23 (t, $^3J_{HH}$ = 9.4 Hz, 1H, H-14), 5.13 (t, $^3J_{HH}$ = 9.7 Hz, 1H, H-15), 5.09 – 5.02 (m, 1H, H-13), 4.63 (d, $^3J_{HH}$ = 7.9 Hz, 1H, H-12), 4.51 (ddd, $^{2,3,4}J_{HH}$ = 12.9, 5.6, 1.6 Hz, 1H, H-17), 4.31 – 4.23 (m, 2H, H-11, H-17‘), 4.18 (ddd, $^{2,3,4}J_{HH}$ = 12.4, 4.9, 2.5 Hz, 1H, H-11‘), 3.95 (s, 3H, H-1), 3.72 (m, 1H, H-16), 2.09 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.02 (s, 3H, OAc).

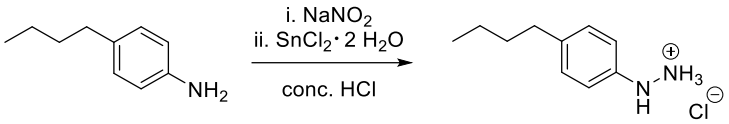
^{13}C-NMR (126 MHz, $CDCl_3$), δ [ppm] = 196.4 (C-8), 170.6 (OAc), 170.3 (OAc), 169.4 (OAc), 169.3 (OAc), 151.7 (C-7), 148.5 (C-6), 131.3 (C-10), 128.5 (C-4), 124.0 (C-9), 122.9 (C-3), 120.4 (C-2), 115.1 (C-5), 99.9 (C-12), 72.8 (C-14), 71.9 (C-16), 71.3 (C-13), 69.7 (C-17), 68.4 (C-15), 61.9 (C-11), 56.3 (C-1), 20.7 (2x OAc), 20.6 (OAc), 20.6 (OAc).

FT-IR ATR, v [cm^{-1}] = 3475 (w), 2942 (w), 2856 (w), 2258 (w), 2115 (w), 2005 (w), 1749 (s), 1655 (m), 1597 (w), 1468 (w), 1432 (w), 1367 (m), 1327 (w), 1219 (s), 1163 (m), 1038 (s), 963 (m), 908 (m), 813 (w), 733 (m), 648 (w), 600 (w), 560 (w).

HR-MS (ESI) Calcd. $[M+Na]^+$: 561.1578, found: 561.1574.

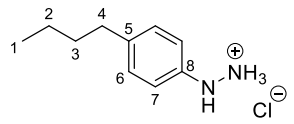
11.2.4 Syntheses of indole derivatives

11.2.4.1 Synthesis of (4-butylphenyl)hydrazine hydrochloride (49a)



56a **49a**

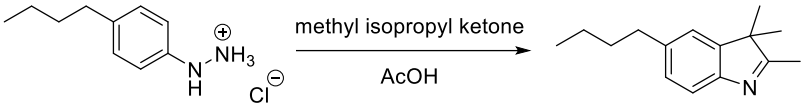
Following a procedure of *Liu et al.*[179], 4.66 mL (29.5 mmol, 1.00 eq.) of 4-butylaniline (**56a**) were added dropwise to 28 mL conc. HCl at 0 °C. A solution of 2.24 g (32.5 mmol, 1.10 eq.) $NaNO_2$ in 28 mL H_2O was added dropwise and the reaction mixture was stirred for 22 h at rt. 13.3 g (59.0 mmol, 2.00 eq.) of $SnCl_2 \cdot 2\ H_2O$ in 28 mL conc. HCl were added and the resulting precipitate was filtered. After washing with cold H_2O 3.24 g (16.2 mmol, 55%) of the desired product **49a** was obtained as brown solid.



M($C_{10}H_{17}ClN_2$)	200.71 g/mol.
^{1}H-NMR	(500 MHz, DMSO-d_6) δ [ppm]: 10.2 (s, 3H, NH_3), 8.14 (s, 1H, NH), 7.09 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-6), 6.94 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-7), 2.60-2.41 (m, 2H, H-4), 1.50 (p, $^3J_{HH}$ = 7.4 Hz, 2H, H-3), 1.27 (ps h, $^3J_{HH}$ = 7.3 Hz, 2H, H-2), 0.88 (t, $^3J_{HH}$ = 7.4 Hz, 3H, H-1).
^{13}C-NMR	(126 MHz, DMSO-d_6), δ [ppm] = 143.4 (C-8), 135.5 (C-5), 128.7 (C-6), 114.8 (C-7), 34.0 (C-4), 33.4 (C-3), 21.7 (C-2), 13.8 (C-1).
FT-IR	ATR, v [cm^{-1}] = 3231 (m), 3000 (m), 2955 (m), 2919 (s), 2871 (s), 2683 (s), 1961 (w), 1765 (w), 1589 (m), 1564 (s), 1534 (s), 1511 (s), 1466 (m), 1322 (w), 1239 (m), 1191 (m), 1123 (w), 1033 (w), 966 (w), 874 (s), 823 (s), 723 (m), 559 (m), 538 (s).

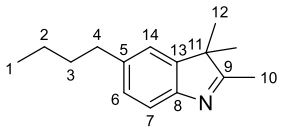
The analytical data are in accordance with the literature.[179]

11.2.4.2 Synthesis of 5-butyl-2,3,3-trimethylindolenine (58a)



49a **58a**

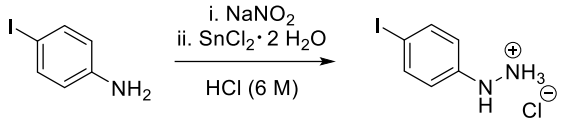
Following a modified literature procedure by *Reifarth et al.*[111], 2.00 g (9.96 mmol, 1.00 eq.) of hydrazine salt **49a** were suspended in 10 mL glacial acetic acid. 1.17 mL (11.0 mmol, 1.10 eq.) methyl isopropyl ketone were added and the resulting suspension was heated to reflux for 17 h. The reaction was terminated by removing the solvent under reduced pressure. The residue was taken up in 100 mL CH_2Cl_2. After washing three times with 20 mL sat. aq. $NaHCO_3$, the org. phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 3:1) to afford 1.50 g (6.97 mmol, 70%, Lit.[111]: 74%) of the desired product **58a** as a red oil.



M($C_{15}H_{21}N$)	215.34 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 3:1) = 0.25.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm]: 7.42 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H-7), 7.10 (dd, $^{3,4}J_{HH}$ = 7.8 Hz, 1.6 Hz, 1H, H-6), 7.08 (s, 1H, H-14), 2.64 (t, $^3J_{HH}$ = 7.8 Hz, 2H, H-4), 2.26 (s, 3H, H-10), 1.61 (p, $^3J_{HH}$ = 7.6 Hz, 2H, H-3), 1.37 (h, $^3J_{HH}$ = 7.4 Hz, 2H, H-2), 1.29 (s, 6H, H-12), 0.94 (t, $^3J_{HH}$ = 7.4 Hz, 3H, H-1).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 187.2 (C-9), 151.8 (C-8), 145.8 (C-13), 140.2 (C-5), 127.7 (C-6), 121.5 (C-14), 119.5 (C-7), 53.6 (C-11), 35.9 (C-4), 34.2 (C-3), 23.4 (C-12), 22.6 (C-2), 15.5 (C-10), 14.1 (C-1).
FT-IR	ATR, v [cm^{-1}] = 2959 (s), 2927 (s), 2859 (m), 2156 (w), 1715 (w), 1579 (m), 1524 (w), 1488 (m), 1461 (s), 1378 (m), 1205 (m), 1103 (w), 945 (w), 825 (s), 730 (w).
HR-MS (EI)	Calcd. $[M]^{\cdot+}$: 215.1669, found: 215.1669.

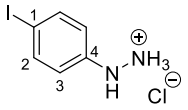
The analytical data are in accordance with the literature.[111]

11.2.4.3 Synthesis of (4-iodophenyl)hydrazine hydrochloride (63)



60 **63**

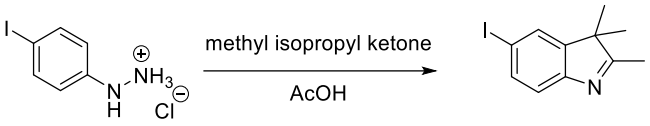
Following a procedure by *L. Finck and M. Oestrich*[180], 100 mL of HCl (6 M) were cooled to 0 °C, 8.76 g (40.0 mmol, 1.00 eq.) of 4-iodoaniline (**60**) were added and the solution was stirred for 20 min. A solution of 3.31 g (48.0 mmol, 1.20 eq.) $NaNO_2$ in 20 mL H_2O was added dropwise and the reaction mixture was stirred for an additional 1 h. A solution of 22.6 g (100 mmol, 2.50 eq.) of $SnCl_2 \cdot 2H_2O$ in 100 mL conc. HCl was added over a course of 50 min. The reaction mixture was stirred for 15 h at rt. The precipitate was filtered off, washed with 80 mL *i*-propanol and 100 mL MTBE. 8.25 g (30.5 mmol, 76%, Lit.[180]: 75%) of the desired product **63** could be obtained as pale brown solid.



M($C_6H_8ICIN_2$)	270.50 g/mol.
^{1}H-NMR	(500 MHz, DMSO-d_6) δ [ppm] = 10.37 (s, 3H, NH_3), 8.49 (s, 1H, NH), 7.58 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H-2), 6.83 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H-3).
^{13}C-NMR	(126 MHz, DMSO-d_6), δ [ppm] = 145.5 (C-4), 137.3 (C-2), 116.8 (C-3), 83.9 (C-1).
FT-IR	ATR, ν [cm^{-1}] = 3231 (w), 2875 (bm), 2681 (m), 1890 (w), 1584 (m), 1563 (m), 1533 (m), 1485 (s), 1401 (w), 1308 (w), 1238 (w), 1189 (w), 1064 (w), 1005 (m), 877 (m), 820 (s), 764 (w), 704 (w), 602 (m), 517 (s).

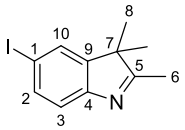
The analytical data are in accordance with the literature[180].

11.2.4.4 Synthesis of 5-iodo-2,3,3-trimethylindolenine (64)



63 **64**

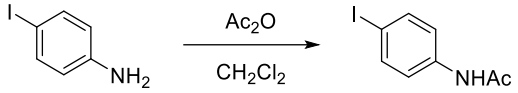
Following a modified literature procedure by *M. Tomasulo et al.*[181], 7.50 g (31.9 mmol, 1.00) of hydrazine salt **63** were suspended in 50 mL glacial acetic acid. 3.73 mL (35.1 mmol, 1.10 eq.) methyl isopropyl ketone were added and the resulting suspension was heated to reflux for 16.5 h. The reaction mixture was terminated by removing the solvent under reduced pressure. The residue was taken up in 100 mL CH_2Cl_2. After washing three times with 60 mL sat. aq. $NaHCO_3$, the org. phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) to afford 5.72 g (20.1 mmol, 63%, Lit.[181]: 64%) of the desired product **64** as a red oil.



M($C_{11}H_{12}IN$)	285.13 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 2:1) = 0.35.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.62 (dd, $^{3,4}J_{HH}$ = 8.0, 1.7 Hz, 1H, H-2), 7.59 (d, $^4J_{HH}$ = 1.6 Hz, 1H, H-10), 7.29 (d, $^3J_{HH}$ = 8.1 Hz, 1H, H-3), 2.26 (s, 3H, H-6), 1.29 (s, 6H, H-8).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 188.5 (C-5), 153.5 (C-4), 148.3 (C-9), 136.8 (C-2), 130.8 (C-10), 121.9 (C-3), 90.0 (C-1), 54.1 (C-7), 23.0 (C-8), 15.5 (C-6).
FT-IR	ATR, v [cm^{-1}] = 2963 (m), 2926 (w), 2867 (w), 1883 (w), 1735 (w), 1606 (w), 1579 (m), 1460 (m), 1445 (s), 1409 (m), 1379 (m), 1279 (w), 1247 (m), 1200 (m), 1120 (w), 1045 (w), 936 (w), 820 (s), 773 (w), 671 (m), 535 (m).
GC-MS	m/z (%) = 284 (100), 269 (37), 207 (6), 158 (18), 143 (19), 127 (15), 115 (46), 91 (20), 51 (12).

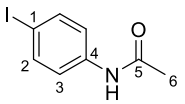
The analytical data are in accordance with the literature[181].

11.2.4.5 Synthesis of *N*-(4-iodophenyl)acetamide (61)



60 **61**

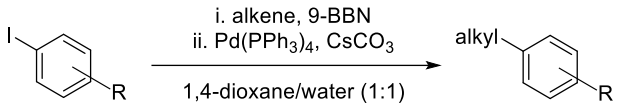
Following a procedure by *S. Kathiravan* and *I. A. Nicholls*[182], 10.0 g (45.7 mmol, 1.00 eq.) of 4-iodoaniline (**60**) were dissolved in 123 mL CH_2Cl_2. At 0 °C 5.20 mL (55.0 mmol, 1.20 eq.) of Ac_2O were added dropwise and the reaction solution was stirred for 1.5 h at rt. The reaction was terminated by the addition of 50 mL sat. aq. Na_2CO_3 at 0 °C. The organic phase was washed two times with 50 mL sat. aq. Na_2CO_3. The aq. phase was extracted four times with 60 mL CH_2Cl_2. The combined org. phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. 6.77 g (25.9 mmol, 57%, Lit.[182]: 99%) of the desired product **61** was obtained as a pale purple solid.



M(C_8H_8INO)	261.06 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:1) = 0.35.
^{1}H-NMR	(500 MHz, $CDCl_3$), δ [ppm] = 7.61 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H-2), 7.28 (d, $^3J_{HH}$ = 8.6 Hz, 2H, H-3), 2.16 (s, 3H, H-6), 1.62 (s, 1H, NH).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 168.4 (C-5), 138.1 (C-2), 137.8 (C-4), 121.8 (C-3), 87.6 (C-1), 24.8 (C-6).
FT-IR	ATR, v [cm^{-1}] = 3287 (w), 3253 (w), 3176 (w), 3101 (w), 3044 (w), 1899 (w), 1664 (m), 1596 (m), 1579 (m), 1526 (m), 1482 (m), 1389 (s), 1307 (m), 1254 (m), 1103 (w), 1002 (m), 944 (w), 815 (s), 734 (s), 603 (w), 503 (s).

The analytical data are in accordance with the literature.[182]

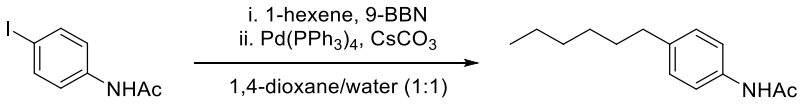
11.2.4.6 *Suzuki* cross-*coupling*: General protocol (GP1)



61/64 **62/58**

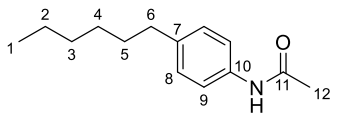
A solution of 9-BBN (1.10-1.70 eq., 0.5 M in THF) was cooled down to 0 °C, the alkene (1.10-1.70 eq.) was added and the reaction mixture was stirred at rt for 3 h. Degassed H_2O, 1,4-dioxane, Cs_2CO_3 (2.50 - 3.50 eq.), $Pd(PPh_3)_4$ (0.4 - 0.5 mol%) and iodoaryl **61**/**64** (1.00 eq.) were added and the resulting suspension was heated to 90 °C for further 2 h. The reaction was terminated by cooling to rt, concentrated under reduced pressure and extracted three times with MTBE. The combined organic phases were dried over MgSO4, stirred with *quadrasil*, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography.

11.2.4.6.1 Synthesis of *N*-(4-hexylphenyl)acetamide (62a)



61 **62a**

According to **GP1**, 26.4 mL (13.2 mmol, 1.70 eq., 0.5 M in THF) of 9-BBN, 1.66 mL (13.2 mmol, 1.70 eq.) of 1-hexene, 8.61 g (26.8 mmol, 3.50 eq.) of Cs_2CO_3, 0.03 g (0.03 mmol, 0.4 mol%) of $Pd(PPh_3)_4$ and 2.00 g (7.66 mmol, 1.00 eq.) of acetamide **61** were reacted in 58 mL H_2O and 58 mL 1,4-dioxane at 90 °C for 5 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1 → 1:1) to afford 1.39 g (6.34 mmol, 83%) of the desired product **62a** as colorless solid.



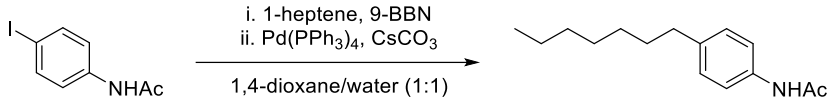
M($C_{14}H_{21}NO$)	219.33 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 3:1) = 0.17.
^{1}H-NMR	(500 MHz, $CDCl_3$), δ [ppm] = 7.54 (s, 1H, NH), 7.39 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-9), 7.10 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H-8), 2.55 (t, $^3J_{HH}$ = 8.4 Hz, 2H, H-6), 2.14 (s, 3H, H-12), 1.64-1.52 (m, 2H, H-5), 1.29 (s, 6H, H-2, H-3, H-4), 0.93-0.85 (m, 3H, H-1).

^{13}C-NMR (126 MHz, $CDCl_3$), δ [ppm] = 168.6 (C-11), 139.2 (C-7), 135.6 (C-10), 128.9 (C-8), 120.2 (C-9), 35.5 (C-6), 31.8 (C-3), 31.6 (C-5), 29.0 (C-4), 24.6 (C-12), 22.7 (C-2), 14.2 (C-1).

FT-IR ATR, v [cm^{-1}] = 3285 (w), 3249 (w), 3122 (w), 3067 (w), 3028 (w), 2958 (w), 2925 (m), 2853 (m), 1902 (w), 1661 (s), 1605 (s), 1553 (s), 1510 (s), 1464 (m), 1409 (s), 1370 (s), 1322 (s), 1268 (m), 1179 (w), 1042 (w), 968 (w), 840 (s), 770 (s), 608 (w), 518 (s).

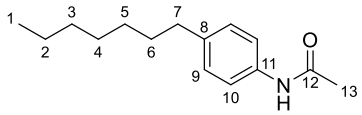
HR-MS (EI) Calcd. $[M]^{\cdot+}$: 219.1618, found: 219.1618.

11.2.4.6.2 Synthesis of *N*-(4-heptylphenyl)acetamide (62b)



61 **62b**

According to **GP1**, 30.0 mL (15.0 mmol, 1.70 eq., 0.5 M in THF) of 9-BBN, 2.10 mL (14.9 mmol, 1.70 eq.) of 1-heptene, 10.1 g (30.9 mmol, 3.50 eq.) of Cs_2CO_3, 0.04 g (0.03 mmol, 0.4 mol%) of $Pd(PPh_3)_4$ and 2.30 g (8.81 mmol, 1.00 eq.) of acetamide **61** were reacted in 67 mL H_2O and 67 mL 1,4-dioxane at 90 °C for 5 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) to afford 1.97 g (8.43 mmol, 96%) of the desired product **62b** as colorless solid.



M($C_{15}H_{23}NO$) 233.36 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 2:1) = 0.34.

^{1}H-NMR (500 MHz, $CDCl_3$), δ [ppm] = 7.48 (s, 1H, NH), 7.39 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-10), 7.11 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H-9), 2.55 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H-7), 2.14 (s, 3H, H-13), 1.63-1.53 (m, 2H, H-6), 1.33-1.23 (m, 8H, H-2, H-3, H-4, H-5), 0.88 (t, $^3J_{HH}$ = 7.0 Hz, 3H, H-1).

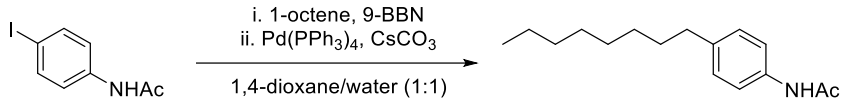
^{13}C-NMR (126 MHz, $CDCl_3$), δ [ppm] = 168.5 (C-12), 139.2 (C-8), 135.6 (C-11), 128.9 (C-9), 120.2 (C-10), 35.5 (C-7), 31.9 (C-3), 31.6 (C-6), 29.3 (C-4), 29.2 (C-5), 24.6 (C-13), 22.8 (C-2), 14.2 (C-1).

FT-IR ATR, v [cm^{-1}] = 3295 (w), 3258 (w), 3191 (w), 3126 (w), 3067 (w), 2955 (w), 2920 (m), 2850 (m), 1901 (w), 1662 (s), 1603 (s), 1548

(s), 1513 (s), 1467 (m), 1410 (s), 1369 (m), 1321 (s), 1265 (m), 1181 (w), 1012 (w), 965 (w), 829 (m), 811 (m), 748 (m), 655 (w), 606 (w), 517 (m).

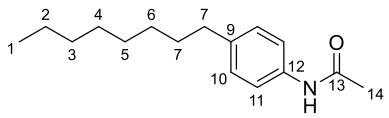
HR-MS (EI) Calcd. $[M]^{\cdot+}$: 233.1776, found: 233.1774.

11.2.4.6.3 Synthesis of *N*-(4-octylphenyl)acetamide (62c)



61 **62c**

According to **GP1**, 26.4 mL (13.2 mmol, 1.70 eq., 0.5 M in THF) of 9-BBN, 2.08 mL (13.2 mmol, 1.70 eq.) of 1-octene, 8.61 g (26.4 mmol, 3.50 eq.) of Cs_2CO_3, 0.03 g (0.03 mmol, 0.4 mol%) of $Pd(PPh_3)_4$ and 2.00 g (7.66 mmol, 1.00 eq.) of acetamide **61** were reacted in 58 mL H_2O and 58 mL 1,4-dioxane at 90 °C for 5 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) to afford 1.86 g (7.51 mmol, 98%) of the desired product **62c** as colorless solid.



M($C_{16}H_{25}NO$) 247.38 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 2:1) = 0.31.

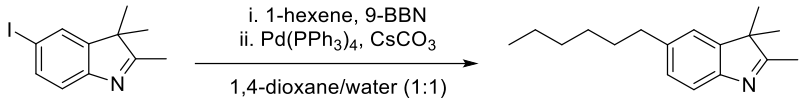
^{1}H-NMR (500 MHz, $CDCl_3$), δ [ppm] = 7.48 (s, 1H, NH), 7.39 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-11), 7.11 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H-10), 2.55 (m, 2H, H-8), 2.14 (s, 3H, H-14), 1.56 (p, $^3J_{HH}$ = 7.3 Hz, 2H, H-7), 1.34-1.23 (m, 10H, H-2, H-3, H-4, H-5, H-6), 0.88 (t, $^3J_{HH}$ = 6.9 Hz, 3H, H-1).

^{13}C-NMR (126 MHz, $CDCl_3$), δ [ppm] = 168.51 (C-13), 139.2 (C-9), 135.6 (C-12), 128.9 (C-10), 120.2 (C-11), 35.5 (C-8), 32.0 (C-3), 31.6 (C-7), 29.6 (C-5), 29.4 (C-4, C-6), 24.6 (C-14), 22.8 (C-2), 14.2 (C-1).

FT-IR ATR, v [cm^{-1}] = 3293 (m), 3257 (m), 3193 (w), 3126 (w), 3068 (w), 2957 (w), 2919 (s), 2849 (m), 2261 (w), 1904 (w) 1661 (s), 1603 (s), 1548 (s), 1513 (s), 1409 (s), 1368 (s), 1320 (s), 1268 (m), 1195 (w), 1123 (w), 1012 (w), 861 (w), 823 (w), 750 (m), 606 (m), 515 (s).

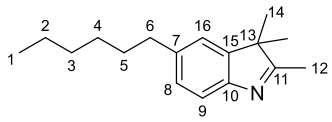
HR-MS (EI) Calcd. $[M]^{\cdot+}$: 247.1931, found: 247.1932.

11.2.4.6.4 Synthesis of 5-hexyl-2,3,3-trimethylindolenine (58b)



64 **58b**

According to **GP1**, 3.40 mL (1.70 mmol, 1.70 eq., 0.5 M in THF) of 9-BBN, 0.21 mL (1.70 mmol, 1.70 eq.) of 1-hexene, 1.14g (3.50 mmol, 3.50 eq.) of Cs_2CO_3, 4.40 mg (0.004 mmol, 0.4 mol%) of $Pd(PPh_3)_4$ and 0.29 g (1.00 mmol, 1.00 eq.) of indole **64** were reacted in 7.60 mL H_2O and 7.60 mL 1,4-dioxane at 90 °C for 5 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 5:1) to afford 0.20 g (0.82 mmol, 82%) of the desired product **58b** as a red oil.



M($C_{17}H_{25}N$) 243.39 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 5:1) = 0.24.

^{1}H-NMR (500 MHz, $CDCl_3$), δ [ppm] = 7.42 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H-9), 7.09 (dd, $^{3,4}J_{HH}$ = 7.8, 1.6 Hz, 1H, H-8), 7.08 (s, 1H, H-16), 2.63 (t, $^3J_{HH}$ = 7.8 Hz, 2H, H-6), 2.25 (s, 3H, H-12), 1.61 (p, $^3J_{HH}$ =7.5 Hz, 2H, H-5), 1.39-1.22 (m, 6H, H-2, H-3, H-4), 1.28 (s, 6H, H-14), 0.88 (t, $^3J_{HH}$ =7.0 Hz, 3H, H-1).

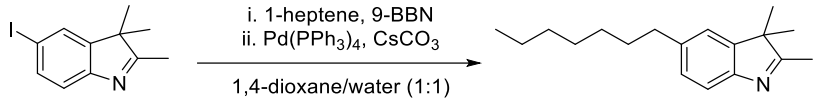
^{13}C-NMR (126 MHz, $CDCl_3$), δ [ppm] = 187.1 (C-11), 151.8 (C-10), 145.8 (C-15), 140.2 (C-7), 127.6 (C-8), 121.5 (C-16), 119.5 (C-9), 53.5 (C-13), 36.2 (C-6), 32.0 (C-5), 31.8, (C-3), 29.2 (C-4), 23.3 (C-14), 22.7 (C-2), 15.5 (C-12), 14.2 (C-1).

FT-IR ATR, v [cm^{-1}] = 3307 (bw), 2959 (m), 2926 (s), 2856 (m), 1714 (w), 1580 (m), 1548 (w), 1462 (s), 1430 (m), 1378 (m), 1251 (w), 1204 (m), 1022 (m), 888 (w), 825 (s), 754 (w), 613 (w).

HR-MS (EI) Calcd. $[M]^{\cdot+}$: 243.1981, found: 243.1981.

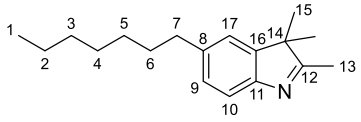
GC-MS m/z (%) = 243 (47), 228 (7), 172 (100), 157 (24), 128 (8), 115 (16), 91 (9), 77 (5).

11.2.4.6.5 Synthesis of 5-heptyl-2,3,3-trimethylindolenine (58c)



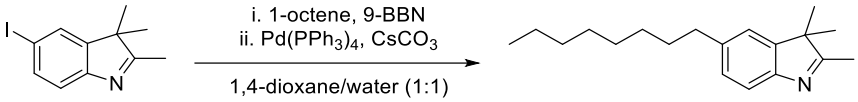
64 **58c**

According to **GP1**, 23.2 mL (11.6 mmol, 1.10 eq., 0.5 M in THF) of 9-BBN, 1.63 mL (11.6 mmol, 1.10 eq.) of 1-heptene, 8.57 g (26.3 mmol, 2.50 eq.) of Cs_2CO_3, 60 mg (0.05 mmol, 0.5 mol%) of $Pd(PPh_3)_4$ and 3.00 g (10.5 mmol, 1.00 eq.) of indole **64** were reacted in 7 mL H_2O and 7 mL 1,4-dioxane at 90 °C for 5 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 3:1) to afford 1.99 g (7.72 mmol, 74%) of the desired product **58c** as a red oil.



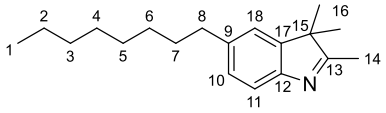
M($C_{18}H_{27}N$)	257.42 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 3:1) = 0.23.
^{1}H-NMR	(500 MHz, $CDCl_3$), δ [ppm] = 7.42 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H-10), 7.10 (dd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.7 Hz, 1H, H-9), 7.08 (s, 1H, H-17), 2.66 - 2.61 (m, 2H, H-7), 2.26 (s, 3H, H-13) 1.66 - 1.59 (m, 2H, H-6), 1.35 - 1.31 (m, 8H, H-5, H-4, H-3, H-2), 1.29 (s, 6H, H-15), 0.91 - 0.85 (m, 3H, H-1).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 187.11 (C-12), 151.51 (C-11), 145.67 (C-16), 140.16 (C-8), 127.53 (C-9), 121.37 (C-17), 119.36 (C-10), 53.43 (C-14), 36.04 (C-7), 31.83 (C-6), 29.38 (C-5, C-4), 23.20 (C-15), 22.67 (C-3, C-2), 15.34 (C-13), 14.11(C-1).
FT-IR	ATR, v [cm^{-1}] = 3791 (w), 3288 (w), 3004 (w), 2958 (s), 2925 (s), 2854 (s), 2352 (w), 2085 (w), 1880 (w), 1740 (m), 1696 (m), 1617 (m), 1579 (s), 1462 (s), 1429 (s), 1377 (m), 1360 (m), 1298 (m), 1249 (m), 1203 (m), 1140 (m), 1121 (m), 1097 (m), 1047 (m), 1031 (m), 944 (m), 883 (m), 826 (s), 773 (m), 723 (m), 677 (m), 649 (m), 634 (m), 612 (m), 536 (m).
HR-MS (EI)	Calcd. $[M]^{\cdot+}$: 257.2138, found: 257.2138.
GC-MS	m/z (%) = 257 (31), 172 (100), 157 (12), 115 (8), 91 (4).

11.2.4.6.6 Synthesis of 5-octyl-2,3,3-trimethylindolenine (58d)



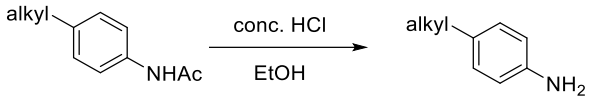
64 **58d**

According to **GP1**, 69.0 mL (34.8 mmol, 1.10 eq., 0.5 M in THF) of 9-BBN, 5.50 mL (34.8 mmol, 1.10 eq.) of 1-octene, 25.7 g (79.0 mmol, 2.50 eq.) of Cs_2CO_3, 0.15 g (0.13 mmol, 0.4 mol%) of $Pd(PPh_3)_4$ and 9.00 g (31.6 mmol, 1.00 eq.) of indole **64** were reacted in 22 mL H_2O and 22 mL 1,4-dioxane at 90 °C for 5 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 5:1) to afford 6.70 g (16.2 mmol, 51%) of the desired product **58d** as a red oil.



M($C_{18}H_{27}N$)	271.45 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 2:1) = 0.38.
^{1}H-NMR	(500 MHz, $CDCl_3$), δ [ppm] = 7.44 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H-11), 7.12 - 7.10 (m, 2H, H-10, H-18), 2.71 - 2.62 (m, 2H, H-8), 2.28 (s, 3H, H-14), 1.65 - 1.63 (m, 3H, H-7), 1.30 (m, 16H, H-2, H-3, H-4, H-5, H-6, H-16), 0.94 - 0.86 (m, 3H, H-1).
^{13}C-NMR	(101 MHz, $CDCl_3$), δ [ppm] = 184.0 (C-13), 150.2 (C-12), 141.7 (C-17), 137.1 (C-9), 127.3 (C-10), 122.8 (C-18), 109.2 (C-11), 44.6 (C-15), 35.7 (C-8), 31.9 (C-7), 31.8 (C-6), 29.4 (C-5), 29.3 (C-4), 29.2 (C-3), 24.4 (C16), 22.6 (C-2), 14.1 (C-1), 14.1 (C-14).
FT-IR	ATR, v [cm^{-1}] = 3205 (w), 3005 (w), 2958 (m), 2924 (s), 2854 (s), 2075 (w), 1880 (w), 1741 (w), 1700 (w), 1618 (w), 1580 (m), 1462 (s), 1429 (m), 1377 (m), 1360 (m), 1299 (m), 1270 (m), 1249 (m), 1204 (m), 1140 (m), 1121 (m), 1097 (m), 1047 (m), 997 (m), 944 (m), 884 (m), 825 (s), 774 (m), 722 (m), 676 (w), 649 (m), 634 (m), 610 (w), 568 (w), 536 (w), 510 (w).
HR-MS (EI)	Calcd. $[M]^{\cdot+}$: 271.2294, found: 271.2291.

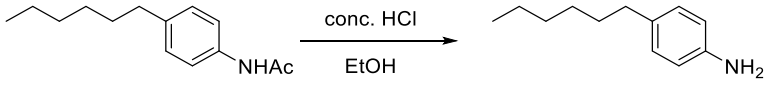
11.2.4.7 Deprotection of Arylamines: General protocol (GP2)



62 **56**

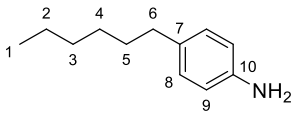
Acetamide **62** (1.00 eq.) was dissolved in EtOH. Conc. HCl was added and the solution was stirred at reflux. After cooling to rt, the reaction was neutralized with sat. aq. $NaHCO_3$. The aq. phase was extracted thrice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure.

11.2.4.7.1 Synthesis of 4-hexylaniline (56b)



62a **56b**

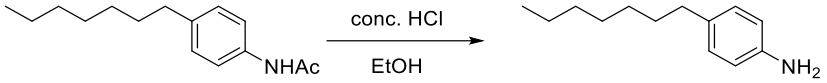
According to **GP2**, 1.20 g (5.47 mmol, 1.00 eq.) of acetamide **62a** were reacted with 6.40 mL conc. HCl in 6.40 mL EtOH for 5.5 h at reflux. 0.98 g (5.60 mmol, quant.) of the desired product **56b** could be obtained as red liquid.



M($C_{12}H_{19}N$)	177.29 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 2:1) = 0.34.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 6.98 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-8), 6.63 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-9), 3.41 (bs, 2H, NH_2), 2.50 (t, $^3J_{HH}$ = 8.0 Hz, 2H, H-6), 1.56 (p, $^3J_{HH}$ = 7.7 Hz, 2H, H-5), 1.32 (m, 6H, H-2, H-3, H-4), 0.93-0.85 (m, 3H, H-1).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 144.1 (C-10), 133.3 (C-7), 129.3 (C-8), 115.4 (C-9), 35.2 (C-6), 31.9 (C-5), 31.9 (C-3), 29.1 (C-4), 22.8 (C-2), 14.2 (C-1).
FT-IR	ATR, v [cm^{-1}] = 3351 (w), 3220 (w), 3017 (w), 3001 (w), 2956 (w), 2924 (m), 2854 (m), 2156 (w), 1875 (w), 1622 (m), 1515 (s), 1466 (w), 1378 (w), 1270 (m), 1179 (w), 1126 (w), 822 (m), 643 (w), 551 (m).
GC-MS	m/z (%) = 177 (24), 106 (100).

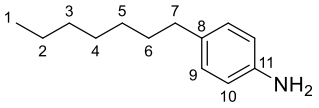
HR-MS (EI) Calcd. $[M]^{\cdot+}$: 177.1511, found: 177.1512.

11.2.4.7.2 Synthesis of 4-heptylaniline (56c)



62b **56c**

According to **GP2**, 1.80 g (7.71 mmol, 1.00 eq.) of acetamide **62b** were reacted with 9.50 mL conc. HCl in 9.50 mL EtOH for 4 h at reflux. 1.47 g (7.68 mmol, 99%.) of the desired product **56c** could be obtained as red liquid.



M($C_{13}H_{21}N$) 191.32 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:1) = 0.81.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 6.98 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-9), 6.63 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-10), 3.51 (s, 2H, NH_2), 2.50 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H-7), 1.63-1.53 (m, 2H, H-6), 1.38-1.25 (m, 8H, H-2, H-3, H-4, H-5), 0.89 (t, $^3J_{HH}$ =7.0 Hz, 3H, H-1).

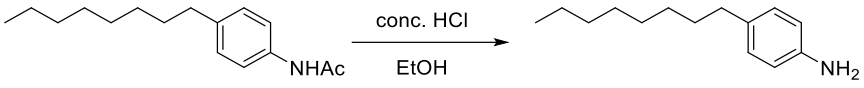
^{13}C-NMR (126 MHz, $CDCl_3$), δ [ppm] = 144.1 (C-10), 133.3 (C-7), 129.3 (C-8), 115.4 (C-9), 35.2 (C-6), 31.9 (C-5), 31.9 (C-3), 29.1 (C-4), 22.8 (C-2), 14.2 (C-1).

FT-IR ATR, v [cm^{-1}] = 3351 (w), 3220 (w), 3017 (w), 3001 (w), 2956 (w), 2924 (m), 2854 (m), 2156 (w), 1875 (w), 1622 (m), 1515 (s), 1466 (w), 1378 (w), 1270 (m), 1179 (w), 1126 (w), 822 (m), 643 (w), 551 (m).

LR-MS (EI) Calcd. $[M]^{\cdot+}$: 191.2, found: 191.5.

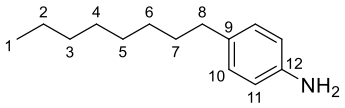
HR-MS (EI) Calcd. $[M]^{\cdot+}$: 191.1668, found: 191.1669.

11.2.4.7.3 Synthesis of 4-octylaniline (56d)



62c **56d**

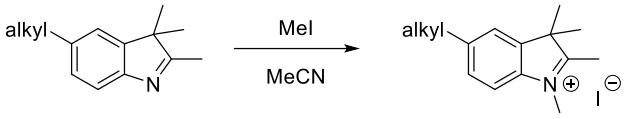
According to **GP2**, 1.70 g (6.87 mmol, 1.00 eq.) of acetamide **62c** were reacted with 8.10 mL conc. HCl in 8 mL EtOH for 4 h at reflux. 1.40 g (6.81 mmol, 99%.) of the desired product **56d** could be obtained as red liquid.



M($C_{14}H_{23}N$)	204.35 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:1) = 0.81.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 6.98 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-10), 6.63 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-11), 3.39 (s, 2H, NH_2), 2.50 (t, $^3J_{HH}$ = 7.9 Hz, 2H, H-8), 1.56 (p, $^3J_{HH}$ = 7.4 Hz, 2H, H-7), 1.31-1.27 (m, 10H, H-2, H-3, H-4, H-5, H-6), 0.89 (t, $^3J_{HH}$ = 7.0 Hz, 3H, H-1).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 144.1 (C-12), 133.3 (C-9), 129.3 (C-10), 115.4 (C-11), 35.2 (C-8), 32.0 (C-7), 32.0 (C-3), 29.7 (C-5), 29.4 (C-4), 29.4 (C-6), 22.8 (C-2), 14.2 (C-1).
FT-IR	ATR, v [cm^{-1}] = 3352 (w), 2956 (w), 2923 (s), 2853 (m), 1874 (w), 1623 (m), 1516 (s), 1465 (w), 1272 (m) 1179 (w), 1125 (w), 1078 (w), 822 (m), 552 (m).
HR-MS (EI)	Calcd. $[M]^{\cdot+}$: 205.1825, found: 205.1823.

The analytical data are in accordance with the literature[183].

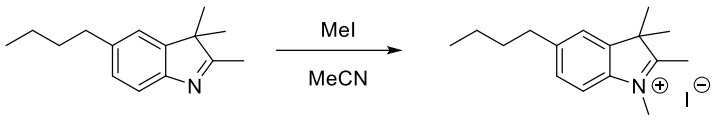
11.2.4.8 *Methylation*: General protocol (GP3)



58 **59**

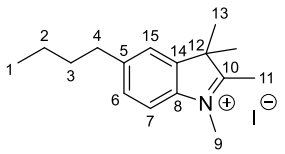
Indole **58** (1.00 eq.) was dissolved in MeCN and MeI (3.00 eq.) was added. The reaction mixture was stirred at reflux. The solvent was removed under reduced pressure and the residue was washed with MTBE.

11.2.4.8.1 Synthesis of 5-butyl-1,2,3,3-tetramethylindolium iodide (59a)



58a **59a**

According to **GP3**, 1.00 g (4.65 mmol, 1.00 eq.) of indole **58a** was reacted with 0.87 mL (13.9 mmol, 3.00 eq) of MeI in 8 mL MeCN at reflux for 16 h. 1.57 g (4.40 mmol, 95%, Lit.: 95%[111]) of the desired product **59a** could be obtained as a hygroscopic purple solid.

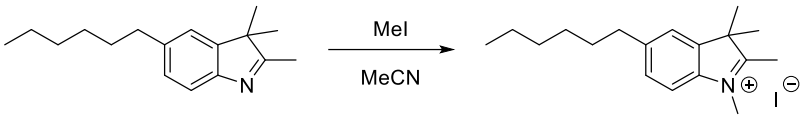


M($C_{16}H_{24}IN$)	357.28 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 2:1) = 0.36.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.55 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H-7), 7.33 (dd, $^{3,4}J_{HH}$ = 8.3 Hz, 1.5 Hz, 1H, H-6), 7.29-7.28 (m, 1H, H-15), 4.23 (s, 3H, H-9), 3.07 (s, 3H, H-11), 2.68 (t, $^3J_{HH}$ = 7.9 Hz, 2H, H-4), 1.61 (s, 6H, H-13), 1.60-1.55 (m, 2H, H-3), 1.35 (h, $^3J_{HH}$ = 7.4 Hz, 2H, H-2), 0.92 (t, $^3J_{HH}$ = 7.4 Hz, 3H, H-1).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 194.7 (C-10), 146.0 (C-5), 141.5 (C-14), 134.0 (C-8), 129.5 (C-6), 122.9 (C-15), 114.9 (C-7), 54.4 (C-12), 37.4 (C-9), 35.7 (C-4), 33.6 (C-3), 23.3 (C-13), 22.4 (C-2), 17.2 (C-11), 13.9 (C-1).
FT-IR	ATR, v [cm^{-1}] = 3446 (w), 3008 (w), 2956 (s), 2928 (s), 2859 (m), 1630 (m), 1614 (m), 1598 (m), 1481 (s), 1366 (s), 1334 (m), 1236 (w), 1161 (w), 1033 (w), 947 (m), 829 (s), 716 (w), 633 (w), 551 (m).

HR-MS (ESI) Calcd. $[M\text{-}I]^+$: 230.1903, found: 230.1898.

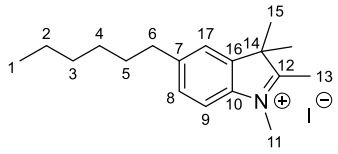
The analytical data are in accordance with the literature[111].

11.2.4.8.2 Synthesis of 5-hexyl-1,2,3,3-tetramethylindolium iodide (59b)



58b **59b**

According to **GP3**, 1.20 g (5.57 mmol, 1.00 eq.) of indole **58b** were reacted with 1.04 mL (16.7 mmol, 3.00 eq) of MeI in 10 mL MeCN at reflux for 16 h. 1.86 g (5.20 mmol, 93%) of the desired product **59b** could be obtained as a hygroscopic red solid.



M($C_{16}H_{24}IN$) 385.33 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:1) = 0.43.

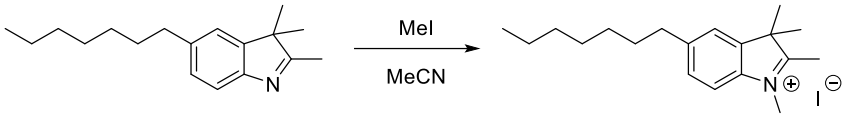
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.53 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H-9), 7.36 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H-8), 7.31 (s, 1H, H-17), 4.25 (s, 3H, H-11), 3.10 (s, 3H, H-13), 2.71 (t, $^3J_{HH}$ = 7.8 Hz, 2H, H-6), 1.65 (s, 6H, H-15), 1.63 - 1.59 (m, 2H, H-5), 1.38 - 1.23 (m, 6H, H-2, H-3, H-4), 0.89 (t, $^3J_{HH}$ = 6.8 Hz, 3H, H-1).

^{13}C-NMR (126 MHz, $CDCl_3$), δ [ppm] = 194.85 (C-12), 146.4 (C-7), 141.6 (C-16), 140.0 (C-10), 129.7 (C-8), 123.1 (C-17), 114.8 (C-9), 54.5 (C-14), 37.3 (C-11), 36.1 (C-6), 31.7 (C-5), 31.6 (C-3), 29.1 (C-4), 23.4 (C-15), 22.7 (C-2), 17.2 (C-13), 14.2 (C-1).

FT-IR ATR, v [cm^{-1}] = 3405 (w), 3008 (w), 2955 (m), 2925 (s), 2855 (s), 2028 (w), 1915 (w), 1630 (m), 1614 (m), 1598 (m), 1481 (s), 1465 (s), 1436 (s), 1393 (m), 1377 (m), 1366 (m), 1334 (m), 1300 (w), 1269 (w), 1236 (w), 1209 (w), 1177 (w), 1162 (w), 1142 (w), 1116 (w), 1092 (w), 1064 (w), 1033 (w), 990 (m), 946 (w), 891 (w), 829 (m), 758 (w), 724 (w), 686 (w), 675 (w), 633 (w), 586 (w), 551 (m).

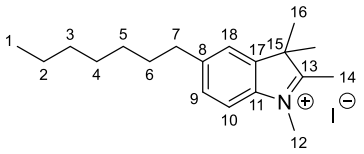
HR-MS (ESI) Calcd. $[M\text{-}I]^{\cdot+}$: 258.2216, found: 258.2215.

11.2.4.8.3 Synthesis of 5-heptyl-1,2,3,3-tetramethylindolium iodide (59c)



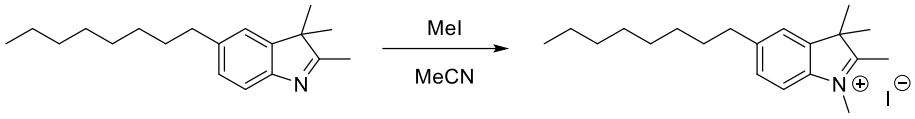
58c **59c**

According to **GP3**, 1.90 g (7.38 mmol, 1.00 eq.) of indole **58c** were reacted with 1.83 mL (29.5 mmol, 4.00 eq) of MeI in 15 mL MeCN at reflux for 2 h. 2.74 g (6.86 mmol, 93%) of the desired product **59c** could be obtained as a red solid.



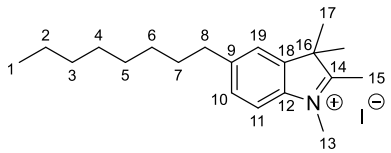
M($C_{19}H_{30}IN$)	399.36 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:1) = 0.57.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.57 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H-10), 7.36 (dd, $^{3,4}J_{HH}$ = 8.2, 1.6 Hz, 1H, H-9), 7.31 (s, 1H, H-18), 4.27 (s, 3H, H-12), 3.11 (s, 3H, H-14), 2.71 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H-7), 1.65 (s, 6H, H-16), 1.63 - 1.62 (m, 2H, H-6) 1.36 - 1.24 (m, 8H, H-5, H-4, H-3, H-2), 0.89 (t, $^3J_{HH}$ = 6.9 Hz, 3H, H-1).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 194.6 (C-13), 146.1 (C-8), 141.4 (C-17), 139.9 (C-11), 129.4 (C-9), 122.8 (C-18), 114.8 (C-10), 54.3 (C-15), 37.3 (C-12), 35.9 (C-7), 31.7 (C-6), 31.4 (C-5), 29.2 (C-4), 29.0 (C-3), 23.2 (C-16), 22.6 (C-2), 17.2 (C-14), 14.0 (C-1).
FT-IR	ATR, v [cm^{-1}] = 3439 (w), 3030 (w), 3010 (w), 2956 (m), 2925 (s), 2854 (s), 1924 (w), 1631 (w), 1615 (w), 1599 (w), 1481 (m), 1464 (s), 1394 (w), 1377 (w), 1361 (w), 1334 (w), 1290 (w), 1275 (w), 1236 (w), 1161 (w), 1142 (w), 1092 (w), 1065 (w), 1034 (w), 991 (w), 950 (w), 891 (w), 833 (w), 821 (m), 757 (w), 722 (w), 686 (w), 674 (w), 633 (w), 586 (w), 552 (w).
HR-MS (ESI)	Calcd. $[M-I]^+$: 272.2372, found: 272.2372.

11.2.4.8.4 Synthesis of 5-octyl-1,2,3,3-tetramethylindolium iodide (59d)



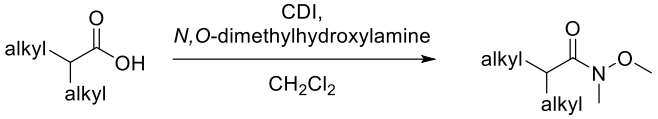
58d **59d**

According to **GP3**, 4.26 g (15.7 mmol, 1.00 eq.) of indole **58d** were reacted with 2.93 mL (47.1 mmol, 3.00 eq) of MeI in 30 mL MeCN at reflux for 16.5 h. 5.31 g (12.8 mmol, 82%) of the desired product **59d** could be obtained as a red solid.



M($C_{20}H_{32}IN$)	413.39 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:1) = 0.59.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.57 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H-11), 7.36 (d, $^3J_{HH}$ = 8.1 Hz, 1H, H-10), 7.31 (s, 1H, H-19), 4.27 (s, 3H, H-15), 3.11 (s, 3H, H-13), 2.74 – 2.67 (m, 2H, H-8), 1.65 (s, 6H, H-17), 1.39 – 1.24 (m, 12H, H-7, H-6, H-5, H-4, H-3, H-2), 0.88 (t, $^3J_{HH}$ = 6.9 Hz, 3H, H-1).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 194.6 (C-14), 146.1 (C-9), 141.4 (C-18), 139.8 (C-12), 129.5 (C-10), 122.8 (C-19), 114.8 (C-11), 54.3 (C-16), 37.3 (C-13), 36.0 (C-8), 31.8 (C-7), 31.4 (C-6), 29.2 (C-5), 29.2 (C-4), 29.2 (C-3), 23.2 (C-17), 22.6 (C-2), 17.2 (C-15), 14.1 (C-1).
FT-IR	ATR, v [cm^{-1}] = 3408 (w), 3010 (w), 2956 (m), 2923 (s), 2853 (s), 1918 (w), 1631 (w), 1615 (w), 1598 (w), 1482 (m), 1465 (m), 1393 (w), 1377 (m), 1366 (m), 1335 (w), 1300 (w), 1272 (w), 1236 (w), 1161 (w), 1142 (w), 1091 (w), 1064 (w), 1034 (w), 990 (w), 948 (w), 888 (w), 829 (m), 757 (w), 721 (w), 686 (w), 633 (w), 587 (w), 551 (w).
HR-MS (ESI)	Calcd. $[M-I]^+$: 286.2529, found: 286.2529.

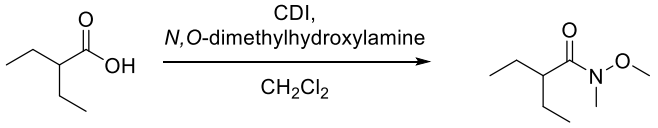
11.2.4.9 Synthesis of *N*-methoxy-*N*-methylamides: General protocol (GP4)



49 **50**

Carboxylic acid **49** (1.00 eq.) was dissolved in CH_2Cl_2. At 0 °C *N*,*O*-dimethylhydroxylamine (1.50 eq.) and CDI (1.50 eq.) were added and the mixture was stirred at rt. The reaction mixture was quenched with H_2O, the layers were separated and the aq. phase was extracted with CH_2Cl_2. The combined org. layers were washed with 2 M HCl and sat. aq. $NaHCO_3$ and dried over $MgSO_4$. The solvent was removed under reduced pressure.

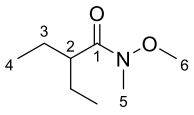
11.2.4.9.1 Synthesis of 2-ethyl-*N*-methoxy-*N*-methylbutanamide (50a)



49a **50a**

According to **GP4**, 1.00 g (8.61 mmol, 1.00 eq.) of 2-ethylbutyric acid **49a** was reacted with 1.26 g (12.9 mmol, 1.50 eq.) of *N*,*O*-dimethylhydroxylamine and 2.09 g (12.9 mmol, 1.50 eq.) of CDI in 17 mL CH_2Cl_2 over 22 h. 1.29 g (8.10 mmol, 94%, Lit.[184]: 84%) of the desired product **50a** were obtained as a colorless oil.

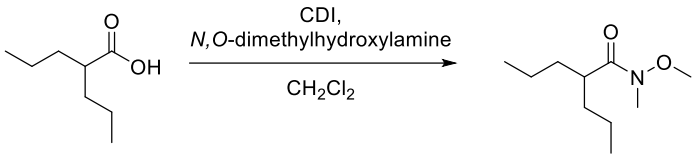
The crude product was used without further purification.



M($C_8H_{17}NO_2$)	159.23 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 3:1) = 0.52.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 3.68 (s, 3H, H-6), 3.21 (s, 3H, H-5), 2.70 (br s, 1H, H-2), 1.68 – 1.59 (m, 2H, H-3), 1.53 – 1.45 (m, 2H, H-3'), 0.88 (t, 6H, $^3J_{HH}$ = 7.4 Hz, H-4).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 176.2 (C-1), 61.3 (C-6), 43.9 (C-2), 36.2 (C-5), 25.4 (C-3), 12.1 (C-4).
FT-IR	ATR, v [cm^{-1}] = 3499 (w), 3204 (w), 2965 (m), 2936 (m), 2876 (w), 2103 (w), 1652 (s), 1529 (w), 1461 (s), 1418 (m), 1388 (m), 1329 (m), 1256 (w), 1177 (m), 1156 (m), 1114 (m), 1096 (m),

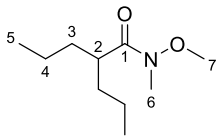
	1064 (m), 1041 (m), 996 (s), 957 (w), 930 (m), 864 (m), 841 (m), 833 (m), 762 (m), 740 (m), 710 (m), 664 (m), 615 (m), 601 (m), 582 (m), 520 (m).
GC-MS	m/z (%) = 159 (9), 130 (8), 99 (90), 71 (100), 61 (67), 55 (76).

11.2.4.9.2 Synthesis of 2-propyl-*N*-methoxy-*N*-methylbutanamide (50b)



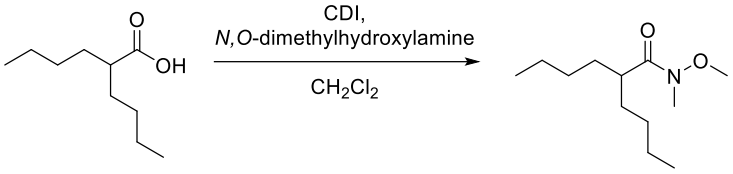
49b **50b**

According to **GP4**, 1.00 g (6.93 mmol, 1.00 eq.) of 2-propylpentanoic acid **49b** was reacted with 1.06 g (10.4 mmol, 1.50 eq.) of *N*,*O*-dimethylhydroxylamine and 1.69 g (10.4 mmol, 1.50 eq.) of CDI in 14 mL CH_2Cl_2 over 22 h. 1.24 g (6.62 mmol, 96%) of the desired product **50b** was obtained as a colorless oil.



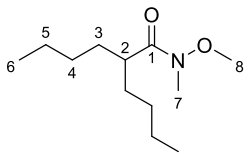
M($C_{10}H_{21}NO_2$)	187.28 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 4:1) = 0.38.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 3.70 (s, 3H, H-7), 3.21 (s, 3H, H-6), 2.87 (br s, 1H, H-2), 1.63 (m, 2H, H-3), 1.44 – 1.24 (m, 6H, H-3, H-4), 0.91 (t, $^3J_{HH}$ = 7.1 Hz, 6H, H-5).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 177.7 (C-1), 61.5 (C-7), 40.4 (C-2), 34.9 (C-3), 32.2 (C-6), 20.9 (C-4), 14.2 (C-5).
FT-IR	ATR, v [cm^{-1}] = 2957 (s), 2932 (s), 2873 (m), 2068 (w), 1731 (m), 1661 (s), 1464 (s), 1415 (m), 1385 (s), 1318 (m), 1235 (m), 1176 (s), 1149 (m), 1118 (m), 1086 (m), 1002 (s), 925 (m), 877 (m), 768 (m), 733 (m), 710 (m), 612 (m), 544 (m).
GC-MS	m/z (%) = 188 (2), 158 (5), 127 (74), 116 (13), 99 (63), 69 (15), 57 (100).
HR-MS (ESI)	Calcd. $[M-I]^{\cdot+}$: 215.1879, found: 216.1956.

11.2.4.9.3 Synthesis of 2-propyl-N-methoxy-N-methylbutanamide (50c)



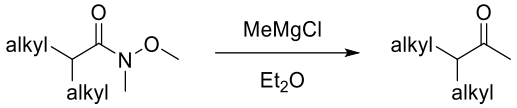
49c **50c**

According to **GP4**, 10.0 g (58.0 mmol, 1.00 eq.) of 2-butylhexanoic acid **49c** were reacted with 6.04 g (87.0 mmol, 1.50 eq.) of *N*,*O*-dimethylhydroxylamine and 1.69 g (10.4 mmol, 1.50 eq.) of CDI in 14 mL CH_2Cl_2 over 22 h. 8.36 g (38.8 mmol, 67%) of the desired product **50c** were obtained as a colorless oil.



M($C_{12}H_{25}NO_2$)	215.34 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 4:1) = 0.26.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 3.68 (s, 3H, H-8), 3.20 (s, 3H, H-7), 2.82 (s, 1H, H-2), 1.66 – 1.58 (m, 2H, H-3), 1.42 (m, 2H,-3), 1.32 - 1.22 (m, 8H, H-4, H-5), 0.88 (t, $^3J_{HH}$ = 7.2 Hz, 6H, H-6).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 178.22 (C-1), 61.40 (C-8), 40.77 (C-2), 32.50 (C-7), 31.96 (C-3), 29.94 (C-4), 22.87 (C-5), 22.64 (C-6).
FT-IR	ATR, v [cm^{-1}] = 2957 (s), 2929 (s), 2872 (m), 2859 (m), 2075 (w), 1732 (m), 1662 (s), 1459 (s), 1414 (m), 1386 (m), 1322 (m), 1175 (s), 1149 (m), 1115 (m), 1088 (m), 992 (s), 907 (m), 784 (w), 729 (m), 710 (m), 613 (m), 547 (m).
HR-MS (EI)	Calcd. $[M-I]^+$: 215.1879 found: 216.1956.
GC-MS	m/z (%) = 214 (1), 155 (45), 127 (23), 85 (78), 71 (100), 57 (76).

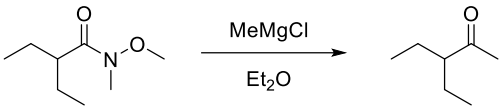
11.2.4.10 Synthesis of long-chain ketones: General protocol (GP5)



50 **36**

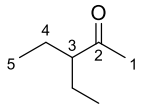
Amide **50** (1.00 eq.) was dissolved in Et_2O and cooled to 0 °C. MeMgCl (2.50 eq., 2.85 M in Et_2O) was added dropwise. After stirring at rt, the reaction mixture was quenched with sat. aq. NH_4Cl. The layers were separated and the aq. phase was extracted with Et_2O. The combined org. layers were washed with H_2O and sat. aq. NaCl and dried over $MgSO_4$. The solvent was removed under reduced pressure.

11.2.4.10.1 Synthesis of 2-ethylpentan-2-one (36b)



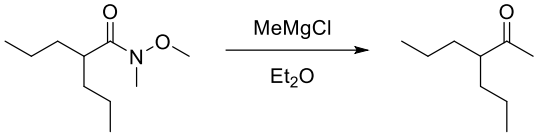
50a **36b**

According to **GP5**, 1.29 g (8.10 mmol, 1.00 eq.) of amide **50a** were reacted with 7.15 g (20.3 mmol, 2.50 eq.) MeMgCl in 32 mL Et_2O for 15 h at rt. 0.79 g (6.92 mmol, 85%) of the desired product **36b** were obtained as colorless oil.



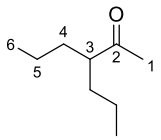
M($C_7H_{14}O$)	114.19 g/mol.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 2.34 – 2.28 (m, 1H, H-3), 2.12 (s, 3H, H-1), 1.66 – 1.56 (m, 2H, H-4), 1.53 – 1.42 (m, 2H, H-4'), 0.87 (t, $^3J_{HH}$ = 7.5 Hz, 6H, H-5).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 213.2 (C-2), 56.5 (C-3), 28.9 (C-1), 24.3 (C-4), 11.9 (C-5).
FT-IR	ATR, ν [cm^{-1}] = 3145 (m), 2960 (m), 2919 (m), 2850 (m), 1991 (w), 1649 (s), 1593 (s), 1456 (s), 1374 (s), 1327 (s), 1257 (s), 1227 (s), 1064 (s), 917 (m), 823 (s), 755 (s), 661 (s), 634 (s).

11.2.4.10.2 Synthesis of 2-propylhexan-2-one (36c)



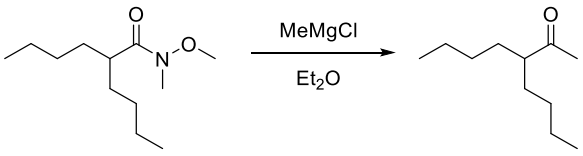
50b **36c**

According to **GP5**, 1.24 g (6.62 mmol, 1.00 eq.) of amide **50b** were reacted with 5.88 g (16.6 mmol, 2.50 eq.) MeMgCl in 27 mL Et_2O for 16 h at rt. 0.77 g (5.44 mmol, 82%) of the desired product **36c** were obtained as colorless oil.



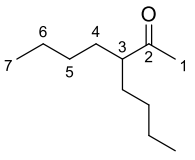
M($C_9H_{18}O$)	142.24 g/mol.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 2.49 – 2.43 (m, 1H, H-3), 2.11 (s, 3H, H-1), 1.60 – 1.52 (m, 2H, H-4), 1.42 – 1.34 (m, 2H, H-4'), 1.30 – 1.21 (m, H-5, 4H), 0.90 (t, $^3J_{HH}$ = 7.3 Hz, 6H, H-6).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 213.3 (C-2), 53.1 (C-3), 34.1 (C-4), 28.7 (C-1), 20.8 (C-5), 14.3 (C-6).
FT-IR	ATR, v [cm^{-1}] = 2958 (s), 2932 (s), 2874 (m), 1709 (s), 1465 (m), 1379 (m), 1353 (m), 1239 (w), 1174 (m), 1136 (m), 1112 (w), 599 (w).
GC-MS	m/z (%) = 143 (23), 98 (12), 69 (47), 59 (100), 55 (52).

11.2.4.10.3 Synthesis of 2-butylheptan-2-one (36d)



50c **36d**

According to **GP5**, 3.83 g (17.8 mmol, 1.00 eq.) of amide **50b** were reacted with 15.9 g (44.5 mmol, 2.50 eq.) MeMgCl in 53 mL Et_2O for 7 h at rt. 2.51 g (14.7 mmol, 83%) of the desired product **36d** were obtained as colorless oil.



M($C_{11}H_{22}O$)	170.30 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 3:1) = 0.83.

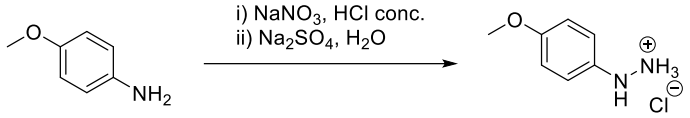
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 2.42 (m, 1H, H-3), 2.11 (s, 3H, H-1), 1.63 – 1.51 (m, 2H, H-4), 1.46 – 1.35 (m, 2H, H-4), 1.35 – 1.24 (m, 4H, H-6), 1.20 (m, 4H, H-5,), 0.88 (t, $^{3}J_{HH}$ = 7.2 Hz, 6H, H-7).

^{13}C-NMR (126 MHz, $CDCl_3$), δ [ppm] = 213.2 (C-2), 53.3 (C-3), 31.4 (C-4), 29.6 (C-6), 28.6 (C-1), 22.8 (C-5), 13.9 (C-7).

FT-IR ATR, v [cm^{-1}] = 2957 (s), 2930 (s), 2873 (m), 2859 (m), 1761 (w), 1710 (s), 1466 (m), 1459 (m), 1376 (m), 1351 (m), 1281 (m), 1219 (m), 1169 (m), 1136 (m), 1115 (m), 1069 (m), 1044 (m), 944 (m), 918 (m), 732 (m), 647 (m), 599 (m), 558 (m).

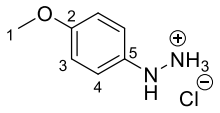
GC-MS m/z (%) = 170 (1), 114 (59), 99 (8), 85 (43), 71 (100), 57 (36).

11.2.4.11 Synthesis of 2-(4-methoxyphenyl)hydrazin-1-ium chloride (35)



34 **35**

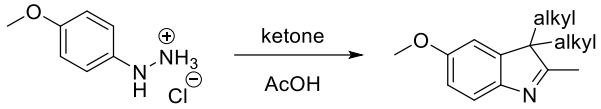
10.0 g (81.2 mmol, 1.00 eq.) of *p*-anisidine (**34**) were added to 25 mL conc. HCl at 0 °C. A solution of 5.60 g (81.2 mmol, 1.00 eq.) of $NaNO_3$ in 25 mL H_2O was added dropwise. The reaction mixture was stirred for 2 h at rt. A solution of 40.9 g (32.5 mmol, 4.00 eq.) of Na_2SO_3 in 150 mL H_2O was added at 0 °C. The reaction mixture was heated to 70 °C for 2 h. The solution was cooled to 0 °C and the resulting precipitation was filtered off and washed with cold H_2O. 10.8 g (62.3 mmol, 77%, Lit.[121]: 91%) of the desired product were obtained as a yellow solid.



M($C_7H_{11}ClN_2O$)	174.63 g/mol.
^{1}H-NMR	(300 MHz, DMSO-d_6) δ [ppm] = 10.12 (s, 1H, NH), 7.75 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H-3), 7.11 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H-4), 4.21 (s, 3H, NH_3), 3.85 (s, 3H, H-1).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 124.4 (C-3), 114.6 (C-4), 55.5 (C-3).
FT-IR	ATR, ν [cm^{-1}] = 3213 (w), 2991 (m), 2932 (m), 2835 (m), 2691 (m), 2060 (w), 1953 (w), 1600 (m), 1591 (m), 1560 (w), 1512 (s), 1497 (s), 1463 (m), 1436 (w), 1414 (w), 1331 (w), 1315 (w), 1303 (m), 1254 (s), 1200 (w), 1176 (m), 1118 (w), 1106 (w), 1045 (m), 1032 (s), 1005 (w), 939 (w), 910 (w), 894 (m), 867 (m), 829 (s), 814 (s), 806 (m), 794 (w), 740 (m), 720 (m), 710 (m), 696 (m), 634 (w), 566 (w), 554 (w), 516 (m).

The analytical data are in accordance with the literature.[121]

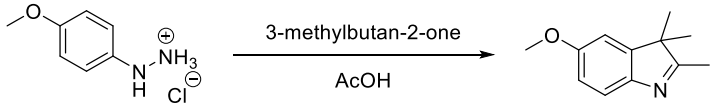
11.2.4.12 *Fischer* indole synthesis: General protocol (GP6)



35 **51**

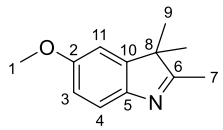
Following a modified procedure by *Balmond et al*.[185], hydrazinium salt **35** (1.00 eq.) was dissolved in glacial acetic acid. The ketone (1.05 - 1.10 eq.) was added and the reaction mixture was stirred at reflux. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed with sat. aq. $NaHCO_3$ and sat. aq. NaCl. The aq. layer was extracted with CH_2Cl_2, the combined org. layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography.

11.2.4.12.1 Synthesis of 5-methoxy-2,3,3-trimethyl-3*H*-indole (33)



35 **33**

According to **GP6**, 16.0 g (92.0 mmol, 1.00 eq.) of hydrazinium salt **35** were reacted with 10.7 mL (102 mmol, 1.10 eq.) of 3-methylbutan-2-one in 80 mL glacial acetic acid at reflux for 5 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1 → 1:1) to afford 16.2 g (85.9 mmol, 93%, Lit.[122]: 97%) of the desired product **33** as a beige solid.

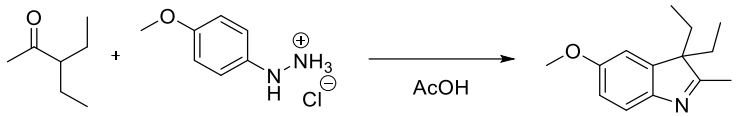


M($C_{12}H_{15}NO$)	189.26 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 2:1) = 0.44.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.43 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H-3), 6.84 – 6.80 (m, 2H, H-4, H-11), 3.83 (s, 3H, H-7), 2.24 (s, 3H, H-1), 1.29 (s, 6H, H-9).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 186.1 (C-6), 158.0 (C-5), 147.0 (C-10), 146.6 (C-2), 120.0 (C-3), 112.1 (C-11), 108.1 (C-4), 55.7 (C-7), 53.7 (C-8), 23.2 (C-9), 15.1 (C-1).

FT-IR	ATR, v [cm^{-1}] = 3212 (w), 2962 (m), 2929 (w), 2865 (w), 2835 (w), 2096 (w), 1875 (w), 1708 (w), 1591 (m), 1513 (m), 1463 (s), 1433 (s), 1381 (m), 1362 (w), 1337 (w), 1286 (s), 1247 (s), 1212 (s), 1179 (s), 1113 (m), 1069 (s), 1029 (s), 944 (w), 866 (m), 814 (s), 750 (w), 719 (w), 698 (w), 683 (w), 617 (m), 587 (m), 565 (w), 519 (w).
GC-MS	m/z (%) = 189 (100), 174 (99), 159 (34), 146 (43), 131 (52), 117 (22), 108 (26), 89 (20), 77 (38), 63 (21), 51 (17).

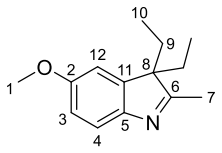
The analytical data are in accordance with the literature.[122]

11.2.4.12.2 Synthesis of 3,3-diethyl-5-methoxy-2-methyl-3H-indole (51a)



36b **35** **51a**

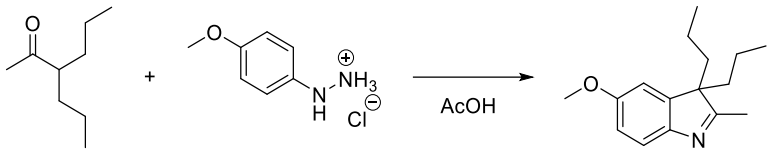
According to **GP6**, 0.54 g (3.10 mmol, 1.00 eq.) of hydrazinium salt **35** were reacted with 0.38 g (3.28 mmol, 1.05 eq.) of ketone **36b** in 2.75 mL glacial acetic acid at reflux for 4.5 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) to afford 0.35 g (1.60 mmol, 52%) of the desired product **51a** as a yellow solid.



M($C_{14}H_{19}NO$)	217.31 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:1) = 0.40.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.41 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H-12), 6.82 (dd, $^{3,4}J_{HH}$ = 8.4, 2.5 Hz, 1H, H-3), 6.74 (d, $^4J_{HH}$ = 2.6 Hz, 1H, H-4), 3.83 (s, 3H, H-1), 2.17 (s, 3H, H-7), 1.87 (m, 2H, H-9), 1.81 – 1.73 (m, 2H, H-9), 0.38 (t, $^3J_{HH}$ = 7.4 Hz, 6H, H-10).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 183.7 (C-6), 157.8 (C-11), 149.5 (C-2), 143.2 (C-5), 119.6 (C-12), 111.8 (C-3), 108.6 (C-4), 63.9 (C-8), 55.6 (C-1), 29.7 (C-9), 15.8 (C-7), 8.2 (C-10).
FT-IR	ATR, v [cm^{-1}] = 3386 (br, w), 2936 (m), 2876 (m), 2855 (w), 1613 (w), 1593 (m), 1579 (m), 1470 (s), 1379 (m), 1270 (s), 1200 (s), 1176 (s), 1082 (m), 1029 (s), 935 (w), 810 (m), 691 (w), 618 (w)

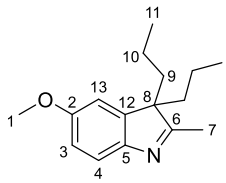
GC-MS	m/z (%) = 218 (13), 202 (100), 188 (40), 174 (19), 145 (14), 115 (7).
HR-MS (ESI)	Calcd. $[M+H]^{\cdot+}$: 218.1539, found: 218.1536.

11.2.4.12.3 Synthesis of 5-methoxy-2-methyl-3,3-dipropyl-3H-indole (51b)



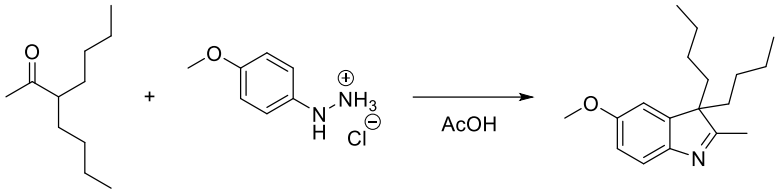
36c **35** **51b**

According to **GP6**, 0.42 g (2.43 mmol, 1.00 eq.) of hydrazinium salt **35** were reacted with 0.38 g (2.67 mmol, 1.10 eq.) of ketone **36c** in 2.15 mL glacial acetic acid at reflux for 4.5 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) to afford 0.27 g (1.08 mmol, 45%) of the desired product **51b** as a yellow solid.



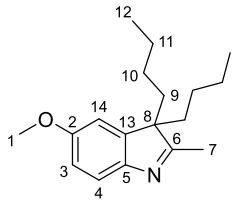
M($C_{16}H_{23}NO$)	245.37 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:1) = 0.50.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.40 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H-13), 6.81 (dd, $^{3,4}J_{HH}$ = 8.3, 2.5 Hz, 1H, H-3), 6.76 (d, $^4J_{HH}$ = 2.5 Hz, 1H, H-4), 3.83 (s, 3H, H-1), 2.21 – 2.13 (m, 3H, H-7), 1.84 – 1.76 (m, 2H, H-9), 1.73 – 1.64 (m, 2H, H-9), 0.81 – 0.70 (m, 9H, H-10, H-11), 0.62 (m, 2H, H-10).
^{13}C-NMR	(126 MHz, $CDCl_3$), δ [ppm] = 184.2 (C-6), 157.7 (C-12), 149.1 (C-2), 144.1 (C-5), 119.6 (C-13), 111.5 (C-3), 108.7 (C-4), 62.9 (C-8), 55.6 (C-1), 39.4 (C-9), 17.0 (C-10), 15.9 (C-7), 14.3 (C-11).
FT-IR	ATR, ν [cm^{-1}] = 2956 (m), 2931 (m), 2872 (m), 1594 (m), 1580 (m), 1476 (s), 1378 (m), 1263 (s), 1196 (s), 1173 (s), 1062 (m), 1033 (m), 821 (m), 768 (m), 623 (m).
GC-MS	m/z (%) = 245 (54), 230 (6), 216 (52), 202 (34), 187 (15), 174 (100), 158 (22), 131 (15), 103 (9), 77 (12), 51 (5).
HR-MS (ESI)	Calcd. $[M+H]^{\cdot+}$: 246.1852, found: 246.1851.

11.2.4.12.4 Synthesis of 3,3-dibutyl-5-methoxy-2-methyl-3H-indole (51c)



36d **35** **51c**

According to **GP6**, 5.51 g (31.6 mmol, 1.00 eq.) of hydrazinium salt **35** were reacted with 5.90 g (34.7 mmol, 1.10 eq.) of ketone **36d** in 2.15 mL glacial acetic acid at reflux for 4.5 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) to afford 2.93 g (11.3 mmol, 33%) of the desired product **51c** as a yellow solid.



M($C_{18}H_{27}NO$) 273.42 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 2:1) = 0.45.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.41 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H-14), 6.82 (dd, $^{3,4}J_{HH}$ = 8.4, 2.5 Hz, 1H, H-3), 6.75 (d, $^4J_{HH}$ = 2.5 Hz, 1H, H-4), 3.84 (s, 3H, H-1), 2.18 (s, 3H, H-7), 1.82 (m, 2H, H-9), 1.71 (m, 2H, H-9), 1.20 – 1.05 (m, 4H, H-10), 0.74 (t, $^3J_{HH}$ = 7.3 Hz, 6H, H-12), 0.73 – 0.64 (m, 2H, H-11), 0.63 – 0.52 (m, 2H, H-11).

^{13}C-NMR (126 MHz, $CDCl_3$), δ [ppm] = 186.1 (C-6), 157.8 (C-13), 149.1 (C-2), 144.0 (C-5), 119.6 (C-14), 111.5 (C-3), 108.7 (C-4), 62.7 (C-8), 55.6 (C-1), 36.9 (C-9), 25.7 (C-11), 22.8 (C-10), 15.9 (C-7), 13.7 (C-12).

FT-IR ATR, ν [cm^{-1}] = 2956 (m), 2929 (m), 2872 (w), 2859 (m), 1731 (w), 1613 (w), 1592 (m), 1579 (m), 1516 (w), 1468 (s), 1437 (m), 1378 (m), 1340 (w), 1277 (m), 1254 (s), 1234 (m), 1195 (m), 1171 (s), 1117 (w), 1102 (w), 1069 (w), 1046 (m), 1027 (m), 970 (w), 925 (w), 903 (w), 866 (w), 846 (m), 821 (m), 811 (s), 755 (w), 747 (w), 703 (w), 687 (w), 624 (m), 602 (m), 574 (w), 536 (w).

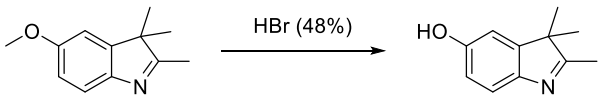
GC-MS	m/z (%) = 273 (52), 258 (6), 230 (47), 216 (46), 207 (6), 188 (12), 174 (100), 158 (18), 145 (6), 131 (13), 115 (9), 91 (8), 77 (9), 55 (5).
HR-MS (ESI)	Calcd. $[M+H]^{\cdot+}$:274.2165410, found: 274.21650. Calcd. $[M+Na]^{+}$: 296.1984857, found: 296.19866.

11.2.4.13 Demethylation of indoles 1: General protocol (GP7)

51 **40**

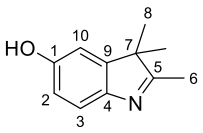
Following a procedure of *Kim et al.*[124], HBr (48%) (4.00 eq.) was added dropwise to indole **51** (1.00 eq.). The reaction mixture was heated to 126 °C. The reaction mixture was neutralized with sat. aq. $NaHCO_3$. The aq. phase was extracted with CH_2Cl_2 and the combined org. layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography.

11.2.4.13.1 Synthesis of 2,3,3-trimethyl-3*H*-indol-5-ol (40a)



33 **40a**

According to **GP7** 18.4 mL (338 mmol, 4.00 eq.) of HBr (48%) were reacted with 16.0 g (84.5 mmol, 1.00 eq.) of indole **33** at 126 °C for 22 h. After purification by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) 9.88 g (56.4 mmol, 67%, Lit.[124]: 84%) of the desired product **40a** were obtained as beige solid.



M($C_{11}H_{13}NO$)	175.23 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:3) = 0.38.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 8.67 (s, 1H, OH), 7.32 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H-2), 6.84 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-10), 6.78 (dd, $^{3,4}J_{HH}$ = 8.3, 2.4 Hz, 1H), 2.26 (s, 3H, H-6), 1.29 (s, 6H, H-8).

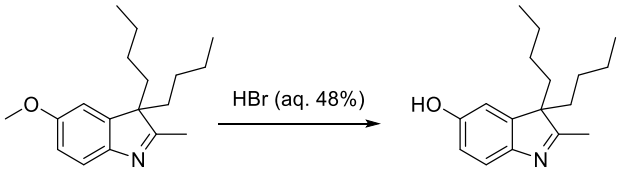
^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 185.8 (C-5), 155.1 (C-9), 147.4 (C-4), 145.7 (C-1), 120.0 (C-2), 114.0 (C-10), 109.6 (C-3), 53.6 (C-7), 23.1 (C-8), 15.0 (C-6).

FT-IR ATR, v [cm^{-1}] = 3025 (w), 2967 (w), 2927 (w), 2839 (w), 2690 (w), 1850 (w), 1702 (w), 1621 (w), 1592 (m), 1582 (m), 1498 (w), 1462 (s), 1429 (m), 1387 (m), 1359 (m), 1293 (s), 1270 (m), 1220 (w), 1201 (m), 1191 (s), 1112 (w), 1061 (m), 1033 (w), 996 (w), 946 (w), 908 (w), 848 (m), 816 (s), 765 (w), 699 (w), 638 (w), 622 (w), 578 (w), 539 (w).

GC-MS m/z (%) = 175 (97), 160 (100), 146 (9), 133 (16), 119 (12), 103 (8), 94 (22), 89 (10), 77 (17), 65 (14), 51 (9).

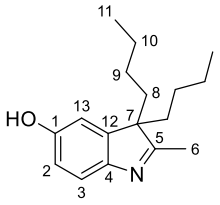
The analytical data are in accordance with the literature.[124]

11.2.4.13.2 Synthesis of 3,3-dibutyl-2-methyl-3*H*-indol-5-ol (40d)



51c **40d**

According to **GP7** 6.20 mL (107 mmol, 10.0 eq.) of HBr (aq. 48%) were reacted with 2.93 g (10.7 mmol, 1.00 eq.) of indole **51c** at 128 °C for 22 h. After purification by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) 0.29 g (1.09 mmol, 10%) of the desired product **40d** were obtained as a beige solid.



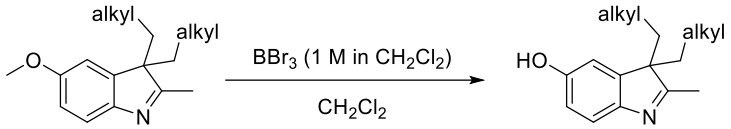
M($C_{17}H_{25}NO$) 259.39 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:1) = 0.59.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.42 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H-3), 6.75 – 6.73 (m, 2H, H-2, H-13), 2.48 (m, 2H, H-8), 1.86 – 1.74 (m, 2H, H-8), 1.58 (s, 1H, OH), 1.51 – 1.40 (m, 2H, H-9), 1.26 (m, 3H, H-6), 1.17 – 1.10 (m, 2H, H-9), 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 3H, H11), 0.90 – 0.77 (m, 2H, H-10), 0.76 (t, $^3J_{HH}$ = 7.4 Hz, 3H, H-11), 0.70 – 0.60 (m, 2H, H-10).

^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 188.6 (C-5), 154.2 (C-12), 149.6 (C-1), 145.7 (C-4), 120.0 (C-3), 114.0 (C-13), 109.4 (C-2), 58.2 (C-7), 37.2 (C-8), 28.7 (C-9), 28.3 (C-8‘), 26.2 (C-10), 22.9 (C-6), 22.9 (C-9‘), 13.8 (C-11), 13.7 (C-11‘).
FT-IR	ATR, ν [cm^{-1}] = 3200 (w), 2960 (m), 2930 (m), 2873 (m), 2860 (m), 2108 (w), 1875 (w), 1676 (s), 1607 (m), 1590 (s), 1522 (m), 1464 (s), 1402 (m), 1354 (m), 1288 (m), 1250 (s), 1210 (s), 1187 (s), 1158 (s), 1117 (m), 1105 (m), 1088 (m), 1066 (m), 1041 (m), 965 (m), 945 (m), 915 (w), 889 (m), 865 (m), 821 (m), 756 (s), 667 (m), 633 (m), 587 (m), 522 (m).
GC-MS	m/z (%) = 259 (59), 216 (68), 202 (55), 173 (22), 160 (100), 131 (11), 103 (7), 77 (9), 55 (5).

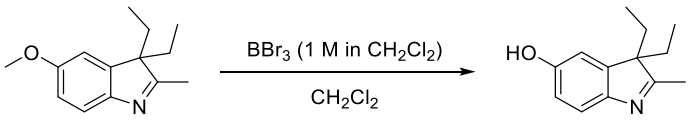
11.2.4.14 Demethylation of indoles 2: General protocol (GP8)



51 **40**

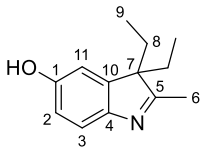
Following a modified procedure by *Stackova et al.*[122], indole **51** (1.00 eq.) was dissolved in CH_2Cl_2. At 0 °C BBr_3 (1.50 eq., 1 M in CH_2Cl_2) was added. After stirring at rt the reaction mixture was quenched with H_2O and neutralized with sat. aq. $NaHCO_3$. The layers were separated and the aq. phase was extracted with CH_2Cl_2. The combined org. layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography.

11.2.4.14.1 Synthesis of 3,3-diethyl-2-methyl-3*H*-indol-5-ol (40b)



51a **40b**

According to **GP8**, 0.68 g (3.14 mmol, 1.00 eq.) of indole **51a** were reacted with 3.14 mL (3.14 mmol, 1.00 eq, 1 M in CH_2Cl_2) in 9 mL CH_2Cl_2 for 17 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH 19:1) 0.53 g (2.60 mmol, 83%) of the desired product **40b** were obtained as yellow solid.



M($C_{13}H_{17}NO$) 203.28 g/mol.

R_f (SiO_2, CH_2Cl_2/MeOH 19:1) = 0.24.

m.p. 154 °C.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.33 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H-3), 6.77 (dd, $^{3,4}J_{HH}$ = 8.2, 2.4 Hz, 1H, H-2), 6.73 (d, $^4J_{HH}$ = 2.3 Hz, 1H, H-11), 2.18 (s, 3H, H-6), 1.92 – 1.81 (m, 2H, H-8), 1.80 – 1.73 (m, 2H, H-8), 1.63 (s, 1H, OH), 0.40 (t, $^3J_{HH}$ = 7.4 Hz, 6H, H-9).

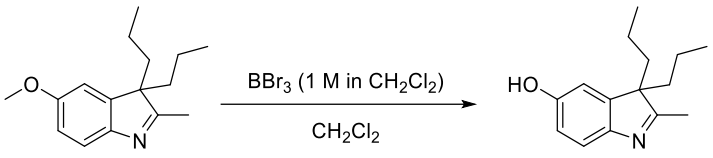
^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 183.8 (C-5), 154.7 (C-10), 148.3 (C-1), 143.3 (C-4), 119.7 (C-3), 114.0 (C-2), 109.8 (C-11), 63.8 (C-7), 29.7 (C-8), 15.6 (C-6), 8.2 (C-9).

FT-IR ATR, v [cm^{-1}] = 3029 (br, m), 2961 (m), 2930 (m), 2855 (m), 2725 (w), 2660 (w), 1621 (w), 1596 (s), 1586 (s), 1458 (s), 1380 (s), 1286 (s), 1246 (m), 1192 (s), 1118 (w), 1037 (w), 878 (m), 815 (s), 622 (w).

GC-MS m/z (%) = 203 (61), 188 (100), 174 (51), 160 (27), 131 (9), 103 (6), 77 (10).

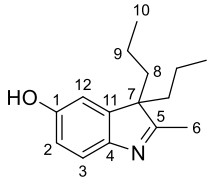
HR-MS (ESI) Calcd. $[M+H]^+$: 204.1382, found: 204.1380.

11.2.4.14.2 Synthesis of 2-methyl-3,3-dipropyl-3*H*-indol-5-ol (40c)



51b **40c**

According to **GP8**, 0.91 g (3.70 mmol, 1.00 eq.) of indole **51b** were reacted with 5.50 mL (5.56 mmol, 1.50 eq, 1 M in CH_2Cl_2) in 9 mL CH_2Cl_2 for 17 h. After column chromatography (SiO_2, *c*Hex/EtOAc 2:1) 0.69 g (3.00 mmol, 81%) of the desired product **40c** could be obtained as beige solid.



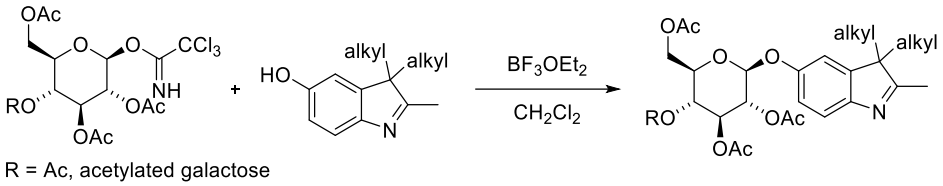
M($C_{15}H_{21}NO$) 231.34 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:1) = 0.43.

m.p. 170 °C.

^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.32 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, H-3), 6.77 – 6.71 (m, 2H, H-2, H-12), 2.19 (s, 3H, H-6), 1.87 – 1.65 (m, 4H, H-8), 0.83 – 0.59 (m, 9H, H-6, H-10).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 184.5 (C-5), 154.4 (C-1), 148.1 (C-11), 144.1 (C-4), 119.7 (C-3), 114.0 (C-2), 109.7 (C-12), 62.9 (C-7), 39.4 (C-8), 17.0 (C-9), 15.7 (C-6), 14.2 (C-10).
FT-IR	ATR, v [cm^{-1}] = 3366 (w), 3241 (w), 3180 (w), 2958 (w), 2929 (w), 2873 (w), 2842 (w), 2704 (w), 2625 (w), 1694 (m), 1608 (w), 1582 (w), 1467 (m), 1381 (m), 1304 (w), 1268 (m), 1226 (w), 1193 (w), 1109 (w), 1057 (w), 951 (w), 929 (w), 867 (w), 823 (s), 779 (w), 747 (w), 667 (w), 648 (m), 627 (m), 586 (w).
GC-MS	m/z (%) = 232 (56), 202 (62), 188 (32), 173 (29), 160 (100), 144 (11), 131 (8), 115 (6), 103 (5), 91 (5), 77 (6).
HR-MS (ESI)	Calcd. $[M+H]^+$: 232.1695, found: 232.1694.

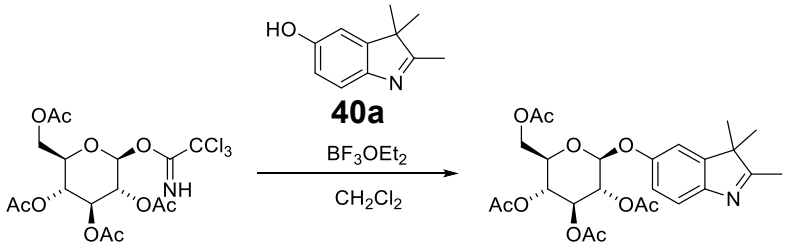
11.2.4.15 *O*-Glycosylation of indoles: General protocol (GP9)



43 **40** **45**

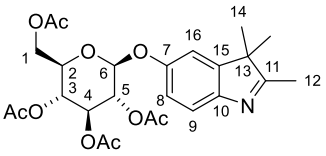
Sugar **43** (1.00 eq) was dissolved in CH_2Cl_2 and indole **40** (1.00 eq.) was added. The solution was cooled to 0 °C and BF_3OEt_2 (1.50 eq.) was added dropwise. After stirring at rt the reaction mixture was quenched with sat. aq. $NaHCO_3$. The layers were separated and the aq. phase was extracted with CH_2Cl_2. The combined org. layers were dried over Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography.

11.2.4.15.1 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2,3,3-trimethyl-3*H*-indol-5-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (45a)



43a **45a**

According to **GP9**, 2.66 g (15.2 mmol, 1.00 eq.) of indole **40a** were reacted with 7.50 g (15.2 mmol, 1.00 eq.) of sugar **43a** and 3.00 mL (22.8 mmol, 1.50 eq.) BF_3OEt_2 in 45 mL CH_2Cl_2 for 17 h at rt. After purification by column chromatography (SiO_2, *c*Hex/EtOAc 1:3) 7.06 g (12.5 mmol, 82%) of the desired product **45a** could be obtained as a light beige solid.



M($C_{25}H_{31}NO_{10}$)	505.52 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:3) = 0.38.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.44 – 7.41 (m, 1H, H-9), 6.93 – 6.91 (m, 2H, H-8, H-16), 5.34 – 5.25 (m, 2H, H-4, H-5), 5.17 (t, $^3J_{HH}$ = 9.4 Hz, 1H, H-3), 5.08 (d, $^3J_{HH}$ = 7.2 Hz, 1H, H-6), 4.28 (dd, $^{2,3}J_{HH}$ = 12.3, 5.4 Hz, 1H, H-1) , 4.18 (dd, $^{2,3}J_{HH}$ = 12.3, 2.4 Hz, 1H, H-1‘),

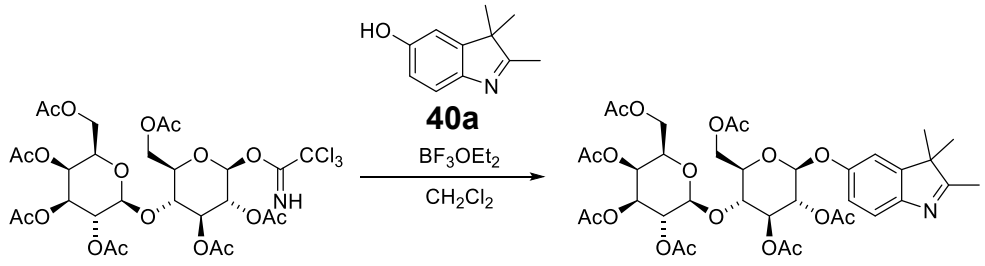
3.87 (ddd, $^{3}J_{HH}$ = 10.0, 5.4, 2.5 Hz, 1H, H-2), 2.25 (s, 3H, H-12), 2.08 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.29 (s, 3H, H-14), 1.28 (s, 3H, H-14).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 187.3 (C-11), 170.5 (OAc), 170.2 (OAc), 169.4 (OAc), 169.3 (OAc), 154.9 (C-15), 149.5 (C-17), 147.3 (C-10), 120.1 (C-9), 115.5 (C-8), 111.6 (C-16), 99.6 (C-6), 72.7 (C-5), 72.0 (C-2), 71.2 (C-4), 68.3 (C-3), 62.0 (C-1), 53.9 (C-13), 23.4 (C-14), 23.1 (C-14), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 15.1 (C-12).

FT-IR ATR, v [cm^{-1}] = 3147 (w), 3051 (w), 2967 (w), 2119 (w), 1744 (s), 1615 (w), 1464 (w), 1432 (w), 1411 (w), 1367 (m), 1211 (s), 1120 (w), 1064 (m), 1034 (s), 985 (w), 910 (w), 826 (w), 772 (w), 696 (w), 636 (w), 599 (w), 563 (w), 505 (w).

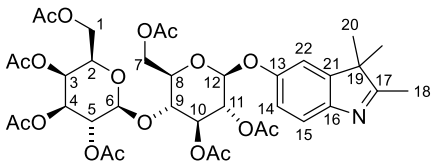
HR-MS (ESI) Calcd. $[M+H]^+$: 506.20207, found: 506.20162.
Calcd. $[M+Na]^+$: 528.18401, found: 528.18360.

11.2.4.15.2 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((2,3,3-trimethyl-3*H*-indol-5-yl)oxy)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (45b)



43b **45b**

According to **GP9**, 1.50 g (8.56mmol, 1.00 eq.) of indole **40a** were reacted with 6.68 g (8.56 mmol, 1.00 eq.) of sugar **43b** and 1.63 mL (12.8 mmol, 1.50 eq.) BF_3OEt_2 in 17 mL CH_2Cl_2 for 17 h at rt. After purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 20:1) 6.75 g (8.50 mmol, 99%) of the desired product **45b** were obtained as a light beige solid.



M($C_{37}H_{47}NO_{18}$) 793.77 g/mol.

R_f (SiO_2, CH_2Cl_2/MeOH 20:1) = 0.23.

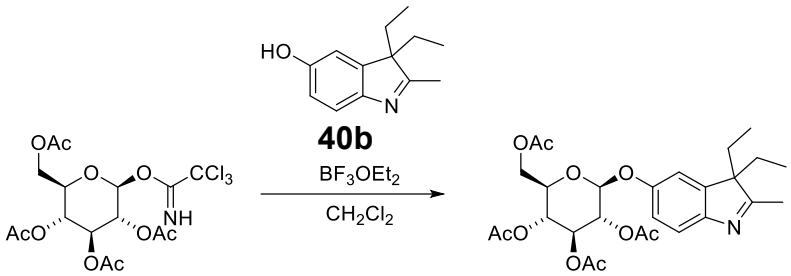
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.43 – 7.40 (m, 1H, H-15), 6.90 (m, 2H, H-14, H-22), 5.36 (d, $^3J_{HH}$ = 3.5 Hz, 1H, H-6), 5.29 (t, $^3J_{HH}$ = 9.0 Hz, 1H, H-4), 5.20 – 5.11 (m, 2H, H-10, H-3), 5.06 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H-12), 4.98 (dd, $^{3,4}J_{HH}$= 10.4, 3.5 Hz, 1H, H-9), 4.52 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H-7), 4.19 – 4.06 (m, 4H, H-7‘, H-1, H-5), 3.92 – 3.88 (m, 2H, H-2, H-11), 3.79 (ddd, $^{3,4}J_{HH}$ = 9.9, 5.7, 2.1 Hz, 1H, H-8), 2.26 (s, 3H, H-18), 2.16 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.29 (s, 3H, H-20), 1.28 (s, 3H, H-20).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 187.3 (C-17), 170.3 (OAc), 170.3 (OAc), 170.1 (OAc), 170.0 (OAc), 169.7 (OAc), 169.6 (OAc), 169.1 (OAc), 154.9 (C-21), 149.3 (C-13), 147.2 (C-16), 120.1 (C-15), 115.6 (C-22), 111.4 (C-14), 101.1 (C-6), 99.2 (C-12), 76.2 (C-2), 72.8 (C-8, C-4), 71.5 (C-3), 70.9 (C-9), 69.1 (C-10, C-11), 66.6 (C-5), 62.0 (C-7), 60.8 (C-1), 53.9 (C-19), 23.1 (C-20), 23.0 (C-20‘), 20.8 (OAc), 20.7 (OAc), 20.7 (OAc), 20.6 (2x OAc), 20.6 (OAc), 20.5 (OAc), 15.3 (C-18).

FT-IR ATR, v [cm^{-1}] = 3362 (w), 2966 (w), 2124 (w), 1724 (s), 1614 (w), 1581 (w), 1463 (w), 1431 (w), 1367 (m), 1213 (s), 1173 (m), 1134 (w), 1109 (w), 954 (w), 902 (w), 825 (m), 772 (w), 738 (w), 706 (w), 671 (w), 602 (m), 512 (w), 492 (w), 451 (w), 424 (w), 402 (w).

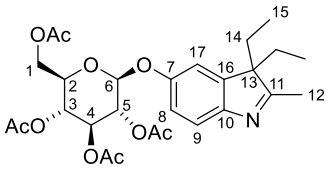
HR-MS (ESI) Calcd. $[M+H]^+$: 794.2865, found: 794.2870.
Calcd. $[M+Na]^+$: 816.2685, found: 816.2665.

11.2.4.15.3 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((3,3-diethyl-2-methyl-3*H*-indol-5-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (45c)



43a **45c**

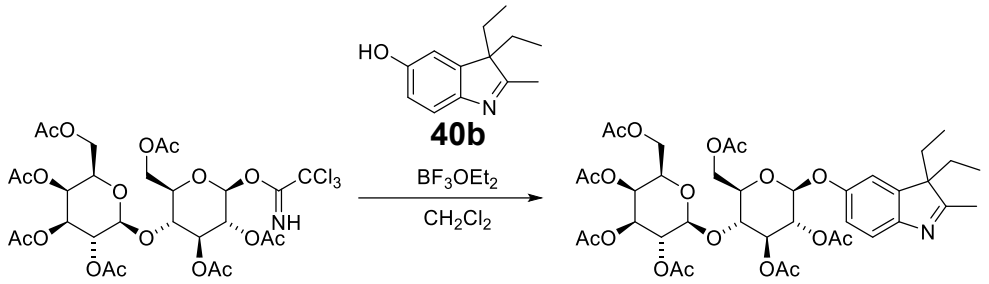
According to **GP9** 0.25 g (1.23 mmol, 1.00 eq.) of indole **40b** were reacted with 0.61 g (1.23 mmol, 1.00 eq.) of sugar **43a** and 0.26 g (1.85 mmol, 1.50 eq.) BF_3OEt_2 in 6.5 mL CH_2Cl_2 for 17 h at rt. After purification by column chromatography (SiO_2, *c*Hex/EtOAc 1:2) 0.44 g (0.83 mmol, 67%) of the desired product **45c** were obtained as a light brown solid.



M($C_{27}H_{35}NO_{10}$)	533.57 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:3) = 0.46.
m.p.	37 - 47 °C.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.41 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H-9), 6.93 (dd, $^{3,4}J_{HH}$ = 8.4, 2.4 Hz, 1H, H-8), 6.84 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-17), 5.33 – 5.25 (m, 2H, H-4, H-5), 5.20 – 5.15 (m, 1H, H-3), 5.08 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H-6), 4.29 (dd, $^{2,3}J_{HH}$ = 12.3, 5.3 Hz, 1H, H-1), 4.18 (dd, $^{2,3}J_{HH}$ = 12.3, 2.3 Hz, 1H, H-1‘), 3.87 (ddd, $^{3,4}J_{HH}$ = 10.0, 5.4, 2.4 Hz, 1H, H-2), 2.18 (s, 3H, H-12), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.87 (m, 2H, H-14), 1.77 (m, 2H, H-14‘), 0.38 (m, 6H, H-15).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 185.5 (C-11), 170.5 (OAc), 170.2 (OAc), 169.4 (OAc), 169.3 (OAc), 154.9 (C-16), 151.4 (C-7), 143.3 (C-10), 119.7 (C-17), 115.5 (C-8), 112.0 (C-9), 99.7 (C-6), 72.7 (C-4), 72.0 (C-2), 71.2 (C-5), 68.3 (C-3), 64.1 (C-13), 62.0 (C-1), 29.5 (C-14), 29.5 (C-14‘), 20.7 (2x OAc), 20.6 (OAc), 20.6 (OAc), 15.9 (C-12), 8.2 (C-15).

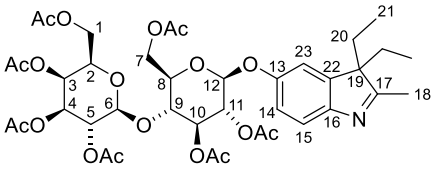
FT-IR	ATR, ν [cm^{-1}] = 2965 (w), 2119 (br, w), 1745 (s), 1581 (w), 1466 (w), 1367 (m), 1213 (s), 1033 (s), 906 (w), 820 (w), 599 (w).
HR-MS (ESI)	Calcd. [M+H]$^+$: 534.2333, found: 534.2327. Calcd. [M+Na]$^+$: 556.2153, found: 556.2150.

11.2.4.15.4 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((3,3-diethyl-2-methyl-3*H*-indol-5-yl)oxy) tetrahydro -2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (45d)



43b **45d**

According to **GP9**, 0.25 g (1.23 mmol, 1.00 eq.) of indole **40b** were reacted with 0.96 g (1.23 mmol, 1.00 eq.) of sugar **43b** and 0.26 g (1.85 mmol, 1.50 eq.) BF_3OEt_2 in 6.5 mL CH_2Cl_2 for 69 h at rt. After purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 10:1) 0.95 g (1.15 mmol, 94%) of the desired product **45d** were obtained as a light brown solid



M($C_{39}H_{51}NO_{18}$)	821.83 g/mol.
R_f	(SiO_2, CH_2Cl_2/MeOH 10:1) = 0.53.
m.p.	42 - 50 °C.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.40 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H-15), 6.92 (dd, $^{3,4}J_{HH}$ = 8.4, 2.4 Hz, 1H, H-14), 6.81 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-23), 5.36 (m, 1H, H-6), 5.30 (t, $^3J_{HH}$ = 9.1 Hz, 1H, H-4), 5.16 (m, 2H, H-10, H-3), 5.06 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H-12), 4.98 (dd, $^{3,4}J_{HH}$ = 10.4, 3.5 Hz, 1H, H-9), 4.54 – 4.48 (m, 2H, H-7, H-5), 4.15 (m, 2H, H-1, H-7‘), 3.93 – 3.87 (m, 2H, H-2, H-11), 3.79 (ddd, $^3J_{HH}$ = 9.8, 5.8, 2.0 Hz, 1H, H-8), 2.18 (s, 3H, H-18), 2.16 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.08 (s, 6H, OAc), 2.07 (s, 3H, OAc), 2.06 (s,

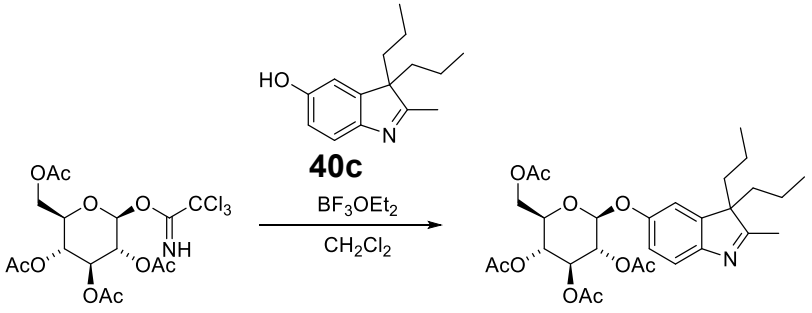
3H, OAc), 1.97 (s, 3H, OAc), 1.87 (m, 2H, H-20), 1.81 – 1.72 (m, 2H, H-20‘), 0.38 (m, 6H, H-21).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 185.4 (C-17), 170.3 (OAc), 170.3 (OAc), 170.1 (OAc), 170.0 (OAc), 169.7 (OAc), 169.6 (OAc), 169.1 (OAc), 154.9 (C-22), 151.4 (C-13), 143.3 (C-16), 119.7 (C-15), 115.5 (C-14), 111.8 (C-23), 101.1 (C-5), 99.4 (C-12), 76.2 (C-11), 72.8 (C-8), 72.7 (C-4), 71.5 (C-10), 70.9 (C-9), 70.7 (C-2), 69.1 (C-3), 66.6 (C-6), 64.1 (C-19), 62.1 (C-7), 60.8 (C-1), 29.5 (C-20), 29.5 (C-20‘), 20.8 (OAc), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 20.5 (OAc), 15.9 (C-18), 8.2 (C-21), 8.2 (C-21‘).

FT-IR ATR, ν [cm^{-1}] = 3369 (m), 3320 (m), 3243 (m), 3186 (w), 2974 (w), 2935 (w), 2900 (w), 2801 (w), 2254 (w), 2131 (w), 1999 (w), 1922 (w), 1720 (m), 1693 (s), 1617 (m), 1545 (w), 1458 (w), 1381 (m), 1355 (m), 1232 (m), 1109 (m), 1083 (m), 1045 (s), 957 (w), 928 (w), 911 (w), 879 (w), 830 (s), 732 (s), 648 (s), 617 (s).

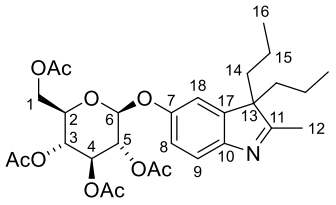
HR-MS (ESI) Calcd. $[M+H]^+$: 822.3178, found: 822.3180.
Calcd. $[M+Na]^+$: 844.2998, found: 844.2999.

11.2.4.15.5 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-methyl-3,3-dipropyl -3*H*-indol-5-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (45e)



43a **45e**

According to **GP9**, 0.69 g (2.98 mmol, 1.00 eq.) of indole **40c** were reacted with 1.47 g (2.98 mmol, 1.00 eq.) of sugar **43a** and 0.57 mL (4.47 mmol, 1.50 eq.) BF_3OEt_2 in 8 mL CH_2Cl_2 for 17 h at rt. After purification by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) 1.38 g (2.29 mmol, 77%) of the desired product **45e** were obtained as a light brown solid.



M($C_{29}H_{39}NO_{10}$) 561.63 g/mol.

R_f (SiO_2, CH_2Cl_2/MeOH 20:1) = 0.34.

m.p. 32 - 35 °C.

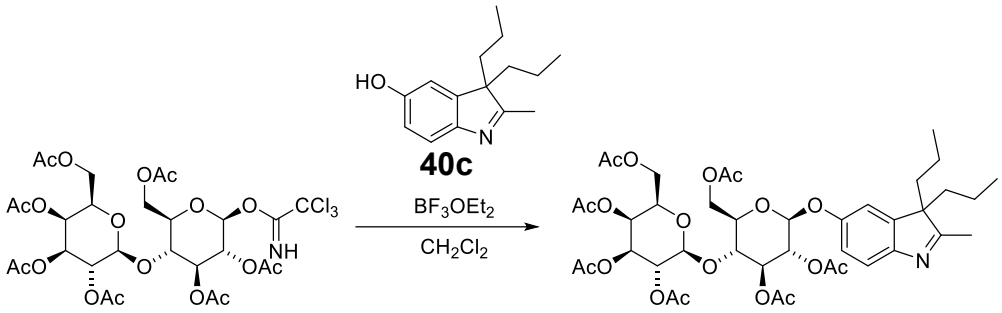
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.40 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H-9), 6.92 (dd, $^{3,4}J_{HH}$ = 8.4, 2.4 Hz, 1H, H-8), 6.85 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-18), 5.35 – 5.24 (m, 2H, H-3, H-4), 5.21 – 5.14 (m, 1H, H-5), 5.08 (d, $^3J_{HH}$ = 7.3 Hz, 1H, H-6), 4.30 (dd, $^{2,3}J_{HH}$ = 12.3, 5.2 Hz, 1H, H-1), 4.18 (dd, $^{2,3}J_{HH}$ = 12.3, 2.4 Hz, 1H, H-1‘), 3.87 (ddd, $^{3,4}J_{HH}$ = 10.0, 5.2, 2.4 Hz, 1H, H-2), 2.19 (s, 3H, H-12), 2.08 (s, 6H, 2x OAc), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.88 – 1.74 (m, 2H, H-14), 1.73 – 1.65 (m, 2H, H-14‘), 0.82 – 0.69 (m, 8H, H-15, H-16), 0.68 – 0.56 (m, 2H, H-15).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 185.9 (C-11), 170.5 (OAc), 170.2 (OAc), 169.4 (OAc), 169.3 (OAc), 154.9 (C-17), 151.0 (C-7), 144.1 (C-10), 119.7 (C-9), 115.2 (C-8), 112.0 (C-18), 99.7 (C-6), 72.7 (C-4), 72.0 (C-2), 71.3 (C-3), 68.3 (C-5), 63.2 (C-13), 62.0 (C-1), 39.2 (C-14), 39.2 (C-14‘), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 17.0 (C-15), 17.0 (C-15‘), 16.0 (C-12), 14.2 (C-16), 14.2 (C-16‘).

FT-IR ATR, v [cm^{-1}] = 3475 (w), 2959 (w), 2935 (w), 2874 (w), 2111 (w), 1747 (s), 1616 (w), 1580 (w), 1467 (m), 1430 (w), 1367 (m), 1328 (w), 1212 (s), 1187 (m), 1120 (w), 1034 (s), 984 (w), 950 (w), 908 (w), 875 (w), 829 (w), 783 (w), 733 (w), 697 (w), 666 (w), 640 (w), 599 (w), 563 (w), 538 (w), 528 (w), 506 (w).

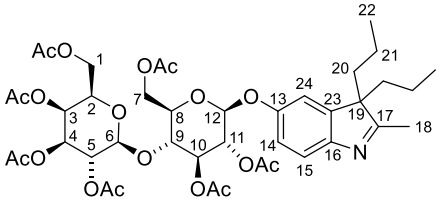
HR-MS (ESI) Calcd. $[M+H]^+$: 562.2646, found: 562.2643.
Calcd. $[M+Na]^+$: 584.2466, found: 548.2464.

11.2.4.15.6 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((3,3-diethyl-2-methyl-3*H*-indol-5-yl) oxy)tetrahydro -2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (45f)



43b **45f**

According to **GP9**, 0.25 g (1.08 mmol, 1.00 eq.) of indole **40c** were reacted with 0.89 g (1.08 mmol, 1.00 eq.) of sugar **43b** and 0.23 g (1.62 mmol, 1.50 eq.) BF_3OEt_2 in 8 mL CH_2Cl_2 for 17 h at rt. After purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 10:1) 0.60 g (0.66 mmol, 65%) of the desired product **45f** were obtained as a light beige solid.



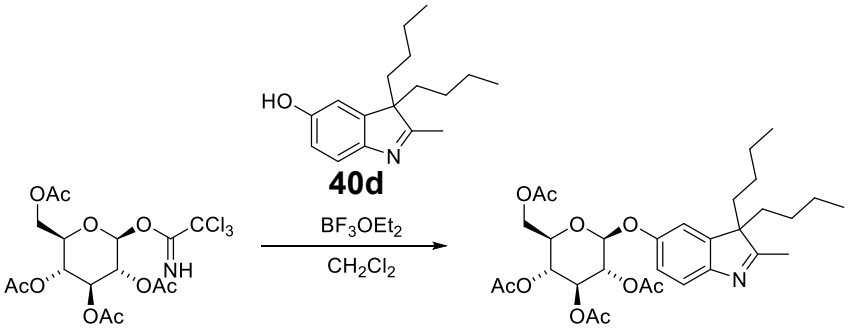
M($C_{41}H_{55}NO_{18}$)	849.88 g/mol.
R_f	(SiO_2, CH_2Cl_2/MeOH 20:1) = 0.53.
m.p.	92 - 100 °C.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.38 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H-15), 6.90 (dd, $^{3,4}J_{HH}$ = 8.4, 2.4 Hz, 1H, H-14), 6.82 (d, $^4J_{HH}$ = 2.3 Hz, 1H, H-24), 5.36 (m, 1H, H-6), 5.30 (t, $^3J_{HH}$ = 9.1 Hz, 1H, H-4), 5.16 (m, 2H, H-3, H-10), 5.05 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H-12), 4.97 (dd, $^{2,3}J_{HH}$ = 10.4, 3.5 Hz, 1H, H-9), 4.54 – 4.46 (m, 2H, H-7, H-5), 4.18 – 4.11 (m, 3H, H-7‘, H-1), 3.93 – 3.87 (m, 2H, H-2, H-11), 3.79 (m, 1H, H-8), 2.18 (s, 3H, H-18), 2.16 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.79 (m, 2H, H-20), 1.69 (m, 2H, H-20‘), 0.74 (m, 8H, H-22, H-21), 0.67 – 0.58 (m, 2H, H-21).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 185.8 (C-17), 170.3 (OAc), 170.2 (OAc), 170.1 (OAc), 170.0 (OAc), 169.7 (OAc), 169.6 (OAc), 169.1 (OAc), 154.9 (C-23), 151.1 (C-13), 144.1 (C-16), 119.7 (C-15),

115.2 (C-14), 111.9 (C-24), 101.1 (C-5), 99.5 (C-12), 76.2 (C-11), 72.8 (C-8), 72.7 (C-4), 71.6 (C-10), 70.9 (C-9), 70.7 (C-2), 69.1 (C-3), 66.6 (C-6), 63.2 (C-19), 62.0 (C-7), 60.8 (C-1), 39.2 (C-20), 20.8 (OAc), 20.8 (OAc), 20.7 (OAc), 20.6 (2x OAc), 20.5 (OAc), 17.0 (C-21), 17.0 (C-21‘), 16.0 (C-18), 14.2 (C-22), 14.2 (C-22‘).

FT-IR ATR, v [cm^{-1}] = 2959 (w), 1745 (s), 1466 (w), 1368 (m), 1214 (s), 1043 (br s), 954 (w), 900 (w), 836 (w), 601 (w).

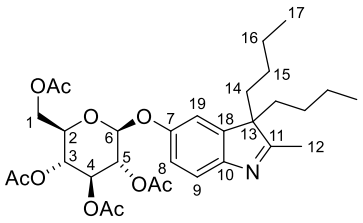
HR-MS (ESI) Calcd. $[M+H]^+$: 850.3491, found: 850.3496.
Calcd. $[M+Na]^+$: 872.3311, found: 872.3311.

11.2.4.15.7 Synthesis of (2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((3,3-dibutyl-2-methyl-3H-indol-5-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (45g)



43a **45g**

According to **GP9**, 0.29 g (1.10 mmol, 1.00 eq.) of indole **40d** were reacted with 0.54 g (1.10 mmol, 1.00 eq.) of sugar **43a** and 0.21 mL (1.65 mmol, 1.50 eq.) BF_3OEt_2 in 3.2 mL CH_2Cl_2 for 16 h at rt. After purification by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) 0.39 g (0.66 mmol, 60%) of the desired product **45g** were obtained as a light beige solid



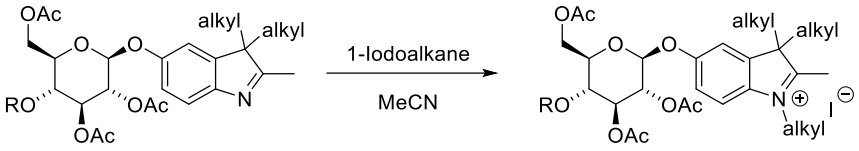
M($C_{31}H_{43}NO_{10}$) 589.68 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 2:1) = 0.27.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.45 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H-9), 6.94 (dd, $^{3,4}J_{HH}$ = 8.4, 2.3 Hz, 1H, H-8), 6.86 (d, $^4J_{HH}$ = 2.3 Hz, 1H, H-19), 5.34 – 5.26 (m, 2H, H-3, H-4), 5.22 – 5.16 (m, 1H, H-5), 5.11 – 5.08 (m, 1H, H-6), 4.31 (dd, $^{2,3}J_{HH}$ = 12.3, 5.2 Hz, 1H, H-1), 4.18 (dd, $^{2,3}J_{HH}$ = 12.3, 2.3 Hz, 1H, H-1‘), 3.87 (ddd, $^{3,4}J_{HH}$ = 9.9, 5.1,

	2.3 Hz, 1H, H-2), 2.24 (s, 3H, H-12), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.84 (m, 2H, H-14), 1.73 (m, 2H, H-14‘), 1.17 – 1.09 (m, 4H, H-15), 0.75 (t, $^{3}J_{HH}$ = 7.3 Hz, 6H, H-17), 0.71 – 0.65 (m, 2H, H-16), 0.61 – 0.54 (m, 2H, H-16‘).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 186.63 (C-11), 170.58 (OAc), 170.27 (OAc), 169.43 (OAc), 169.37 (OAc), 155.25 (C-18), 149.60 (C-7), 144.23 (C-10), 119.66 (C-9), 115.28 (C-8), 112.17 (C-19), 99.77 (C-6), 72.69 (C-3), 72.13 (C-2), 71.28 (C-4), 68.25 (C-5), 63.00 (C-13), 61.96 (C-1), 36.78 (C-14), 36.72 (C-14‘), 25.71 (C-16), 22.81 (C-15), 22.78 (C-15‘), 20.73 (OAc), 20.68 (OAc), 20.64 (OAc), 20.61 (OAc), 15.88 (C-12), 13.73 (C-17), 13.70 (C-17‘).
FT-IR	ATR, v [cm^{-1}] = 3491 (w), 2958 (w), 2933 (w), 2861 (w), 1747 (s), 1616 (w), 1580 (w), 1467 (w), 1430 (w), 1367 (m), 1212 (s), 1121 (w), 1033 (s), 905 (w), 827 (w), 771 (w), 698 (w), 641 (w), 599 (w), 564 (w), 507 (w).
HR-MS (ESI)	Calcd. $[M+H]^+$: 590.2959, found: 590.2953. Calcd. $[M+Na]^+$: 612.2779, found: 612.2774.

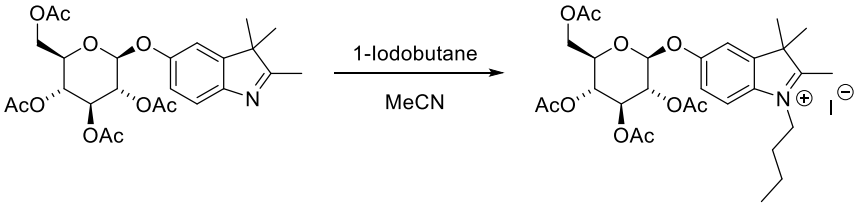
11.2.4.16 *N*-Alkylation of indoles: General protocol (GP10)



45 **46**

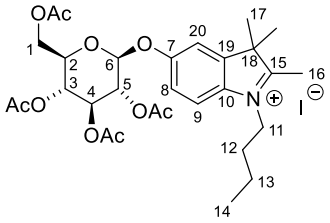
Indole **45** (1.00 eq.) was dissolved in MeCN and alkyl iodide (4.00 eq.) was added. The reaction mixture was stirred at reflux. After cooling to rt, the solvent was removed under reduced pressure and the crude product was washed with MTBE.

11.2.4.16.1 Synthesis of 1-butyl-2,3,3-trimethyl-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-3*H*-indol-1-ium iodide (46a)



45a **46a**

According to **GP10**, 5.25 g (10.4 mmol, 1.00 eq.) of indole **45a** were reacted with 4.72 mL (41.6 mmol, 4.00 eq.) of butyl iodide in 30 mL MeCN for 17 h at reflux. After purification 6.53 g (9.47 mmol, 91%) of the desired product **46a** were obtained as a brown solid.



M($C_{29}H_{40}NO_{10}$)	689.54 g/mol.
R_f	(SiO_2, CH_2Cl_2/MeOH 10:1) = 0.42.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.62 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H-9), 7.29 (d, $^4J_{HH}$ = 2.3 Hz, 1H, H-20), 7.21 (dd, $^{3,4}J_{HH}$ = 8.8, 2.3 Hz, 1H, H-8), 5.33 (m, 3H, H-3, H-4, H-6), 5.21 (t, $^3J_{HH}$ = 9.5 Hz, 1H, H-5), 4.63 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H-11), 4.30 (dd, $^{2,3}J_{HH}$ = 12.5, 4.6 Hz, 1H, H-2), 4.23 (dd, $^{2,3}J_{HH}$ = 12.7, 2.8 Hz, 1H, H-1‘), 4.13 (m, 1H, H-6), 3.02 (s, 3H, H-16), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.90 (m, 2H, H-12), 1.68 (s,

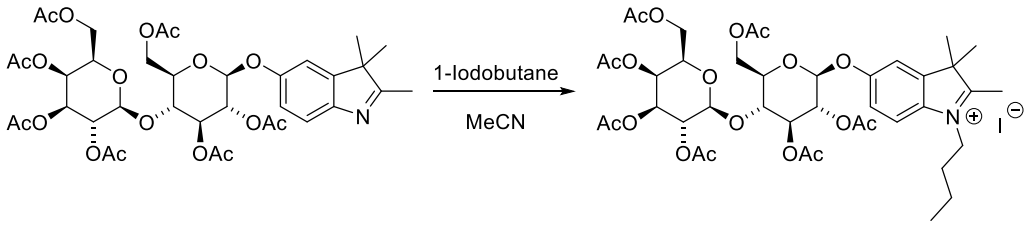
3H, H-17), 1.66 (s, 3H, H-17‘), 1.51 – 1.44 (m, 2H, H-13), 1.01 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, H-14).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 193.8 (C-15), 170.5 (OAc), 170.0 (OAc), 169.4 (OAc), 169.4 (OAc), 158.0 (C-19), 143.6 (C-7), 136.1 (C-10), 117.3 (C-8), 116.5 (C-9), 112.7 (C-20), 98.2 (C-6), 72.5 (C-4), 72.2 (C-2), 71.0 (C-3), 67.9 (C-5), 61.7 (C-(C-1), 54.6 (C-18), 50.2 (C-11), 29.9 (C-12), 23.3 (C-17), 23.0 (C-17‘), 20.8 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 20.2 (C-13), 16.5 (C-16), 13.7 (C-14).

FT-IR ATR, v [cm^{-1}] = 3633 (w), 3451 (w), 2961 (w), 2877 (w), 1746 (s), 1614 (w), 1481 (w), 1458 (w), 1433 (w), 1379 (w), 1367 (w), 1334 (w), 1286 (w), 1246 (m), 1215 (s), 1165 (w), 1117 (w), 1067 (m), 1035 (s), 986 (w), 958 (w), 920 (w), 909 (w), 894 (w), 828 (w), 756 (w), 726 (w), 707 (w), 676 (w), 659 (w), 642 (w), 600 (w), 560 (w), 535 (w), 507 (w).

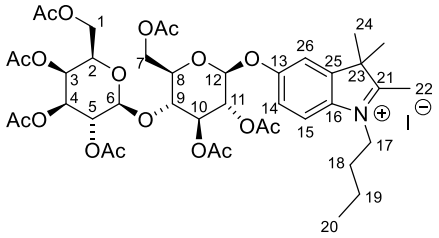
HR-MS (ESI) Calcd. $[M\text{-}I]^+$: 562.2646728, found: 562.26324.

11.2.4.16.2 Synthesis of 1-butyl-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4-diacetoxy-6-(acetoxymethyl)-5-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)-2,3,3-trimethyl-3*H*-indol-1-ium iodide (46f)



45b **46f**

According to **GP10**, 3.50 g (4.40 mmol, 1.00 eq.) of indole **45b** were reacted with 2.00 mL (17.6 mmol, 4.00 eq.) of butyl iodide in 15 mL MeCN for 17 h at reflux. After purification 3.68 g (4.32 mmol, 98%) of the desired product **46f** were obtained as a brown solid.



M($C_{41}H_{56}NO_{18}$) 977.79 g/mol.

R_f (SiO_2, CH_2Cl_2/MeOH 10:1) = 0.47.

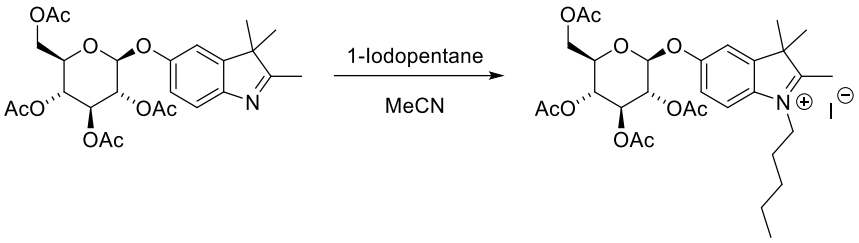
^{1}H-NMR (500 MHz, DMSO-d_6) δ [ppm] = 7.92 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H-15), 7.47 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-26), 7.17 (dd, $^{3,4}J_{HH}$ = 8.9, 2.4 Hz, 1H, H-14), 5.67 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H-6), 5.31 – 5.23 (m, 2H, H-4, H-3), 5.18 (dd, $^{3,4}J_{HH}$ = 10.3, 3.6 Hz, 1H, H-10), 5.04 – 4.99 (m, 1H, H-5), 4.87 (m, 1H, H-9), 4.78 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H-12), 4.43 (d, $^3J_{HH}$ = 7.5 Hz, 2H, H-17), 4.36 (d, $^3J_{HH}$ = 10.7 Hz, 1H, H-7), 4.24 (m, 2H, H-8, H-11), 4.07 (dd, $^{2,3}J_{HH}$ = 12.3, 6.7 Hz, 1H, H-7‘), 4.05 – 4.01 (m, 2H, H-1), 3.94 (d, $^3J_{HH}$ = 9.4 Hz, 1H, H-2), 2.79 (s, 3H, H-22), 2.11 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.01 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.91 (s, 3H, OAc), 1.82 – 1.76 (m, 2H, H-18), 1.51 (s, 6H, H-24), 1.39 (m, 2H, H-19), 0.93 (t, $^3J_{HH}$ = 7.3 Hz, 3H, H-20).

^{13}C-NMR (126 MHz, DMSO-d_6) δ [ppm] = 195.3 (C-21), 170.6 (OAc), 170.3 (2x OAc), 169.9 (OAc), 169.8 (OAc), 169.6 (OAc), 169.5 (OAc), 157.6 (C-25), 144.3 (C-13), 136.4 (C-16), 117.1 (C-15), 116.4 (C-14), 112.2 (C-26), 100.4 (C-12), 96.7 (C-6), 76.4 (C-2), 72.6 (C-3), 72.5 (C-11), 71.1 (C-5), 70.7 (C-10), 70.1 (C-8), 69.3 (C-9), 67.5 (C-4), 62.5 (C-7), 61.3 (C-1), 54.5 (C-23), 47.9 (C-17), 29.8 (C-18), 22.5 (C-24), 22.4 (C-24‘), 21.0 (OAc), 20.9 (OAc), 20.8 (OAc), 20.8 (2x OAc), 20.8 (OAc), 20.7 (OAc), 19.7 (C-19), 14.2 (C-22), 14.0 (C-20).

FT-IR ATR, v [cm^{-1}] = 3453 (w), 2961 (w), 2120 (w), 1744 (s), 1611 (w), 1480 (w), 1431 (w), 1368 (m), 1220 (s), 1179 (w), 1156 (w), 1134 (w), 1116 (w), 1047 (s), 980 (w), 956 (w), 908 (w), 824 (w), 744 (w), 711 (w), 695 (w), 632 (w), 603 (w), 590 (w), 569 (w), 510 (w).

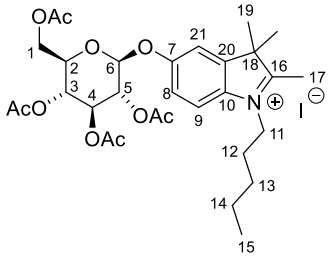
HR-MS (ESI) Calcd. $[M-I]^+$: 850.3491, found: 850.3502.

11.2.4.16.3 Synthesis of 2,3,3-trimethyl-1-pentyl-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-3*H*-indol-1-ium iodide (46b)



45a **46b**

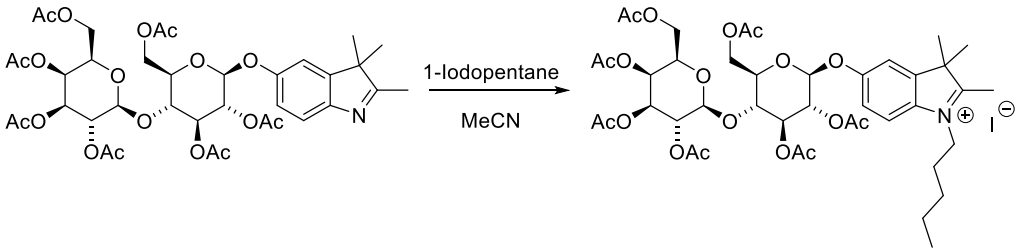
According to **GP10**, 0.30 g (0.60 mmol, 1.00 eq.) of indole **45a** were reacted with 0.31 mL (2.40 mmol, 4.00 eq.) of pentyl iodide in 2 mL MeCN for 20 h at reflux. After purification, 0.35 g (0.50 mmol, 85%) of the desired product **46b** were obtained as a brown solid.



M($C_{30}H_{42}NO_{10}$)	703.57 g/mol.
R_f	(SiO_2, *c*Hex:EtOAc 1:3) = 0.44.
m.p.	80 – 82 °C.
^{1}H-NMR	(500 MHz, MeOD) δ [ppm] = 7.81 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H-9), 7.45 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-21), 7.28 (dd, $^{3,4}J_{HH}$ = 8.9, 2.4 Hz, 1H, H-8), 5.54 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H-2), 5.40 (t, $^3J_{HH}$ = 9.5 Hz, 1H, H-5), 5.21 (dd, $^3J_{HH}$ = 9.6, 7.8 Hz, 1H, H-4), 5.14 (t, $^3J_{HH}$ = 9.7 Hz, 1H, H-3), 4.50 – 4.43 (m, 2H, H-11), 4.32 – 4.25 (m, 1H, H-1), 4.22 – 4.16 (m, 2H, H-1‘, H-6), 2.04 (s, 6H, 2x OAc), 2.04 (s, 6H, 2x OAc), 2.00 (s, 3H, H-17), 1.98 – 1.91 (m, 2H, H-12), 1.60 (s, 3H, H-19), 1.60 (s, 3H, H-19‘), 1.46 (m, 4H, H-13, H-14), 0.99 - 0.90 (m, 3H, H-15).
^{13}C-NMR	(126 MHz, MeOD) δ [ppm] = 195.2 (C-16), 170.7 (OAc), 170.1 (OAc), 169.7 (OAc), 169.5 (OAc), 158.1 (C-20), 144.0 (C-7), 136.0 (C-10), 117.0 (C-8), 116.2 (C-9), 111.8 (C-21), 97.6 (C-2), 72.6 (C-5), 71.8 (C-6), 71.1 (C-4), 68.0 (C-3), 61.5 (C-1), 54.5 (C-18), 48.0 (C-11), 28.3 (C-13), 27.2 (C-12), 21.9 (C-14), 21.3 (C-19), 21.3 (C-19’), 19.2 (C-17), 19.1 (4x OAc), 12.7 (C-15).

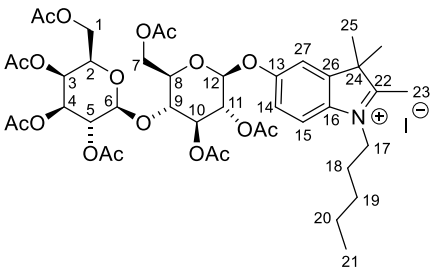
FT-IR	ATR, v [cm^{-1}] = 3475 (w), 2958 (w), 2870 (w), 2118 (w), 1745 (s), 1610 (w), 1478 (w), 1365 (w), 1211 (s), 1118 (w), 1065 (m), 1034 (s), 959 (w), 908 (w), 825 (w),726 (w), 701 (w), 644 (w), 598 (w), 562 (w), 532 (w), 505 (w), 483 (w), 454 (w), 424 (w), 406 (w).
HR-MS (ESI)	Calcd. $[M-I]^+$: 576.2803, found: 576.2795.

11.2.4.16.4 Synthesis of 5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4-diacetoxy-6-(acetoxymethyl)-5-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)-2,3,3-trimethyl-1-pentyl-3*H*-indol-1-ium iodide (46g)



45b **46g**

According to **GP10**, 0.70 g (0.88 mmol, 1.00 eq.) of indole **45b** were reacted with 0.46 mL (3.53 mmol, 4.00 eq.) of pentyl iodide in 3 mL MeCN for 20 h at reflux. After purification, 0.72 g (0.73 mmol, 82%) of the desired product **46g** were obtained as a brown solid.



M($C_{42}H_{58}NO_{18}$)	991.82 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:3) = 0.29.
m.p.	152 - 154 °C.
^{1}H-NMR	(500 MHz, MeOD) δ [ppm] = 7.81 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H-15), 7.43 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-27), 7.25 (dd, $^{3,4}J_{HH}$ = 8.9, 2.4 Hz, 1H, H-14), 5.48 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H-6), 5.37 (m, 1H, H-3), 5.35 – 5.30 (m, 1H, H-4), 5.17 – 5.11 (m, 2H, H-10, H-5), 5.03 (m, 1H, H-9), 4.75 (d, $^3J_{HH}$ = 7.9 Hz, 1H, H-12), 4.57 (dd, $^{2,3}J_{HH}$ = 12.1, 1.8 Hz, H-7), 4.50 – 4.44 (m, 2H, H-17), 4.20 – 4.16 (m, 3H, H-7‘, H-1, H-1‘), 4.12 – 4.04 (m, 2H, H-11, H-2), 4.01 – 3.97 (m, 1H, H-8), 2.14 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.07

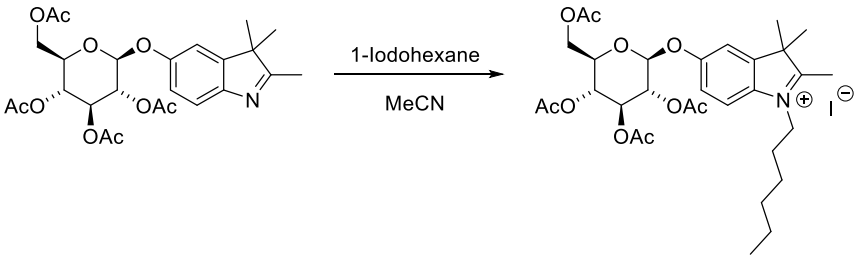
(s, 3H, OAc), 2.05 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.93 (s, 3H, OAc), 1.60 (s, 6H, H-25), 1.45 (m, 4H, H-19, H-20), 1.37 (m, 2H, H-18), 1.19 (s, 3H, H-23), 0.94 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, H-21).

^{13}C-NMR (126 MHz, MeOD) δ [ppm] = 194.7 (C-22), 170.7 (OAc), 170.6 (OAc), 170.5 (OAc), 170.2 (OAc), 170.0 (OAc), 169.7 (OAc), 158.2 (C-26), 144.0 (C-13), 135.9 (C-16), 116.9 (C-14), 116.1 (C-15), 111.7 (C-27), 100.7 (C-12), 97.5 (C-6), 75.8 (C-8), 72.8 (C-4), 71.3 (C-2), 71.0 (C-10), 70.4 (C-11), 69.3 (C-9), 67.1 (C-3), 62.0 (C-7), 60.8 (C-1), 54.4 (C-24), 48.0 (C-17), 28.3 (C-19), 27.2 (C-18), 25.8 (C-23), 21.9 (C-20), 21.4 (C-25), 21.3 (C-25‘), 19.7 (OAc), 19.4 (OAc), 19.3 (OAc), 19.2 (OAc), 19.1 (OAc), 19.0 (OAc), 12.7 (C-23).

FT-IR ATR, v [cm^{-1}] = 3463 (w), 2961 (w), 2121 (w), 1746 (s), 1611 (w), 1481 (w), 1435 (w), 1368 (m), 1219 (s), 1172 (w), 1134 (w), 1046 (s), 953 (w), 901 (w), 825 (w), 742 (w), 724 (w), 693 (w), 632 (w), 511 (w), 493 (w), 451 (w), 412 (w), 402 (w).

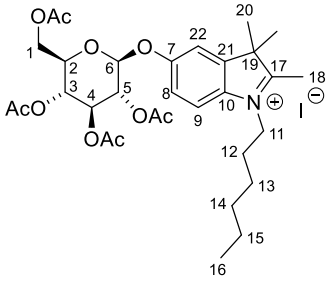
HR-MS (ESI) Calcd. [M-I]$^{+}$: 864.3648, found: 864.3650.

11.2.4.16.5 Synthesis of 1-hexyl-2,3,3-trimethyl-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-3*H*-indol-1-ium iodide (46c)



45a **46c**

According to **GP10**, 0.30 g (0.60 mmol, 1.00 eq.) of indole **45a** were reacted with 0.39 mL (2.40 mmol, 4.00 eq.) of hexyl iodide in 2 mL MeCN for 20 h at reflux. After purification, 0.42 g (0.57 mmol, 96%) of the desired product **46c** were obtained as a brown solid.



M($C_{31}H_{44}NO_{10}$) 717.60 g/mol.

m.p. 121 – 123 °C.

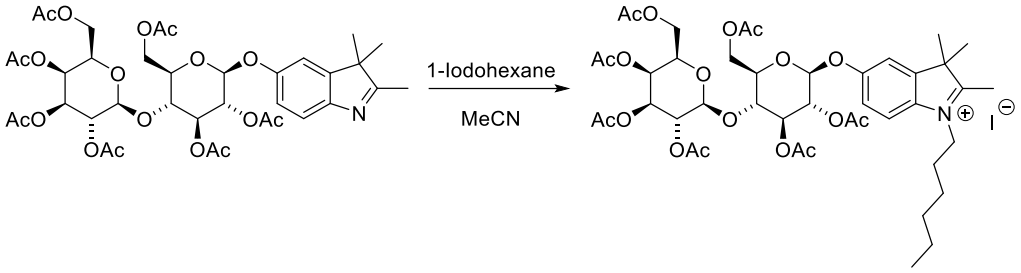
^{1}H-NMR (500 MHz, MeOD) δ [ppm] = 7.81 (d, $^{3}J_{HH}$ = 8.9 Hz, 1H, H-9), 7.45 (d, $^{4}J_{HH}$ = 2.4 Hz, 1H, H-22), 7.28 (dd, $^{3,4}J_{HH}$ = 8.9, 2.4 Hz, 1H, H-8), 5.54 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, H-2), 5.40 (t, $^{3}J_{HH}$ = 9.5 Hz, 1H, H-5), 5.21 (m, 1H, H-4), 5.14 (t, $^{3}J_{HH}$ = 9.7 Hz, 1H, H-3), 4.50 - 4.44 (m, 2H, H-11), 4.29 (dd, $^{2,3}J_{HH}$ = 12.5, 4.8 Hz, 1H, H-1), 4.22 - 4.17 (m, 2H, H-1‘, H-6), 2.04 (s, 6H, 2x OAc), 2.04 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.97 - 1.90 (m, 2H, H-12), 1.60 (s, 3H, H-20), 1.60 (s, 3H, H-20‘), 1.50 - 1.45 (m, 2H, H-13), 1.43 - 1.38 (m, 2H, H-14), 1.35 - 1.30 (m, 2H, H-15), 1.19 (s, 3H, H-18), 0.93 - 0.89 (m, 3H, H-16).

^{13}C-NMR (126 MHz, MeOD) δ [ppm] = 194.7 (C-17), 170.7 (OAc), 170.1 (OAc), 169.7 (OAc), 169.5 (OAc), 158.1 (C-21), 144.0 (C-7), 136.0 (C-10), 117.0 (C-9), 116.2 (C-8), 111.8 (C-22), 97.6 (C-2), 72.6 (C-5), 71.8 (C-6), 71.1 (C-4), 68.0 (C-3), 61.5 (C-1), 54.5 (C-19), 47.0 (C-11), 31.3 (C-15), 28.5 (C-14), 27.5 (C-12), 26.2 (C-13), 25.8 (C-18), 21.3 (C-20), 21.3 (C-20‘), 19.2 (OAc), 19.1 (3x OAc), 19.1 (C-16).

FT-IR ATR, v [cm^{-1}] = 3476 (w), 2928 (w), 2858 (w), 2112 (w), 1747 (m), 1610 (w), 1478 (w), 1366 (w), 1212 (s), 1066 (m), 1034 (s), 960 (w), 908 (w), 894 (w), 750 (w), 724 28 (w), 701 (w), 642 (w), 598 (w), 562 (w), 504 (w), 483 (w), 454 (w), 422 (w).

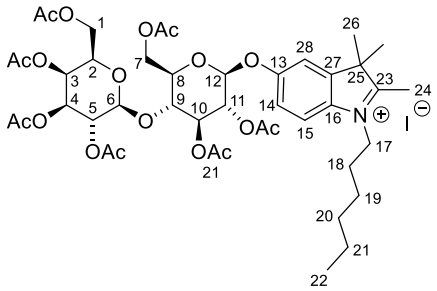
HR-MS (ESI) Calcd. $[M-I]^{+}$: 590.2959, found: 590.2970.

11.2.4.16.6 Synthesis of 5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4-diacetoxy-6-(acetoxymethyl)-5-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl) oxy) tetrahydro-2*H*-pyran-2-yl)oxy)-1-hexyl-2,3,3-trimethyl-3*H*-indol-1-ium iodide (46h)



45b **46h**

According to **GP10**, 0.70 g (0.84 mmol, 1.00 eq.) of indole **45b** were reacted with 0.58 mL (3.35 mmol, 4.00 eq.) of hexyl iodide in 3 mL MeCN for 20 h at reflux. After purification, 0.64 g (0.63 mmol, 71%) of the desired product **46h** were obtained as a brown solid.



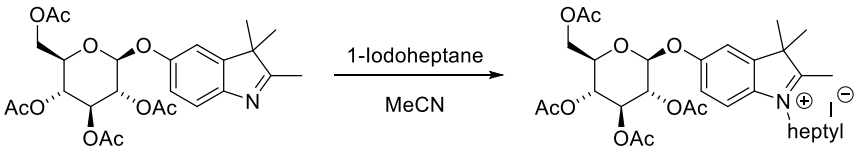
M($C_{43}H_{60}NO_{18}$)	1005.90 g/mol.
m.p.	179 - 181 °C.
^{1}H-NMR	(500 MHz, DMSO-d_6) δ [ppm] = 7.92 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H-15), 7.47 (d, $^4J_{HH}$ = 2.5 Hz, 1H, H-28), 7.18 (dd, $^{3,4}J_{HH}$ = 8.9, 2.4 Hz, 1H, H-14), 5.67 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H-6), 5.30 – 5.23 (m, 2H, H-3, H-4), 5.18 (m, 1H, H-5), 5.02 (m, 1H, H-10), 4.87 (m, 1H, H-9), 4.78 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H-12), 4.41 (t, $^3J_{HH}$ = 7.7 Hz, 2H, H-17), 4.37 (dd, $^{2,3}J_{HH}$ = 12.1, 1.9 Hz, 1H, H-7), 4.26 – 4.22 (m, 1H, H-11), 4.19 – 4.14 (m, 1H, H-2), 4.10 – 4.06 (m, 1H, H-7‘), 4.04 (m, 2H, H-1), 3.93 (m, 1H, H-8), 2.11 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.01 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.91 (s, 3H, OAc), 1.80 (m, 2H, H-18), 1.51 (s, 6H, H-26), 1.41 – 1.22 (m, 6H, H-19, H-20, H-21), 1.11 (s, 3H, H-24), 0.86 (t, $^3J_{HH}$ = 6.9 Hz, 3H, H-22).

^{13}C-NMR (126 MHz, DMSO-d_6) δ [ppm] = 195.2 (C-23), 170.6 (OAc), 170.3 (2x OAc), 169.9 (OAc), 169.8 (OAc), 169.6 (OAc), 169.5 (OAc), 157.6 (C-27), 144.3 (C-13), 136.4 (C-16), 117.0 (C-15), 116.4 (C-14), 112.2 (C-28), 100.4 (C-12), 96.7 (C-6), 76.4 (C-8), 72.7 (C-3), 72.5 (C-2), 71.1 (C-10), 70.7 (C-5), 70.1 (C-11), 69.3 (C-9), 67.5 (C-4), 62.5 (C-7), 61.3 (C-1), 48.1 (C-17), 31.4 (C-19), 28.7 (C-20), 27.7 (C-18), 27.3 (C-24), 26.2 (C-25), 22.5 (C-26), 22.4 (C-21), 21.0 (2x OAc), 20.9 (OAc), 20.8 (OAc), 20.8 (OAc), 20.8 (OAc), 20.7 (OAc), 14.3 (C-22).

FT-IR ATR, v [cm^{-1}] = 2932 (w), 1745 (m), 1611 (w), 1481 (w), 1437 (w), 1368 (m), 1220 (s), 1175 (w), 1134 (w), 1047 (m), 953 (w), 903 (w), 850 (w), 825 (w), 744 (w), 724 (w), 633 (w), 601 (w), 493 (w), 452 (w), 436 (w), 403 (w).

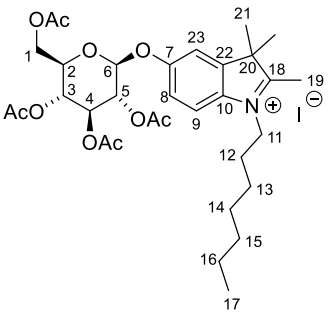
HR-MS (ESI) Calcd. [M-I]$^+$: 878.3804, found: 878.3812.

11.2.4.16.7 Synthesis of 1-heptyl-2,3,3-trimethyl-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tri acetoxy -6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-3*H*-indol-1-ium iodide (46d)



45a **46d**

According to **GP10**, 2.10 g (4.15 mmol, 1.00 eq.) of indole **45a** were reacted with 2.72 mL (16.6 mmol, 4.00 eq.) of heptyl iodide in 8 mL MeCN for 17 h at reflux. After purification, 3.03 g (4.14 mmol, >99%) of the desired product **46d** were obtained as a brown solid.



M($C_{32}H_{46}NO_{10}$) 731.62 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:2) = 0.50.

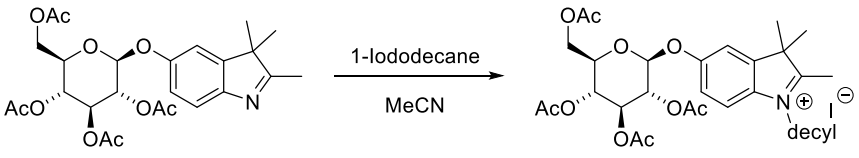
^{1}H-NMR (500 MHz, MeOD) δ [ppm] = 7.82 (d, $^{3}J_{HH}$ = 8.9 Hz, 1H, H-9), 7.46 (d, $^{4}J_{HH}$ = 2.4 Hz, 1H, H-23), 7.28 (dd, $^{3,4}J_{HH}$ = 8.9, 2.4 Hz, 1H, H-8), 5.55 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, H-2), 5.40 (t, $^{3}J_{HH}$ = 9.5 Hz, 1H, H-5), 5.21 – 5.19 (m, 1H, H-4), 5.14 (t, $^{3}J_{HH}$ = 9.6 Hz, 1H, H-3), 4.50 – 4.44 (m, 2H, H-11), 4.29 (dd, $^{2,3}J_{HH}$ = 12.9, 5.2 Hz, 1H, H-1), 4.19 (m, 2H, H-1‘, H-6), 2.04 (s, 9H, 3x OAc), 2.00 (s, 3H, OAc), 1.97 – 1.91 (m, 2H, H-12), 1.61 (s, 3H, H-21), 1.60 (s, 3H, H-21‘), 1.50 – 1.31 (m, 8H, H-13, H-14, H-15, H-16), 0.95 (t, $^{3}J_{HH}$ = 6.9 Hz, 3H, H-17).

^{13}C-NMR (126 MHz, MeOD) δ [ppm] = 194.8 (C-18), 170.7 (OAc), 170.1 (OAc), 169.8 (OAc), 169.6 (OAc), 158.1 (C-22), 144.0 (C-7), 136.0 (C-10), 117.0 (C-8), 116.3 (C-9), 111.7 (C-23), 97.6 (C-2), 72.6 (C-5), 71.8 (C-6), 71.1 (C-4), 68.0 (C-3), 61.5 (C-1), 54.5 (C-20) 47.8 (C-11), 33.1 (C-14), 32.3 (C-15), 28.3 (C-13), 27.2 (C-12), 21.9 (C-19), 21.4 (C-21), 21.3 (C-21‘), 21.2 (C-16), 19.1 (OAc), 19.1 (2x OAc), 19.1 (OAc), 12.7 (C-17).

FT-IR ATR, v [cm^{-1}] = 3456 (w), 2928 (w), 2857 (w), 1747 (m), 1611 (w), 1478 (w), 1437 (w), 1366 (w), 1286 (w), 1212 (s), 1120 (w), 1065 (m), 1035 (s), 961 (w), 908 (w), 895 (w), 825 (w), 751 (w), 724 (w), 702 (w), 645 (w), 598 (w), 562 (w), 533 (w), 505 (w).

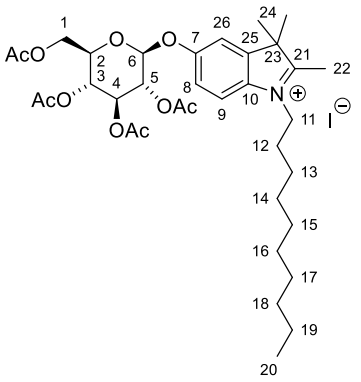
HR-MS (ESI) Calcd. [M-I]$^{+}$: 604.3116, found: 604.3108.

11.2.4.16.8 Synthesis of 1-decyl-2,3,3-trimethyl-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tri acetoxy -6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-3*H*-indol-1-ium iodide (46e)



45a **46e**

According to **GP10**, 2.10 g (4.15 mmol, 1.00 eq.) of indole **45a** were reacted with 3.54 mL (16.6 mmol, 4.00 eq.) of decyl iodide in 8 mL MeCN for 16 h at reflux. After purification, 3.20 g (4.15 mmol, >99%) of the desired product **46e** were obtained as a brown solid.



M($C_{35}H_{52}NO_{10}$) 773.70 g/mol.

R_f (SiO_2, cHex/EtOAc 1:2) = 0.85.

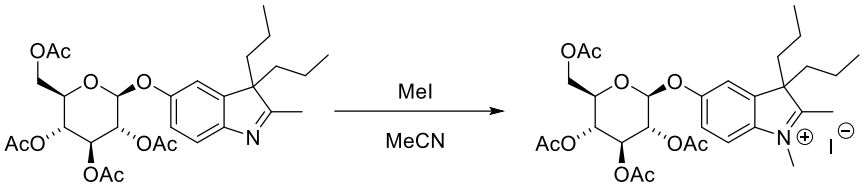
^{1}H-NMR (500 MHz, MeOD) δ [ppm] = 7.82 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H-9), 7.46 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-26), 7.28 (dd, $^{3,4}J_{HH}$ = 8.9, 2.4 Hz, 1H, H-8), 5.56 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H-2), 5.40 (t, $^3J_{HH}$ = 9.5 Hz, 1H, H-5), 5.23 – 5.19 (m, 1H, H-4), 5.17 – 5.12 (m, 1H, H-3), 4.47 (t, $^3J_{HH}$ = 7.8 Hz, 2H, H-11), 4.28 (dd, $^{2,3}J_{HH}$ = 4.8, 2.6 Hz, 1H, H-1), 4.20 (m, 2H, H-6, H-1‘), 2.04 (m, 9H, 3x OAc), 2.00 (s, 3H, OAc), 1.97 – 1.91 (m, 2H, H-12), 1.61 (s, 3H, H-24), 1.60 (s, 3H, H-24‘), 1.51 – 1.44 (m, 2H, H-13), 1.43 – 1.37 (m, 2H, H-14), 1.33 (s, 3H, H-22), 1.29 (m, 10H, H-15, H-16, H-17, H-18, H-19), 0.89 (m, 3H, H-20).

^{13}C-NMR (126 MHz, MeOD) δ [ppm] = 194.7 (C-21), 170.7 (OAc), 170.1 (OAc), 169.8 (OAc), 169.6 (OAc), 158.1 (C-25), 144.0 (C-7), 136.0 (C-10), 117.0 (C-8), 116.3 (C-9), 111.7 (C-26), 97.6 (C-2), 72.6 (C-5), 71.8 (C-6), 71.1 (C-4), 68.0 (C-3), 61.5 (C-1), 47.8 (C-11), 31.6 (C-16), 29.1 (C-14), 29.1 (C-17), 28.9 (C-23), 28.8 (C-13), 27.5 (C-12), 26.2 (C-18), 22.3 (C-19), 21.8 (C-22), 21.4 (C-24), 21.3 (C-24’), 19.2 (OAc), 19.1 (2x OAc), 19.1 (OAc), 13.0 (C-20).

FT-IR ATR, v [cm^{-1}] = 3456 (w), 2925 (w), 2854 (w), 2116 (w), 1748 (m), 1611 (w), 1479 (w), 1436 (w), 1366 (w), 1287 (w), 1212 (s), 1120 (w), 1065 (m), 1035 (s), 961 (w), 908 (w), 825 (w), 723 (w), 702 (w), 644 (w), 599 (w), 562 (w), 532 (w), 505 (w).

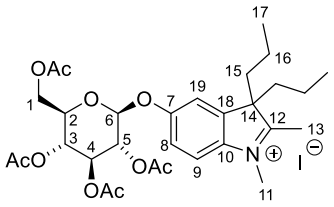
HR-MS (ESI) Calcd. $[M-I]^+$: 646.3585, found: 646.3583.

11.2.4.16.9 Synthesis of 1,2-dimethyl-3,3-dipropyl-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacet-oxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-3*H*-indol-1-ium iodide (52a)



45e **52a**

According to **GP10**, 0.15 g (0.26 mmol, 1.00 eq.) of indole **45e** were reacted with 0.05 mL (0.78 mmol, 3.00 eq.) of methyl iodide in 0.5 mL MeCN for 3 h at reflux. After purification, 0.15 g (0.21 mmol, 82%) of the desired product **52a** were obtained as a brown solid.



M($C_{30}H_{42}NO_{10}$) 703.57 g/mol.

^{1}H-NMR (500 MHz, MeOD) δ [ppm] = 7.81 (d, $^3J_{HH}$ = 8.7 Hz, 1H, H-9), 7.39 (dd, $^{3,4}J_{HH}$ = 8.9, 2.4 Hz, 1H, H-8), 7.14 (d, $^3J_{HH}$ = 2.3 Hz, 1H, H-19), 5.37 – 5.26 (m, 2H, H-4, H-6), 5.23 – 5.17 (m, 1H, H-5), 4.41 (s, 3H, H-11), 4.31 (dd, $^{2,3}J_{HH}$ = 12.5, 4.6 Hz, 1H, H-1), 4.30 – 4.19 (m, H1, H-1‘), 4.08 – 4.02 (m, 2H, H-2, H-3), 3.08 (s, 3H, H-13), 2.14 – 2.13 (m, 2H, H-15), 2.10 (s, 6H, 2x OAc), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.00 – 0.92 (m, 2H, H-15‘), 0.86 - 0.78 (m, 10H, H-16, H-17).

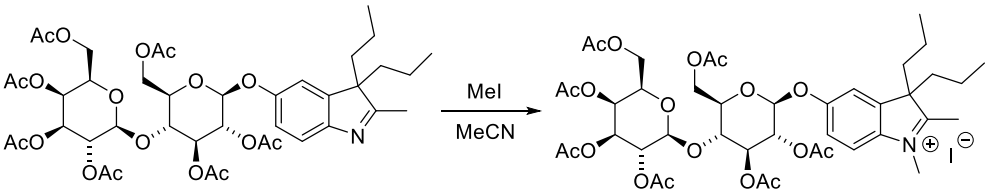
^{13}C-NMR (126 MHz, MeOD) δ [ppm] = 194.4 (C-12), 170.5 (OAc), 170.0 (2x OAc), 169.4 (OAc), 158.0 (C-18), 140.6 (C-7), 138.1 (C-10), 116.9 (C-8), 113.4 (C-9), 112.5 (C-19), 72.4 (C-6), 71.0 (C-3), 70.5 (C-4), 69.0 (C-2), 67.9 (C-5), 63.9 (C-14), 61.7 (C-1), 39.1 (C-15), 38.1 (C-11), 20.8 (OAc), 20.8 (OAc), 20.7 (OAc), 20.6 (OAc), 17.7 (C-16), 17.7 (C-16‘), 17.1 (C-13), 14.0 (C-17), 14.0 (C-17‘).

FT-IR ATR, v [cm^{-1}] = 3476 (w), 2960 (w), 2933 (w), 2873 (w), 2131 (w), 2027 (w), 1749 (s), 1610 (w), 1555 (w), 1475 (w), 1406 (w), 1367 (m), 1228 (s), 1117 (w), 1069 (m), 1038 (s), 962 (w),

908 (w), 820 (w), 771 (w), 699 (w), 640 (w), 601 (w), 559 (w), 532 (w), 506 (w).

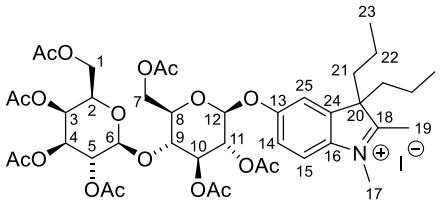
HR-MS (ESI) Calcd. $[M-I]^+$: 576.2803, found: 576.2790.

11.2.4.16.10 Synthesis of 5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4-diacetoxy-6-(acetoxymethyl)-5-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)-1,2-dimethyl-3,3-dipropyl-3*H*-indol-1-ium iodide (52b)



45f **52b**

According to **GP10**, 0.48 g (0.56 mmol, 1.00 eq.) of indole **45f** were reacted with 010 mL (1.68 mmol, 3.00 eq.) of methyl iodide in 1.10 mL MeCN for 3 h at reflux. After purification, 0.53 g (0.53 mmol, 95%) of the desired product **52b** were obtained as a brown solid.



M($C_{42}H_{58}NO_{18}$) 991.82 g/mol.

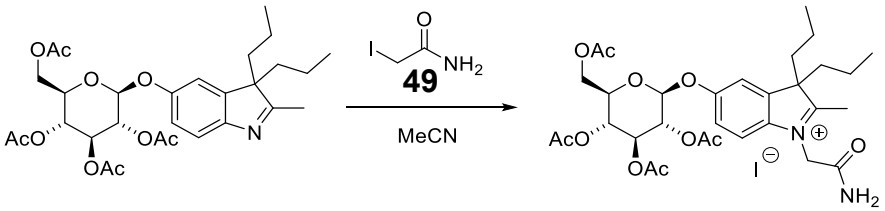
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.81 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H-15), 7.24 (dd, $^{3,4}J_{HH}$ = 8.9, 2.4 Hz, 1H, H-14), 7.14 (d, $^4J_{HH}$ = 2.5 Hz, 1H, H-25), 5.39 – 5.35 (m, 1H, H-5), 5.32 (t, $^3J_{HH}$ = 8.8 Hz, 1H, H-4), 5.26 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H-6), 5.21 (m, 1H, H-3), 5.15 - 5.10 (m, 1H, H-10), 5.01 - 4.96 (m, 1H, H-9), 4.59 - 4.48 (m, 2H, H-7, H-12), 4.41 (s, 3H, H-17), 4.21 – 4.08 (m, 3H, H-7‘, H-1, H-1‘), 4.01 – 3.98 (m, 1H, H-8), 3.95 – 3.87 (m, 2H, H-2, H-11), 3.09 (s, 3H, H-19), 2.16 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.09 (s, 6H, 2x OAc), 2.08 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.07 - 2.04 (m, 2H, H-21), 1.98 (s, 3H, OAc), 1.00 - 0.88 (m, 2H, H-21‘), 0.86 - 0.76 (m, 10H, H-22, H-23).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 194.5 (C-18), 170.3 (OAc), 170.1 (OAc), 170.1 (OAc), 170.0 (OAc), 169.6 (OAc), 169.6 (OAc), 169.1 (OAc), 158.0 (C-24), 140.6 (C-13), 138.1 (C-16), 117.1 (C-14), 116.5 (C-15), 113.2 (C-25), 101.1 (C-12), 98.2 (C-6), 75.7 (C-2), 73.1 (C-8), 72.5 (C-4), 71.3 (C-3), 70.9 (C-9), 70.7 (C-11), 69.0 (C-10), 66.6 (C-5), 63.9 (C-20), 61.6 (C-7), 60.7 (C-1), 39.1 (C-21), 38.1 (C-17), 21.0 (OAc), 20.8 (OAc), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 20.5 (OAc), 17.6 (C-22), 17.1 (C-19), 14.0 (C-23).

FT-IR ATR, v [cm^{-1}] = 3400 (w), 2967 (w), 2936 (w), 2901 (w), 2877 (w), 2126 (w), 1927 (w), 1746 (s), 1634 (w), 1612 (w), 1481 (w), 1455 (w), 1431 (w), 1369 (m), 1325 (w), 1218 (s), 1173 (w), 1152 (w), 1124 (w), 1071 (s), 1044 (s), 986 (w), 951 (w), 903 (w), 880 (w), 823 (w), 745 (w), 710 (w), 680 (w), 633 (w), 604 (w), 591 (w), 555 (w), 528 (w).

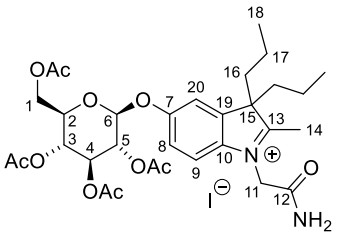
HR-MS (ESI) Calcd. $[M-I]^+$: 864.3648401, found: 864.36504.

11.2.4.16.11 Synthesis of 1-(2-amino-2-oxoethyl)-2-methyl-3,3-dipropyl-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl) oxy)-3*H*-indol-1-ium iodide (52c)



45e **52c**

According to **GP10**, 3.13 g (5.57 mmol, 1.00 eq.) of indole **45e** were reacted with 4.12 g (22.3 mmol, 4.00 eq.) of 2-iodoacetamide (**49**) in 23 mL MeCN for 16.5 h at reflux. After purification, 4.10 g (5.49 mmol, 99%) of the desired product **52c** were obtained as a brown solid.



M($C_{31}H_{43}NO_{11}$) 746.59 g/mol.

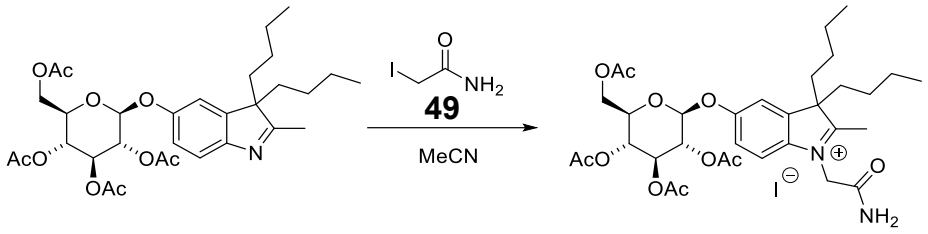
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.18 (s, 1H, *N*H), 8.06 (d, $^{3}J_{HH}$ = 8.9 Hz, 1H, H-9), 7.28 (m, 1H, H-8), 7.10 (d, $^{4}J_{HH}$ = 2.3 Hz, 1H, H-20), 5.86 – 5.78 (m, 3H, *N*H, H-11), 5.36 – 5.30 (m, 2H, H-4, H-5), 5.25 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H, H-6), 5.19 (t, $^{3}J_{HH}$ = 9.4 Hz, 1H, H-3), 4.30 (dd, $^{2,3}J_{HH}$ = 12.4, 5.0 Hz, 1H, H-1), 4.19 (dd, $^{2,3}J_{HH}$ = 12.5, 2.4 Hz, 1H, H-1‘), 3.99 – 3.95 (m, 1H, H-2), 2.82 (s, 3H, H-14), 2.17 – 2.12 (m, 2H, H-16), 2.11 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.04 – 1.98 (m, 2H, H-16‘), 1.06 – 0.92 (m, 2H, H-17), 0.89 – 0.75 (m, 8H, H-17‘, H-18).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 196.9 (C-13), 170.5 (OAc), 170.1 (OAc), 169.4 (OAc), 169.4 (OAc), 163.3 (C-12), 158.1 (C-19), 140.1 (C-7), 137.6 (C-10), 117.2 (C-9), 116.7 (C-8), 113.5 (C-20), 98.4 (C-6), 72.5 (C-2), 72.4 (C-5), 71.0 (C-4), 67.9 (C-3), 64.3 (C-15), 61.6 (C-1), 51.8 (C-11), 40.0 (C-16), 39.9 (C-16‘), 20.9 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 17.5 (C-17), 17.4 (C-17‘), 15.6 (C-14), 14.1 (C-18), 14.0 (C-18‘).

FT-IR ATR, ν [cm^{-1}] = 3903 (w), 3750 (w), 3423 (m), 3333 (m), 3187 (m), 2960 (m), 2935 (w), 2873 (w), 2325 (w), 2115 (w), 1943 (w), 1747 (s), 1669 (s), 1610 (m), 1480 (m), 1430 (m), 1368 (s), 1229 (s), 1122 (m), 1066 (s), 1040 (s), 987 (m), 910 (m), 886 (m), 821 (m), 772 (m), 598 (m), 577 (m).

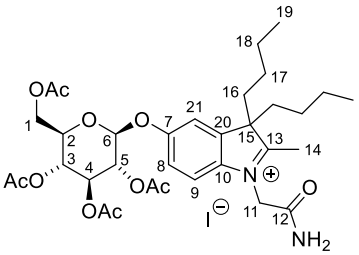
HR-MS (ESI) Calcd. $[M-I]^{+}$: 619.2861, found: 619.2855.

11.2.4.16.12 Synthesis of 1-(2-amino-2-oxoethyl)-3,3-dibutyl-2-methyl-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-3*H*-indol-1-ium iodide (52d)



45g **52d**

According to **GP10**, 0.39 g (0.66 mmol, 1.00 eq.) of indole **45g** were reacted with 0.49 g (2.63 mmol, 4.00 eq.) of 2-iodoacetamide (**49**) in 2.5 mL MeCN for 17 h at reflux. After purification, 0.51 g (0.66 mmol, >99%) of the desired product **52d** were obtained as a brown solid.



M($C_{33}H_{47}NO_{11}$) 774.65 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.32 (s, 1H, *N*H), 8.07 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H-9), 7.29 (dd, $^3J_{HH}$ = 8.8, 2.3 Hz, 1H, H-8), 7.09 (d, $^4J_{HH}$ = 2.3 Hz, 1H, H-21), 5.79 (m, 3H, *N*H, H-11), 5.36 – 5.31 (m, 2H, H-5, H-4), 5.24 (d, $^3J_{HH}$ = 7.3 Hz, 1H, H-6), 5.19 (t, $^3J_{HH}$ = 9.6 Hz, 1H, H-3), 4.32 (dd, $^3J_{HH}$ = 12.5, 4.9 Hz, 1H, H-1), 4.19 (dd, $^3J_{HH}$ = 12.4, 2.3 Hz, 1H, H-1‘), 3.97 (m, 1H, H-2), 2.80 (s, 3H, H-14), 2.17 (m, 2H, H-16), 2.11 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.04 – 2.02 (m, 2H, H-16‘), 1.23 (m, 4H, H-17), 0.99 – 0.86 (m, 2H, H-18), 0.81 (m, 6H, H-19), 0.74 (m, 2H, H-18‘).

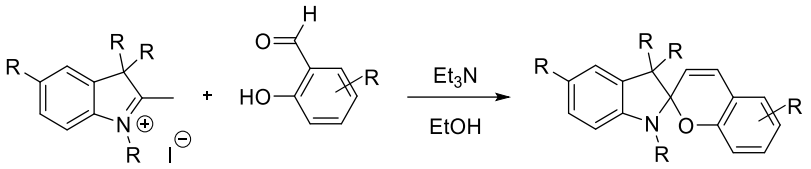
^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 196.5 (C-13), 172.4 (OAc), 170.5 (OAc), 169.4 (OAc), 169.0 (OAc), 163.2 (C-12), 158.2 (C-20), 140.1 (C-7), 137.6 (C-10), 117.3 (C-9), 116.7 (C-8), 113.6 (C-21), 98.6 (C-6), 72.5 (C-5), 72.4 (C-2), 71.0 (C-4), 67.8 (C-3), 64.1 (C-15), 61.6 (C-1), 51.7 (C-11), 37.5 (C-16), 25.9 (C-18), 25.0

(C-18‘), 22.6 (C-17), 22.6 (C-17‘), 20.9 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 15.5 (C-14), 13.5 (C-19).

FT-IR ATR, v [cm^{-1}] = 3424 (w), 3335 (w), 3187 (w), 2957 (w), 2934 (w), 2871 (w), 2111 (w), 1935 (w), 1748 (s), 1672 (s), 1610 (m), 1480 (m), 1456 (w), 1430 (m), 1368 (m), 1226 (s), 1120 (m), 1067 (m), 1039 (s), 985 (w), 961 (w), 913 (w), 816 (w), 758 (w), 698 (w), 599 (m), 513 (w).

HR-MS (ESI) Calcd. $[M\text{-}I]^+$: 647.3174, found: 647.3173.

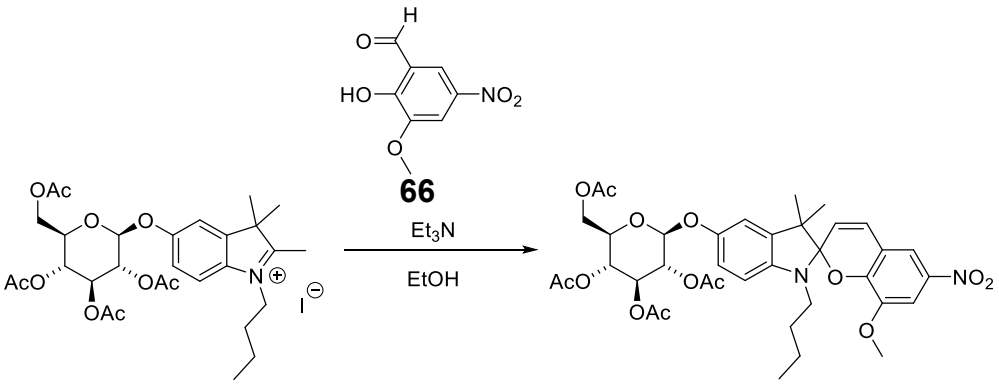
11.2.5 Condensation of indoles and aromatic aldehydes: General protocol (GP17)



31 **32** **28**

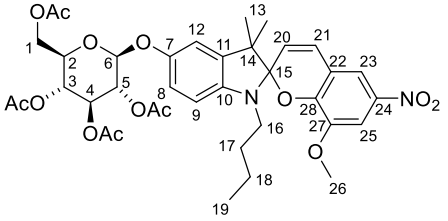
Indole **31** (1.00 eq.) was dissolved in EtOH. The aromatic aldehyde **32** (1.00 eq.) and Et_3N (1.00 eq.) were added and the mixture was heated to reflux. After full conversion the mixture was cooled to rt and the solvent was removed under reduced pressure. The crude product was washed with MTBE or Et_2O.

11.2.5.1 Synthesis of (2*R*,3*R*,4*S*,5*R*)-2-(acetoxymethyl)-6-((1'-butyl-8-methoxy-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (93)



46a **93**

According to **GP17**, 2.00 g (2.90 mmol, 1.00 eq.) of indole **46a** were reacted with 0.57 g (2.90 mmol, 1.00 eq.) of aldehyde **66** and 0.40 mL (2.90 mmol, 1.00 eq.) Et_3N in 6 mL EtOH for 24 h. After purification, 2.10 g (2.83 mmol, 98%) of spiropyran **93** were obtained as blue solid.



M($C_{37}H_{44}N_2O_{14}$) 740.76 g/mol.

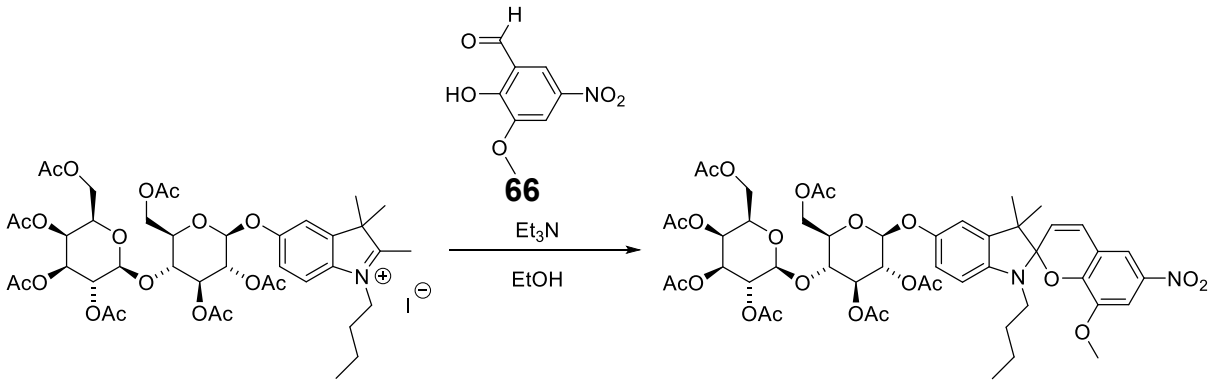
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.69 - 7.68 (m, 1H, H-23), 7.63 - 7.62 (m, 1H, H-25), 6.84 (d, $^{3}J_{HH}$ = 10.4 Hz, 1H, H-20), 6.80 (dt, $^{3,4}J_{HH}$ = 8.3, 2.6 Hz, 1H, H-8), 6.76 – 6.75 (m, 1H, H-12), 6.43 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, H-9), 5.81 (dd, $^{3,4}J_{HH}$ = 10.3, 1.0 Hz, 1H, H-21), 5.39 – 5.23 (m, 2H, H-4, H-5), 5.21 – 5.09 (m, 1H, H-3), 5.03 – 5.00 (m, 1H, H-6), 4.29 (m, 1H, H-1), 4.19 (dd, $^{2,3}J_{HH}$ = 12.2, 2.5 Hz, 1H, H-1‘), 3.86 – 3.83 (m, 1H, H-2), 3.77 (s, 3H, H-26), 3.21 – 3.14 (m, 1H, H-16), 3.11 – 3.06 (m, 1H, H-16‘), 2.10 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.04 (m, 6H, 2x OAc), 1.66 – 1.54 (m, 1H, H-17), 1.51 – 1.49 (m, 1H, H-17‘), 1.39 – 1.29 (m, 2H, H-18), 1.24 (d, $^{4}J_{HH}$ = 4.2 Hz, 3H, H-13), 1.16 (d, $^{3}J_{HH}$ = 3.8 Hz, 3H, H-13‘), 0.88 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, H-19).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.6 (OAc), 170.3 (OAc), 169.4 (OAc), 169.3 (OAc), 150.5 (C-7), 149.4 (C-28), 147.3 (C-27), 143.5 (C-11), 140.3 (C-24), 137.6 (C-10), 128.1 (C-20), 121.8 (C-21), 118.2 (C-22), 116.1 (C-8), 115.3 (C-23), 112.8 (C-12), 107.9 (C-25), 107.0 (C-15), 106.4 (C-9), 100.5 (C-6), 72.8 (C-4), 71.9 (C-2), 71.3 (C-5), 68.3 (C-3), 62.0 (C-1), 56.3 (C-26), 52.6 (C-14), 43.5 (C-16), 31.0 (C-17), 25.9 (C-13), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 20.4 (C-18), 13.9 (C-19).

FT-IR ATR, v [cm^{-1}] = 3475 (w), 2961 (w), 2871 (w), 2132 (w), 1754 (s), 1655 (w), 1592 (w), 1520 (m), 1487 (m), 1366 (w), 1336 (m), 1221 (s), 1173 (w), 1115 (w), 1087 (m), 1067 (m), 1041 (m), 984 (w), 910 (w), 853 (w), 818 (w), 790 (w), 743 (w), 698 (w), 646 (w), 599 (w).

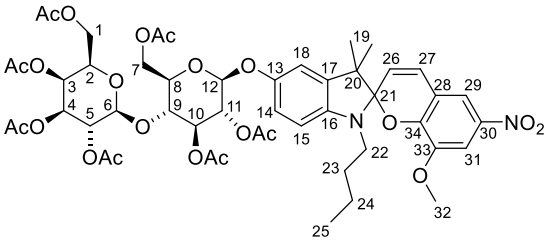
HR-MS (ESI) Calcd. $[M+H]^+$: 741.2865, found: 741.2868.
Calcd. $[M+Na]^+$: 763.2685, found: 763.2684.
Calcd. $[M+H+Na]^{2+}$: 779.2424, found: 779.2428.

11.2.5.2 Synthesis of (2R,3S,4S,5R)-2-acetoxymethyl)-6-(((2R,3R,4S,5R)-4,5-di acetoxy-2-(acetoxymethyl)-6-((1'-butyl-8-methoxy-3',3'-dimethyl-6-nitrospiro [chromene-2,2'-indolin]-5'-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (95)



46f **95**

According to **GP17**, 1.60 g (1.88 mmol, 1.00 eq.) of indole **46f** were reacted with 0.37 g (1.88 mmol, 1.00 eq.) of aldehyde **66** and 0.26 mL (1.88 mmol, 1.00 eq.) Et_3N in 4 mL EtOH for 16.5 h. After purification, 1.78 g (1.73 mmol, 92%) of spiropyran **95** were obtained as a blue solid.



M($C_{49}H_{60}N_2O_{22}$) 1029.01 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.68 - 7.68 (m, 1H, H-29), 7.63 - 7.61 (m, 1H, H-31), 6.84 (d, $^3J_{HH}$ = 10.4 Hz, 1H, H-26), 6.78 (dd, $^{3,4}J_{HH}$ = 8.3, 2.1 Hz, 1H, H-14), 6.74 – 6.73 (m, 1H, H-18), 6.41 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H-15), 5.81 (dd, $^{3,4}J_{HH}$ = 10.4, 1.3 Hz, 1H, H-27), 5.37 – 5.36 (m, 1H, H-12), 5.30 – 5.25 (m, 1H, H-6), 5.17 – 5.10 (m, 2H, H-3, H-5), 5.01 – 4.95 (m, 2H, H-4, H-11), 4.54 – 4.51 (m, 3H, H-1, H-10), 4.18 – 4.11 (m, 2H, H-7), 3.92 – 3.87 (m, 2H, H-2, H-8), 3.77 (s, 3H, H-32), 3.76 – 3.75 (m, 1H, H-9), 3.18 – 3.05 (m, 2H, H-22), 2.16 (s, 3H, OAc), 2.10 – 2.08 (m, 9H, 3x OAc), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.63 - 1.56 (m, 2H, H-23), 1.52 - 1.45 (m, 2H, H-24), 1.24 - 1.23 (m, 3H, H-19), 1.16 - 1.15 (m, 3H, H-19'), 0.88 (t, $^3J_{HH}$ = 7.4 Hz, 3H, H-25).

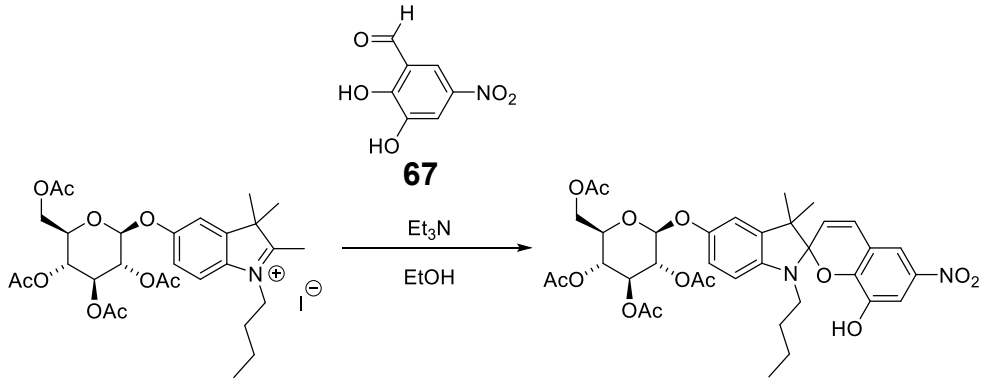
^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.3 (OAc), 170.3 (OAc), 170.1 (OAc), 170.0 (OAc), 169.8 (OAc), 169.6 (OAc), 169.1 (OAc), 150.5

(C-13), 149.4 (C-34), 147.3 (C-33), 143.4 (C-17), 140.3 (C-30), 137.4 (C-16), 128.1 (C-26), 121.8 (C-27), 118.2 (C-28), 116.1 (C-14), 115.6 (C-29), 112.7 (C-18), 107.8 (C-31), 107.0 (C-21), 106.3 (C-15), 101.1 (C-10), 100.1 (C-11), 76.2 (C-2), 72.8 (C-6), 72.7 (C-9), 71.7 (C-3), 70.9 (C-4), 70.7 (C-8), 69.1 (C-5), 66.6 (C-12), 62.0 (C-7), 60.8 (C-1), 56.2 (C-32), 52.6 (C-20), 43.5 (C-22), 31.0 (C-23), 21.0 (OAc), 20.8 (OAc), 20.8 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 20.5(OAc), 20.47 (C-24), 19.7 (C-19), 19.7 (C-19‘), 13.9 (C-25).

FT-IR ATR, v [cm^{-1}] = 3475 (w), 2962 (w), 2872 (w), 2255 (w), 2123 (w), 1750 (s), 1660 (w), 1592 (w), 1520 (w), 1486 (w), 1369 (m), 1338 (w), 1222 (s), 1172 (w), 1114 (w), 1051 (m), 984 (w), 958 (w), 911 (w), 823 (w), 789 (w), 733 (w), 648 (w), 602 (w).

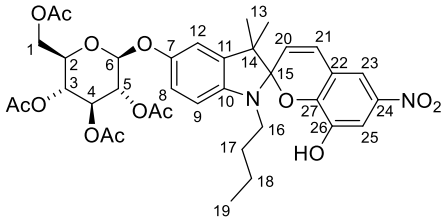
HR-MS (ESI) Calcd. $[M+H]^+$: 1029.3710, found: 1029.3714.
Calcd. $[M+Na]^+$: 1051.3529, found: 1051.3533.

11.2.5.3 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((1'-butyl-8-hydroxy-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (94)



46a **94**

According to **GP17**, 0.40 g (0.58 mmol, 1.00 eq.) of indole **46a** were reacted with 0.11 g (0.58 mmol, 1.00 eq.) of aldehyde **67** and 0.08 mL (0.58 mmol, 1.00 eq.) Et_3N in 1.20 mL EtOH for 24 h. After purification, 0.42 g (0.58 mmol, >99%) of spiropyran **94** were obtained as a blue solid.



M($C_{36}H_{42}N_2O_{14}$) 726.73 g/mol.

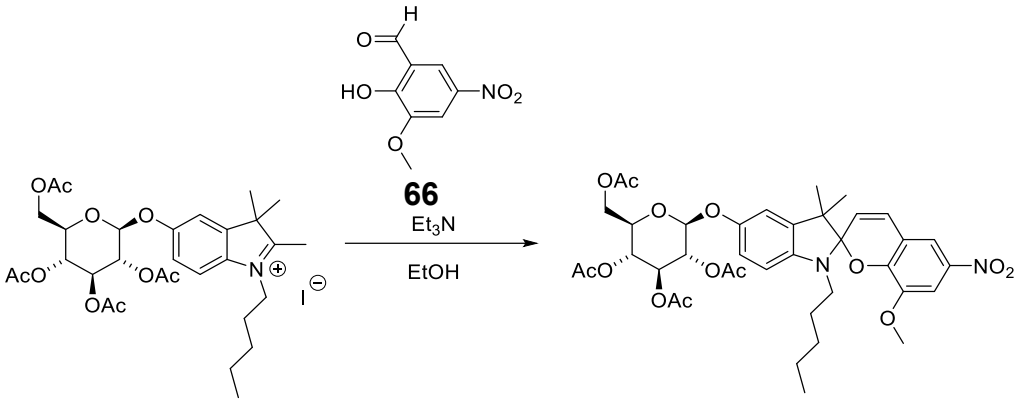
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.24 (br s, 1H, *O*H), 8.19 (d, $^4J_{HH}$ = 2.6 Hz, 1H, H-23), 8.04 (d, $^4J_{HH}$ = 2.6 Hz, 1H, H-25), 6.90 (d, $^3J_{HH}$ = 10.4 Hz, 1H, H-21), 6.86 – 6.82 (m, 1H, H-8), 6.77 – 6.75 (m, 1H, H-12), 6.47 – 6.44 (m, 1H, H-9), 5.85 (d, $^3J_{HH}$ = 10.4 Hz, 1H, H-20), 5.37 – 5.25 (m, 3H, H-3, H-4, H-5), 5.05 – 5.01 (m, 1H, H-6), 4.30 – 4.14 (m, 2H, H-1), 3.924 - 3.90 (m, 1H, H-2), 3.20 - 3.05 (m, 2H, H-16), 2.11 – 2.08 (m, 6H, 2x OAc), 2.06 - 2.04 (m, 6H, 2x OAc), 1.95 - 1.87 (m, 2H, H-17), 1.53 - 1.44 (m, 2H, H-18), 1.24 (m, 3H, H-13), 1.18 (m, 3H, H-13‘), 1.03 (t, $^3J_{HH}$ = 7.3 Hz, 3H, H-19).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 195.6 (C-26), 169.4 (OAc), 169.4 (OAc), 169.4 (OAc), 169.2 (OAc), 153.5 (C-24), 149.9 (C-7), 145.7 (C-27), 144.2 (C-11), 137.3 (C-10), 129.9 (C-21), 121.3 (C-20), 120.0 (C-23), 117.9 (C-22), 116.5 (C-8), 115.8 (C-25), 112.8 (C-12), 108.5 (C-15), 106.8 (C-9), 100.2 (C-6), 72.4 (C-5), 72.3 (C-2), 71.1 (C-4), 68.1 (C-3), 61.9 (C-1), 43.6 (C-16), 29.6 (C-17), 28.1 (C-13), 28.1 (C-13‘), 20.7 (OAc), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.4 (C-14), 20.3 (C-18), 13.7 (C-19).

FT-IR ATR, v [cm^{-1}] = 3365 (br w), 2963 (w), 1755 (m), 1664 (w), 1592 (w), 1565 (w), 1521 (w), 1474 (w), 1446 (w), 1368 (w), 1340 (w), 1287 (m), 1235 (s), 1114 (w), 1076 (w), 1041 (w), 953 (w), 910 (w), 825 (w), 774 (w), 745 (w), 598 (w).

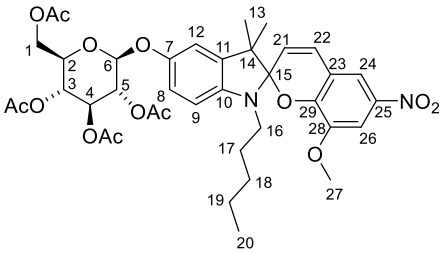
HR-MS (ESI) Calcd. $[M+H]^+$: 727.7088, found: 727.2710.
Calcd. $[M+Na]^+$: 749.2528, found: 749.2529.

11.2.5.4 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((8-methoxy-3',3'-dimethyl-6-nitro-1'-pentylspiro[chromene-2,2'-indolin]-5'-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (96)



46b **96**

According to **GP17**, 2.00 g (2.84 mmol, 1.00 eq.) of indole **46b** were reacted with 0.56 g (2.84 mmol, 1.00 eq.) of aldehyde **66** and 0.40 mL (2.84 mmol, 1.00 eq.) Et_3N in 6 mL EtOH for 18 h. After purification, 2.03 g (2.69 mmol, 95%) of spiropyran **96** were obtained as blue solid.

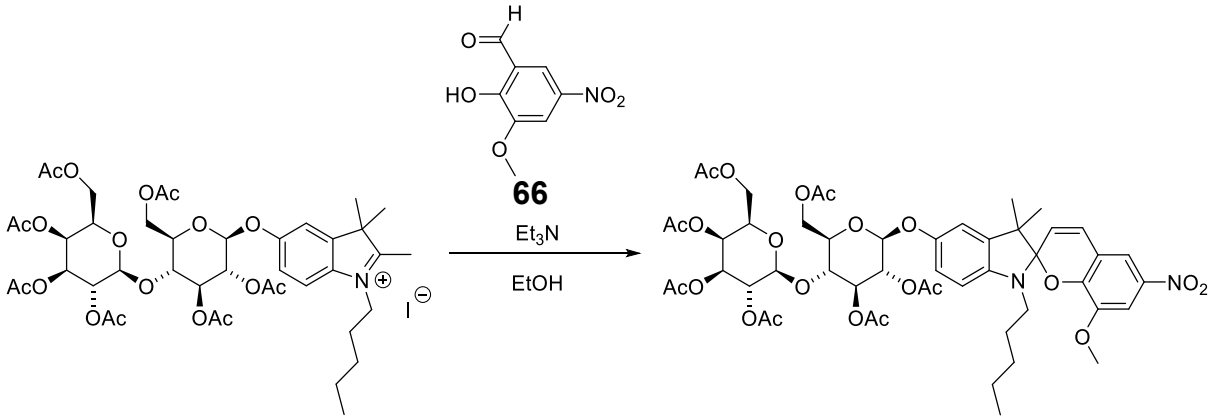


M($C_{38}H_{46}N_2O_{14}$) 754.79 g/mol.

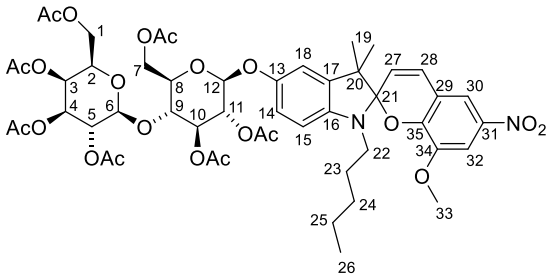
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.69 - 7.68 (m, 1H, H-24), 7.63 - 7.62 (m, 1H, H-26), 6.84 (d, $^3J_{HH}$ = 10.3 Hz, 1H, H-22), 6.80 (dt, $^{3,4}J_{HH}$ = 8.3, 2.5 Hz, 1H, H-8), 6.76 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-12), 6.42 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H-9), 5.81 (d, $^3J_{HH}$ = 10.2 Hz, 1H, H-21), 5.33 - 5.24 (m, 2H, H-2, H-5), 5.20 - 5.16 (m, 1H, H-4), 5.02 - 5.00 (m, 1H, H-6), 4.30 - 4.26 (m, 1H, H-1), 4.19 (dd, $^{2,3}J_{HH}$ = 12.2, 2.4 Hz, 1H, H-1‘), 3.86 - 3.82 (m, 1H, H-2), 3.77 (s, 3H, H-27), 3.20 - 3.03 (m, 2H, H-16), 2.11 - 2.08 (m, 6H, OAc), 2.07 - 2.04 (m, 6H, OAc), 1.62 - 1.57 (m, 2H, H-17), 1.29 - 1.27 (m, 4H, H-17, H-18), 1.24 - 1.23 (m, 3H, H-13), 1.16 (m, 3H, H-13‘), 0.85 (t, $^3J_{HH}$ = 6.8 Hz, 3H, H-20).

^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 170.6 (OAc), 170.3 (OAc), 169.4 (OAc), 169.3 (OAc), 150.5 (C-7), 149.4 (C-29), 147.3 (C-28), 143.5 (C-11), 140.3 (C-25), 137.6 (C-10), 128.1 (C-22), 121.8 (C-21), 118.2 (C-23), 115.6 (C-8), 115.4 (C-24), 112.8 (C-12), 107.8 (C-26), 107.0 (C-15), 106.3 (C-9), 100.5 (C-6), 72.2 (C-5), 71.9 (C-2), 71.3 (C-3), 68.3 (C-4), 62.1 (C-1), 56.3 (C-27), 52.6 (C-14), 43.8 (C-16), 29.4 (C-18), 28.5 (C-17), 22.4 (C-19), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 19.7 (C-13), 14.0 (C-20).
FT-IR	ATR, v [cm^{-1}] = 2960 (w), 2870 (w), 1756 (s), 1656 (w), 1592 (w), 1520 (m), 1487 (m), 1366 (w), 1337 (m), 1283 (m), 1227 (s), 1171 (w), 1115 (w), 1089 (m), 1067 (m), 1041 (m), 981 (w), 914 (w), 809 (w), 790 (w), 779 (w), 743 (w), 646 (w), 599 (w).
HR-MS (ESI)	Calcd. $[M+H]^+$: 755.3021, found: 755.3014. Calcd. $[M+Na]^+$: 777.2841, found: 777.2827.

11.2.5.5 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((8-methoxy-3',3'-dimethyl-6-nitro-1'-pentyl spiro[chro mene-2,2'-indolin]-5'-yl)oxy)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (97)



According to **GP17**, 2.00 g (2.02 mmol, 1.00 eq.) of indole **46g** were reacted with 0.40 g (2.02 mmol, 1.00 eq.) of aldehyde **66** and 0.28 mL (2.02 mmol, 1.00 eq.) Et_3N in 4.5 mL EtOH for 17.5 h. After purification, 2.10 g (2.01 mmol, >99%) of spiropyran **97** were obtained as a blue solid.



M($C_{50}H_{62}N_2O_{22}$) 1043.04 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.69 – 7.68 (m, 1H, H-30), 7.62 (m, 1H, H-32), 6.84 (d, $^3J_{HH}$ = 10.4 Hz, 1H, H-28), 6.79 - 6.77 (m, 1H, H-14), 6.74 – 6.73 (m, 1H, H-18), 6.41 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H-15), 5.81 (d, $^3J_{HH}$ = 10.4 Hz, 1H, H-27), 5.39 - 5.35 (m, 1H, H-12), 5.30 – 5.27 (m, 1H, H-6), 5.20 - 5.10 (m, 2H, H-3, H-5), 5.03 - 4.95 (m, 2H, H-4, H-11), 4.57 - 4.47 (m, 3H, H-1, H-10), 4.19 - 4.13 (m, 2H, H-7), 3.94 – 3.86 (m, 2H, H-2, H-8), 3.77 (s, 3H, H-33), 3.76 – 3.74 (m, 1H, H-9), 3.17 - 3.04 (m, 2H, H-22), 2.16 (s, 3H, OAc), 2.12 – 2.02 (m, 15H, OAc), 1.97 (s, 3H, OAc), 1.65 - 1.58 (m, 2H, H-23), 1.31 - 1.28 (m, 4H, H-24, H-25), 1.23 (m, 3H, H-19), 1.16 - 1.15 (m, 3H, H-19‘), 0.85 (t, $^3J_{HH}$ = 7.0 Hz, 3H, H-26).

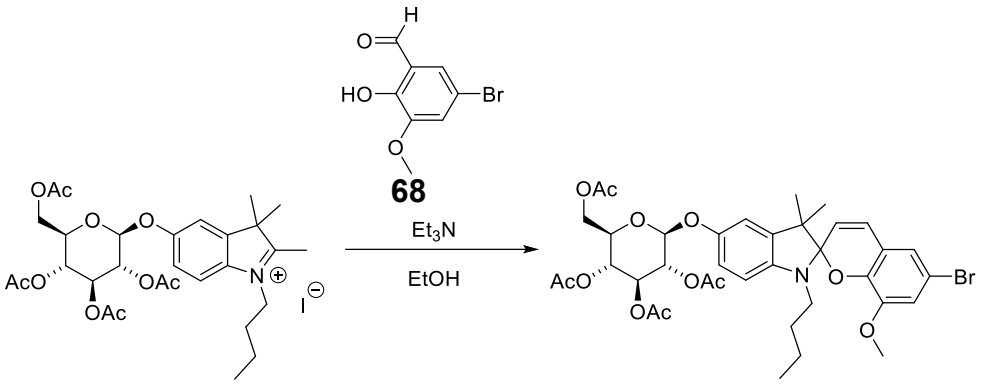
^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.3 (OAc), 170.3 (OAc), 170.1 (2x OAc), 169.8 (OAc), 169.6 (OAc), 169.1 (OAc), 150.5 (C-13), 149.4 (C-35), 147.3 (C-34), 143.4 (C-17), 140.3 (C-31), 137.5 (C-16), 128.1 (C-28), 121.8 (C-27), 118.2 (C-29), 116.1 (C-14), 115.4 (C-30), 112.7 (C-18), 107.8 (C-32), 107.0 (C-21), 106.3 (C-15), 101.1 (C-10), 100.1 (C-11), 76.2 (C-2), 72.8 (C-6), 72.7 (C-9), 71.7 (C-5), 70.9 (C-4), 70.7 (C-8), 69.1 (C-3), 66.6 (C-12), 62.0 (C-1), 60.8 (C-7), 56.3 (C-33), 52.6 (C-20), 43.7 (C-22), 29.4 (C-24), 28.5 (C-23), 22.4 (C-25), 20.8 (OAc), 20.8 (OAc), 20.7 (2 x OAc), 20.6 (OAc), 20.6 (OAc), 20.5 (OAc), 19.7 (C-19), 19.7 (C-19‘), 14.0 (C-26).

FT-IR ATR, v [cm^{-1}] = 3456 (w), 3355 (w), 2963 (w), 2871 (w), 2119 (w), 1749 (s), 1660 (w), 1592 (w), 1521 (w), 1486 (w), 1369 (m), 1338 (w), 1220 (s), 1172 (w), 1048 (s), 982 (w), 957 (w), 913 (w), 825 (w), 790 (w), 742 (w), 634 (w), 603 (w).

HR-MS (ESI) Calcd. $[M+H]^+$: 1043.3866, found: 1043.3867.

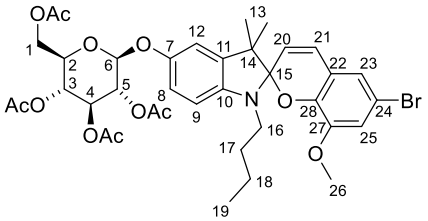
Calcd. [M+Na]$^+$: 1065.3686, found: 1065.3693.

11.2.5.6 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((6-bromo-1'-butyl-8-methoxy-3',3'-dimethylspiro[chromene-2,2'-indolin]-5'-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (100)



46a **100**

According to **GP17**, 2.00 g (2.90 mmol, 1.00 eq.) of indole **46a** were reacted with 0.67 g (2.90 mmol, 1.00 eq.) of aldehyde **68** and 0.40 mL (2.90 mmol, 1.00 eq.) Et_3N in 6 mL EtOH for 18 h. After purification, 2.24 g (2.90 mmol, >99%) of spiropyran **100** were obtained as a blue solid.



M($C_{37}H_{44}BrNO_{12}$) 774.66 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 6.83 (t, $^4J_{HH}$ = 2.0 Hz, 1H, H-23), 6.81 (t, $^4J_{HH}$ = 2.0 Hz, 1H, H-25), 6.78 - 6.76 (m, 1H, H-8), 6.74 - 6.73 (m, 1H, H-12), 6.70 (d, $^3J_{HH}$ = 10.3 Hz, 1H, H-21), 6.38 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H-9), 5.69 (d, $^3J_{HH}$ = 10.2 Hz, 1H, H-20), 5.32 - 5.21 (m, 2H, H-4, H-5), 5.20 - 5.12 (m, 1H, H-3), 5.00 – 4.98 (m, 1H, H-6), 4.31 - 4.24 (m, 1H, H-1), 4.18 (dd, $^{2,3}J_{HH}$ = 12.2, 2.4 Hz, 1H, H-1‘), 3.86 - 3.80 (m, 1H, H-2), 3.67 (s, 3H, H-26), 3.22 - 3.13 (m, 1H, H-16), 3.08 – 3.02 (m, 1H, H-16‘), 2.10 - 2.08 (m, 6H, OAc), 2.05 - 2.04 (m, 6H, OAc), 1.65 - 1.55 (m, 1H, H-17), 1.53 - 1.47 (m, 1H, H-17‘), 1.38 - 1.27 (m, 2H,

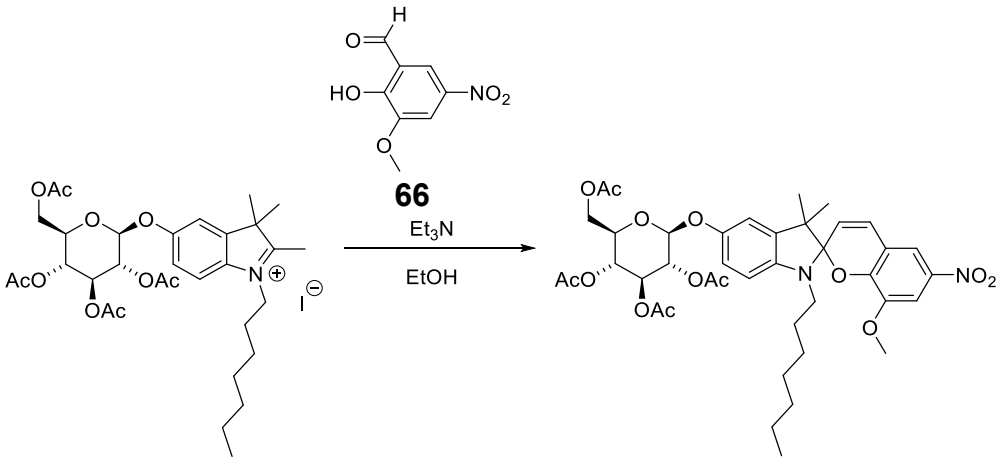
H-18), 1.23 (d, $^4J_{HH}$ = 3.7 Hz, 3H, H-13), 1.13 (d, $^4J_{HH}$ = 3.8 Hz, 3H, H-13‘), 0.88 (t, $^3J_{HH}$ = 7.3 Hz, 3H, H-19).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.6 (OAc), 170.3 (OAc), 169.4 (OAc), 169.3 (OAc), 150.2 (C-7), 148.0 (C-28), 143.9 (C-10), 142.9 (C-22), 137.9 (C-11), 128.1 (C-21), 121.5 (C-25), 121.3 (C-20), 120.6 (C-27), 116.5 (C-23), 116.0 (C-8), 112.8 (C-12), 111.1 (C-24), 106.0 (C-9), 105.2 (C-15), 100.6 (C-6), 72.8 (C-4), 71.9 (C-2), 71.3 (C-5), 68.3 (C-3), 62.0 (C-1), 56.5 (C-26), 52.2 (C-14), 43.5 (C-16), 31.1 (C-17), 25.8 (C-13), 25.8 (C-13‘), 20.7 (2x OAc), 20.6 (OAc), 20.6 (OAc), 20.4 (C-18), 13.9 (C-19).

FT-IR ATR, v [cm^{-1}] = 3475 (w), 2961 (w), 2871 (w), 2119 (w), 1755 (s), 1659 (w), 1602 (w), 1568 (w), 1487 (m), 1478 (m), 1444 (w), 1381 (w), 1247 (s), 1220 (s), 1171 (w), 1114 (w), 1066 (m), 1043 (m), 987 (w), 960 (w), 912 (w), 831 (w), 808 (w), 759 (w), 734 (w), 637 (w), 599 (w).

HR-MS (ESI) Calcd. $[M+H]^+$: 774.2119, found: 774.2116.
Calcd. $[M+Na]^+$: 796.1939, found: 796.1925.

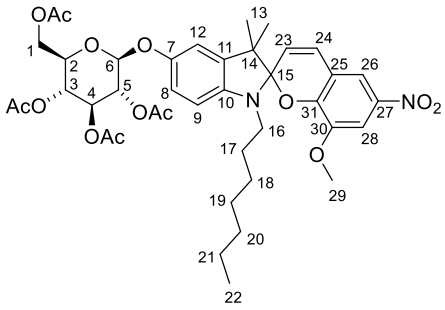
11.2.5.8 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((1'-heptyl-8-methoxy -3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)oxy)tetrahydro -2*H*-pyran-3,4,5-triyl triacetate (98)



46d **98**

According to **GP17**, 2.00 g (2.73 mmol, 1.00 eq.) of indole **46d** were reacted with 0.54 g (2.73 mmol, 1.00 eq.) of aldehyde **66** and 0.38 mL (2.73 mmol, 1.00 eq.) Et_3N

in 6 mL EtOH for 20 h. After purification, 2.03 g (2.60 mmol, 95%) of spiropyran **98** were obtained as a blue solid.



M($C_{40}H_{50}N_2O_{14}$) 782.84 g/mol.

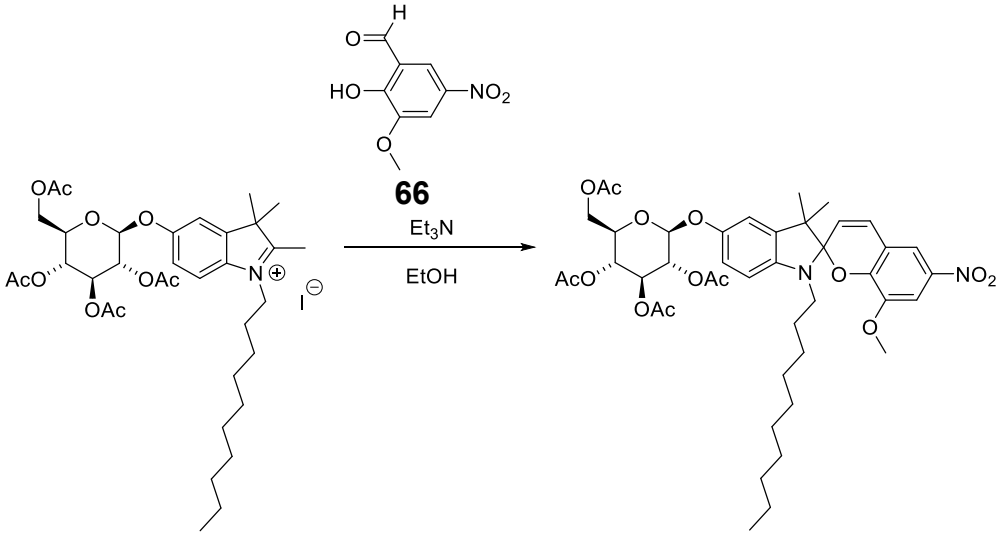
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.69 - 7.68 (m, 1H, H-26), 7.63 - 7.61 (m, 1H, H-28), 6.84 (d, $^3J_{HH}$ = 10.4 Hz, 1H, H-24), 6.83 - 6.79 (m, 1H, H-8), 6.76 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-12), 6.42 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H-9), 5.81 (d, $^3J_{HH}$ = 10.3 Hz, 1H, H-23), 5.33 – 5.23 (m, 2H, H-3, H-4), 5.20 – 5.15 (m, 1H, H-5), 5.02 - 5.01 (m, 1H, H-6), 4.31 – 4.26 (m, 1H, H-1), 4.19 (dd, $^{2,3}J_{HH}$ = 12.1, 2.4 Hz, 1H, H-1‘), 3.86 – 3.82 (m, 1H, H-2), 3.77 (s, 3H, H-29), 3.19 – 3.14 (m, 1H, H-16), 3.09 – 3.05 (m, 1H, H-16‘), 2.11 – 2.03 (m, 12H, OAc), 1.63 - 1.57 (m, 1H, H-17), 1.53 – 1.49 (m, 1H, H-17‘), 1.41 - 1.20 (m, 11H, H-18, H-19, H-20, H-21, H-13), 1.16 (d, $^4J_{HH}$ = 4.0 Hz, 3H, H-13‘), 0.86 (t, $^3J_{HH}$ = 7.0 Hz, 3H, H-22).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.6 (OAc), 170.3 (OAc), 169.4 (OAc), 169.3 (OAc), 150.5 (C-7), 149.4 (C-31), 147.3 (C-30), 143.4 (C-11), 140.3 (C-27), 137.6 (C-10), 128.1 (C-24), 121.8 (C-23), 118.2 (C-25), 115.6 (C-8), 115.4 (C-26), 112.8 (C-12), 107.8 (C-28), 107.0 (C-15), 106.3 (C-9), 100.5 (C-6), 72.8 (C-4), 71.9 (C-2), 71.3 (C-5), 68.3 (C-3), 62.0 (C-1), 56.2 (C-29), 52.6 (C-14), 43.8 (C-16), 31.7 (C-18), 29.0 (C-19), 28.8 (C-17), 27.2 (C-20), 22.6 (C-21), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 19.7 (C-13), 14.0 (C-22).

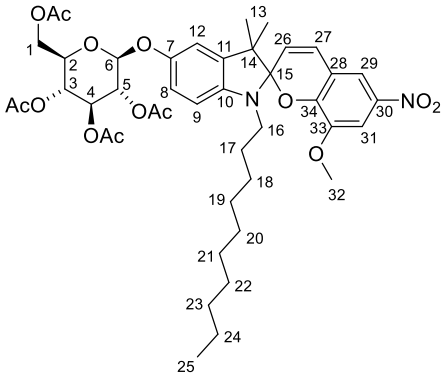
FT-IR ATR, v [cm^{-1}] = 3484 (w), 3092 (w), 2958 (w), 2930 (w), 2857 (w), 2259 (w), 2111 (w), 1753 (s), 1657 (w), 1580 (w), 1520 (m), 1486 (m), 1480 (m), 1453 (w), 1366 (m), 1336 (m), 1268 (m), 1216 (s), 1169 (w), 1115 (m), 1088 (m), 1066 (m), 1040 (s), 983 (w), 909 (m), 809 (w), 790 (w), 780 (w), 743 (w), 698 (w), 674 (w), 641 (w), 599 (w), 529 (w).

HR-MS (ESI) Calcd. $[M+H]^+$: 783.3334, found: 783.3333.
Calcd. [M+Na]: 805.3154, found: 805.3150.

11.2.5.9 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((1'-decyl-8-methoxy-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)oxy)tetrahydro-2*H*-pyran -3,4,5-triyl triacetate (99)



According to **GP17**, 2.70 g (3.49 mmol, 1.00 eq.) of indole **46e** were reacted with 0.69 g (3.49 mmol, 1.00 eq.) of aldehyde **66** and 0.49 mL (3.49 mmol, 1.00 eq.) Et_3N in 6 mL EtOH for 24 h. After purification, 2.75 g (3.33 mmol, 95%) of spiropyran **99** were obtained as a blue solid.



M($C_{43}H_{56}N_2O_{14}$) 824.92 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.69 – 7.68 (m, 1H, H-29), 7.63 - 7.62 (m, 1H, H-31), 6.84 (d, $^3J_{HH}$ = 10.4 Hz, 1H, H-27), 6.80 (dt, $^{3,4}J_{HH}$ = 8.4, 2.7 Hz, 1H, H-8), 6.76 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-12), 6.42 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H-9), 5.81 (d, $^3J_{HH}$ = 10.4 Hz, 1H, H-26), 5.33 – 5.23 (m, 2H, H-3, H-4), 5.20 – 5.16 (m, 1H, H-5), 5.02 – 5.00 (m, 1H, H-6), 4.31 – 4.26 (m, 1H, H-1), 4.19 (dd, $^{2,3}J_{HH}$ = 12.3,

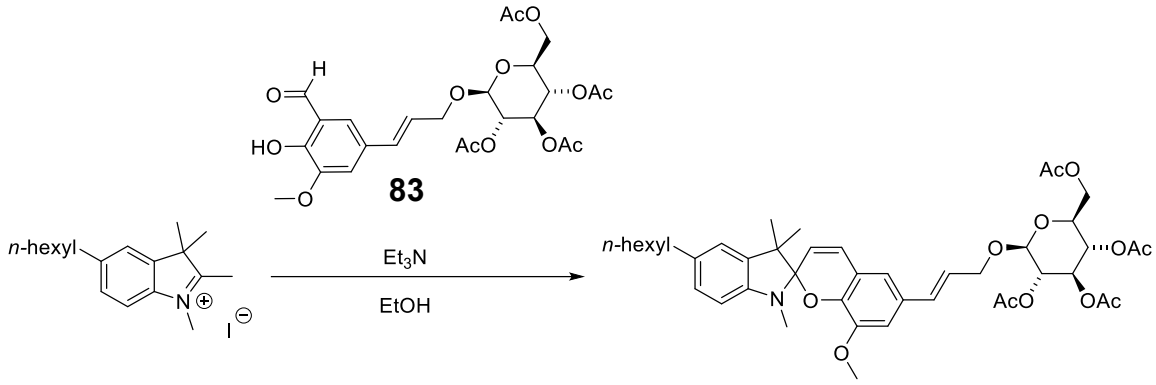
2.5 Hz, 1H, H-1‘), 3.85 – 3.82 (m, 1H, H-2), 3.77 (s, 3H, H-32), 3.16 – 3.09 (m, 1H, H-16), 3.08 – 3.05 (m, 1H, H-16‘), 2.10 – 2.04 (m, 12H, OAc), 1.64 – 1.57 (m, 1H, H-17), 1.54 – 1.45 (m, 1H, H-17‘), 1.41 – 1.32 (m, 1H, H-18), 1.32 – 1.19 (m, 16H, H-18‘, H-19, H-20, H-21, H-22, H-23, H-24, H-13), 1.16 (d, $^{4}J_{HH}$ = 3.9 Hz, 3H, H-13‘), 0.88 – 0.86 (m, 3H, H-25).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.6 (OAc), 170.3 (OAc), 169.4 (OAc), 169.3 (OAc), 150.5 (C-7), 149.4 (C-34), 147.3 (C-33), 143.5 (C-11), 140.3 (C-30), 137.4 (C-10), 128.1 (C-27), 121.8 (C-26), 118.2 (C-28), 115.6 (C-8), 115.3 (C-29), 112.8 (C-12), 107.8 (C-31), 107.0 (C-15), 106.3 (C-9), 100.5 (C-6), 72.8 (C-2), 71.9 (C-3), 71.3 (C-4), 68.3 (C-5), 62.0 (C-1), 56.2 (C-32), 52.6 (C-14), 43.8 (C-16), 31.8 (C-18), 29.5 (C-17, C-19, C-20), 29.4 (C-21), 29.3 (C-22), 27.3 (C-23), 22.6 (C-24), 20.7 (OAc), 20.6 (2x OAc), 20.6 (OAc), 19.7 (C-13), 14.1 (C-25).

FT-IR ATR, v [cm^{-1}] = 3660 (w), 3484 (w), 3092 (w), 2926 (w), 2855 (w), 2112 (w), 2012 (w), 1754 (s), 1657 (w), 1581 (w), 1521 (m), 1487 (m), 1454 (w), 1366 (m), 1336 (m), 1282 (m), 1216 (s), 1115 (m), 1066 (m), 1039 (s), 983 (w), 962 (w), 908 (m), 809 (w), 790 (w), 779 (w), 743 (w), 698 (w), 675 (w), 641 (w), 599 (w), 529 (w).

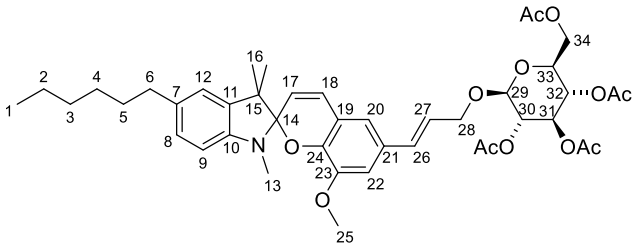
HR-MS (ESI) Calcd. $[M+H]^+$: 825.3804, found: 825.3804.
Calcd. $[M+Na]^+$: 847.3623, found: 847.3619.

11.2.5.10 Synthesis of (2*S*,3*S*,4*R*,5*S*,6*S*)-2-(acetoxymethyl)-6-(((*E*)-3-(5'-hexyl-8-methoxy-1',3',3'-trimethylspiro[chromene-2,2'-indolin]-6-yl)allyl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (101)



59b **101**

According to **GP17**, 0.06 g (0.15 mmol, 1.00 eq.) of indole **59b** were reacted with 0.08 g (0.15 mmol, 1.00 eq.) of aldehyde **83** and 0.02 mL (0.15 mmol, 1.00 eq.) Et_3N in 0.3 mL EtOH for 24 h. After purification, 0.10 g (0.13 mmol, 89%) of spiropyran **101** were obtained as a blue solid.



M($C_{43}H_{55}NO_{12}$) 777.91 g/mol.

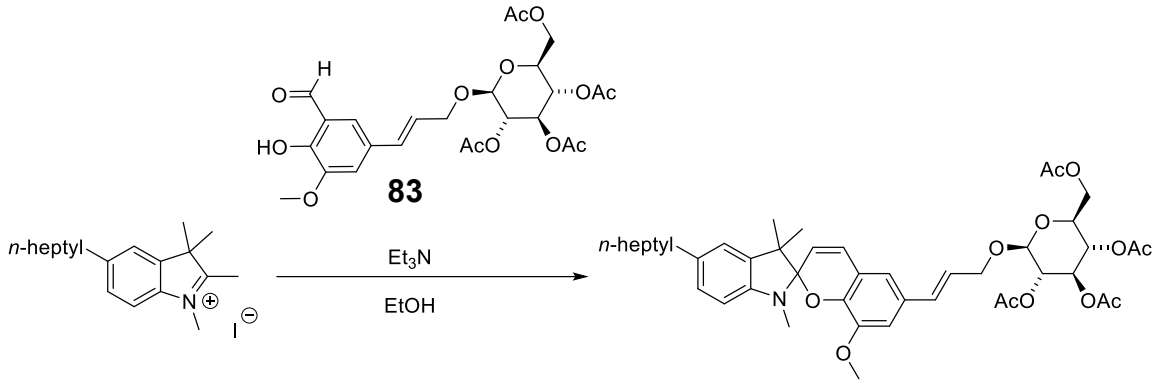
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 6.94 (dd, $^{3,4}J_{HH}$ = 7.8, 1.8 Hz, 1H, H-8), 6.86 (d, $^4J_{HH}$ = 1.7 Hz, 1H, H-12), 6.82 – 6.76 (m, 2H, H-18, H-20), 6.71 (d, $^4J_{HH}$ = 2.0 Hz, 1H, H-22), 6.46 (d, $^3J_{HH}$ = 16.0 Hz, 1H, H-26), 6.41 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H-9), 6.07 – 5.99 (m, 1H, H-27), 5.69 (d, $^3J_{HH}$ = 10.2 Hz, 1H, H-17), 5.23 – 5.16 (m, 1H, H-30), 5.11 (t, $^3J_{HH}$ = 9.6 Hz, 1H, H-31), 5.04 (dd, $^{3,3}J_{HH}$ = 9.6, 7.9 Hz, 1H, H-32), 4.61 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H-29), 4.48 - 4.44 (m, 1H, H-28), 4.29 – 4.23 (m, 2H, H-28‘, H-34), 4.22 – 4.12 (m, 1H, H-34‘), 3.71 – 3.66 (m, 4H, H-25, H-33), 2.71 (s, 3H, H-13), 2.57 – 2.54 (m, 2H, H-6), 2.09 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.64 – 1.57 (m, 2H, H-5), 1.36 – 1.31 (m, 6H, H-4, H-3, H-2), 1.29 (s, 3H, H-16), 1.15 (s, 3H, H-16‘), 0.91 – 0.88 (m, 3H, H-1).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.7 (OAc), 170.3 (OAc), 169.4 (OAc), 169.3 (OAc), 147.2 (C-23), 146.0 (C-7), 144.3 (C-24), 136.7 (C-10), 133.5 (C-11), 133.1 (C-26), 128.8 (C-18), 128.1 (C-21), 126.9 (C-8), 122.0 (C-27), 121.6 (C-12), 120.5 (C-17), 119.6 (C-14), 118.0 (C-22), 112.0 (C-20), 106.3 (C-9), 104.8 (C-19), 99.3 (C-29), 72.9 (C-30), 71.8 (C-33), 71.3 (C-32), 70.0 (C-28), 68.4 (C-31), 61.9 (C-34), 56.7 (C-25), 51.7 (C-15), 35.7 (C-6), 32.0 (C-5), 31.7 (C-4), 29.1 (C-3), 28.9 (C-13), 22.6 (C-2), 20.7 (2x OAc), 20.6 (OAc), 20.6 (OAc), 14.1 (C-1).

FT-IR ATR, v [cm^{-1}] = 3491 (w), 2957 (w), 2928 (w), 2856 (w), 2113 (w), 2010 (w), 1756 (s), 1647 (w), 1617 (w), 1581 (w), 1489 (w), 1467 (w), 1366 (m), 1294 (w), 1225 (s), 1184 (w), 1155 (w), 1114 (w), 1040 (m), 983 (w), 927 (w), 848 (w), 809 (w), 733 (w), 701 (w), 649 (w), 598 (w), 560 (w), 534 (w).

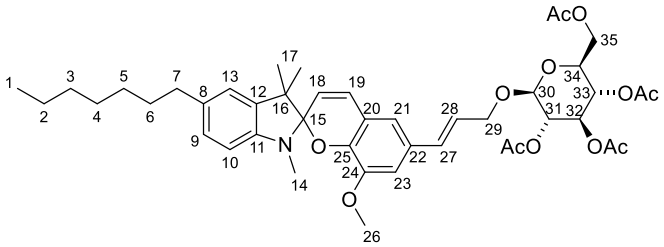
HR-MS (ESI) Calcd. $[M+H]^+$: 778.3797, found: 778.3796.

11.2.5.11 Synthesis of (2*S*,3*S*,4*R*,5*S*,6*S*)-2-(acetoxymethyl)-6-(((*E*)-3-(5'-heptyl-8-methoxy-1',3',3'-trimethylspiro[chromene-2,2'-indolin]-6-yl)allyl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (102)



59c **102**

According to **GP17** 0.06 g (0.15 mmol, 1.00 eq.) of indole **59c** were reacted with 0.08 g (0.15 mmol, 1.00 eq.) of aldehyde **83** and 0.02 mL (0.15 mmol, 1.00 eq.) Et_3N in 0.3 mL EtOH for 24 h. After purification, 0.10 g (0.13 mmol, 89%) of spiropyran **102** weree obtained as a blue solid.



M($C_{44}H_{57}NO_{12}$) 791.94 g/mol.

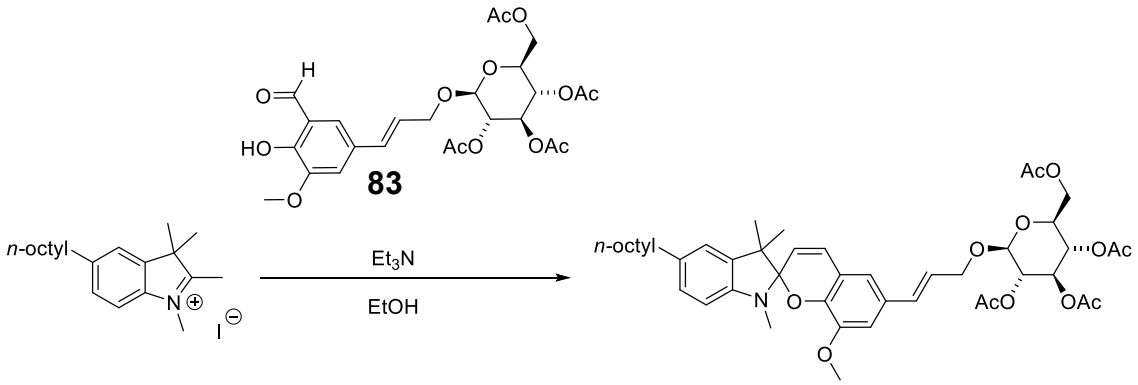
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 6.94 (dd, $^{3,4}J_{HH}$ = 7.8, 1.8 Hz, 1H, H-9), 6.86 (d, $^4J_{HH}$ = 1.8 Hz, 1H, H-13), 6.81 - 6.77 (m, 2H, H-21, H-19), 6.71 (d, $^4J_{HH}$ = 2.0 Hz, 1H, H-23), 6.46 (d, $^3J_{HH}$ = 16.0 Hz, 1H, H-27), 6.41 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H-10), 6.04 (ddd, $^{3,3,3}J_{HH}$ = 15.9, 6.9, 5.6 Hz, 1H, H-28), 5.72 - 5.67 (m, 1H, H-18), 5.24 - 5.18 (m, 1H, H-31), 5.11 (t, $^3J_{HH}$ = 9.6 Hz, 1H, H-32), 5.06 – 5.00 (m, 1H, H-33), 4.62 (d, $^3J_{HH}$ = 7.9 Hz, 1H, H-30), 4.46 (ddd, $^{2,3,4}J_{HH}$ = 12.6, 5.6, 1.6 Hz, 1H, H-29), 4.29 - 4.23 (m, 2H, H-29‘, H-35), 4.17 (dd, $^{2,3}J_{HH}$ = 12.3, 2.5 Hz, 1H, H-35‘), 3.72 - 3.64 (m, 4H, H-34, H-26), 2.71 (s, 3H, H-14), 2.58 - 2.51 (m, 2H, H-7), 2.09 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.65 – 1.52 (m, 2H, H-6), 1.35 - 1.25 (m, 11H, H-5, H-4, H-3, H-2, H-17), 1.16 (s, 3H, H-17‘), 0.92 - 0.84 (m, 3H, H-1).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.7 (OAc), 170.3 (OAc), 169.4 (OAc), 169.3 (OAc), 147.2 (C-24), 146.0 (C-8), 144.3 (C-25), 136.7 (C-11), 133.6 (C-12), 133.1 (C-27), 128.8 (C-19), 128.1 (C-22), 126.9 (C-9), 122.0 (C-28), 121.6 (C-13), 120.5 (C-18), 119.6 (C-15), 118.0 (C-23), 112.0 (C-21), 106.3 (C-10), 104.8 (C-20), 99.3 (C-30), 72.9 (C-31), 71.8 (C-34), 71.3 (C-33), 70.0 (C-29), 68.4 (C-32), 61.9 (C-35), 56.7 (C-26), 51.7 (C-16), 35.7 (C-7), 32.0 (C-6), 31.8 (C-5), 29.4 (C-4), 29.2 (C-3), 28.9 (C-14), 25.9 (C-17), 22.6 (C-2), 20.7 (2x OAc), 20.6 (OAc), 20.6 (OAc), 20.3 (C-17‘), 14.1 (C-1).

FT-IR ATR, v [cm^{-1}] = 3484 (w), 2957 (w), 2927 (w), 2855 (w), 2157 (w), 2006 (w), 1757 (s), 1648 (w), 1617 (w), 1581 (w), 1489 (w), 1467 (w), 1366 (w), 1294 (w), 1225 (s), 1184 (w), 1155 (w), 1114 (w), 1040 (m), 982 (w), 928 (w), 847 (w), 807 (w), 736 (w), 601 (w), 560 (w).

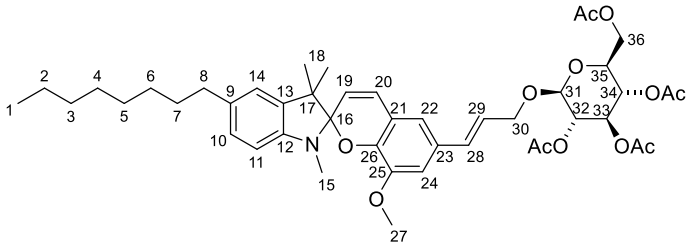
HR-MS (ESI) Calcd. $[M+H]^+$: 792.3954, found: 792.3958.

11.2.5.12 Synthesis of (2*S*,3*S*,4*R*,5*S*,6*S*)-2-(acetoxymethyl)-6-(((*E*)-3-(8-methoxy-1',3',3'-trimethyl-5'-octylspiro[chromene-2,2'-indolin]-6-yl)allyl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (103)



59d **103**

According to **GP17**, 0.06 g (0.15 mmol, 1.00 eq.) of indole **59d** were reacted with 0.08 g (0.15 mmol, 1.00 eq.) of aldehyde **83** and 0.02 mL (0.15 mmol, 1.00 eq.) Et_3N in 0.3 mL EtOH for 24 h. After purification, 0.10 g (0.13 mmol, 89%) of spiropyran **103** were obtained as a blue solid.



M($C_{45}H_{59}NO_{12}$) 805.96 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 6.94 (dd, $^{3,4}J_{HH}$ = 7.8, 1.7 Hz, 1H, H-10), 6.86 (d, $^{4}J_{HH}$ = 1.7 Hz, 1H, H-14), 6.81 – 6.77 (m, 2H, H-20, H-22), 6.71 (d, $^{4}J_{HH}$ = 1.9 Hz, 1H, H-24), 6.46 (dd, $^{3,4}J_{HH}$ = 15.3, 4.7 Hz, 1H, H-28), 6.41 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, H-11), 6.04 (ddd, $^{2,3,4}J_{HH}$ = 15.8, 6.9, 5.6 Hz, 1H, H-29), 5.69 (d, $^{3}J_{HH}$ = 10.2 Hz, 1H, H-19), 5.23 - 5.18 (m, 1H, H-32), 5.11 (t, $^{3}J_{HH}$ = 9.6 Hz, 1H, H-33), 5.04 (dd, $^{3,3}J_{HH}$ = 9.6, 7.9 Hz, 1H, H-34), 4.61 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, H-31), 4.46 (ddd, $^{2,3,4}J_{HH}$ = 12.7, 5.6, 1.5 Hz, 1H, H-30), 4.29 - 4.23 (m, 2H, H-30‘, H-36), 4.17 (dd, $^{2,3}J_{HH}$ = 12.3, 2.5 Hz, H-36‘), 3.72 – 3.67 (m, 4H, H-27, H-35), 2.71 (s, 3H, H-15), 2.57 - 2.52 (m, 2H, H-8), 2.09 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.64 - 1.56 (m, 2H, H-7), 1.36 - 1.24 (m, 13H, H-6, H-5, H-4, H-3, H-2, H-18), 1.16 (s, 3H, H18‘), 0.90 - 0.87 (m, 3H, H-1).

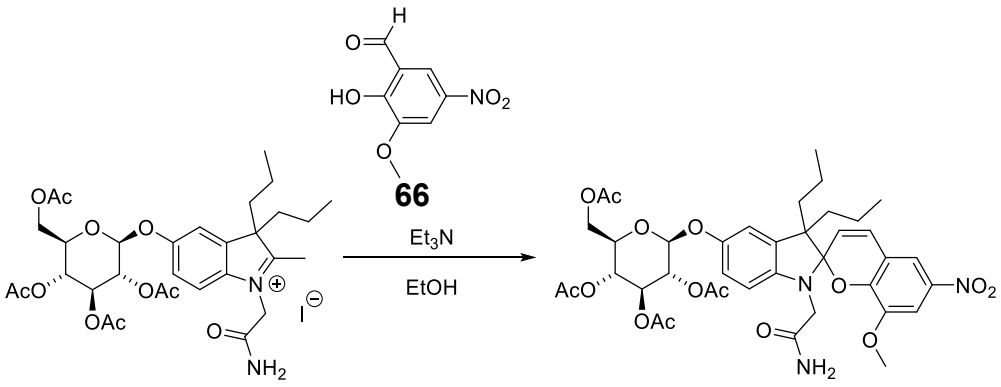
^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.7 (OAc), 170.3 (OAc), 169.4 (OAc), 169.3 (OAc), 147.2 (C-25), 146.0 (C-9), 144.3 (C-26), 136.7 (C-12), 133.6 (C-13), 133.1 (C-28), 128.8 (C-20), 128.1 (C-23), 126.9 (C-10), 122.0 (C-29), 121.6 (C-14), 120.5 (C-19), 119.6 (C-16), 118.0 (C-24), 112.0, (C-22) 106.3 (C-11), 104.8 (C-21), 99.4 (C-31), 72.9 (C-32), 71.8 (C-34), 71.3 (C-35), 70.0 (C-30), 68.4 (C-33), 61.9 (C-36), 56.7 (C-27), 51.7 (C-17), 35.7 (C-8), 32.0 (C-7), 31.9 (C-6), 29.5 (C-5), 29.4 (C-4), 29.3 (C-3), 28.9 (C-15), 22.70 (C-2), 20.77 (OAc), 20.74 (OAc), 20.64 (OAc), 20.62 (OAc), 20.3 (C-18), 14.1 (C-1).

FT-IR ATR, v [cm^{-1}] = 3662 (w), 3484 (w), 2957 (w), 2926 (m), 2855 (w), 2114 (w), 2024 (w), 1756 (s), 1651 (w), 1616 (w), 1582 (w), 1490 (w), 1466 (w), 1393 (w), 1365 (m), 1293 (w), 1224 (s),

1184 (w), 1155 (w), 1115 (w), 1040 (m), 981 (w), 927 (w), 848 (w), 808 (w), 733 (w), 649 (w), 599 (w), 560 (w), 529 (w).

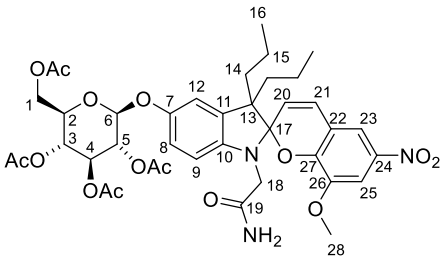
HR-MS (ESI) Calcd. $[M+H]^+$: 806.4110, found: 806.4106.

11.2.5.13 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((1'-(2-amino-2-oxo ethyl)-8-methoxy-6-nitro-3',3'-dipropylspiro[chromene-2,2'-indolin]-5'-yl)oxy) tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (106)



52c **106**

According to **GP17**, 3.00 g (4.02 mmol, 1.00 eq.) of indole **52c** were reacted with 0.79 g (4.02 mmol, 1.00 eq.) of aldehyde **66** and 0.56 mL (4.02 mmol, 1.00 eq.) Et_3N in 8 mL EtOH for 20 h. After purification, 2.95 g (3.71 mmol, 92%) of spiropyran **106** were obtained as a blue solid.



M($C_{39}H_{47}N_3O_{15}$) 797.81 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.72 (t, $^4J_{HH}$ = 2.2 Hz, 1H, H-23), 7.68 (t, $^4J_{HH}$ = 2.2 Hz, 1H, H-25), 6.89 (d, $^3J_{HH}$ = 10.5 Hz, 1H, H-20), 6.85 - 6.82 (m, 1H, H-8), 6.78 (d, $^4J_{HH}$ = 2.5 Hz, 1H, H-12), 6.39 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H-9), 5.91 (dd, $^{3,4}J_{HH}$ = 10.4, 3.0 Hz, 1H, H--21), 5.36 - 5.33 (m, 1H, H-3), 5.27 - 5.22 (m, 2H, H-4, H-5), 5.06 – 5.03 (m, 1H, H-6), 4.33 – 4.28 (m, 2H, H-1), 4.03 (s, 3H, H-28), 3.86 (m, 1H, H-2), 3.82 (s, 2H, H-18), 2.13 - 2.02 (m, 12H, 4x OAc), 1.23 - 1.17 (m, 4H, H-14), 0.95 - 0.92 (m, 2H, H-15),

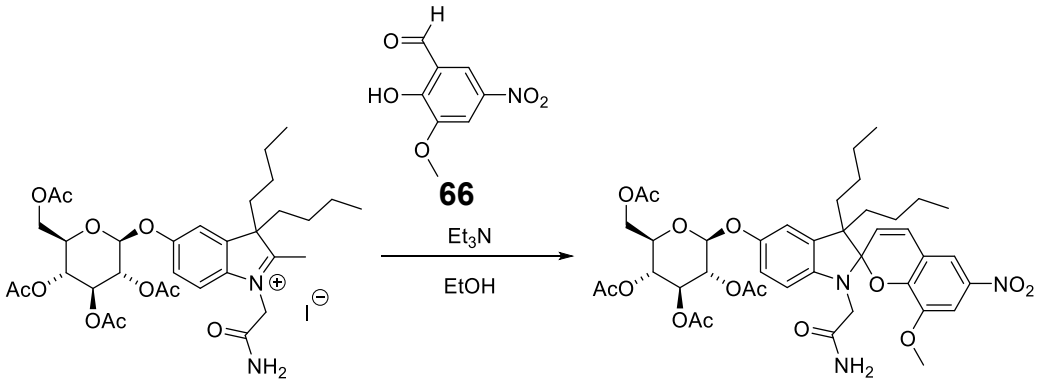
0.89 - 0.81 (m, 3H, H-16), 0.79 - 0.73 (m, 2H, H-15‘), 0.66 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, H-16‘).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 172.19 (C-19), 170.60 (OAc), 170.29 (OAc), 169.68 (OAc), 169.44 (OAc), 151.24 (C-7), 149.05 (C-26), 147.26 (C-27), 141.55 (C-11), 140.98 (C-24), 135.30 (C-10), 128.01 (C-20), 121.34 (C-21), 117.49 (C-22), 115.80 (C-8), 115.51 (C-23), 115.04 (C-12), 107.90 (C-25), 107.20 (C-9), 105.56 (C-17), 100.07 (C-6), 72.73 (C-3), 72.01 (C-2), 71.30 (C-4), 68.23 (C-5), 62.00 (C-1), 58.34 (C-13), 56.82 (C-28), 47.16 (C-18), 20.76 (OAc), 20.71 (OAc), 20.62 (2x OAc), 17.35 (C-14), 17.15 (C-14‘), 16.87 (C-15), 16.72 (C-15‘), 14.85 (C-16), 14.53 (C-16‘).

FT-IR ATR, v [cm^{-1}] = 3449 (w), 3348 (w), 3204 (w), 3100 (w), 2961 (w), 2874 (w), 2132 (w), 1753 (m), 1685 (m), 1591 (w), 1526 (w), 1485 (w), 1369 (w), 1339 (m), 1226 (s), 1066 (m), 1041 (s), 986 (w), 960 (w), 909 (w), 823 (w), 788 (w), 766 (w), 743 (w), 600 (w).

HR-MS (ESI) Calcd. $[M+H]^+$: 798.3079, found: 798.3085.
Calcd. [M+Na]: 820.2899, found: 820.2903.

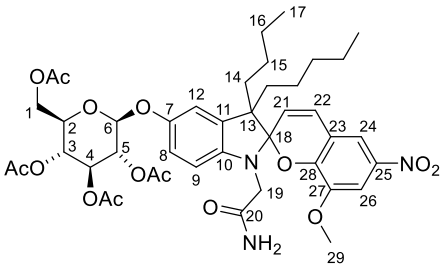
11.2.5.14 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((1'-(2-amino-2-oxoethyl)-8-methoxy-6-nitro-3',3'-dibutylspiro[chromene-2,2'-indolin]-5'-yl)oxy) tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (107)



52d **107**

According to **GP17**, 0.60 g (0.78 mmol, 1.00 eq.) of indole **52c** were reacted with 0.15 g (0.78 mmol, 1.00 eq.) of aldehyde **66** and 0.11 mL (0.78 mmol, 1.00 eq.) Et_3N in 18 mL EtOH for 20 h. After purification, 0.56 g (0.68 mmol, 87%) of spiropyran **107**

were obtained as a blue solid.



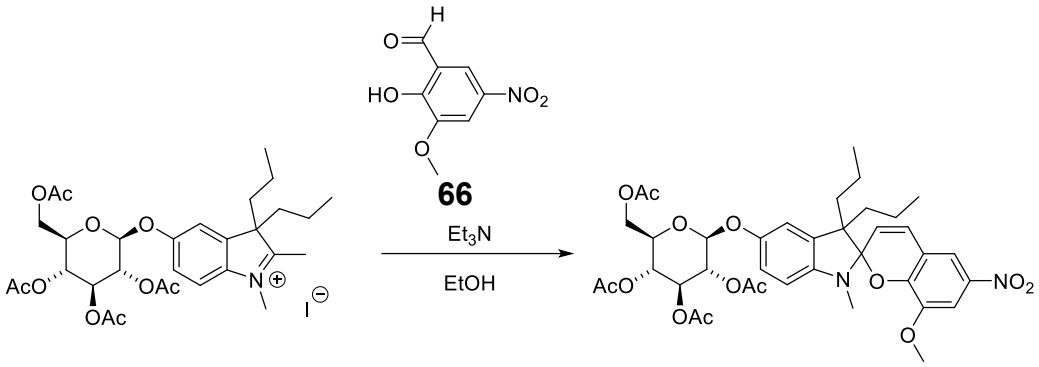
M($C_{41}H_{51}N_3O_{15}$) 825.86 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.73 (t, $^4J_{HH}$ = 2.4 Hz, 1H, H-24), 7.67 (t, $^4J_{HH}$ = 2.6 Hz, 1H, H-26), 6.88 (d, $^3J_{HH}$ = 10.4 Hz, 1H, H-21), 6.83 (td, $^{3,4}J_{HH}$ = 8.5, 2.4 Hz, 1H, H-8), 6.79 - 6.78 (m, 1H, H-12), 6.39 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H-9), 5.90 (dd, $^{3,4}J_{HH}$ = 10.4, 2.3 Hz, 1H, H-22), 5.33 – 5.24 (m, 2H, H-3, H-4), 5.19 (t, $^3J_{HH}$ = 9.5 Hz, 1H, H-5), 5.03 (t, $^3J_{HH}$ = 7.0 Hz, 1H, H-6), 4.33 – 4.29 (m, 2H, H-1), 4.03 (s, 3H, H-29), 3.91 - 3.83 (m, 1H, H-2), 3.81 (s, 2H, H-19), 2.11 - 2.05 (m, 12H, 4x OAc), 1.22 - 1.07 (m, 6H, H-14, H-14‘, H-15), 1.02 - 0.90 (m, 4H, H-15‘, H-16), 0.87 - 0.81 (m, 3H, H-17), 0.78 - 0.73 (m, 2H, H-16‘), 0.60 (td, $^{3,4}J_{HH}$ = 7.3, 1.6 Hz, 3H, H-17‘).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 171.4 (C-20), 170.6 (OAc), 170.4 (OAc), 169.9 (OAc), 169.4 (OAc), 151.3 (C-7), 148.2 (C-27), 147.7 (C-28), 141.4 (C-11), 140.2 (C-25), 135.0 (C-10), 127.8 (C-21), 122.0 (C-22), 118.8 (C-23), 115.2 (C-26), 114.7 (C-8), 114.6 (C-12), 114.6 (C-18), 107.9 (C-24), 107.3 (C-13), 106.9 (C-9), 100.3 (C-6), 72.5 (C-3), 72.2 (C-2), 71.3 (C-4), 68.2 (C-5), 62.2 (C-1), 56.8 (C-29), 47.5 (C-19), 25.5 (C-14), 23.1 (C-15), 22.5 (C-16), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 14.2 (C-17), 13.5 (C-17‘).

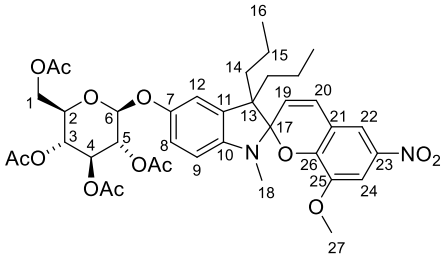
FT-IR ATR, v [cm^{-1}] = 3347 (w), 2957 (w), 2935 (w), 2872 (w), 2157 (w), 1972 (w), 1752 (s), 1686 (w), 1591 (w), 1525 (w), 1491 (w), 1466 (w), 1438 (w), 1367 (w), 1338 (m), 1225 (s), 1066 (m), 1042 (m), 985 (w), 907 (w), 825 (w), 805 (w), 745 (w), 697 (w), 682 (w), 649 (w), 642 (w), 601 (w), 559 (w), 536 (w).

11.2.5.15 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((3'-butyl-8-methoxy-1'-methyl-6-nitro-3'-propylspiro[chromene-2,2'-indolin]-5'-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (104)



52a **104**

According to **GP17**, 0.91 g (0.13 mmol, 1.00 eq.) of indole **52a** were reacted with 0.03 g (0.13 mmol, 1.00 eq.) of aldehyde **66** and 0.02 mL (0.13 mmol, 1.00 eq.) Et_3N in 6 mL EtOH for 20 h. After purification, 0.07 g (0.09 mmol, 68%) of spiropyran **104** were obtained as a blue solid.



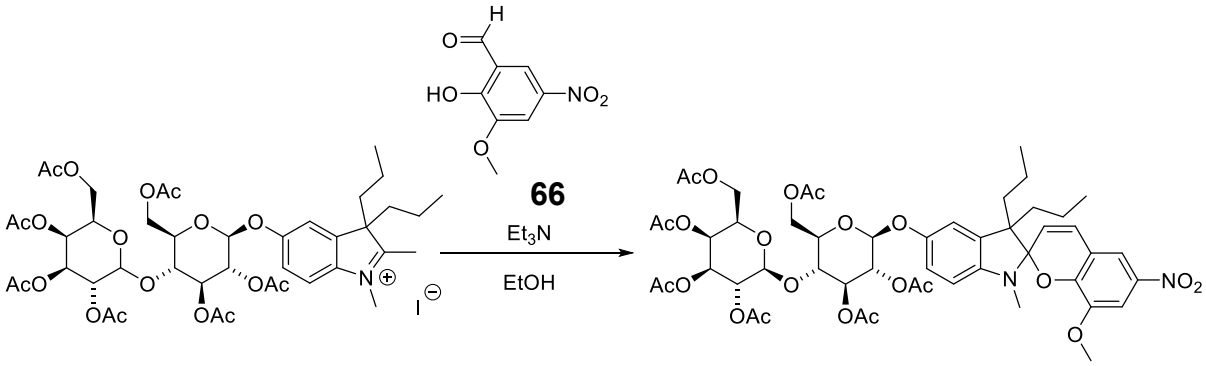
M($C_{38}H_{46}N_2O_{14}$) 754.79 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.40 (d, $^4J_{HH}$ = 2.7 Hz, 1H, H-24), 7.60 (d, $^3J_{HH}$ = 8.8 Hz, 1H, H-9), 7.53 – 7.51 (s, 1H, H-22), 7.30 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-12), 7.23 (dd, $^{3,4}J_{HH}$ = 8.8, 2.4 Hz, 1H, H-8), 5.47 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H-20), 5.40 - 5.38 (m, 1H, H-5), 5.19 – 5.11 (m, 1H, H-4), 5.07 - 5.04 (m, 1H, H.6), 4.77 (d, $^3J_{HH}$ = 7.9 Hz, 1H, H-19), 4.20 - 4.15 (m, 3H, H-1, H-3), 3.99 (s, 3H, H-27), 3.89 - 3.97 (m, 1H, H-2), 3.91 (s, 3H, H-18), 2.52 - 2.40 (m, 2H, H-14), 2.40 - 2.30 (m, 2H, H-14‘), 2.18 - 1.91 (m, 12H, 4x OAc), 0.92 - 0.88 (m, 4H, H-15, H-15‘), 0.80 - 0.77 (m, 6H, H-16, H-16‘).

^{13}C-NMR (101 MHz, MeOD) δ [ppm] = 170.6 (OAc), 170.5 (OAc), 170.0 (OAc), 169.9 (OAc), 161.8 (C-7), 157.2 (C-26), 155.8 (C-10), 151.3 (C-25), 150.1 (C-21), 138.6 (C-11), 133.9 (C-23), 122.2 (C-24), 117.0 (C-8), 113.4 (C-9), 110.7 (C-12), 105.8 (C-22), 100.7 (C-19),

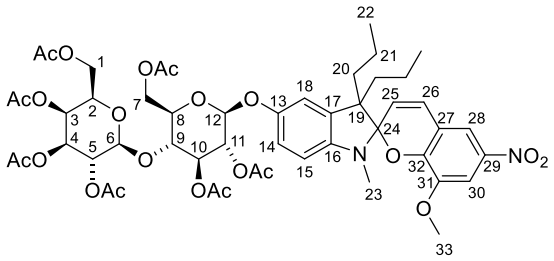
	100.3 (C-17), 97.8 (C-20), 77.0 (C-13), 71.1 (C-4), 69.9 (C-6), 69.3 (C-3), 67.2 (C-5), 61.5 (C-1), 55.5 (C-2), 55.0 (C-27), 43.9 (C-14), 30.9 (C-18), 19.2 (OAc), 19.2 (OAc), 19.0 (2x OAc), 16.9 (C-15), 16.5 (C-15‘), 12.9 (C-16), 12.8 (C-16‘).
FT-IR	ATR, v [cm^{-1}] = 3660 (w), 3384 (w), 3103 (w), 2960 (w), 2934 (w), 2222 (w), 2070 (w), 1971 (w), 1748 (m), 1590 (w), 1562 (w), 1521 (m), 1491 (m), 1465 (m), 1405 (w), 1378 (w), 1337 (m), 1283 (m), 1230 (s), 1067 (m), 1046 (m), 975 (w), 936 (w), 905 (w), 820 (w), 795 (w), 745 (w), 690 (w), 641 (w), 601 (w), 560 (w).
HR-MS (ESI)	Calcd. $[M+H]^+$: 755.3022, found: 755.3023. Calcd. [M+Na]: 777.2841, found: 777.2849. Calcd. [M+H+Na]: 778.2920, found: 778.2913.

11.2.5.16 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((3'-butyl-8-methoxy-1'-methyl-6-nitro-3'-propylspiro[chromene-2,2'-indolin]-5'-yl)oxy)tetrahydro-2*H*-pyran-3-yl)oxy) tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (105)



52b **105**

According to **GP17**, 0.53 g (0.53 mmol, 1.00 eq.) of indole **52b** were reacted with 0.10 g (0.53 mmol, 1.00 eq.) of aldehyde **66** and 0.07 mL (0.53 mmol, 1.00 eq.) Et_3N in 6 mL EtOH for 20 h. After purification, 0.47 g (0.46 mmol, 87%) of spiropyran **105** were obtained as a blue solid.



M($C_{50}H_{62}N_2O_{22}$) 1043.04 g/mol.

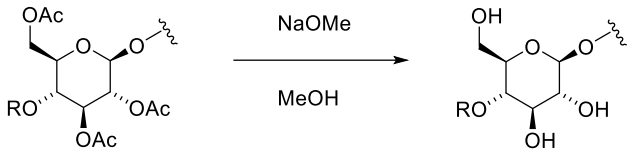
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.23 (d, $^4J_{HH}$ = 2.5 Hz, 1H, H-30), 7.94 (d, $^4J_{HH}$ = 2.5 Hz, 1H, H-28), 7.31 – 7.29 (m, 1H, H-14), 7.12 - 7.05 (m, 1H, H-15), 7.01 (d, $^4J_{HH}$ = 2.3 Hz, 1H, H-18), 6.82 (d, $^3J_{HH}$ = 10.5 Hz, 1H, H-25), 5.92 (dd, $^{3,4}J_{HH}$ = 10.5, 1.9 Hz, 1H, H-26), 5.38 - 5.36 (m, 2H, H-11, H-5), 5.25 - 5.16 (m, 3H, H-3, H-10, H-12), 5.00 - 4.96 (m, 2H, H-4, H-6), 4.61 - 4.53 (m, 1H, H-1), 4.22 – 4.14 (m, 3H, H-7, H-1‘), 4.03 (s, 3H, H-33), 3.96 - 3.91 (m, 2H, H-2, H-8), 3.83 – 3.80 (m, 1H, H-9), 3.71 (s, 3H, H-23), 2.34 – 2.20 (m, 4H, H-20), 2.21 – 2.07 (m, 21H, 7x OAc), 0.94 - 0.82 (m, 2H, H-21), 0.79 - 0.74 (m, 6H, H-22), 0.61 - 0.57 (m, 2H, H-21‘).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.4 (OAc), 170.3 (OAc), 170.3 (OAc), 170.1 (OAc), 170.1 (OAc), 170.1 (OAc), 170.0 (OAc), 157.4 (C-32), 156.2 (C-13), 149.7 (C-31), 140.8 (C-16), 139.7 (C-29), 139.2 (C-17), 127.0 (C-26), 122.0 (C-25), 120.4 (C-27), 120.4 (C-30), 112.7 (C-18), 111.3 (C-15), 111.3 (C-28), 105.3 (C-24), 104.7 (C-19), 104.3 (C-14), 101.1 (C-6), 99.2 (C-12), 75.8 (C-8), 73.1 (C-11), 71.2 (C-10), 70.8 (C-5), 70.7 (C-2), 69.1 (C-3), 66.7 (C-5), 62.0 (C-1), 61.1 (C-4), 56.8 (C-33), 55.8 (C-9), 44.4 (C-20), 32.0 (C-23), 20.8 (OAc), 20.8 (OAc), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.5 (OAc), 20.4 (OAc), 18.2 (C-21), 17.4 (C-21‘), 14.0 (C-22), 12.0 (C-22‘).

FT-IR ATR, v [cm^{-1}] = 3371 (s), 2963 (w), 2931 (w), 2509 (w), 2120 (w), 1779 (w), 1648 (m), 1558 (s), 1495 (m), 1411 (s), 1346 (m), 1284 (m), 1248 (m), 1208 (m), 1170 (m), 1075 (s), 1050 (s), 1021 (s), 962 (w), 928 (m), 651 (s), 621 (s).

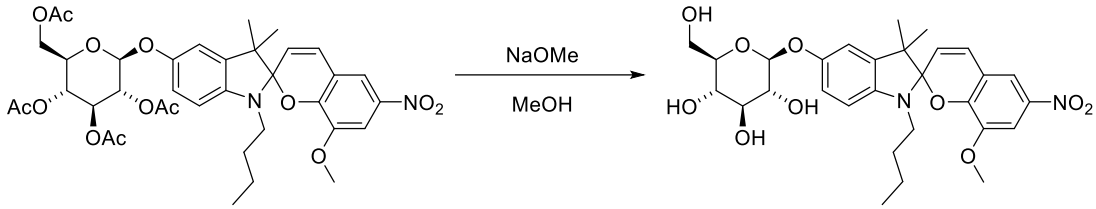
HR-MS (ESI) Calcd. $[M+H]^+$: 1042.3866, found: 1043.3864.
Calcd. [M+Na]: 1065.3686, found: 1065.3689.

11.2.6 Deacetylation of sugar compounds: General protocol (GP18)



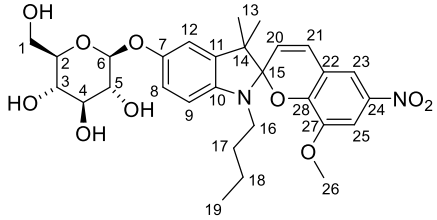
The sugar compound (1.00 eq.) was dissolved in MeOH and cooled to 0 °C. A solution of NaOMe in MeOH (0.5 M, 0.5 eq.) was added dropwise. The reaction mixture was stirred at rt for 0.5 – 1 h. The solution was neutralized with the acidic *Amberlite IR-120* ion exchanger and stirred for further 10 min. The mixture was filtered, washed with MTBE and the solvent was removed under reduced pressure.

11.2.6.1 Synthesis of (2*S*,3*R*,4*S*,5*S*,6*R*)-2-((1'-butyl-8-methoxy-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)oxy)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (108)



93 **108**

According to **GP18**, 2.15 g (2.90 mmol, 1.00 eq.) of spiropyran **93** was deprotected with 2.90 mL (1.45 mmol, 0.50 eq.) of NaOMe (0.5 M in MeOH) in 12 mL MeOH. After purification, 1.57 g (2.74 mmol, 95%) of the desired product **108** were obtained as a blue solid.



M($C_{29}H_{36}N_2O_{10}$) 572.61 g/mol.

^{1}H-NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.29 (d, $^4J_{HH}$ = 2.8 Hz, 1H, H-25), 7.56 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H-9), 7.43 (d, $^4J_{HH}$ = 2.5 Hz, 2H, H-23, H-12), 7.28 (dd, $^{3,4}J_{HH}$ = 8.8, 2.4 Hz, 1H, H-8), 5.02 – 5.01 (m, 1H, H-21), 4.41 (t, $^3J_{HH}$ = 7.5 Hz, 2H, H-16), 3.98 – 3.94 (m, 1H, H-1), 3.86 (s, 3H, H-26), 3.74 – 3.69 (m, 1H, H-1‘), 3.53 – 3.45 (m, 4H, H-20, H-3, H-4, H-6), 3.42 – 3.39 (m, 1H, H-2), 1.96 – 1.88 (m,

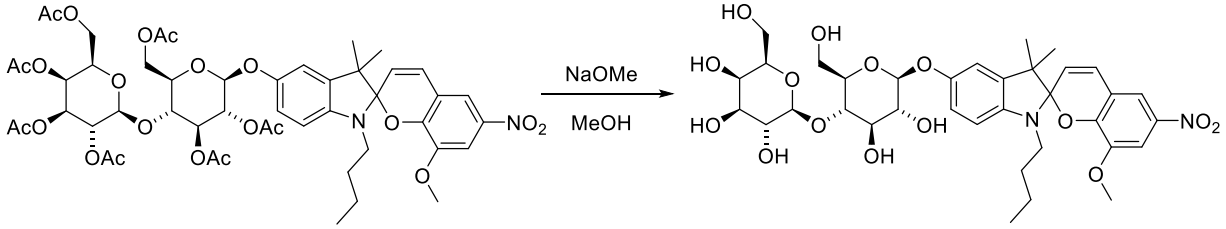
2H, H-17), 1.81 (s, 6H, H-13), 1.57 – 1.52 (m, 2H, H-18), 1.05 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, H-19).

^{13}C-NMR (126 MHz, MeOD-d_4) δ [ppm] = 180.5 (C-28), 173.0 (C-27), 158.0 (C-22), 152.6 (C-7), 144.7 (C-10), 135.7 (C-11), 133.0 (C-24), 123.6 (C-25), 119.8 (C-15), 117.2 (C-8), 114.0 (C-9), 111.2 (C-12), 104.7 (C-23), 101.0 (C-21), 76.9 (C-3), 76.6 (C-4), 76.6 (C-20), 73.4 (C-6), 70.1 (C-2), 61.2 (C-1), 54.7 (C-26), 51.3 (C-14), 48.4 (C-5), 45.5 (C-16), 29.7 (C-17), 26.2 (C-13), 19.8 (C-18), 12.7 (C-19).

FT-IR ATR, v [cm^{-1}] = 3361 (m), 2961 (w), 2931 (w), 2872 (w), 2120 (w), 2070 (w), 2003 (w), 1932 (w), 1591 (m), 1560 (m), 1512 (m), 1484 (m), 1448 (m), 1417 (m), 1370 (m), 1334 (m), 1305 (m), 1277 (s), 1238 (s), 1196 (s), 1128 (m), 1097 (s), 1072 (s), 1044 (s), 1020 (m), 981 (m), 936 (w), 885 (w), 851 (w), 818 (w), 790 (w), 774 (w), 744 (w), 706 (w), 677 (w), 653 (w), 629 (w), 537 (w).

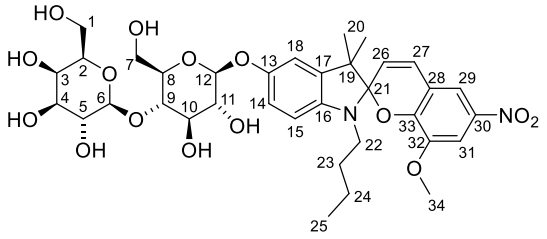
HR-MS (ESI) Calcd. [M+H]$^{+}$: 573.2443, found: 573.2432.
Calcd. [M+Na]$^{+}$: 595.2262, found: 595.2257.

11.2.6.2 Synthesis of (2*S*,3*R*,4*S*,5*R*,6*R*)-2-(((2*R*,3*S*,4*R*,5*R*,6*S*)-6-((1'-butyl-8-methoxy-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)oxy)-4,5-dihydroxy-2-(hydroxymethyl)tetrahydro-2*H*-pyran-3-yl)oxy)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (110)



95 **110**

According to **GP18**, 1.78 g (1.73 mmol, 1.00 eq.) of spiropyran **95** was deprotected with 1.70 mL (0.86 mmol, 0.50 eq.) of NaOMe (0.5 M in MeOH) in 8 mL MeOH. After purification, 1.18 g (1.60 mmol, 93%) of the desired product **110** were obtained as a blue solid.



M($C_{35}H_{46}N_2O_{22}$) 734.75 g/mol.

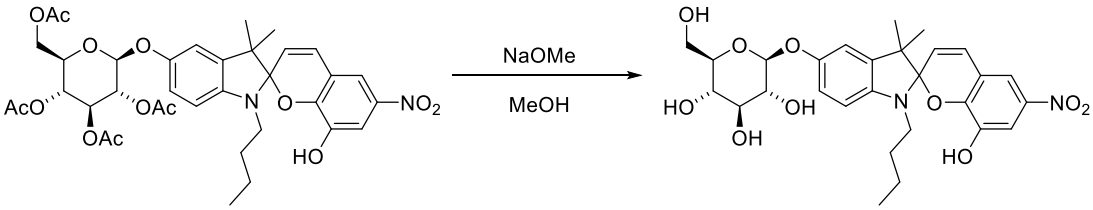
^{1}H-NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.23 (d, $^4J_{HH}$ = 2.9 Hz, 1H, H-31), 7.53 (d, $^4J_{HH}$ = 2.9 Hz, 1H, H-29), 7.15 (d, $^4J_{HH}$ = 2.6 Hz, 1H, H-18), 7.09 - 7.06 (m, 1H, H-14), 6.96 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H-15), 4.83 - 4.75 (m, 1H, H-26), 4.42 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H-12), 3.96 - 3.90 (m, 3H, H-7, H-6), 3.86 (s, 3H, H-34), 3.83 - 3.79 (m, 2H, H-1), 3.72 - 3.50 (m, 8H, H-2, H-3, H-4, H-5, H-8, H-10, H-11, H-27), 3.37 - 3.35 (m, 1H, H-9), 1.71 - 1.63 (m, 2H, H-22), 1.40 - 1.31 (m, 2H, H-24), 1.34 (s, 6H, H-20), 1.31 (m, 2H, H-23), 0.97 (t, $^3J_{HH}$ = 7.9 Hz, 3H, H-25).

^{13}C-NMR (101 MHz, MeOD-d_4) δ [ppm] = 154.1 (C-32), 153.0 (C-13), 147.0 (C-33), 143.7 (C-30), 136.5 (C-16), 130.3 (C-17), 119.7 (C-31), 118.2 (C-28), 116.0 (C-14), 112.7 (C-18), 109.0 (C-15), 106.0 (C-29), 103.7 (C-12), 101.7 (C-26), 78.3 (C-27), 75.7 (C-5), 75.7 (C-3), 75.7 (C-11), 74.8 (C-10), 73.3 (C-4), 73.3 (C-8), 71.1 (C-2), 68.9 (C-6), 61.1 (C-1), 60.3 (C-7), 54.7 (C-34), 47.9 (C-9), 29.1 (C-23), 29.1 (C-22), 22.8 (C-20), 19.5 (C-24), 12.7 (C-25).

FT-IR ATR, v [cm^{-1}] = 3393 (s), 2960 (w), 2934 (w), 2520 (w), 1982 (w), 1665 (w), 1597 (m), 1564 (w), 1515 (w), 1496 (w), 1445 (w), 1384 (w), 1285 (s), 1244 (s), 1168 (w), 1076 (s), 960 (w), 893 (w), 830 (w), 788 (w), 767 (w), 748 (w), 724 (w), 703 (w), 673 (w), 663 (w), 577 (w), 544 (w).

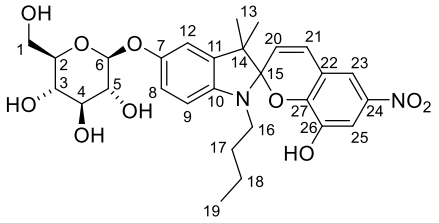
HR-MS (ESI) Calcd. $[M+H]^+$: 735.2970, found: 735.2972.
Calcd. $[M+Na]^+$: 757.2790, found: 757.2777.

11.2.6.3 Synthesis of (2*S*,3*R*,4*S*,5*S*,6*R*)-2-((1'-butyl-8-hydroxy-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)oxy)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (109)



94 **109**

According to **GP18**, 0.42 g (0.58 mmol, 1.00 eq.) of spiropyran **94** was deprotected with 0.60 mL (0.29 mmol, 0.50 eq.) of NaOMe (0.5 M in MeOH) in 2.4 mL MeOH. After purification, 0.31 g (0.55 mmol, 95%) of the desired product **109** were obtained as a blue solid.



M($C_{28}H_{34}N_2O_{10}$) 558.58 g/mol.

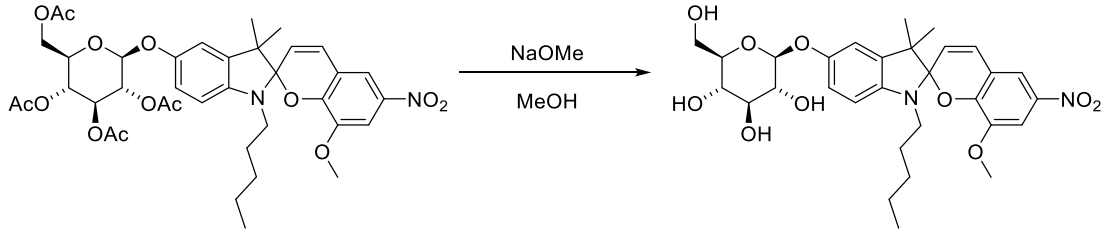
^{1}H-NMR (400 MHz, MeOD-*d*$_4$) δ [ppm] = 8.21 (d, $^4J_{HH}$ = 2.8 Hz, 1H, H-25), 7.57 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H-9), 7.43 (d, $^4J_{HH}$ = 2.2 Hz, 1H, H-12), 7.42 (d, $^4J_{HH}$ = 2.7 Hz, 1H, H-23), 7.28 (dd, $^{3,4}J_{HH}$ = 8.8, 2.4 Hz, 1H, H-8), 5.03 – 5.01 (m, 1H, H-20), 4.43 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H-16), 3.96 (dd, $^{2,3}J_{HH}$ = 12.3, 2.4 Hz, 1H, H-1), 3.72 (dd, $^{2,3}J_{HH}$ = 11.9, 6.1 Hz, 1H, H-1‘), 3.60 - 3.51 (m, 3H, H-2, H-5, H-21), 3.48 - 3.39 (m, 3H, H-6, H-3, H-4), 1.93 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H-17), 1.82 (s, 6H, H-13), 1.60 - 1.53 (m, 2H, H-18), 1.05 (t, $^3J_{HH}$ = 7.3 Hz, 3H, H-19).

^{13}C-NMR (101 MHz, MeOD-*d*$_4$) δ [ppm] = 171.5 (C-27), 158.1 (C-7), 152.7 (C-26), 150.5 (C-22), 145.2 (C-10), 144.7 (C-15), 135.6 (C-11), 133.6 (C-24), 128.6 (C-15), 124.1 (C-25), 117.2 (C-8), 114.5 (C-9), 111.2 (C-23), 105.7 (C-12), 101.0 (C-21), 76.9 (C-2), 76.6 (C-3), 76.5 (C-5), 73.6 (C-4), 73.4 (C-20), 70.1 (C-6), 61.2 (C-1), 51.3 (C-14), 45.6 (C-16), 29.7 (C-17), 26.2 (C-13), 26.2 (C-13‘), 19.7 (C-18), 12.7 (C-19).

FT-IR ATR, v [cm^{-1}] = 3332 (m), 2962 (w), 2931 (w), 2873 (w), 2228 (w), 2130 (w), 2071 (w), 1998 (w), 1948 (w), 1718 (w), 1606 (w), 1587 (w), 1561 (m), 1516 (m), 1481 (m), 1444 (m), 1427 (s), 1371 (m), 1331 (s), 1282 (s), 1248 (s), 1195 (s), 1131 (m), 1073 (s), 1043 (s), 1018 (s), 961 (m), 951 (m), 883 (w), 820 (w), 796 (w), 770 (w), 745 (m), 704 (w), 667 (w), 650 (w), 596 (w), 574 (w), 506 (w).

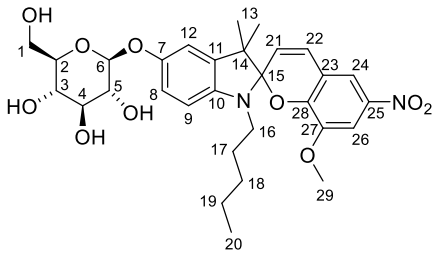
HR-MS (ESI) Calcd. $[M+H]^+$: 559.2286, found: 559.2276.
Calcd. $[M+Na]^+$: 581.2106, found: 581.2102.

11.2.6.4 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(hydroxymethyl)-6-((8-methoxy-3',3'-dimethyl-6-nitro-1'-pentylspiro[chromene-2,2'-indolin]-5'-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triol (111)



96 **111**

According to **GP18**, 2.03 g (2.69 mmol, 1.00 eq.) of spiropyran **96** were deprotected with 2.70 mL (1.35 mmol, 0.50 eq.) of NaOMe (0.5 M in MeOH) in 12 mL MeOH. After purification, 1.53 g (2.60 mmol, 97%) of the desired product **111** were obtained as a blue solid.

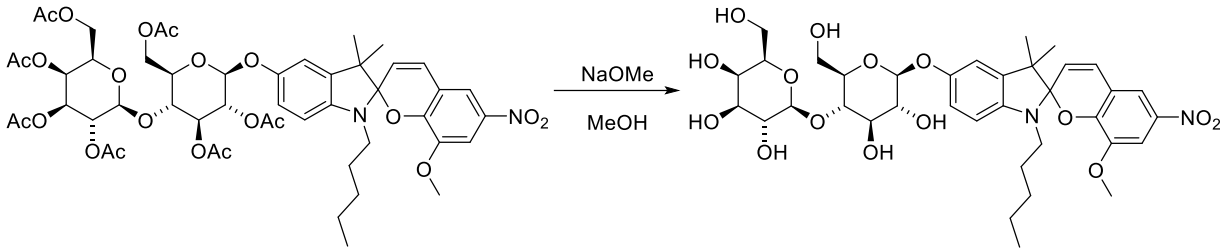


M($C_{30}H_{38}N_2O_{10}$) 586.64 g/mol.

^{1}H-NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.29 (d, $^4J_{HH}$ = 2.8 Hz, 1H, H-26), 7.55 (d, $^3J_{HH}$ = 8.8 Hz, 1H, H-9), 7.42 (t, $^4J_{HH}$ = 2.4 Hz, 2H, H-12, H-24), 7.28 (dd, $^{3,4}J_{HH}$ = 8.8, 2.2 Hz, 1H, H-8), 5.02 – 5.01 (m, 1H, H-22), 4.40 (t, $^3J_{HH}$ = 7.5 Hz, 2H, H-16), 4.01 – 3.92 (m, 1H, H-1), 3.86 (s, 3H, H-29), 3.74 – 3.67 (m, 1H, H-1‘), 3.56 – 3.53 (m, 1H, H-4), 3.54 -3.52 (m, 2H, H-21, H-5), 3.48 – 3.45 (m, 1H, H-6),

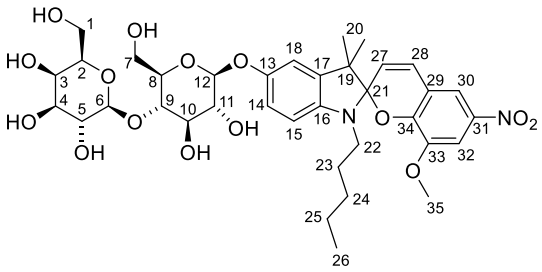
	3.43 - 3.38 (m, 2H, H-2, H-3), 1.97 - 1.91 (m, 2H, H-17), 1.53 - 1.42 (m, 4H, H-18, H-19), 0.95 (t, $^3J_{HH}$ = 6.9 Hz, 3H, H-20).
^{13}C-NMR	(126 MHz, MeOD-d_4) δ [ppm] = 180.5 (C-28), 173.3 (C-27), 158.0 (C-23), 152.7 (C-7), 144.6 (C-10), 135.7 (C-11), 132.9 (C-25), 127.8 (C-26), 119.8 (C-15), 117.2 (C-8), 114.0 (C-9), 111.2 (C-24), 104.6 (C-12), 101.0 (C-22), 76.9 (C-4), 76.6 (C-5), 76.6 (C-3), 73.6 (C-6), 73.4 (C-21), 70.1 (C-2), 61.2 (C-1), 54.7 (C-29), 51.3 (C-14), 45.6 (C-16), 28.6 (C-18), 27.3 (C-17), 26.3 (C-13), 26.2 (C-13‘), 22.0 (C-19), 12.8 (C-20).
FT-IR	ATR, v [cm^{-1}] = 3369 (m), 2959 (w), 2932 (w), 2871 (w), 2072 (w), 1687 (w), 1588 (m), 1563 (w), 1515 (m), 1493 (m), 1465 (m), 1421 (m), 1372 (w), 1337 (m), 1279 (s), 1240 (s), 1191 (m), 1097 (m), 1074 (s), 973 (w), 938 (w), 891 (w), 816 (w), 793 (w), 745 (w), 707 (w), 676 (w), 655 (w), 596 (w).
HR-MS (ESI)	Calcd. [M+H]$^+$: 587.2599, found: 587.2592. Calcd. [M+Na]$^+$: 609.2418, found: 609.2416.

11.2.6.5 Synthesis of (2*S*,3*R*,4*S*,5*R*,6*R*)-2-(((2*R*,3*S*,4*R*,5*R*,6*S*)-4,5-dihydroxy-2-(hydroxymethyl)-6-((8-methoxy-3',3'-dimethyl-6-nitro-1'-pentylspiro[chromene-2,2'-indolin]-5'-yl)oxy)tetrahydro-2*H*-pyran-3-yl)oxy)-6-(hydroxymethyl)tetra hydro-2*H*-pyran-3,4,5-triol (112)



97 **112**

According to **GP18**, 2.10 g (2.01 mmol, 1.00 eq.) of spiropyran **97** were deprotected with 2.00 mL (1.00 mmol, 0.50 eq.) of NaOMe (0.5 M in MeOH) in 8 mL MeOH. After purification, 1.39 g (1.85 mmol, 92%) of the desired product **112** were obtained as a blue solid.



M($C_{36}H_{48}N_2O_{15}$) 748.78 g/mol.

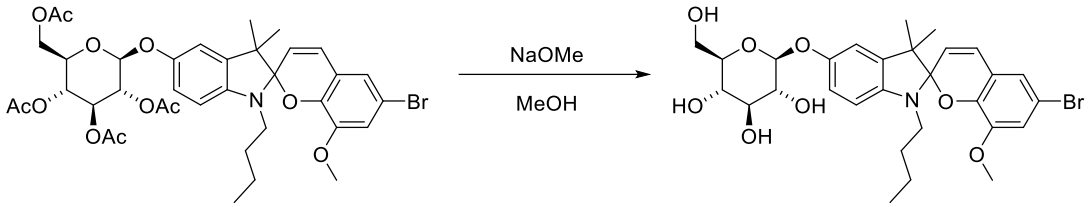
^{1}H-NMR (500 MHz, DMSO-d_6) δ [ppm] = 7.90 (d, $^4J_{HH}$ = 2.6 Hz, 1H, H-30), 7.65 (d, $^4J_{HH}$ = 2.7 Hz, 1H, H-32), 7.63 (d, $^3J_{HH}$ = 8.9 Hz, 1H, H-15), 7.19 (d, $^4J_{HH}$ = 2.9 Hz, 1H, H-18), 7.19 - 7.12 (m, 2H, H-14, H--27), 5.95 (d, $^3J_{HH}$ = 10.3 Hz, 1H, H-27), 4.25 (d, $^3J_{HH}$ = 7.2 Hz, 1H, H-12), 3.80 - 3.79 (m, 1H, H-7), 3.69 (s, 3H, H-35), 3.65 - 3.62 (m, 3H, H-7‘, H-6, H-3), 3.55 - 3.51 (m, 4H, H-1, H-8, H-2), 3.51 - 3.47 (m, 5H, H-4, H-5, H-9, H-10, H-11), 1.85 - 1.80 (m, 2H, H-22), 1.74 (s, 3H, H-20), 1.73 (s, 3H, H-20‘), 1.47 - 1.37 (m, 2H, H-23), 1.28 – 1.19 (m, 2H, H-25), 0.87 (t, $^3J_{HH}$ = 6.9 Hz, 3H, H-26).

^{13}C-NMR (126 MHz, DMSO-d_6) δ [ppm] = 157.3 (C-13), 154.2 (C-33), 149.3 (C-34), 144.7 (C-16), 142.3 (C-21), 140.2 (C-31), 136.0 (C-17), 128.5 (C-28), 121.9 (C-27), 118.8 (C-29), 116.7 (C-14), 115.8 (C-30), 114.6 (C-15), 107.7 (C-32), 105.5 (C-18), 104.3 (C-12), 80.8 (C-9), 76.0 (C-8), 75.4 (C-2), 75.3 (C-6), 73.7 (C-4), 73.5 (C-5), 73.4 (C-11), 71.0 (C-10), 68.6 (C-3), 60.8 (C-1), 60.6 (C-7), 55.4 (C-35), 51.1 (C-19), 29.2 (C-24), 28.7 (C-23), 27.4 (C-22), 27.3 (C-20), 22.2 (C-25), 14.3 (C-26).

FT-IR ATR, v [cm^{-1}] = 3366 (m), 2966 (w), 2929 (w), 2512 (w), 2130 (w), 2070 (w), 2006 (w), 1947 (w), 1721 (w), 1671 (w), 1594 (w), 1564 (w), 1515 (w), 1489 (w), 1464 (w), 1421 (w), 1333 (m), 1280 (s), 1248 (s), 1167 (w), 1075 (s), 1051 (s), 892 (w), 830 (w), 788 (w), 745 (w), 681 (w), 625 (w), 591 (w).

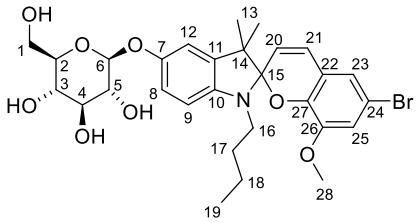
HR-MS (ESI) Calcd. $[M+H]^+$: 749.3127, found: 749.3129.
Calcd. $[M+Na]^+$: 771.2946, found: 771.2952.

11.2.6.6 Synthesis of (2*S*,3*R*,4*S*,5*S*,6*R*)-2-((6-bromo-1'-butyl-8-methoxy-3',3'-dimethylspiro[chromene-2,2'-indolin]-5'-yl)oxy)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (115)



100 **115**

According to **GP18**, 2.24 g (2.90 mmol, 1.00 eq.) of spiropyran **100** were deprotected with 2.90 mL (1.45 mmol, 0.50 eq.) of NaOMe (0.5 M in MeOH) in 12 mL MeOH. After purification, 1.67 g (2.75 mmol, 95%) of the desired product **115** were obtained as a blue solid.



M($C_{29}H_{36}BrNO_8$) 606.51 g/mol.

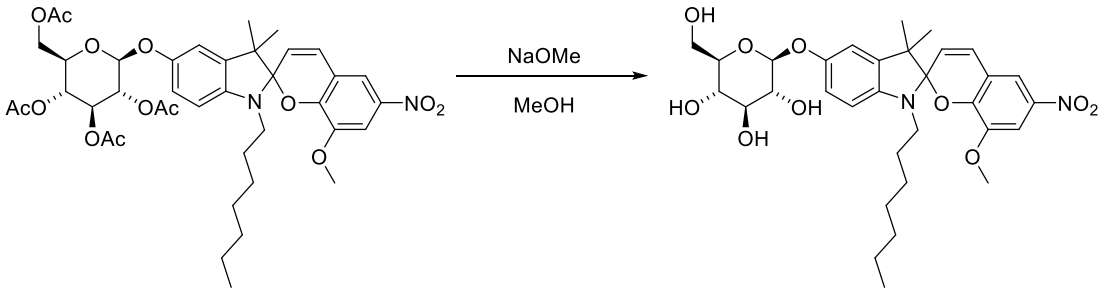
^{1}H-NMR (500 MHz, MeOD-*d*$_4$) δ [ppm] = 6.93 - 6.87 (m, 4H, H-8, H-12, H-23, H-25), 6.84 – 6.81 (m, 1H, H-21), 6.41 (d, $^3J_{HH}$ = 8.7 Hz, 1H, H-9), 5.79 (d, $^3J_{HH}$ = 10.2 Hz, 1H, H-20), 4.76 - 4.72 (m, 1H, H-6), 3.92 – 3.88 (m, 1H, H-1), 3.72 – 3.68 (m, 1H, H-1‘), 3.66 (s, 3H, H-28), 3.45 – 3.42 (m, 2H, H-4, H-5), 3.41 - 3.35 (m, 2H, H-3, H-2), 3.21 - 3.14 (m, 1H, H-16), 3.09 - 2.98 (m, 1H, H-16‘), 1.67 - 1.59 (m, 1H, H-17), 1.53 - 1.48 (m, 1H, H-17‘), 1.37 - 1.25 (m, 2H, H-18), 1.23 (s, 3H, H-13), 1.13 (s, 3H, H-13‘), 0.88 (t, $^3J_{HH}$ = 7.4 Hz, 3H, H-19).

^{13}C-NMR (126 MHz, MeOD-*d*$_4$) δ [ppm] = 151.4 (C-7), 147.9 (C-26), 143.1 (C-27), 142.7 (C-10), 137.4 (C-11), 127.9 (C-21), 121.1 (C-12), 121.1 (C-20), 120.8 (C-22), 115.8 (C-25), 115.5 (C-23), 112.2 (C-8), 110.8 (C-24), 105.9 (C-9), 105.3 (C-15), 102.8 (C-6), 76.6 (C-3, C-4), 73.7 (C-5), 70.2 (C-2), 61.2 (C-1), 55.5 (C-28), 51.9 (C-14), 43.2 (C-16), 30.9 (C-17), 20.1 (C-18), 18.7 (C-13), 18.6 (C-13‘), 12.9 (C-19).

FT-IR ATR, v [cm^{-1}] = 3354 (m), 2961 (w), 2932 (w), 2873 (w), 2251 (w), 2124 (w), 2072 (w), 1682 (m), 1574 (m), 1486 (m), 1466 (m), 1444 (m), 1421 (m), 1388 (m), 1354 (m), 1272 (m), 1236 (m), 1198 (m), 1073 (s), 1047 (s), 896 (w), 860 (w), 836 (w), 813 (w), 738 (w), 705 (w), 633 (w), 596 (w), 578 (m), 529 (w).

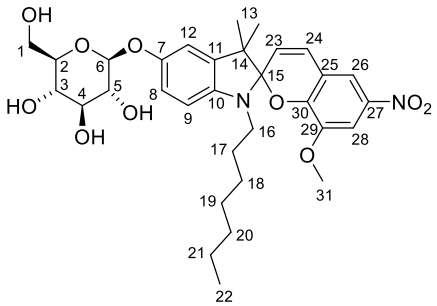
HR-MS (ESI) Calcd. $[M+H]^+$: 606.1697, found: 606.1693.
Calcd. $[M+Na]^+$: 628.1517, found: 628.1513.

11.2.6.7 Synthesis of (2*S*,3*R*,4*S*,5*S*,6*R*)-2-((1'-heptyl-8-methoxy-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)oxy)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (114)



98 **114**

According to **GP18**, 2.03 g (2.60 mmol, 1.00 eq.) of spiropyran **98** was deprotected with 2.60 mL (1.30 mmol, 0.50 eq.) of NaOMe (0.5 M in MeOH) in 12 mL MeOH. After purification, 1.55 g (2.53 mmol, 97%) of the desired product **114** were obtained as a blue solid.

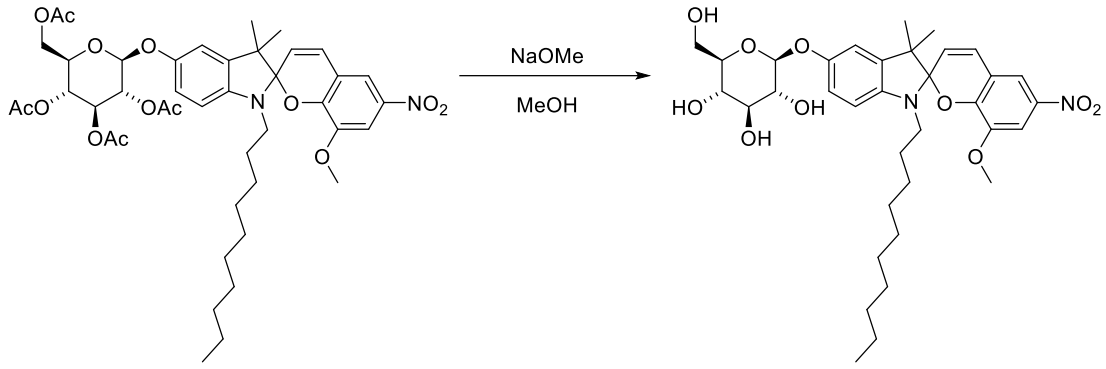


M($C_{32}H_{42}N_2O_{10}$) 614.69 g/mol.

^{1}H-NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.33 (d, $^4J_{HH}$ = 2.8 Hz, 1H, H-28), 7.57 (d, $^3J_{HH}$ = 8.8 Hz, 1H, H-9), 7.48 (d, $^4J_{HH}$ = 2.7 Hz, 1H, H-26), 7.44 (d, $^4J_{HH}$ = 2.3 Hz, 1H, H-12), 7.29 (dd, $^{3,4}J_{HH}$ = 8.7, 2.4 Hz, 1H, H-8), 5.04 – 5.00 (m, 1H, H-24), 4.43 (t, $^3J_{HH}$ = 7.5 Hz, 2H, H-16), 4.00 – 3.95 (m, 1H, H-1), 3.88 (s, 3H, H-31), 3.72 (ddd, $^{2,3,4}J_{HH}$ = 12.1, 5.9, 3.9 Hz, 1H, H-1‘), 3.56 – 3.53 (m, 1H, H-4),

	3.53 – 3.50 (m, 2H, H-23, H-5), 3.48 - 3.43 (m, 1H, H-6), 3.42 - 3.39 (m, 2H, H-2, H-3), 1.97 - 1.92 (m, 2H, H-17), 1.83 (s, 6H, H-13), 1.54 - 1.48 (m, 2H, H-18), 1.46 - 1.41 (m, 2H, H-19), 1.33 - 1.30 (m, 4H, H-20, H-21), 0.89 (t, $^3J_{HH}$ = 6.9 Hz, 3H, H-22).
^{13}C-NMR	(126 MHz, MeOD-d_4) δ [ppm] = 180.5 (C-30), 172.4 (C-29), 158.1 (C-25), 152.5 (C-7), 144.7 (C-10), 135.7 (C-11), 133.3 (C-27), 127.8 (C-28), 119.8 (C-15), 117.2 (C-8), 114.1 (C-9), 111.2 (C-26), 104.8 (C-12), 101.0 (C-24), 76.9 (C-4), 76.6 (C-3), 76.6 (C-5), 73.6 (C-6), 73.4 (C-23), 70.1 (C-2), 61.2 (C-1), 54.7 (C-31), 51.3 (C-14), 45.7 (C-16), 31.4 (C-20), 28.6 (C-19), 27.6 (C-17), 26.4 (C-18), 26.2 (C-13), 26.2 (C-13‘), 22.1 (C-21), 12.9 (C-41).
FT-IR	ATR, v [cm^{-1}] = 3350 (w), 2927 (w), 2857 (w), 2123 (w), 2069 (w), 1996 (w), 1927 (w), 1681 (w), 1587 (m), 1563 (m), 1513 (m), 1490 (m), 1463 (m), 1418 (m), 1370 (m), 1335 (m), 1277 (s), 1237 (s), 1207 (s), 1180 (m), 1095 (s), 1071 (s), 1044 (s), 1017 (s), 977 (m), 937 (m), 893 (w), 815 (w), 792 (w), 744 (m), 706 (w), 676 (w), 652 (w), 594 (w), 538 (w).
HR-MS (ESI)	Calcd. [M+H]$^+$: 615.2912, found: 615.2906. Calcd. [M+Na]$^+$: 637.2731, found: 637.2731.

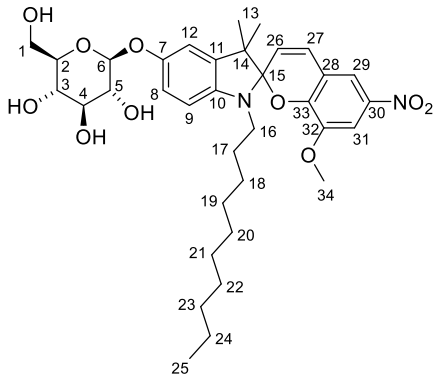
11.2.6.8 Synthesis of (2*S*,3*R*,4*S*,5*S*,6*R*)-2-((1'-decyl-8-methoxy-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)oxy)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (113)



99 **113**

According to **GP18**, 2.75 g (3.33 mmol, 1.00 eq.) of spiropyran **99** were deprotected with 3.30 mL (1.66 mmol, 0.50 eq.) of NaOMe (0.5 M in MeOH) in 13.5 mL MeOH.

After purification, 2.10 g (3.20 mmol, 96%) of the desired product **113** were obtained as a blue solid.



M($C_{35}H_{48}N_2O_{10}$) 656.77 g/mol.

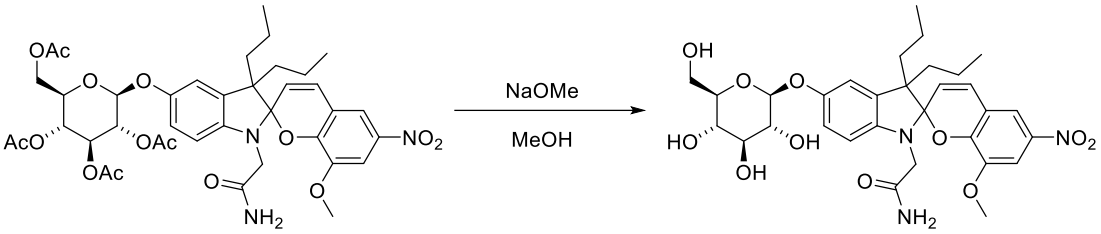
^{1}H-NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.31 (d, $^4J_{HH}$ = 2.9 Hz, 1H, H-31), 7.56 (d, $^3J_{HH}$ = 8.8 Hz, 1H, H-9), 7.45 - 7.43 (m, 2H, H-29, H-12), 7.28 (dd, $^{3,4}J_{HH}$ = 8.8, 2.4 Hz, 1H, H-8), 5.04 – 5.01 (m, 1H, H-27), 4.42 (t, 1H, $^3J_{HH}$ = 7.3 Hz, H-16), 4.01 - 3.94 (m, 1H, H-1), 3.87 (s, 3H, H-34), 3.72 (ddd, $^{2,3,4}J_{HH}$ = 12.1, 5.9, 3.5 Hz, 1H, H-1‘), 3.58 - 3.54 (m, 1H, H-5), 3.53 - 3.51 (m, 2H, H-4, H-26), 3.49 - 3.44 (m, 1H, H-6), 3.42 - 3.38 (m, 2H, H-2, H-3), 1.98 - 1.92 (m, 2H, H-17), 1.82 (s, 6H, H-13), 1.52 - 1.46 (m, 2H, H-18), 1.42 (t, $^3J_{HH}$ = 6.8 Hz, 2H, H-24), 1.35 - 1.22 (m, 10H, H-19, H-20, H-21, H-22, H-23), 0.87 (t, $^3J_{HH}$ = 6.9 Hz, 3H, H-25).

^{13}C-NMR (126 MHz, MeOD-d_4) δ [ppm] = 180.5 (C-33), 173.2 (C-32), 158.0 (C-28), 152.7 (C-7), 144.7 (C-10), 135.7 (C-11), 133.0 (C-30), 127.8 (C-31), 119.8 (C-15), 117.2 (C-8), 114.0 (C-9), 111.2 (C-29), 104.7 (C-12), 101.0 (C-27), 76.9 (C-5), 76.6 (C-3), 76.6 (C-4), 73.6 (C-6), 73.4 (C-26), 70.1 (C-2), 61.2 (C-1), 54.7 (C-34), 51.3 (C-14), 45.6 (C-16), 31.6 (C-21), 29.2 (C-17), 29.1 (C-22), 29.0 (C-20), 28.8 (C-19), 27.6 (C-23), 26.3 (C-18), 26.3 (C-13), 26.2 (C-13‘), 22.3 (C-24), 13.0 (C-25).

FT-IR ATR, v [cm^{-1}] = 3369 (w), 2926 (m), 2855 (w), 2131 (w), 1684 (w), 1587 (w), 1563 (w), 1514 (m), 1484 (w), 1466 (m), 1420 (w), 1372 (w), 1336 (w), 1279 (m), 1241 (s), 1210 (m), 1098 (m), 1074 (m), 1046 (m), 976 (w), 937 (w), 887 (w), 817 (w), 791 (w), 745 (w), 710 (w), 676 (w), 650 (w), 596 (w), 536 (w).

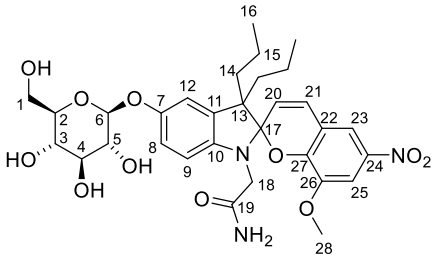
HR-MS (ESI) Calcd. [M+H]$^+$: 657.3381, found: 657.3379.
Calcd. [M+Na]$^+$: 679.3201, found: 679.3201.

11.2.6.9 Synthesis of 2-(8-methoxy-6-nitro-3',3'-dipropyl-5'-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)spiro-[chromene-2,2'-indolin]-1'-yl)acetamide (121)



106 **121**

According to **GP18**, 2.95 g (3.70 mmol, 1.00 eq.) of spiropyran **106** were deprotected with 3.70 mL (1.85 mmol, 0.50 eq.) of NaOMe (0.5 M in MeOH) in 15 mL MeOH. After purification, 2.10 g (3.20 mmol, 96%) of the desired product **121** were obtained as a blue solid.



M($C_{31}H_{39}N_3O_{11}$) 629.66 g/mol.

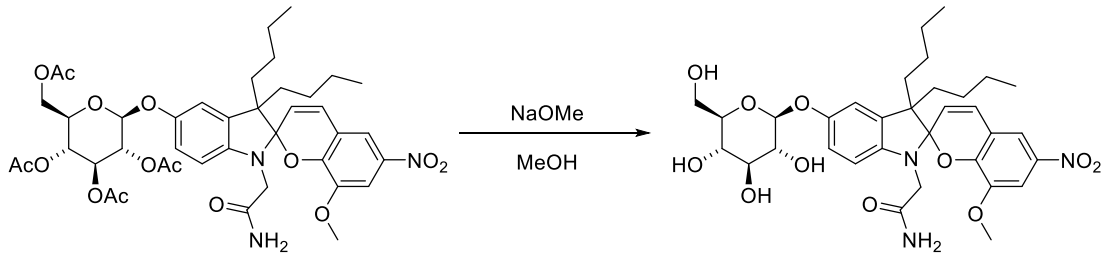
^{1}H-NMR (400 MHz, MeOD-*d_4*) δ [ppm] = 8.06 (s, 1H, H-25), 7.86 – 7.79 (m, 1H, H-23), 7.47 – 7.44 (m, 1H, H-9), 7.38 – 7.25 (m, 1H, H-12), 7.30 – 7.26 (m, 1H, H-8), 6.96 – 6.91 (m, 1H, H-21), 6.34 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H-20), 4.84 – 4.76 (m, 1H, H-6), 4.03 – 4.01 (m, 1H, H-1), 3.86 (s, 3H, H-28), 3.74 – 3.73 (m, 1H, H-1‘), 3.53 – 3.50 (m, 2H, H-3, H-5), 3.43 – 3.39 (m, 2H, H-2, H-4), 2.47 – 2.36 (m, 2H, H-18), 1.79 – 1.73 (m, 2H, H-14), 1.55 – 1.50 (m, 2H, H-14‘), 1.29 – 1.23 (m, 4H, H-15), 0.92 – 0.83 (m, 3H, H-16), 0.79 – 0.76 (m, 3H, H-16‘).

^{13}C-NMR (101 MHz, MeOD-*d_4*) δ [ppm] = 215.2 (C-19), 157.2 (C-7), 151.2 (C-27), 141.0 (C-26), 139.9 (C-10), 136.8 (C-20), 133.4 (C-11), 127.3 (C-25), 123.0 (C-22), 119.2 (C-9), 115.6 (C-21), 112.9 (C-8), 110.8 (C-12), 109.7 (C-24), 106.6 (C-23), 101.7 (C-6), 95.1 (C-18), 87.9 (C-17), 77.6 (C-5), 76.6 (C-4), 73.5 (C-3), 69.2 (C-2), 61.1 (C-1), 54.6 (C-28), 45.5 (C-13), 33.4 (C-14), 16.3 (C-15), 16.2 (C-15‘), 12.9 (C-16), 12.8 (C-16‘).

FT-IR ATR, v [cm^{-1}] = 3356 (m), 2960 (w), 2933 (w), 2873 (w), 2523 (w), 2072 (w), 2035 (w), 1999 (w), 1940 (w), 1675 (s), 1595 (m), 1562 (w), 1508 (m), 1486 (m), 1415 (m), 1380 (w), 1338 (m), 1276 (s), 1234 (s), 1100 (s), 1074 (s), 960 (w), 944 (w), 893 (w), 827 (w), 766 (w), 746 (w), 724 (w), 660 (w), 633 (w), 602 (w), 591 (w), 538 (w).

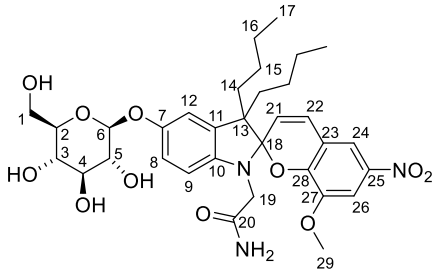
HR-MS (ESI) Calcd. [M+H]$^+$: 630.2657, found: 630.2661.
Calcd. [M+Na]$^+$: 652.2477, found: 652.2485.

11.2.6.10 Synthesis of 2-(3',3'-dibutyl-8-methoxy-6-nitro-5'-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)spiro[chromene-2,2'-indolin]-1'-yl)acetamide (122)



107 **122**

According to **GP18**, 0.56 g (0.68 mmol, 1.00 eq.) of spiropyran **107** were deprotected with 0.68 mL (0.34 mmol, 0.50 eq.) of NaOMe (0.5 M in MeOH) in 2.8 mL MeOH. After purification, 0.36 g (0.54 mmol, 79%) of the desired product **122** were obtained as a blue solid.



M($C_{33}H_{43}N_3O_{11}$) 657.72 g/mol.

^{1}H-NMR (400 MHz, MeOD-d_4) δ [ppm] = 8.22 (d, $^4J_{HH}$ = 2.9 Hz, 1H, H-26), 7.52 (d, $^4J_{HH}$ = 2.9 Hz, 1H, H-24), 7.46 – 7.45 (m, 1H, H-9), 7.37 (d, $^4J_{HH}$ = 2.3 Hz, 1H, H-12), 7.30 – 7.28 (m, 1H, H-8), 6.97 – 6.94 (m, 1H, H-22), 6.35 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H-21), 5.06 – 5.02 (m, 1H, H-6), 3.93 – 3.92 (m, 1H, H-1), 3.86 (s, 3H, H-29), 3.75 – 3.72 (m, 1H, H-1‘), 3.53 – 3.51 (m, 1H, H-5), 3.46 – 3.41 (m, 3H, H-2,

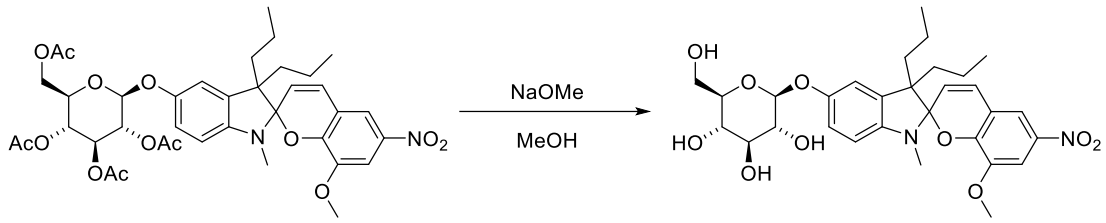
H-3, H-4), 2.54 – 2.44 (m, 2H, H-14), 2.41 – 2.35 (m, 2H, H-14), 1.28 – 1.17 (m, 4H, H-15), 1.02 – 0.97 (m, 2H, H-16), 0.75 (t, $^{3}J_{HH}$ = 7.3 Hz, 6H, H-17), 0.65 – 0.60 (m, 2H, H-16‘).

^{13}C-NMR (101 MHz, MeOD-d_4) δ [ppm] = 208.7 (C-20), 157.8 (C-7), 153.7 (C-27), 151.8 (C-28), 141.3 (C-10), 133.2 (C-11), 131.9 (C-23), 119.7 (C-25), 119.2 (C-26), 116.9 (C-8), 115.7 (C-22), 114.6 (C-18), 113.1 (C-9), 110.2 (C-12), 106.1 (C-21), 105.5 (C-24), 100.8 (C-6), 76.8 (C-3), 76.6 (C-5), 73.4 (C-4), 70.4 (C-2), 61.2 (C-1), 54.6 (C-29), 51.1 (C-13), 41.5 (C-19), 28.7 (C-14), 25.6 (C-15), 22.4 (C-16), 12.6 (C-17).

FT-IR ATR, v [cm^{-1}] = 3350 (m), 2956 (w), 2933 (m), 2871 (w), 2439 (w), 2071 (w), 1999 (w), 1947 (w), 1671 (m), 1595 (m), 1562 (w), 1511 (m), 1486 (s), 1466 (m), 1417 (m), 1379 (w), 1337 (m), 1283 (s), 1243 (s), 1231 (s), 1098 (s), 1073 (s), 962 (w), 940 (w), 894 (w), 821 (w), 789 (w), 767 (w), 745 (w), 723 (w), 654 (w), 592 (w).

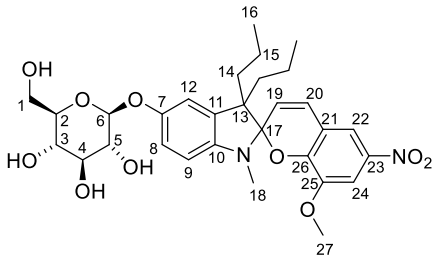
HR-MS (ESI) Calcd. [M+H]$^{+}$: 658.2970, found: 658.2970.
Calcd. [M+Na]$^{+}$: 680.2789, found: 680.2795.

11.2.6.11 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(hydroxymethyl)-6-((8-methoxy-1'-methyl-6-nitro-3',3'-dipropylspiro[chromene-2,2'-indolin]-5'-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triol (119)



104 **119**

According to **GP18**, 50.0 mg (0.06 mmol, 1.00 eq.) of spiropyran **104** were deprotected with 0.06 mL (0.03 mmol, 0.50 eq.) of NaOMe (0.5 M in MeOH) in 0.4 mL MeOH. After purification, 30.0 mg (0.05 mmol, 83%) of the desired product **119** were obtained as a blue solid.



M($C_{30}H_{38}N_2O_{11}$) 586.64 g/mol.

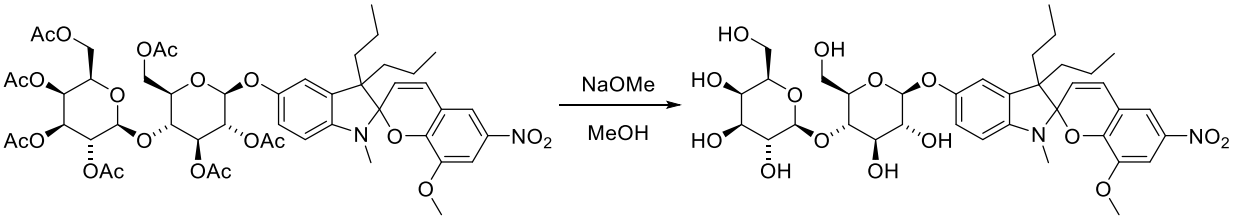
^{1}H-NMR (400 MHz, MeOD-d_4) δ [ppm] = 8.60 (s, 1H, H-12), 8.42 (d, $^4J_{HH}$ = 2.7 Hz, 1H, H-24), 8.02 (d, $^3J_{HH}$ = 2.7 Hz, 1H, H-8), 7.80 (d, $^3J_{HH}$ = 2.7 Hz, 1H, H-9), 7.61 (dd, $^{3\,4}J_{HH}$ = 8.8, 2.6 Hz, 1H, H-20), 7.57 (d, $^4J_{HH}$ = 2.7 Hz, 1H, H-22), 7.33 - 7.31 (m, 1H, H-19), 5.08 - 5.03 (m, 1H, H-6), 3.99 (s, 3H, H-18), 3.92 (s, 3H, H-27), 3.77 - 3.69 (m, 2H, H-1), 3.55 - 3.50 (m, 2H, H-3, H-4), 3.45 - 3.39 (m, 2H, H-2, H-5), 2.48 – 2.33 (m, 4H, H-14), 0.92 - 0.90 (m, 2H, H-15), 0.78 (t, $^3J_{HH}$ = 7.1 Hz, 6H, H-16), 0.64 - 0.61 (m, 4H, H-15‘).

^{13}C-NMR (101 MHz, MeOD-d_4) δ [ppm] = 179.4 (C-7), 169.9 (C-10), 159.0 (C-26), 151.1 (C-25), 151.1 (C-23), 150.6 (C-12), 145.7 (C-17), 142.3 (C-21), 122.4 (C-11), 121.7 (C-24), 117.1 (C-19), 115.8 (C-8), 113.9 (C-20), 105.8 (C-9), 105.5 (C-22), 100.5 (C-6), 76.9 (C-3), 72.4 (C-4), 70.6 (C-5), 70.3 (C-2), 65.0 (C-13), 60.2 (C-1), 55.5 (C-27), 43.6 (C-14), 30.9 (C-18), 14.4 (C-15), 12.8 (C-16), 12.8 (C-16‘).

FT-IR ATR, v [cm^{-1}] = 3370 (w), 2959 (w), 2932 (w), 2874 (w), 2253 (w), 2130 (w), 2069 (w), 2025 (w), 2002 (w), 1987 (w), 1971 (w), 1964 (w), 1895 (w), 1589 (m), 1561 (w), 1518 (m), 1491 (m), 1465 (m), 1405 (m), 1336 (m), 1283 (s), 1234 (s), 1203 (m), 1096 (m), 1075 (s), 1015 (m), 975 (w), 938 (w), 891 (w), 868 (w), 808 (w), 793 (w), 777 (w), 769 (w), 762 (w), 745 (w), 730 (w), 708 (w), 692 (w), 685 (w), 678 (w), 671 (w), 662 (w), 655 (w), 638 (w), 632 (w), 616 (w), 609 (w), 603 (w), 587 (w), 579 (w), 572 (w), 562 (w), 556 (w), 549 (w), 533 (w), 526 (w), 510 (w), 503 (w).

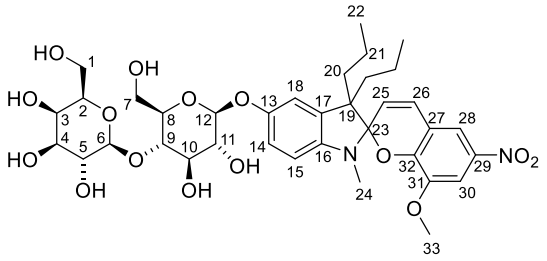
HR-MS (ESI) Calcd. $[M+H]^+$: 587.2599, found: 587.2597.
Calcd. $[M+Na]^+$: 609.2418, found: 609.2418.

11.2.6.12 Synthesis of (2*S*,3*R*,4*S*,5*R*,6*R*)-2-(((2*R*,3*S*,4*R*,5*R*,6*S*)-4,5-dihydroxy-2-(hydroxymethyl)-6-((8-methoxy-1'-methyl-6-nitro-3',3'-dipropylspiro[chromene-2,2'-indolin]-5'-yl)oxy)tetrahydro-2*H*-pyran-3-yl)oxy)-6-(hydroxymethyl)tetra hydro-2*H*-pyran-3,4,5-triol (120)



105 **120**

According to **GP18**, 0.48 g (0.46 mmol, 1.00 eq.) of spiropyran **105** were deprotected with 0.46 mL (0.28 mmol, 0.50 eq.) of NaOMe (0.5 M in MeOH) in 2 mL MeOH. After purification, 0.32 g (0.43 mmol, 94%) of the desired product **119** were obtained as a blue solid.



M($C_{36}H_{48}N_2O_{15}$) 748.78 g/mol.

^{1}H-NMR (400 MHz, MeOD-d_4) δ [ppm] = 8.60 (s, 1H, H-18), 8.40 (d, $^4J_{HH}$ = 2.7 Hz, 1H, H-30), 8.02 (d, $^3J_{HH}$ = 2.6 Hz, 1H, H-14), 7.80 (d, $^3J_{HH}$ = 2.7 Hz, 1H, H-15), 7.60 (d, $^3J_{HH}$ = 8.8 Hz, 1H, H-25), 7.53 (d, $^4J_{HH}$ = 2.7 Hz, 1H, H-28), 7.31 (dd, $^{3,4}J_{HH}$ = 8.8, 2.4 Hz, 1H, H-26), 5.11 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H-12), 4.43 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H-6), 4.03 - 4.01 (m, 1H, H-9), 3.99 (s, 3H, H-24), 3.96 - 3.94 (m, 1H, H-1), 3.91 (s, 3H, H-33), 3.86 - 3.84 (m, 3H, H-1‘, H-5, H-7), 3.73 – 3.70 (m, 3H, H-7‘, H-4, H-11), 3.64 - 3.58 (m, 3H, H-2, H-3, H-10), 3.54 -3.51 (m, 1H, H-8), 2.49 -2.42 (m, 2H, H-20), 2.37 – 2.29 (m, 2H, H-20‘), 0.94 - 0.89 (m, 2H, H-21), 0.78 (t, $^3J_{HH}$ = 7.1 Hz, 6H, H-22), 0.69 - 0.60 (m, 2H, H-21‘).

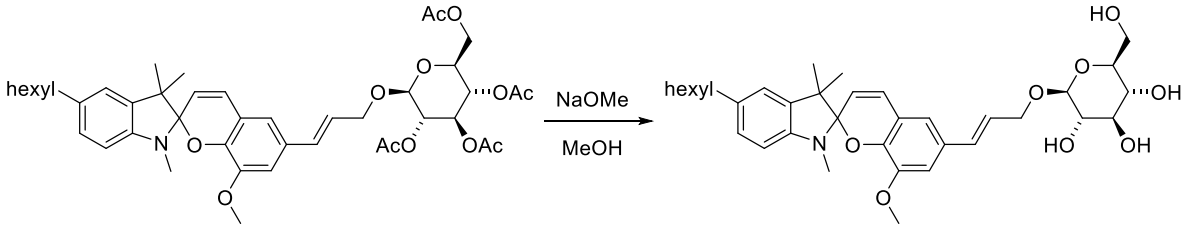
^{13}C-NMR (101 MHz, MeOD-d_4) δ [ppm] = 179.4 (C-13), 171.0 (C-16), 158.0 (C-23), 152.4 (C-31), 151.4 (C-18), 150.9 (C-29), 141.6 (C-23), 133.9 (C-27), 123.2 (C-30), 121.7 (C-17), 117.0 (C-26), 115.7 (C-14), 113.8 (C-25), 105.8 (C-15), 105.2 (C-28), 103.7 (C-6), 100.4 (C-12), 78.9 (C-4), 75.7 (C-3), 74.9 (C-11), 73.6 (C-8), 73.4

(C-10), 71.1 (C-2), 68.9 (C-5), 61.3 (C-19), 61.1 (C-7), 61.0 (C-1), 55.5 (C-9), 54.8 (C-33), 43.4 (C-20), 32.1 (C-24), 16.9 (C-21), 16.9 (C-21‘), 12.8 (C-22), 12.8 (C-22‘).

FT-IR ATR, v [cm^{-1}] = 3370 (m), 2959 (w), 2932 (w), 2875 (w), 2220 (w), 2128 (w), 2070 (w), 1983 (w), 1589 (m), 1561 (m), 1515 (m), 1492 (m), 1458 (m), 1405 (m), 1382 (m), 1336 (m), 1284 (s), 1235 (s), 1203 (m), 1075 (s), 975 (m), 938 (w), 892 (w), 820 (w), 791 (w), 759 (w), 745 (w), 706 (w), 660 (w), 617 (w), 558 (w).

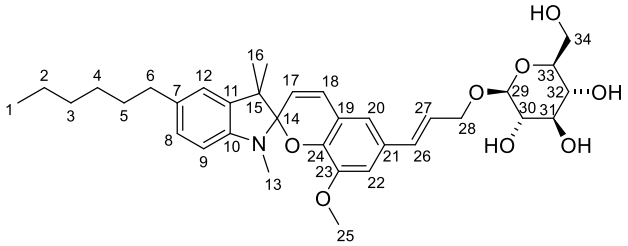
HR-MS (ESI) Calcd. $[M+H]^+$: 749.3127, found: 749.3132.
Calcd. $[M+Na]^+$: 771.2947, found 771.2950.

11.2.6.13 Synthesis of (2*S*,3*S*,4*R*,5*R*,6*S*)-2-(((*E*)-3-(5'-hexyl-8-methoxy-1',3',3'-trimethylspiro[chromene-2,2'-indolin]-6-yl)allyl)oxy)-6-(hydroxymethyl)tetra hydro-2*H*-pyran-3,4,5-triol (116)



101 **116**

According to **GP18**, 0.10 g (0.13 mmol, 1.00 eq.) of spiropyran **101** were deprotected with 0.03 mL (0.13 mmol, 1.00 eq.) of NaOMe (5.4 M in MeOH) in 0.5 mL MeOH. After purification, 0.61 g (0.12 mmol, 92%) of the desired product **116** were obtained as a blue solid.



M($C_{35}H_{47}NO_8$) 609.76 g/mol.

^{1}H-NMR (400 MHz, MeOD-d_4) δ [ppm] = 7.14 (s, 1H, H-12), 7.13 - 7.11 (m, 1H, H-9), 6.92 (s, 1H, H-22), 6.90 (s, 1H, H-20), 6.88 (m, 1H, H-9), 4.44 - 4.30 (m, 1H, H-26), 3.91 - 3.79 (m, 4H, H-28, H-17, H-34), 3.73 - 3.68 (m, 1H, H-18, H-34‘), 3.39 - 3.34 (m, 3H, H-31, H-32, H-33), 3.31 - 3.29 (m, 3H, H-30, H-29, H-27), 3.22 (s, 3H, H-25),

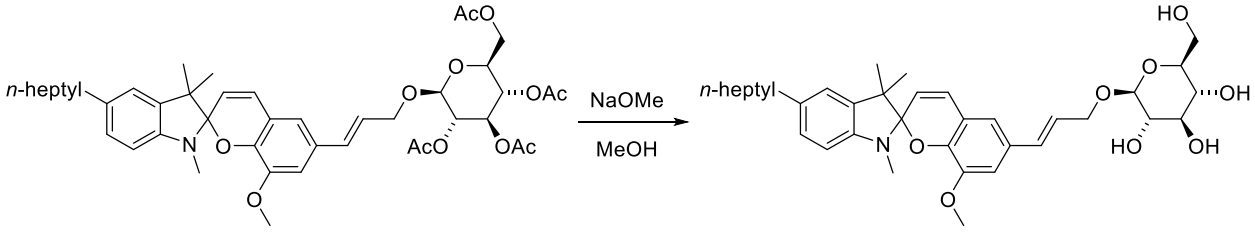
2.60 - 2.52 (m, 2H, H-6), 1.63 (s, 3H, H-13), 1.65 - 1.62 (m, 2H, H-5), 1.38 - 1.30 (m, 12H, H-4, H-3, H-2, H-16), 0.93 - 0.90 (m, 3H, H-1).

^{13}C-NMR (101 MHz, MeOD-d_4) δ [ppm] = 148.9 (C-17), 147.8 (C-18), 145.6 (C-24), 144.1 (C-23), 140.1 (C-7), 137.6 (C-19), 135.1 (C-14), 134.9 (C-21), 127.3 (C-8), 127.0 (C-22), 126.8 (C-10), 122.1 (C-12), 121.8 (C-9), 121.7 (C-11), 108.0 (C-20), 102.2 (C-26), 76.9 (C-33), 73.8 (C-27), 73.7 (C-31), 70.2 (C-32), 61.5 (C-28), 61.4 (C-36), 54.9 (C-30), 54.0 (C-29), 44.2 (C-15), 35.2 (C-6), 31.6 (C-5), 31.4 (C-4), 28.5 (C-3), 25.1 (C-25), 23.1 (C-16), 22.9 (C-13), 22.2 (C-2), 12.9 (C-1).

FT-IR ATR, ν [cm^{-1}] = 3357 (w), 2957 (m), 2926 (m), 2855 (m), 2336 (w), 2248 (w), 2119 (w), 2080 (w), 1995 (w), 1846 (w), 1803 (w), 1713 (w), 1647 (m), 1595 (s), 1495 (s), 1464 (s), 1422 (m), 1381 (m), 1349 (s), 1302 (m), 1246 (m), 1192 (m), 1152 (m), 1100 (s), 1072 (s), 1045 (s), 1020 (s), 966 (m), 891 (w), 869 (w), 807 (m), 752 (m), 723 (m), 704 (m), 610 (m), 585 (m), 557 (m), 527 (m).

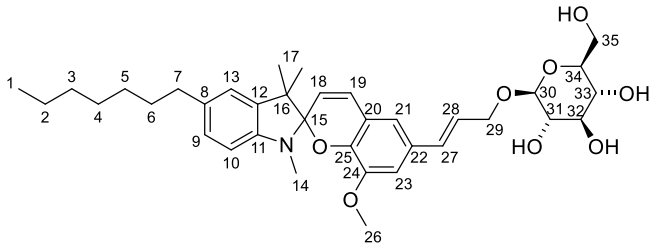
HR-MS Calcd. [M+H]$^+$: 610.3374, found: 610.3374.

11.2.6.14 Synthesis of (2*S*,3*S*,4*R*,5*R*,6*S*)-2-(((*E*)-3-(5'-heptyl-8-methoxy-1',3',3'-trimethylspiro[chromene-2,2'-indolin]-6-yl)allyl)oxy)-6-(hydroxymethyl)tetra hydro-2*H*-pyran-3,4,5-triol (117)



102 **117**

According to **GP18**, 0.10 g (0.13 mmol, 1.00 eq.) of spiropyran **102** were deprotected with 0.03 mL (0.13 mmol, 1.00 eq.) of NaOMe (5.4 M in MeOH) in 0.5 mL MeOH. After purification, 0.08 g (0.13 mmol, >99%) of the desired product **117** were obtained as a blue solid.



M($C_{36}H_{49}NO_8$) 623.79 g/mol.

^{1}H-NMR (400 MHz, MeOD-*d_4*) δ [ppm] = 6.95 - 6.89 (m, 4H, H-9, H-10, H--23, H-18), 6.88 (d, $^4J_{HH}$ = 1.7 Hz, 1H, H-21), 6.83 (d, $^4J_{HH}$ = 1.9 Hz, 1H, H-13), 6.44 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H-19), 4.52 (ddd, $^{2,3,4}J_{HH}$ = 12.5, 5.9, 1.6 Hz, 1H, H-29), 4.38 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H-27), 4.35 - 4.29 (m, 1H, H-29‘), 3.93 - 3.88 (m, 1H, H-35), 3.70 (s, 3H, H-26), 3.66 -3.67 (m, 1H, H-35‘), 3.39 - 3.36 (m, 1H, H-31), 3.30 – 3.22 (m, 2H, H-28, H-33), 2.71 (s, 3H, H-14), 2.56 (t, $^3J_{HH}$ = 7.7 Hz, 2H, H-7), 1.61 - 1.60 (m, 2H, H-6), 1.33 - 1.31 (m, 8H, H-5, H-4, H-3, H-2), 1.28 (s, 3H, H-17), 1.15 (s, 3H, H-17‘), 0.93 - 0.91 (m, 3H, H-1).

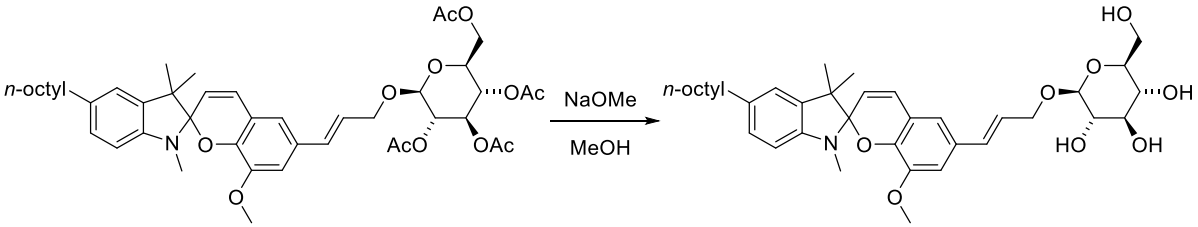
^{13}C-NMR (101 MHz, MeOD-*d_4*) δ [ppm] = 148.2 (C-25), 147.1 (C-8), 146.8 (C-24), 146.2 (C-11), 133.4 (C-20), 128.9 (C-23), 128.3 (C-22), 126.7 (C-9), 121.1 (C-21), 117.7 (C-13), 112.7 (C-10), 111.35 (C-18), 110.8 (C-10), 106.2 (C-19), 101.7 (C-27), 76.7 (C-32), 76.6 (C-31), 73.7 (C-33), 73.5 (C-28), 70.3 (C-30), 69.5 (C-29), 61.4 (C-35), 55.5 (C-26), 51.4 (C-16), 47.8 (C-34), 35.2 (C-7), 31.8 (C-6), 31.6 (C-5), 29.0 (C-4), 29.0 (C-3), 27.8 (C-14), 22.3 (C-2), 19.0 (C-17), 19.0 (C-17‘), 13.0 (C-1).

FT-IR ATR, v [cm^{-1}] = 3365 (m), 2956 (m), 2924 (s), 2854 (m), 2116 (w), 2077 (w), 2007 (w), 1972 (w), 1714 (w), 1618 (m), 1599 (m), 1579 (m), 1492 (s), 1465 (s), 1421 (m), 1379 (m), 1360 (s), 1291 (m), 1252 (s), 1188 (m), 1158 (m), 1123 (s), 1101 (s), 1075 (s), 1043 (s), 1018 (s), 959 (m), 885 (m), 805 (m), 755 (w), 721 (w), 645 (m), 630 (m), 613 (m), 597 (m), 585 (m), 564 (m), 552 (m), 538 (m), 518 (m), 505 (m).

HR-MS (ESI) Calcd. $[M+H]^+$: 624.3530, found: 624.3525.

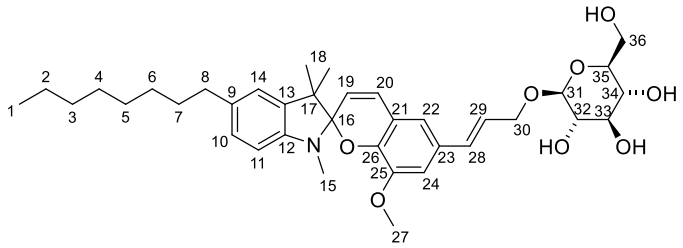
Calcd. $[M+Na]^+$: 646.3350, found: 646.3352.

11.2.6.14 Synthesis of (2*S*,3*R*,4*R*,5*S*,6*S*)-2-(hydroxymethyl)-6-(((*E*)-3-(8-methoxy-1',3',3'-trimethyl-5'-octylspiro[chromene-2,2'-indolin]-6-yl)allyl)oxy)tetrahydro-2*H*-pyran-3,4,5-triol (118)



103 **118**

According to **GP18**, 0.10 g (0.13 mmol, 1.00 eq.) of spiropyran **103** were deprotected with 0.03 mL (0.13 mmol, 1.00 eq.) of NaOMe (5.4 M in MeOH) in 0.5 mL MeOH. After purification, 80.0 mg (0.12 mmol, 92%) of the desired product **118** were obtained as a blue solid.



M($C_{37}H_{51}NO_8$) 637.81 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 6.96 – 6.89 (m, 4H, H-10, H-11, H-19, H-24), 6.88 (d, $^4J_{HH}$ = 1.7 Hz, 1H, H-14), 6.83 (d, $^4J_{HH}$ = 1.9 Hz, 1H, H-22), 6.59 (d, $^3J_{HH}$ = 16.0 Hz, 1H, H-28), 6.44 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H-20), 6.24 (dt, $^{3,3}J_{HH}$ = 15.9, 6.3 Hz, 1H, H-29), 4.57 – 4.48 (m, 1H, H-30), 4.38 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H-28), 4.32 (dd, $^{2,3}J_{HH}$ = 12.6, 6.7 Hz, 2H, H-30), 3.96 – 3.81 (m, 1H, H-36), 3.70 (s, 3H, H-27), 3.70 – 3.66 (m, 1H, H-36‘), 3.40 – 3.35 (m, 2H, H-34, H-25), 3.30 – 3.21 (m, 2H, H-32, H-33), 2.71 (s, 3H, H-24), 2.58 – 2.53 (m, 2H, H-8), 1.64 – 1.59 (m, 2H, H-7), 1.38 – 1.31 (m, 10H, H-6, H-5, H-4, H-3, H-2), 1.28 (s, 3H, H-18), 1.15 (s, 3H, H-18‘), 0.92 (t, $^3J_{HH}$ = 6.6 Hz, 3H, H-1).

^{13}C-NMR (101 MHz, $CDCl_3$) δ [ppm] = 146.8 (C-25), 146.2 (C-12), 143.6 (C-26), 136.6 (C-21), 133.4 (C-13), 132.3 (C-28), 128.8 (C-24), 126.7 (C-10), 123.0 (C-29), 121.1 (C-14), 120.8 (C-19), 119.5 (C-9), 117.6 (C-22), 111.2 (C-11), 106.2 (C-20), 104.7 (C-16), 101.7 (C-31), 76.7 (C-34), 76.6 (C-35), 73.7 (C-33), 70.3 (C-30, C-32), 69.5 (C-23), 61.4 (C-36), 55.4 (C-27), 51.4 (C-17), 35.3

(C-8), 31.9 (C-7), 31.6 (C-5), 29.0 (C-6), 28.9 (C-4), 27.8 (C-15), 22.3 (C-3, C-2), 19.0 (C-18), 13.0 (C-1).

FT-IR ATR, v [cm^{-1}] = 3365 (m), 2957 (m), 2925 (s), 2854 (s), 2132 (w), 1999 (w), 1959 (w), 1639 (m), 1617 (m), 1579 (m), 1491 (s), 1466 (s), 1421 (m), 1360 (m), 1293 (m), 1254 (m), 1187 (w), 1157 (m), 1101 (s), 1076 (s), 1044 (s), 1019 (s), 962 (m), 881 (w), 805 (w), 755 (w), 719 (w), 659 (w), 651 (w), 609 (w), 574 (w).

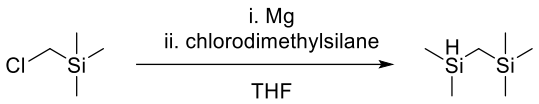
HR-MS Calcd. $[M+H]^+$: 638.3687, found: 638.3682.
Calcd. $[M+Na]^+$: 660.3506, found: 660.3504.

Part 2: Novel fluorescent silicon-based surfactants

11.3 Synthesis of fluorescent carbosilane surfactants

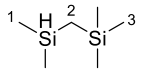
11.3.1 Synthesis of carbosilane chains

11.3.1.1 Synthesis of ((dimethylsilyl)methyl)trimethylsilane (150a)



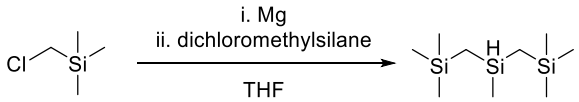
143 **150a**

2.58 g (106 mmol, 1.60 eq.) of Mg were suspended in 60 mL THF. A solution of 11.4 mL (81.7 mmol, 1.25 eq.) silane **143** in 20 mL THF were added dropwise. After complete addition and initiation of the reaction the mixture was heated to 80 °C for 2 h. At rt, 7.30 mL (65.4 mmol, 1.00 eq.) of chlorodimethylsilane were added and the reaction mixture was stirred at 80 °C for further 14.5 h. The mixture was cooled to rt and quenched with H_2O. The layers were separated and the aq. phase was extracted with MTBE. The combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. 5.61 g (38.3 mmol, 59%, Lit.[171, 186],[186]:89 – 91%) of the desired product **150a** was obtained as colorless oil.



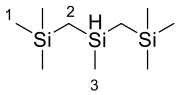
M($C_6H_{18}Si_2$)	146.38 g/mol.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 3.94 (m, 1H, SiH), 0.07 (s, 3H, H-1), 0.06 (s, 3H, H-1'), 0.00 (s, 9H, H-3), -0.27 (d, $^3J_{HH}$ = 3.8 Hz, 2H, H-2).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 1.4 (C-2), 0.7 (C-3), -1.5 (C-1).
FT-IR	ATR, v [cm^{-1}] = 2955 (m), 2900 (w), 2868 (w), 2108 (m), 1750 (m), 1420 (w), 1375 (w), 1305 (w), 1250 (s), 1045 (s), 999 (w), 869 (s), 829 (s), 785 (m), 774 (m), 756 (w), 733 (w), 690 (m), 626 (m), 560 (w).

11.3.1.2 Synthesis of ((methylsilanediyl)bis(methylene))bis(trimethylsilane) (150b)



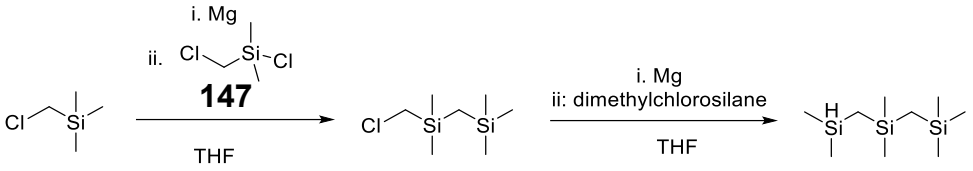
143 **150b**

2.58 g (106 mmol, 3.25 eq.) of Mg were suspended in 60 mL THF. A solution of 11.4 mL (81.7 mmol, 2.50 eq.) silane **143** in 20 mL THF were added dropwise. After complete addition and initiation of the reaction, the mixture was heated to 80 °C for 2 h. At rt, 3.42 mL (65.4 mmol, 1.00 eq.) of dichloromethylsilane were added and the reaction mixture was stirred at 80 °C for further 6.5 h. The mixture was cooled to rt and quenched with H_2O. The layers were separated and the aq. phase was extracted with MTBE. The combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. 7.10 g (32.5 mmol, 99%, Lit.[172]: 100%), of the desired product **150b** was obtained as colorless oil.



M($C_9H_{26}Si_3$)	218.56 g/mol.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 4.00 – 3.92 (m, 1H, SiH), 0.04 (s, 4H, H-2), 0.00 (s, 18H, H-1), -0.26 (dd, $^{3,4}J_{HH}$ = 8.0, 3.8 Hz, 3H, H-3).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 2.5 (C-2), 0.8 (C-1), -3.5 (C-3).
^{29}Si-NMR	(69 MHz, $CDCl_3$) δ [ppm] = 0.4, -16.9.
FT-IR	ATR, v [cm^{-1}] = 2954 (w), 2900 (w), 2869 (w), 2103 (w), 1935 (w), 1420 (w), 1356 (w), 1248 (m), 1041 (m), 889 (m), 828 (s), 791 (m), 779 (m), 769 (s), 730 (w), 707 (w), 687 (m), 650 (w), 629 (w), 605 (w), 570 (w).

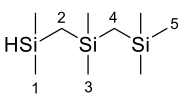
11.3.1.3 Synthesis of ((dimethylsilyl)methyl)dimethyl((trimethylsilyl)methyl) silane (150c)



143 **148** **150c**

2.58 g (106 mmol, 1.40 eq.) of Mg were suspended in 60 mL THF. A solution of 11.4 mL (81.7 mmol, 1.10 eq.) silane **143** in 20 mL THF were added dropwise. After complete addition and initiation of the reaction, the mixture was heated to 80 °C for 2 h. At rt, 9.82 mL (74.3 mmol, 1.00 eq.) of chlorosilane **147** were added and the reaction mixture was stirred at 80 °C for further 6.5 h. The mixture was cooled to rt and quenched with H_2O. The layers were separated and the aq. phase was extracted with MTBE. The combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. 12.5 g (64.0 mmol, 86%) of the desired product **148** was obtained as colorless oil.

1.79 g (73.6 mmol, 1.15 eq.) of Mg were suspended in 80 mL THF and 12.5 g (64.0 mmol, 1.00 eq.) of chlorosilane **148** were added dropwise. After complete addition and initiation of the reaction, the mixture was heated to 80 °C for 5 h. At rt, 7.12 mL (64.0 mmol, 1.00 eq.) of dimethylchlorosilane were added and the reaction mixture was stirred at 80 °C for further 15.5 h. The mixture was cooled to rt and quenched with H_2O. The layers were separated and the aq. phase was extracted with MTBE. The combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, 100% *c*Hex) to afford 8.75 g (40.0 mmol, 63%, Lit.[173],[187]: 72 – 80%) of the desired product **150c** as colorless oil.

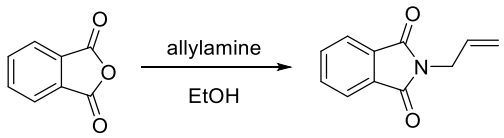


M($C_9H_{26}Si_3$)	218.56 g/mol.
R_f	(SiO_2, 100% cHex) = 0.76.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 3.99 (dp, $^{3,4}J_{HH}$ = 7.4, 3.7 Hz, 1H, SiH), 0.12 (s, 3H, H-1), 0.11 (s, 3H, H-1), 0.08 (s, 6H, H-3), 0.04 (s, 12H, H-5), -0.21 (m, 4H, H-2, H-4).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 5.1 (C-4), 2.8 (C-2), 1.8 (C-3), 1.3 (C-1), -1.4 (C-5).

^{29}Si-NMR (69 MHz, $CDCl_3$) δ [ppm] = 0.8, 0.1, -16.6.

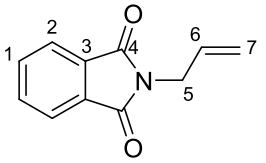
FT-IR ATR, v [cm^{-1}] = 3725 (w), 2954 (w), 2898 (w), 2862 (w), 2109 (m), 1932 (w), 1595 (w), 1355 (w), 1249 (s) 1052 (s), 890 (s), 860 (m), 826 (s), 763 (s), 684 (s), 659 (w), 630 (w), 589 (w), 540 (w).

11.3.1.4 Synthesis of 2-allylisoindoline-1,3-dione (156b)



160 **156b**

5.00 g (33.8 mmol, 1.10 eq.) of phthalic anhydride (**160**) were dissolved in 50 mL EtOH, 3.00 mL (40.5 mmol, 1.10 eq.) of allylamine were added and the reaction mixture was stirred at 80 °C for 48 h. The reaction mixture was cooled to rt and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) to afford 9.95 g (53.1 mmol, 78%) of the desired product **156b** as a colorless solid.



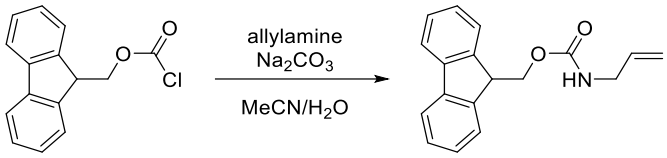
M($C_{11}H_9NO_2$) 187.20 g/mol.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.86 (dd, $^{3,4}J_{HH}$ = 5.4, 3.0 Hz, 2H, H-2), 7.72 (dd, $^{3,4}J_{HH}$ = 5.4, 3.0 Hz, 2H, H-1), 5.89 (m, 1H, H-6), 5.35-4.94 (m, 2H, H-7), 4.30 (m, 2H, H-5).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 167.9 (C-4), 133.9 (C-1), 132.1 (C-3), 131.5 (C-6), 123.1 (C-2), 117.8 (C-7), 40.0 (C-5).

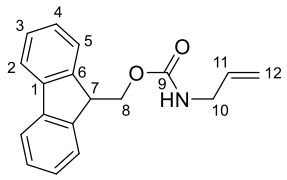
FT-IR ATR, v [cm^{-1}] = 3456 (w), 3086 (w), 2949 (w), 2921 (w), 1768 (w), 1481 (w), 1467 (w), 1355 (m), 1322 (m), 1171 (w), 971 (w), 946 (s), 894 (m), 847 (m), 724 (s), 707 (s), 695 (m), 649 (m), 553 (w).

11.3.1.5 Synthesis of (9*H*-fluoren-9-yl)methyl allylcarbamate (156a)



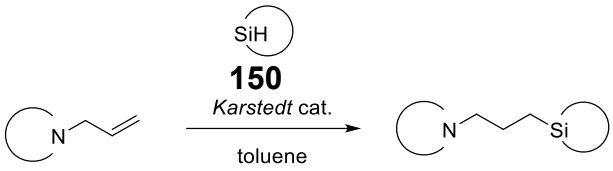
172 **156a**

0.30 mL (4.00 mmol, 1.00 eq.) of allylamine and 1.00 g (4.00 mmol, 1.00 eq.) of Fmoc (**172**) were dissolved in 10 mL MeCN/H_2O (1:1). 0.71 g (6.66 mmol, 1.70 eq.) Na_2CO_3 were added and the reaction mixture was stirred for 15 min at rt. MeCN was removed under reduced pressure and the aq. phase was acidified with conc. HCl to pH 4 - 5 and extracted with EtOAc. The combined org. layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. 1.01 g (3.84 mmol, 98%) of the desired product **156a** was obtained as colorless solid.



M($C_{18}H_{17}NO_2$)	279.33 g/mol.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.80 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H-5), 7.64 - 7.60 (m, 2H, H-3), 7.46 - 7.40 (m, 2H, H-4), 7.34 (td, $^{3,4}J_{HH}$ = 7.5, 1.2 Hz, 2H, H-2), 5.88 (m, 1H, H-11), 5.21 (dd, $^{2,3}J_{HH}$ = 17.1, 2.1 Hz, 1H, H-12), 5.16 (dd, $^{2,3}J_{HH}$ = 10.2, 1.5 Hz, 1H, H-12‘), 4.87 (s, 1H, NH), 4.46 (d, $^3J_{HH}$ = 6.9 Hz, 2H, H-8), 4.26 (t, $^3J_{HH}$ = 7.0 Hz, 1H, H-7), 3.86 (t, $^3J_{HH}$ = 4.8 Hz, 2H, H-10).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 156.4 (C-9), 144.1 (C-6), 141.5 (C-5), 134.5 (C-11), 127.8 (C-3), 127.2 (C-2), 125.2 (C-1), 120.1 (C-4), 116.3 (C-12), 66.8 (C-8), 47.4 (C-7), 43.6 (C-10).
FT-IR	ATR, v [cm^{-1}] = 3319 (m), 2942 (w), 1751 (w), 1693 (s), 1645 (w), 1536 (s), 1478 (w), 1464 (w), 1446 (m), 1343 (w), 1256 (s), 1142 (m), 1103 (w), 1082 (w), 1033 (m), 989 (m), 921 (m), 865 (w), 779 (w), 758 (m), 741 (s), 733 (s), 675 (w), 641 (m), 622 (w), 587 (w), 564 (w), 521 (w), 505 (w).
HR-MS (ESI)	Calcd. $[M+H]^+$: 280.1337, found: 280.1336. Calcd. $[M+Na]^+$: 302.1157, found: 302.1155.

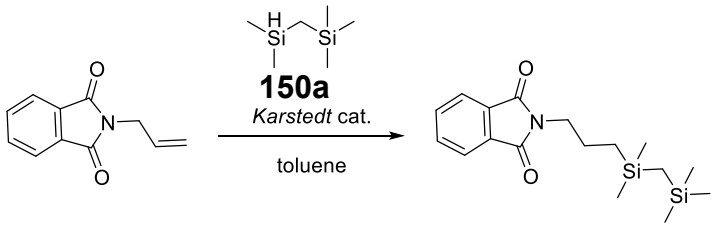
11.3.1.6 Hydrosilylation: General protocol (GP13)



156 **158/154**

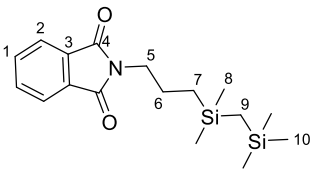
Allyl compound **153** (1.00 eq.) and silane **150** (1.00 eq.) were dissolved in toluene and heated to 80 °C. 100 ppm of *Karstedt* cat. (Platinum-divinyltetramethyldisiloxane complex in xylene, 2.10 - 2.40% Pt) were added and stirred at 80 °C. The mixture was cooled to rt, the solvent was removed under reduced pressure and the residue was dissolved in $CHCl_3$. $MgSO_4$ and activated carbon were added, the mixture was stirred for 5 - 15 min and filtered over a pad of $MgSO_4$. The solvent was removed under reduced pressure.

11.3.1.6.1 Synthesis of 2-(3-(dimethyl((trimethylsilyl)methyl)silyl)propyl)iso indoline-1,3-dione (158a)



156b **158a**

According to **GP13**, 3.50 g (18.7 mmol, 1.00 eq.) of phthalimide **156b** were reacted with 3.28 g (22.4 mmol, 1.20 eq.) of silane **150a** and 98 µL *Karstedt* cat. in 98 µL toluene. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 20:1) to afford 1.23 g (3.70 mmol, 20%) of the desired product **158a** as a colorless oil.



M($C_{17}H_{27}NO_2Si_2$)	333.58 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 20:1) = 0.21.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.84 (dd, $^{3,4}J_{HH}$ = 5.4, 3.0 Hz, 2H, H-2), 7.71 (dd, $^{3,4}J_{HH}$ = 5.4, 3.0 Hz, 2H, H-1), 3.66 (t, $^{3}J_{HH}$ =

7.4 Hz, 2H, H-5), 1.68 – 1.61 (m, 2H, H-6), 0.55 - 0.49 (m, 2H, H-7), -0.00 (s, 15H, H-8, H-10), -0.30 (s, 2H, H-9).

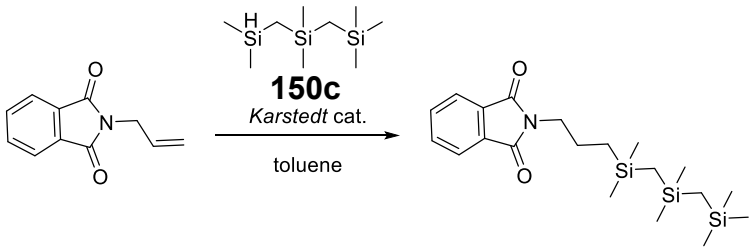
^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 168.5 (C-4), 133.8 (C-2), 132.2 (C-3), 123.1 (C-1), 41.1 (C-5), 23.3 (C-6), 15.0 (C-7), 2.4 (C-9), 1.3 (C-10), -0.7 (C-8).

FT-IR ATR, ν [cm^{-1}] = 3355 (w), 2951 (m), 2894 (m), 1773 (m), 1713 (s), 1612 (m), 1524 (m), 1467 (m), 1450 (m), 1437 (m), 1395 (s), 1361 (m), 1309 (m), 1249 (s), 1188 (m), 1134 (m), 1051 (s), 970 (m), 917 (w), 836 (s), 792 (m), 759 (m), 740 (m), 718 (s), 688 (m), 621 (m), 591 (m), 559 (m), 530 (m).

HR-MS (ESI) Calcd. $[M+Na]^+$: 356.1472, found: 356.1475.

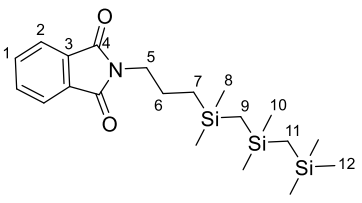
GC-MS m/z (%) = 333 (33), 318 (100), 304 (84), 276 (9), 246 (54), 204 (7), 172 (9), 160 (40), 145 (85), 130 (66), 115 (20), 73 (62), 59 (15).

11.3.1.6.2 Synthesis of 2-(3-(((dimethyl((trimethylsilyl)methyl)silyl)methyl) dimethylsilyl)propyl)isoindoline-1,3-dione (158b)



156b **158b**

According to **GP13**, 3.50 g (18.7 mmol, 1.00 eq.) of phthalimide **156b** were reacted with 4.90 g (22.4 mmol, 1.20 eq.) of silane **150c** and 98 µL *Karstedt* cat. in 98 mL toluene. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 20:1) to afford 6.44 g (15.9 mmol, 85%) of the desired product **158b** as a colorless oil.



M($C_{20}H_{35}NO_2Si_3$) 405.76 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 20:1) = 0.27.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.84 (dd, $^{3,4}J_{HH}$ = 5.4, 3.1 Hz, 2H, H-2), 7.70 (dd, $^{3,4}J_{HH}$ = 5.5, 3.0 Hz, 2H, H-1), 3.65 (t, $^{3}J_{HH}$ =

7.4 Hz, 2H, H-5), 1.65 - 1.63 (m, 2H, H-6), 0.58 - 0.45 (m, 2H, H-7), 0.02 (m, 6H, H-8), -0.00 (s, 9H, H-12), -0.00 (s, 6H, H-10), -0.29 (m, 4H, H-9, H-11).

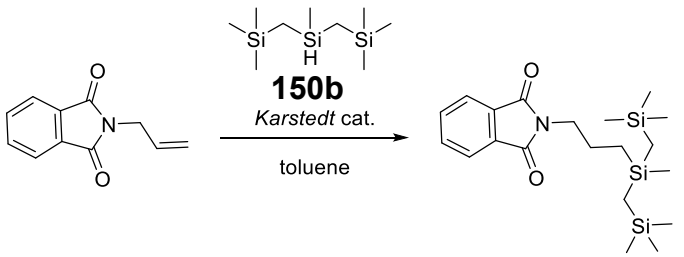
^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 168.5 (C-4), 133.8 (C-2), 132.2 (C-3), 123.1 (C-1), 41.1 (C-5), 23.3 (C-6), 15.1 (C-7), 5.7 (C-9), 3.9 (C-11), 2.4 (C-8), 1.4 (C-12), -0.6 (C-10).

GC-MS m/z (%) = 405 (28), 390 (100), 376 (17), 318 (47), 246 (93), 217 (19), 201 (52), 187 (22), 172 (11), 160 (40), 145 (26), 129 (82), 102 (12), 73 (90), 59 (16).

FT-IR ATR, v [cm^{-1}] = 3676 (w), 3473 (w), 3061 (w), 2952 (w), 2897 (w), 2476 (w), 1923 (w), 1839 (w), 1774 (w), 1713 (s), 1616 (w), 1468 (w), 1456 (w), 1436 (w), 1393 (m), 1360 (m), 1336 (w), 1310 (w), 1248 (m), 1217 (w), 1188 (w), 1171 (w), 1050 (m), 1014 (w), 998 (w), 969 (w), 861 (m), 829 (s), 808 (s), 759 (m), 715 (s), 686 (m), 626 (w), 603 (w), 571 (w), 529 (m).

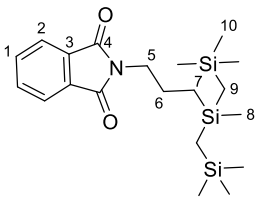
HR-MS (ESI) Calcd. $[M+M]^+$: 406.2048, found: 406.2052.
Calcd. $[M+Na]^+$: 428.1867, found: 428.1873.

11.3.1.6.3 Synthesis of 2-(3-(methylbis((trimethylsilyl)methyl)silyl)propyl)iso indoline-1,3-dione (158c)



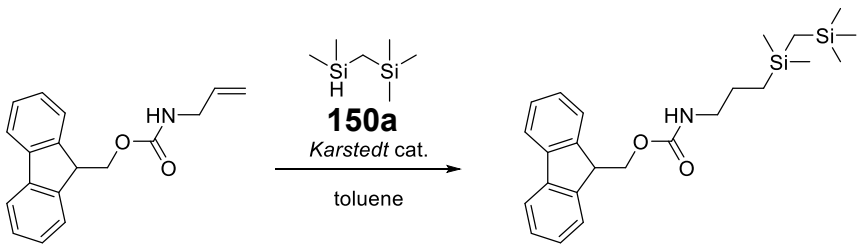
156b **158c**

According to **GP13**, 2.00 g (10.7 mmol, 1.00 eq.) of phthalimide **156b** were reacted with 2.80 g (12.8 mmol, 1.20 eq.) of silane **150b** and 50 µL *Karstedt* cat. in 25 mL toluene. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 20:1) to afford 3.30 g (8.13 mmol, 76%) of the desired product **158c** as a colorless oil.



M($C_{20}H_{35}NO_2Si_3$)	405.76 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 10:1) = 0.41.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.86 - 7.81 (m, 2H, H-2), 7.74 - 7.69 (m, 2H, H-1), 3.66 (t, $^3J_{HH}$ =7.4 Hz, 2H, H-5), 1.71 - 1.59 (m, 2H, H-6), 0.59 - 0.48 (m, 2H, H-7), 0.03 - 0.02 (m, 18H, H-10), 0.01 (s, 3H, H-8), -0.27 (m, 4H, H-9).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 168.4 (C-4), 133.8 (C-1), 132.1 (C-3), 123.1 (C-2), 41.0 (C-5), 23.3 (C-6), 15.1 (C-7), 3.4 (C-9), 1.5 (C-10), -0.61 (C-8).
FT-IR	ATR, v [cm^{-1}] = 3676 (w), 3424 (w), 2952 (w), 2899 (w), 2156 (w), 1774 (w), 1713 (s), 1664 (w), 1616 (w), 1591 (w),1468 (w), 1436 (w), 1393 (m), 1360 (m), 1310 (w), 1248 (m),1218 (w), 1188 (w), 1171 (w), 1052 (s), 1015 (w), 998 (w), 968 (w),829 (s), 797 (s), 761 (m), 715 (s), 686 (m), 647 (w), 625 (w), 604 (w), 573 (w), 529 (m).
HR-MS (ESI)	Calcd.: $[M+H]^+$: 406.2048, found: 406.2051. Calcd.: $[M+Na]^+$: 428.1868, found: 428.1870.
GC-MS	m/z (%) = 405 (64), 390 (100), 376 (27), 355 (12), 318 (41), 281 (8), 246 (8), 201 (37), 187 (13), 160 (24), 129 (68), 115 (7), 73 (90), 59 (11).

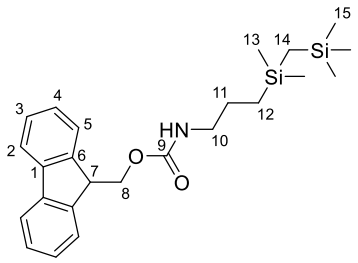
11.3.1.6.4 Synthesis of (9*H*-fluoren-9-yl)methyl(3-(dimethyl((trimethylsilyl) methyl) silyl)propyl)carbamate (157a)



156a **157a**

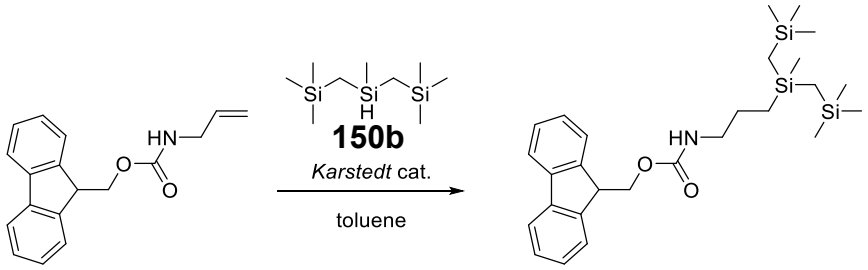
According to **GP13**, 1.00 g (3.57 mmol, 1.00 eq.) of allyl carbamate **156a** were reacted with 0.64 g (4.34 mmol, 1.22 eq.) of silane **150a** and 50 µL *Karstedt* cat. in 30 mL toluene. The crude product was purified by column chromatography (SiO_2,

*c*Hex/EtOAc 6:1) to afford 0.46 g (1.06 mmol, 30%) of the desired product **157a** as a colorless oil.



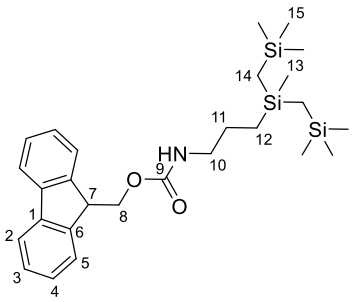
M($C_{24}H_{35}NO_2Si_2$)	435.72 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 5:1) = 0.46.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 7.77 (d, $^3J_{HH}$ = 7.5 Hz, 2H, H-5), 7.60 (d, $^3J_{HH}$ = 7.5 Hz, 2H, H-2), 7.43 - 7.38 (m, 2H, H-3), 7.32 (t, $^3J_{HH}$ = 7.4 Hz, 2H, H-4), 4.81 (s, 1H, *N*H), 4.40 (d, $^3J_{HH}$ = 6.9 Hz, 2H, H-8), 4.25 - 4.20 (m, 1H, H-7), 3.21 - 3.14 (m, 2H, H-10), 1.53 - 1.46 (m, 2H, H-11), 0.56 - 0.45 (m, 2H, H-12), 0.03 (s, 9H, H-15), 0.02 (s, 6H, H-13), -0.28 (s, 2H, H-14).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 156.2 (C-9), 144.2 (C-6), 141.5 (C-1), 127.8 (C-3), 127.2 (C-2), 125.2 (C-5), 120.1 (C-4), 66.7 (C-8), 47.5 (C-7), 44.5 (C-10), 27.1 (C-11), 24.9 (C-12), 15.1 (C-14), 1.6 (C-15), -0.5 (C-13).

11.3.1.6.5 Synthesis of (9*H*-fluoren-9-yl)methyl (3-(methylbis((trimethylsilyl) methyl)silyl)propyl)carbamate (157b)



156a **157b**

According to **GP13**, 1.00 g (3.80 mmol, 1.00 eq.) of allyl carbamate **156a** were reacted with 1.00 g (4.58 mmol, 1.20 eq.) of silane **150b** and 20 µL *Karstedt* cat. in 15 mL toluene. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) to afford 1.03 g (2.11 mmol, 56%) of the desired product **157b** as a colorless oil.



M($C_{27}H_{43}NO_2Si_3$) 497.89 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 2:1) = 0.70.

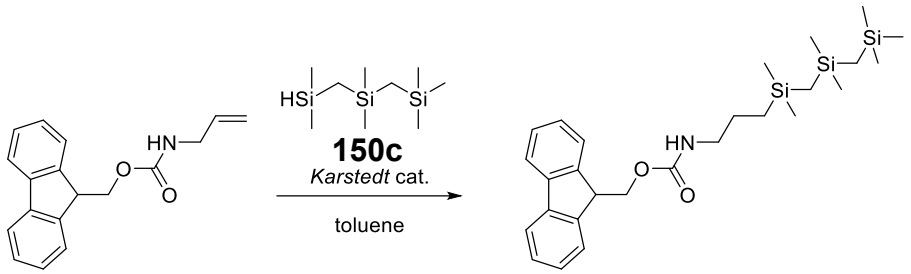
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.77 (d, $^3J_{HH}$ = 7.5 Hz, 2H, H-5), 7.60 (d, $^3J_{HH}$ = 7.5 Hz, 2H, H-2), 7.40 (t, $^3J_{HH}$ = 7.5 Hz, 2H, H-3), 7.32 (t, $^3J_{HH}$ = 7.4 Hz, 2H, H-4), 4.81 (s, 1H, *N*H), 4.40 (d, $^3J_{HH}$ = 6.9 Hz, 2H, H-8), 4.29 - 4.17 (m, 1H, H-7), 3.17 (s, 2H, H-10), 1.56 - 1.39 (m, 2H, H-11), 0.56 - 0.39 (m, 2H, H-12), 0.03 - 0.05 (m, 18H, H-15), 0.02 - 0.03 (m, 3H, H-13), -0.25 (s, 4H, H-14).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 156.4 (C-9), 144.0 (C-6), 141.3 (C-1), 127.6 (C-3), 127.0 (C-2), 125.0 (C-5), 119.9 (C-4), 66.5 (C-8), 47.3 (C-7), 44.3 (C-10), 24.8 (C-11), 15.6 (C-12), 3.5 (C-14), 1.5 (C-15), 0.5 (C-13).

FT-IR ATR, v [cm^{-1}] = 3336 (w), 3066 (w), 2953 (w), 1915 (w), 1689 (m), 1611 (w), 1541 (m), 1478 (w), 1464 (w), 1450 (w), 1355 (w), 1304 (w), 1279 (m), 1247 (s), 1166 (w), 1148 (w), 1054 (m), 1003 (w), 988 (w), 946 (w), 829 (s), 812 (s), 796 (s), 757 (s), 732 (s), 686 (m), 645 (m), 621 (m), 588 (w), 539 (w), 508 (w).

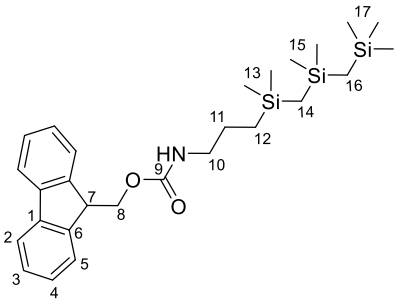
HR-MS (ESI) Calcd.: $[M+H]^+$: 498.2674, found: 498.2677.
Calcd.: $[M+Na]^+$: 520.2494, found: 520.2496.

11.3.1.6.6 Synthesis of ((9*H*-fluoren-9-yl)methyl(3-(((dimethyl((trimethylsilyl) methyl)silyl)methyl)dimethylsilyl)propyl)carbamate (157c)



156a **157c**

According to **GP13**, 1.93 g (6.89 mmol, 1.00 eq.) of allyl carbamate **156a** were reacted with 1.51 g (6.90 mmol, 1.00 eq.) of silane **150c** and 20 µL *Karstedt* cat. in 15 mL toluene. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) to afford 1.89 g (3.79 mmol, 55%) of the desired product **157c** as a colorless oil.



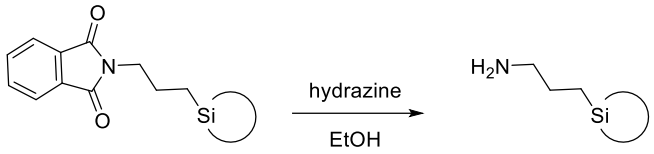
M($C_{27}H_{43}NO_2Si_3$) 497.90 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 5:1) = 0.58.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.77 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H-5), 7.60 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H-2), 7.43 - 7.38 (m, 2H, H-3), 7.32 (t, $^3J_{HH}$ = 7.4 Hz, 2H, H-4), 4.83 - 4.76 (m, 1H, *N*H), 4.40 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H-8), 4.25 - 4.20 (m, 1H, H-7), 3.18 - 3.17 (m, 2H, H-10), 1.56 - 1.39 (m, 2H, H-11), 0.51 - 0.45 (m, 2H, H-12), 0.06 - 0.05 (m, 9H, H-17), 0.02 - 0.03 (m, 12H, H-13, H-15), -0.25 (s, 2H, H-14), -0.26 (s, 2H, H-16).

11.3.1.7 Deprotection of amine function

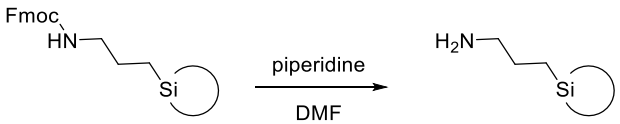
Route 1: Hydrazinolysis: General protocol (GP14)



158 **159**

Phthalimide **158** (1.00 eq.) was dissolved in EtOH. Hydrazine monohydrate (64%) (10.0 eq.) was added and the reaction mixture was stirred at 80 °C. The precipitate was filtered off, washed with EtOH and dried under reduced pressure. The solid was suspended in EtOAc, acidified with conc. HCl to pH 6 and washed with H_2O. The layers were separated and the org. phase was washed with aq. NaOH (2 M). The org. layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure.

Route 2: Fmoc cleavage: General protocol (GP15)

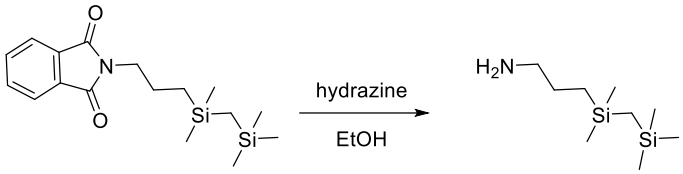


158 **159**

Carbosilane **158** (1.00 eq.) was dissolved in DMF, piperidine (10.0 - 12.0 eq.) was added and the reaction mixture was stirred at rt. The solvent was removed under reduced pressure, the residue was dissolved in EtOAc and washed with sat. aq. $NaHCO_3$. The aq. phase was extracted with EtOAc and the combined org. layers were dried over $MgSO_4$. The solvent was removed under reduced pressure.

11.3.1.7.1 Synthesis of 3-(dimethyl((trimethylsilyl)methyl)silyl)propan-1-amine (159b)

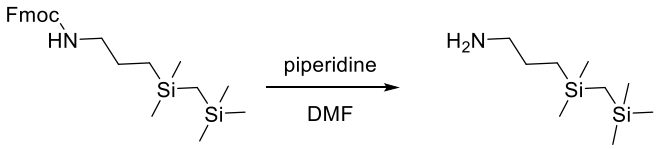
Route 1:



158a **159b**

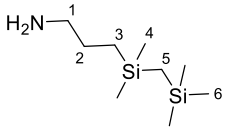
According to **GP14**, 1.23 g (3.70 mmol, 1.00 eq.) of phthalimide **158a** were reacted with 2.89 g (37.0 mmol, 10.0 eq.) of hydrazine monohydrate (64%) in 12 mL EtOH for 4 h. 0.46 g (2.25 mmol, 61%) of the desired product **159b** could be obtained as colorless oil.

Route 2:



157a **159b**

According to **GP15** 0.44 g (1.03 mmol, 1.00 eq.) of carbosilane **157a** were deprotected with 1.00 mL (10.1 mmol, 10.0 eq.) of piperidine. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 3:1 + 5% Et_3N) to afford 0.21 g (1.02 mmol, 99%) of the desired product **159b** as colorless oil.



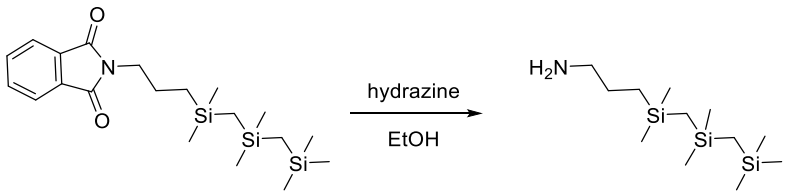
M($C_9H_{25}NSi_2$)	203.48 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 3:1 + 5% Et_3N) = 0.07.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 2.67 - 2.64 (m, 2H, H-1), 2.04 (br s, 2H, NH_2), 1.99 – 1.93 (m, 2H, H-2), 0.49 - 0.43 (m, 2H, H-3), 0.02 - 0.00 (m, 15H, H-4, H-6), -0.29 (s, 2H, H-5).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 45.7 (C-1), 28.3 (C-2), 15.1 (C-3), 2.7 (C-4), 1.5 (C-5), -0.5 (C-6).
^{29}Si-NMR	(60 MHz, $CDCl_3$) δ [ppm] = 31.39, 0.40.
FT-IR	ATR, v [cm^{-1}] = 2951 (w), 2925 (w), 2896 (w), 2859 (w), 1744 (w), 1652 (m), 1557 (m), 1435 (m), 1375 (m), 1302 (w), 1250 (s), 1178

(w), 1051 (s), 831 (s), 762 (m), 681 (m), 617 (w), 589 (w), 554 (w).

HR-MS (EI) Calcd. $[M-H]^+$: 202.1441, found: 202.1438.

11.3.1.7.2 Synthesis of 3-(((dimethyl((trimethylsilyl)methyl)silyl)methyl) dimethyl silyl)propan-1-amine (159c)

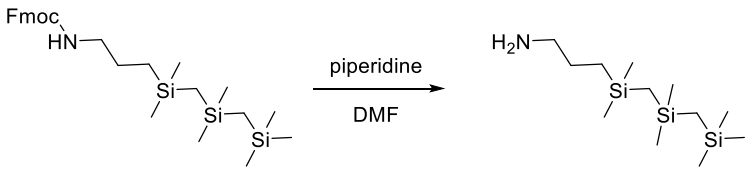
Route 1:



158b **159c**

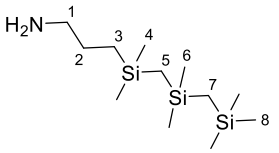
According to **GP14**, 6.44 g (16.0 mmol, 1.00 eq.) of phthalimide **158b** were reacted with 12.5 g (160 mmol, 10.0 eq.) of hydrazine monohydrate (64%) in 50 mL EtOH for 5.5 h. 4.10 g (14.9 mmol, 93%) of the desired product **159c** could be obtained as colorless oil.

Route 2:



157c **159c**

According to **GP15**, 1.80 g (1.37 mmol, 1.00 eq.) of carbosilane **157c** were deprotected with 1.36 mL (13.7 mmol, 10.0 eq.) of piperidine. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 3:1 + 5% Et_3N) to afford 0.98 g (3.57 mmol, 99%) of the desired product **159b** as colorless oil.



M($C_{12}H_{33}NSi_3$) 275.65 g/mol.

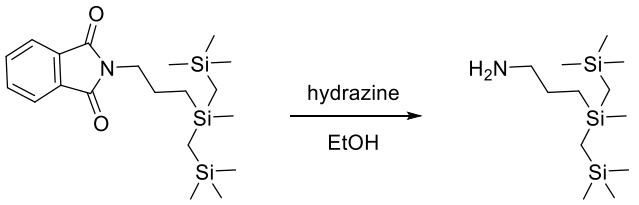
R_f (SiO_2, CH_2Cl_2/MeOH 10:1) = 0.15.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 2.75 (t, $^3J_{HH}$ = 7.1 Hz, 2H, H-1), 2.62 (br s, 2H, NH_2), 1.55 – 1.47 (m, 2H, H-2), 0.53 – 0.46 (m, 2H,

	H-3), 0.05 (d, $^3J_{HH}$ = 1.8 Hz, 6H, H-4), 0.03 – -0.00 (m, 15H, H-6, H-8), -0.27 (m, 4H, H-5, H-7).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 44.6 (C-1), 26.4 (C-2), 15.0 (C-3), 5.7 (C-7), 3.9 (C-5), 2.4 (C-4), 1.4 (C-8), -0.5 (C-6).
^{29}Si-NMR	(60 MHz, $CDCl_3$) δ [ppm] = 1.78, 0.61, 0.05
FT-IR	ATR, v [cm^{-1}] = 2951 (w), 2925 (w), 2896 (w), 2859 (w), 1744 (w), 1652 (m), 1557 (m), 1435 (m), 1375 (m), 1302 (w), 1250 (s), 1178 (w), 1051 (s), 831 (s), 762 (m), 681 (m), 617 (w), 589 (w), 554 (w).
HR-MS (EI)	Calcd. $[M-H]^+$: 272.1680, found: 272.1675.

11.3.1.7.3 Synthesis of 3-(methylbis((trimethylsilyl)methyl)silyl)propan-1-amine (159a)

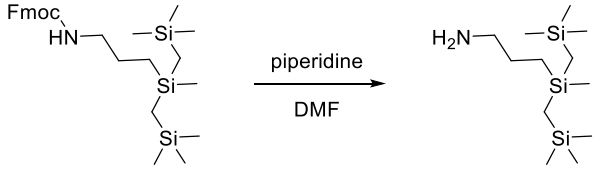
Route 1:



158c **159a**

According to **GP14**, 3.00 g (7.39 mmol, 1.00 eq.) of phthalimide **158c** were reacted with 3.70 mL (73.9 mmol, 10.0 eq.) of hydrazine monohydrate (64%) in 30 mL EtOH for 2 h. 1.22 g (4.44 mmol, 60%) of the desired product **159a** were obtained as a colorless oil.

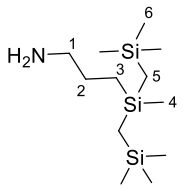
Route 2:



157b **159a**

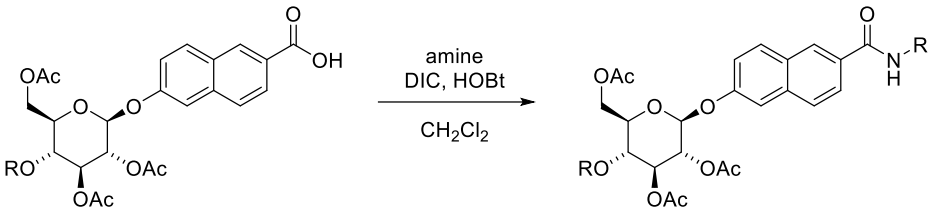
According to **GP15** 0.30 g (0.61 mmol, 1.00 eq.) of carbosilane **157b** were deprotected with 0.61 mL (6.16 mmol, 10.1 eq.) of piperidine. The crude product was purified by

column chromatography (SiO_2, *c*Hex/EtOAc 3:1 + 5% Et_3N) to afford 0.13 g (0.49 mmol, 80%) of the desired product **159a** as colorless oil.



M($C_{12}H_{33}NSi_3$)	275.65 g/mol.
R_f	(SiO_2, CH_2Cl_2/MeOH 10:1) = 0.13.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 8.33 (s, 2H, *N*H_2), 2.04 - 2.97 (m, 2H, H-1), 1.79 – 1.68 (m, 2H, H-2), 0.60 – 0.55 (m, 2H, H-3), 0.15 - -0.00 (m, 21H, H-4, H-6), -0.21 - -0.26 (m, 3H, H-4).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 41.3 (C-1), 21.0 (C-2), 14.1 (C-3), 1.8 (C-5), 0.0 (C-6), -0.1 (C-4).
^{29}Si-NMR	(60 MHz, $CDCl_3$) δ [ppm] = 0.62, 0.20, 0.05.
FT-IR	ATR, v [cm^{-1}] = 2957 (m), 2894 (w), 2859 (w), 1672 (w), 1574 (w), 1412 (w), 1354 (w), 1300 (w), 1248 (s), 1175 (w), 1054 (s), 834 (s), 684 (m), 644 (w), 601 (w), 537 (w).
HR-MS (ESI)	Calcd. $[M+H]^+$: 276.1994, found: 276.1995.

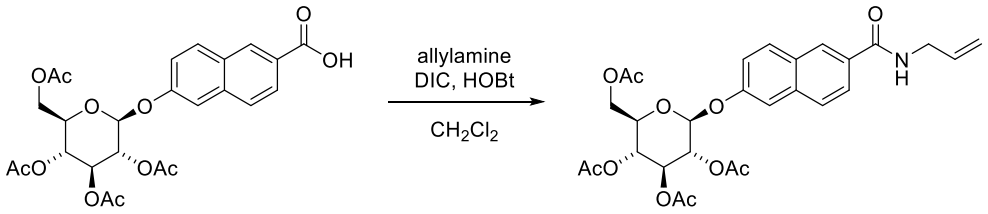
11.3.2 Amide coupling: General protocol (GP16)



138 **153/154**

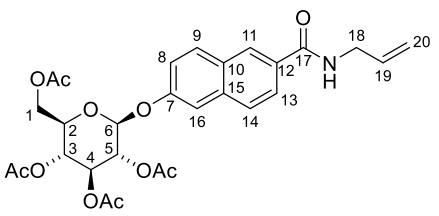
Naphthoic acid **138** (1.00 eq.) was dissolved in CH_2Cl_2 and cooled to 0 °C. DIC (1.50 eq.) and HOBt (0.20 eq.) were added and the mixture was allowed to warm up to rt. The amine (1.20 eq.) was added and the reaction mixture was stirred at rt. H_2O was added, the layers were separated and the org. phase was washed with sat. aq. NaCl. The aq. phase was extracted with CH_2Cl_2, the combined org. layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure.

11.3.2.1 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((6-(allylcarbamoyl) naphthalen-2-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (153a)



138a **153a**

According to **GP16**, 0.50 g (0.96 mmol, 1.00 eq.) of naphthoic acid **138a** were reacted with 0.23 mL (1.44 mmol, 1.50 eq.) of DIC, 0.03 g (0.19 mmol, 0.20 eq.) of HOBt and 0.09 mL (1.16 mmol, 1.20 eq.) of allylamine in 6 mL CH_2Cl_2 at rt for 24 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) to afford 0.53 g (0.95 mmol, 99%) of the desired amide **153a** as a colorless solid.



$M(C_{28}H_{31}NO_{11})$ 557.55 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:1) = 0.19.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.26 (s, 1H, H-11), 7.89 - 7.82 (m, 2H, H-13, H-14), 7.78 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H-9), 7.35 (d, $^4J_{HH}$ = 2.5 Hz, 1H, H-16), 7.24 (dd, $^{3,4}J_{HH}$ = 8.9, 2.4 Hz, 1H, H-8), 6.32

(t, $^{3}J_{HH}$ = 5.8 Hz, 1H, *N*H), 6.02 – 5.95 (m, 1H, H-19), 5.37 - 5.32 (m, 3H, H-4, H-6, H-18), 5.28 (m, 1H, H-18‘), 5.24 - 5.19 (m, 2H, H-5, H-3), 4.31 (dd, $^{2,3}J_{HH}$ = 12.3, 5.6 Hz, 1H, H-1), 4.22 (dd, $^{2,3}J_{HH}$ = 12.3, 2.5 Hz, 1H, H-1‘), 4.16 – 4.15 (m, 2H, H-20), 3.99 – 3.98 (m, 1H, H-2), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc).

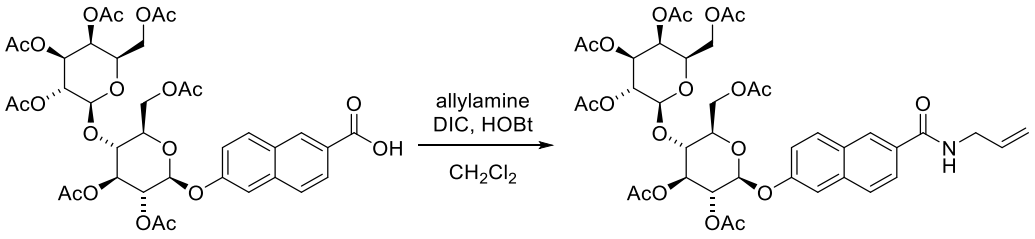
^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.5 (OAc), 170.2 (OAc), 169.4 (OAc), 169.3 (OAc), 167.1 (C-17), 155.9 (C-7), 135.7 (C-12), 134.1 (C-19), 130.8 (C-13), 130.6 (C-10), 129.2 (C-15), 127.6 (C-9), 127.2 (C-11), 124.4 (C-14), 119.7 (C-8), 116.9 (C-18), 111.0 (C-16), 98.7 (C-6), 72.6 (C-4), 72.2 (C-2), 71.1 (C-5), 68.3 (C-3), 62.0 (C-1), 42.5 (C-20), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 20.6 (OAc).

FT-IR ATR, v [cm^{-1}] = 3330 (w), 2971 (w), 2133 (w), 1756 (s), 1640 (w), 1545 (w), 1505 (w), 1478 (w), 1430 (w), 1367 (w), 1215 (s), 1169 (w), 1127 (w), 1067 (m), 1041 (m), 985 (w), 908 (w), 814 (w), 767 (w), 598 (w), 536 (w), 512 (w).

HR-MS (ESI) Calcd. $[M+H]^+$: 558.1969, found: 558.1971.

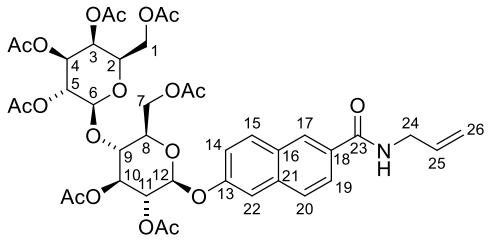
Calcd. $[M+Na]^+$: 580.1789, found: 580.1788.

11.3.2.2 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*, 6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((6-(allylcarbamoyl)naphthalen-2-yl)oxy) tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (153b)



138b **153b**

According to **GP16**, 1.00 g (1.24 mmol, 1.00 eq.) of naphthoic acid **138b** was reacted with 0.29 mL (0.1.86 mmol, 1.50 eq.) of DIC, 40 mg (0.25 mmol, 0.20 eq.) of HOBt and 0.11 mL (1.49 mmol, 1.20 eq.) of allylamine in 7 mL CH_2Cl_2 at rt for 18 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1 → 1:2) to afford 1.03 g (1.22 mmol, 98%) of the desired amide **153b** as a colorless solid.



M($C_{40}H_{47}NO_{19}$) 845.80 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:2) = 0.41.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.24 (s, 1H, H-17), 7.82 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H-19, H-20), 7.75 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H-15), 7.32 - 7.30 (m, 1H, H-22), 7.20 (dd, $^{3,4}J_{HH}$ = 8.9, 2.2 Hz, 1H, H-14), 6.42 (s, 1H, *N*H), 5.97 – 5.96 (m, 1H, H-25), 5.35 – 5.34 (m, 1H, H-3), 5.34 - 5.28 (m, 2H, H-26, H-10), 5.25 – 5.24 (m, 2H, H-12, H-11), 5.19 (d, $^3J_{HH}$ = 10.2 Hz, 1H, H-26'), 5.13 (d, $^3J_{HH}$ = 2.4 Hz, 1H, H-5), 4.98 - 4.96 (m, 1H, H-4), 4.60 - 4.44 (m, 3H, H-7, H-6), 4.14 - 4.09 (m, 4H, H-24, H-1), 3.90 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H-2, H-8, H-9), 2.15 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.06 (s, 6H, 2x OAc), 2.03 (s, 6H, 2x OAc), 1.96 (s, 3H, OAc).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.4 (OAc), 170.3 (OAc), 170.2 (OAc), 170.1 (OAc), 169.8 (OAc), 169.7 (OAc), 169.2 (OAc), 167.2 (C-23), 155.9 (C-13), 135.8 (C-21), 134.2 (C-25), 130.8 (C-15), 130.6 (C-18), 129.2 (C-16), 127.6 (C-14), 127.3 (C-17), 124.5 (C-19), 119.7 (C-20), 116.9 (C-26), 111.0 (C-22), 101.2 (C-6), 98.4 (C-12), 76.3 (C-8), 73.0 (C-9), 72.9 (C-10), 71.5 (C-11), 70.8 (C-4), 69.2 (C-2), 66.7 (C-5), 62.2 (C-3), 60.9 (C-7), 42.7 (C-1), 42.6 (C-24), 20.9 (OAc), 20.8 (OAc), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc).

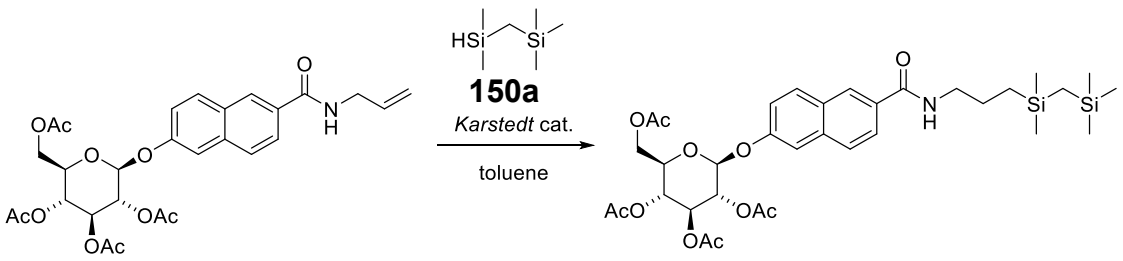
FT-IR ATR, v [cm^{-1}] = 3340 (w), 2968 (w), 1745 (s), 1617 (m), 1568 (m), 1463 (w), 1437 (w), 1367 (m), 1212 (s), 1169 (m), 1130 (m), 1044 (s), 956 (m), 902 (m), 866 (m), 814 (w), 766 (w), 747 (w), 633 (m), 602 (m), 527 (w), 477 (m), 457 (w), 414 (w).

HR-MS (ESI) Calcd. $[M+H]^+$: 846.2815, found: 846.2825.

Calcd. $[M+Na]^+$: 868.2634, found: 868.2638.

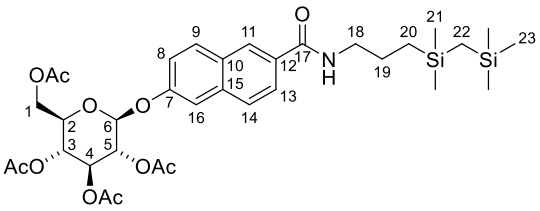
11.3.3 Hydrosilylation of allylamides

11.3.3.1 Synthesis of (2*R*,3*R*,4*S*,5*R*,6S)-2-(acetoxymethyl)-6-((6-((3-(dimethyl((trimethylsilyl)methyl)silyl)propyl)carbamoyl)naphthalen-2-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (154a)



153a **154a**

According to **GP13**, 0.53 g (0.95 mmol, 1.00 eq.) of amide **153a** were reacted with 0.17 g (1.14 mmol, 1.20 eq.) of silane **150a** and 5 µL *Karstedt* cat. in 5 mL toluene for 16 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) to afford 0.24 g (0.34 mmol, 36%) of the desired product **154a** as a colorless solid.



M($C_{34}H_{49}NO_{11}Si_2$) 703.93 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:1) = 0.43.

^{1}H-NMR (600 MHz, $CDCl_3$) δ [ppm] = 8.26 (s, 1H, H-11), 7.90 - 7.78 (m, 3H, H-13, H-4, H-9), 7.37 (s, 1H, H-16), 7.28 - 7.24 (m, 1H, H-8), 6.31 (s, 1H, *N*H), 5.37 - 5.36 (m, 2H, H-4, H-5), 5.32 - 5.20 (m, 2H, H-3, H-6), 4.34 (dd, $^{2,3}J_{HH}$ = 12.3, 5.0 Hz, 1H, H-1), 4.24 (d, $^{3}J_{HH}$ = 12.2 Hz, 1H, H-1'), 4.00 (s, 1H, H-2), 3.51 (s, 2H, H-18), 2.10 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.64 (s, 2H, H-19), 0.62 - 0.59 (m, 2H, H-20), 0.06 (s, 6H, H-21), 0.05 (s, 9H, H-23), -0.24 (s, 2H, H-22).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.5 (OAc), 170.2 (OAc), 169.4 (OAc), 169.3 (OAc), 167.3 (C-17), 155.8 (C-7), 135.6 (C-10), 131.0 (C-15), 130.8 (C-14), 129.2 (C-12), 127.5 (C-11), 127.1 (C-13), 124.4 (C-9), 119.7 (C-8), 111.0 (C-16), 98.8 (C-6), 72.6 (C-4), 72.2 (C-2), 71.1 (C-5), 68.3 (C-3), 62.0 (C-1), 43.4 (C-18),

24.5 (C-19), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 20.6 (OAc), 15.2 (C-20), 2.5 (C-22), 1.4 (C-23), -0.6 (C-21).

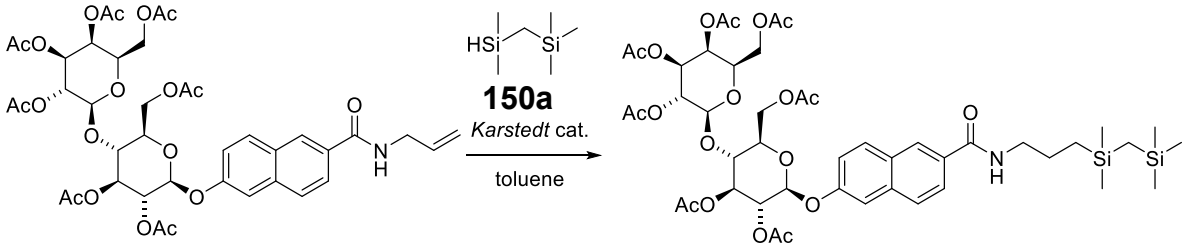
^{29}Si-NMR (119 MHz, $CDCl_3$) δ [ppm] = 1.98, 0.40.

FT-IR ATR, ν [cm^{-1}] = 3319 (w), 2953 (w), 2896 (w), 1756 (s), 1639 (w), 1604 (w), 1536 (w), 1504 (w), 1478 (w), 1433 (w), 1368 (w), 1215 (s), 1181 (w), 1118 (w), 1048 (m), 985 (w), 907 (w), 839 (m), 789 (w), 765 (w), 688 (w), 598 (w), 560 (w), 536 (w).

HR-MS (ESI) Calcd. $[M+H]^+$: 704.2916, found: 704.2914.

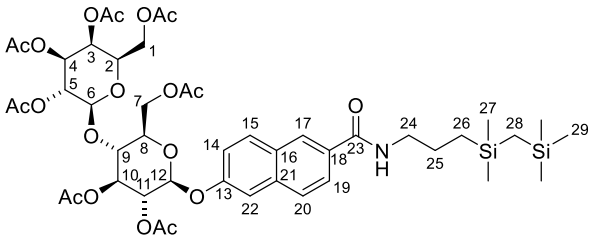
Calcd. $[M+Na]^+$: 726.2736, found: 726.2733.

11.3.3.2 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*, 6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((6-((3-(dimethyl((trimethylsilyl)methyl)silyl) propyl)carbamoyl)naphthalen-2-yl)oxy)tetrahydro-2*H*-pyran-3-yl)oxy)tetra hydro -2*H*-pyran-3,4,5-triyl triacetate (154b)



153b **154b**

According to **GP13**, 1.00 g (1.18 mmol, 1.00 eq.) of amide **153b** were reacted with 0.21 g (1.42 mmol, 1.20 eq.) of silane **150a** and 6.2 µL *Karstedt* cat. in 6.2 mL toluene for 18 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1 → 1:1) to afford 0.52 g (0.49 mmol, 41%) of the desired product **154b** as a colorless solid.



M($C_{46}H_{65}NO_{19}Si_2$) 992.18 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:1) = 0.37.

^{1}H-NMR (600 MHz, $CDCl_3$) δ [ppm] = 8.26 (s, 1H, H-17), 7.89 - 7.79 (m, 3H. H-19, H-20, H-15), 7.38 - 7.36 (m, 1H, H-22), 7.24 (dd, $^{3,4}J_{HH}$ = 8.8, 2.3 Hz, 1H, H-14), 6.30 (s, 1H, *N*H), 5.49 – 5.48 (m, 1H, H-6), 5.45 - 5.33 (m, 3H, H-12, H-11, H-5), 5.21 – 5.19 (m, 1H, H-4), 5.12 - 5.05 (m, 1H, H-3), 4.92 - 4.89 (m, 1H, H-10), 4.54 (dd, $^{2,3}J_{HH}$ = 12.1, 2.7 Hz, 1H, H-7), 4.34 - 4.25 (m, 2H, H-7‘, H-1), 4.19 - 4.13 (m, 1H, H-9), 4.10 – 4.09 (m, 1H, H-1‘), 4.03 - 3.99 (m, 2H, H-2, H-8), 3.52 – 3.51 (m, 2H, H-24), 2.13 (s, 3H, OAc), 2.08 (s, 9H, 3x OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.66 – 1.65 (m, 2H, H-25), 0.62 - 0.58 (m, 2H, H-26), 0.06 (s, 6H, H-27), 0.05 (s, 9H, H-29), -0.24 (s, 2H, H-28).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.5 (2x OAc), 170.3 (OAc), 170.2 (OAc), 169.9 (OAc), 169.6 (OAc), 169.4 (OAc), 167.3 (C-23), 155.7 (C-13), 151.2 (C-16), 135.6 (C-21), 130.7 (C-15), 129.2 (C-18), 127.5 (C-19), 127.1 (C-17), 124.4 (C-20), 119.6 (C-14), 111.0 (C-22), 98.1 (C-12), 95.7 (C-6), 75.3 (C-11), 72.8 (C-8), 72.4 (C-9), 72.0 (C-5), 70.0 (C-10), 69.3 (C-3), 68.6 (C-2), 68.0 (C-4), 62.9 (C-7), 61.6 (C-1), 43.3 (C-24), 24.4 (C-25), 20.9 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 20.6 (OAc), 20.6 (OAc), 20.5 (OAc), 15.2 (C-26), 2.5 (C-28), 1.4 (C-29), -0.6 (C-27).

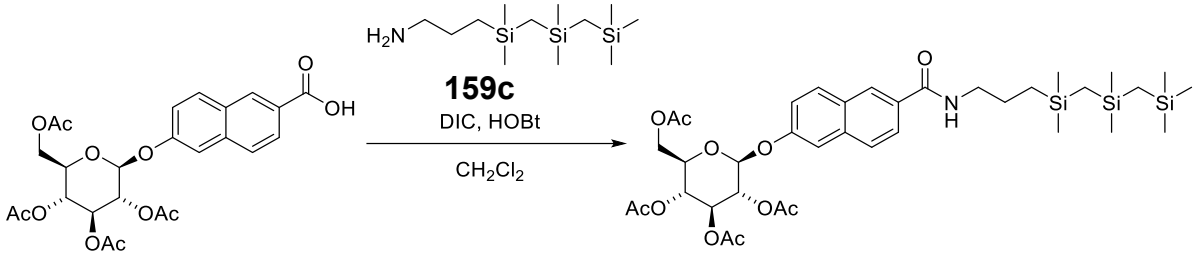
^{29}Si-NMR (119 MHz, $CDCl_3$) δ [ppm] = 1.98, 0.40.

FT-IR ATR, v [cm^{-1}] = 3337 (w), 2954 (w), 1749 (s), 1642 (w), 1604 (w), 1537 (w), 1504 (w), 1478 (w), 1435 (w), 1368 (w), 1229 (s), 1138 (w), 1043 (m), 940 (w), 900 (w), 838 (w), 788 (w), 765 (w), 733 (w), 688 (w), 602 (w), 558 (w), 520 (w).

HR-MS (ESI) Calcd. $[M+H]^+$: 992.3762, found: 992.3764.

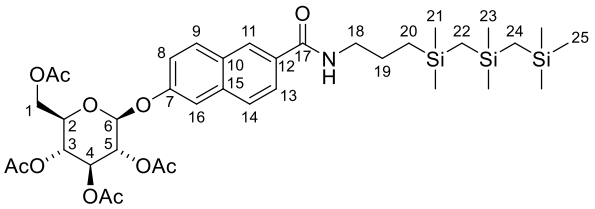
Calcd. $[M+Na]^+$: 1014.3581, found: 1014.3573.

11.3.3.3 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((6-((3-(((dimethyl((trimethylsilyl)methyl)silyl)methyl)dimethylsilyl)propyl)carbamoyl)naphthalen-2-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (164a)



138a **164a**

According to **GP16**, 0.50 g (0.69 mmol, 1.00 eq.) of naphthoic acid **138a** was reacted with 0.23 mL (1.44 mmol, 1.50 eq.) of DIC, 30 mg (0.19 mmol, 0.20 eq.) of HOBt and 0.32 g (1.16 mmol, 1.20 eq.) of silane **159c** in 6 mL CH_2Cl_2 at rt for 18 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) to afford 0.38 g (0.49 mmol, 51%) of the desired amide **164a** as a colorless solid.



M($C_{37}H_{57}NO_{11}Si_3$) 776.11 g/mol.

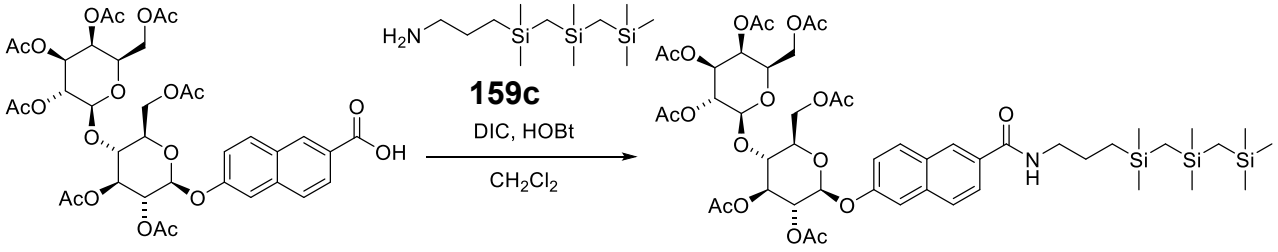
R_f (SiO_2, *c*Hex/EtOAc 1:1) = 0.53.

^{1}H-NMR (600 MHz, $CDCl_3$) δ [ppm] = 8.30 (s, 1H, H-11), 7.90 (m, 3H, H-13, H-14, H-9), 7.38 (s, 1H, H-16), 7.27 (s, 1H, H-8), 6.32 - 6.22 (m, 1H, *N*H), 5.47– 5.11 (m, 4H, H-6, H-5, H-4, H-3), 4.34 (d, $^3J_{HH}$ = 11.6 Hz, 1H, H-1), 4.25 (d, $^3J_{HH}$ = 11.9 Hz, 1H, H-1‘), 4.03 - 3.99 (m, 1H, H-2), 3.52 (s, 2H, H-18), 2.15 (s, 3H, OAc), 2.15 - 2.08 (m, 9H, OAc), 1.65 (s, 2H, H-19), 0.62 - 0.60 (m, 2H, H-20), 0.08 (s, 6H, H-21), 0.07 (s, 6H, H-23), 0.04 (s, 9H, H-25), -0.21 - -0.24 (m, 4H, H-22, H-24).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.5 (OAc), 170.2 (OAc), 169.4 (OAc), 169.4 (OAc), 155.8 (C-17), 151.3 (C-7), 143.2 (C-10), 135.6 (C-15), 132.9 (C-12), 130.3 (C-13), 129.2 (C-9), 125.1 (C-14), 124.5 (C-11), 120.1 (C-16), 119.7 (C-8), 98.8 (C-6), 72.7 (C-2), 71.1 (C-5), 70.9 (C-3), 68.3 (C4), 62.1 (C-1), 43.4 (C-18),

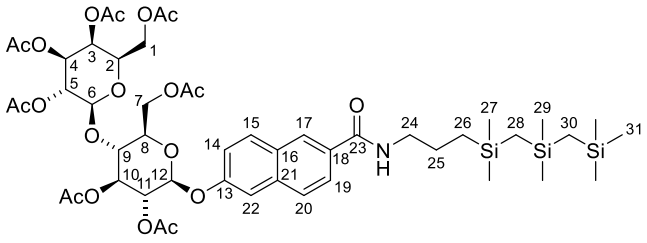
	24.5 (C-19), 20.8 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 15.4 (C-20), 5.8 (C-22), 3.9 (C-24), 2.4 (C-21), 1.4 (C-25), -0.5 (C-23).
^{29}Si-NMR	(119 MHz, $CDCl_3$) δ [ppm] = 1.80, 0.64, 0.06.
FT-IR	ATR, ν [cm^{-1}] = 3301 (w), 2953 (w), 2898 (w), 1755 (s), 1639 (w), 1603 (w), 1539 (w), 1502 (w), 1477 (w), 1432 (w), 1368 (m), 1217 (s), 1046 (s), 907 (w), 836 (s), 812 (m), 686 (w), 600 (w), 535 (w).
HR-MS (ESI)	Calcd. $[M+H]^+$: 776.3312, found: 776.3315.
	Calcd. $[M+Na]^+$: 798.3131, found: 798.3133.

11.3.3.4 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*, 6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((6-((3-(((dimethyl((trimethylsilyl)methyl) silyl)methyl)dimethylsilyl)propyl)carbamoyl)naphthalen-2-yl)oxy)tetrahydro-2*H*-pyran-3-yl)oxy)tetra hydro-2*H*-pyran-3,4,5-triyl triacetate (164b)



138b **164b**

According to **GP16**, 0.80 g (0.99 mmol, 1.00 eq.) of naphthoic acid **138b** were reacted with 0.23 mL (1.49 mmol, 1.50 eq.) of DIC, 0.03 g (0.20 mmol, 0.20 eq.) of HOBt and 0.33 g (1.19 mmol, 1.20 eq.) of silane **159c** in 6 mL CH_2Cl_2 at rt for 17 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1 → 1:2) to afford 0.59 g (0.55 mmol, 56%) of the desired amide **164b** as a colorless solid.



M($C_{49}H_{73}NO_{19}Si_3$)	1064.40 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:1) = 0.46.

^{1}H-NMR (600 MHz, $CDCl_3$) δ [ppm] = 8.26 (s, 1H, H-17), 7.90 - 7.79 (m, 3H, H-15, H-19, H-20), 7.37 (d, $^{4}J_{HH}$ = 2.3 Hz, 1H, H-22), 7.24 (dd, $^{3,4}J_{HH}$ = 8.9, 2.2 Hz, 1H, H-14), 6.30 (s, 1H, *N*H), 5.49 – 5.48 (m, 1H, H-6), 5.43 - 5.33 (m, 3H, H-12, H-11, H-5), 5.20 – 5.19 (m, 1H, H-4), 5.10 – 5.09 (m, 1H, H-3), 4.92 - 4.88 (m, 1H, H-10), 4.60 – 4.52 (m, 1H, H-7), 4.31 – 4.30 (m, 2H, H-7‘, H-1), 4.20 - 4.14 (m, 1H, H-9), 4.09 (dd, $^{2,3}J_{HH}$ = 12.5, 2.3 Hz, 1H, H-1‘), 4.04 – 3.99 (m, 2H, H-2, H-8), 3.51 (s, 2H, H-24), 2.12 (s, 3H, OAc), 2.08 (s, 9H, 3x OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.66 (s, 2H, H-25), 0.64 – 0.58 (m, 2H, H-26), 0.07 (s, 6H, H-27), 0.06 (s, 6H, H-19), 0.04 (s, 9H, H-31), -0.23 (s, 2H, H-28), -0.23 (s, 2H, H-30).

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 170.5 (2x OAc), 170.3 (OAc), 170.2 (OAc), 169.9 (OAc), 169.6 (OAc), 169.4 (OAc), 167.3 (C-23), 155.7 (C-13), 135.6 (C-16), 131.0 (C-21), 130.7 (C-19), 129.2 (C-18), 127.6 (C-20), 127.1 (C-17), 124.4 (C-15), 119.6 (C-14), 111.0 (C-22), 98.1 (C-12), 95.7 (C-6), 75.3 (C-11), 72.8 (C-9), 72.4 (C-8), 72.0 (C-4), 70.0 (C-10), 69.3 (C-5), 68.6 (C-2), 68.0 (C-3), 62.9 (C-7), 61.6 (C-1), 43.4 (C-24), 24.5 (C-25), 20.9 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 20.6 (OAc), 20.6 (OAc), 20.5 (OAc), 15.3 (C-26), 5.8 (C-28), 3.9 (C-30), 2.4 (C-29), 1.4 (C-31), -0.5 (C-27).

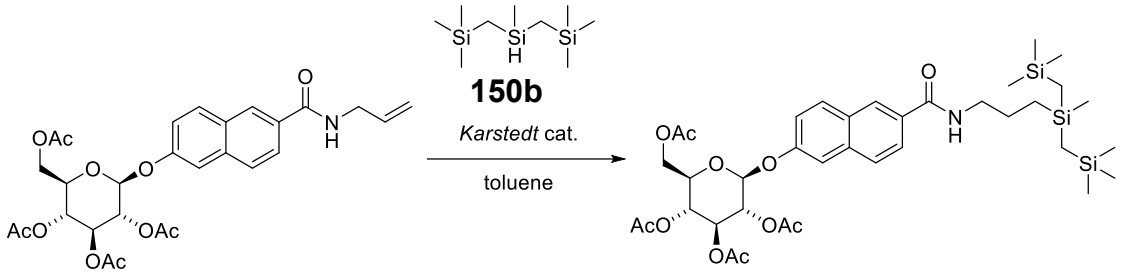
^{29}Si-NMR (119 MHz, $CDCl_3$) δ [ppm] = 1.79, 0.64, 0.06.

FT-IR ATR, ν [cm^{-1}] = 3320 (w), 2953 (w), 1752 (s), 1641 (w), 1535 (w), 1477 (w), 1432 (w), 1368 (m), 1232 (s), 1047 (s), 940 (w), 900 (w), 837 (m), 813 (w), 687 (w), 602 (w), 562 (w).

HR-MS (ESI) Calcd. $[M+H]^+$: 1064.4157, found: 1064.4162.

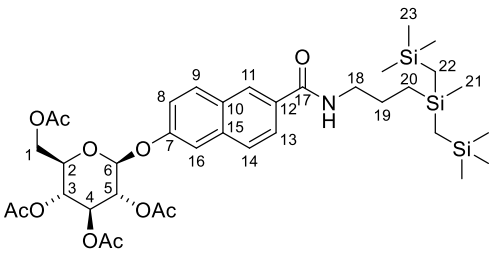
Calcd. $[M+Na]^+$: 1086.3976, found: 1086.3970.

11.3.3.5 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((6-((3-(methylbis((trimethylsilyl)methyl)silyl)propyl)carbamoyl)naphthalen-2-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (165a)



153a **165a**

According to **GP13**, 0.15 g (0.27 mmol, 1.00 eq.) of amide **153a** were reacted with 80 mg (0.27 mmol, 1.00 eq.) of silane **150b** and 8 µL *Karstedt* cat. in 6 mL toluene for 18 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) to afford 61 mg (0.08 mmol, 30%) of the desired product **165a** as a colorless solid.



M($C_{37}H_{57}NO_{11}Si_3$) 776.11 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 1:1) = 0.42.

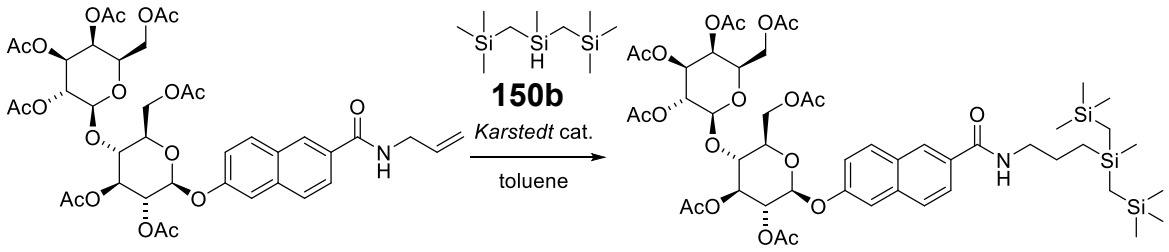
^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.23 (s, 1H, H-11), 7.87 - 7.72 (m, 3H, H-9, H-13, H-14), 7.33 (s, 1H, H-16), 7.22 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H-8), 6.40 (s, 1H, *N*H), 5.35 – 5.34 (m, 2H, H-4, H-3), 5.23 - 5.20 (m, 2H, H-6, H-4), 4.34 - 4.25 (m, 1H, H-1), 4.21 (d, $^3J_{HH}$ = 12.1 Hz, 1H, H-1‘), 3.99 - 3.93 (m, 1H, H-2), 3.52 - 3.43 (m, 2H, H-18), 2.07 - 2.04 (m, 12H, OAc), 1.64 – 1.62 (m, 2H, H-19), 0.62 - 0.54 (m, 3H, H-20), 0.04 – 0.03 (m, 18H, H-23), 0.01 – 0.00 (m, 3H, H-21), -0.24 - -0.28 (m, 4H, H-22).

^{13}C-NMR (75 MHz, $CDCl_3$) δ [ppm] = 170.6 (OAc), 170.3 (OAc), 169.5 (OAc), 169.4 (OAc), 167.5 (s, C-17), 155.9 (s, C-7), 135.7 (C-10), 131.0 (C-12), 130.9 (C-13), 129.3 (C-15), 127.6 (C-14), 127.3 (C-11), 124.6 (C-9), 119.8 (C-8), 111.1 (C-16), 98.8 (C-4), 72.8 (C-5), 72.3 (C-2), 71.3(C-3), 68.45 (C-6), 62.2 (C-1), 43.5

	(C-18), 24.5 (C-19), 20.8 (OAc), 20.7 (OAc), 20.7 (OAc), 20.7 (OAc), 15.4 (C-20), 4.0 (C-21), 4.1 (C-23), 1.6 (C-22).
^{29}Si-NMR	(119 MHz, $CDCl_3$) δ [ppm] = 0.64, 0.21, -0.06.
FT-IR	ATR, ν [cm^{-1}] = 3333 (w), 2953 (w), 2121 (w), 1737 (s), 1635 (m), 1603 (w), 1534 (m), 1504 (w), 1478 (w), 1432 (w), 1367 (m), 1252 (m), 1220 (s), 1205 (s), 1127 (m), 1114 (w), 1101 (m), 1082 (m), 1067 (m), 1034 (s), 983 (m), 932 (m), 909 (m), 897 (m), 869 (w), 836 (m), 819 (m), 769 (w), 755 (w), 698 (w), 660 (w), 649 (w), 623 (m), 602 (m), 565 (w), 535 (w), 511 (m).
HR-MS (ESI)	Calcd. $[M+H]^+$: 776.3312, found: 776.3317.
	Calcd. $[M+Na]^+$: 798.3132, found: 798.3137.

11.3.3.6 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((6-((3-(methylbis((trimethylsilyl)methyl)silyl)propyl)carbamoyl)naphthalen-2-yl)oxy)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (165b)

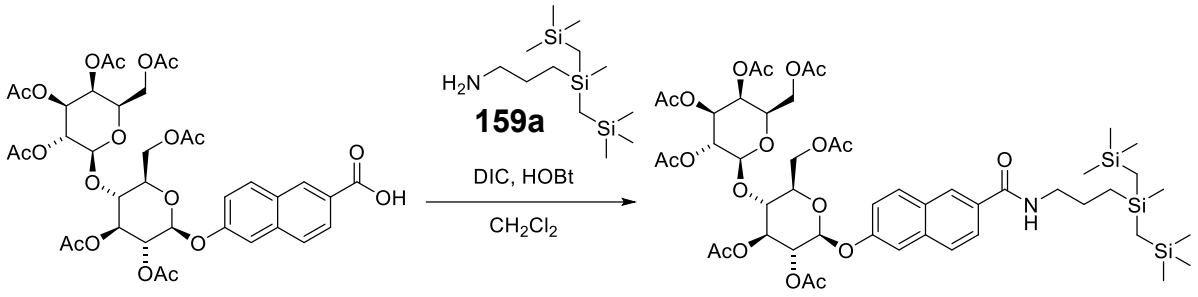
Route 1:



153b **165b**

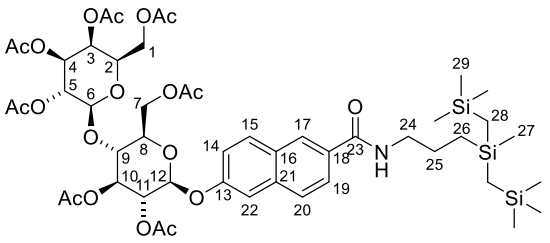
According to **GP13**, 0.27 g (0.32 mmol, 1.00 eq.) of amide **153b** were reacted with 0.14 g (0.64 mmol, 2.00 eq.) of silane **150b** and 20 µL *Karstedt* cat. in 5 mL toluene for 20 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) to afford 40 mg (0.04 mmol, 13%) of the desired product **165b** as a colorless solid.

Route 2:



138b **165b**

According to **GP16**, 0.50 g (0.62 mmol, 1.00 eq.) of naphthoic acid **138b** was reacted with 0.15 mL (0.93 mmol, 1.50 eq.) of DIC, 0.02 g (0.12 mmol, 0.20 eq.) of HOBt and 0.21 g (0.74 mmol, 1.20 eq.) of silane **159c** in 4 mL CH_2Cl_2 at rt for 15 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1 → 1:2) to afford 0.33 g (0.31 mmol, 50%) of the desired amide **165b** as a colorless solid.



M($C_{49}H_{73}NO_{19}Si_3$) 1064.40 g/mol.

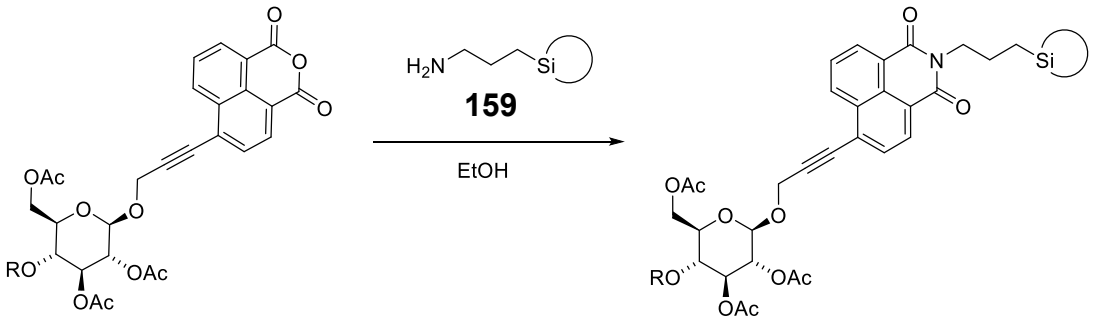
R_f (SiO_2, *c*Hex/EtOAc 1:2) = 0.78.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.26 (s, 1H, H-17), 7.89 - 7.79 (m, 3H, H-15, H-19, H-20), 7.37 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-22), 7.24 (dd, $^{3,4}J_{HH}$ = 8.9, 2.4 Hz, 1H, H-14), 6.30 (s, 1H, *N*H), 5.49 (dd, $^3J_{HH}$ = 5.8, 4.0 Hz, 1H, H-6), 5.42 - 5.32 (m, 3H, H-5, H-11, H-12), 5.19 (m, 1H, H-10), 5.09 – 5.08 (m, 1H, H-4), 4.91 – 4.90 (m, 1H, H-3), 4.54 (dd, $^{2,3}J_{HH}$ = 12.0, 2.7 Hz, 1H, H-7), 4.34 - 4.25 (m, 2H, H-7‘, H-1), 4.19 - 4.13 (m, 1H, H-9), 4.09 (dd, $^{2,3}J_{HH}$ = 12.5, 2.3 Hz, 1H, H-1‘), 4.02 – 4.01 (m, 2H, H-2, H-8), 3.52 - 3.51 (m, 2H, H-24), 2.12 (s, 3H, OAc), 2.08 (m, 9H, 3x OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.74 - 1.62 (m, 2H, H-25), 0.65 - 0.57 (m, 2H, H-26), 0.07 (s, 3H, H-27), 0.05 (s, 9H, H-29), 0.04 (s, 9H, H-29‘), -0.20 – -0.25 (m, 4H, H-28).

^{13}C-NMR (75 MHz, $CDCl_3$) δ [ppm] = 170.5 (2x OAc), 170.3 (OAc), 170.2 (OAc), 169.9 (OAc), 169.6 (OAc), 169.4 (OAc), 167.3 (C-23),

	155.7 (C-13), 135.6 (C-16), 131.1 (C-18), 130.7 (C-19), 129.2 (C-21), 127.5 (C-15), 127.1 (C-17), 124.4 (C-20), 119.6 (C-14), 111.0 (C-22), 98.1 (C-12), 95.7 (C-6), 75.3 (C-5), 72.8 (C-9), 72.4 (C-8), 72.0 (C-10), 70.0 (C-3), 69.3 (C-11), 68.6 (C-2), 68.0 (C-4), 62.9 (C-7), 61.6 (C-1), 43.3 (C-24), 24.5 (C-25), 20.9 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 20.6 (OAc), 20.6 (OAc), 20.5 (OAc), 15.9 (C-26), 3.9 (C-28), 3.5 (C-28‘), 1.5 (C-29), 1.4 (C-29‘), -0.5 (C-27).
^{29}Si-NMR	(119 MHz, $CDCl_3$) δ [ppm] = 2.34, 1.79, 0.21.
FT-IR	ATR, ν [cm^{-1}] = 3300 (w), 2953 (w), 2899 (w), 1743 (s), 1636 (m), 1536 (w),1504 (w),1478 (w), 1437 (w), 1368 (m), 1246 (s), 1226 (s), 1213 (s),1180 (m), 1149 (m), 1114 (m), 1048 (s), 980 (m), 959 (w), 904 (m), 832 (s), 810 (s), 764 (m), 686 (m), 643 (m), 603 (m), 589 (m), 564 (w), 523 (w), 494 (m), 474 (w), 452 (w).
HR-MS (ESI)	Calcd. $[M+H]^+$: 1064.4157, found: 1064.4170. Calcd. $[M+Na]^+$: 1086.3976, found: 1086.3984.

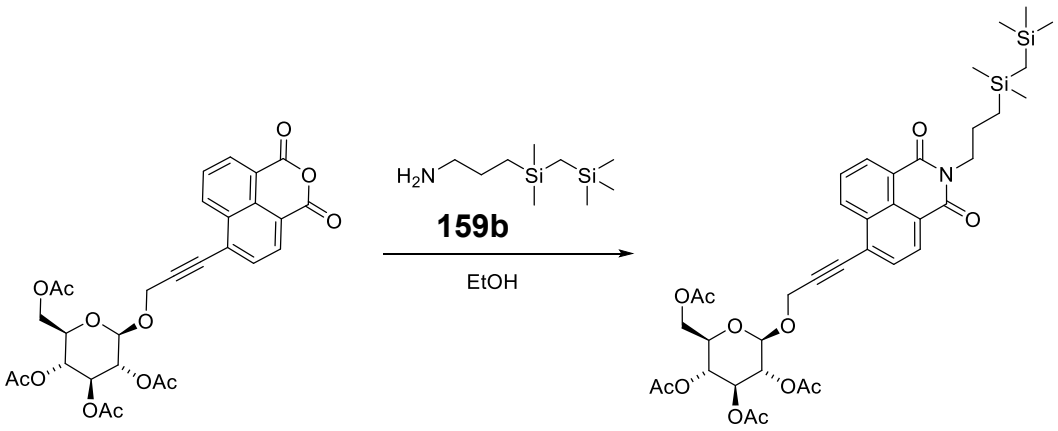
11.3.4 Naphthalimide synthesis: General protocol (GP17)



141 **161**

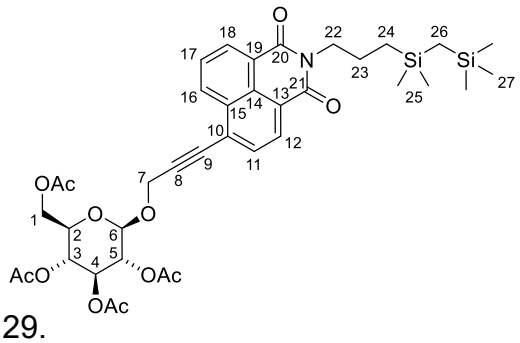
Anhydride **141** (1.00 eq.) was dissolved in EtOH and silane **159** (1.20 eq.) was added. The reaction mixture was heated to 60 °C for 16 – 20 h. The mixture was cooled to rt and the solvent was removed under reduced pressure.

11.3.4.1 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-((3-(2-(3-(dimethyl((trimethylsilyl)methyl)silyl)propyl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[de]isoquinolin-6-yl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (161a)



141a **161a**

According to **GP17**, 0.50 g (0.86 mmol, 1.00 eq.) of anhydride **141a** were reacted with 0.21 g (1.03 mmol, 1.20 eq.) of silane **159b** in 5 mL EtOH for 17 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) to afford 0.23 g (0.30 mmol, 34%) of the desired naphthalimide **161a** as an orange solid.



M($C_{38}H_{49}NO_{12}Si_2$) 767.97 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 2:1) = 0.29.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.67 (dd, $^{3,4}J_{HH}$ = 7.3, 1.2 Hz, 1H, H-16), 8.63 (dd, $^{3,4}J_{HH}$ = 8.4, 1.2 Hz, 1H, H-18), 8.57 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-12), 7.91 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-11), 7.86 (dd, $^{3,3}J_{HH}$ = 8.4, 7.3 Hz, 1H, H-17), 5.31 (t, $^{3}J_{HH}$ = 9.5 Hz, 1H, H-5), 5.18 (t, $^{3}J_{HH}$ = 9.7 Hz, 1H, H-4), 5.13 (dd, $^{3,3}J_{HH}$ = 9.5, 7.9 Hz, 1H, H-3), 4.95 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, H-6), 4.80 (d, $^{2}J_{HH}$ = 3.5 Hz, 2H, H-7), 4.33 (dd, $^{2,3}J_{HH}$ = 12.3, 4.5 Hz, 1H, H-1), 4.22 (dd, $^{2,3}J_{HH}$ = 12.4, 2.4 Hz, 1H, H-1‘), 4.19 – 4.15 (m, 2H, H-22), 3.82 (m, 1H, H-1), 2.11 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.78 – 1.69 (m, 2H, H-23), 0.66 – 0.59 (m, 2H, H-24), 0.04 (s, 6H, H-25), 0.03 (s, 9H, H-27), -0.26 (s, 2H, H-26).

^{13}C-NMR (75 MHz, $CDCl_3$) δ [ppm] = 170.6 (OAc), 170.3 (OAc), 169.4 (OAc), 169.3 (OAc), 163.8 (C-20), 163.6 (C-21), 131.9 (C-18), 131.7 (C-14), 131.6 (C-16), 131.0 (C-11), 130.2 (C-12), 128.0 (C-19), 127.7 (C-17), 126.1 (C-10), 123.1 (C-15), 122.8 (C-10), 98.8 (C-6), 93.0 (C-9), 83.9 (C-8), 72.7 (C-5), 72.1 (C-2), 71.1 (C-3), 68.2 (C-4), 61.8 (C-1), 56.9 (C-7), 43.5 (C-22), 22.7 (C-23), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 15.3 (C-24), 2.5 (C-26), 1.3 (C-27), -0.6 (C-25).

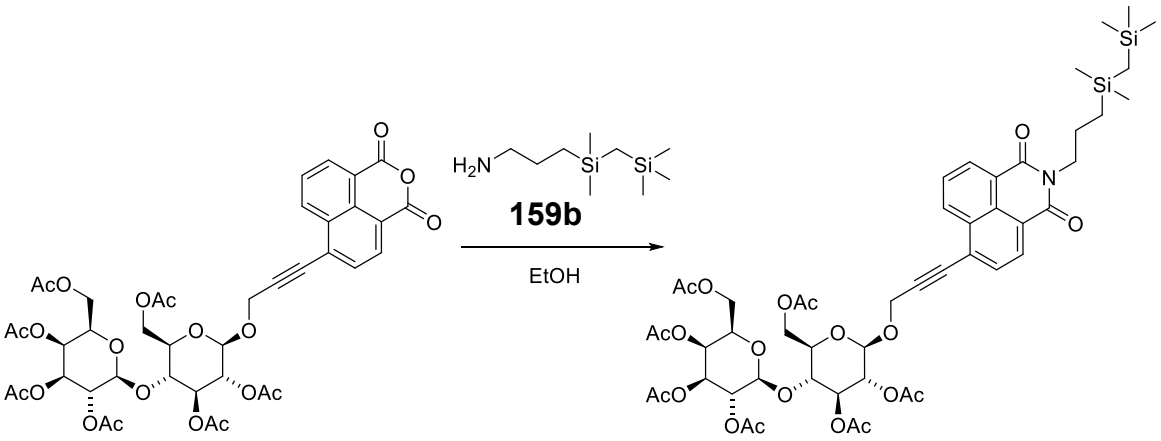
^{29}Si-NMR (119 MHz, $CDCl_3$) δ [ppm] = 1.93, 0.37.

FT-IR ATR, ν [cm^{-1}] = 2953 (w), 2895 (w), 1757 (s), 1701 (m), 1661 (s), 1615 (w), 1591 (w), 1511 (w), 1440 (w), 1382 (m), 1354 (m), 1226 (s), 1168 (w), 1052 (s), 979 (w), 905 (w), 839 (m), 785 (m), 756 (w), 688 (w), 600 (w), 560 (w).

HR-MS (ESI) Calcd. $[M+H]^+$: 768.2866, found: 768.2868.

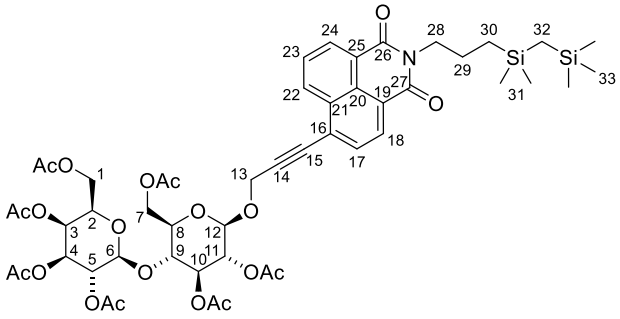
Calcd. $[M+Na]^+$: 790.2685, found: 790.2687.

11.3.4.2 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*R*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((3-(2-(3-(dimethyl((trimethylsilyl)methyl) silyl)propyl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[de]isoquinolin-6-yl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (161b)



141b **161b**

According to **GP17**, 0.71 g (0.82 mmol, 1.00 eq.) of anhydride **141b** were reacted with 0.20 g (0.98 mmol, 1.20 eq.) of silane **159b** in 5 mL EtOH for 15.5 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) to afford 0.63 g (0.59 mmol, 72%) of the desired naphthalimide **161b** as an orange solid.



M($C_{50}H_{65}NO_{20}Si_2$) 1056.20 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 2:1) = 0.23.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.67 (dd, $^{3,4}J_{HH}$ = 7.3, 1.2 Hz, 1H, H-24), 8.63 (dd, $^{3,4}J_{HH}$ = 8.3, 1.2 Hz, 1H, H-22), 8.58 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-18), 7.92 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-17), 7.89 – 7.87 (m, 1H, H-23), 5.46 (d, $^{3}J_{HH}$ = 4.0 Hz, 1H, H-12), 5.39 – 5.33 (m, 2H, H-9, H-10), 5.10 – 5.07 (m, 1H, H-5), 4.99 – 4.94 (m, 2H, H-6, H-4), 4.89 – 4.86 (m, 1H, H-11), 4.78 (d, $^{4}J_{HH}$ = 2.4 Hz, 2H, H-13), 4.57 (dd, $^{2,3}J_{HH}$ = 12.2, 2.7 Hz, 1H, H-1), 4.28 (m, 2H, H-1‘, H-7), 4.19 – 4.15 (m, 2H, H-28), 4.15 – 4.05 (m, 2H, H-7‘,

H-3), 4.00 – 3.97 (m, 1H, H-2), 3.82 – 3.79 (m, 1H, H-8), 2.16 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.05 (m, 9H, OAc), 2.02 (s, 3H, OAc), 1.77 – 1.69 (m, 2H, H-29), 0.65 – 0.62 (m, 2H, H-30), 0.04 (s, 6H, H-31), 0.03 (s, 9H, H-33), -0.26 (s, 2H, H-32).

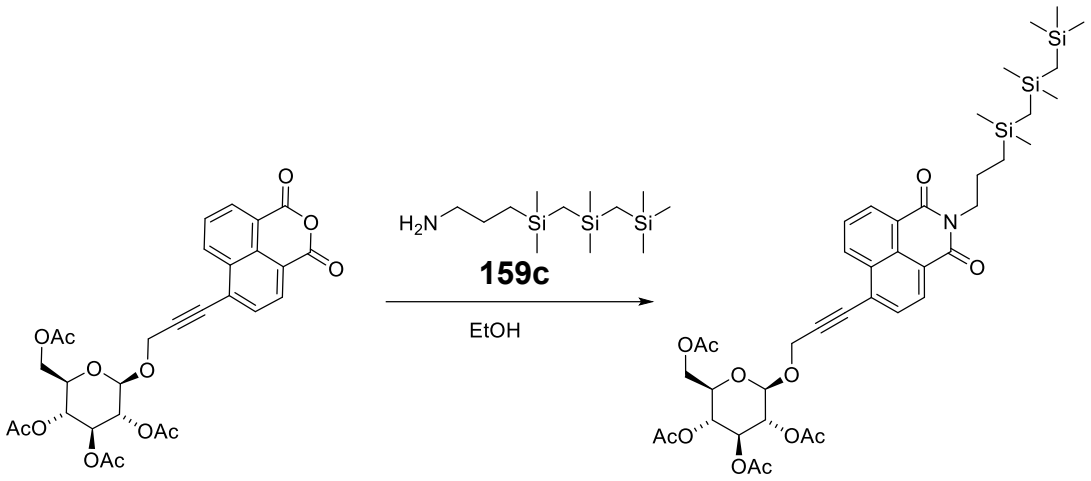
^{13}C-NMR (75 MHz, $CDCl_3$) δ [ppm] = 170.5 (OAc), 170.5 (OAc), 170.4 (OAc), 170.2 (OAc), 169.9 (OAc), 169.6 (OAc), 169.3 (OAc), 163.8 (C-26), 163.6 (C-27), 131.9 (C-22), 131.7 (C-24), 131.1 (C-17), 130.2 (C-18), 128.0 (C-20), 127.7 (C-23), 126.1 (C-21), 123.1 (C-25), 122.8 (C-19), 98.1 (C-6), 95.6 (C-12), 92.9 (C-16), 83.9 (C-15), 75.3 (C-9), 72.5 (C-4), 72.4 (C-8), 72.0 (C-4), 70.0 (C-11), 69.2 (C-10), 68.5 (C-2), 68.0 (C-5), 62.6 (C-1), 61.4 (C-14), 60.3 (C-7), 56.8 (C-13), 43.5 (C-28), 22.7 (C-29), 20.9 (OAc), 20.8 (OAc), 20.7 (OAc), 20.6 (OAc), 20.5 (OAc), 20.5 (2x OAc), 15.3 (C-30), 2.5 (C-32), 1.3 (C-33), -0.6 (C-31).

^{29}Si-NMR (119 MHz, $CDCl_3$) δ [ppm] = 1.93, 0.37.

FT-IR ATR, ν [cm^{-1}] = 3484 (w), 2954 (w), 2896 (w), 2124 (w), 1931 (w), 1752 (s), 1702 (w), 1662 (m), 1616 (w), 1591 (w), 1510 (w), 1439 (w), 1382 (w), 1366 (w), 1229 (s), 1168 (w), 1136 (w), 1047 (s), 958 (w), 938 (w), 899 (w), 839 (w), 785 (w), 756 (w), 733 (w), 688 (w), 651 (w), 601 (w), 554 (w).

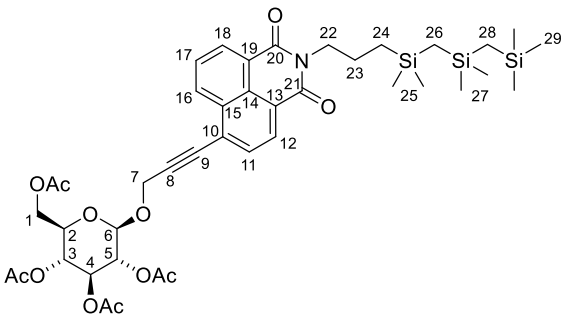
HR-MS (ESI) Calcd. $[M+Na]^+$: 1078.3530, found: 1078.3525.

11.3.4.3 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-((3-(2-(3-(((dimethyl((trimethylsilyl)methyl)silyl)methyl)dimethylsilyl)propyl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[de]isoquinolin-6-yl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (162a)



141a **162a**

According to **GP17**, 1.00 g (1.72 mmol, 1.00 eq.) of anhydride **141a** was reacted with 0.57 g (2.06 mmol, 1.20 eq.) of silane **159c** in 10 mL EtOH for 15.5 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) to afford 0.55 g (0.65 mmol, 38%) of the desired naphthalimide **162a** as an orange solid.



M($C_{41}H_{57}NO_{12}Si_3$) 840.16 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 2:1) = 0.18.

^{1}H-NMR (600 MHz, $CDCl_3$) δ [ppm] = 8.68 – 8.67 (m, 1H, H-16), 8.63 (dd, $^{3,4}J_{HH}$ = 8.4, 1.2 Hz, 1H, H-18), 8.57 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-12), 7.91 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-11), 7.86 (dd, $^{3,3}J_{HH}$ = 8.4, 7.3 Hz, 1H, H-17), 5.31 (t, $^{3}J_{HH}$ = 9.5 Hz, 1H, H-5), 5.18 (m, 1H, H-4), 5.15 – 5.11 (m, 1H, H-3), 4.95 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, H-6), 4.80 (d, $^{2}J_{HH}$ = 5.0 Hz, 2H, H-7), 4.33 (dd, $^{2,3}J_{HH}$ = 12.3, 4.6 Hz, 1H, H-1), 4.22 (dd, $^{2,3}J_{HH}$ = 12.3, 2.4 Hz, 1H, H-1‘), 4.20 – 4.15 (m, 2H, H-22), 3.82 (m, 1H, H-2), 2.11 (s, 3H, OAc), 2.07 (s, 3H,

OAc), 2.06 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.73 (m, 3H, H-23), 0.66 – 0.60 (m, 2H, H-24), 0.06 (s, 6H, H-25), 0.04 (s, 6H, H-27), 0.03 (s, 9H, H-29), -0.24 (s, 2H, H-26), -0.25 (s, 2H, H-28).

^{13}C-NMR (75 MHz, $CDCl_3$) δ [ppm] = 170.6 (OAc), 170.2 (OAc), 169.3 (OAc), 169.3 (OAc), 163.8 (C-20), 163.5 (C-21), 131.9 (C-18), 131.7 (C-16), 131.0 (C-11), 130.2 (C-12), 128.0 (C-19), 127.6 (C-17), 126.1 (C-13), 123.1 (C-14), 122.8 (C-15), 98.8 (C-6), 93.0 (C-10), 83.9 (C-9), 72.6 (C-5), 72.1 (C-2), 71.1 (C-3), 68.2 (C-4), 61.8 (C-1), 60.3 (C-8), 56.9 (C-7), 43.5 (C-22), 22.7 (C-23), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.5 (OAc), 15.3 (C-24), 7.2 (C-26), 4.0 (C-28), 2.4 (C-25), 1.4 (C-29), -0.5 (C-27).

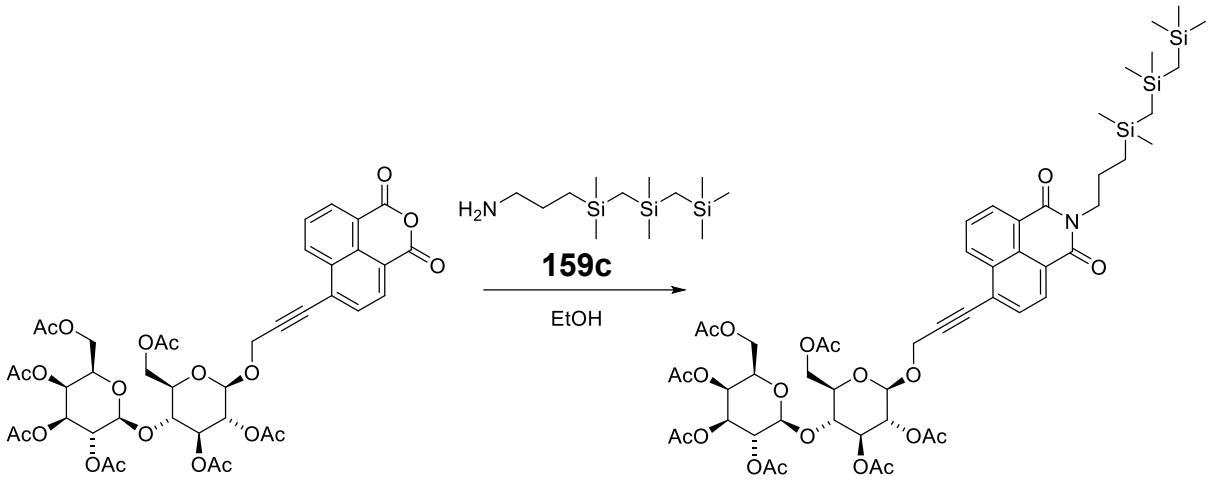
^{29}Si-NMR (119 MHz, $CDCl_3$) δ [ppm] = 1.75, 0.60, 0.04.

FT-IR ATR, ν [cm^{-1}] = 3485 (w), 2953 (w), 2897 (w), 1757 (s), 1702 (m), 1662 (s), 1616 (w), 1591 (w), 1511 (w), 1439 (w), 1382 (m), 1354 (m), 1244 (s), 1224 (s), 1168 (w), 1123 (w), 1045 (s), 979 (w), 904 (w), 836 (s), 813 (m), 785 (m), 756 (w), 687 (w), 600 (w), 582 (w), 540 (w).

HR-MS (ESI) Calcd. $[M+H]^+$: 840.3261, found: 840.3268.

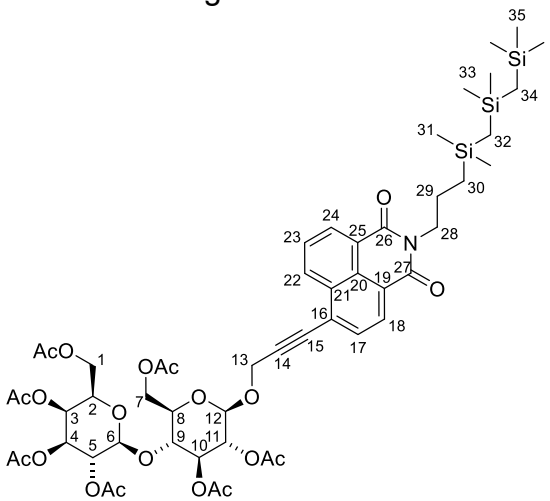
Calcd. $[M+Na]^+$: 862.3080, found: 862.3086.

11.3.4.4 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*R*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((3-(2-(3-(((dimethyl((trimethylsilyl)methyl)silyl)methyl)dimethylsilyl)propyl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[de]isoquinolin-6-yl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (162b)



141b **162b**

According to **GP17**, 1.00 g (1.15 mmol, 1.00 eq.) of anhydride **141b** was reacted with 0.38 g (1.38 mmol, 1.20 eq.) of silane **159c** in 7 mL EtOH for 15 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 2:1) to afford 0.72 g (0.63 mmol, 55%) of the desired naphthalimide **162b** as a beige solid.



M($C_{53}H_{73}NO_{20}Si_3$) 1128.40 g/mol.

R_f (SiO_2, *c*Hex/EtOAc 2:1) = 0.24.

^{1}H-NMR (600 MHz, $CDCl_3$) δ [ppm] = 8.67 (dd, $^{3,4}J_{HH}$ = 7.3, 1.2 Hz, 1H, H-24), 8.63 (dd, $^{3,4}J_{HH}$ = 8.4, 1.2 Hz, 1H, H-22), 8.57 (s, 1H, H-18), 7.92 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-17), 7.88 (dd, $^{3,3}J_{HH}$ = 8.4, 7.3 Hz, 1H, H-23), 5.46 (d, $^{3}J_{HH}$ = 4.0 Hz, 1H, H-12), 5.41 – 5.32 (m, 2H, H-9, H-10), 5.09 (t, $^{3}J_{HH}$ = 9.9 Hz, 1H, H-5), 5.00 – 4.93

(m, 2H, H-6, H-4), 4.88 (m, 1H, H-11), 4.78 (d, $^{2}J_{HH}$ = 1.8 Hz, 2H, H-13), 4.57 (dd, $^{2,3}J_{HH}$ = 12.2, 2.7 Hz, 1H, H-1), 4.28 (m, 2H, H-1‘, H-7), 4.21 – 4.15 (m, 2H, H-28), 4.08 (m, 2H, H-7‘, H-3), 4.00 - 3.97 (m, 1H, H-2), 3.82 – 3.79 (m, 1H, H-8), 2.17 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.05 (m, 9H, OAc), 2.02 (s, 3H, OAc), 1.75 – 1.70 (m, 2H, H-29), 0.66 – 0.60 (m, 2H, H-30), 0.06 (s, 6H, H-31), 0.04 (s, 6H, H-33), 0.03 (s, 9H, H-35), -0.24 (s, 2H, H-32), -0.25 (s, 2H, H-34).

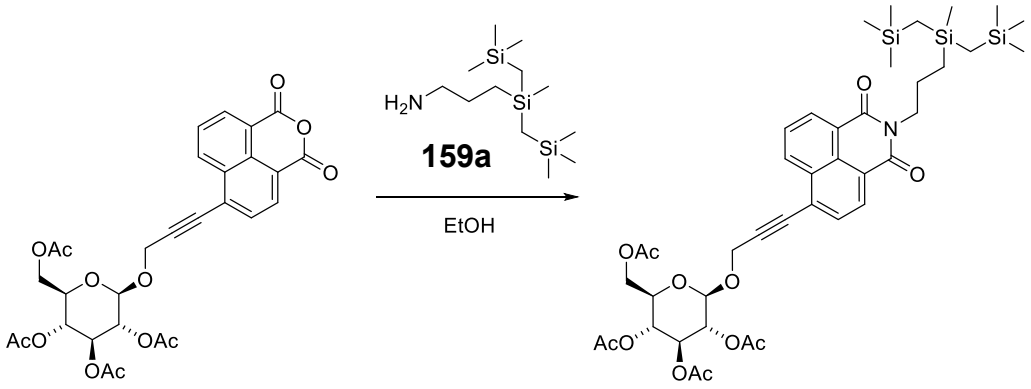
^{13}C-NMR (75 MHz, $CDCl_3$) δ [ppm] = 170.5 (OAc), 170.4 (OAc), 170.2 (OAc), 169.9 (OAc), 169.6 (OAc), 169.4 (OAc), 163.8 (C-26), 163.6 (C-27), 132.0 (C-22), 131.7 (C-24), 131.1 (C-17), 130.2 (C-18), 128.0 (C-25), 127.7 (C-23), 126.1 (C-19), 123.1 (C-20), 122.8 (C-21), 98.1 (C-6), 95.6 (C-12), 92.9 (C-16), 83.9 (C-15), 75.3 (C-9), 72.5 (C-3), 72.4 (C-8), 71.9 (C-4), 70.0 (C-11), 69.2 (C-10), 68.5 (C-2), 68.0 (C-5), 62.6 (C-1), 61.4 (C-7), 60.4 (C-14), 56.8 (C-13), 43.5 (C-28), 22.7 (C-29), 20.9 (OAc), 20.8 (OAc), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.6 (OAc), 20.5 (OAc), 15.3 (C-30), 5.7 (C-32), 4.0 (C-34), 2.4 (C-31), 1.4 (C-35), -0.5 (C-33).

^{29}Si-NMR (119 MHz, $CDCl_3$) δ [ppm] = 1.75, 0.60, 0.04.

FT-IR ATR, ν [cm^{-1}] = 3490 (w), 2953 (w), 2898 (w), 2131 (w), 1751 (s), 1702 (w), 1662 (m), 1616 (w), 1591 (w), 1511 (w), 1439 (w), 1382 (w), 1366 (m), 1230 (s), 1167 (w), 1136 (w), 1045 (s), 992 (w), 958 (w), 938 (w), 899 (w), 836 (m), 813 (m), 786 (w), 756 (w), 735 (w), 686 (w), 602 (w), 582 (w), 554 (w).

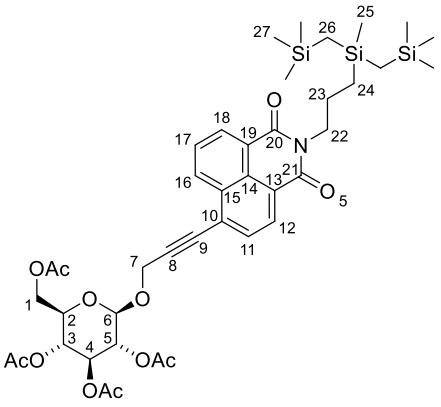
HR-MS (ESI) Calcd. $[M+Na]^+$: 1150.3925, found: 1150.3924.

11.3.4.5 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-((3-(2-(3-(methylbis((trimethylsilyl)methyl)silyl)propyl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[de]isoquinolin-6-yl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (163a)



141a **163a**

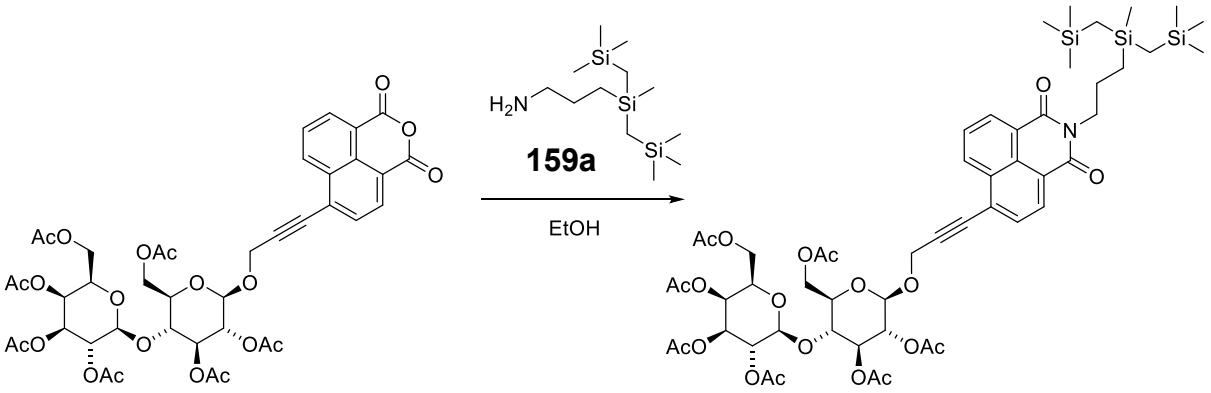
According to **GP17**, 0.43 g (0.71 mmol, 1.00 eq.) of anhydride **141a** were reacted with 0.24 g (0.86 mmol, 1.20 eq.) of silane **159a** in 10 mL EtOH for 15 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:1) to afford 0.48 g (0.57 mmol, 80%) of the desired naphthalimide **163a** as an orange solid.



M($C_{41}H_{57}NO_{12}Si_3$)	840.15 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:1) = 0.62.
m.p.	97 – 98 °C.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 8.64 (dt, $^{3,4}J_{HH}$ = 7.3, 1.1 Hz, 1H, H-18), 8.59 (dd, $^{3,4}J_{HH}$ = 8.4, 1.2 Hz, 1H, H-16), 8.54 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-12), 7.87 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-11), 7.83 (dd, $^{3,3}J_{HH}$ = 8.3, 7.3 Hz, 1H, H-17), 5.28 (t, $^{3}J_{HH}$ = 9.5 Hz, 1H, H-5), 5.15 (t, $^{3}J_{HH}$ = 9.7 Hz, 1H. H-4), 5.09 (dd, $^{3,3}J_{HH}$ = 9.5, 7.9 Hz, 1H, H-3), 4.92 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, H-6), 4.77 (d, $^{2}J_{HH}$ = 3.4 Hz, 2H, H-7), 4.30 (dd, $^{2,3}J_{HH}$ = 12.4, 4.5 Hz, 1H, H-1), 4.18 (dd, $^{2,3}J_{HH}$ = 12.4, 2.4 Hz, 1H, H-1), 4.16 – 4.11 (m, 2H, H-22),

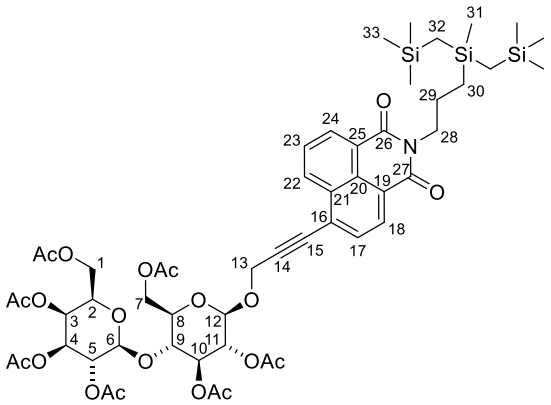
	3.79 - 3.78 (m, 1H, H-2), 2.07 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.73 – 1.65 (m, 2H, H-23), 0.64 – 0.58 (m, 2H, H-24), 0.02 (s, 3H, H-25), -0.00 (m, 18H, H-26), -0.27 (m, 4H, H-25).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 170.6 (OAc), 170.2 (OAc), 169.3 (OAc), 169.3 (OAc), 163.8 (C-20), 163.5 (C-21), 131.9 (C-16), 131.7 (C-18), 131.6 (C-19), 131.0 (C-11), 130.2 (C-12), 128.0 (C-13), 127.6 (C-17), 126.1 (C-10), 123.1 (C-14), 122.8 (C-15), 98.7 (C-6), 93.0 (C-9), 83.9 (C-8), 72.7 (C-5), 72.1 (C-2), 71.1 (C-3), 68.2 (C-4), 61.7 (C-1), 56.9 (C-7), 43.5 (C-22), 22.7 (C-23), 20.7 (OAc), 20.7 (OAc), 20.6 (OAc), 20.5 (OAc), 16.0 (C-24), 3.5 (C-26), 1.5 (C-27), 1.4 (C-25).
^{29}Si-NMR	(119 MHz, $CDCl_3$) δ [ppm] = 0.18, 0.04.
FT-IR	ATR, ν [cm^{-1}] = 3659 (w), 2953 (w), 2899 (w), 2119 (w), 1752 (s), 1700 (m), 1660 (m), 1616 (w), 1590 (m), 1510 (w), 1439 (w), 1381 (m), 1352 (m), 1214 (s), 1167 (w), 1125 (w), 1038 (s), 977 (w), 904 (w), 832 (s), 801 (s), 783 (s), 755 (m), 686 (m), 598 (m).
HR-MS (ESI)	Calcd. $[M+H]^+$: 850.3261, found: 840.3260. Calcd. $[M+Na]^+$: 862.3081, found: 862.3078.

11.3.4.6 Synthesis of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*R*)-4,5-diacetoxy-2-(acetoxymethyl)-6-((3-(2-(3-(methylbis((trimethylsilyl)methyl) silyl)propyl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[de]isoquinolin-6-yl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (163b)



141b **163b**

According to **GP17**, 0.80 g (0.92 mmol, 1.00 eq.) of anhydride **141b** were reacted with 0.31 g (1.10 mmol, 1.20 eq.) of silane **159a** in 15 mL EtOH for 18 h. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc 1:3) to afford 0.63 g (0.56 mmol, 61%) of the desired naphthalimide **163b** as an orange solid.

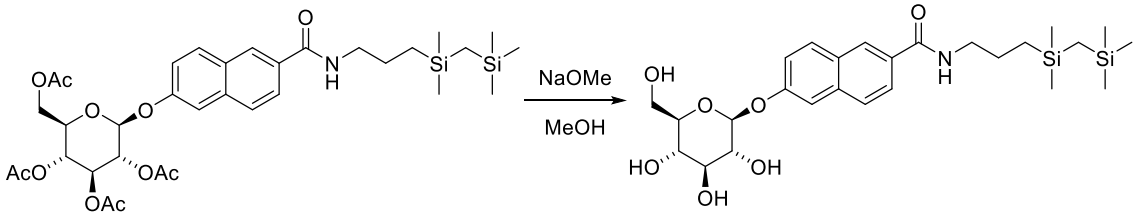


M($C_{53}H_{73}NO_{20}Si_3$)	1128.40 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc 1:3) = 0.79.
m.p.	84 – 86 °C.
^{1}H-NMR	(500 MHz, $CDCl_3$) δ [ppm] = 8.67 (d, $^3J_{HH}$ = 7.3 Hz, 1H, H-24), 8.61 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H-22), 8.57 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H-18), 7.90 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H-17), 7.88 – 7.84 (m, 1H, H-23), 5.37 (m, 1H, H-12), 5.30 (t, $^3J_{HH}$ = 9.2 Hz, 1H, H-9), 5.13 (dd, $^{3,3}J_{HH}$ = 10.4, 7.9 Hz, 1H, H-10), 5.04 – 4.96 (m, 2H, H-4, H-5), 4.91 (d, $^3J_{HH}$ = 7.9 Hz, 1H, H-6), 4.76 (d, $^2J_{HH}$ = 5.4 Hz,

	2H, H-13), 4.57 (dd, $^{2,3}J_{HH}$ = 12.1, 2.1 Hz, 1H, H-1), 4.53 (m, 1H, H-11), 4.16 (m, 4H, H-28, H-1‘, H-7), 4.12 – 4.08 (m, 1H, H-7‘), 3.92 – 3.86 (m, 2H, H-2, H-3), 3.73 – 3.69 (m, 1H, H-8), 2.17 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.06 (s, 6H, OAc), 1.98 (s, 3H, OAc), 1.72 (m, 2H, H-29), 0.67 – 0.61 (m, 2H, H-30), 0.05 (s, 3H, H-31), 0.04 – 0.02 (m, 18H, H-33), -0.24 (m, 4H, H-32).
^{13}C-NMR	(126 MHz, $CDCl_3$) δ [ppm] = 170.3 (OAc), 170.3 (OAc), 170.1 (OAc), 170.0 (OAc), 169.7 (OAc), 169.6 (OAc), 169.0 (OAc), 163.8 (C-26), 163.5 (C-27), 131.9 (C-22), 131.7 (C-24), 131.6 (C-25), 131.0 (C-17), 130.2 (C-18), 127.9 (C-19), 127.7 (C-23), 126.1 (C-16), 123.1 (C-20), 122.8 (C-21), 101.1 (C-11), 98.5 (C-6), 92.9 (C-15), 83.9 (C-14), 76.0 (C-3), 72.9 (C-8), 72.7 (C-9), 71.4 (C-5), 70.9 (C-4), 70.7 (C-2), 69.1 (C-10), 66.5 (C-12), 61.7 (C-1), 60.7 (C-7), 56.8 (C-13), 43.5 (C-28), 22.7 (C-29), 20.8 (OAc), 20.8 (OAc), 20.7 (OAc), 20.6 (3x OAc), 20.5 (OAc), 16.0 (C-30), 3.5 (C-32), 2.4 (C-31), 1.5 (C-33).
^{29}Si-NMR	(119 MHz, $CDCl_3$) δ [ppm] = 0.60, 0.18.
FT-IR	ATR, v [cm^{-1}] = 3662 (w), 2956 (w), 2901 (w), 1748 (s), 1701 (w), 1661 (m), 1590 (w), 1439 (w), 1367 (m), 1215 (s), 1171 (w), 1131 (w), 1047 (s), 955 (w), 900 (w), 833 (s), 801 (m), 783 (m), 755 (w), 686 (w), 601 (w).
HR-MS (ESI)	Calcd. $[M+Na]^+$: 1150.3925, found: 1150.3924.

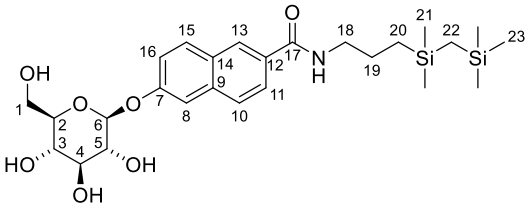
11.3.5 Deprotection of sugar units and preservation of final carbosilane surfactants

11.3.5.1 Synthesis of *N*-(3-(dimethyl((trimethylsilyl)methyl)silyl)propyl)-6-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl) oxy)-2-naphthamide (166a)



154a **166a**

According to **GP18**, 0.24 g (0.34 mmol, 1.00 eq.) of compound **154a** were deprotected with 0.34 mL (0.17 mmol, 0.50 eq.) NaOMe in MeOH (0.5 M) in 2 mL MeOH. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 4:4:1) to afford 0.18 g (0.33 mmol, 98%) of the desired product **166a** as a colorless solid.



M($C_{26}H_{41}NO_7Si_2$)	535.78 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) = 0.44.
^{1}H-NMR	(400 MHz, MeOD-d_4) δ [ppm] = 8.33 – 8.32 (m, 1H, H-13), 7.93 (d, $^3J_{HH}$ = 9.0 Hz, 1H, H-15), 7.87 – 7.85 (m, 2H, H-10, H-11), 7.56 (d, $^4J_{HH}$ = 2.5 Hz, 1H, H-8), 7.39 (dd, $^{3,4}J_{HH}$ = 9.0, 2.5 Hz, 1H, H-16), 5.14 – 5.11 (m, 1H, H-6), 3.97 (dd, $^{2,3}J_{HH}$ = 12.1, 2.3 Hz, 1H, H-1), 3.75 (dd, $^{2,3}J_{HH}$ = 12.1, 5.8 Hz, 1H, H-1‘), 3.60 - 3.58 (m, 1H, H-2), 3.56 – 3.53 (m, 2H, H-4, H-5), 3.47 - 3.41 (s, 1H, H-3), 3.41 (t, $^3J_{HH}$ = 7.2 Hz, 2H, H-18), 1.71 - 1.63 (m, 2H, H-19), 0.66 – 0.61 (m, 2H, H-20), 0.07 (s, 6H, H-21), 0.05 (s, 9H, H-23), -0.21 (s, 2H, H-22).
^{13}C-NMR	(101 MHz, MeOD-d_4) δ [ppm] = 168.8 (C-17), 156.9 (C-7), 136.0 (C-14), 130.13 (C-15), 130.0 (C-12), 128.8 (C-9), 127.1 (C-13), 127.0 (C-11), 123.9 (C-10), 119.5 (C-16), 110.3 (C-8),

100.7 (C-6), 76.9 (C-2), 76.6 (C-5), 73.5 (C-4), 70.0 (C-3), 61.1 (C-1), 42.9 (C-18), 23.8 (C-19), 14.7 (C-20), 1.7 (C-22), 0.1 (C-23), -1.8 (C-21).

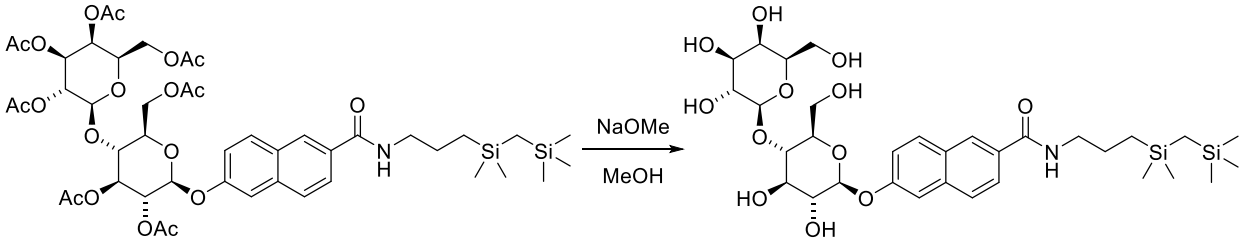
^{29}Si-NMR (119 MHz, MeOD-d_4) δ [ppm] = 1.87, 0.24.

FT-IR ATR, ν [cm^{-1}] = 3343 (s), 2951 (m), 2486 (m), 2123 (w), 1631 (s), 1543 (m), 1485 (s), 1449 (m), 1410 (m), 1364 (m), 1312 (m), 1252 (m), 1224 (m), 1194 (m), 1149 (m), 1045 (s), 835 (s), 784 (s), 763 (s), 747 (s), 686 (s), 656 (s), 619 (s), 580 (s).

HR-MS (ESI) Calcd. $[M+H]^+$: 536.2494, found: 536.2496.

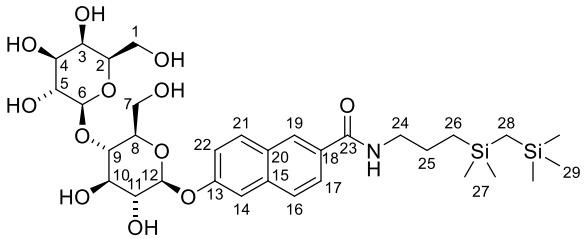
Calcd. $[M+Na]^+$: 558.2313, found: 558.2313.

11.3.5.2 Synthesis of 6-(((2*S*,3*R*,4*R*,5*S*,6*R*)-3,4-dihydroxy-6-(hydroxymethyl)-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl) oxy)tetrahydro-2*H*-pyran-2-yl)oxy)-*N*-(3-(dimethyl((trimethylsilyl)methyl)silyl) propyl)-2-naphth amide (166b)



154b **166b**

According to **GP18**, 0.50 g (0.50 mmol, 1.00 eq.) of compound **154b** were deprotected with 0.50 mL (0.25 mmol, 0.50 eq.) NaOMe in MeOH (0.5 M) in 3.5 mL MeOH. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) to afford 0.31 g (0.44 mmol, 88%) of the desired product **166b** as a colorless solid.



M($C_{32}H_{51}NO_{12}Si_2$) 697.93 g/mol.

R_f (SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) = 0.11.

^{1}H-NMR (400 MHz, MeOD-d_4) δ [ppm] = 8.32 (s, 1H, H-19), 7.93 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H, H-21), 7.87 (m, 2H, H-16, H-17), 7.55 (d, $^{4}J_{HH}$ = 2.4 Hz, 1H, H-14), 7.38 (dd, $^{3,4}J_{HH}$ = 9.0, 2.4 Hz, 1H, H-22), 5.25 (d, $^{3}J_{HH}$ = 3.8 Hz, 1H, H-12), 5.16 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, H-6), 4.03 – 3.96 (m, 1H, H-7), 3.93 – 3.85 (m, 2H, H-7‘, H-1), 3.84 - 3.78 (m, 1H, H-1‘), 3.77 – 3.66 (m, 4H, H-2, H-3, H-4, H-8, H-10), 3.64 – 3.59 (m, 1H, H-5), 3.51 – 3,47 (m, 1H, H-11), 3.41 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, H-24), 3.32 – 3.28 (m, 1H, H-9), 1.73 - 1.63 (m, 2H, H-25), 0.66 – 0.58 (m, 2H, H-26), 0.07 (s, 6H, H-27), 0.05 (s, 9H, H-29), -0.21 (s, 2H, H-28).

^{13}C-NMR (101 MHz, MeOD-d_4) δ [ppm] = 168.8 (C-23), 156.8 (C-13), 136.0 (C-20), 130.1 (C-21), 130.0 (C-18), 128.8 (C-15), 127.1 (C-19), 127.1 (C-17), 124.0 (C-16), 119.5 (C-22), 110.2 (C-14), 101.5 (C-6), 100.5 (C-12), 79.5 (C-8), 76.3 (C-4), 75.4 (C-3), 73.7 (C-10), 73.4 (C-2), 73.1 (C-11), 72.7 (C-5), 70.1 (C-9), 61.3 (C-7), 60.6 (C-1), 42.9 (C-24), 23.8 (C-25), 14.7 (C-26), 1.7 (C-28), 0.1 (C-29), -1.8 (C-27).

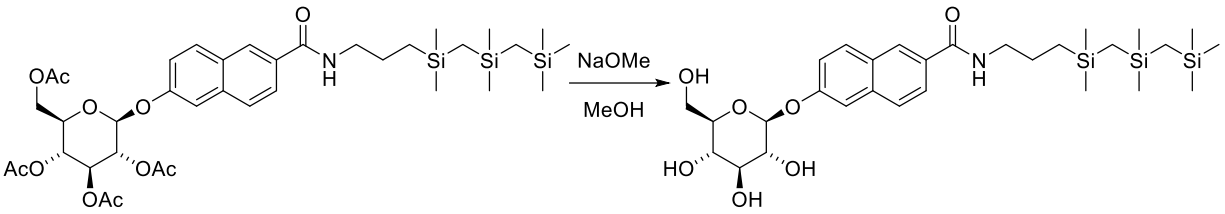
^{29}Si-NMR (119 MHz, MeOD-d_4) δ [ppm] = 1.87, 0.24.

FT-IR ATR, ν [cm^{-1}] = 3379 (w), 2953 (w), 2923 (w), 2438 (w), 2124 (w), 2079 (w), 1915 (w), 1622 (s), 1604 (m), 1575 (w), 1545 (w), 1486 (m), 1455 (m), 1436 (m), 1406 (w), 1363 (w), 1312 (w), 1251 (m), 1224 (m), 1194 (m), 1170 (w), 1143 (w), 1118 (w), 1076 (s), 1048 (s), 1026 (s), 970 (m), 894 (w), 832 (s), 786 (s), 763 (s), 748 (m), 686 (m), 657 (m), 630 (m), 618 (m), 589 (m), 530 (m).

HR-MS (ESI) Calcd. $[M+H]^+$: 698.3022, found: 698.3022.

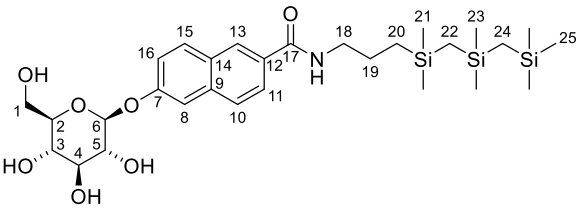
Calcd. $[M+Na]^+$: 720.2842, found: 720.2839.

11.3.5.3 Synthesis of *N*-(3-(((dimethyl((trimethylsilyl)methyl)silyl)methyl) dimethylsilyl)propyl)-6-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl) tetrahydro-2*H*-pyran-2-yl)oxy)-2-naphthamide (167a)



164a **167a**

According to **GP18**, 0.37 g (0.67 mmol, 1.00 eq.) of compound **164a** were deprotected with 0.68 mL (0.34 mmol, 0.50 eq.) NaOMe in MeOH (0.5 M) in 4 mL MeOH. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 5:5:1) to afford 0.26 g (0.42 mmol, 63%) of the desired product **167a** as a colorless solid.



M($C_{29}H_{49}NO_7Si_3$) 607.97 g/mol.

R_f (SiO_2, *c*Hex/EtOAc/MeOH 4:4:1) = 0.28.

^{1}H-NMR (400 MHz, MeOD-d_4) δ [ppm] = 8.32 (m, 1H, H-13), 7.93 (d, $^3J_{HH}$ = 9.0 Hz, 1H, H-15), 7.87 (m, 2H, H-10, H-11), 7.56 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H8), 7.39 (dd, $^{3,4}J_{HH}$ = 9.0, 2.5 Hz, 1H, H-16), 5.15 – 5.09 (m, 1H, H-6), 3.97 (dd, $^{2,4}J_{HH}$ = 12.0, 2.3 Hz, 1H, H-1), 3.75 (dd, $^{2,3}J_{HH}$ = 12.1, 5.8 Hz, 1H, H-1‘), 3.61 – 3.56 (m, 1H, H-2), 3.56 – 3.53 (m, 2H, H-4, H-5), 3.474 – 3.38 (m, 3H, H-3, H-18), 1.73 – 1.62 (m, 2H, H-19), 0.67 – 0.59 (m, 2H, H-20), 0.09 (s, 6H, H-21), 0.07 (s, 6H, H-23), 0.03 (s, 9H, H-25), -0.18 (s, 2H, H-22), -0.20 (s, 2H, H-24).

^{13}C-NMR (101 MHz, MeOD-d_4) δ [ppm] = 168.8 (C-17), 156.9 (C-7), 136.0 (C-14), 130.1 (C-15), 130.0 (C-12), 128.8 (C-9), 127.1 (C-13), 127.0 (C-11), 123.9 (C-10), 119.5 (C-16), 110.3 (C-8), 100.7 (C-6), 76.9 (C-2), 76.6 (C-5), 73.5 (C-4), 70.0 (C-3), 61.1

(C-1), 42.9 (C-18), 23.8 (C-19), 14.8 (C-20), 5.1 (C-22), 3.3 (C-24), 1.4 (C-21), 0.2 (C-25), -1.7 (C-23).

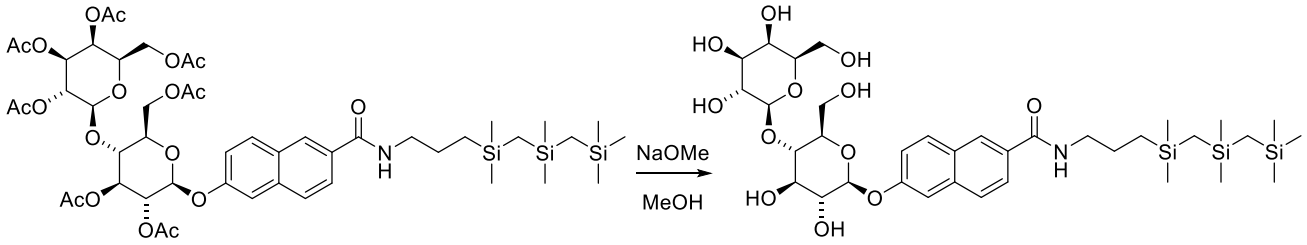
^{29}Si-NMR (119 MHz, MeOD-d_4) δ [ppm] = 1.64, 0.56, -0.06.

FT-IR ATR, ν [cm^{-1}] = 3352 (s), 2952 (m), 2472 (m), 2080 (w), 1625 (s), 1605 (m), 1545 (m), 1485 (s), 1454 (m), 1408 (m), 1363 (m), 1313 (m), 1250 (s), 1221 (m), 1194 (m), 1142 (m), 1116 (m), 1101 (m), 1076 (s), 1048 (s), 971 (m), 833 (s), 812 (s), 754 (s), 684 (s), 657 (s), 631 (s), 541 (s).

HR-MS (ESI) Calcd. $[M+H]^+$: 608.2889, found: 608.2894.

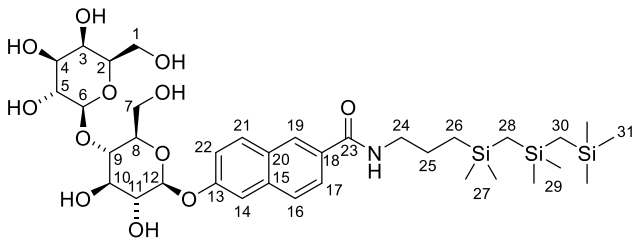
Calcd. $[M+Na]^+$: 630.2709, found: 630.2713.

11.3.5.4 Synthesis of 6-(((2*S*,3*R*,4*R*,5*S*,6*R*)-3,4-dihydroxy-6-(hydroxymethyl)-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)-*N*-(3-(((dimethyl((trimethylsilyl)methyl)silyl)methyl)dimethylsilyl)propyl)-2-naphthamide (167b)



164b **167b**

According to **GP18**, 0.57 g (0.54 mmol, 1.00 eq.) of compound **164b** were deprotected with 0.54 mL (0.27 mmol, 0.50 eq.) NaOMe in MeOH (0.5 M) in 3 mL MeOH. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) to afford 0.32 g (0.41 mmol, 76%) of the desired product **167b** as a colorless solid.



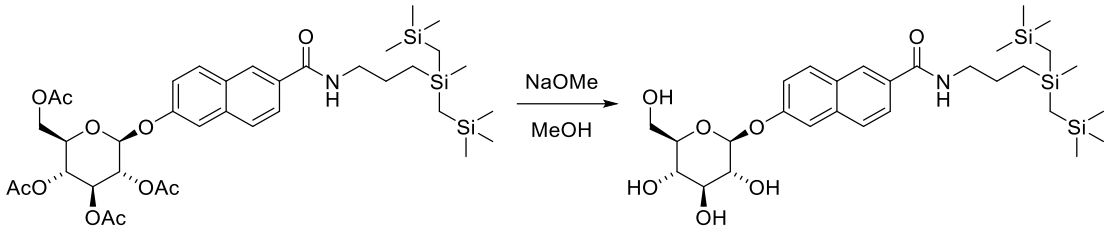
M($C_{35}H_{59}NO_{12}Si_3$) 770.11 g/mol.

R_f (SiO_2, *c*Hex/EtOAc/MeOH 4:4:1) = 0.28.

^{1}H-NMR (600 MHz, MeOD-d_4) δ [ppm] = 8.32 (s, 1H, H-19), 7.93 (d, $^3J_{HH}$ = 9.0 Hz, 1H, H-21), 7.87 (m, 2H, H-16, H-17), 7.55 (d, $^4J_{HH}$ =

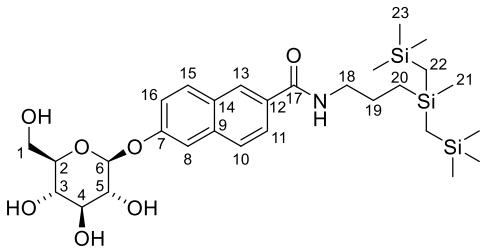
	2.5 Hz, 1H, H-14), 7.38 (dd, $^{3,4}J_{HH}$ = 8.9, 2.4 Hz, 1H, H-22), 5.25 (d, $^{4}J_{HH}$ = 3.8 Hz, 1H, H-12), 5.16 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, H-6), 3.99 (dd, $^{2,4}J_{HH}$ = 12.4, 1.3 Hz, 1H, H-7), 3.91 – 3.86 (m, 2H, H-1, H-7‘), 3.83 – 3.80 (m, 1H, H-4), 3.75 (m, 1H, H-2), 3.72 – 3.69 (m, 3H, H-1‘, H-3, H-8), 3.69 – 3.64 (m, 1H, H-10), 3.61 (dd, $^{3}J_{HH}$ = 9.4, 7.7 Hz, 1H, H-5), 3.50 (m, 1H, H-11), 3.42 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, H-24), 3.32 – 3.29 (m, 1H, H-9), 1.73 - 1.64 (m, 2H, H-25), 0.66 – 0.61 (m, 2H, H-26), 0.09 (s, 6H, H-27), 0.08 (s, 6H, H-29), 0.03 (s, 9H, H-31),-0.18 (s, 2H, H-28), -0.21 (s, 2H, H-30).
^{13}C-NMR	(151 MHz, MeOD-d_4) δ [ppm] = 168.8 (C-23), 156.8 (C-13), 136.0 (C-20), 130.1 (C-21), 130.0 (C-18), 128.8 (C-15), 127.1 (C-19), 127.2 (C-17), 124.0 (C-16), 119.4 (C-22), 110.3 (C-14), 101.5 (C-6), 100.5 (C-12), 79.5 (C-8), 76.3 (C-4), 75.4 (C-3), 73.7 (C-10), 73.4 (C-2), 73.1 (C-11), 72.8 (C-5), 70.1 (C-9), 61.3 (C-7), 60.6 (C-1), 42.9 (C-24), 23.8 (C-25), 14.8 (C-26), 5.1 (C-28), 3.3 (C-30), 1.4 (C-27), 0.2 (C-31), -1.7 (C-29).
^{29}Si-NMR	(119 MHz, MeOD-d_4) δ [ppm] = 1.64, 0.55, -0.06.
FT-IR	ATR, ν [cm^{-1}] = 3343 (m), 2951 (m), 2896 (w), 2478 (m), 2240 (w), 2133 (w), 2071 (w), 1924 (w), 1631 (m), 1603 (m), 1485 (s), 1452 (m), 1391 (m), 1364 (m), 1312 (m), 1251 (m), 1225 (m), 1194 (m), 1150 (m), 1118 (m), 1043 (s), 976 (s), 861 (s), 835 (s), 813 (s), 764 (m), 686 (m), 659 (m), 629 (m), 566 (m), 535 (m).
HR-MS (ESI)	Calcd. $[M+H]^+$: 770.3417, found: 770.3423. Calcd. $[M+Na]^+$: 792.3237, found: 792.3240.

11.3.5.5 Synthesis of *N*-(3-(methylbis((trimethylsilyl)methyl)silyl)propyl)-6-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl) oxy)-2-naphthamide (168a)



165a **168a**

According to **GP18**, 0.23 g (0.30 mmol, 1.00 eq.) of compound **165a** were deprotected with 0.30 mL (0.15 mmol, 0.50 eq.) NaOMe in MeOH (0.5 M) in 10 mL MeOH. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) to afford 0.15 g (0.24 mmol, 80%) of the desired product **168a** as a colorless solid.



M($C_{29}H_{49}NO_7Si_3$) 607.97 g/mol.

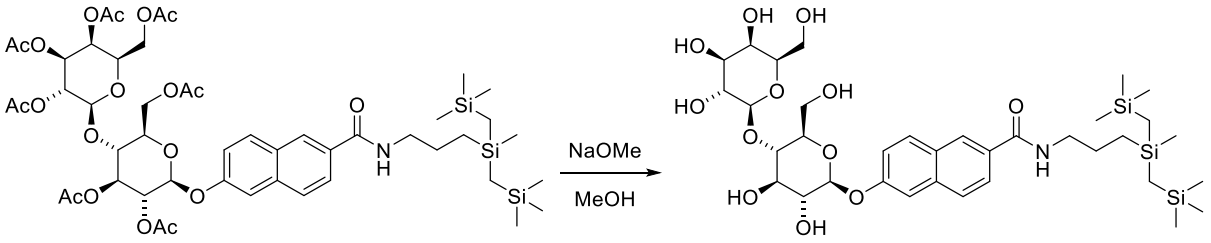
R_f (SiO_2, CH_2Cl_2/MeOH 4:1) = 0.28.

^{1}H-NMR (600 MHz, MeOD-*d_4*) δ [ppm] = 8.35 – 8.30 (m, 1H, H-13), 7.92 (dd, $^{3,4}J_{HH}$ = 9.2, 1.3 Hz, 1H, H-15), 7.87 (m, 2H, H-10, H-11), 7.56 (d, $^{4}J_{HH}$ = 2.5 Hz, 1H, H-8), 7.39 (dd, $^{3,4}J_{HH}$ = 9.0, 2.4 Hz, 1H, H-16), 5.15 – 5.10 (m, 1H, H-6), 3.97 (dd, $^{2,4}J_{HH}$ = 12.0, 2.3 Hz, 1H, H-1), 3.75 (dd, $^{2,3}J_{HH}$ = 12.0, 5.8 Hz, 1H, H-1‘), 3.62 - 3.57 (m, 1H, H-5), 3.56 – 3.53 (m, 2H, H-4, H-3), 3.48 - 3.44 (m, 1H, H-2), 3.42 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, H-18), 1.71 - 1.63 (m, 2H, H-19), 0.67 – 0.58 (m, 2H, H-20), 0.08 (s, 3H, H-21), 0.06 (s, 9H, H-23), 0.03 (s, 9H, H-23‘), -0.18 (s, 2H, H-22), -0.21 (s, 2H, H-22‘).

^{13}C-NMR (101 MHz, MeOD-*d_4*) δ [ppm] = 168.8 (C-17), 156.9 (C-7), 136.0 (C-14), 130.1 (C-12), 130.0 (C-15), 128.8 (C-9), 127.1 (C-13), 127.0 (C-11), 123.9(C-10), 119.51 (C-16), 110.3 (C-8),

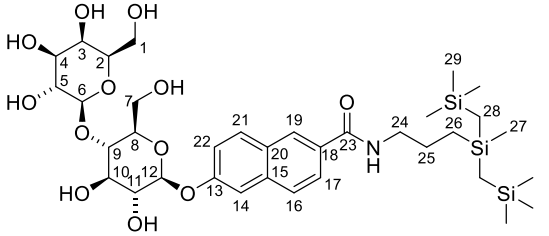
	100.7 (C-6), 76.9 (C-2), 76.6 (C-5), 73.5 (C-4), 70.0 (C-3), 61.1 (C-1), 42.9 (C-18), 23.8 (C-19), 14.8 (C-20), 3.3 (C-22), 1.4 (C-21), 0.3 (C-23), 0.2 (C-23‘).
^{29}Si-NMR	(119 MHz, MeOD-d_4) δ [ppm] = 0.56, -0.06.
FT-IR	ATR, ν [cm^{-1}] = 3288 (w), 2952 (w), 2896 (w), 1722 (w), 1635 (m), 1605 (w), 1539 (m), 1503 (w), 1478 (w), 1408 (w), 1362 (w), 1311 (w), 1249 (m), 1214 (m), 1178 (w), 1045 (s), 934 (w), 896 (w), 831 (s), 807 (s), 756 (m), 685 (m), 627 (m), 530 (m), 473 (m), 424 (w), 417 (w).
HR-MS (ESI)	Calcd. [M+H]$^+$: 608.2889, found: 608.2817.
	Calcd. [M+Na]$^+$: 630.2709, found: 630.2710.

11.3.5.6 Synthesis of 6-(((2*S*,3*R*,4*R*,5*S*,6*R*)-3,4-dihydroxy-6-(hydroxymethyl)-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)-*N*-(3-(methylbis((trimethylsilyl)methyl)silyl)propyl)-2-naphthamide (168b)



165b **168b**

According to **GP18**, 0.32 g (0.30 mmol, 1.00 eq.) of compound **165b** were deprotected with 0.30 mL (0.15 mmol, 0.50 eq.) NaOMe in MeOH (0.5 M) in 2 mL MeOH. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) to afford 0.18 g (0.24 mmol, 80%) of the desired product **168b** as a colorless solid.



M($C_{35}H_{59}NO_{12}Si_3$)	770.11 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) = 0.37.

^{1}H-NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.32 (m, 1H, H-19), 7.93 (m, 1H, H-21), 7.87 (m, 2H, H-16, H-17), 7.55 (d, $^{4}J_{HH}$ = 2.5 Hz, 1H, H-14), 7.38 (dd, $^{3,4}J_{HH}$ = 8.9, 2.5 Hz, 1H, H-22), 5.25 (d, $^{3}J_{HH}$ = 3.8 Hz, 1H, H-12), 5.16 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, H-6), 4.00 - 3.97 (m, 1H, H-7), 3.92 – 3.85 (m, 2H, H-1, H-7‘), 3.84 - 3.79 (m, 1H, H-4), 3.75 (m, 1H, H-2), 3.70 (m, 3H, H-1‘, H-3, H-8), 3.68 – 3.65 (m, 1H, H-10), 3.61 (m, 1H, H-5), 3.50 (m, 1H, H-11), 3.42 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, H-24), 3.32 – 3.28 (m, 1H, H-9), 1.72 – 1.62 (m, 2H, H-25), 0.70 – 0.58 (m, 2H, H-26), 0.11 – 0.03 (m, 21H, H-27, H-29), -0.17 – -0.22 (m, 4H, H-28).

^{13}C-NMR (126 MHz, MeOD-d_4) δ [ppm] = 168.8 (C-23), 156.8 (C-13), 136.0 (C-18), 130.1 (C-20), 130.1 (C-21), 128.8 (C-15), 127.1 (C-19), 127.1 (C-17), 124.0 (C-16), 119.4 (C-22), 110.3 (C-14), 101.5 (C-6), 100.5 (C-12), 79.5 (C-8), 76.3 (C-4), 75.4 (C-3), 73.7 (C-10), 73.4 (C-2), 73.1 (C-11), 72.7 (C-5), 70.1 (C-9), 61.3 (C-7), 60.6 (C-1), 42.9 (C-24), 23.8 (C-25), 14.8 (C-26), 2.9 (C-28), 1.4 (C-27), 0.3 (C-29).

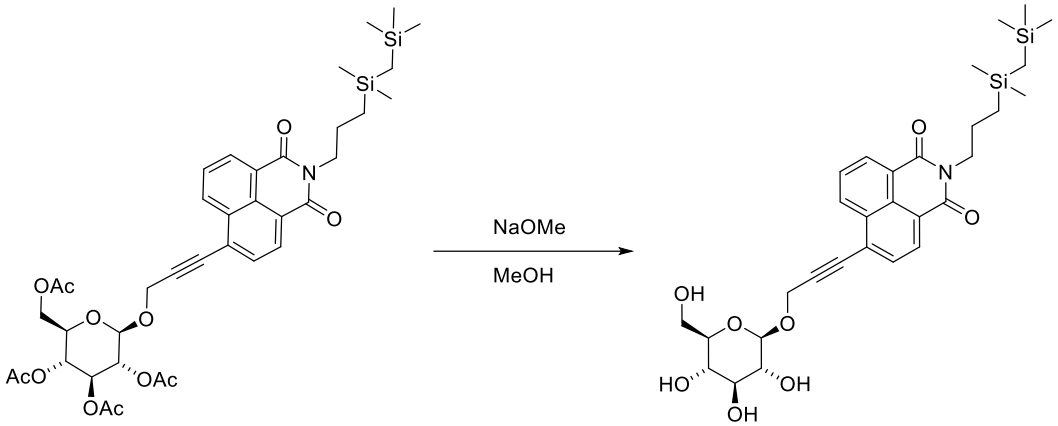
^{29}Si-NMR (119 MHz, MeOD-d_4) δ [ppm] = 1.64, 0.07.

FT-IR ATR, ν [cm^{-1}] = 3351 (m), 2951 (m), 2896 (m), 2481 (m), 2236 (w), 2134 (w), 2074 (w), 1631 (m), 1603 (m), 1485 (s), 1451 (m), 1408 (m), 1392 (m), 1364 (m), 1312 (m), 1249 (s), 1224 (m), 1194 (m), 1149 (m), 1116 (m), 1044 (s), 975 (m), 897 (m), 835 (s), 811 (s), 764 (s), 686 (s), 659 (s), 630 (s), 579 (m).

HR-MS (ESI) Calcd. $[M+H]^+$: 770.3417, found: 770.3423.

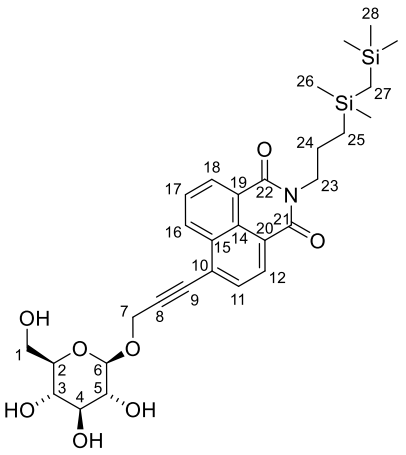
Calcd. $[M+Na]^+$: 792.3237, found: 792.3238.

11.3.5.7 Synthesis of (2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-((3-(2-(3-(dimethyl((trimethylsilyl)methyl)silyl)propyl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[de]isoquinoline-6-yl)prop-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (169a)



161a **169a**

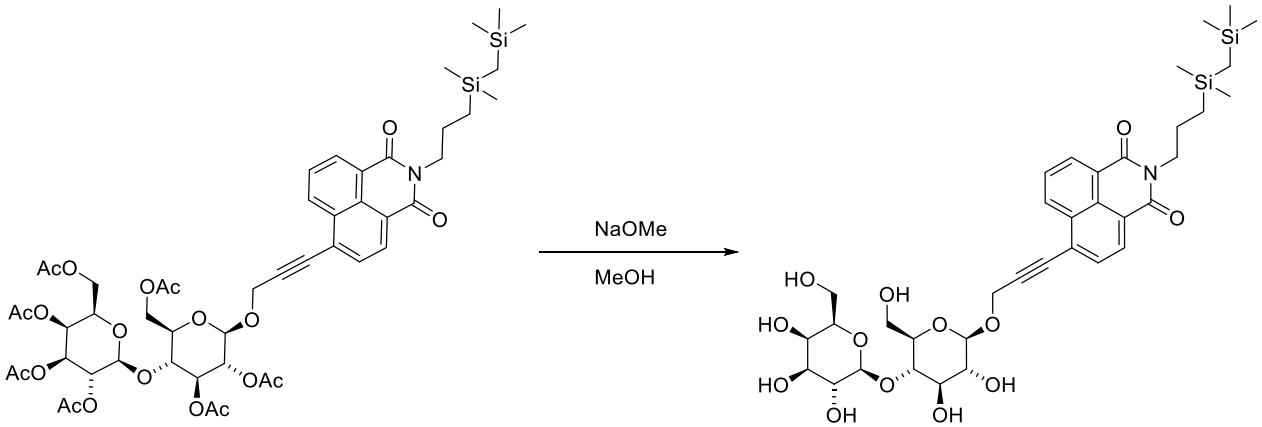
According to **GP18**, 0.23 g (0.30 mmol, 1.00 eq.) of compound **161a** were deprotected with 0.30 mL (0.15 mmol, 0.50 eq.) NaOMe in MeOH (0.5 M) in 2 mL MeOH. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 10:10:1) to afford 0.68 g (0.11 mmol, 38%) of the desired product **169a** as an orange solid.



M($C_{30}H_{41}NO_8Si_2$)	599.83 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc/MeOH 5:5:1) = 0.60.
^{1}H-NMR	(500 MHz, MeOD-d_4) δ [ppm] = 8.53 (dd, $^{3,4}J_{HH}$ = 8.4, 1.2 Hz, 1H, H-16), 8.43 (dd, $^{3,4}J_{HH}$ = 7.3, 1.2 Hz, 1H, H-18), 8.31 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-12), 7.78 – 7,74 (m, 2H, H-11, H-17), 4.89 (s, 2H, H-7), 4.66 (s, 1H, H-6), 4.06 – 4.02 (m, 2H, H-23), 3.96 (dd, $^{2,3}J_{HH}$ = 11.9, 2.1 Hz, 1H, H-1), 3.78 – 3.74 (m, 1H, H-1‘), 3.48 - 3.46 (m, 1H, H-3), 3.39 – 3.36 (m, 2H, H-2, H-5),

	1.74 – 1.67 (m, 2H, H-24), 0.64 – 0.58 (m, 2H, H-25), 0.05 (s, 6H, H-26), 0.03 (s, 9H, H-28), -0.20 - -0.24 (2H, H-27).
^{13}C-NMR	(101 MHz, MeOD-d_4) δ [ppm] = 163.6 (C-22), 163.3 (C-21), 132.0 (C-16), 131.2 (C-19), 131.0 (C-18), 130.5 (C-17), 129.6 (C-12), 127.4 (C-11), 127.3 (C-20), 126.5 (C-10), 122.3 (C-14), 121.8 (C-15), 101.3 (C-6), 94.7 (C-9), 82.4 (C-8), 76.8 (C-2), 76.6 (C-4), 73.6 (C-3), 70.2 (C-5), 61.4 (C-1), 56.1 (C-7), 42.9 (C-23), 22.2 (C-24), 14.6 (C-25), 1.7 (C-28), 0.1 (C-26), -1.7 (C-27).
FT-IR	ATR, ν [cm^{-1}] = 3370 (m), 2952 (m), 2896 (w), 2119 (w), 1775 (w), 1701 (m), 1660 (s), 1615 (w), 1590 (m), 1514 (w), 1441 (w), 1385 (m), 1351 (s), 1247 (s), 1156 (m), 1075 (s), 1051 (s), 860 (m), 836 (s), 784 (s), 755 (m), 734 (m), 687 (m), 649 (m), 620 (m), 581 (m).
HR-MS (ESI)	Calcd. [M+H]$^+$: 600.2443, found: 600.2444.
	Calcd. [M+Na]$^+$: 622.2262, found: 622.2264.

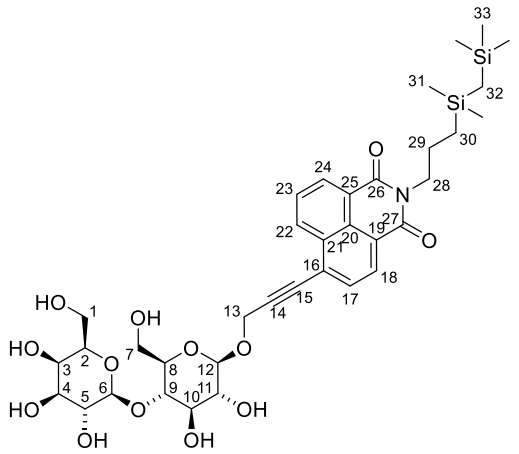
11.3.5.8 Synthesis of 6-(3-(((2*R*,3*R*,4*R*,5*S*,6*R*)-3,4-dihydroxy-6-(hydroxymethyl)-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)-2-(3-(dimethyl((trimethylsilyl)methyl)silyl)propyl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione (169b)



161b **169b**

According to **GP18**, 0.63 g (0.59 mmol, 1.00 eq.) of compound **161a** were deprotected with 0.60mL (0.30 mmol, 0.50 eq.) NaOMe in MeOH (0.5 M) in 4 mL MeOH. The crude

product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) to afford 0.32 g (0.41 mmol, 70%) of the desired product **169b** as an orange solid.



M($C_{36}H_{51}NO_{13}Si_2$) 761.97 g/mol.

R_f (SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) = 0.47.

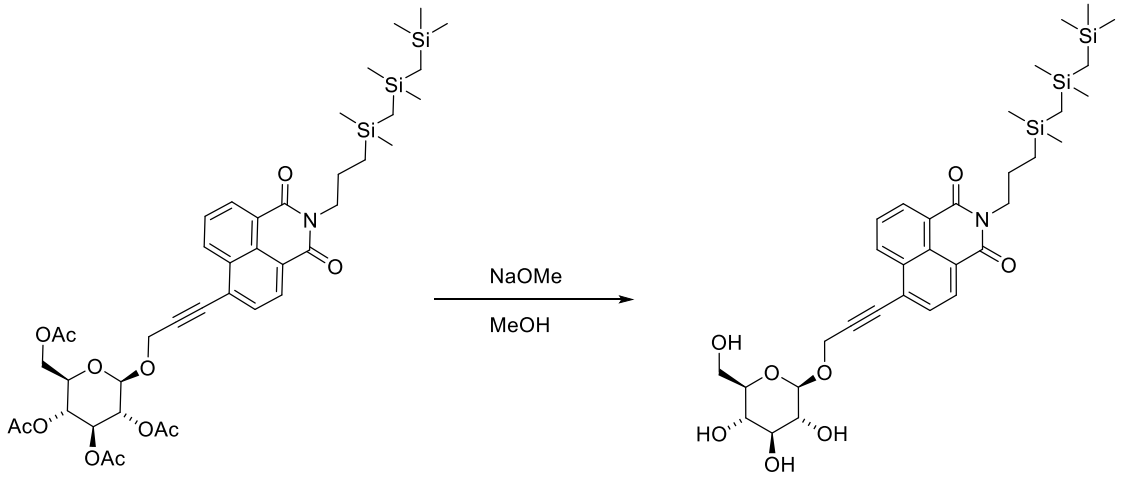
^{1}H-NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.73 (dd, $^{3,4}J_{HH}$ = 8.4, 1.2 Hz, 1H, H-22), 8.60 (dd, $^{3,4}J_{HH}$ = 7.3, 1.2 Hz, 1H, H-24), 8.50 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-18), 7.94 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-17), 7.93 - 7.90 (m, 1H, H-23), 5.21 (d, $^{4}J_{HH}$ = 3.8 Hz, 1H, H-12), 4.89 (m, 2H, H-13), 4.67 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, H-6), 4.15 – 4.10 (m, 2H, H-28), 3.97 (dd, $^{2,4}J_{HH}$ = 12.2, 2.1 Hz, 1H, H-7), 3.89 – 3.83 (m, 2H, H-1, H-7‘), 3.74 – 3.69 (m, 3H, H-1‘, H-3, H-11), 3.66 – 3.58 (m, 2H, H-4, H-10), 3.53 – 3.44 (m, 2H, H-2, H-8), 3.40 – 3.36 (m, 1H, H-5), 3.29 (m, 1H, H-9), 1.79 – 1.69 (m, 2H, H-29), 0.67 - 0.58 (m, 2H, H-30), 0.06 (s, 6H, H-31), 0.03 (s, 9H, H-33), -0.22 (s, 2H, H-32).

^{13}C-NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.9 (C-26), 163.6 (C-27), 132.2(C-22), 131.59 (C-25), 131.2 (C-24), 130.7 (C-17), 129.8 (C-18), 127.6 (C-19), 127.5 (C-23), 126.7 (C-16), 122.6 (C-20), 122.2 (C-21), 101.5 (C-12), 101.3 (C-6), 94.5 (C-15), 82.5 (C-14), 79.8 (C-10), 76.4 (C-11), 75.4 (C-8), 73.6 (C-4), 73.4 (C-3), 73.1 (C-5), 72.7 (C-2), 70.1 (C-9), 61.3 (C-1), 60.8 (C-7), 56.1 (C-13), 42.8 (C-28), 22.2 (C-29), 14.6 (C-30), 1.7 (C-32), 0.1 (C-33), -1.8 (C-31).

^{29}Si-NMR (119 MHz, MeOD-d_4) δ [ppm] = 1.87, 0.24.

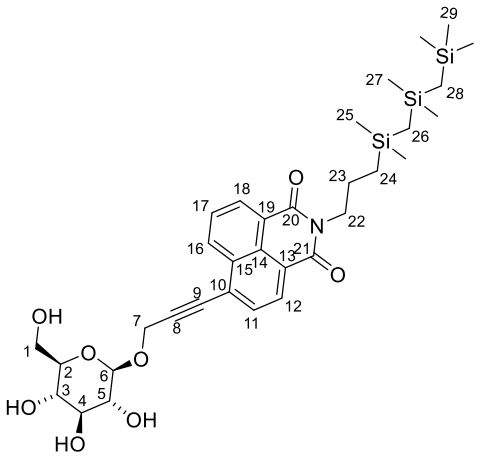
FT-IR	ATR, ν [cm^{-1}] = 3350 (m), 2952 (m), 2895 (w), 2481 (m), 2239 (m), 2137 (w), 2073 (m), 1927 (w), 1700 (m), 1652 (m), 1614 (m), 1589 (m), 1509 (w), 1441 (m), 1385 (m), 1354 (s), 1247 (m), 1150 (m), 1118 (s), 1076 (s), 1047 (s), 974 (s), 837 (s), 783 (s), 755 (s), 705 (m), 687 (s), 582 (s), 559 (s).
HR-MS (ESI)	Calcd. $[M+H]^+$: 762.2971, found: 762.2986.
	Calcd. $[M+Na]^+$: 784.2791, found: 784.2794.

11.3.5.9 Synthesis of 2-(3-(((dimethyl((trimethylsilyl)methyl)silyl)methyl) dimethylsilyl)propyl)-6-(3-(((2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl) tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione (170a)



162a **170a**

According to **GP18**, 0.55 g (0.66 mmol, 1.00 eq.) of compound **162a** were deprotected with 0.06mL (0.33 mmol, 0.50 eq.) NaOMe in MeOH (5.4 M) in 4 mL MeOH. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 10:10:1) to afford 0.22 g (0.32 mmol, 49%) of the desired product **170a** as an orange solid.



M($C_{33}H_{49}NO_8Si_3$) 672.01 g/mol.

R_f (SiO_2, *c*Hex/EtOAc/MeOH 5:5:1) = 0.13.

^{1}H-NMR (400 MHz, MeOD-*d*$_4$) δ [ppm] = 8.75 – 8.66 (m, 1H, H-16), 8.63 - 8.53 (m, 1H, H-18), 8.51 – 8.43 (m, 1H, H-12), 7.96 - 7.85 (m, 2H, H-11, H-17), 4.89 (s, 2H, H-7), 4.66 (dd, $^{3,4}J_{HH}$ = 7.7, 0.9 Hz, 1H, H-6), 4.12 (m, 2H, H-22), 3.98 – 3.92 (m, 1H, H-1), 3.73 (dd, $^{2,3}J_{HH}$ = 11.9, 5.4 Hz, 1H, H-1‘), 3.48 – 3.34 (m, 4H, H-2, H-3, H-4, H-5), 1.78 – 1.69 (m, 2H, H-23), 0.66 – 0.58 (m, 2H, H-24), 0.06 (s, 6H, H-25), 0.05 (s, 6H, H-27), 0.01 (s, 9H, H-29), -0.20 (s, 2H, H-26), -0.23 (s, 2H, H-28).

^{13}C-NMR (101 MHz, MeOD-*d*$_4$) δ [ppm] = 163.8 (C-20), 163.5 (C-21), 132.2 (C-16), 131.5 (C-19), 131.2 (C-18), 130.6 (C-11), 129.8 (C-12), 127.6 (C-13), 127.5 (C-17), 126.7 (C-10), 122.6 (C-14), 122.1 (C-15), 101.3 (C-6), 94.6 (C-9), 82.4 (C-8), 76.8 (C-4), 76.6 (C-5), 73.5 (C-3), 70.2 (C-2), 61.4 (C-1), 56.0 (C-7), 42.8 (C-22), 22.2 (C-23), 14.6 (C-24), 5.0 (C-26), 3.3 (C-28), 1.3 (C-25), 0.2 (C-29), -1.6 (C-27).

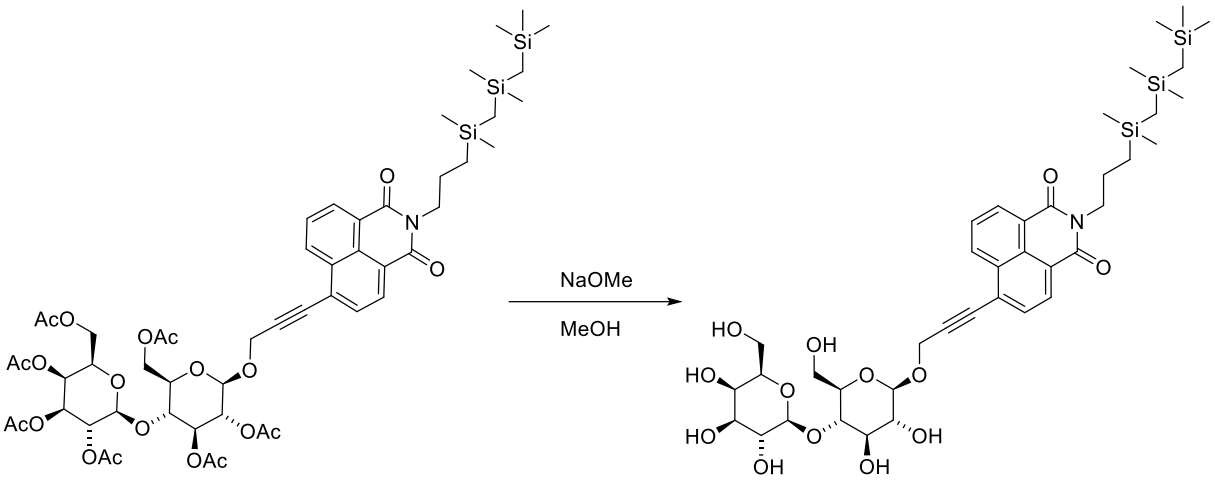
^{29}Si-NMR (79 MHz, MeOD-*d*$_4$) δ [ppm] = 1.70, 0.51, -0.07.

FT-IR ATR, ν [cm^{-1}] = 3353 (s), 2952 (m), 2897 (w), 2488 (m), 2079 (w), 1700 (m), 1651 (s), 1615 (m), 1591 (m), 1440 (m), 1405 (m), 1385 (m), 1351 (m), 1247 (s), 1157 (m), 1115 (m), 1046 (s), 974 (m), 833 (s), 811 (s), 785 (s), 755 (s), 685 (s), 597 (s).

HR-MS (ESI) Calcd. $[M+H]^+$: 672.2838, found: 672.2846.

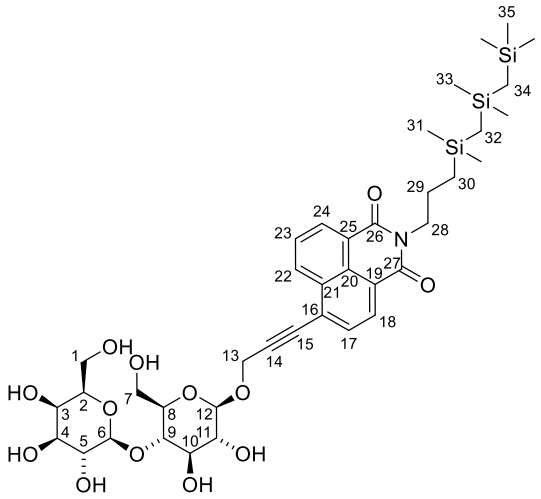
Calcd. $[M+Na]^+$: 694.2658, found: 694.2664.

11.3.5.10 Synthesis of 6-(3-(((2*R*,3*R*,4*R*,5*S*,6*R*)-3,4-dihydroxy-6-(hydroxymethyl)-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)-2-(3-(((dimethyl((trimethylsilyl)methyl)silyl)methyl)dimethylsilyl)propyl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione (170b)



162b **170b**

According to **GP18**, 0.72 g (0.63 mmol, 1.00 eq.) of compound **162b** were deprotected with 0.64mL (0.32 mmol, 0.50 eq.) NaOMe in MeOH (0.5 M) in 4 mL MeOH. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 5:5:1) to afford 0.33 g (0.39 mmol, 61%) of the desired product **170b** as an orange solid.



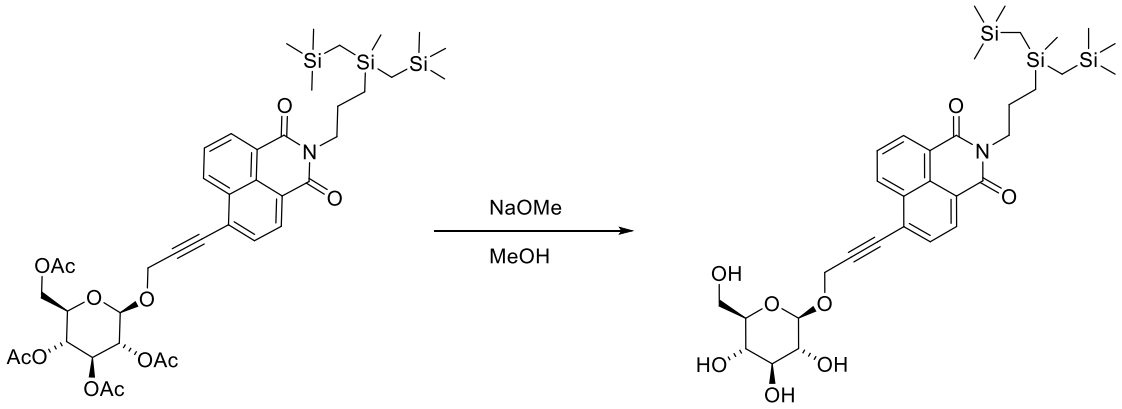
M($C_{39}H_{59}NO_{13}Si_3$) 834.15 g/mol.

R_f (SiO_2, *c*Hex/EtOAc/MeOH 5:5:1) = 0.55.

^{1}H-NMR (600 MHz, MeOD-d_4) δ [ppm] = 8.72 (dd, $^{3,4}J_{HH}$ = 8.4, 1.1 Hz, 1H, H-22), 8.59 (dd, $^{3,4}J_{HH}$ = 7.3, 1.1 Hz, 1H, H-24), 8.49 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-18), 7.93 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-17), 7.90 (dd, $^{3,3}J_{HH}$ = 8.4, 7.3 Hz, 1H, H-23), 5.21 (d, $^{3}J_{HH}$ = 3.8 Hz,

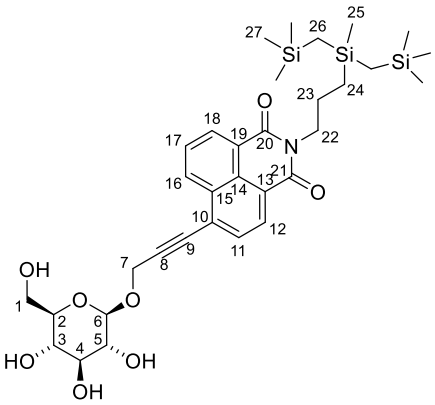
	1H, H-12), 4.92 – 4.86 (m, 2H, H-13), 4.67 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, H-6), 4.15 – 4.10 (m, 2H, H-28), 3.97 (dd, $^{2,4}J_{HH}$ = 12.3, 2.1 Hz, 1H, H-7), 3.88 – 3.83 (m, 2H, H-1, H-7‘), 3.73 – 3.68 (m, 3H, H-3, H-4, H-1‘), 3.65 – 3.58 (m, 2H, H-10, H-11), 3.50 - 3.45 (m, 2H, H-2, H-8), 3.38 (dd, $^{3,3}J_{HH}$ = 9.3, 7.7 Hz, 1H, H-5), 3.29 (m, 1H, H-9), 1.77 – 1.70 (m, 2H, H-29), 0.65 – 0.60 (m, 2H, H-30), 0.06 (s, 6H, H-31), 0.06 (s, 6H, H-33), 0.01 (s, 9H, H-35), -0.20 (s, 2H, H-32), -0.23 (s, 2H, H-34).
^{13}C-NMR	(151 MHz, MeOD-d_4) δ [ppm] = 163.8 (C-26), 163.5 (C-27), 132.2 (C-22), 131.5 (C-25), 131.2 (C-24), 130.7 (C-17), 129.8 (C-18), 127.6 (C-19), 127.5 (C-23), 126.7 (C-16), 122.6 (C-20), 122.1 (C-21), 101.5 (C-12), 101.3 (C-6), 94.6 (C-15), 82.5 (C-14), 79.8 (C-2), 76.4 (C-4), 75.4 (C-8), 73.6 (C-10), 73.4 (C-3), 73.1 (C-5), 72.7 (C-11), 70.1 (C-9), 61.3 (C-1), 60.8 (C-7), 56.1 (C-13), 42.8 (C-28), 22.2 (C-29), 14.6 (C-30), 5.0 (C-32), 3.3 (C-34), 1.3 (C-31), 0.2 (C-35), -1.6 (C-33).
^{29}Si-NMR	(119 MHz, MeOD-d_4) δ [ppm] = 1.70, 0.50, -0.08.
FT-IR	ATR, ν [cm^{-1}] = 3339 (s), 2953 (m), 2499 (w), 2199 (w), 2080 (w), 1699 (m), 1648 (m), 1590 (m), 1509 (w), 1441 (m), 1385 (m), 1354 (m), 1248 (m), 1149 (m), 1042 (m), 976 (m), 833 (s), 783 (s), 754 (s), 681 (s), 603 (s), 594 (s).
HR-MS (ESI)	Calcd. [M+Na]$^{+}$: 856.3186, found: 856.3189.

11.3.5.11 Synthesis of 2-(3-(methylbis((trimethylsilyl)methyl)silyl)propyl)-6-(3-(((2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)-1H-benzo[de]isoquinoline-1,3(2*H*)-dione (171a)



163a **171a**

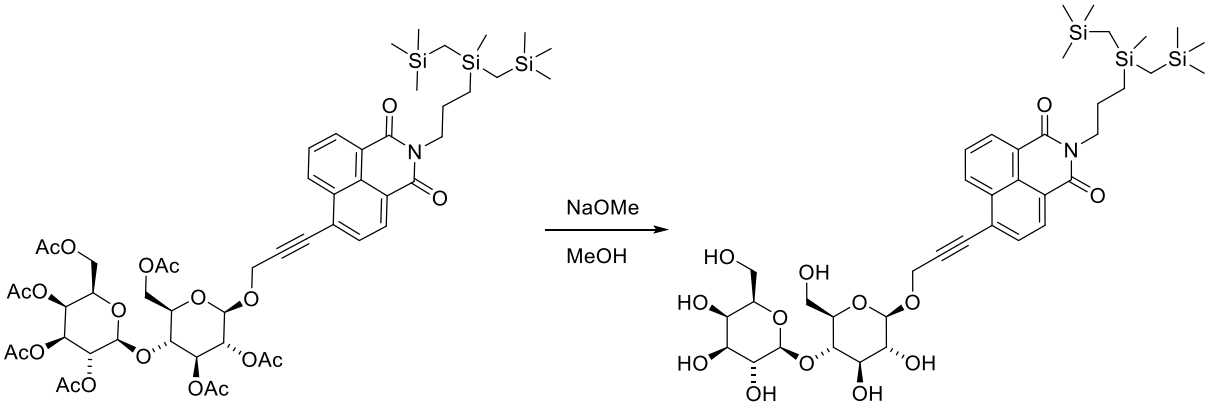
According to **GP18**, 0.26 g (0.31 mmol, 1.00 eq.) of compound **163a** were deprotected with 0.20mL (0.10 mmol, 0.30 eq.) NaOMe in MeOH (0.5M) in 10 mL MeOH. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) to afford 0.20 g (0.30 mmol, 95%) of the desired product **171a** as a red solid.



M($C_{33}H_{49}NO_8Si_3$)	672.01 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) = 0.33.
m.p.	165 – 166 °C.
^{1}H-NMR	(400 MHz, MeOD-d_4) δ [ppm] = 8.60 (m, 1H, H-16), 8.49 (m, 1H, H-18), 8.37 (dd, $^{3,4}J_{HH}$ = 7.6, 1.3 Hz, 1H, H-12), 7.82 (m, 2H, H-11, H-17), 4.90 (s, 2H, H-7), 4.67 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H-6), 4.08 (m, 2H, H-22), 3.96 (dd, $^{2,3}J_{HH}$ = 11.9, 2.2 Hz, 1H, H-1), 3.74 (dd, $^{2,3}J_{HH}$ = 11.9, 5.7 Hz, 1H, H-1‘), 3.47 (t, $^3J_{HH}$ = 8.9 Hz, 1H, H-4), 3.43 – 3.34 (m, 3H, H-2, H-3, H-5), 1.72 (m,

	2H, H-23), 0.62 (m, 2H, H-24), 0.06 – 0.01 (s, 21H, H-25, H-27), -0.19 – -0.27 (m, 4H, H-26).
^{13}C-NMR	(126 MHz, MeOD-*d*$_4$) δ [ppm] = 163.7 (C-20), 163.4 (C-21), 132.0 (C-16), 131.3 (C-19), 131.1 (C-18), 130.6 (C-11), 129.7 (C-12), 127.4 (C-17), 127.4 (C-13), 126.6 (C-10), 122.4 (C-14), 121.9 (C-15), 101.3 (C-6), 94.6 (C-9), 82.4 (C-8), 76.8 (C-4), 76.6 (C-5), 73.6 (C-3), 70.2 (C-2), 61.4 (C-1), 56.1 (C-7), 42.8 (C-22), 22.2 (C-23), 14.7 (C-24), 2.9 (C-26), 0.3 (C-27), -1.6 (C-25).
^{29}Si-NMR	(99 MHz, MeOD-*d*$_4$) δ [ppm] = 1.70, 0.04.
FT-IR	ATR, ν [cm^{-1}] = 3663 (w), 3388 (w), 2953 (m), 2901 (w), 1702 (m), 1660 (m), 1614 (w), 1589 (m), 1509 (w), 1440 (w), 1384 (m), 1350 (m), 1244 (s), 1153 (w), 1047 (s), 830 (s), 800 (s), 781 (s), 753 (s), 685 (m), 650 (m), 597 (m), 580 (m), 527 (m).
HR-MS (ESI)	Calcd. $[M+H]^+$: 672.2839, found: 672.2844. Calcd. $[M+Na]^+$: 694.2658, found: 694.2663.

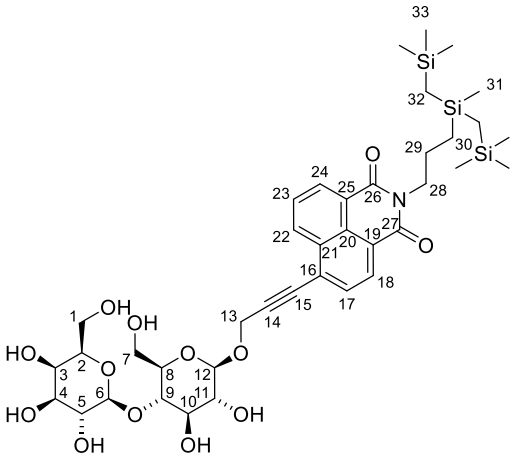
11.3.5.12 Synthesis of 6-(3-(((2*R*,3*R*,4*R*,5*S*,6*R*)-3,4-dihydroxy-6-(hydroxymethyl)-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)-2-(3-(methylbis((trimethylsilyl)methyl)silyl)propyl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione (171b)



163b **171b**

According to **GP18**, 0.37 g (0.33 mmol, 1.00 eq.) of compound **163a** were deprotected with 0.20 mL (0.10 mmol, 0.30 eq.) NaOMe in MeOH (0.5 M) in 10 mL MeOH. The

crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 1:1:1) to afford 0.14 g (0.17 mmol, 51%) of the desired product **171b** as a red solid.



M($C_{39}H_{59}NO_{13}Si_3$) 834.14 g/mol.

R_f (SiO_2, *c*Hex/EtOAc/MeOH 1:1:1) = 0.42.

m.p. 178 – 180 °C.

^{1}H-NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.57 (m, 1H, H-22), 8.47 (m, 1H, H-24), 8.35 (m, 1H, H-18), 7.83 – 7.77 (m, 2H, H-17, H-23), 5.22 (d, $^3J_{HH}$ = 3.8 Hz, 1H, H-12), 4.89 (m, 2H, H-13), 4.69 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H-6), 4.09 – 4.05 (m, 2H, H-28), 3.98 (dd, $^{2,3}J_{HH}$ = 12.2, 2.0 Hz, 1H, H-7), 3.92 – 3.84 (m, 2H, H-1, H-7‘), 3.77 – 3.61 (m, 6H, H-1‘, H-3, H-4, H-10, H-11), 3.53 – 3.47 (m, 2H, H-2, H-8), 3.42 – 3.39 (m, 1H, H-5), 3.30 (t, $^3J_{HH}$ = 9.3 Hz, 1H, H-9), 1.72 (m, 2H, H-29), 0.66 – 0.56 (m, 2H, H-30), 0.07 – 0.00 (m, 21H, H-31, H-33), -0.18 – -0.25 (m, 4H, H-32).

^{13}C-NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.6 (C-26), 163.3 (C-27), 132.0 (C-22), 131.3 (C-25), 131.1 (C-24), 130.6 (C-17), 129.7 (C-18), 127.4 (C-23), 127.3 (C-19), 126.6 (C-16), 122.4 (C-20), 121.9 (C-21), 101.5 (C-12), 101.3 (C-6), 94.6 (C-15), 82.5 (C-14), 79.8 (C-2), 76.4 (C-4), 75.4 (C-8), 73.6 (C-10), 73.4 (C-3), 73.1 (C-5), 72.7 (C-11), 70.1 (C-9), 61.3 (C-1), 60.8 (C-7), 56.2 (C-13), 42.8 (C-28), 22.3 (C-29), 14.7 (C-30), 2.9 (C-32), 1.4 (C-33), 0.3 (C-31).

^{29}Si-NMR (99 MHz, MeOD-d_4) δ [ppm] = 1.70, 0.03.

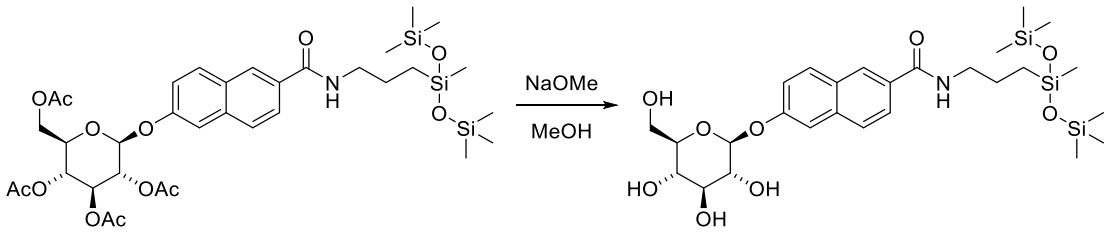
FT-IR ATR, ν [cm^{-1}] = 3376 (w), 2953 (w), 2901 (w), 1750 (w), 1702 (m), 1662 (m), 1615 (w), 1590 (w), 1511 (w), 1440 (w),

	1383 (m), 1350 (m), 1244 (m), 1154 (w), 1048 (s), 891 (w), 831 (s), 800 (s), 782 (s), 754 (s), 686 (m), 665 (m), 597 (m), 581 (m).
HR-MS (ESI)	Calcd. $[M+Na]^+$: 856.3186, found: 856.3185.

11.4 Synthesis of fluorescent siloxane surfactants

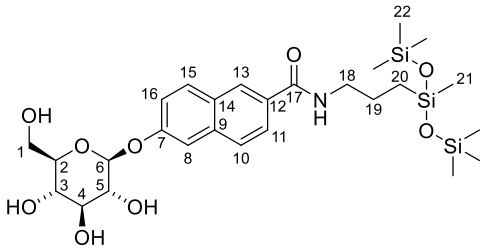
11.4.1 Deprotection of sugar units and preservation of final siloxane surfactants

11.4.1.1 Synthesis of *N*-(3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propyl)-6-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)-2-naphthamide (132a)



140a **132a**

According to **GP18**, 0.50 g (0.64 mmol, 1.00 eq.) of compound **140a** were deprotected with 0.06 mL (0.32 mmol, 0.50 eq.) NaOMe in MeOH (5.4 M) in 12 mL MeOH. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) to afford 0.20 g (0.33 mmol, 52%) of the desired product **132a** as a yellow solid.



M($C_{27}H_{45}NO_9Si_3$) 611.91 g/mol.

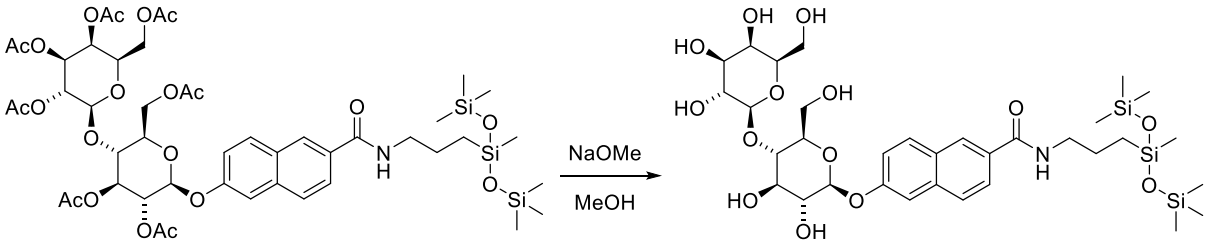
R_f (SiO_2, *c*Hex/EtOAc/MeOH 1:1:1) = 0.59.

^{1}H-NMR (300 MHz, MeOD-d_4) δ [ppm] = 8.34 – 8.31 (m, 1H, H-13), 7.92 (d, $^3J_{HH}$ = 9.0 Hz, 1H, H-15), 7.86 (m, 2H, H-10, H-11), 7.55 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H-8), 7.38 (dd, $^{3,4}J_{HH}$ = 8.9, 2.5 Hz, 1H, H-16), 5.15 – 5.09 (m, 1H, H-6), 3.97 (dd, $^{2,4}J_{HH}$ = 12.0, 2.2 Hz, 1H, H-1), 3.75 (dd, $^{2,3}J_{HH}$ = 12.1, 5.7 Hz, 1H, H-1‘), 3.63 – 3.53 (m, 3H, H-2, H-3, H-4), 3.48 – 3.38 (m, 3H, H-5, H-18), 1.77 - 1.63 (m, 2H, H-19), 0.66 – 0.54 (m, 2H, H-20), 0.10 (m, 21H, H-21, H-22).

^{13}C-NMR (75 MHz, MeOD-d_4) δ [ppm] = 168.8 (C-17), 156.9 (C-7), 136.0 (C-14), 130.1 (C-15), 130.0 (C-12), 128.8 (C-9), 127.1 (C-13),

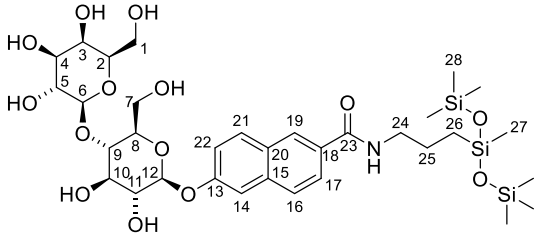
	127.0 (C-11), 123.9 (C-10), 119.5 (C-8), 110.3 (C-16), 100.7 (C-6), 76.9 (C-2), 76.6 (C-5), 73.5 (C-4), 70.0 (C-3), 61.1 (C-1), 42.6 (C-18), 23.1 (C-19), 14.6 (C-20), 0.5 (C-22), -1.5 (C-21).
^{29}Si-NMR	(60 MHz, MeOD-d_4) δ [ppm] = 7.45, -21.67.
FT-IR	ATR, ν [cm^{-1}] = 3316 (w), 2958 (w), 2115 (w), 1786 (w), 1740 (w), 1632 (m), 1604 (w), 1537 (m), 1504 (w), 1478 (w), 1390 (w), 1366 (w), 1301 (w), 1252 (m), 1212 (m), 1036 (s), 935 (w), 896 (w), 837 (s), 796 (m), 782 (s), 753 (s), 687 (m), 653 (m), 623 (m), 599 (m), 573 (m), 511 (m).
HR-MS (ESI)	Calcd. $[M+H]^+$: 612.2475, found: 612.2481.
	Calcd. $[M+Na]^+$: 634.2294, found: 634.2299.

11.4.1.2 Synthesis of 6-(((2*S*,3*R*,4*R*,5*S*,6*R*)-3,4-dihydroxy-6-(hydroxymethyl)-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)-*N*-(3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propyl)-2-naphthamide (132b)



140b **132b**

According to **GP18**, 0.18 g (0.17 mmol, 1.00 eq.) of compound **140b** were deprotected with 0.20 mL (0.08 mmol, 0.50 eq.) NaOMe in MeOH (0.5 M) in 12 mL MeOH. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 10:1) to afford 0.07 g (0.09 mmol, 57%) of the desired product **132b** as a colorless solid.



M($C_{33}H_{55}NO_{14}Si_3$)	774.05 g/mol.
R_f	(SiO_2, *c*Hex/EtOAc/MeOH 1:1:1) = 0.56.

^{1}H-NMR (300 MHz, MeOD-d_4) δ [ppm] = 8.32 (s, 1H, H-19), 7.93 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H, H-21), 7.87 (m, 2H, H-16, H-17), 7.54 (d, $^{4}J_{HH}$ = 2.5 Hz, 1H, H-14), 7.38 (dd, $^{3,4}J_{HH}$ = 8.9, 2.4 Hz, 1H, H-22), 5.17 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-12), 4.44 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, H-6), 3.96 (m, 2H, H-1, H-7), 3.87 – 3.78 (m, 2H, H-1‘, H-7‘), 3.81 – 3.69 (m, 4H, H-2, H-3, H-4, H-10), 3.71 – 3.56 (m, 3H, H-11, H-5, H-8), 3.52 (m, 1H, H-9), 3.41 (t, $^{3}J_{HH}$ = 7.1 Hz, 2H, H-24), 1.76 – 1.65 (m, 2H, H-25), 0.62 – 0.57 (m, 2H, H-26), 0.19 – 0.04 (m, 21H, H-27, H-28).

^{13}C-NMR (151 MHz, MeOD-d_4) δ [ppm] = 163.6 (C-23), 156.8 (C-13), 136.0 (C-18), 130.1 (C-21), 130.1 (C-20), 128.8 (C-15), 127.1 (C-19), 127.0 (C-17), 124.2 (C-16), 119.4 (C-22), 110.8 (C-14), 103.7 (C-6), 100.4 (C-12), 78.8 (C-8), 75.7 (C-4), 75.3 (C-3), 74.9 (C-10), 73.4 (C-2), 73.2 (C-11), 71.1 (C-5), 68.9 (C-9), 61.1 (C-7), 60.3 (C-1), 42.6 (C-24), 23.1 (C-25), 14.5 (C-26), 0.5 (C-28), 0.5 (C-27).

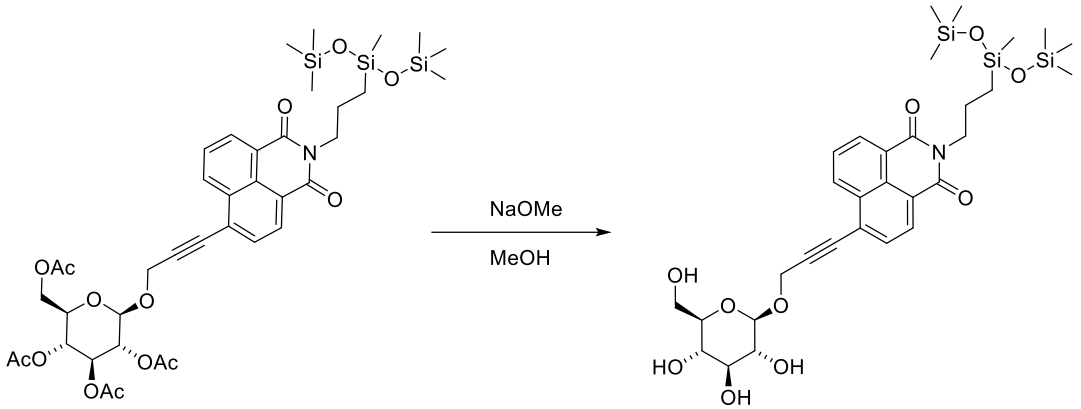
^{29}Si-NMR (60 MHz, MeOD-d_4) δ [ppm] = 7.46, -21.67.

FT-IR ATR, v [cm^{-1}] = 3333 (w), 2954 (w), 2122 (w), 1737 (s), 1635 (m), 1603 (w), 1535 (m), 1504 (w), 1478 (w), 1432 (w), 1415 (w), 1368 (m), 1253 (m), 1220 (s), 1205 (s), 1172 (m), 1127 (m), 1082 (s), 1067 (s), 1035 (s), 985 (m), 933 (m), 909 (m), 896 (m), 868 (m), 838 (m), 819 (m), 785 (w), 769 (w), 755 (w), 699 (m), 649 (m), 623 (m), 603 (m), 565 (w), 535 (m), 511 (m).

HR-MS (ESI) Calcd. $[M+H]^+$: 774.3003, found: 774.3011.

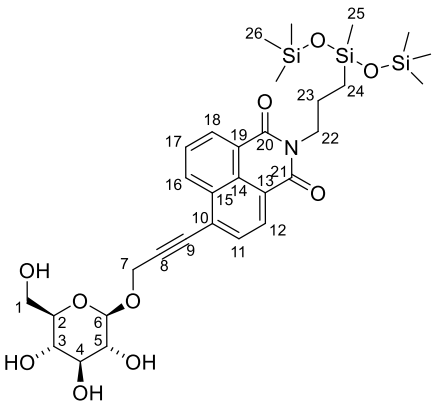
Calcd. $[M+Na]^+$: 796.2822, found: 796.2827.

11.4.1.3 Synthesis of 2-(3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propyl)-6-(3-(((2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl) oxy)prop-1-yn-1-yl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione (131a)



142a **131a**

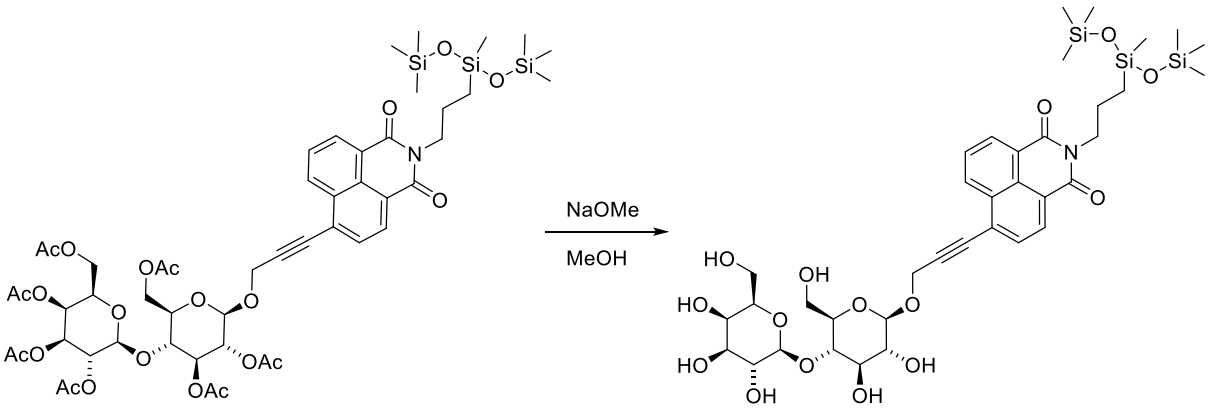
According to **GP18,** 0.44 g (0.52 mmol, 1.00 eq.) of compound **142a** were deprotected with 0.40 mL (0.20 mmol, 0.30 eq.) NaOMe in MeOH (0.5 M) in 10 mL MeOH. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) to afford 0.32 g (0.48 mmol, 92%) of the desired product **131a** as a red solid.



M($C_{31}H_{45}NO_{10}Si_3$)	675.95g/mol.
R_f	(SiO_2, *c*Hex/EtOAc/MeOH 2:2:1) = 0.33.
^{1}H-NMR	(500 MHz, MeOD-d_4) δ [ppm] = 8.49 (dd, $^{3,4}J_{HH}$ = 8.4, 1.1 Hz, 1H, H-16), 8.41 (dd, $^{3,4}J_{HH}$ = 7.3, 1.2 Hz, 1H, H-18), 8.29 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-12), 7.77 – 7.72 (m, 2H, H-11, H-17), 4.90 (s, 2H, H-7), 4.68 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, H-6), 4.08 – 4.02 (m, 2H, H-22), 3.97 (dd, $^{2,4}J_{HH}$ = 11.9, 2.2 Hz, 1H, H-1), 3.76 (dd, $^{2,3}J_{HH}$ = 11.9, 5.8 Hz, 1H, H-1‘), 3.49 (m, 1H, H-4), 3.43 (m, 1H, H-1), 3.40 – 3.35 (m, 1H, H-5), 1.79 – 1.70 (m, 2H, H-23), 0.61 – 0.54 (m, 2H, H-24), 0.11 (s, 18H, H-26), 0.07 (C-25).

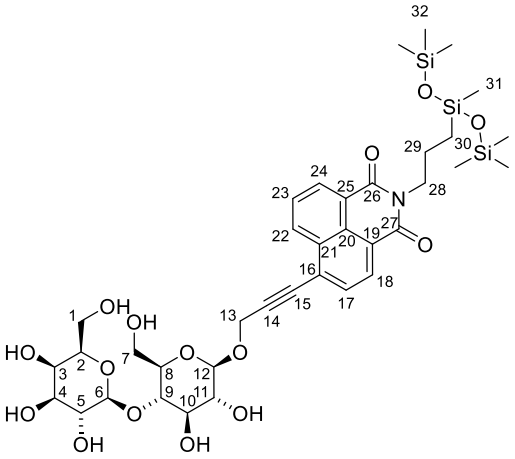
^{13}C-NMR	(126 MHz, MeOD-*d*$_4$) δ [ppm] = 163.5 (C-20), 163.2 (C-21), 131.9 (C-16), 131.2 (C-19), 131.0 (C-18), 130.5 (C-11), 129.6 (C-12), 127.4 (C-17), 127.2 (C-13), 126.5 (C-10), 122.2 (C-14), 121.7 (C-15), 101.3 (C-6), 94.7 (C-9), 82.4 (C-8), 76.8 (C-4), 76.6 (C-5), 73.6 (C-3), 70.2 (C-2), 61.4 (C-1), 56.1 (C-7), 42.6 (C-22), 21.4 (C-23), 14.5 (C-24), 0.6 (C-26), -1.5 (C-25).
^{29}Si-NMR	(99 MHz, MeOD-*d*$_4$) δ [ppm] = 7.46, -21.95.
FT-IR	ATR, ν [cm^{-1}] = 3396 (w), 2957 (w), 2901 (w), 1702 (m), 1660 (m), 1615 (w), 1590 (m), 1510 (w), 1441 (w), 1384 (w), 1352 (m), 1249 (m), 1185 (w), 1153 (w), 1028 (s), 837 (s), 782 (s), 753 (s), 687 (m), 652 (m), 635 (m), 603 (m), 580 (m).
HR-MS (ESI)	Calcd. [M+Na]$^+$: 698.2243, found: 698.2247.

11.4.1.4 Synthesis of 6-(3-(((2*R*,3*R*,4*R*,5*S*,6*R*)-3,4-dihydroxy-6-(hydroxymethyl)-5-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)-2-(3-(1,1,1,3,5,5,5-hepta methyl trisiloxan-3-yl)propyl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione (131b)



142b **131b**

According to **GP18**, 0.38 g (0.34 mmol, 1.00 eq.) of compound **142b** were deprotected with 0.20 mL (0.10 mmol, 0.30 eq.) NaOMe in MeOH (0.5 M) in 10 mL MeOH. The crude product was purified by column chromatography (SiO_2, *c*Hex/EtOAc/MeOH 1:1:1) to afford 0.31 g (0.26 mmol, 77%) of the desired product **131b** as an orange solid.



M($C_{37}H_{55}NO_{15}Si_3$) 838.09 g/mol.

R_f (SiO_2, *c*Hex/EtOAc/MeOH 1:1:1) = 0.40.

^{1}H-NMR (500 MHz, MeOD-d_4) δ [ppm] = 8.53 (dd, $^{3,4}J_{HH}$ = 8.4, 1.2 Hz, 1H, H-22), 8.45 (dd, $^{3,4}J_{HH}$ = 7.3, 1.2 Hz, 1H, H-24), 8.33 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H-18), 7.82 – 7.74 (m, 2H, H-17, H-23), 5.23 (d, $^{3}J_{HH}$ = 3.9 Hz, 1H, H-12), 4.89 (m, 2H, H-13), 4.69 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, H-6), 4.10 – 4.04 (m, 2H, H-28), 3.99 (dd, $^{2,4}J_{HH}$ = 12.2, 2.0 Hz, 1H, H-7), 3.91 – 3.82 (m, 2H, H-1, H-7‘), 3.77 - 3.59 (m, 6H, H-1‘, H-3, H-4, H-10, H-11), 3.53 (m, 1H, H-8), 3.49 (m, 1H, H-2), 3.41 (dd, $^{3,3}J_{HH}$ = 9.4, 7.8 Hz, 1H, H-5), 3.29 (m, 1H, H-9), 1.75 (m, 2H, H-29), 0.60 – 0.55 (m, 2H, H-30), 0.11 (s, 18H, H-32), 0.07 (s, 3H, H-31).

^{13}C-NMR (126 MHz, MeOD-d_4) δ [ppm] = 163.6 (C-26), 163.3 (C-27), 132.0 (C-22), 131.2 (C-25), 131.0 (C-24), 130.5 (C-17), 129.7 (C-18), 127.4 (C-23), 127.3 (C-19), 126.5 (C-16), 122.3 (C-20), 121.8 (C-21), 101.5 (C-12), 101.3 (C-6), 94.6 (C-15), 82.4 (C-14), 79.8 (C-2), 76.4 (C-4), 75.4 (C-8), 73.6 (C-10), 73.4 (C-3), 73.1 (C-5), 72.7 (C-11), 70.1 (C-9), 61.3 (C-1), 60.8 (C-7), 56.2 (C-13), 42.6 (C-28), 21.4 (C-29), 14.5 (C-30), 0.5 (C-32), -1.5 (C-31).

^{29}Si-NMR (99 MHz, MeOD-d_4) δ [ppm] = 7.47, -21.95.

FT-IR ATR, ν [cm^{-1}] = 3352 (w), 2957 (w), 1702 (w), 1660 (m), 1615 (w), 1590 (w), 1510 (w), 1441 (w), 1385 (w), 1352 (m), 1249 (m), 1146 (w), 1021 (s), 838 (s), 782 (s), 753 (s), 687 (m), 635 (m), 597 (m), 580 (m).

HR-MS (ESI) Calcd. $[M+Na]^+$: 860.2771, found: 860.2776

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13 Appendix

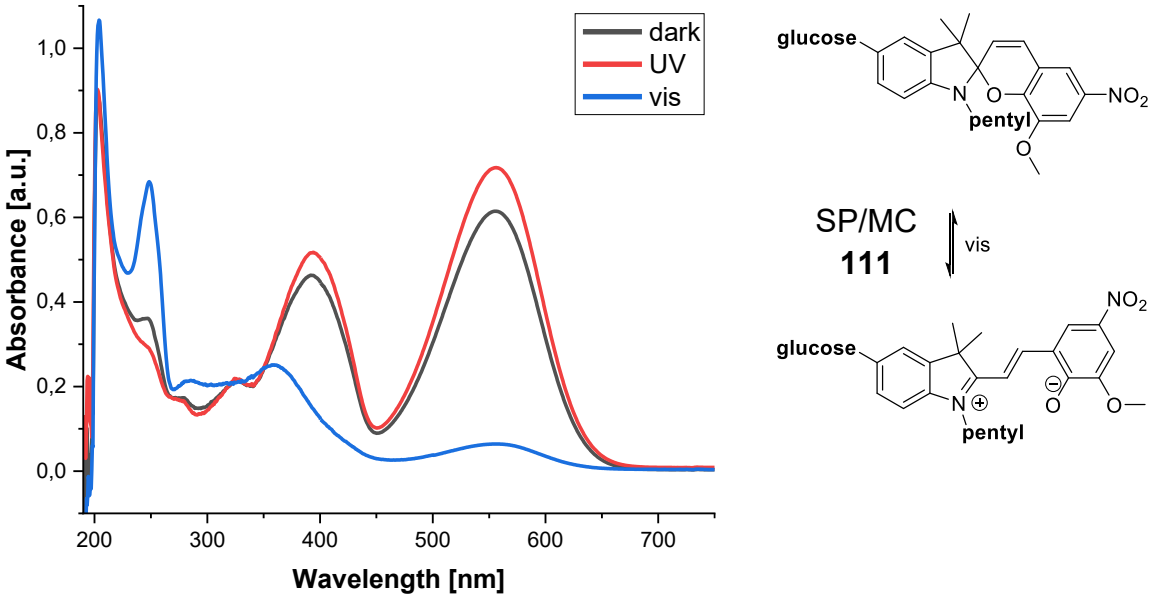
13.1 List of abbreviations

A_{min}	Minimale head group requirement
Ac	Acetate
aq.	aqueous
BBN	Borabicyclononane
Bn	Benzyl
c	Concentration
cat.	catalyzed
CDI	1,1'-Carbonyldiimidazole
*c*Hex	Cyclohexane
cmc	Critical micelle concentration
conc.	concentrated
d	Cuvette thickness
DHPs	Dihydropyrenes
DIBAL-H	Di*iso*butylaluminium hydride
DIC	Diisopropylcarbodiimide
DMAP	4-Dimethylaminopyridine
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DMP	Dess-Martin periodinane
E	Absorbance
eq.	Equivalents
ESI	Electron spray ionization
Et	Ethyl
et al.	et alii
EtOAc	Ethyl acetate
Fmoc	Fluorenylmethoxycarbonyl
GC	Gas chromatography
HBPin	Pinacolborane
HOBt	1-Hydroxybenzotriazole
IC	Internal conversion
ISC	Intersystem crossing
LC	Liquid chromatography
Lit.	Literature
MC	Merocyanine
Me	Methyl
MS	Mass spectroscopy
MTBE	Methyl *tert*-butyl ether
m. p.	Melting point
NMR	Nuclear magnetic resonance
PPTS	Pyridinium *p*-toluenesulfonate

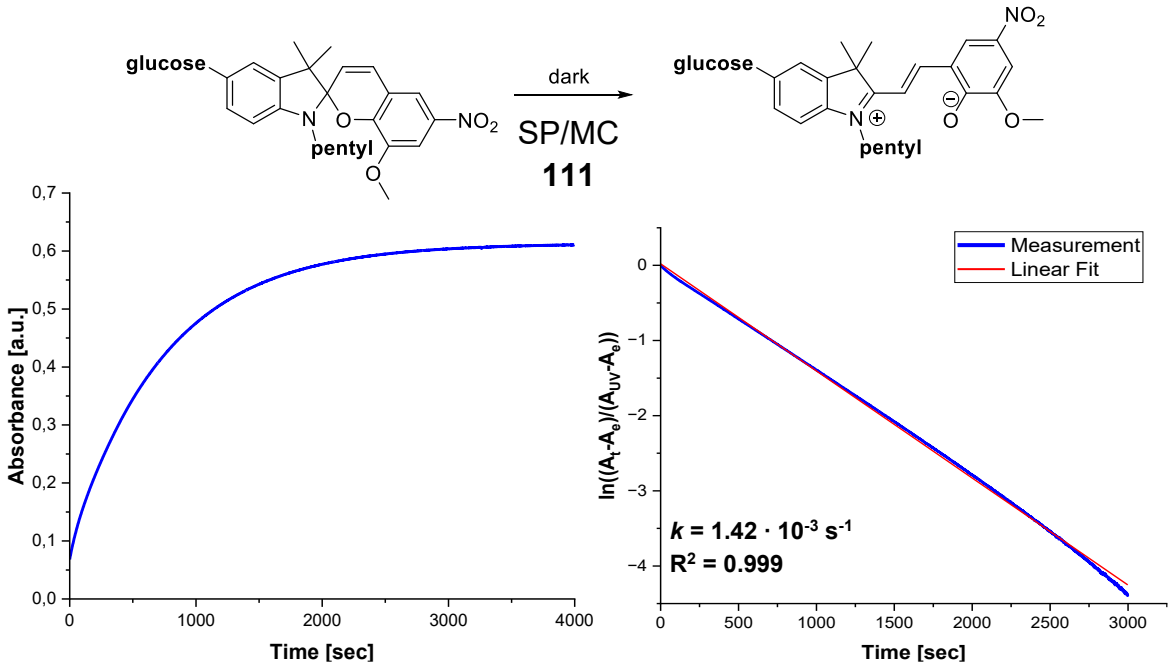
quant.	quantitative
R_f	Retention factor
rt	Room temperature
sat.	saturated
SP	Spiropyran
THF	Tetrahydrofuran
Tf	Triflate
TLC	Thin layer chromatography
TMS	Trimethysilyl
UV	ultraviolet
vis	visible
σ	Surface tension
Γ	Surface concentration
Γ_∞	maximum surface concentration
ε	Extinction coefficient

13.2 UV-vis spectra of spiropyran-based surfactants

Scheme 76 shows the UV-vis spectra of surfactant **111**.

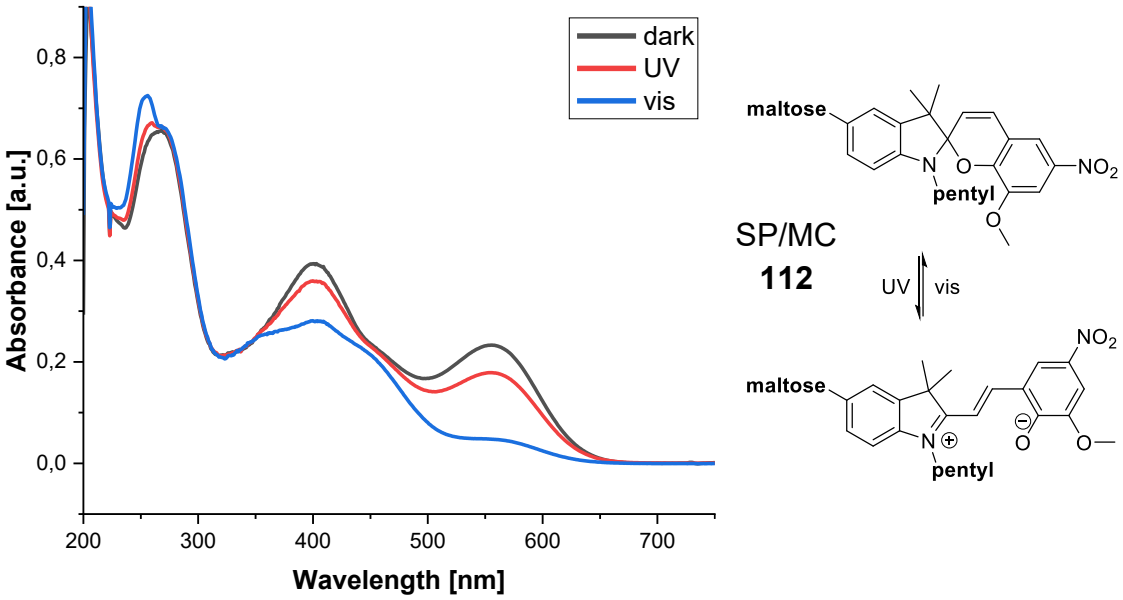


*Scheme 76: UV-vis spectra of SP/MC **111** (0.025 mM in MeOH) at the thermal equilibrium in the dark (black) and after irradiation with UV (red) and visible (blue) light.*

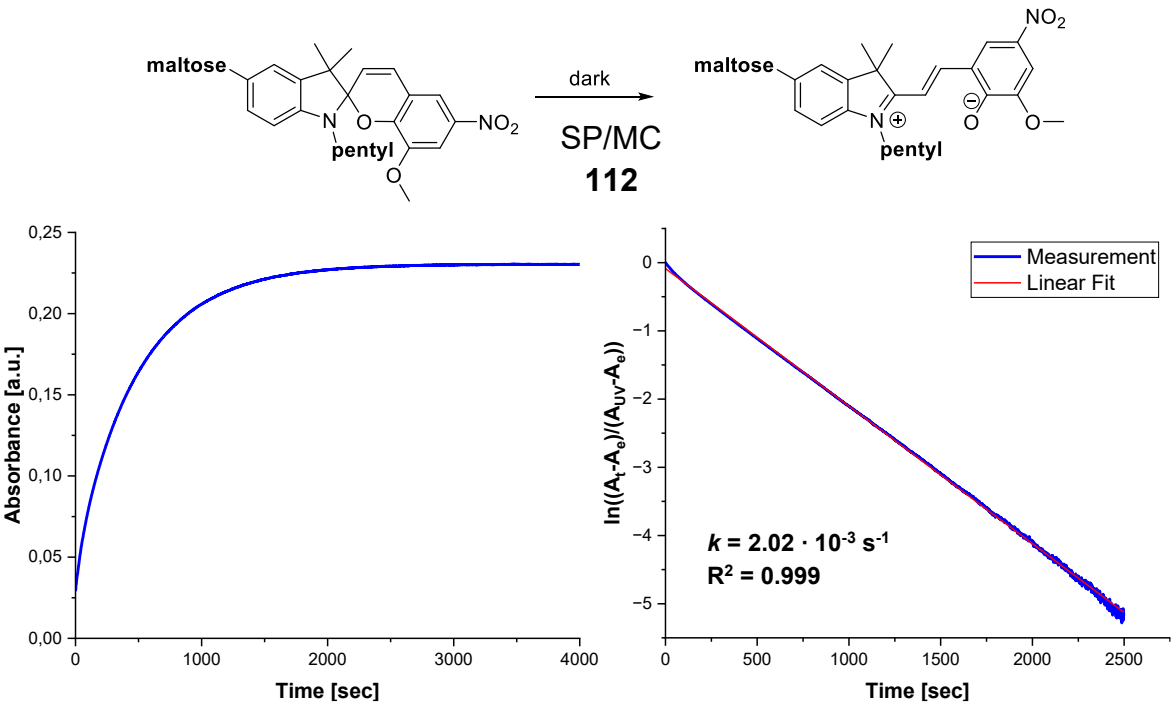


*Scheme 77: Kinetics for the ring opening reaction of spiropyran **111** to the corresponding merocyanine. Plot of the absorbance at the absorption maximum of the merocyanine against time (left) and the logarithmic plot of the conversion to determine the rate constant k (right).*

Scheme 78 shows the UV-vis spectra of surfactant surfactant **112**.

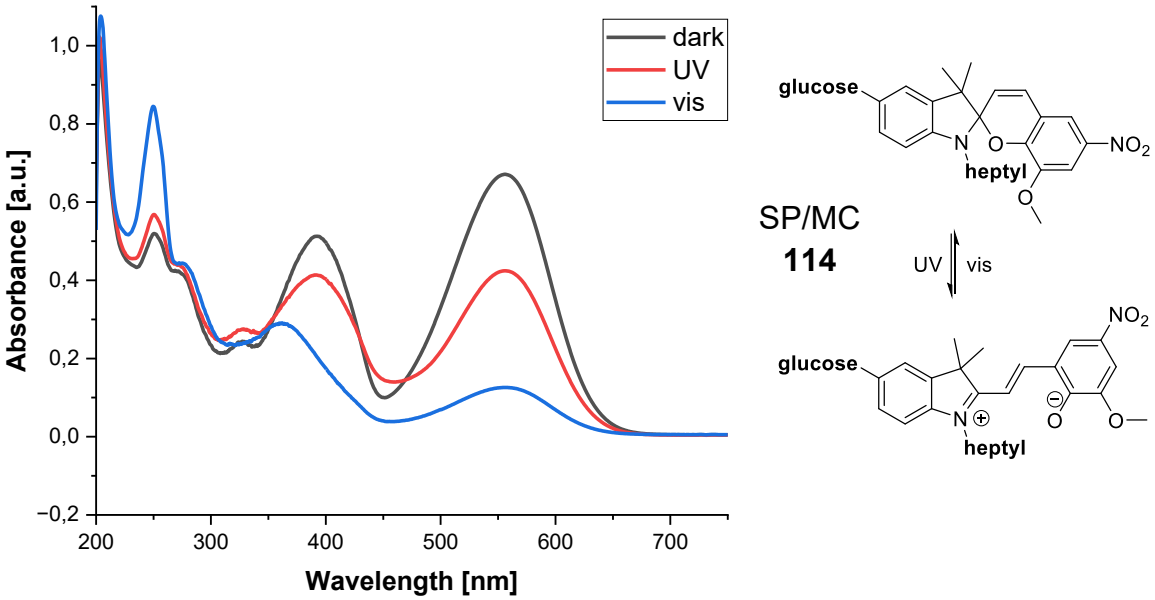


*Scheme 78: UV-vis spectra of SP/MC **112** (0.025 mM in MeOH) at the thermal equilibrium in the dark (black) and after irradiation with UV (red) and visible (blue) light.*

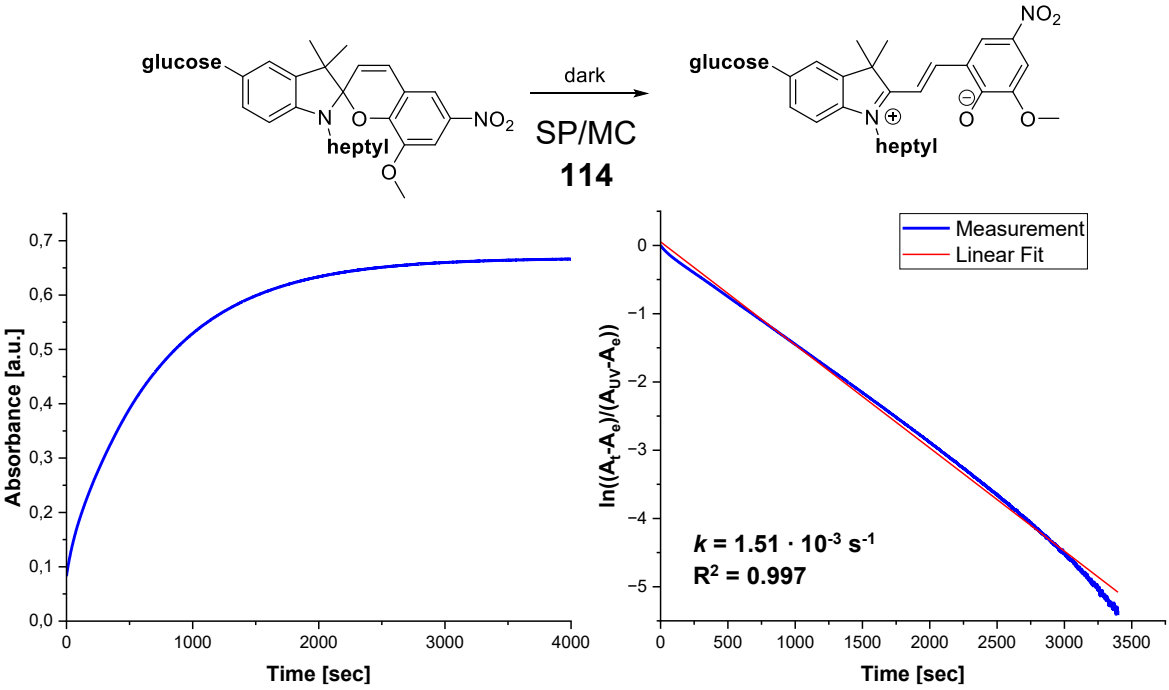


*Scheme 79: Kinetics for the ring opening reaction of spiropyran **112** to the corresponding merocyanine. Plot of the absorbance at the absorption maximum of the merocyanine against time (left) and the logarithmic plot of the conversion to determine the rate constant k (right).*

Scheme 80 shows the UV-vis spectra of surfactant surfactant **114**.

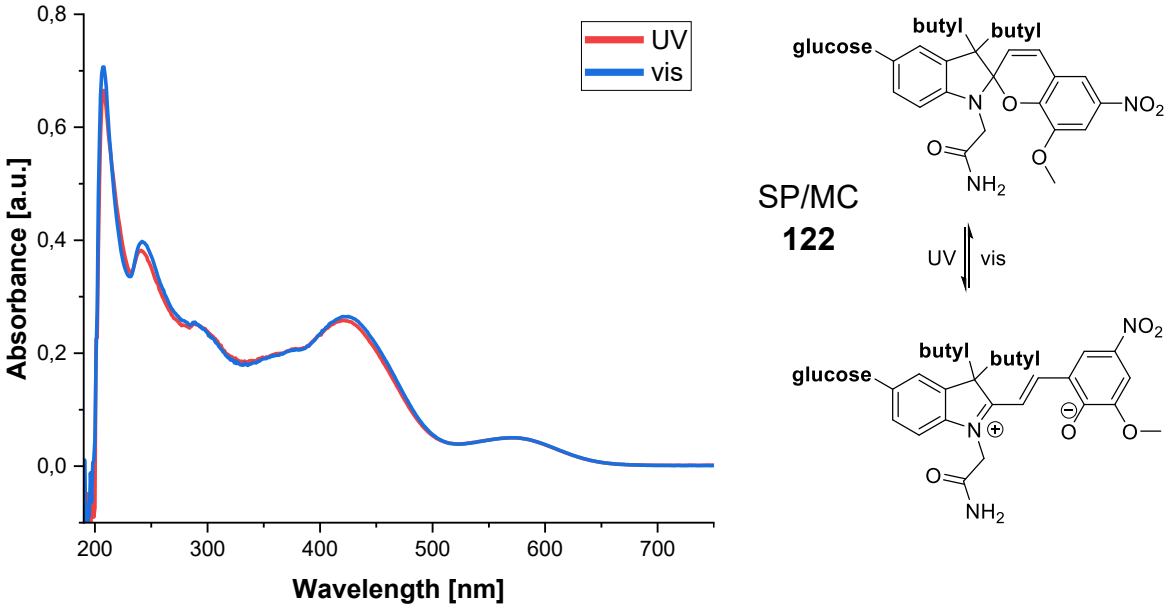


*Scheme 80: UV-vis spectra of SP/MC **114** (0.025 mM in MeOH) at the thermal equilibrium in the dark (black) and after irradiation with UV (red) and visible (blue) light.*



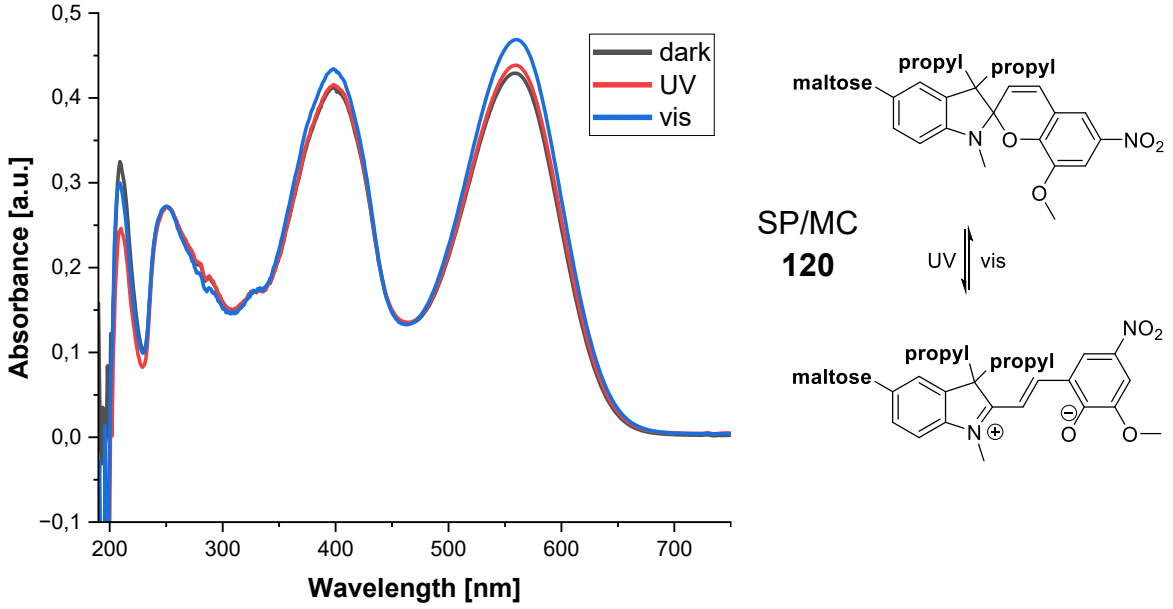
*Scheme 81: Kinetics for the ring opening reaction of spiropyran **114** to the corresponding merocyanine. Plot of the absorbance at the absorption maximum of the merocyanine against time (left) and the logarithmic plot of the conversion to determine the rate constant k (right).*

Scheme 82 shows the UV-vis spectra of surfactant surfactant **122**.

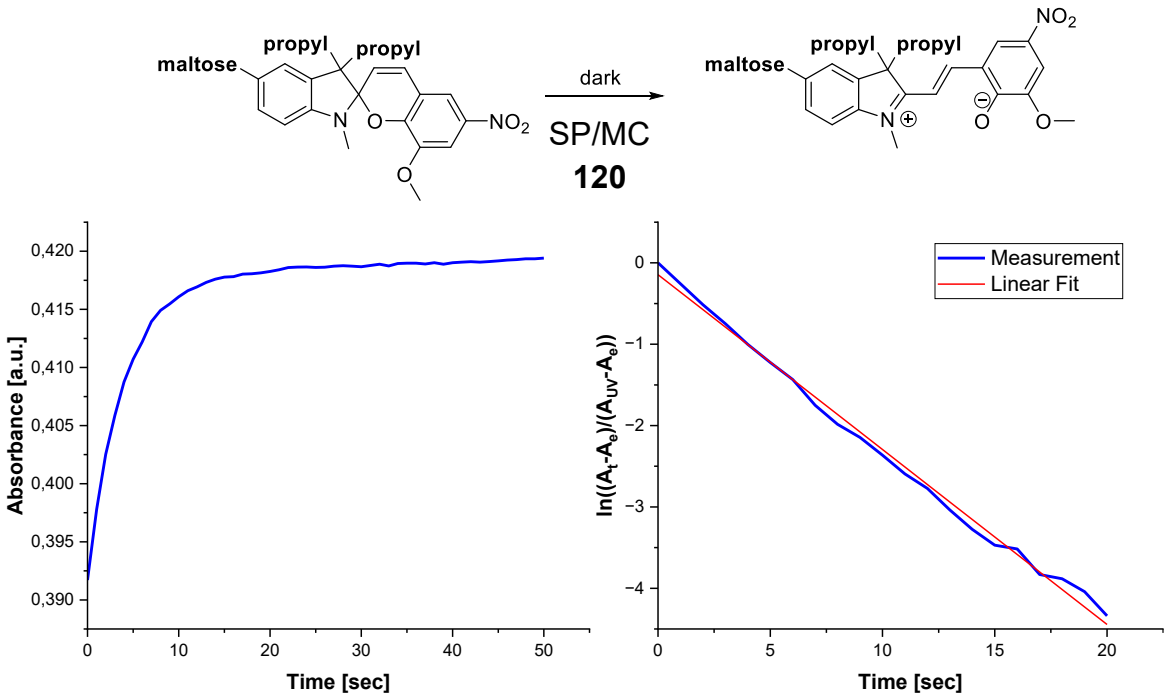


*Scheme 82: UV-vis spectra of SP/MC **122** (0.025 mM in MeOH) after irradiation with UV (red) and visible (blue) light.*

Scheme 83 shows the UV-vis spectra of surfactant surfactant **120**.

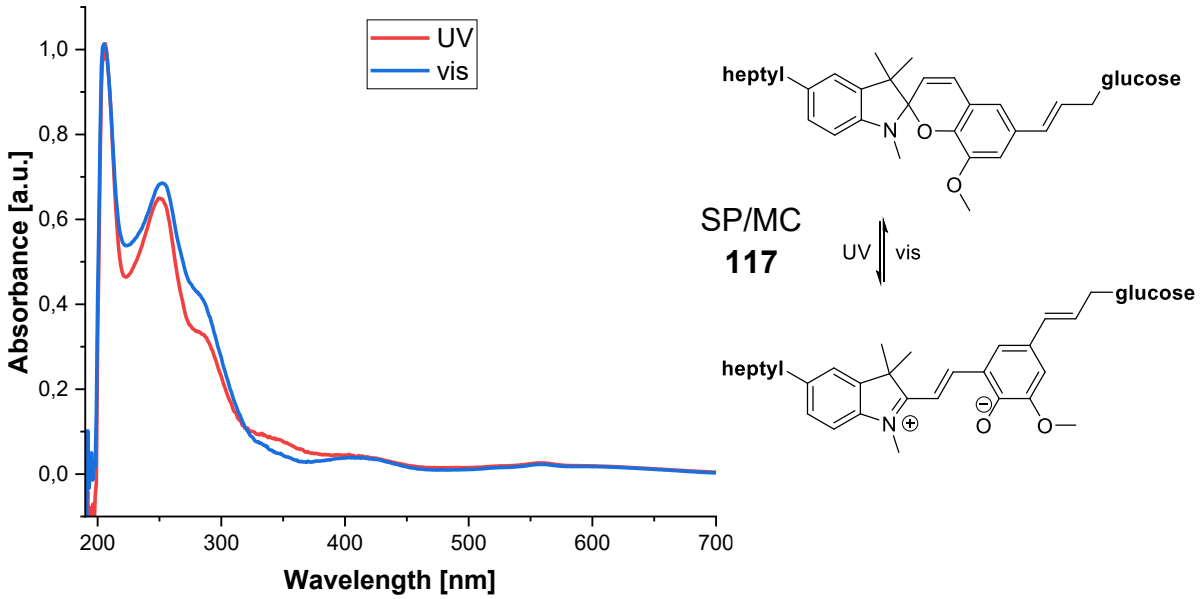


*Scheme 83: UV-vis spectra of SP/MC **122** (0.025 mM in MeOH) at the thermal equilibrium in the dark (black) and after irradiation with UV (red) and visible (blue) light.*



*Scheme 84: Kinetics for the ring opening reaction of spiropyran **120** to the corresponding merocyanine. Plot of the absorbance at the absorption maximum of the merocyanine against time (left) and the logarithmic plot of the conversion to determine the rate constant k (right).*

Scheme 85 shows the UV-vis spectra of surfactant surfactant **117**.



*Scheme 85: UV-vis spectra of SP/MC **117** (0.025 mM in MeOH) after irradiation with UV (red) and visible (blue) light.*

13.3 Absorption and emission spectra of the silicon-based surfactants

The absorption and emission spectra of surfactant **166a** is shown in Figure 49

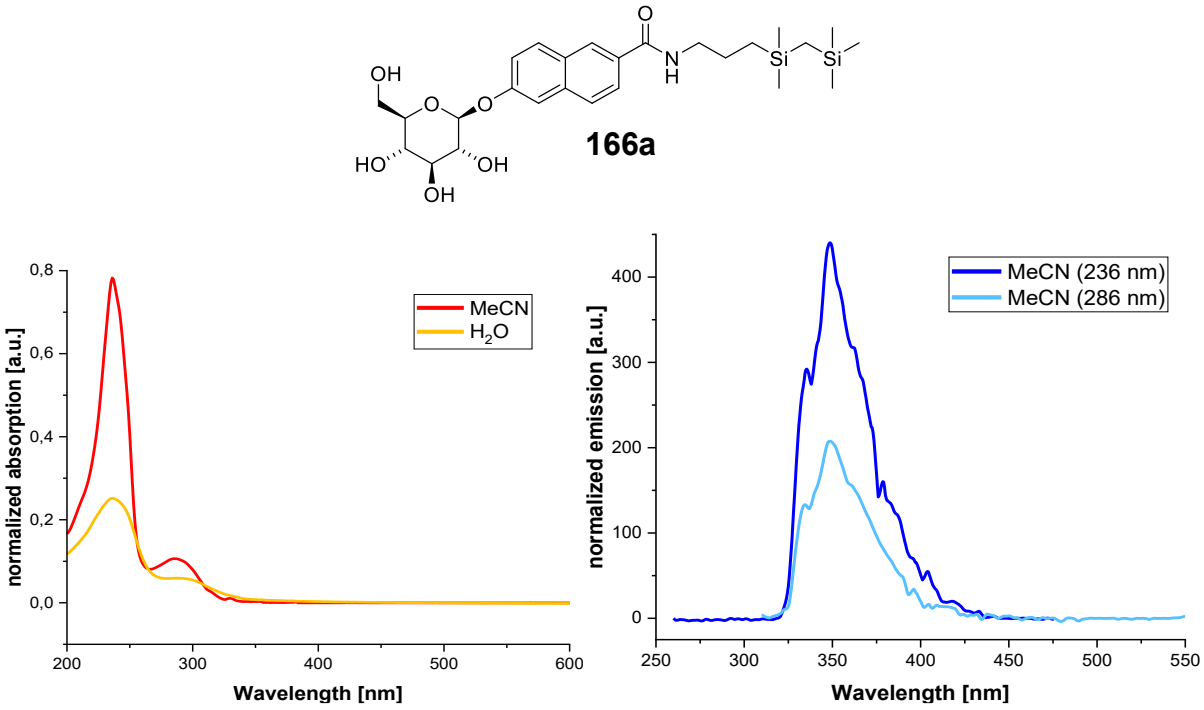


*Figure 49: Absorption (left) and emission (right) spectra of solutions of surfactant **166a** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The absorption maxima are in the same range as for the previous molecule. But in comparison, the intensities of the maxima are lower in MeCN and somewhat stronger in water. It is possible that the molecule dissolves better in the polar solvent due to the shorter carbosilane chain.

The intensity of the emission spectrum in water is so low and blurred that it was not depicted here. In MeCN, the absorption maxima are shifted into the longer wavelength range and are at 355 nm.

The absorption and emission spectra of surfactant **167a** are shown in Figure 50.

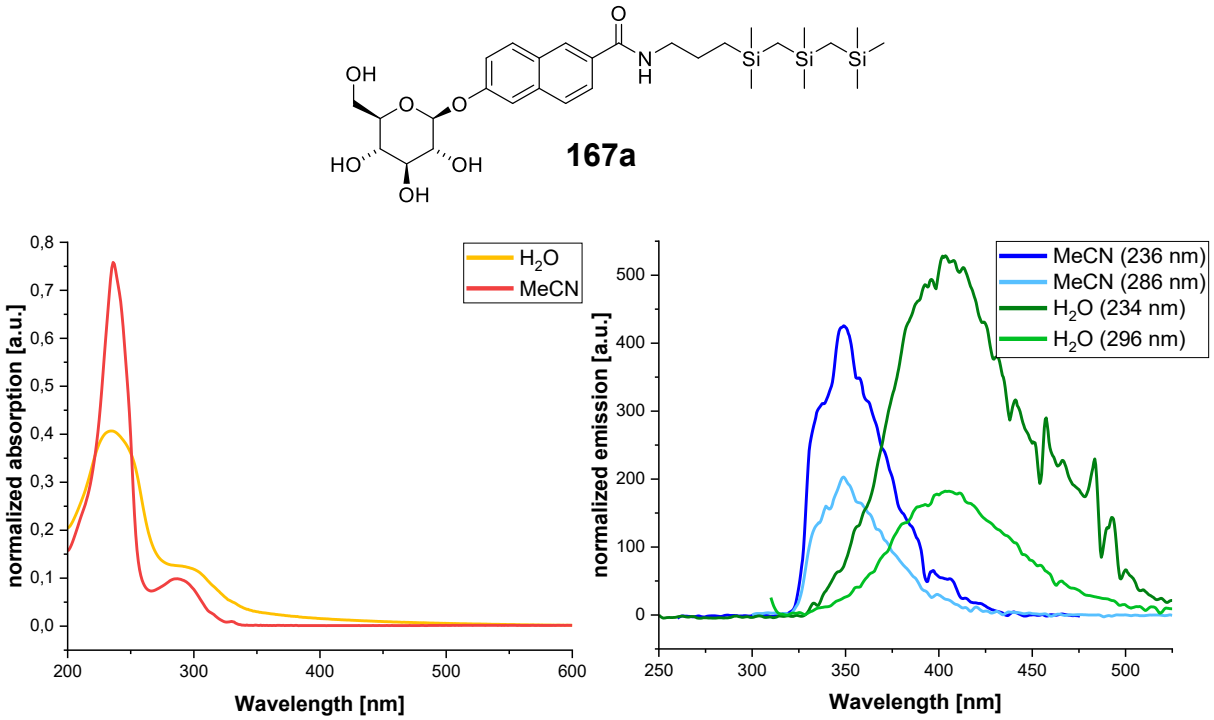


*Figure 50: Absorption (left) and emission (right) spectra of solutions of surfactant **167a** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

Here, the absorption maxima are also at 236 and 296 nm. The intensities in MeCN and in water are similar to those in the previous spectra. In the emission spectrum, the intensity of the maxima at 410 nm increases sharply and in some cases is higher than for the measurement in MeCN. The T-shaped surfactant appears to have significantly different interactions with water than the surfactants with the linear chains. The polar solvent therefore does not inhibit the fluorescence.

The absorption and emission spectra of surfactant **166b** are shown in Figure 51.

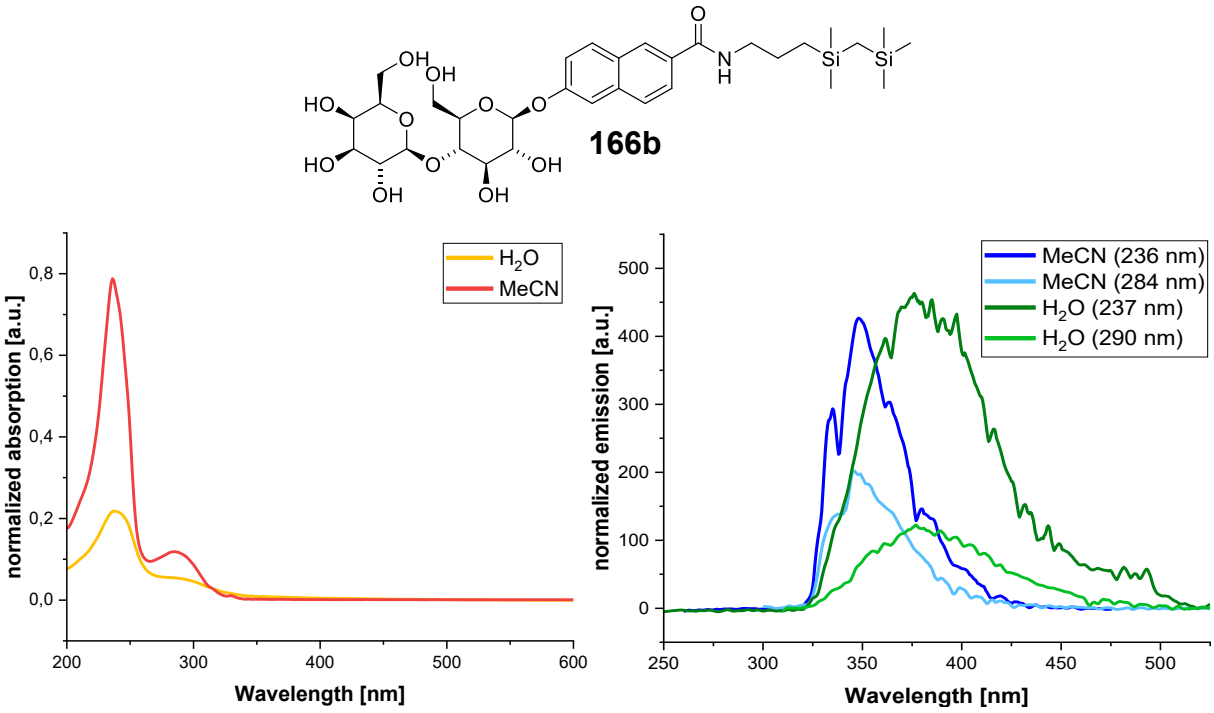


*Figure 51: Absorption (left) and emission (right) spectra of solutions of surfactant **166b** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The absorption maxima and their intensity are in the same range as in the previous spectra. However, the emission bands are slightly shifted. Although they show a *Stoke* shift, the maxima are at 345 nm (MeCN) and 365 nm (H_2O). The intensity in water is strong and is partially above the values of MeCN-solution.

The absorption and emission spectra of surfactant **167b** are shown Figure 52.

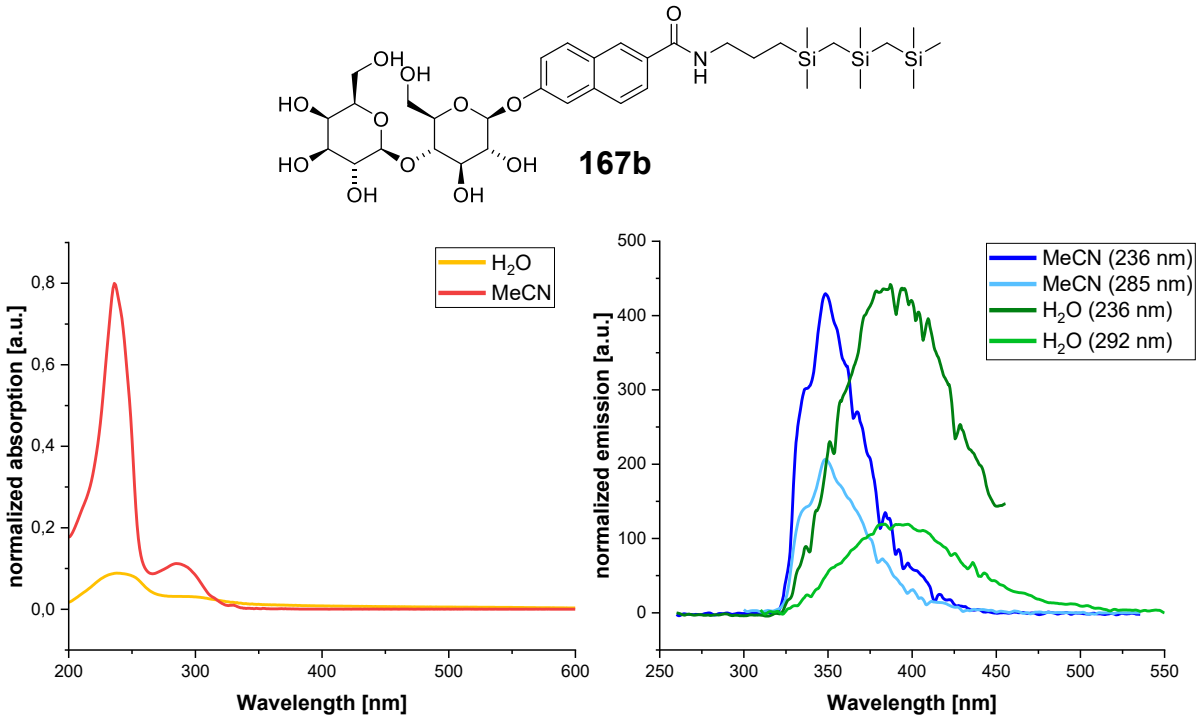
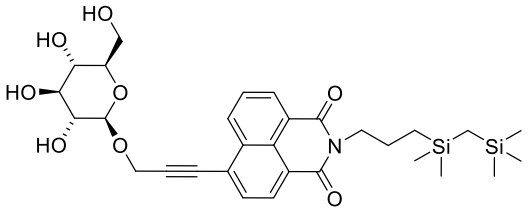


*Figure 52: Absorption (left) and emission (right) spectra of solutions of surfactant **167b** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The length of the carbosilane chain does not appear to have a significant effect on the absorption and emission properties. The intensity of absorption of the aqueous solution is slightly lower, but the intensity and wavelength region in the emission spectrum are in the same range as for the previous compound with the disaccharide as the head group.

In Figure 53 the absorption and emission spectra of surfactant **169a** are shown.



169a

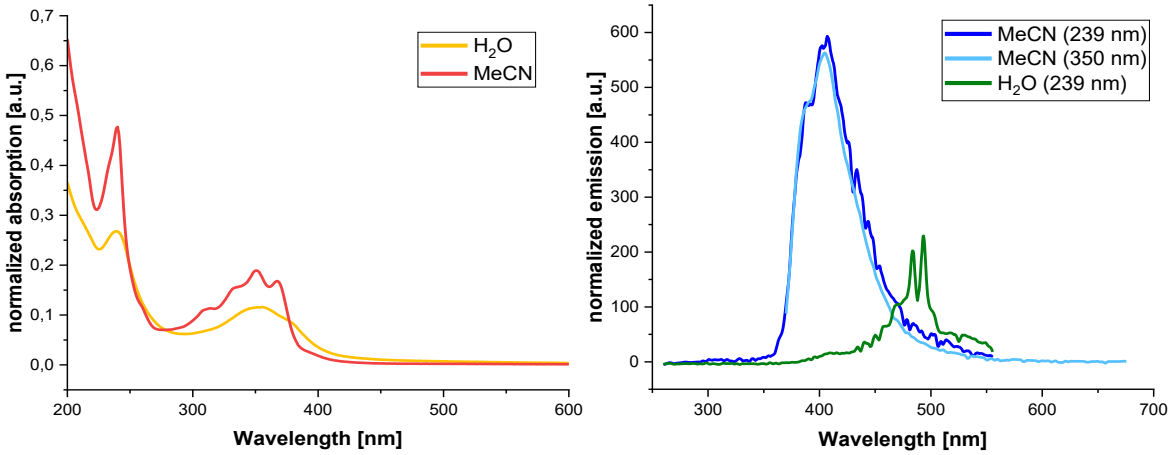
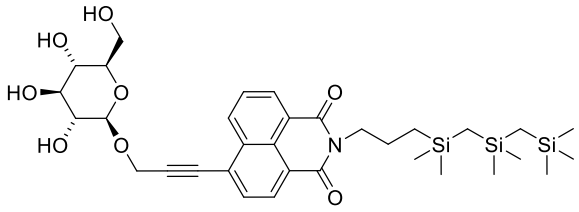


*Figure 53: Absorption (left) and emission (right) spectra of solutions of surfactant **169a** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The absorption spectrum of naphthalimide **169a** shows three maxima. In MeCN, a sharp band is visible at 239 nm and two smaller bands at 350 nm and 355 nm. A slight red shift can be seen in H_2O. In addition, the smaller maxima have merged to form a broad band.

The emission spectrum of the solution in MeCN shows a maximum at 406 nm. The measurement of the aqueous solution results in a spectrum with a weak band at 490 nm with many irregularities. By exciting with the wavelength of the smaller absorption maxima, it was not possible to measure an emission band with sufficient intensity.

In Figure 54 the absorption and emission spectra of surfactant **170a** are shown



170a

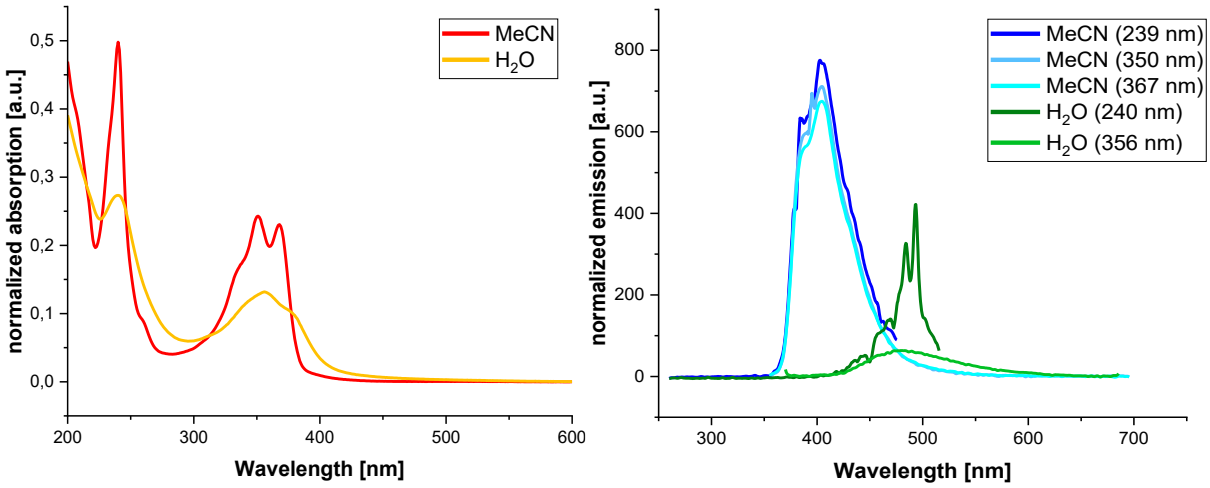


*Figure 54: Absorption (left) and emission (right) spectra of solutions of surfactant **170a** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The absorption spectrum is similar to the spectrum of the previous naphthalimide. The sharp band at 239 nm also has the same intensity. The two maxima at 350 nm and 367 nm are sharper and more intense. The emission spectrum of the MeCN solution shows maxima at 400 nm and for the aqueous solution a bathochromic shift to 490 nm and 500 nm.

In Figure 55 the absorption and emission spectrum of surfactant **169b** with the disaccharide as the head group are shown.

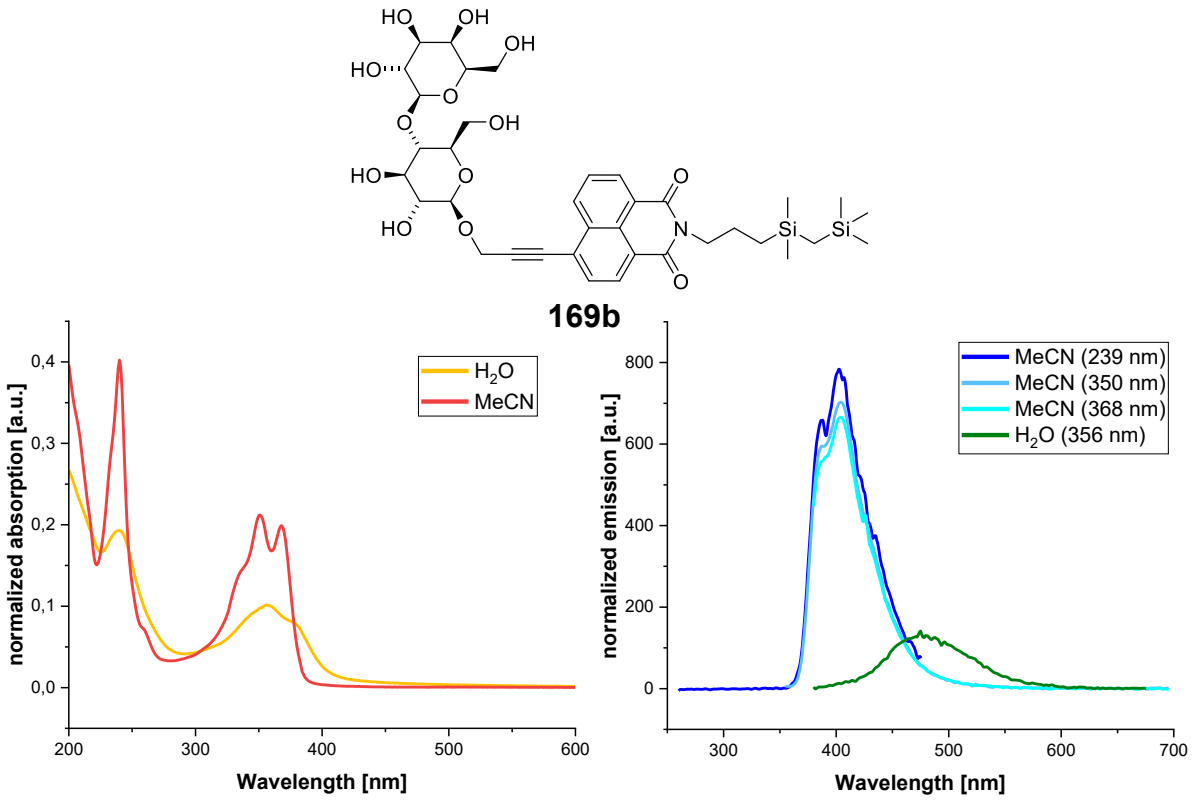


*Figure 55: Absorption (left) and emission (right) spectra of solutions of surfactant **169b** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The spectra also show similar absorption and emission lines as the previous compound with a monosaccharide as head group, but the intensities of the lines of the aqueous solution are low in intensity. Therefore, no emission spectrum could be obtained by excitation at 239 nm. The sugar unit seems to influence the absorption and emission behavior. This could be due to strong interactions of the hydroxy groups with the polar solvent.

In Figure 56 the absorption and emission spectra of surfactant **170b** are shown.

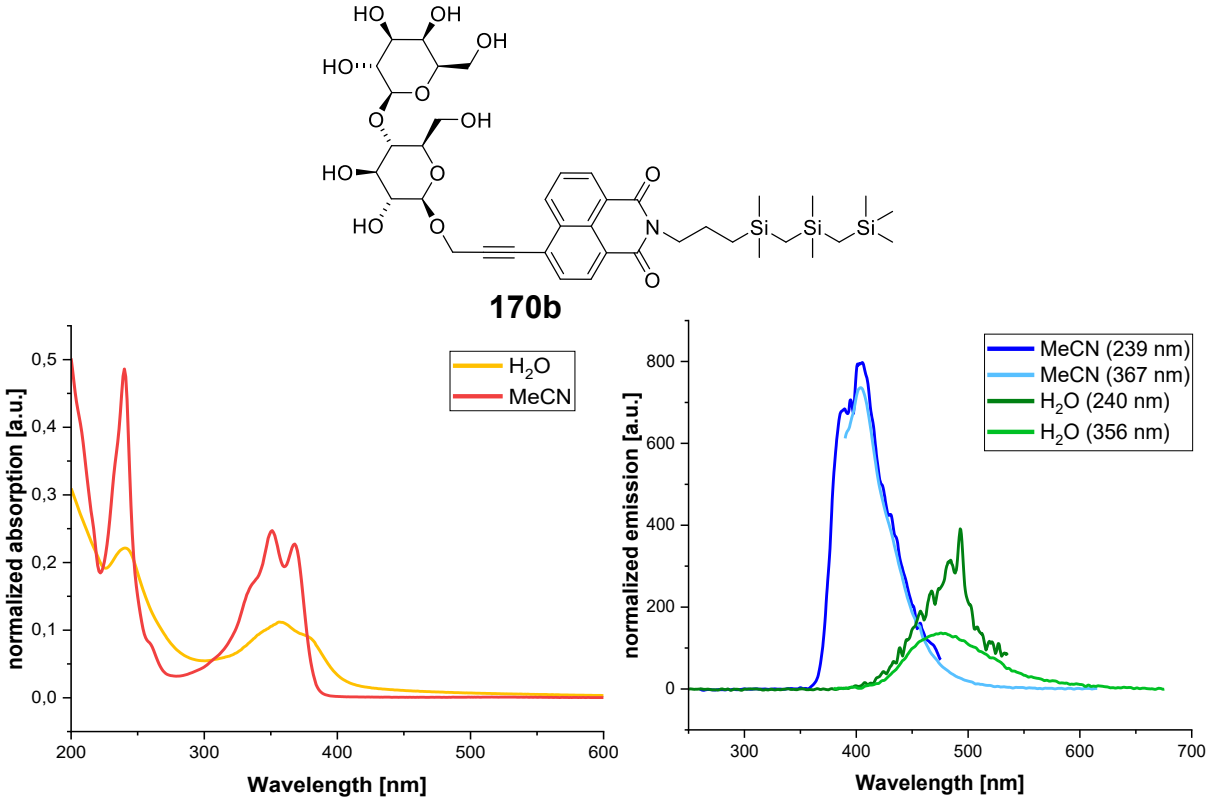


*Figure 56: Absorption (left) and emission (right) spectra of solutions of surfactant **170b** in MeCN and H_2O. The excitation wavelengths of the emission are indicated after the solvent in the caption.*

The spectra of surfactant **170b** are almost identical to the previous spectra of compound **169b**. However, an emission line could also be obtained here by excitation at 240 nm.

13.4 Selected NMR spectra

13.4.1 NMR spectra of photoswitchable surfactants

In most cases, the spectra of the photoswitches show the SP and MC forms, as the compounds were in equilibrium between the two isomers during the NMR measurements.

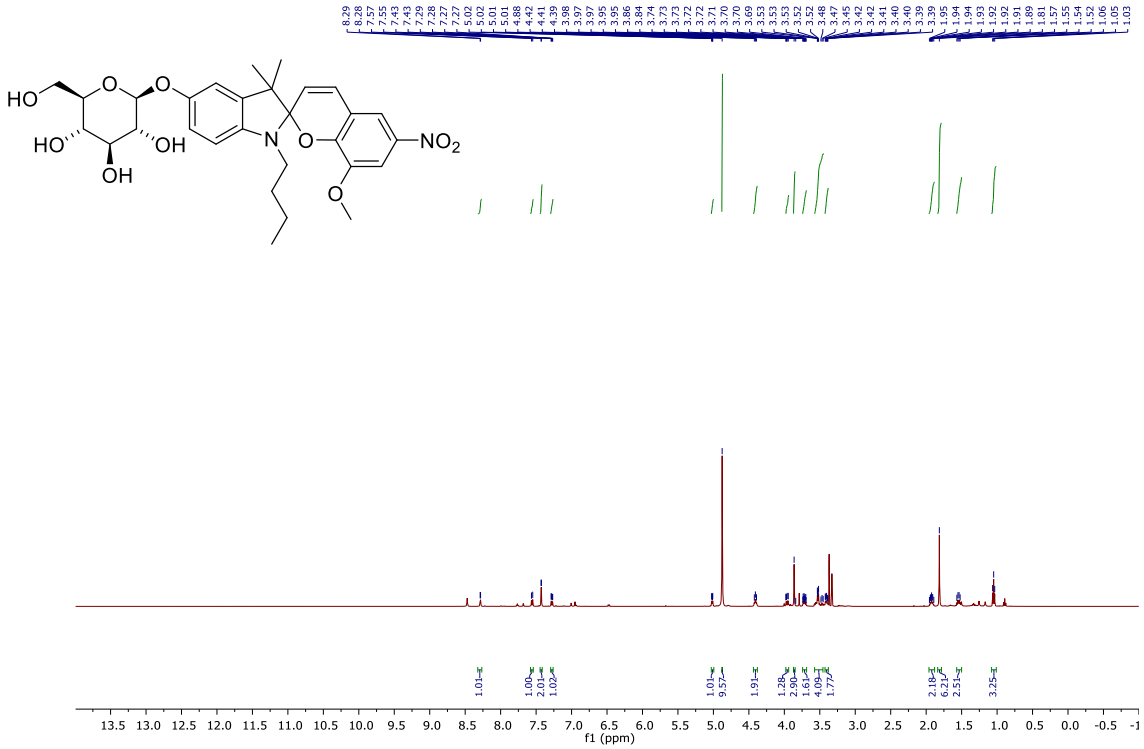


*Figure 57: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **108**.*

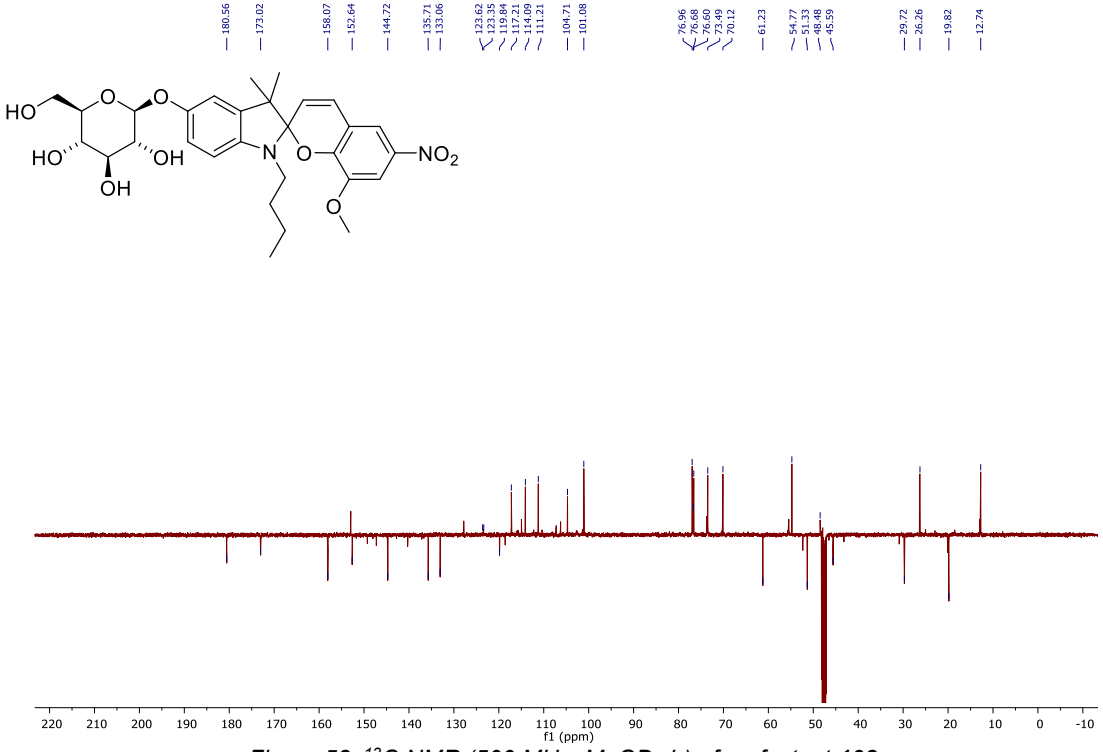


*Figure 58: ^{13}C NMR (500 MHz, MeOD-d$_4$) of surfactant **108**.*

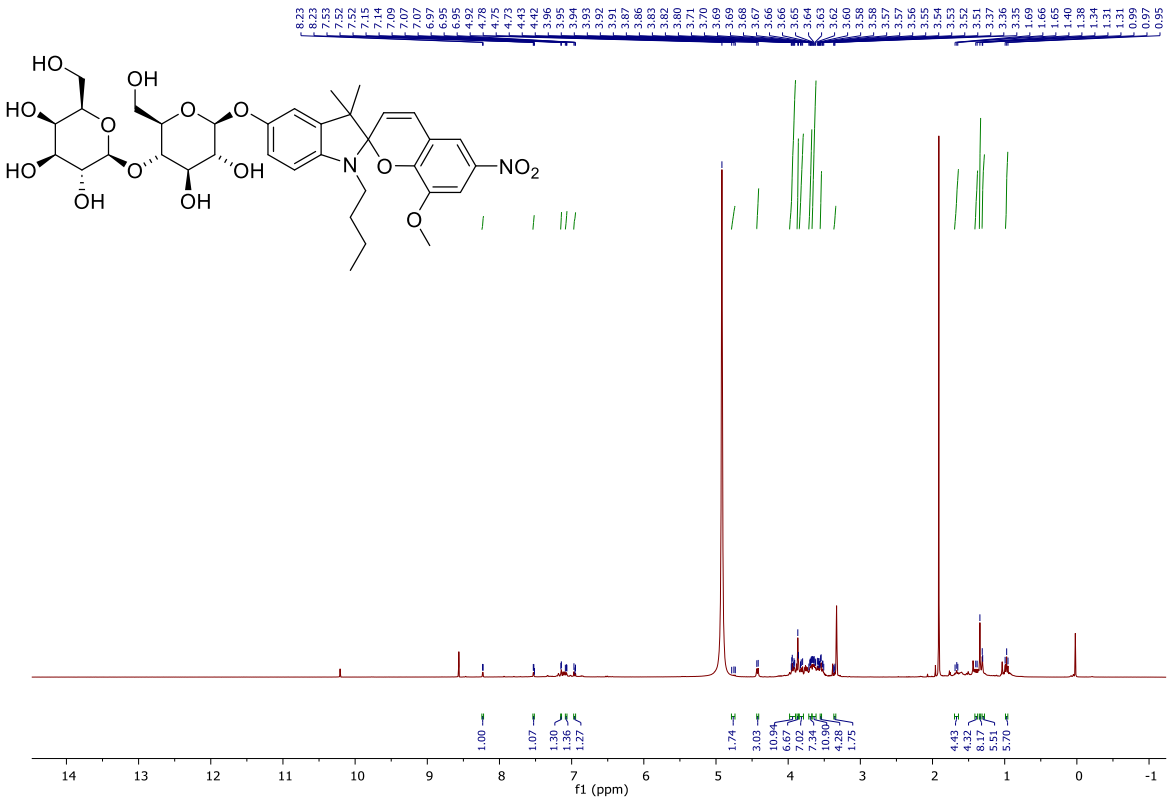


*Figure 59: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **110**.*

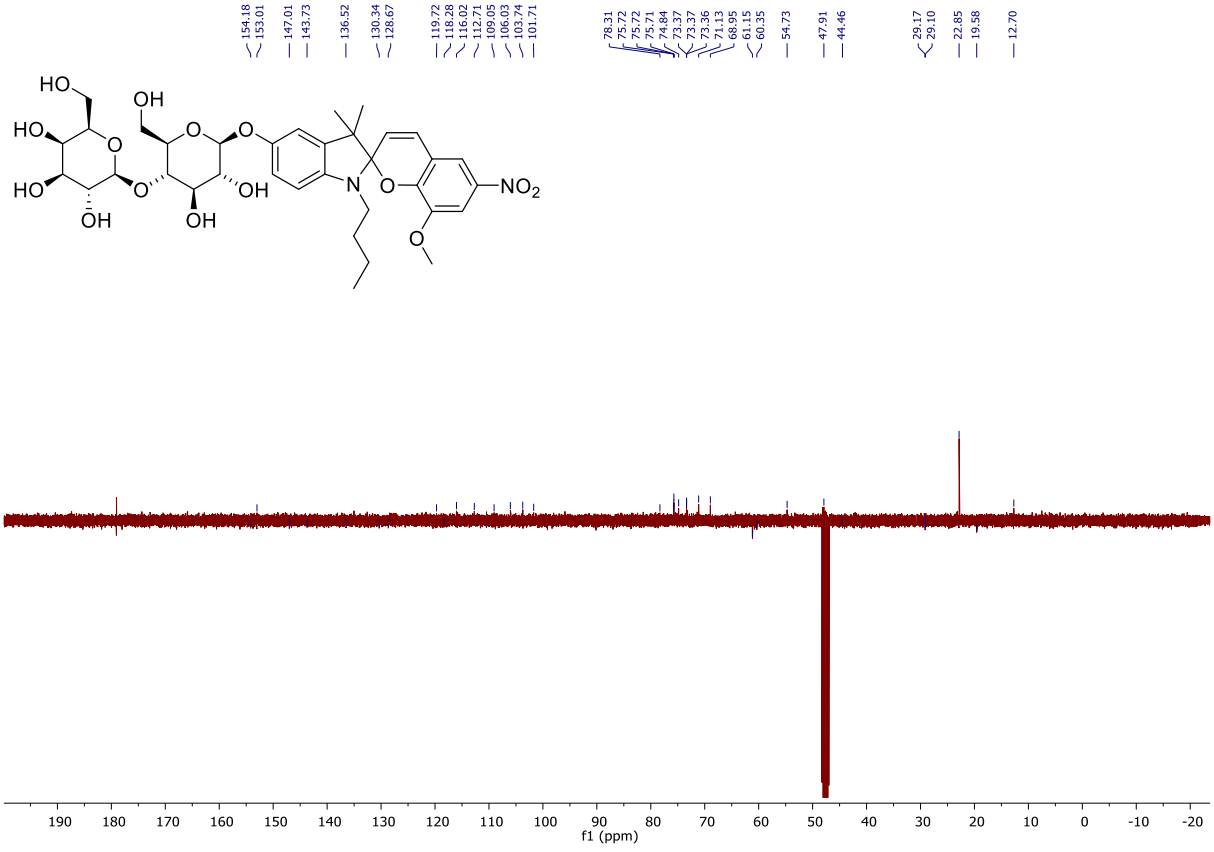


*Figure 60: ^{13}C NMR (500 MHz, MeOD-d$_4$) of surfactant **110**.*

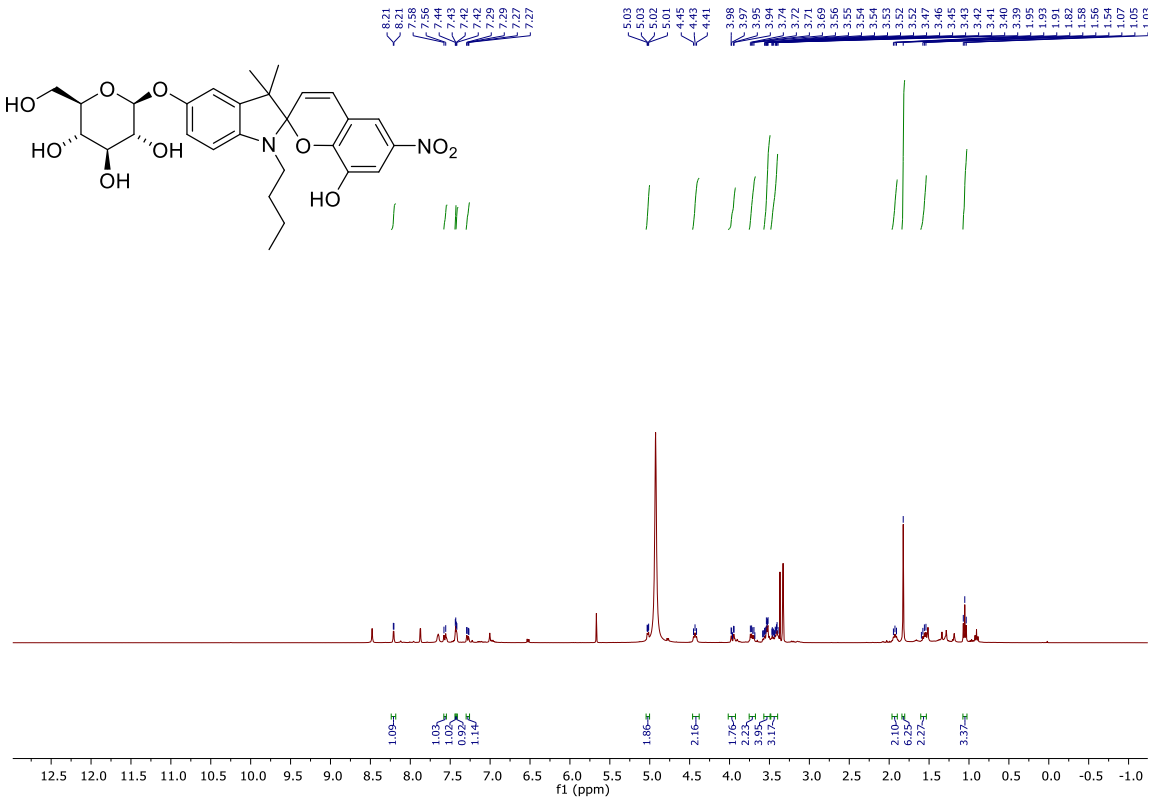


*Figure 61: ^{1}H NMR (500 MHz, MeOD-d_4) of surfactant **109**.*

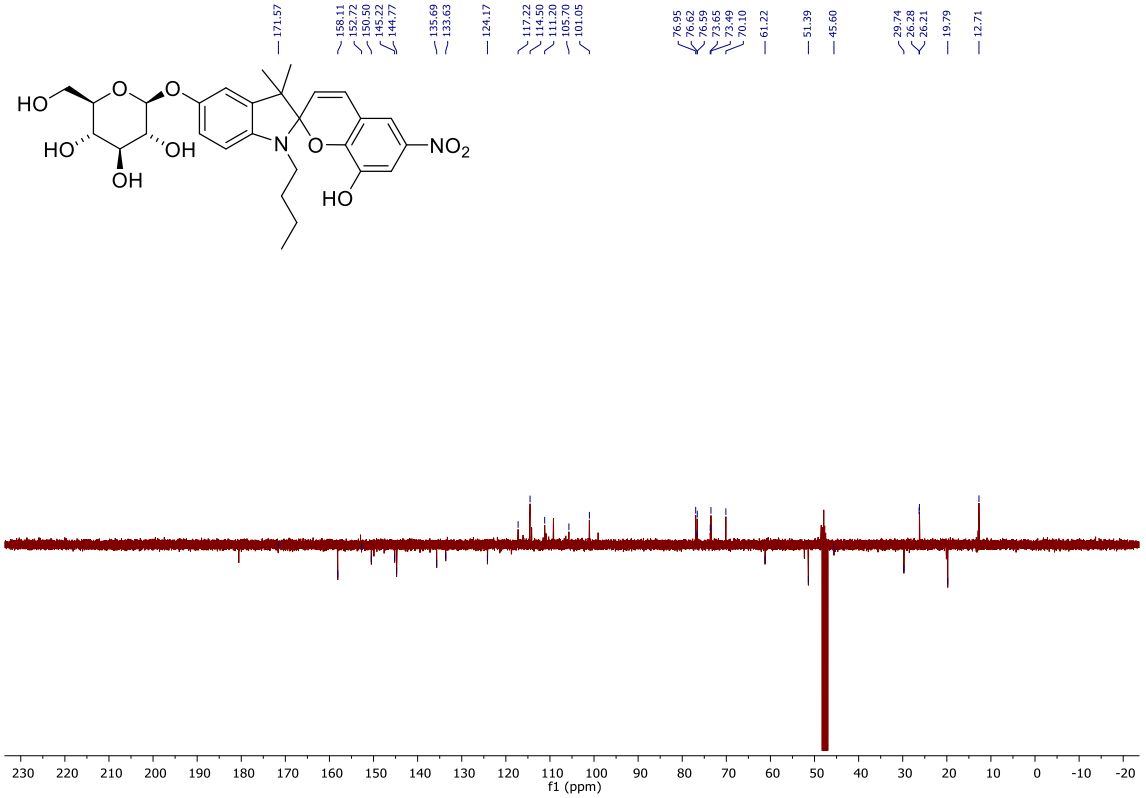


*Figure 62: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **109**.*

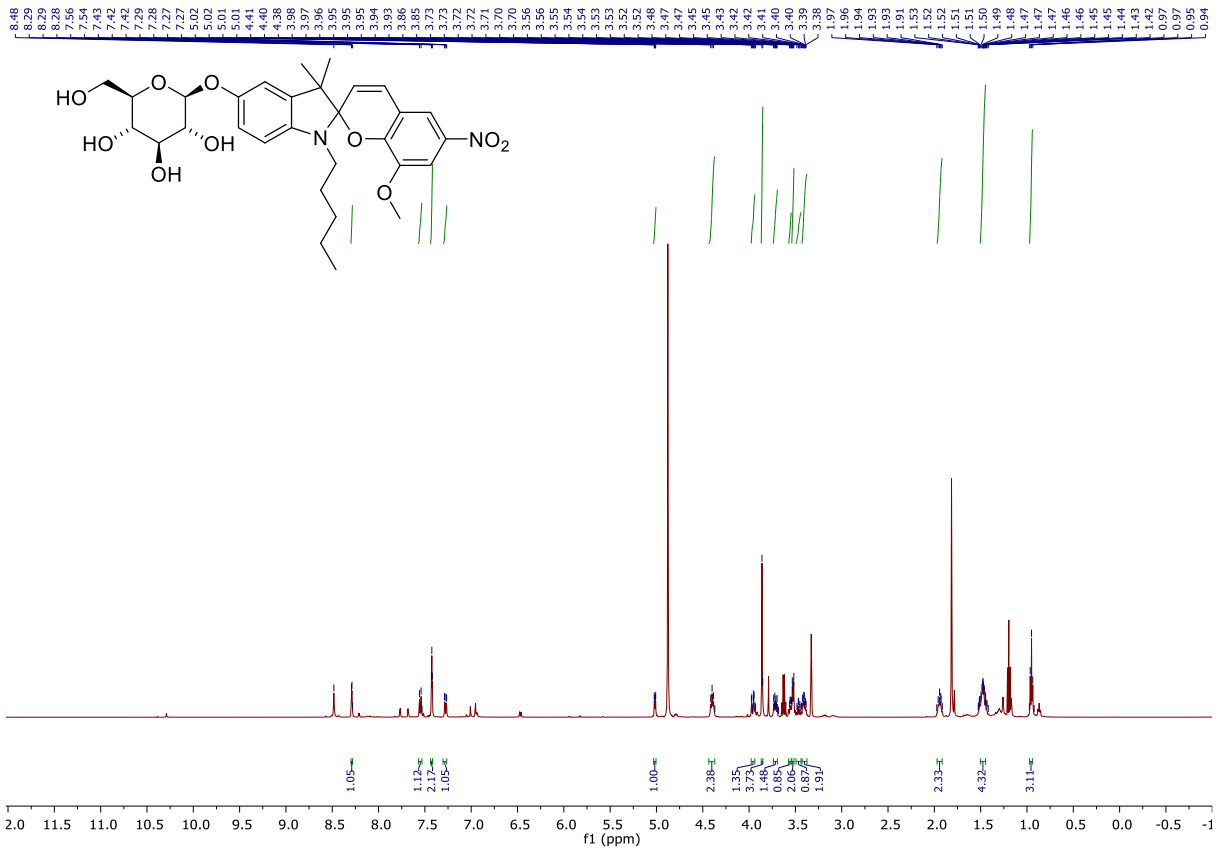


*Figure 63: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **111**.*

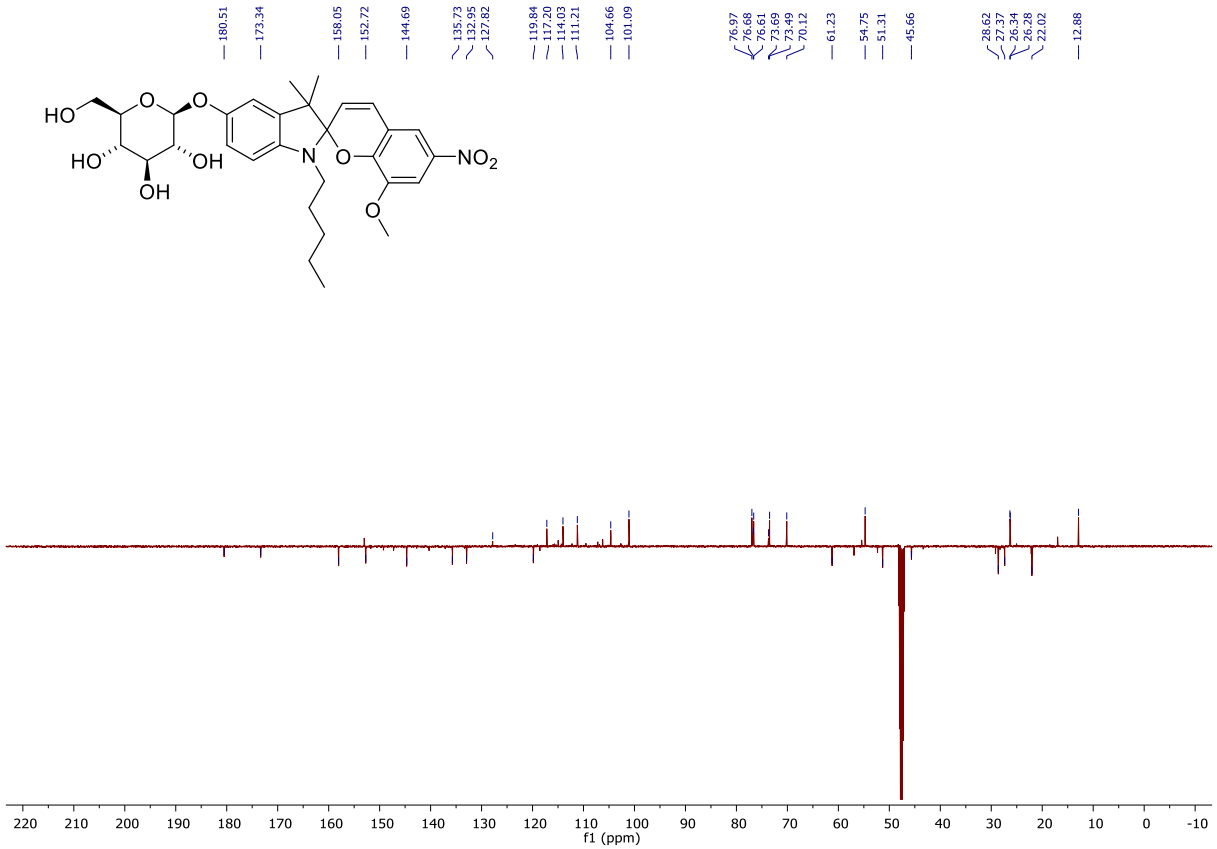


*Figure 64: ^{13}C NMR (500 MHz, MeOD-d$_4$) of surfactant **111**.*

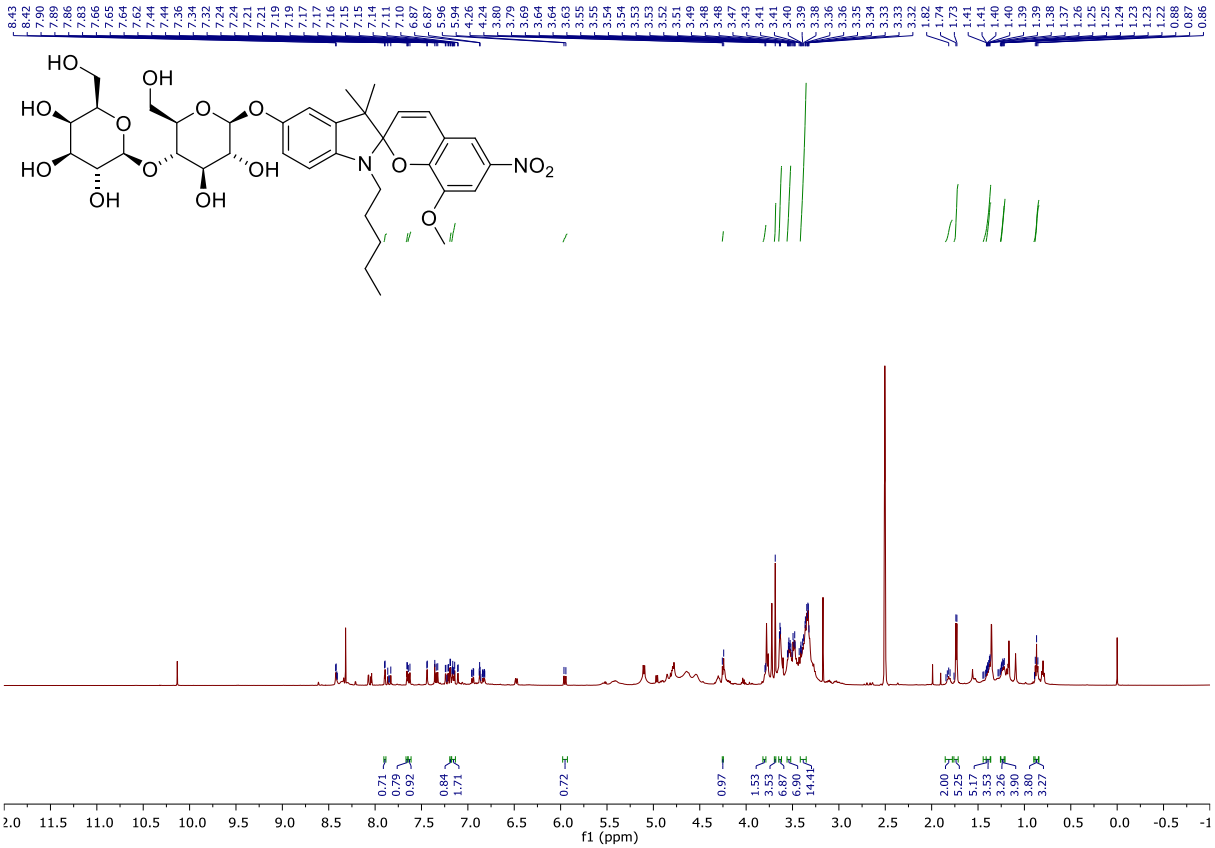


*Figure 65: ^{1}H NMR (500 MHz, MeOD-d_4) of surfactant **112**.*

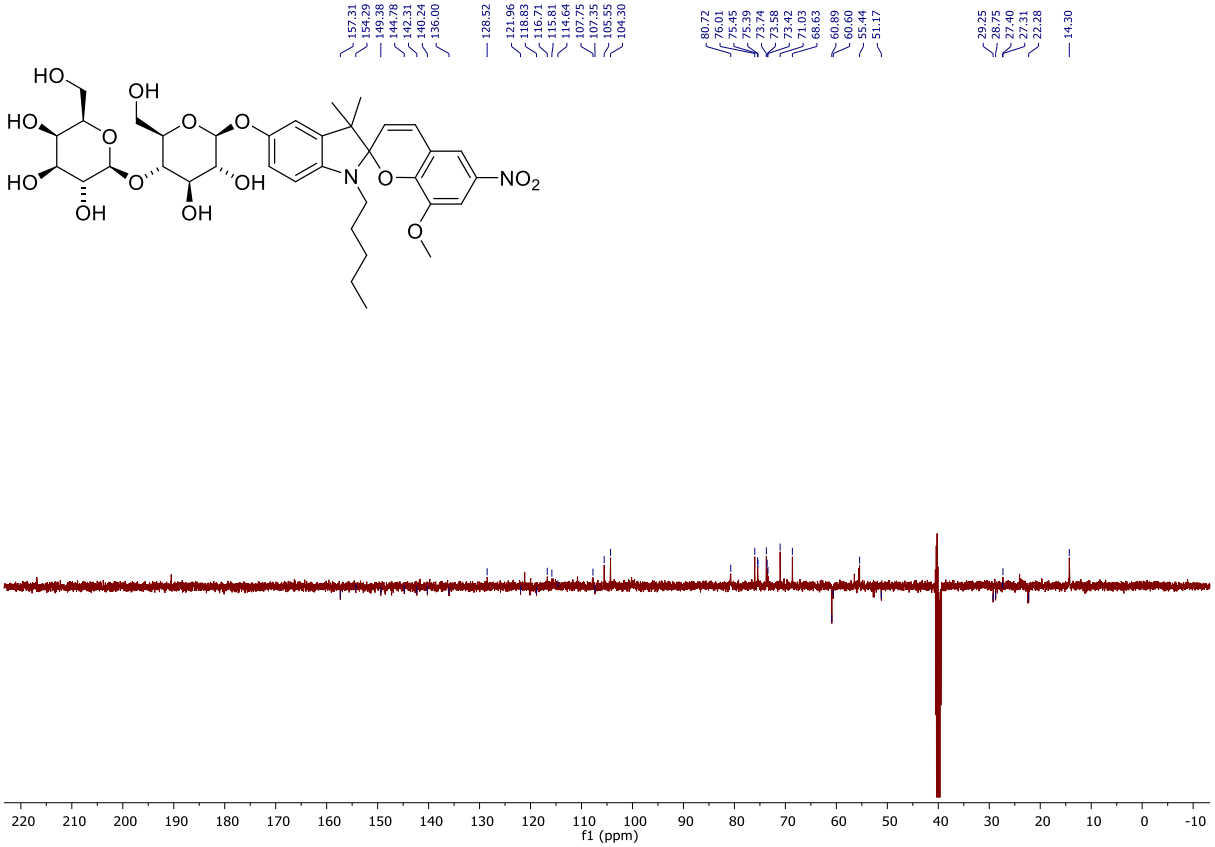


*Figure 66: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **112**.*

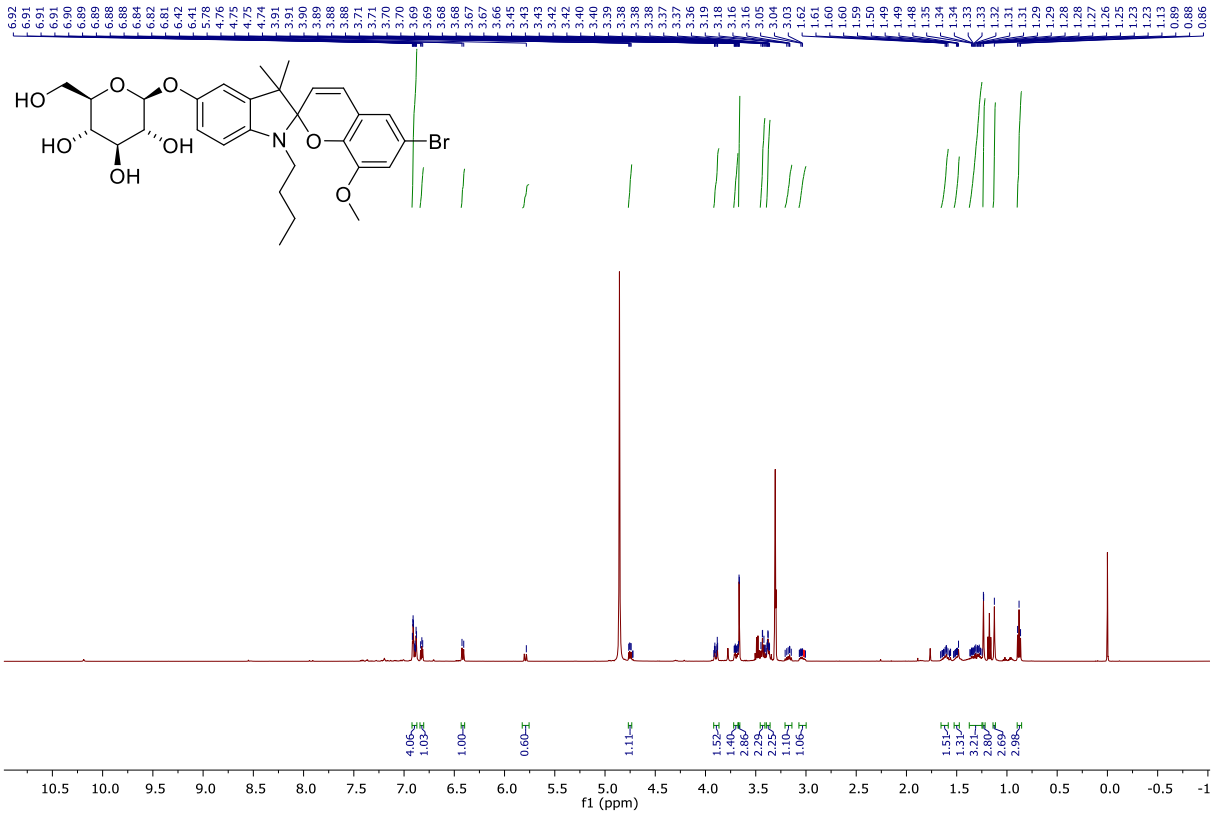


*Figure 67: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **115**.*

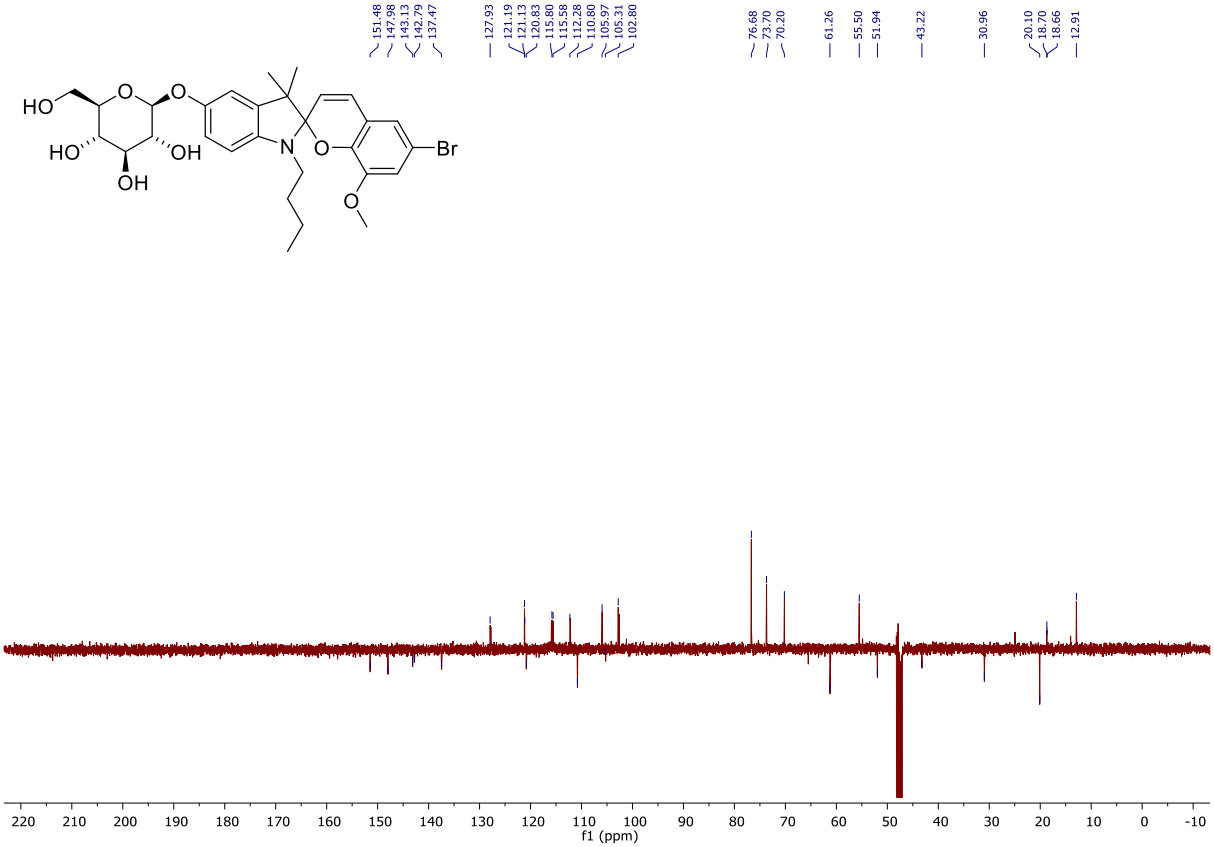


*Figure 68: ^{13}C NMR (500 MHz, MeOD-d$_4$) of surfactant **115***

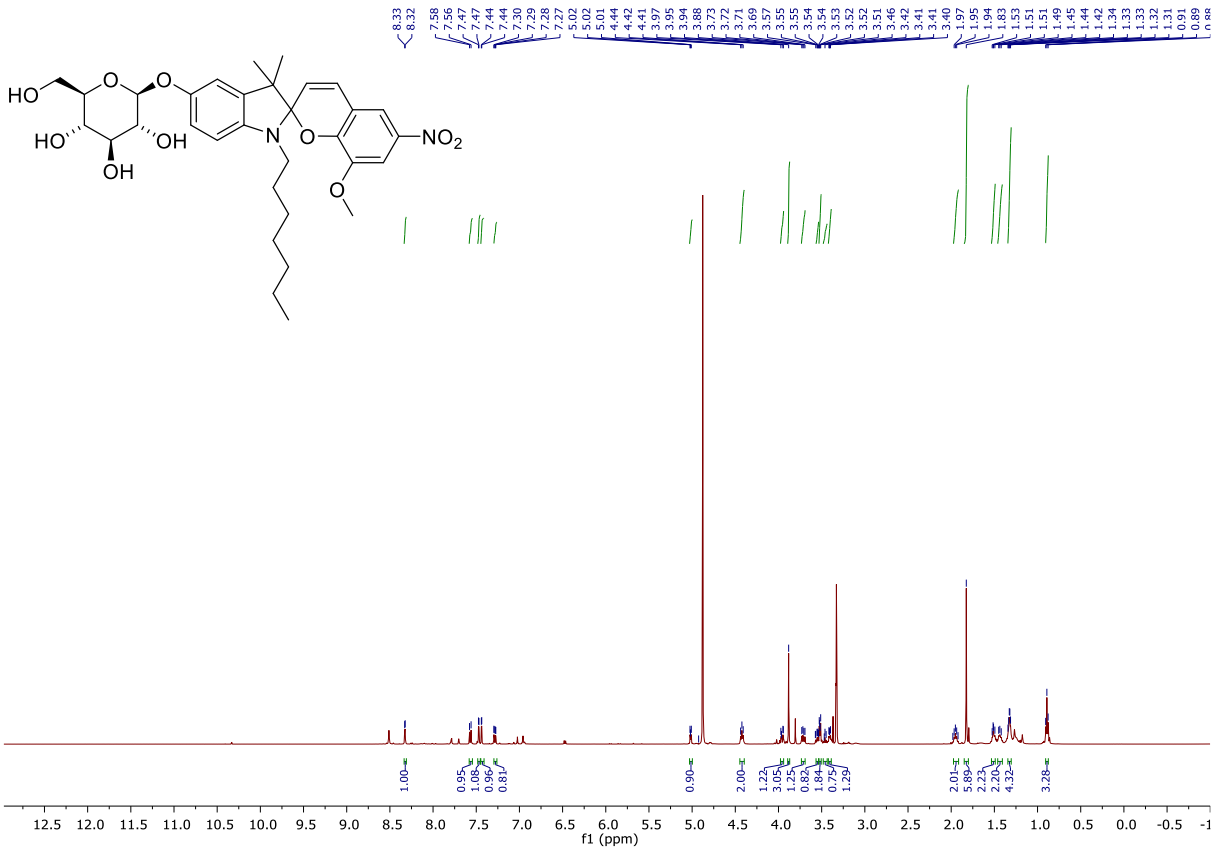


*Figure 69: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **114**.*

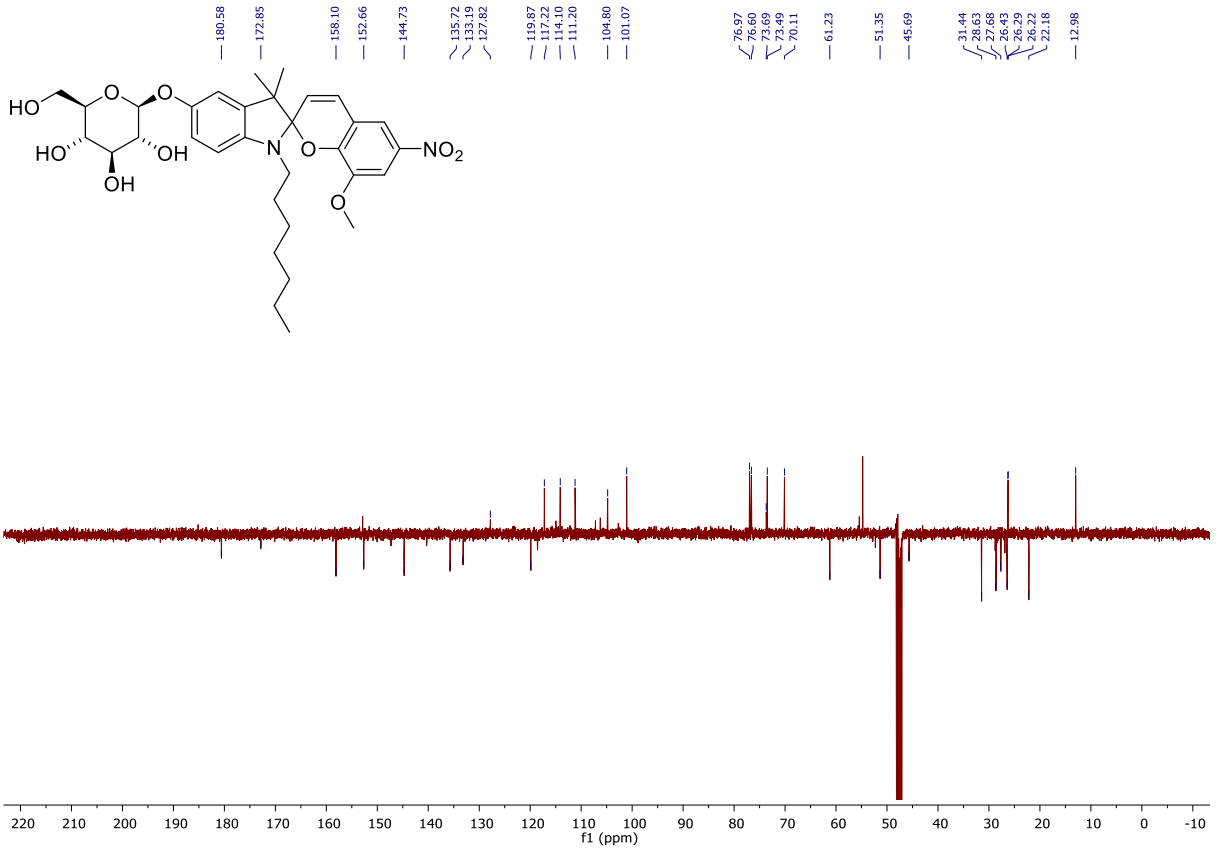


*Figure 70: ^{13}C NMR (500 MHz, MeOD-d$_4$) of surfactant **114***

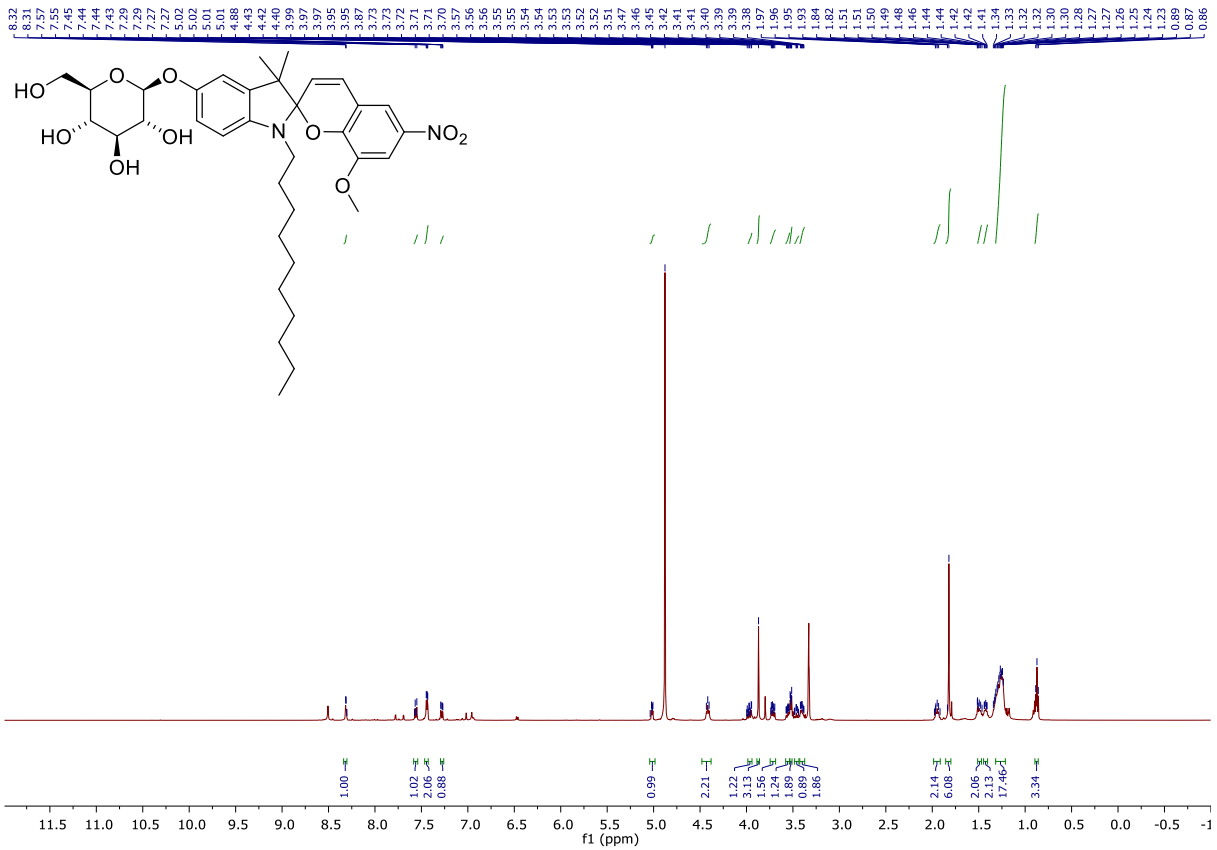


*Figure 71: ^{1}H NMR (500 MHz, MeOD-d_4) of surfactant **113**.*

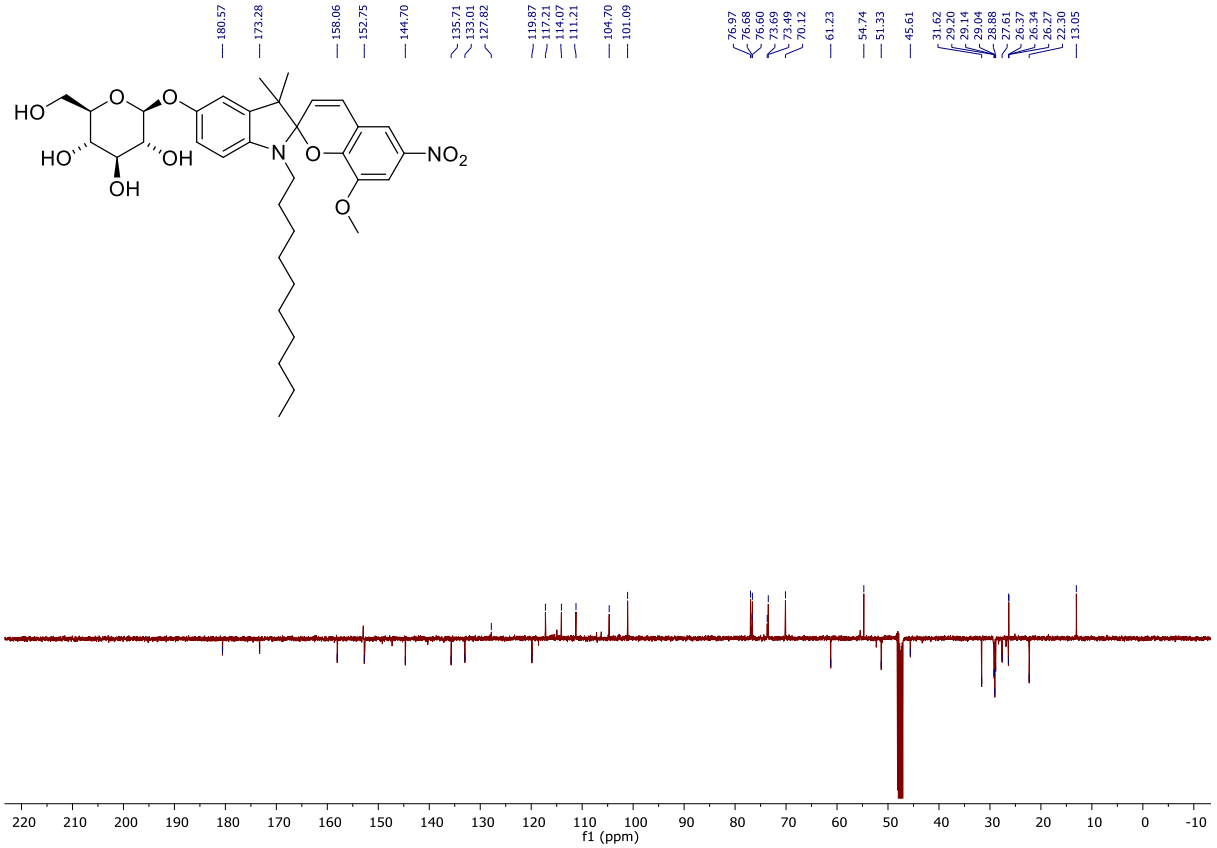


*Figure 72: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **113***

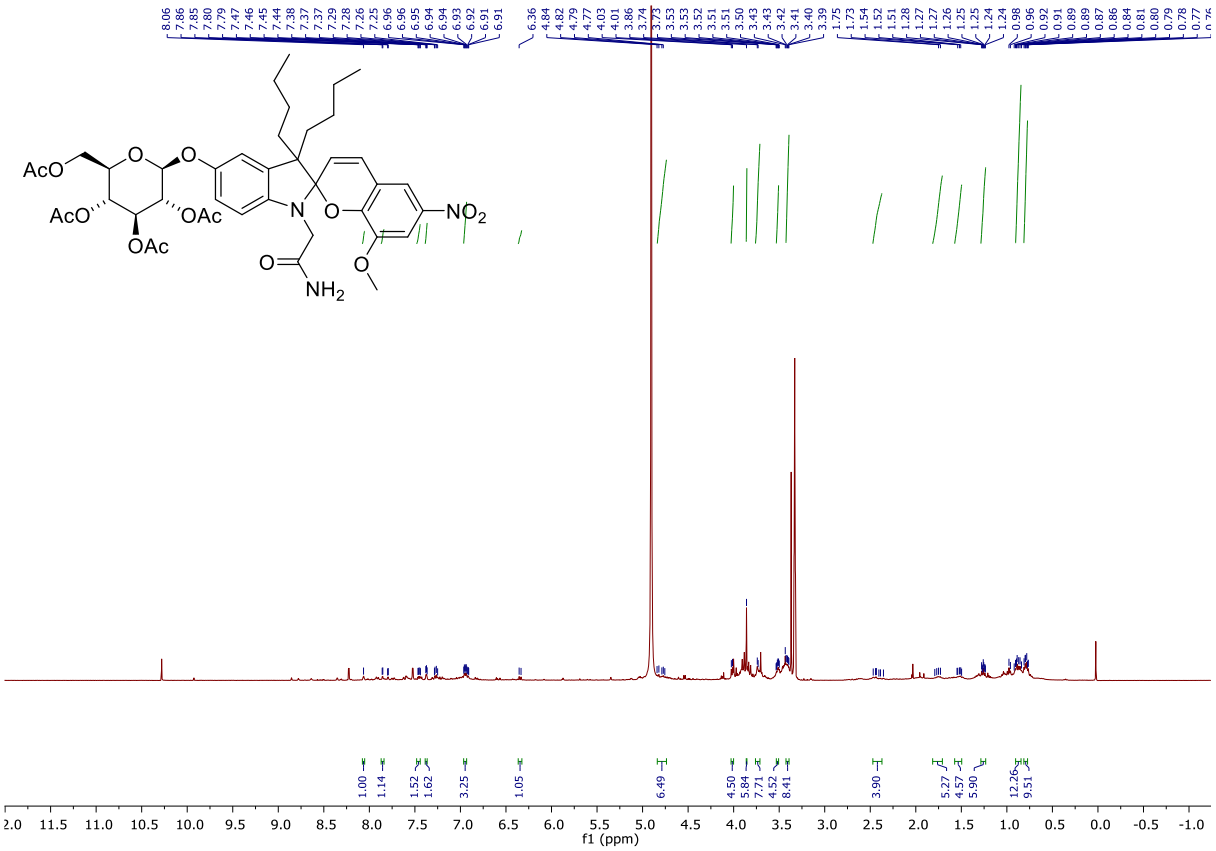


*Figure 73: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **121**.*

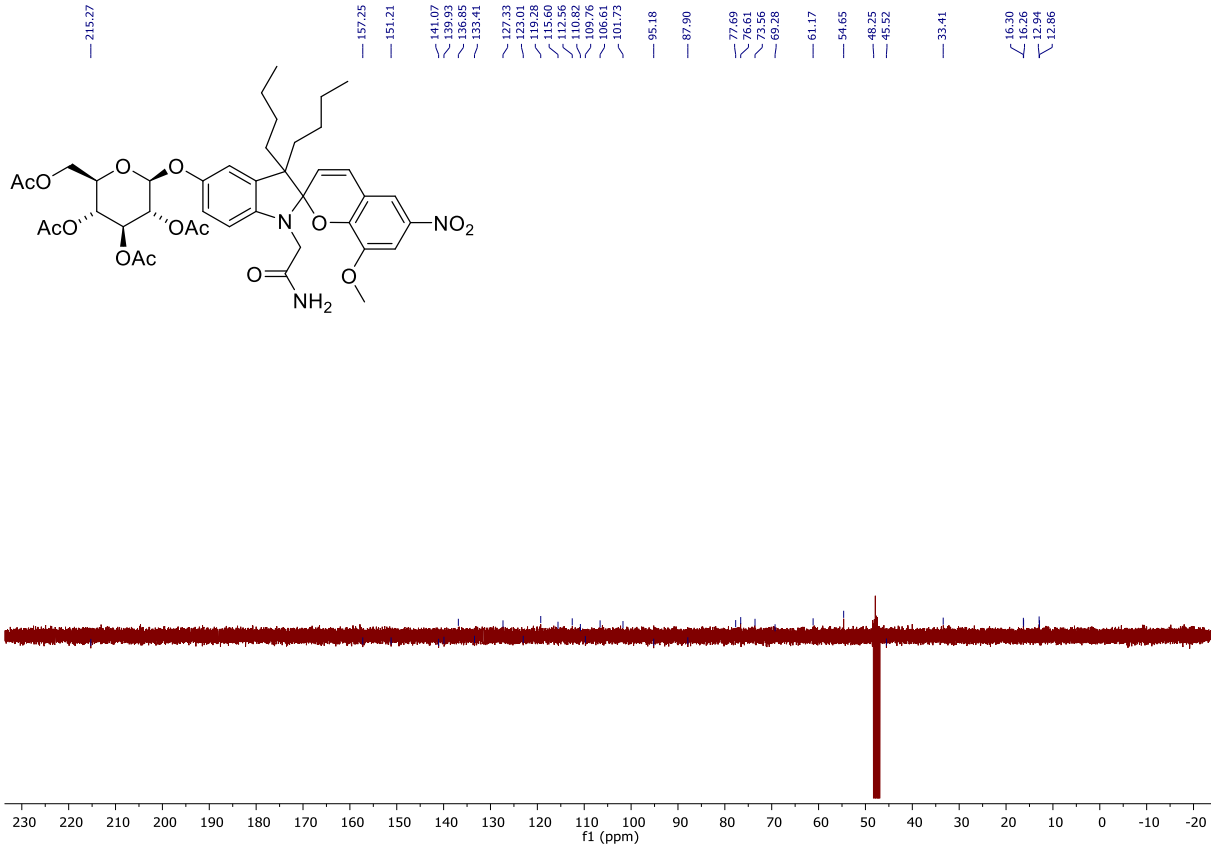


*Figure 74: ^{13}C NMR (500 MHz, MeOD-d$_4$) of surfactant **121***

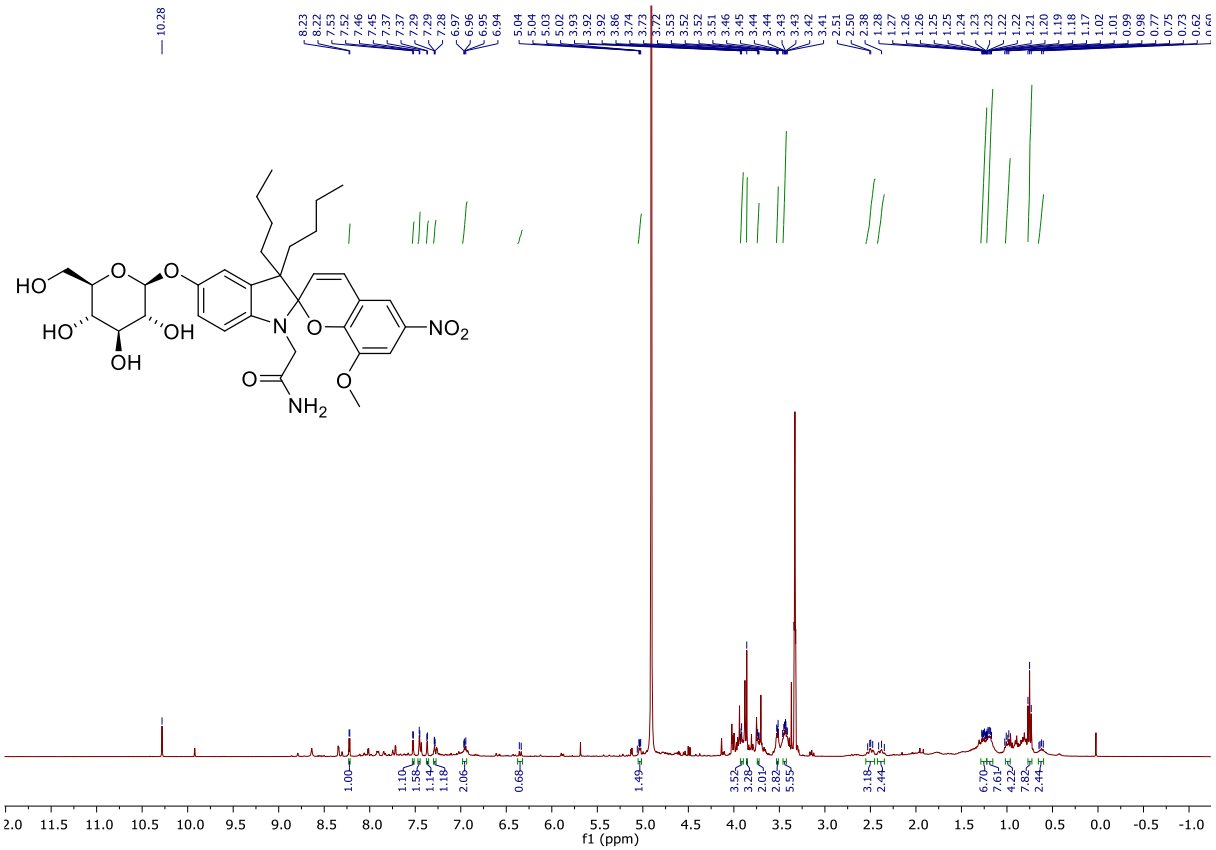


*Figure 75: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **122**.*

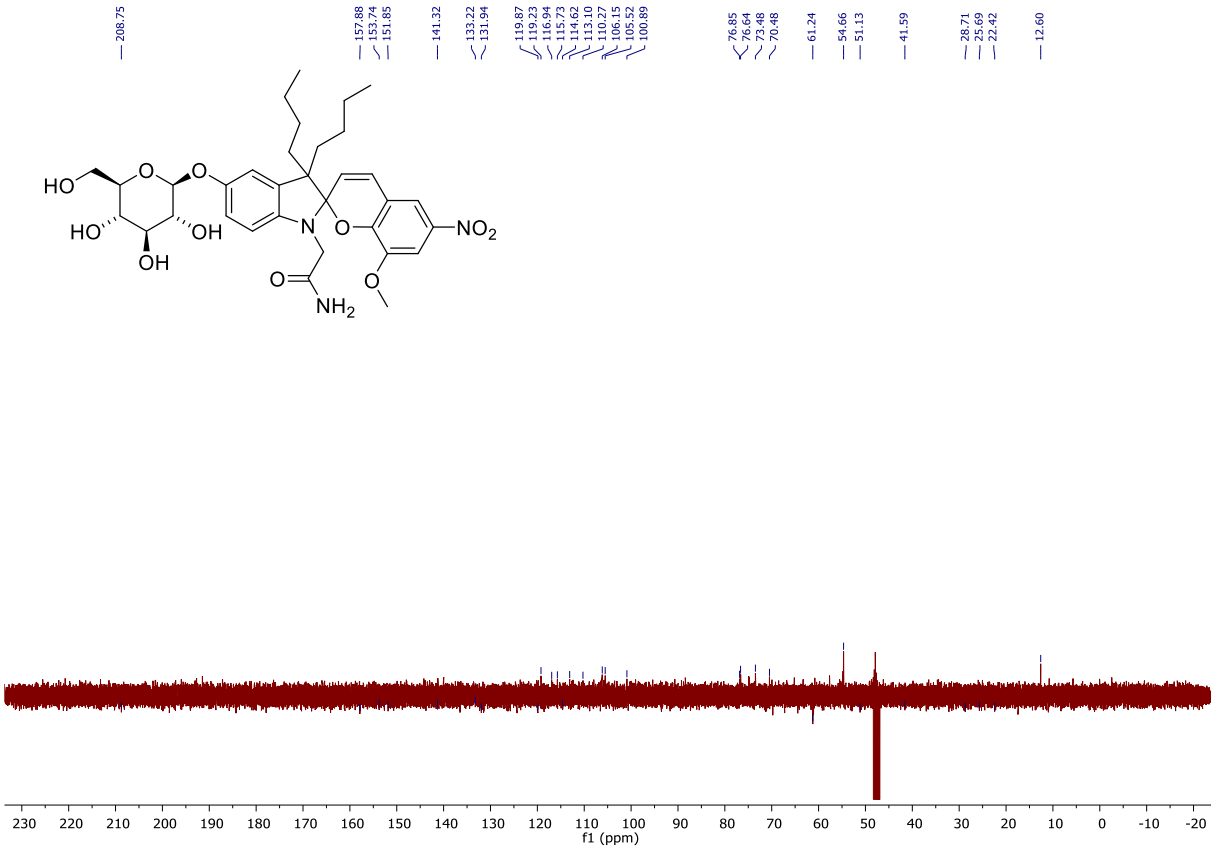


*Figure 76: ^{13}C NMR (500 MHz, MeOD-d$_4$) of surfactant **122**.*

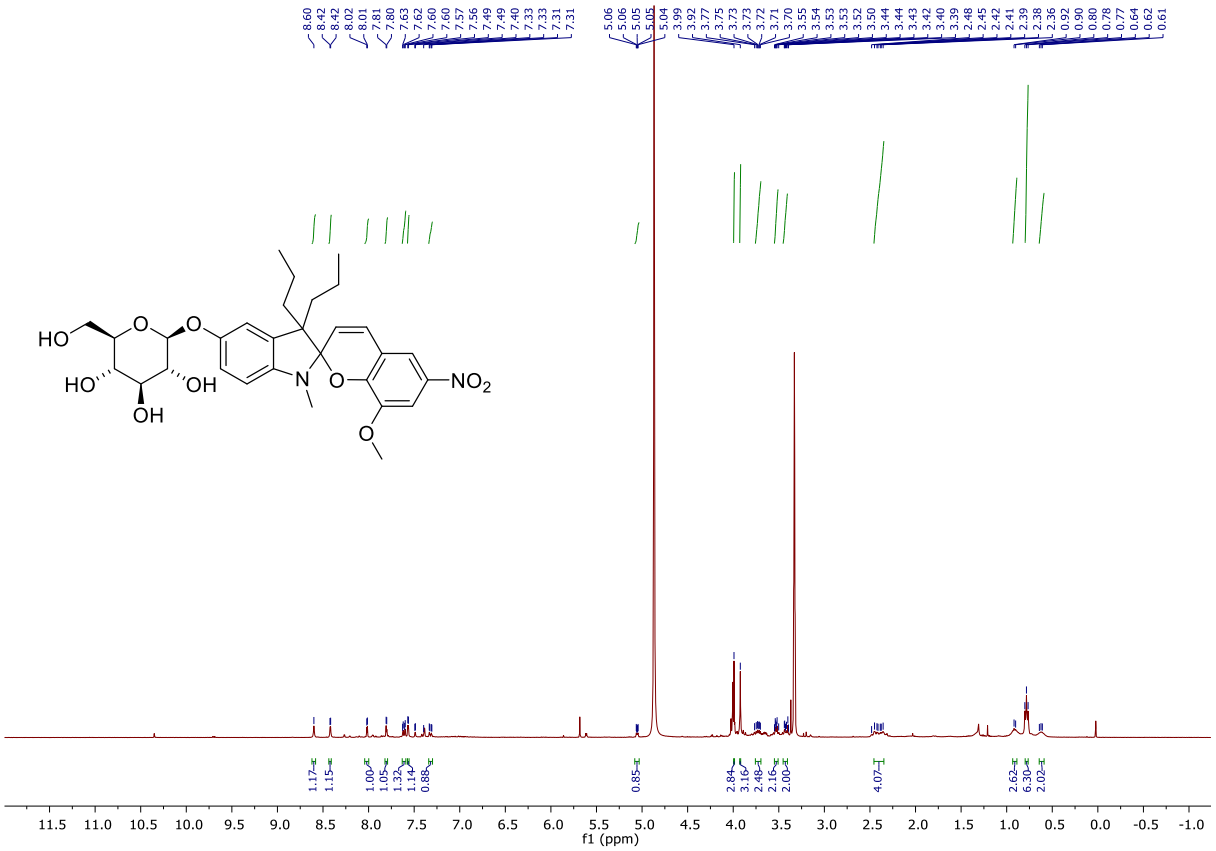


*Figure 77: [1]H NMR (500 MHz, MeOD-d4) of surfactant **119**.*

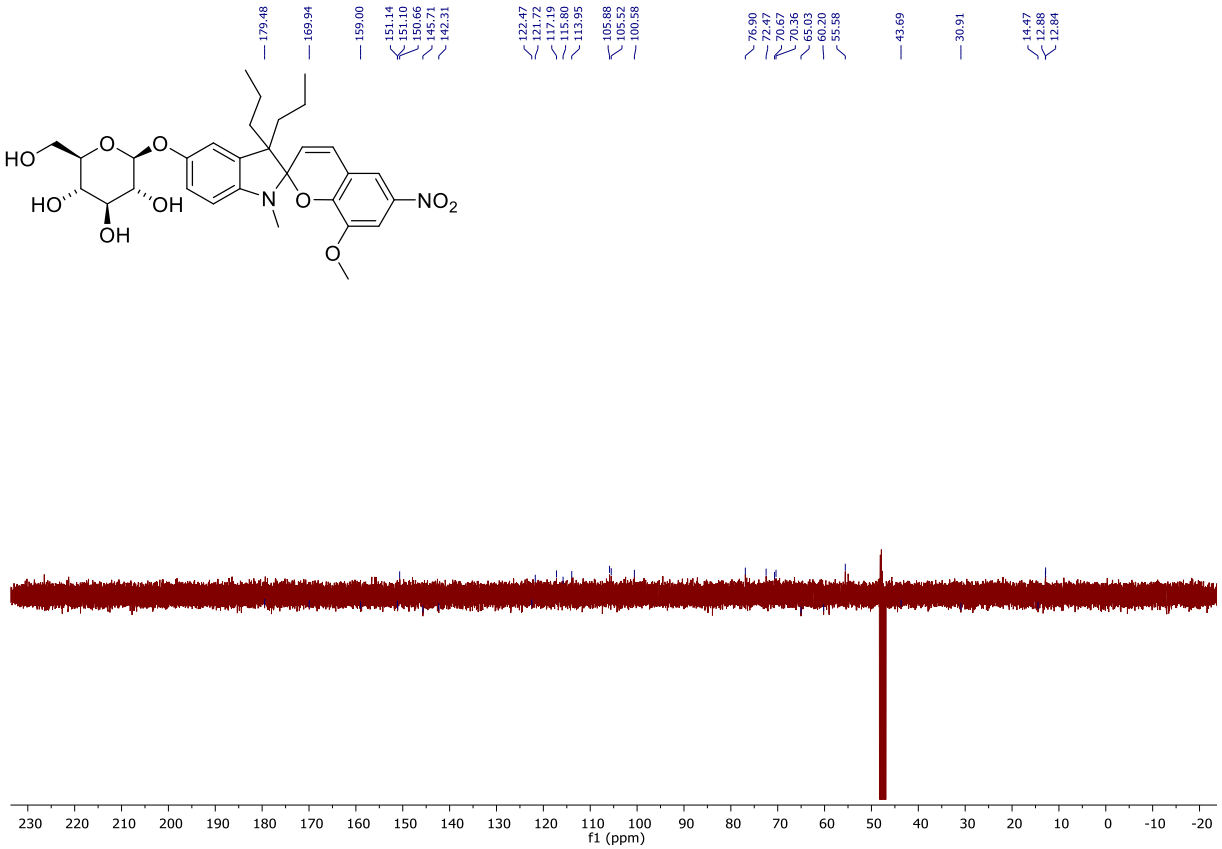


*Figure 78: [13]C NMR (500 MHz, MeOD-d4) of surfactant **119**.*

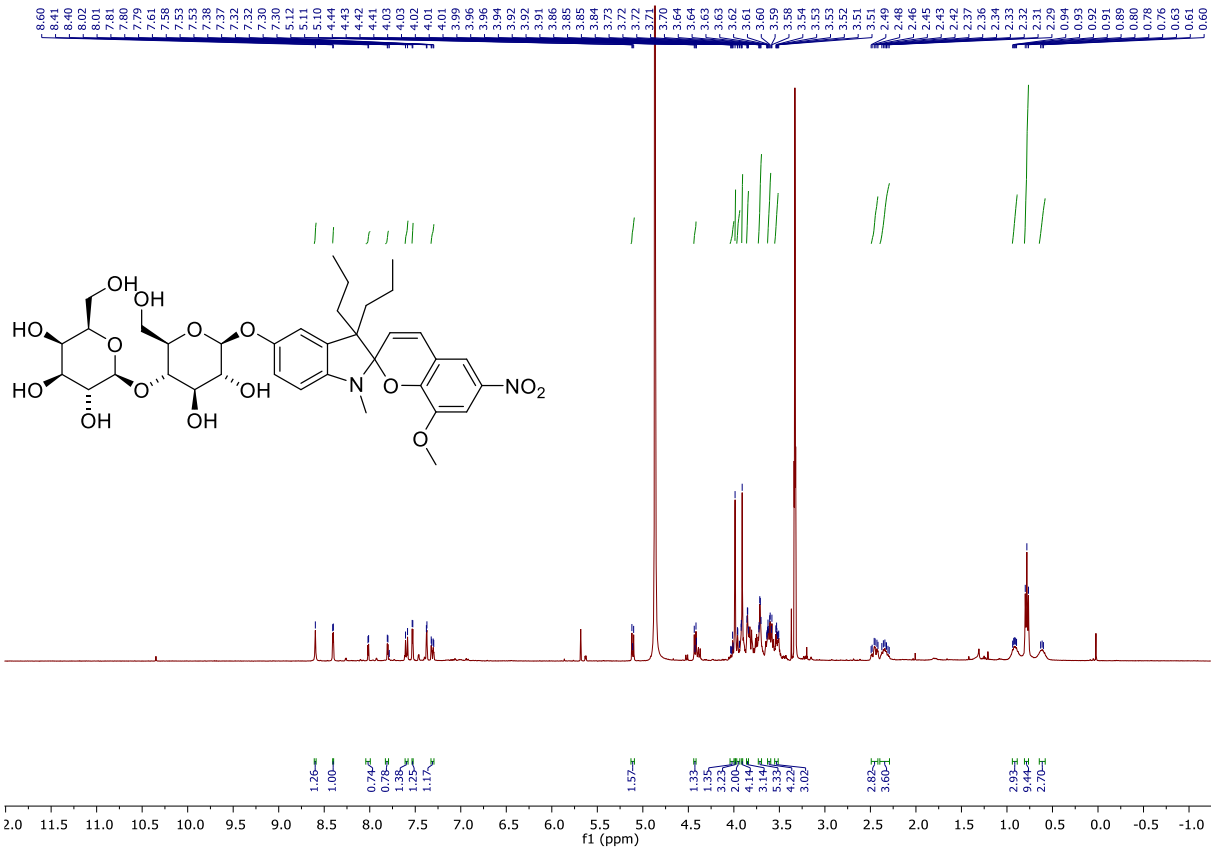


*Figure 79: ^{1}H NMR (500 MHz, MeOD-d_4) of surfactant **120**.*

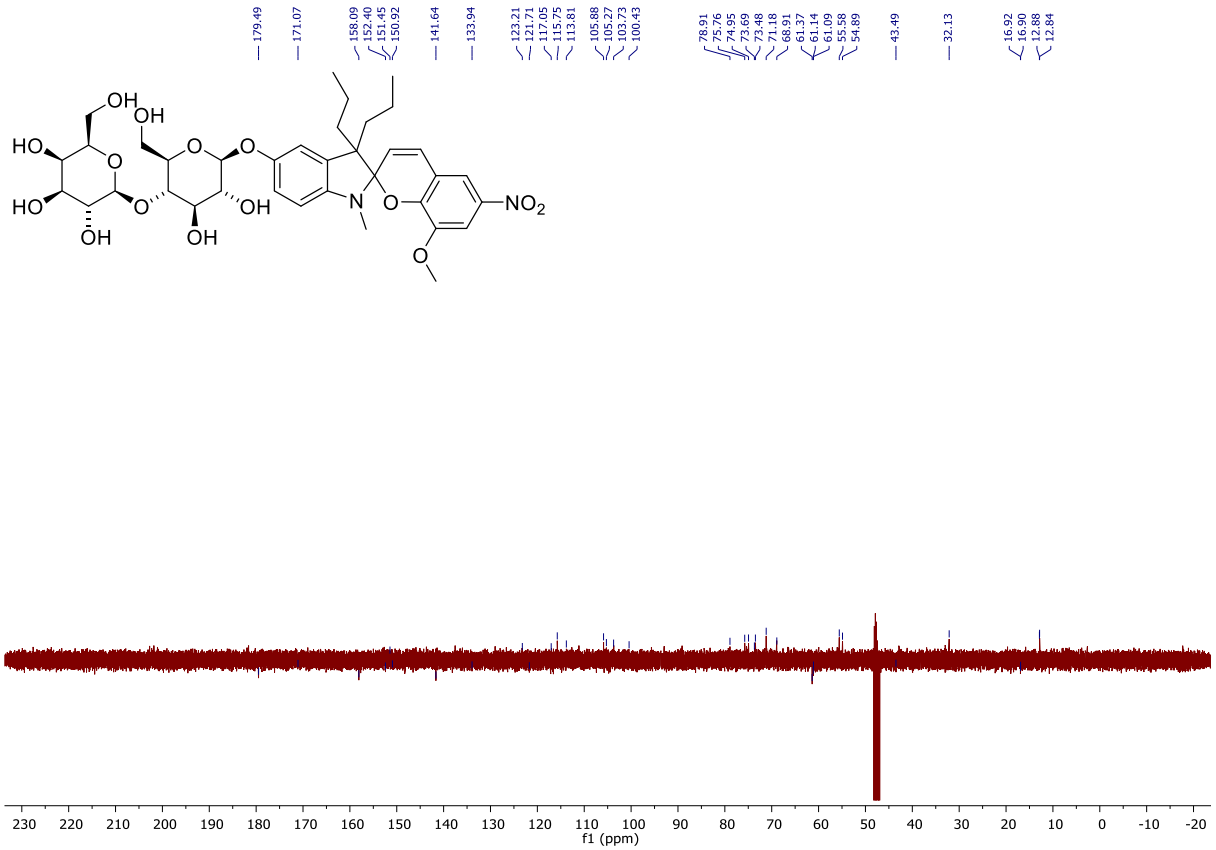


*Figure 80: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **120**.*

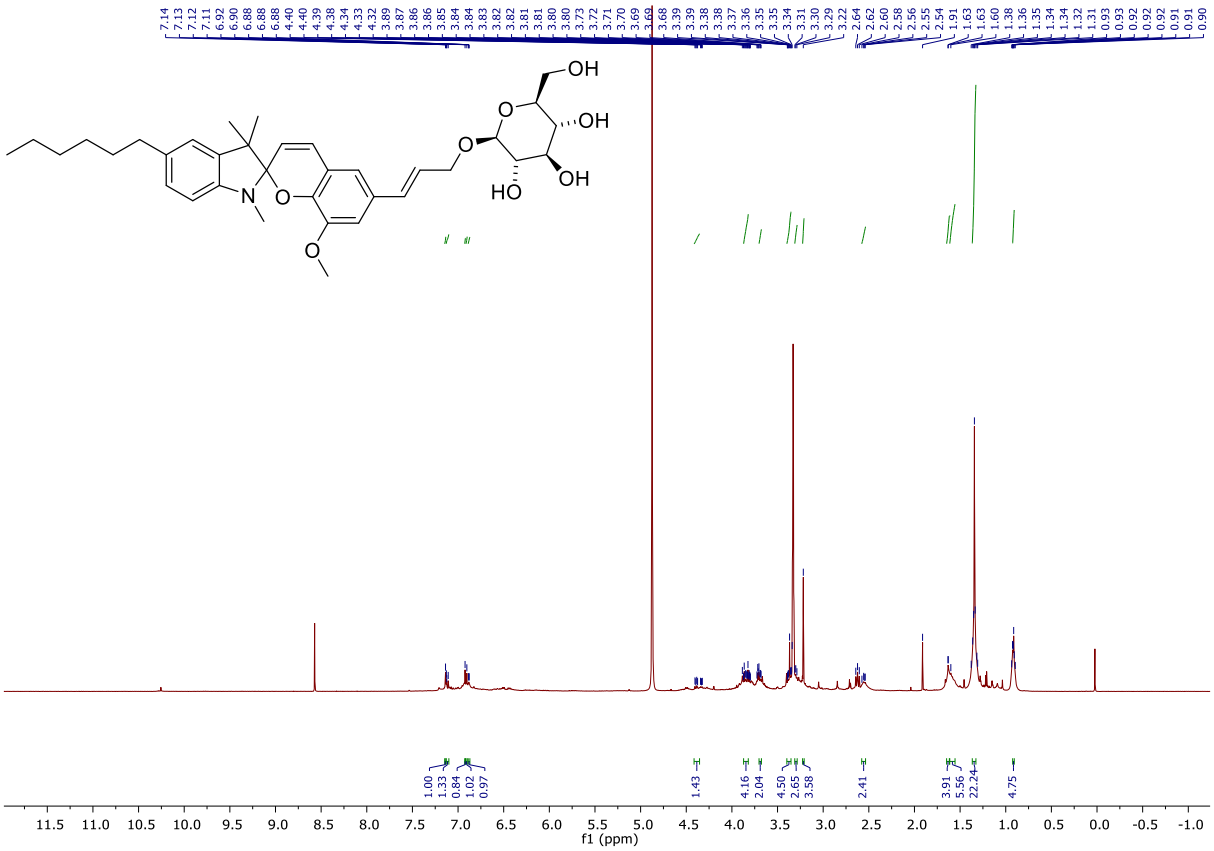


*Figure 81: ^{1}H NMR (500 MHz, $CDCl_3$) of surfactant **116**.*

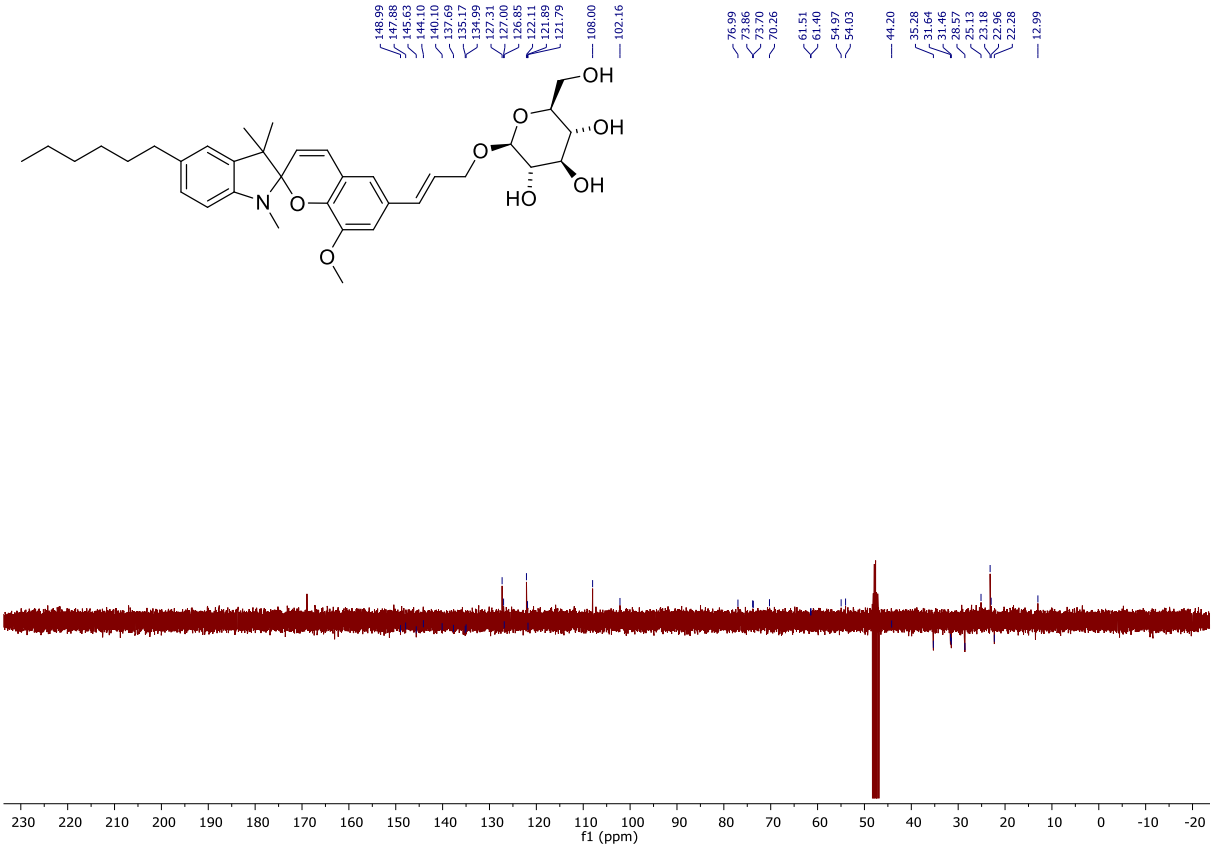


*Figure 82: ^{13}C NMR (500 MHz, $CDCl_3$) of surfactant **116**.*

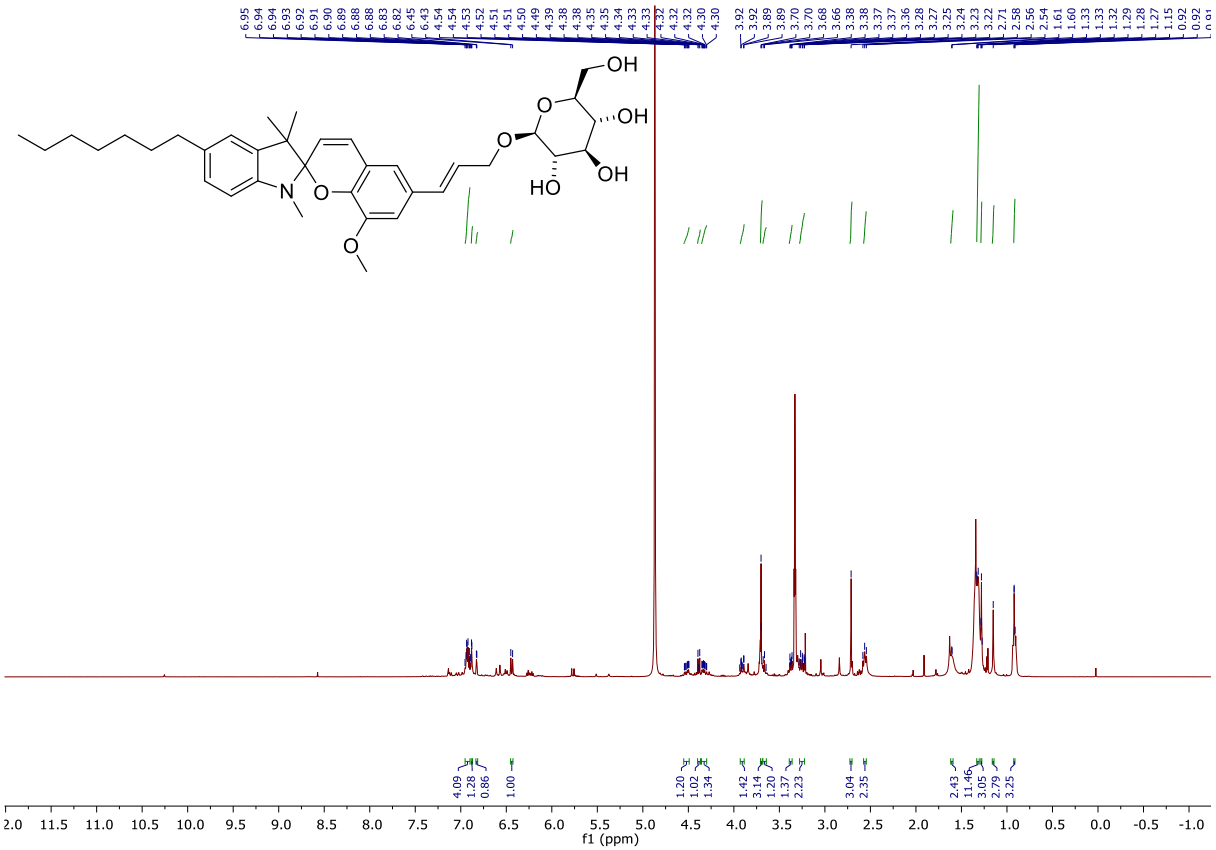


*Figure 83: ^{1}H NMR (500 MHz, $CDCl_3$) of surfactant **117**.*

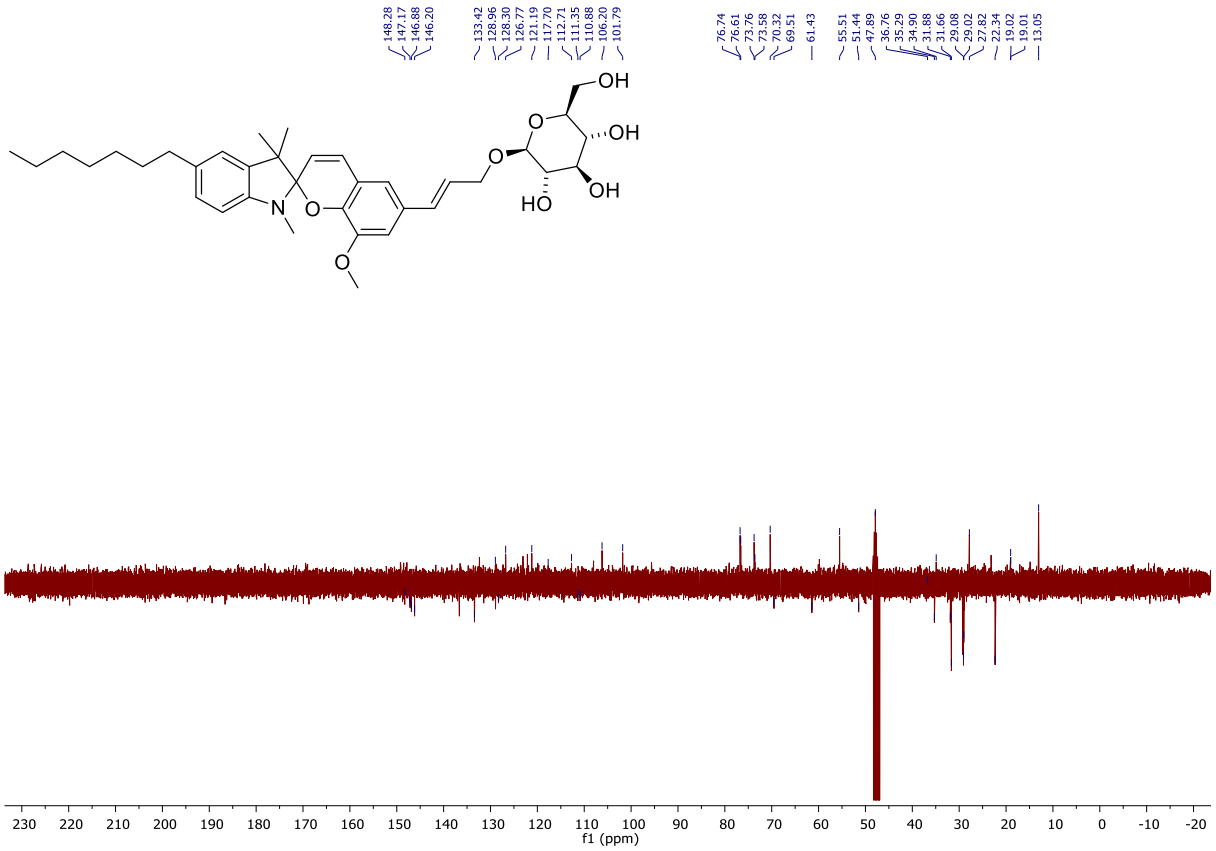


*Figure 84: ^{13}C NMR (500 MHz, $CDCl_3$) of surfactant **117**.*

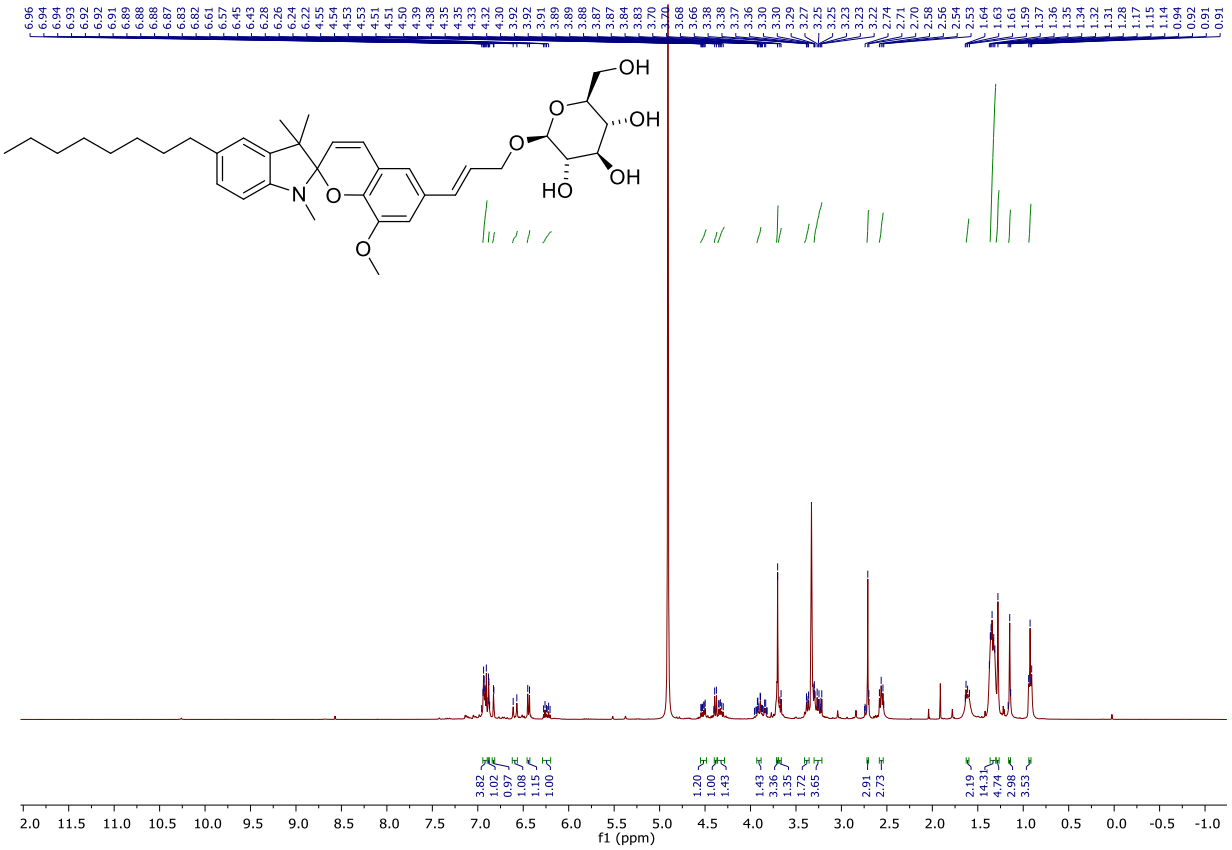


*Figure 85: ^{1}H NMR (500 MHz, $CDCl_3$) of surfactant **117**.*

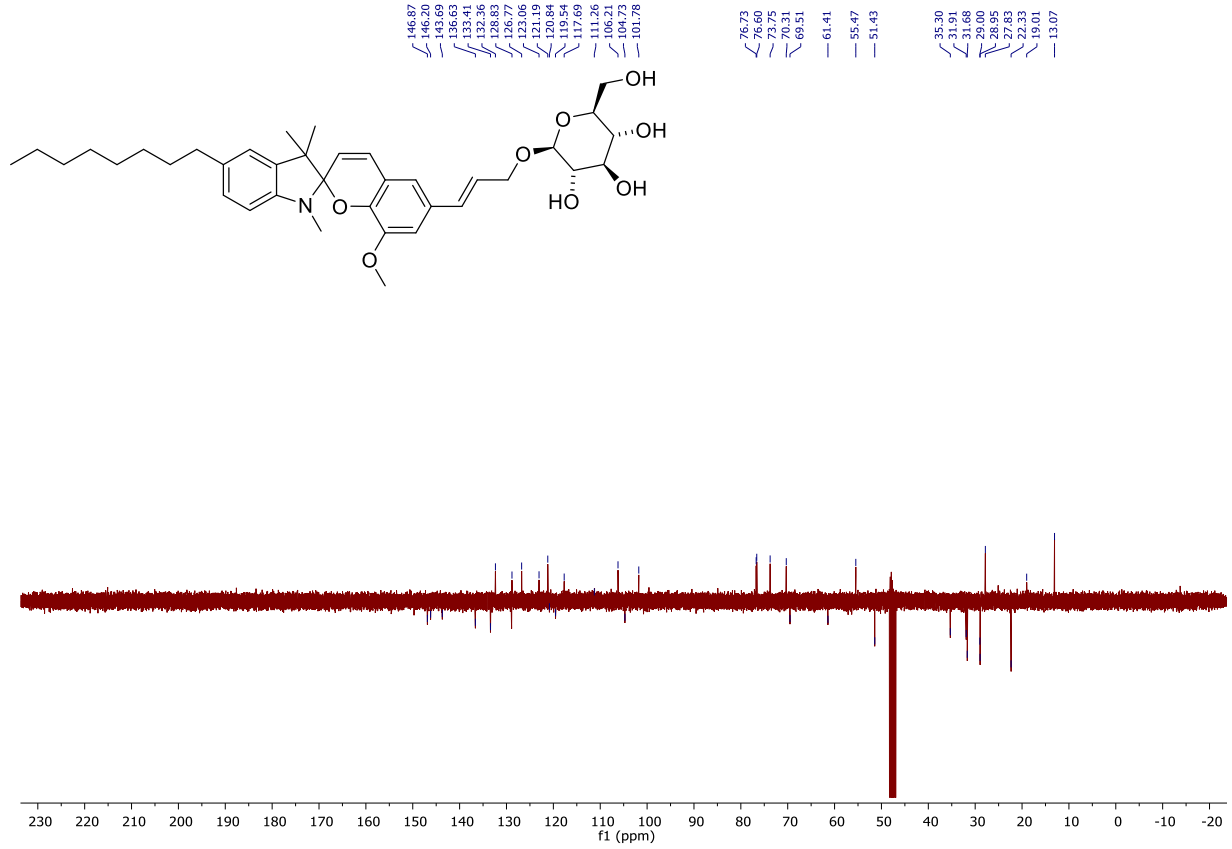


*Figure 86: ^{13}C NMR (500 MHz, $CDCl_3$) of surfactant **117**.*

13.4.2 NMR spectra of fluorescent silicon-based surfactants

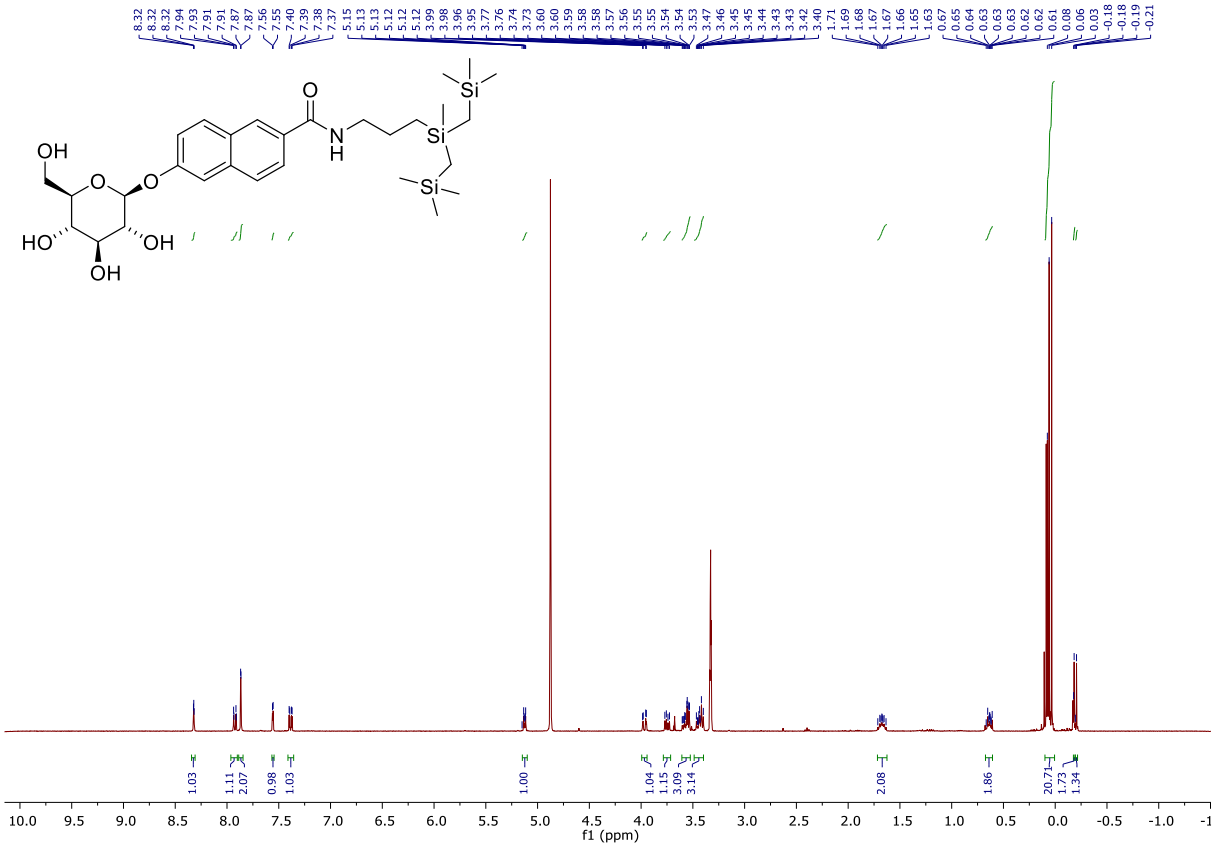


*Figure 87: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **168a**.*

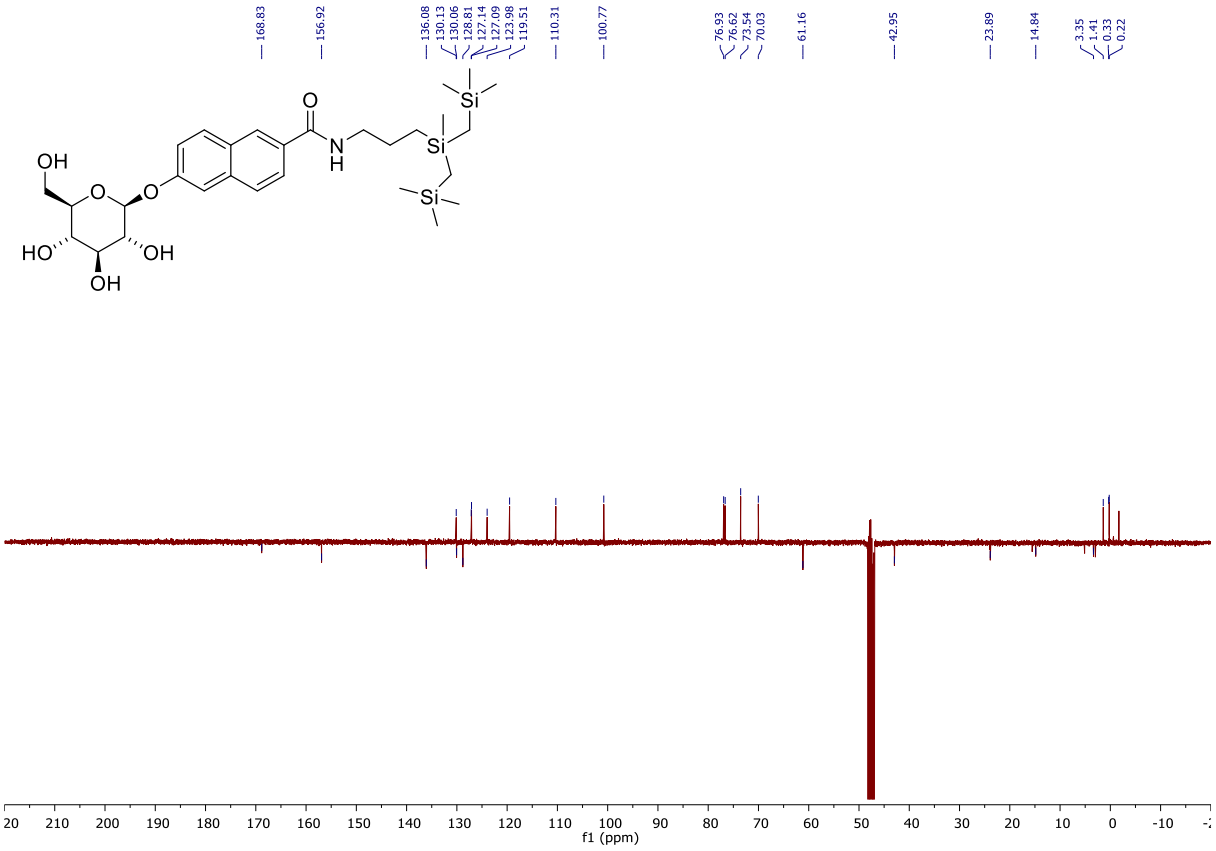


*Figure 88: ^{13}C NMR (500 MHz, MeOD-d$_4$) of surfactant **168a**.*

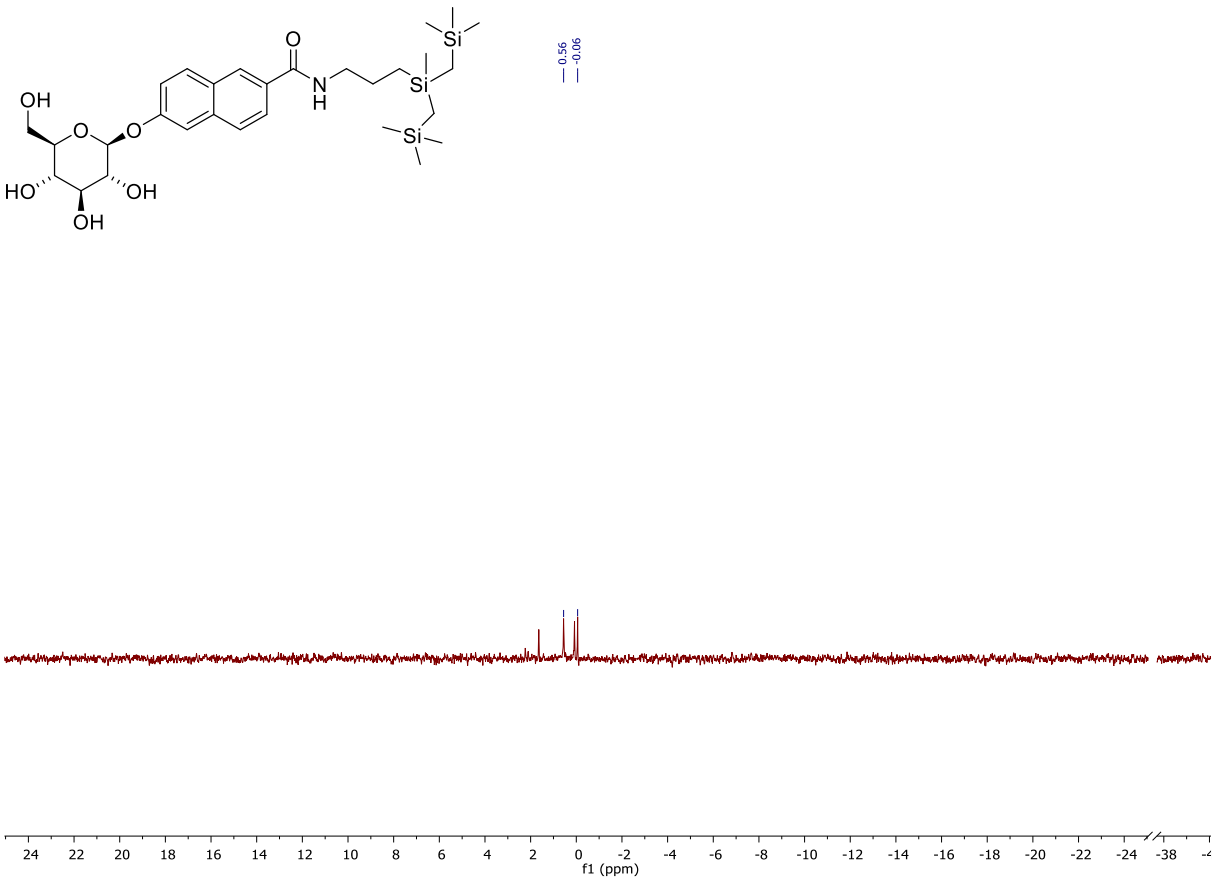


*Figure 89: ^{29}Si NMR (500 MHz, MeOD-d$_4$) of surfactant **168a**.*

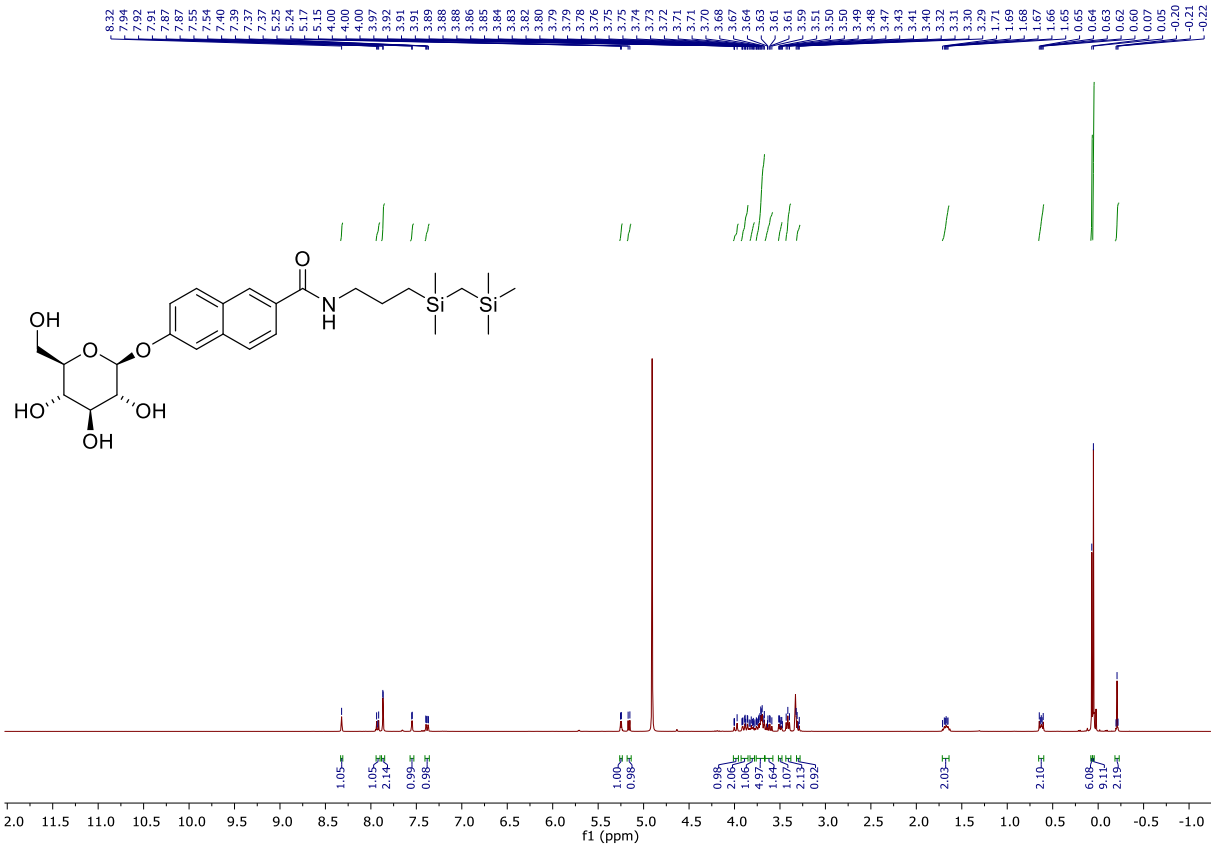


*Figure 90: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **166a**.*

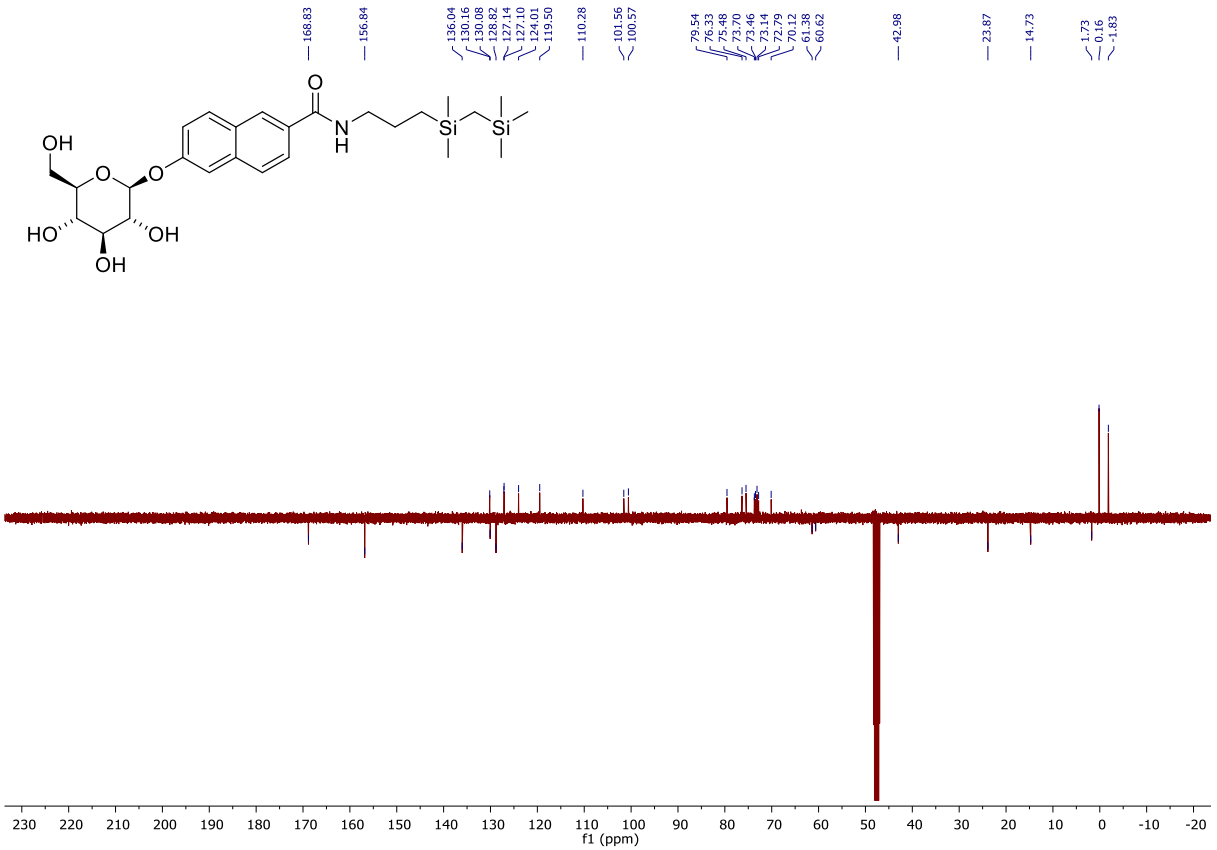


*Figure 91: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **166a**.*

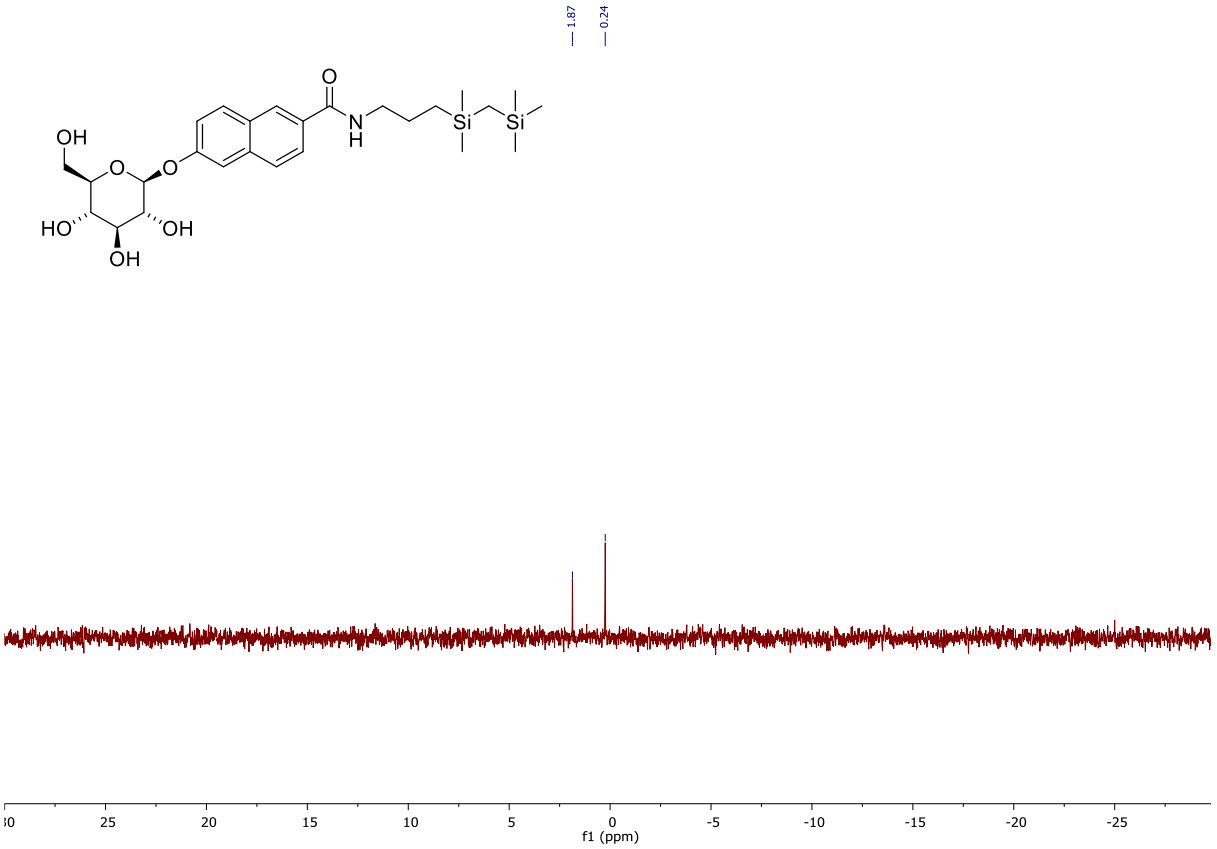


*Figure 92: ^{29}Si NMR (500 MHz, MeOD-d_4) of surfactant **166a**.*

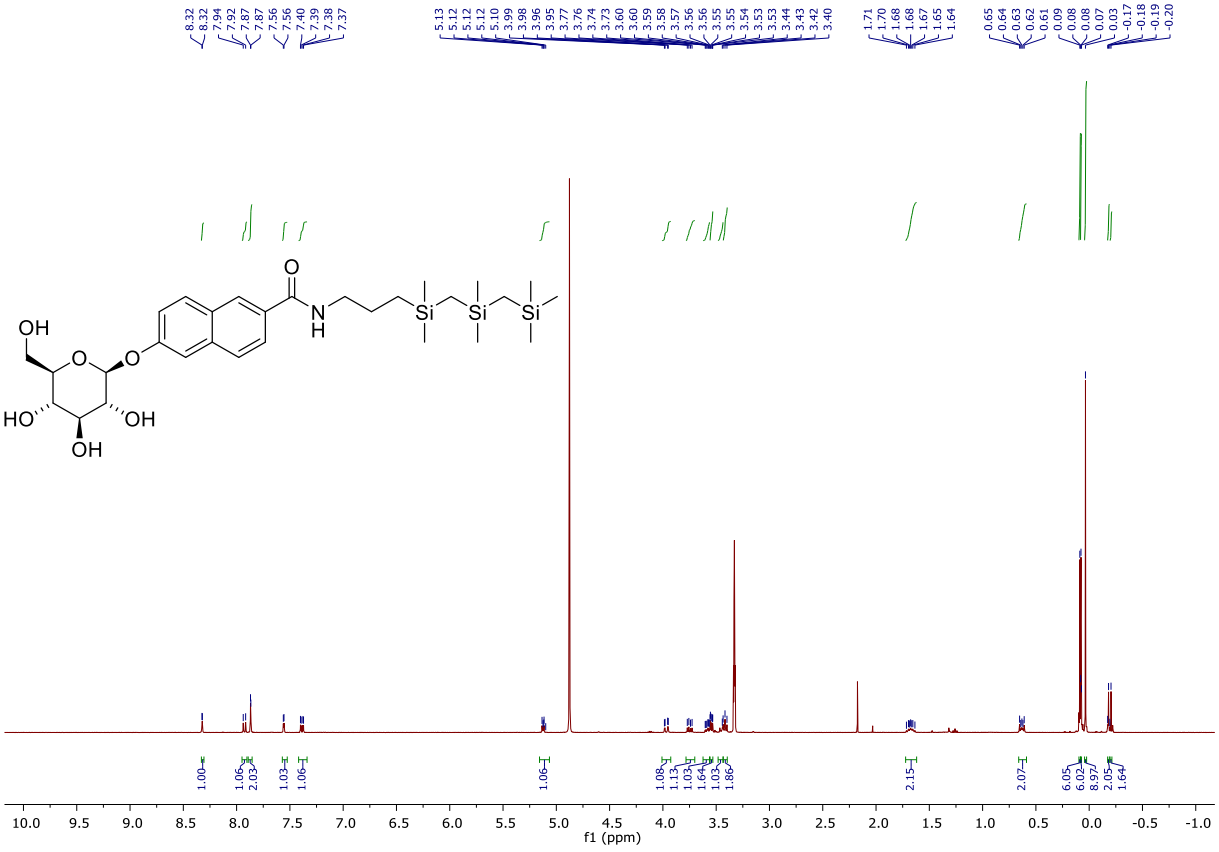


*Figure 93: ^{1}H NMR (500 MHz, MeOD-d_4) of surfactant **167a**.*

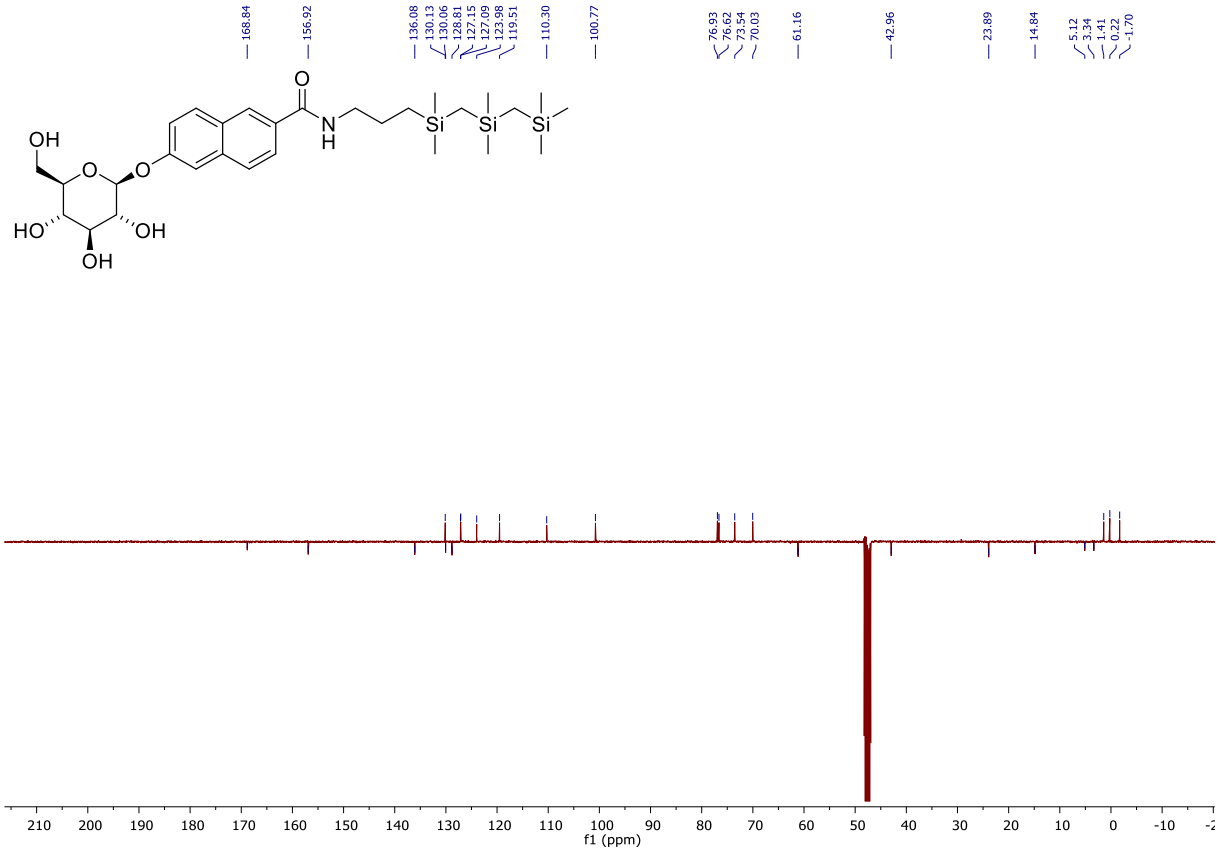


*Figure 94: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **167a**.*

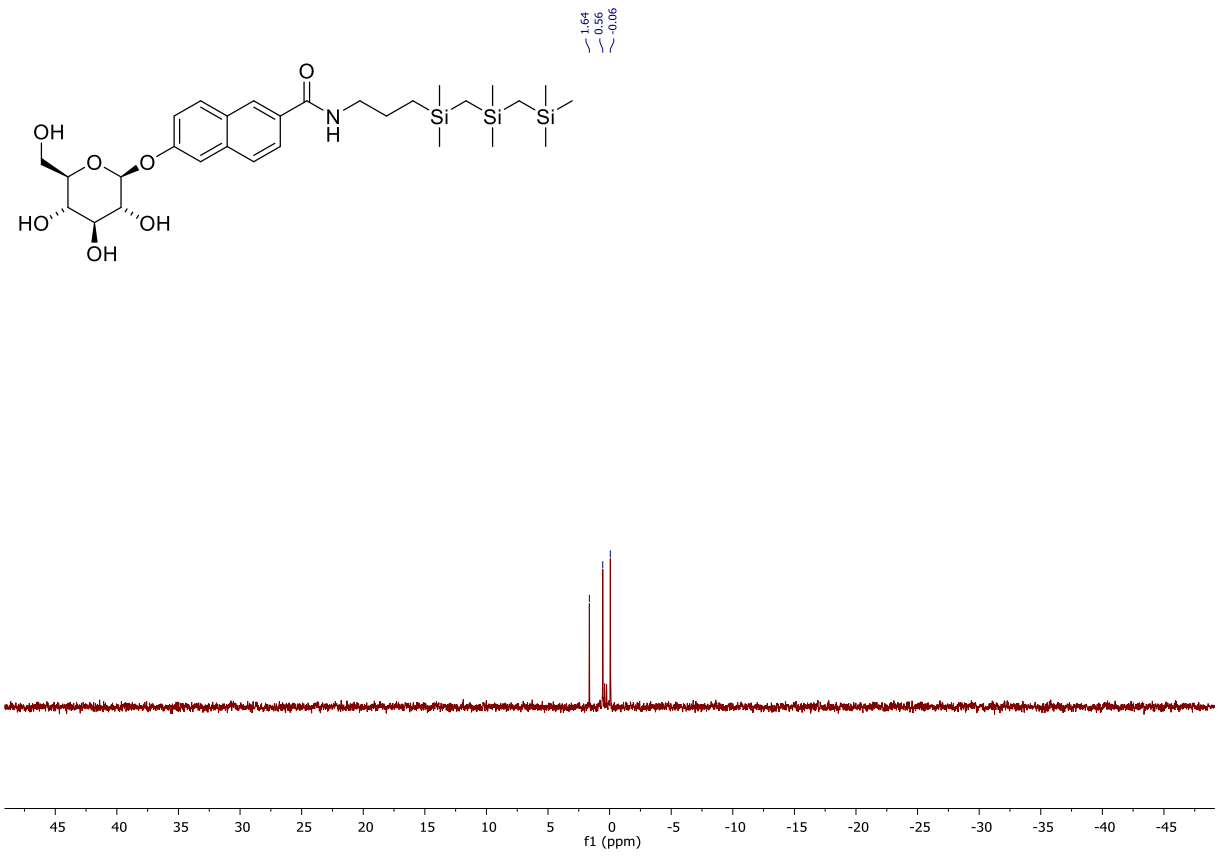


*Figure 95: ^{29}Si NMR (500 MHz, MeOD-d$_4$) of surfactant **167a**.*

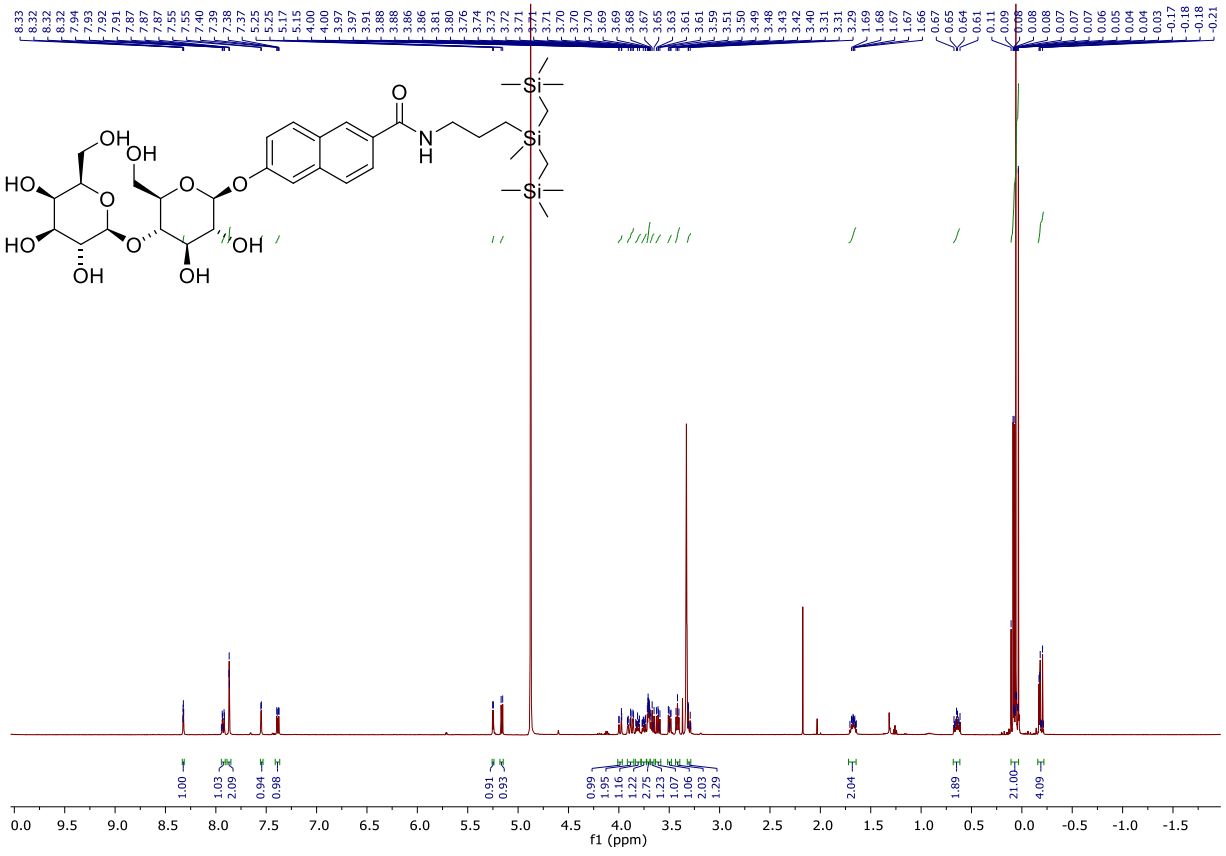


*Figure 96: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **168b**.*

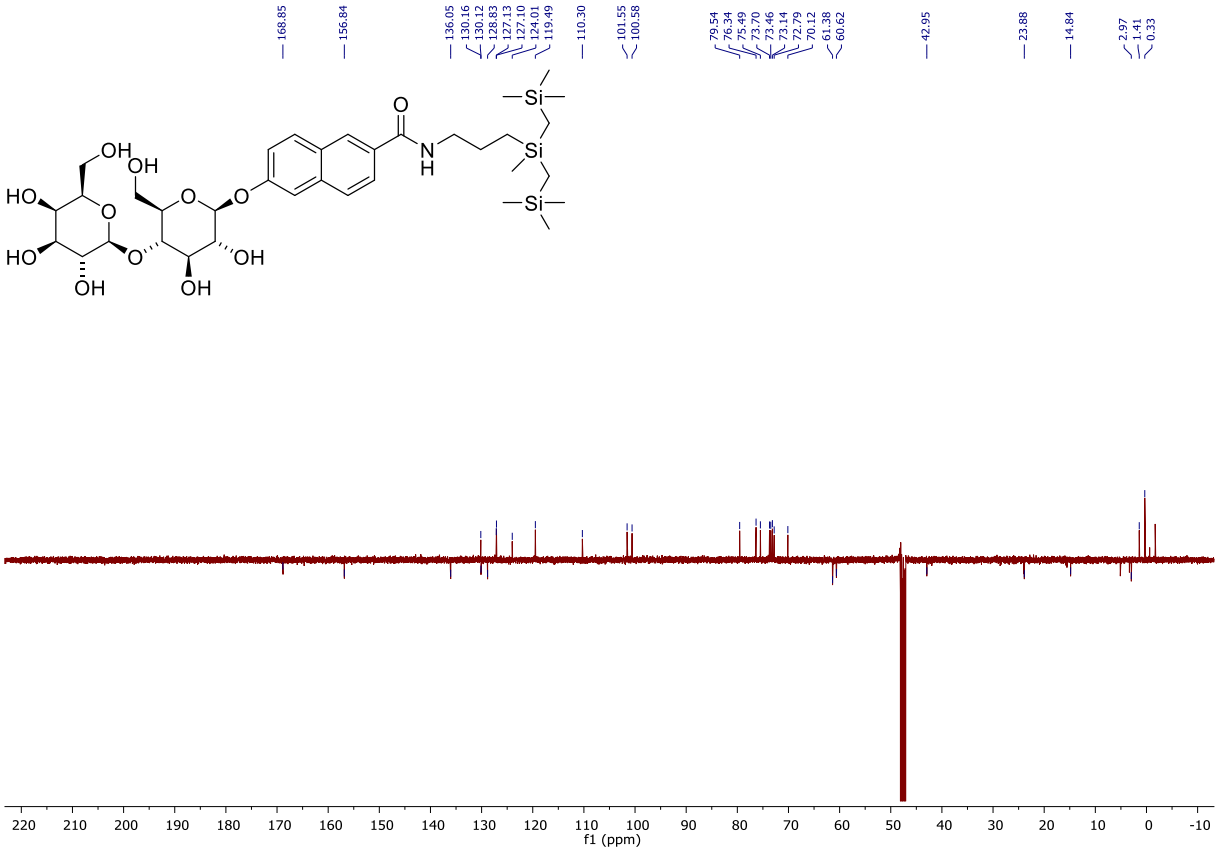


*Figure 97: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **168b**.*

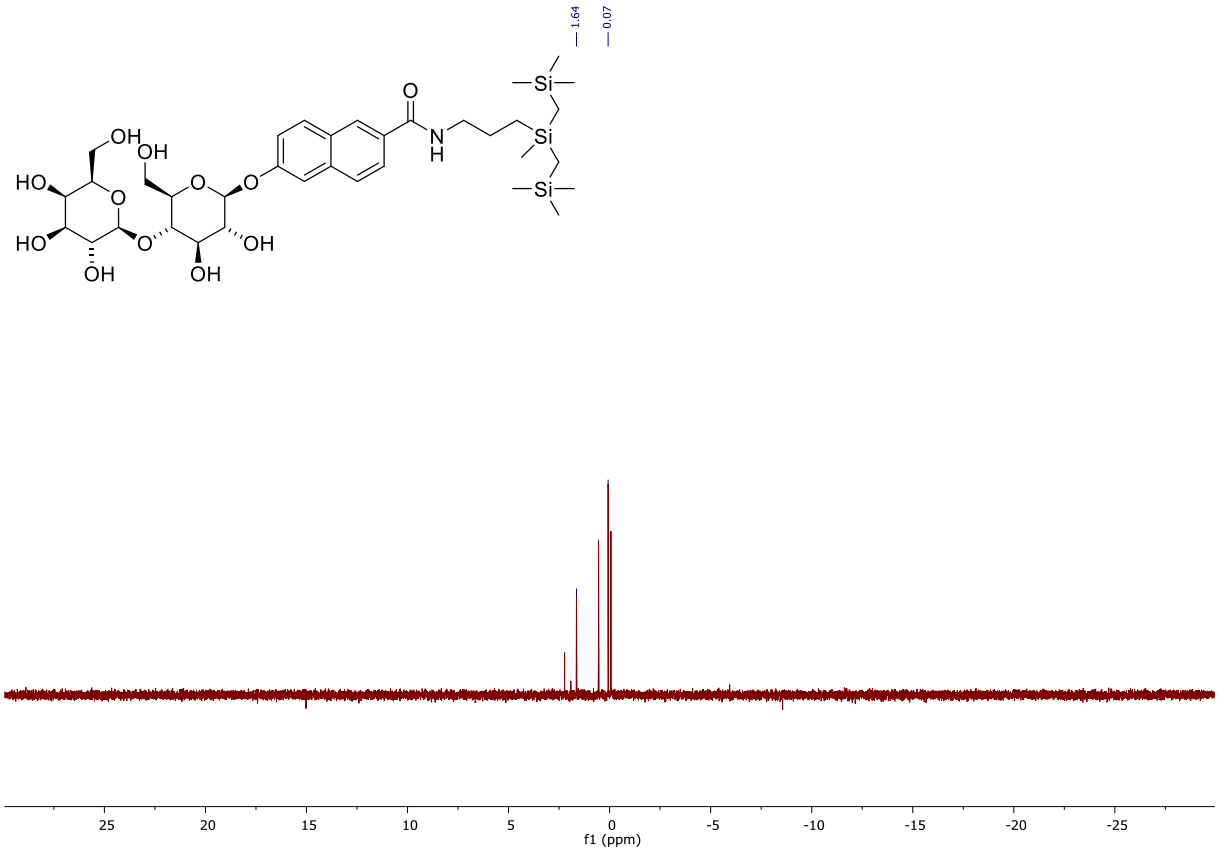


*Figure 98: ^{29}Si NMR (500 MHz, MeOD-d_4) of surfactant **168b**.*

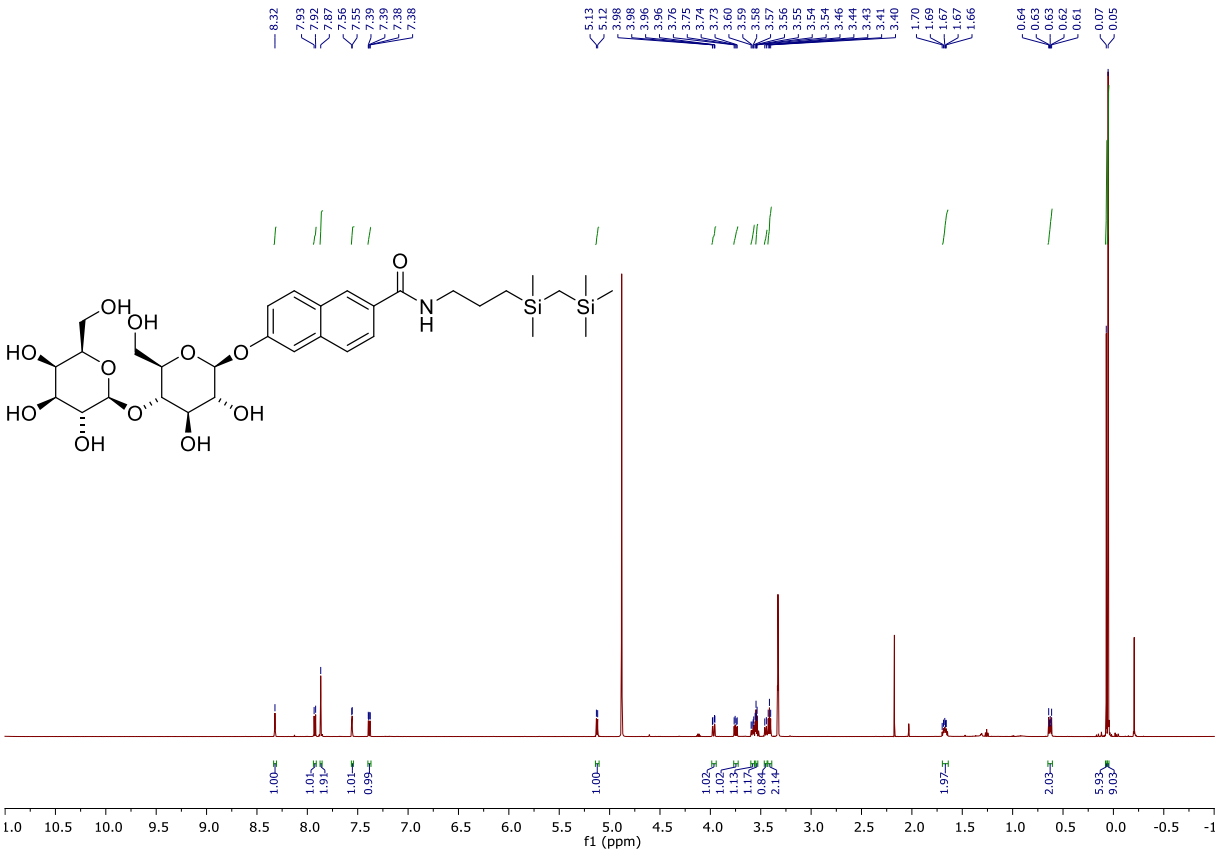


*Figure 99: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **166b**.*

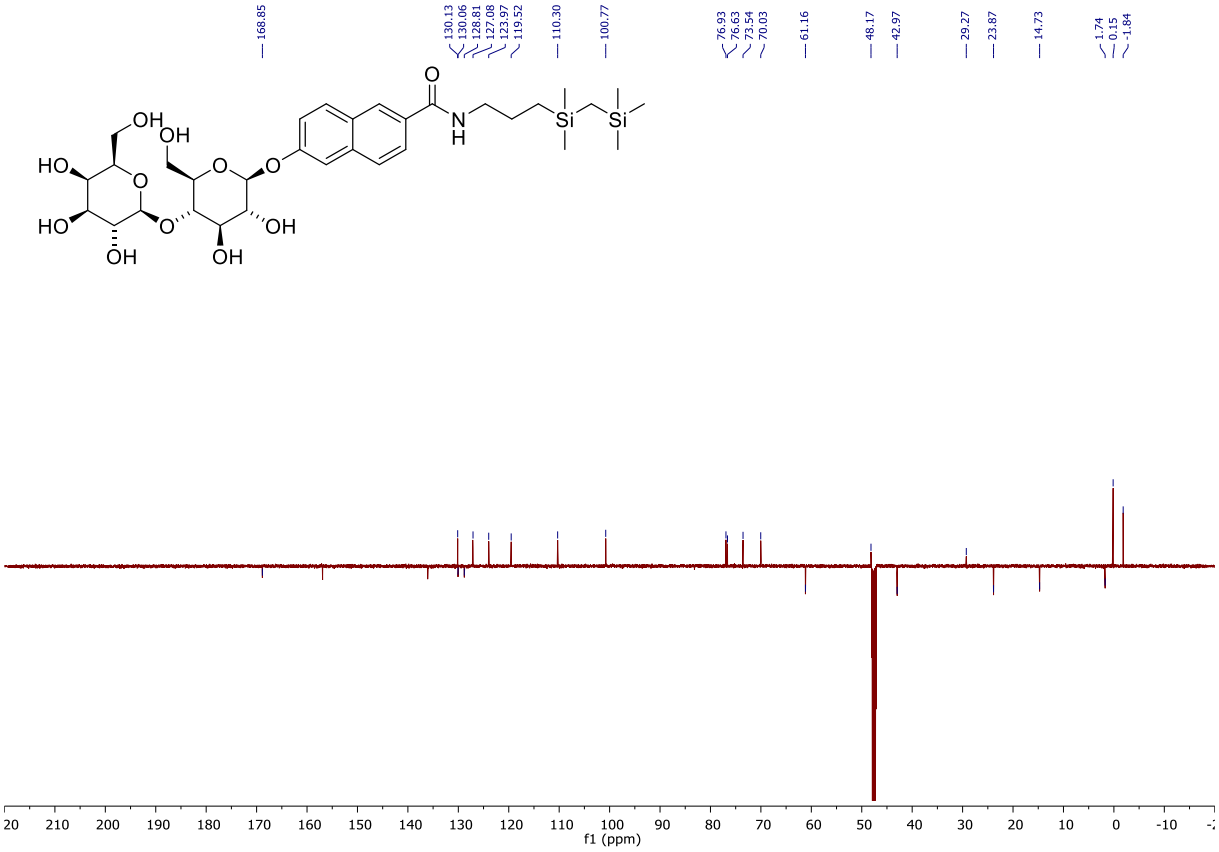


*Figure 100: ^{13}C NMR (500 MHz, MeOD-d$_4$) of surfactant **166b**.*

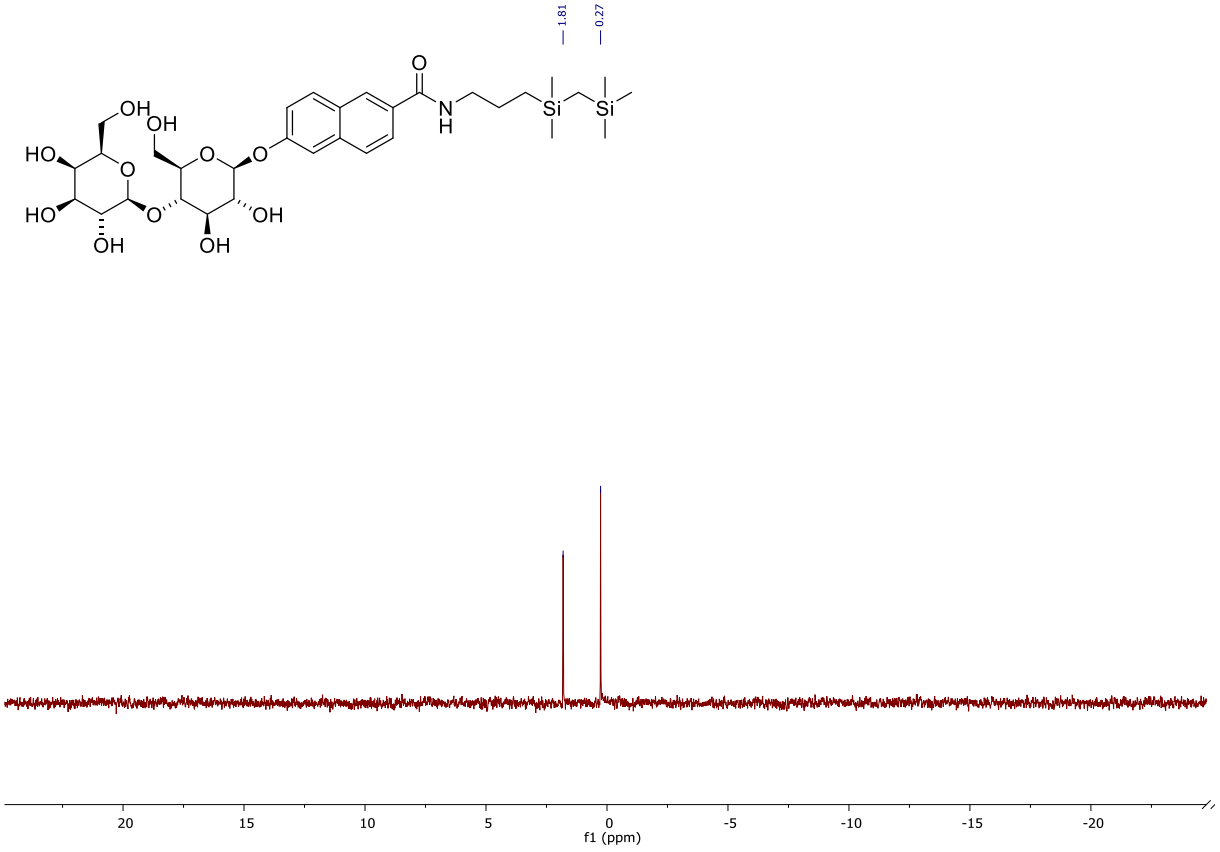


*Figure 101: ^{29}Si NMR (500 MHz, MeOD-d$_4$) of surfactant **166b**.*

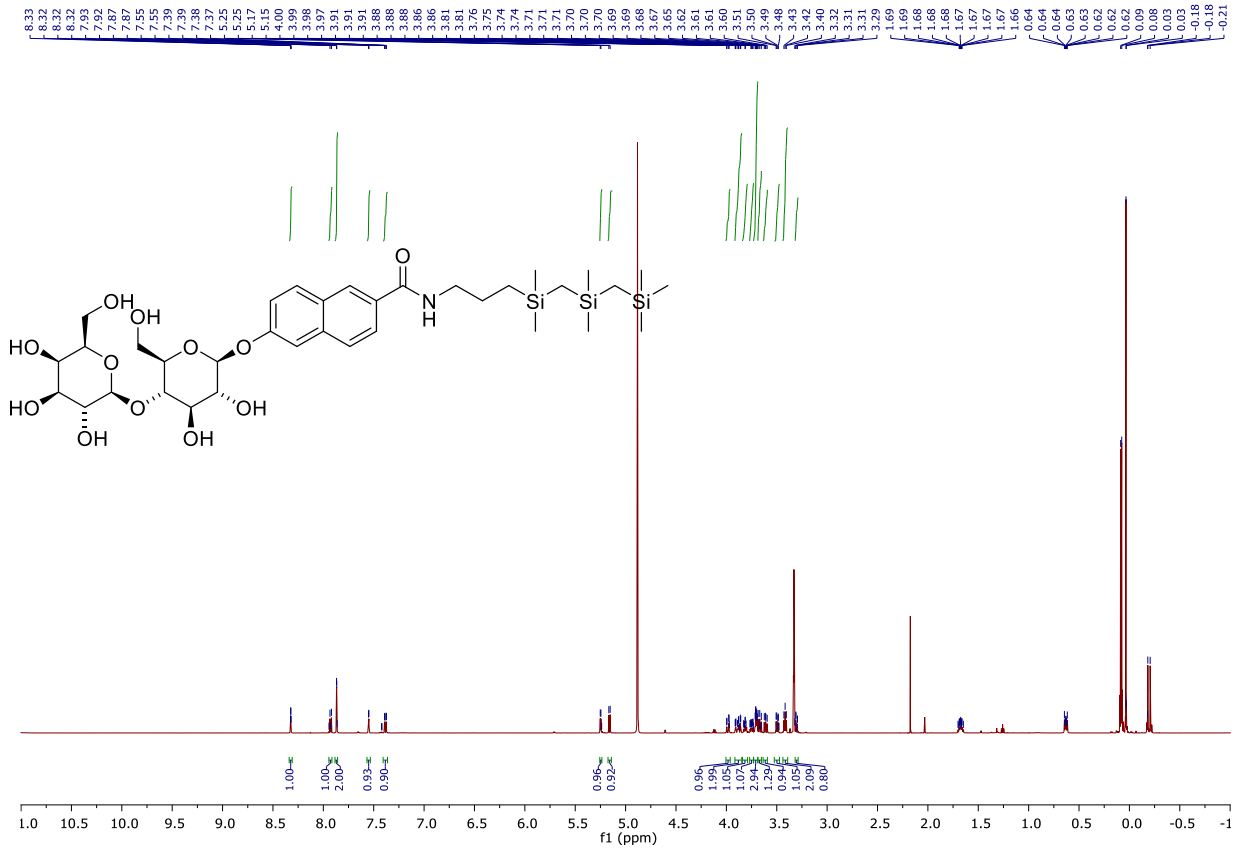


*Figure 102: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **167b**.*

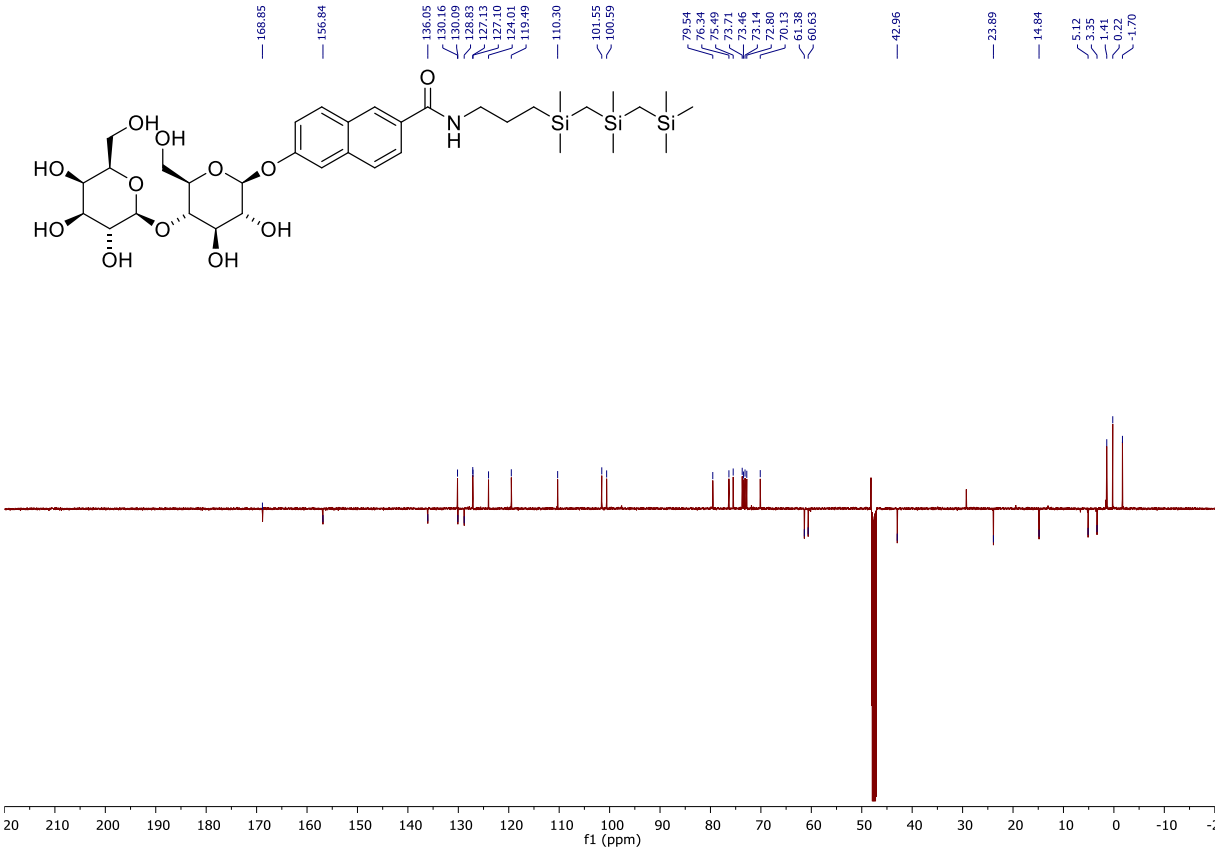


*Figure 103: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **167b**.*

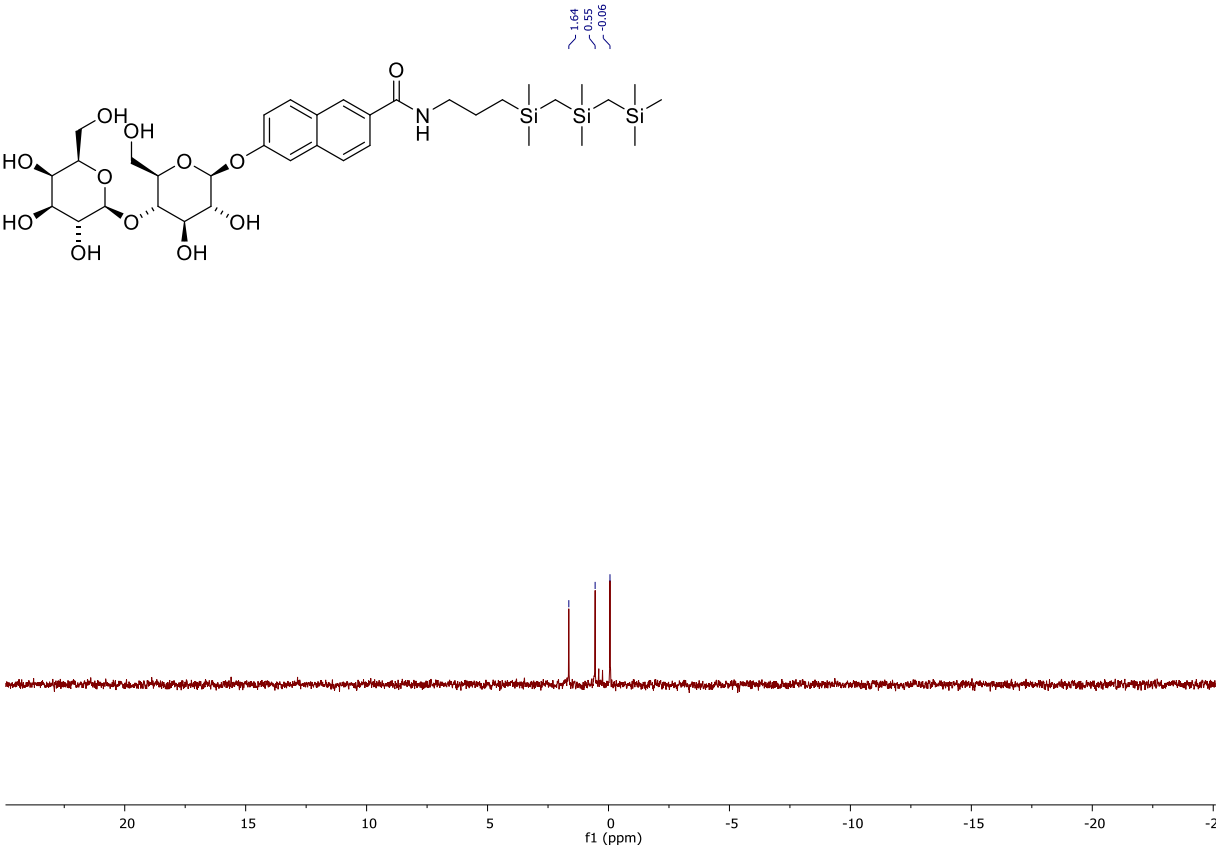


*Figure 104: ^{29}Si NMR (500 MHz, MeOD-d_4) of surfactant **167b**.*

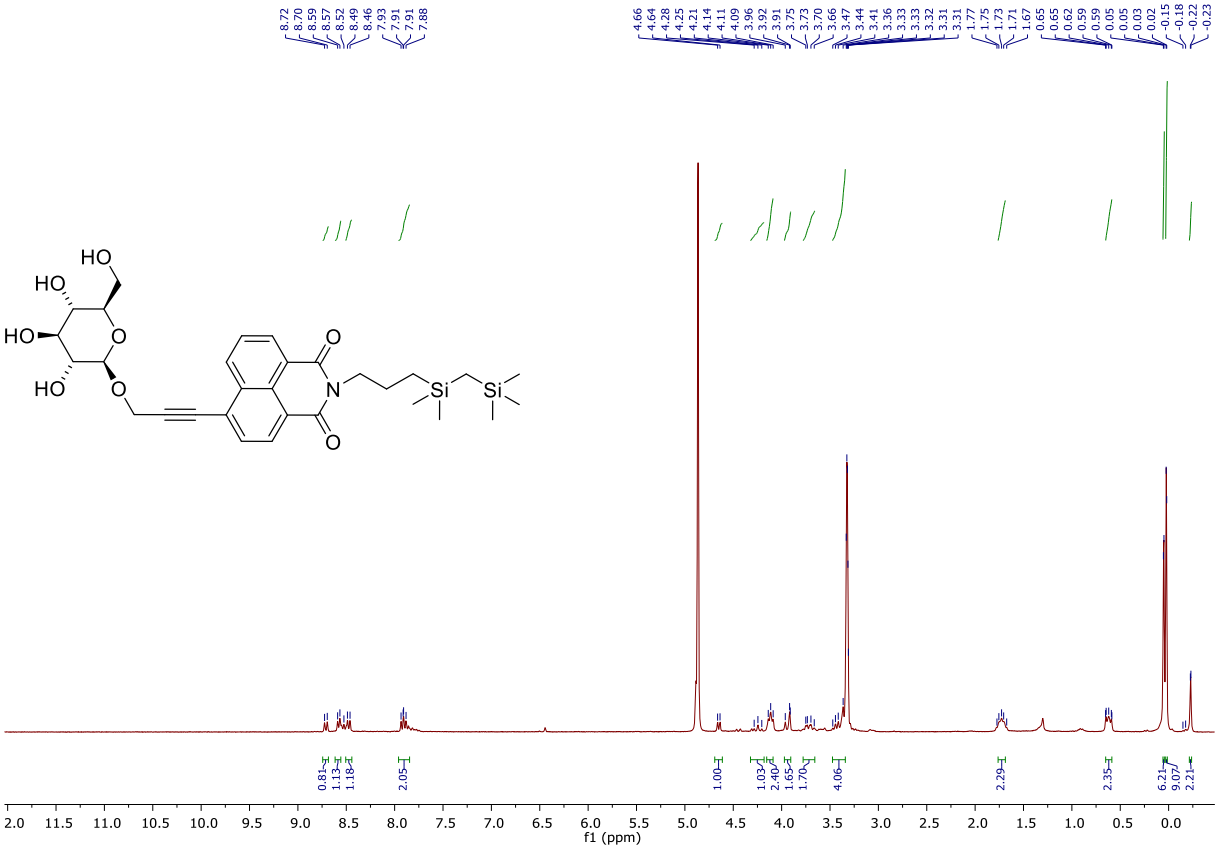


*Figure 105: ^{1}H NMR (500 MHz, MeOD-d_4) of surfactant **169a**.*

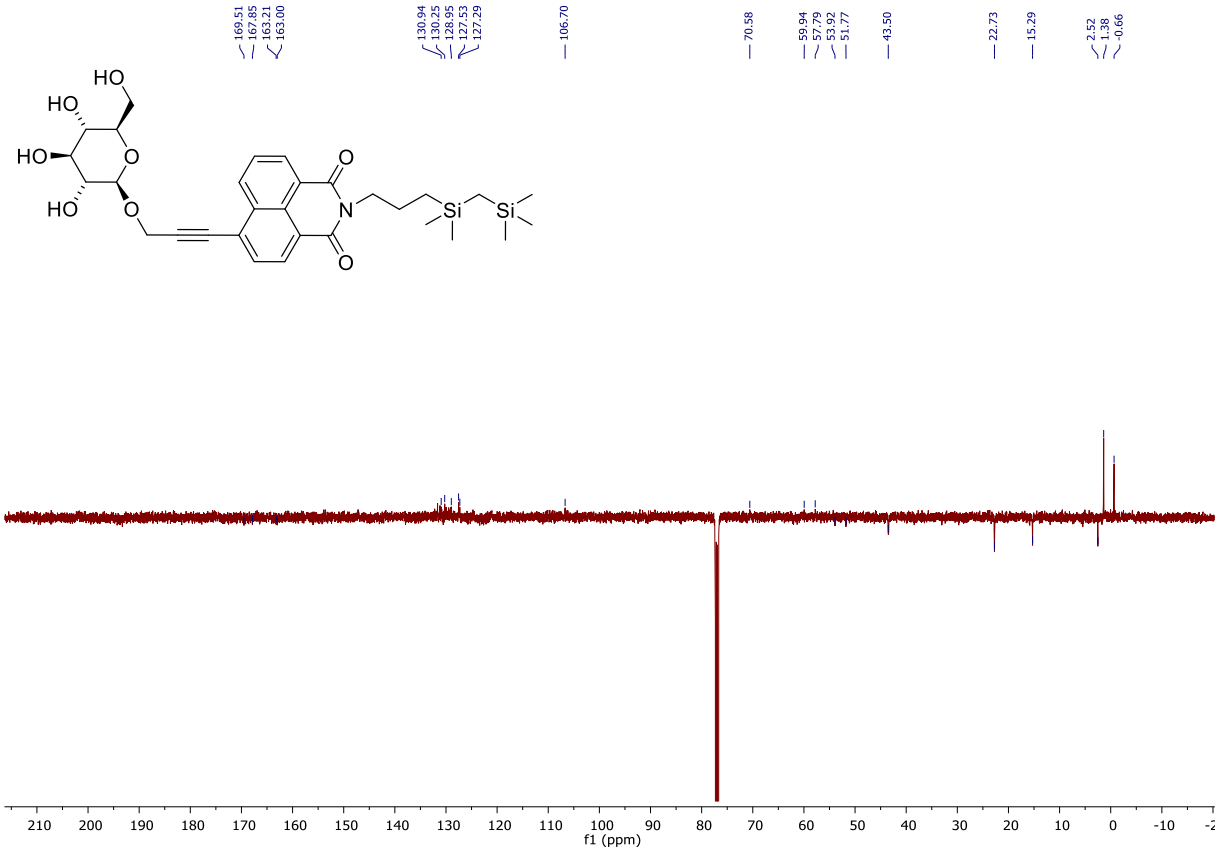


*Figure 106: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **169a**.*

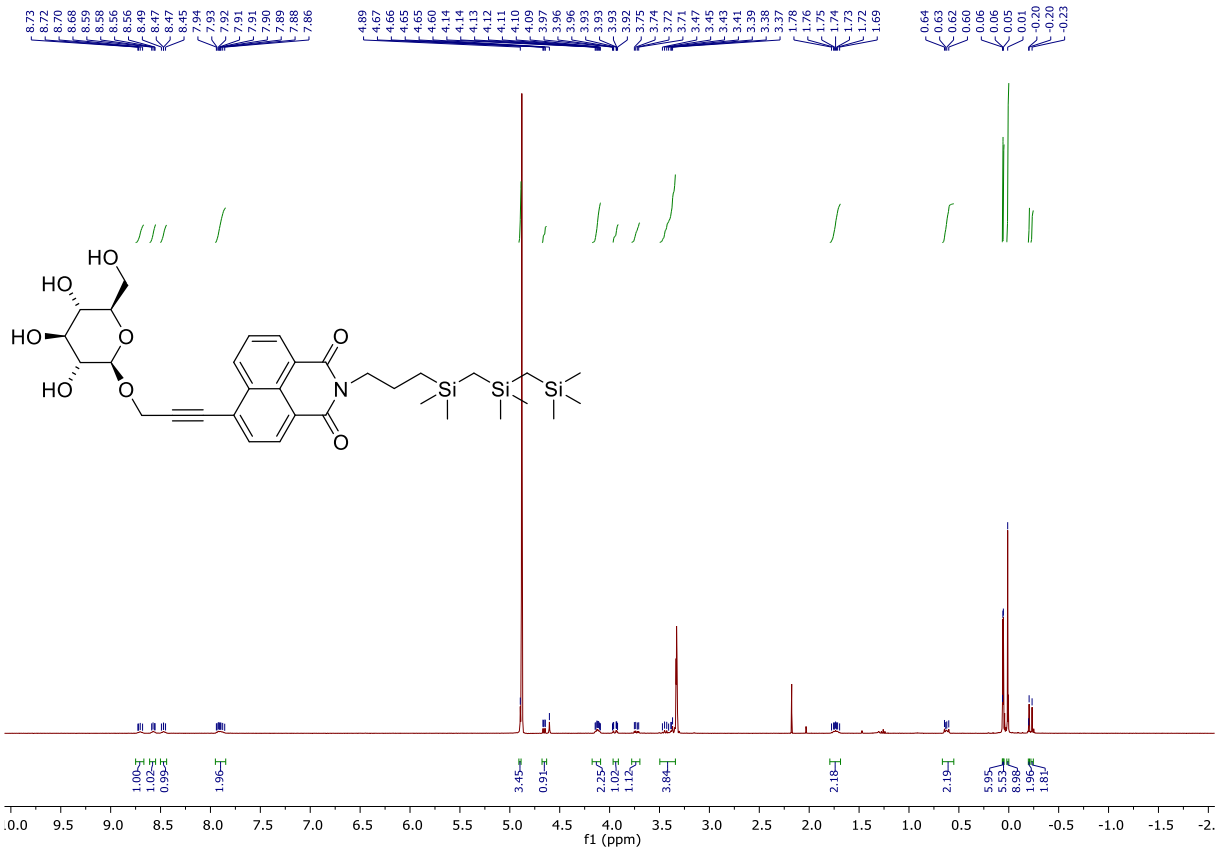


*Figure 107: ^{1}H NMR (500 MHz, MeOD-d_4) of surfactant **170a**.*

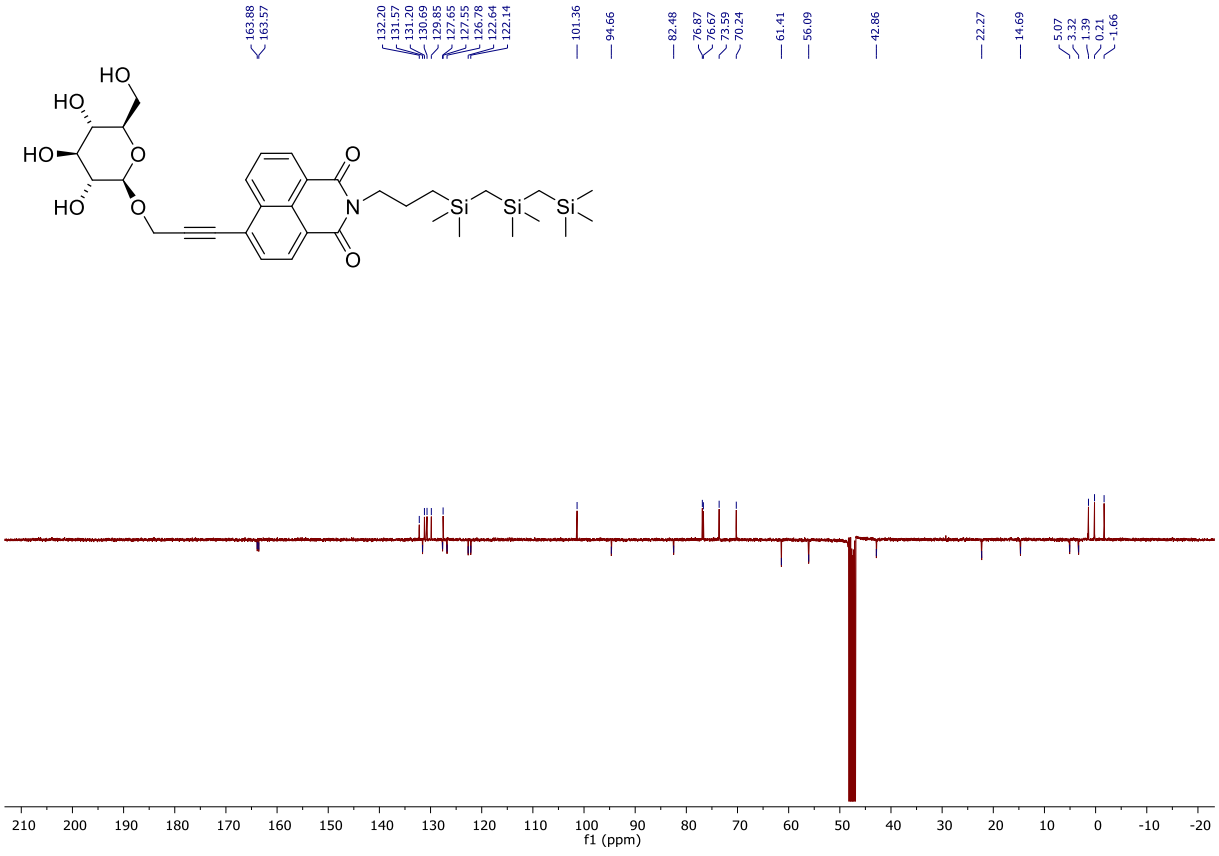


*Figure 108: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **170a**.*

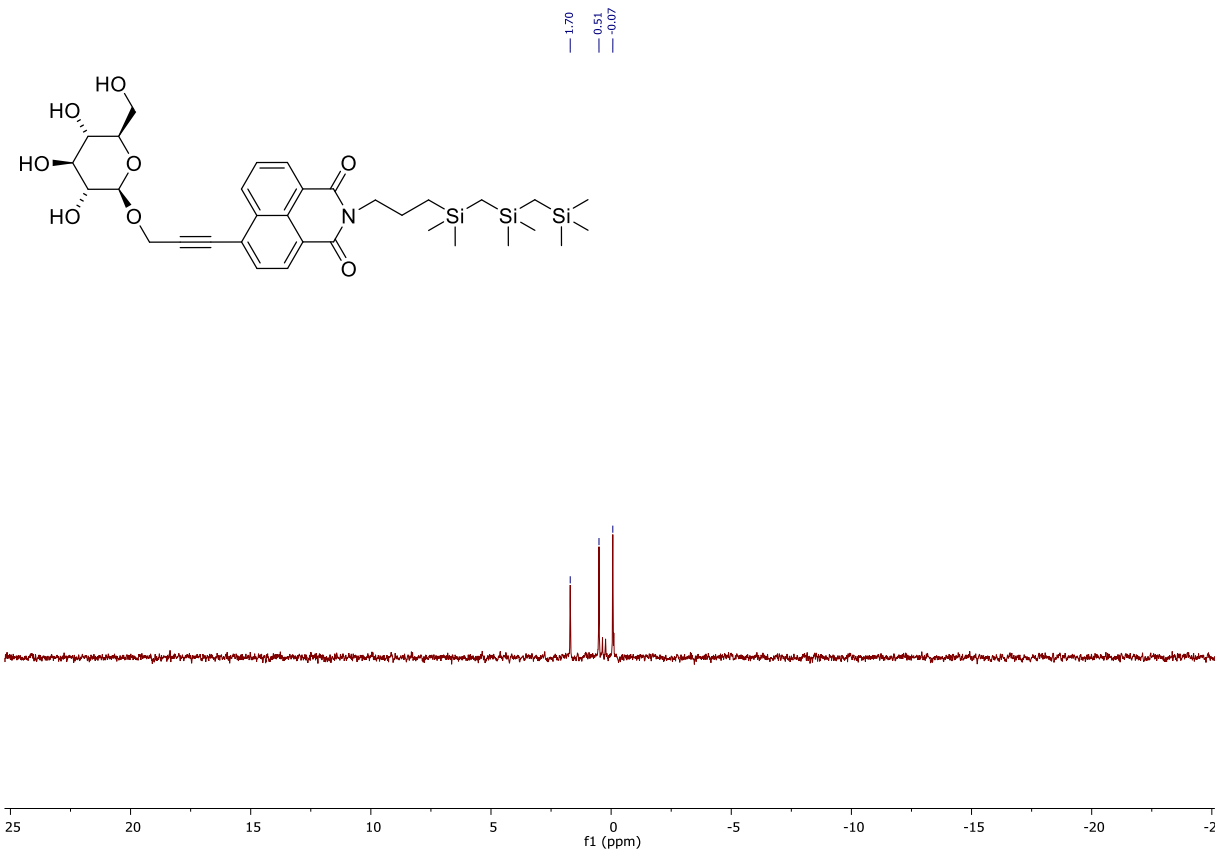


*Figure 109: ^{29}Si NMR (500 MHz, MeOD-d$_4$) of surfactant **170a**.*

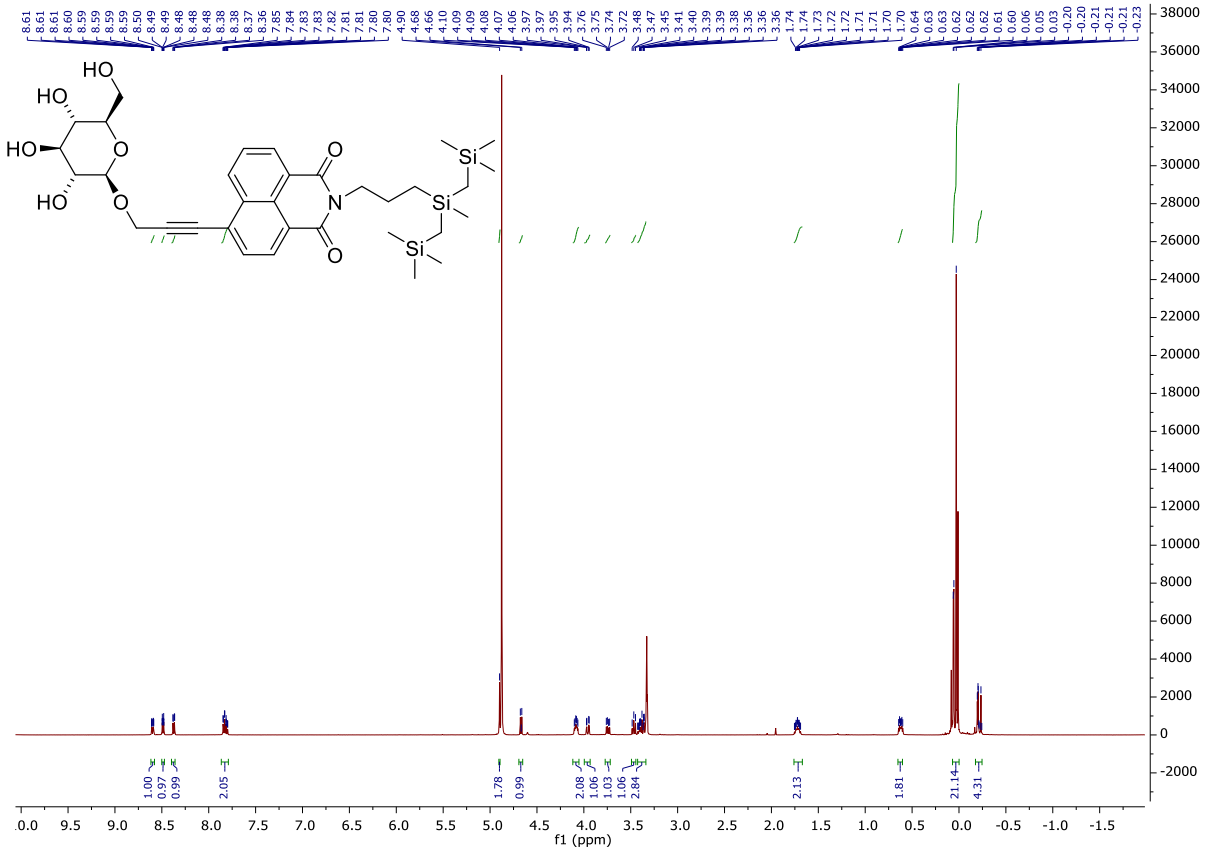


*Figure 110: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **171a**.*

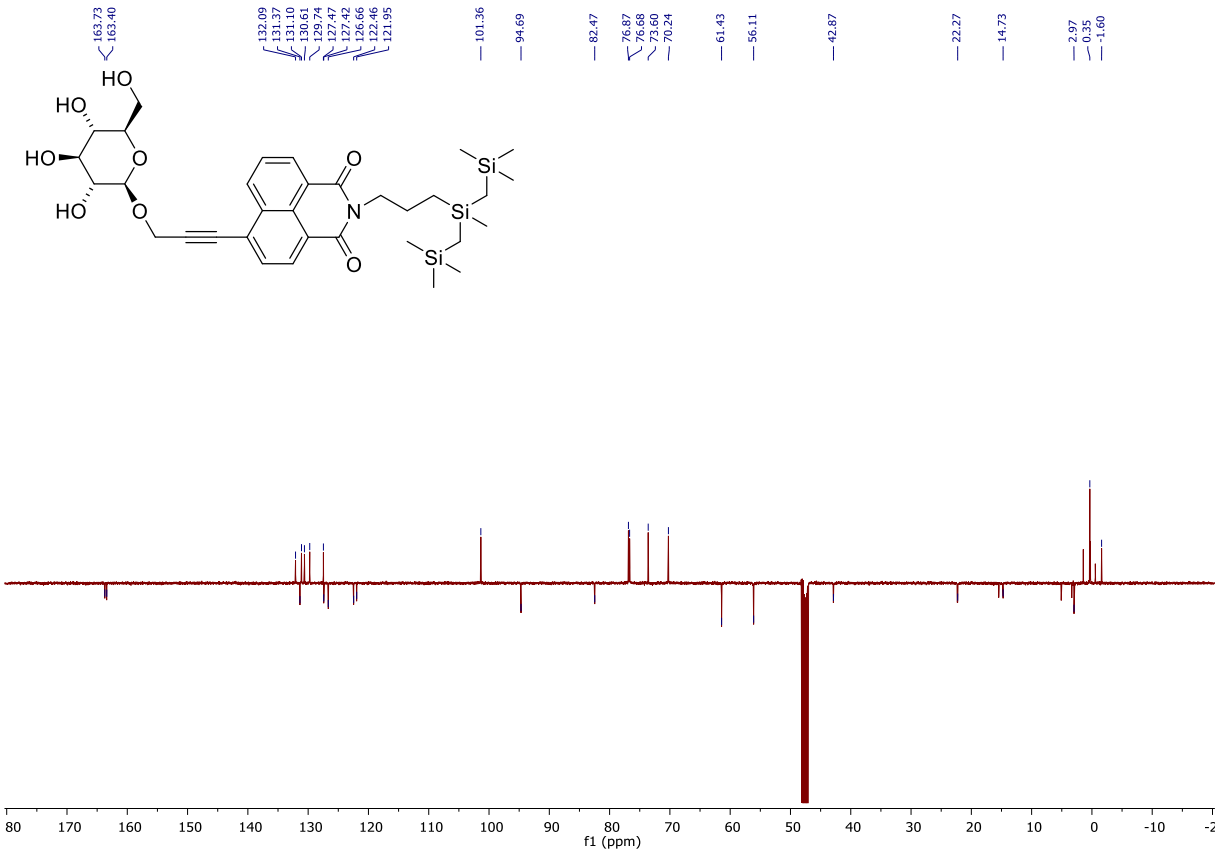


*Figure 111: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **171a**.*

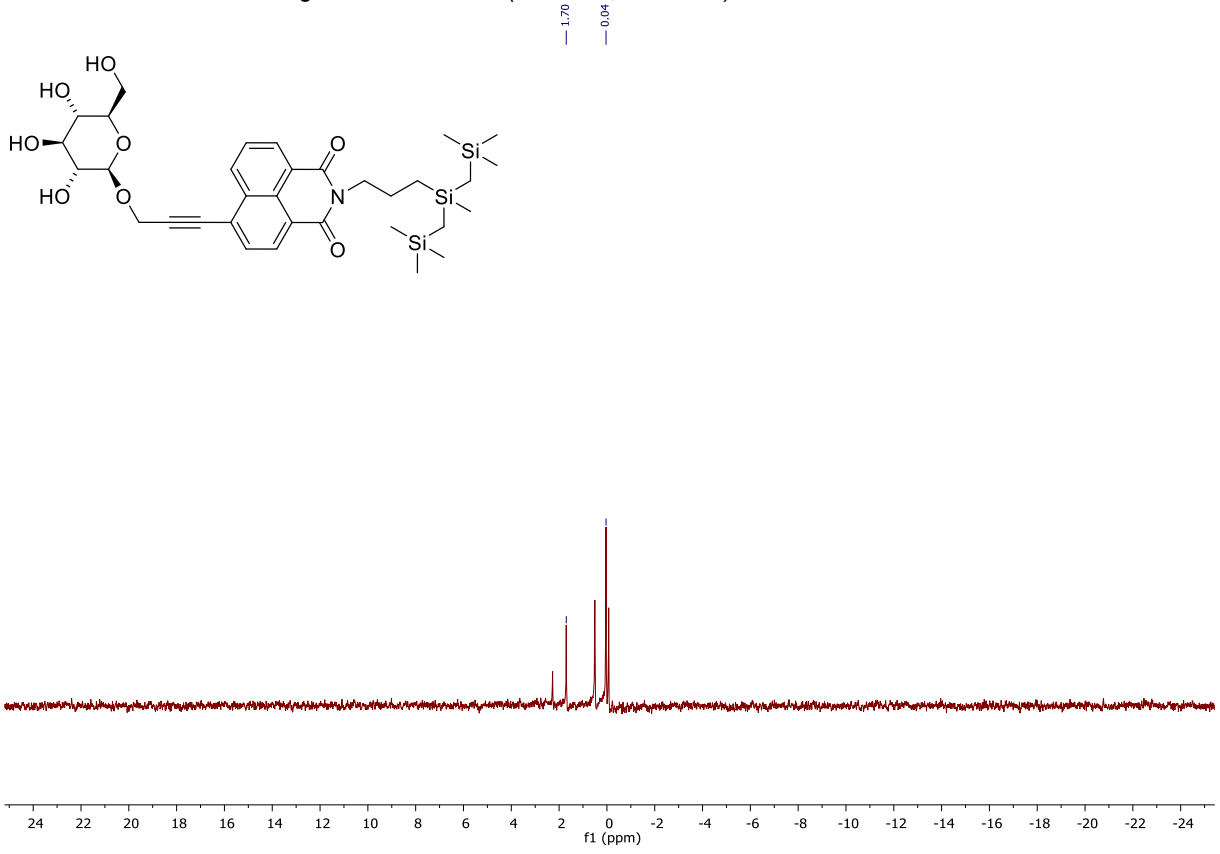


*Figure 112: ^{29}Si NMR (500 MHz, MeOD-d_4) of surfactant **171a**.*

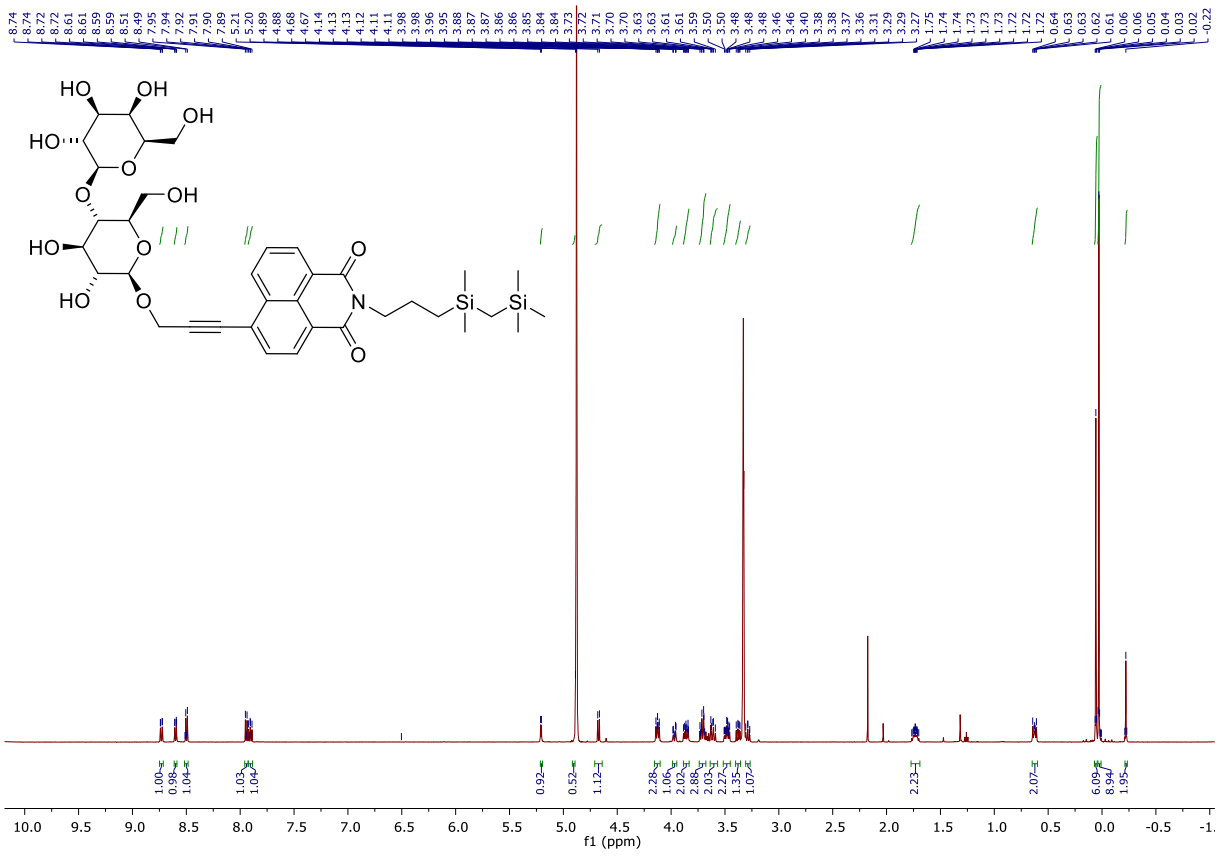


*Figure 113: ^{1}H NMR (500 MHz, MeOD-d_4) of surfactant **169b**.*

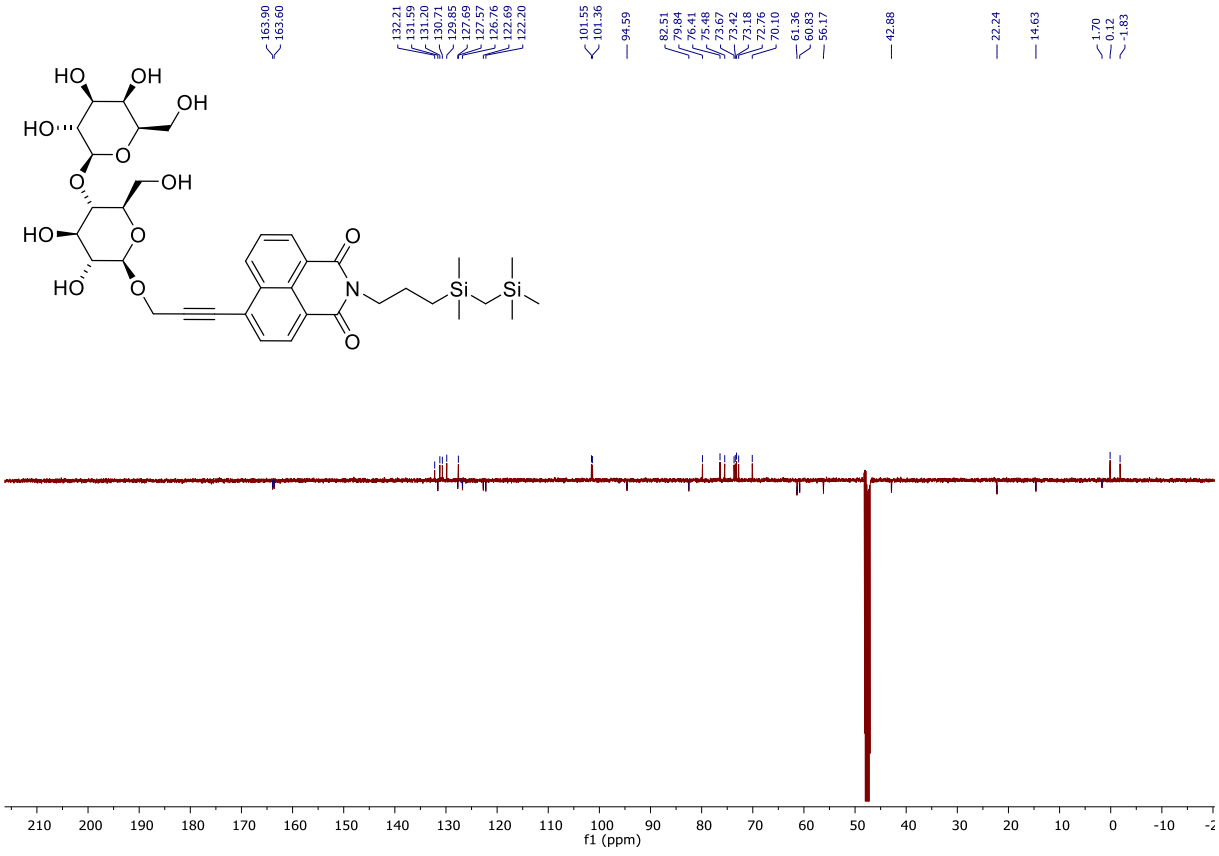


*Figure 114: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **169b**.*

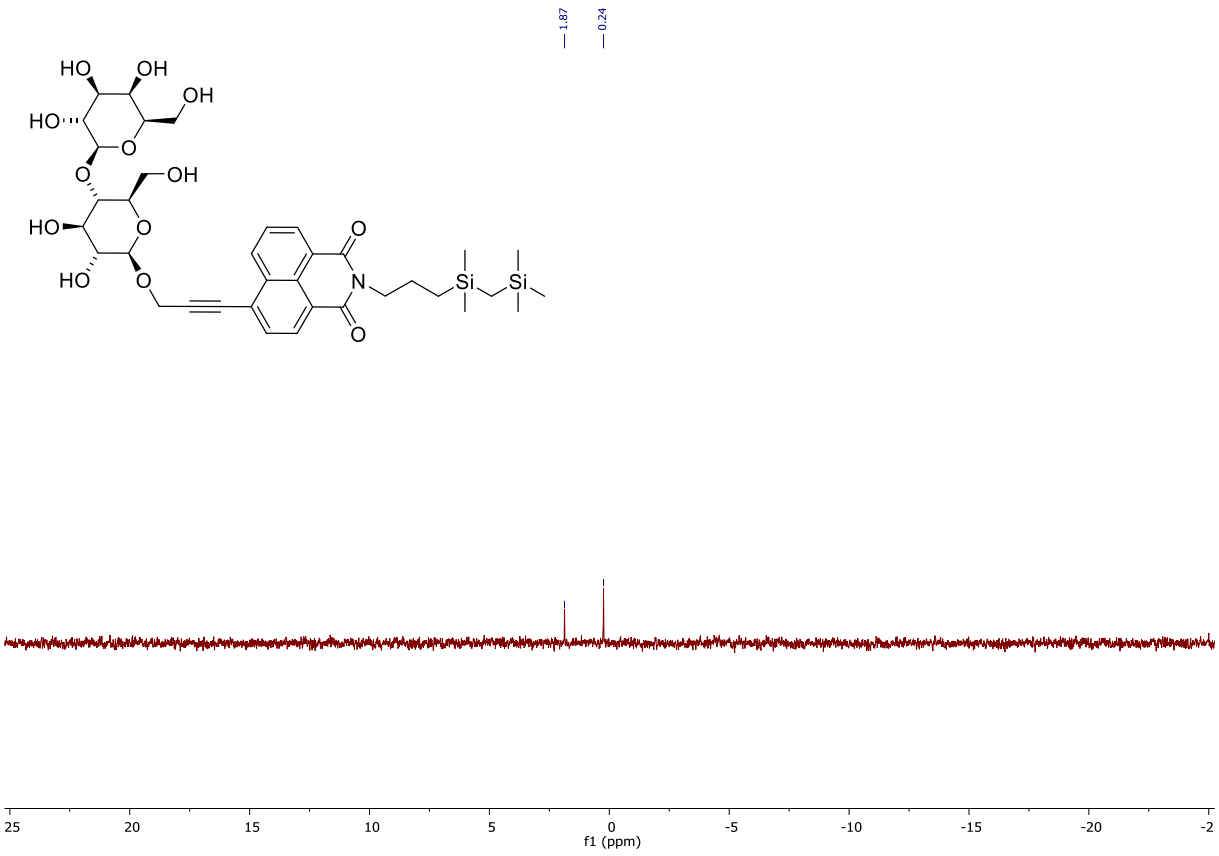


*Figure 115: ^{29}Si NMR (500 MHz, MeOD-d$_4$) of surfactant **169b**.*

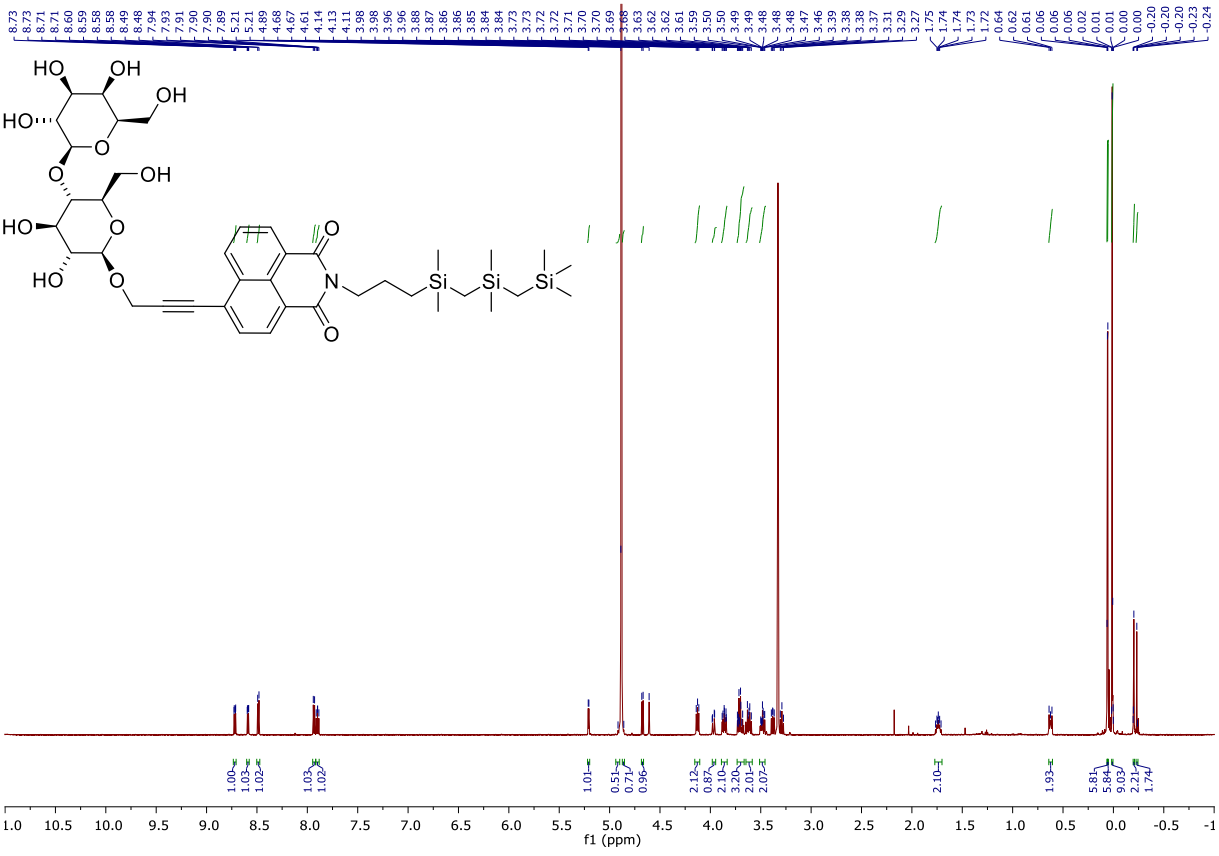


*Figure 116: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **170b**.*

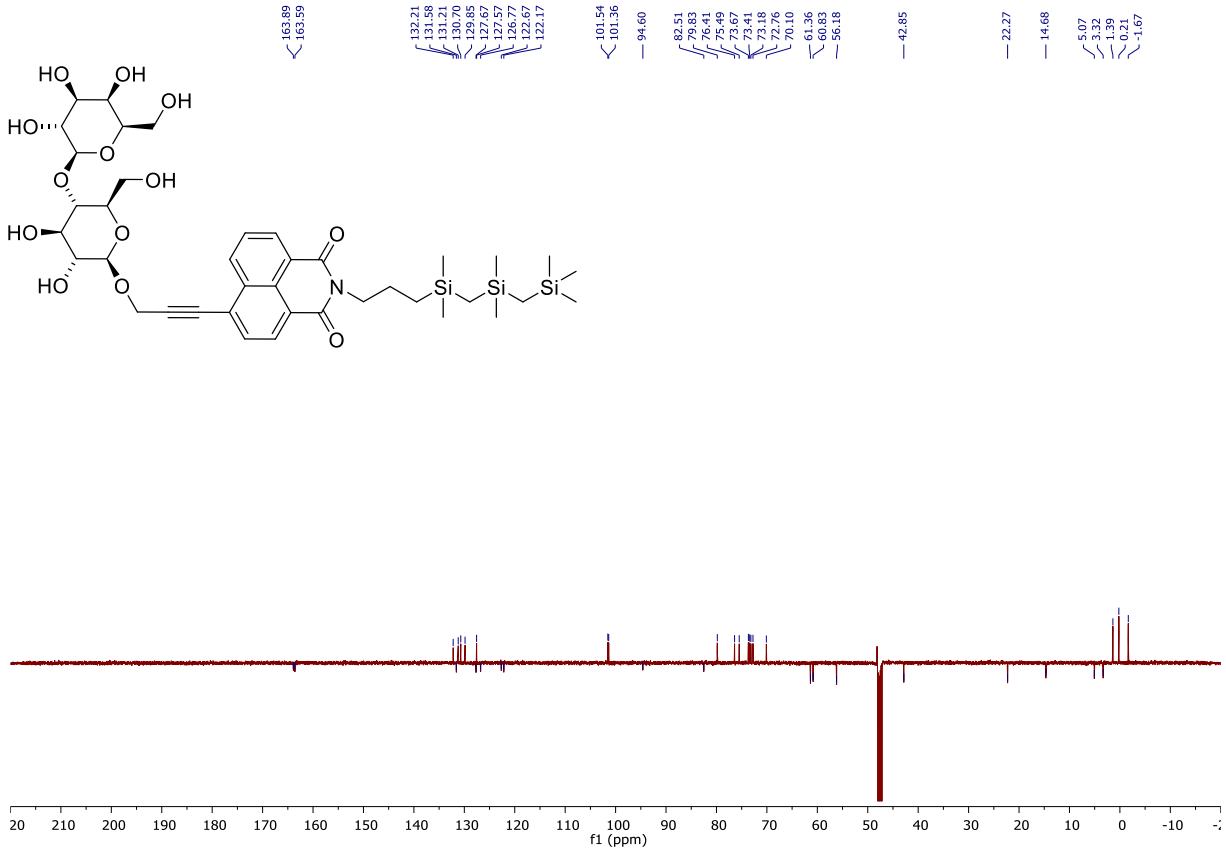


*Figure 117: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **170b**.*

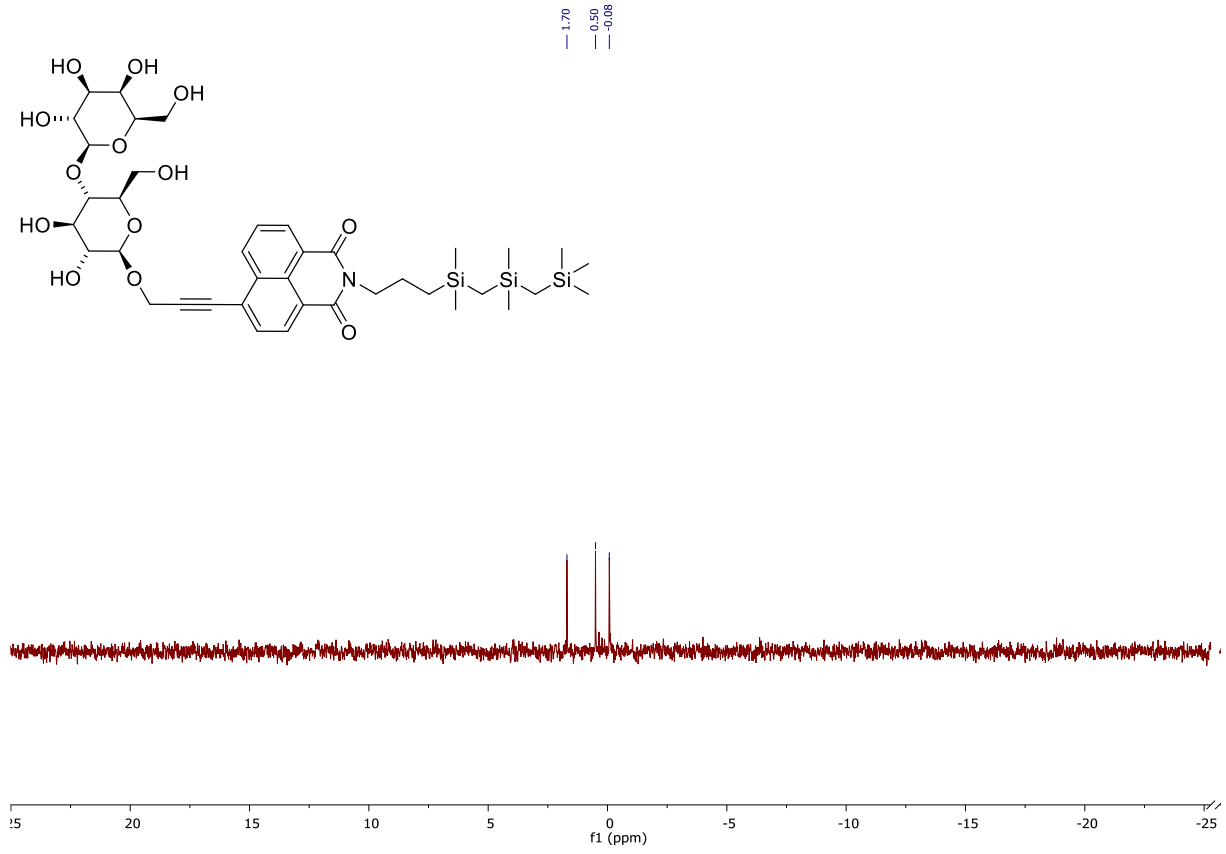


*Figure 118: ^{29}Si NMR (500 MHz, MeOD-d_4) of surfactant **170b**.*

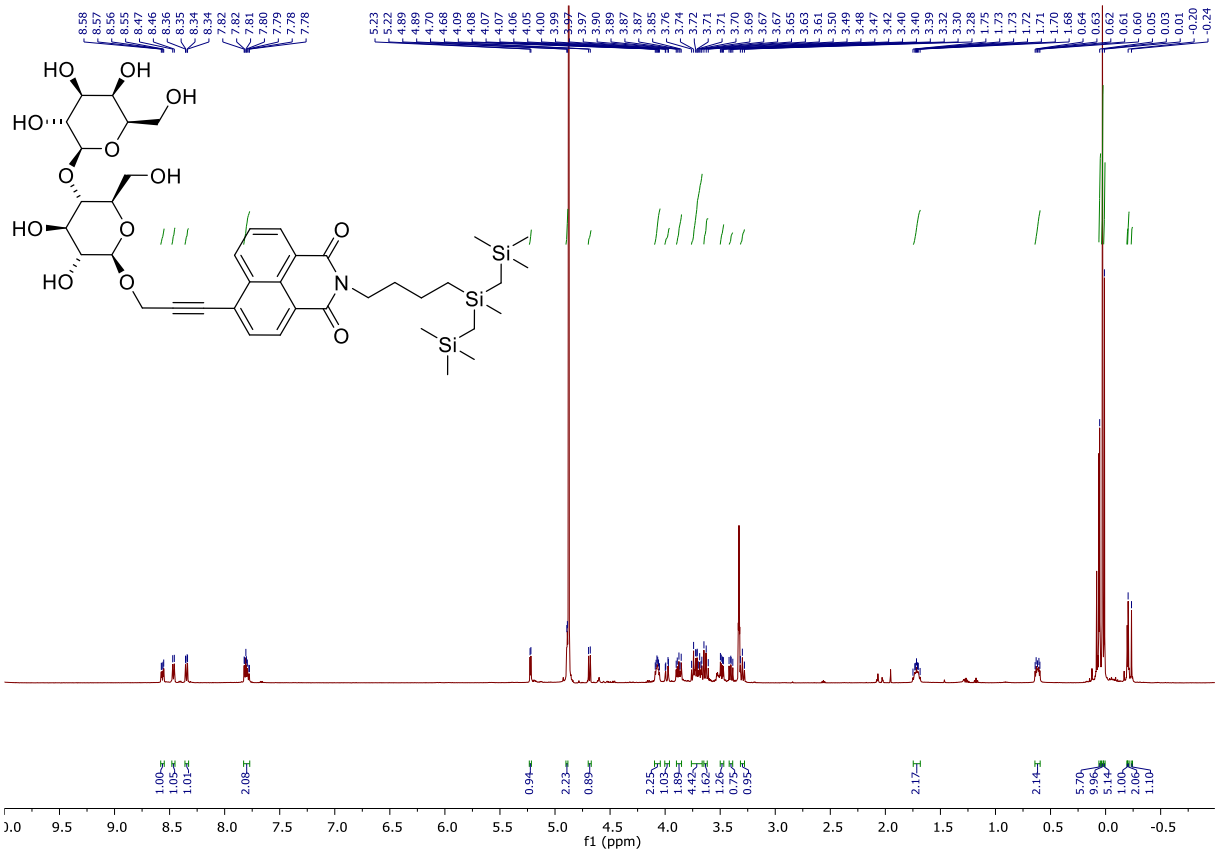


*Figure 119: ^{1}H NMR (500 MHz, MeOD-d_4) of surfactant **171b**.*

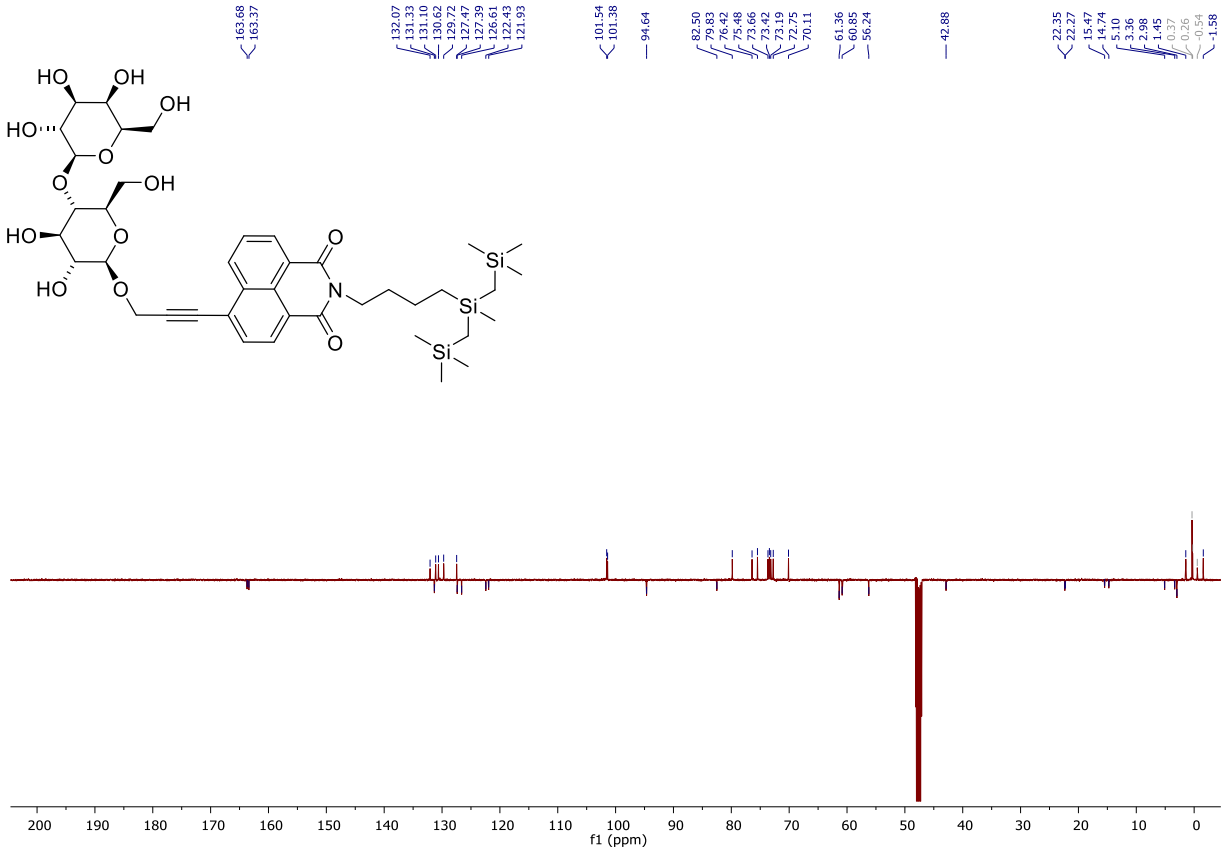


*Figure 120: ^{13}C NMR (500 MHz, MeOD-d_4) of surfactant **171b**.*

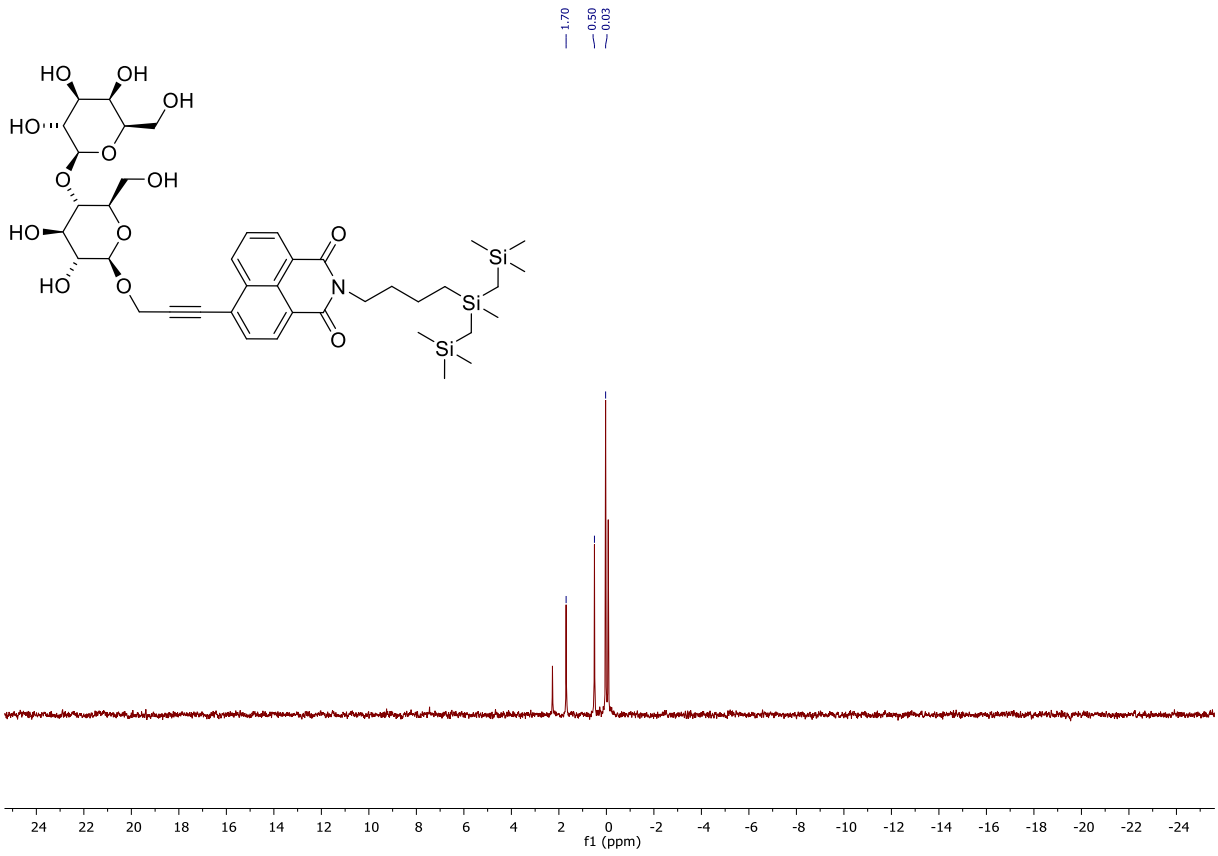


*Figure 121: ^{29}Si NMR (500 MHz, MeOD-d$_4$) of surfactant **171b**.*

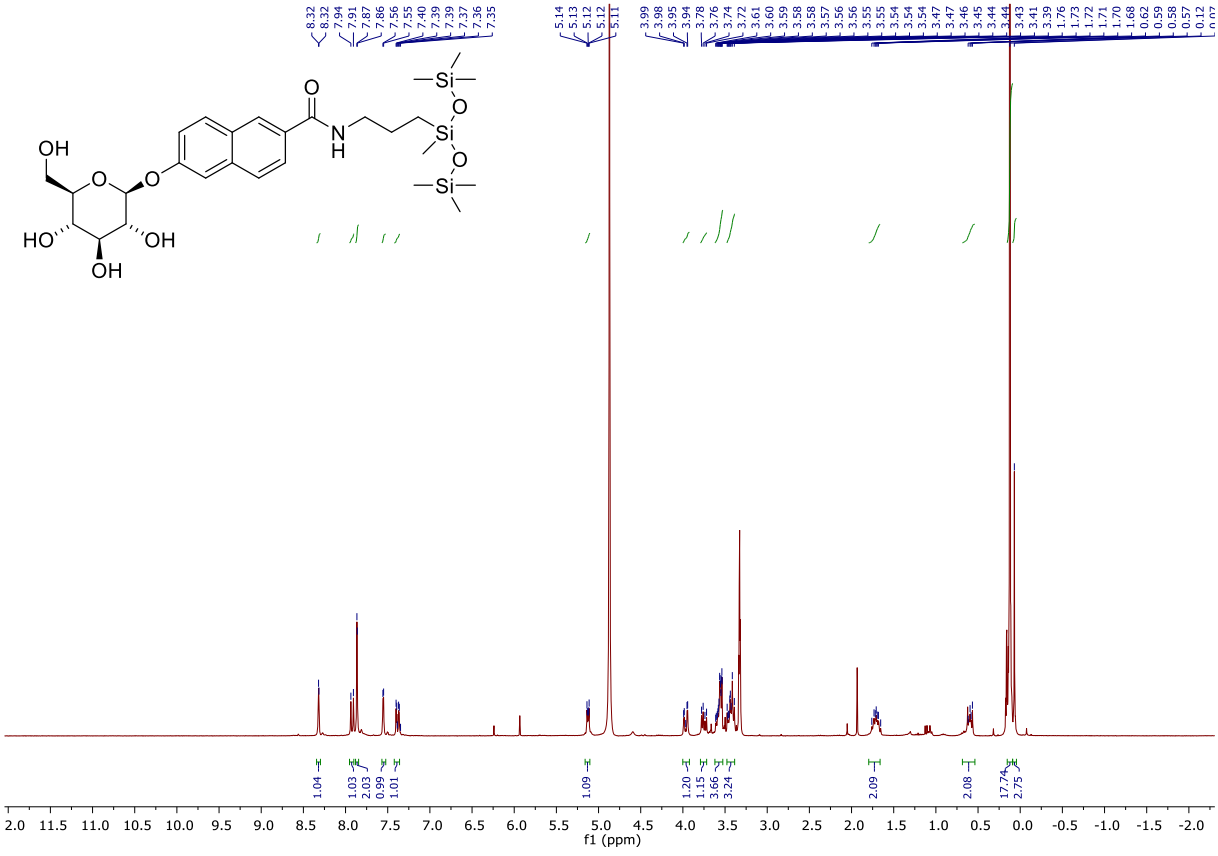


*Figure 122: ^{1}H NMR (300 MHz, MeOD-d$_4$) of surfactant **132a**.*

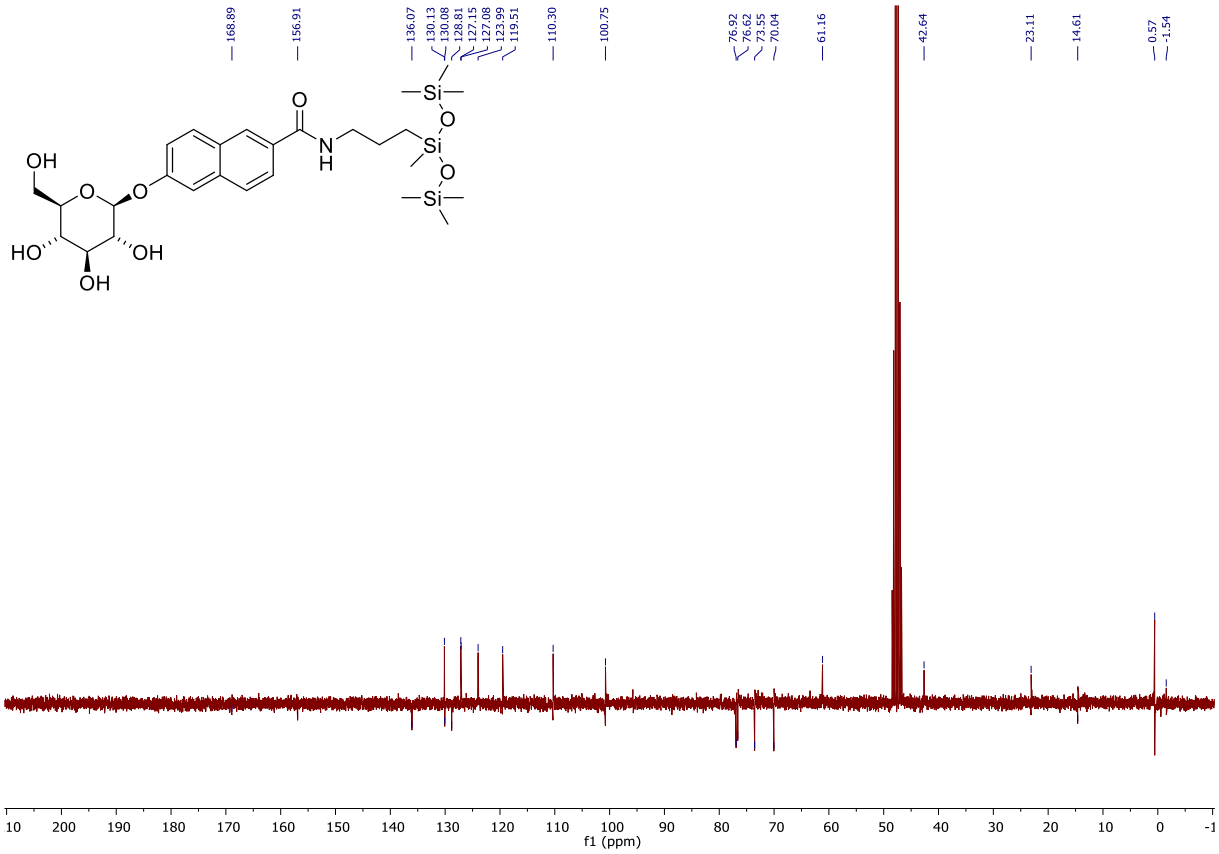


*Figure 123: ^{13}C NMR (300 MHz, MeOD-d$_4$) of surfactant **132a***

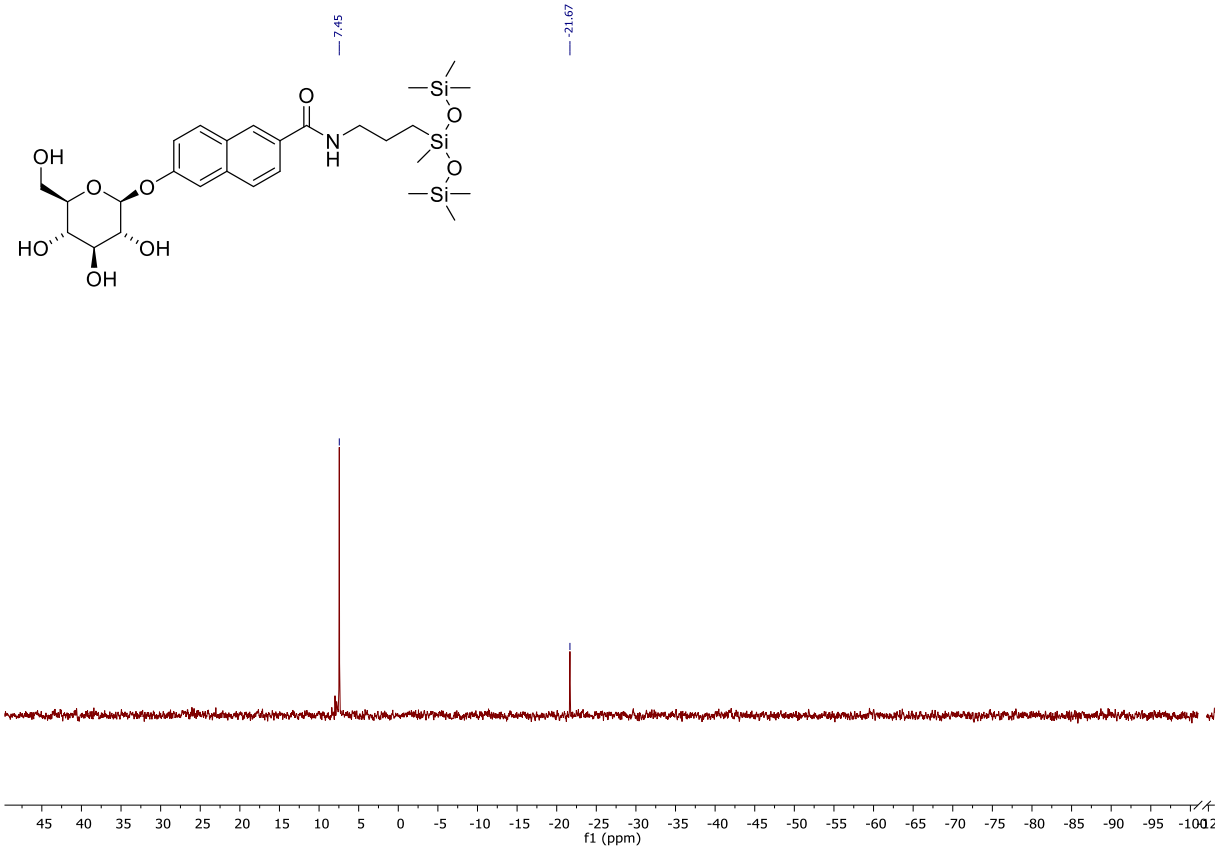


*Figure 124: ^{29}Si NMR (300 MHz, MeOD-d$_4$) of surfactant **132a**.*

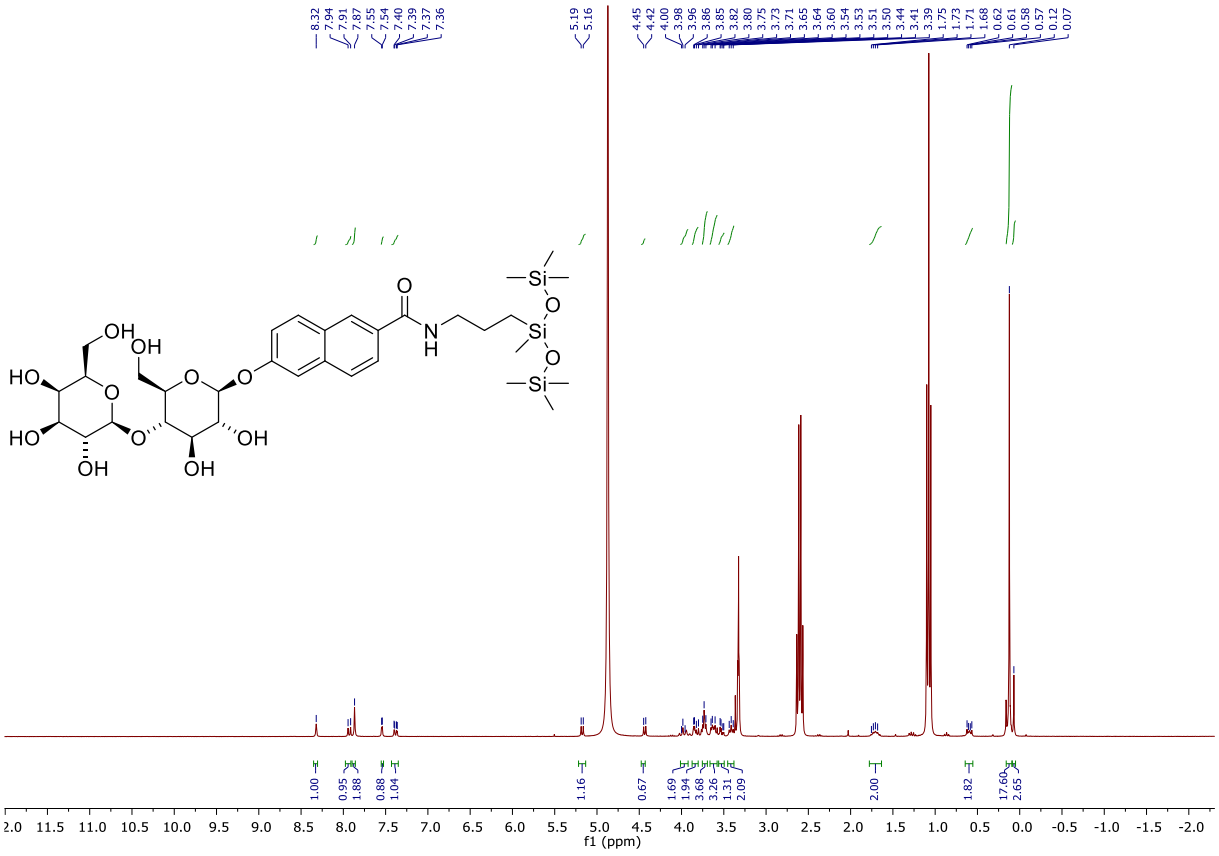


*Figure 125: ^{1}H NMR (300 MHz, MeOD-d_4) of surfactant **132b**.*

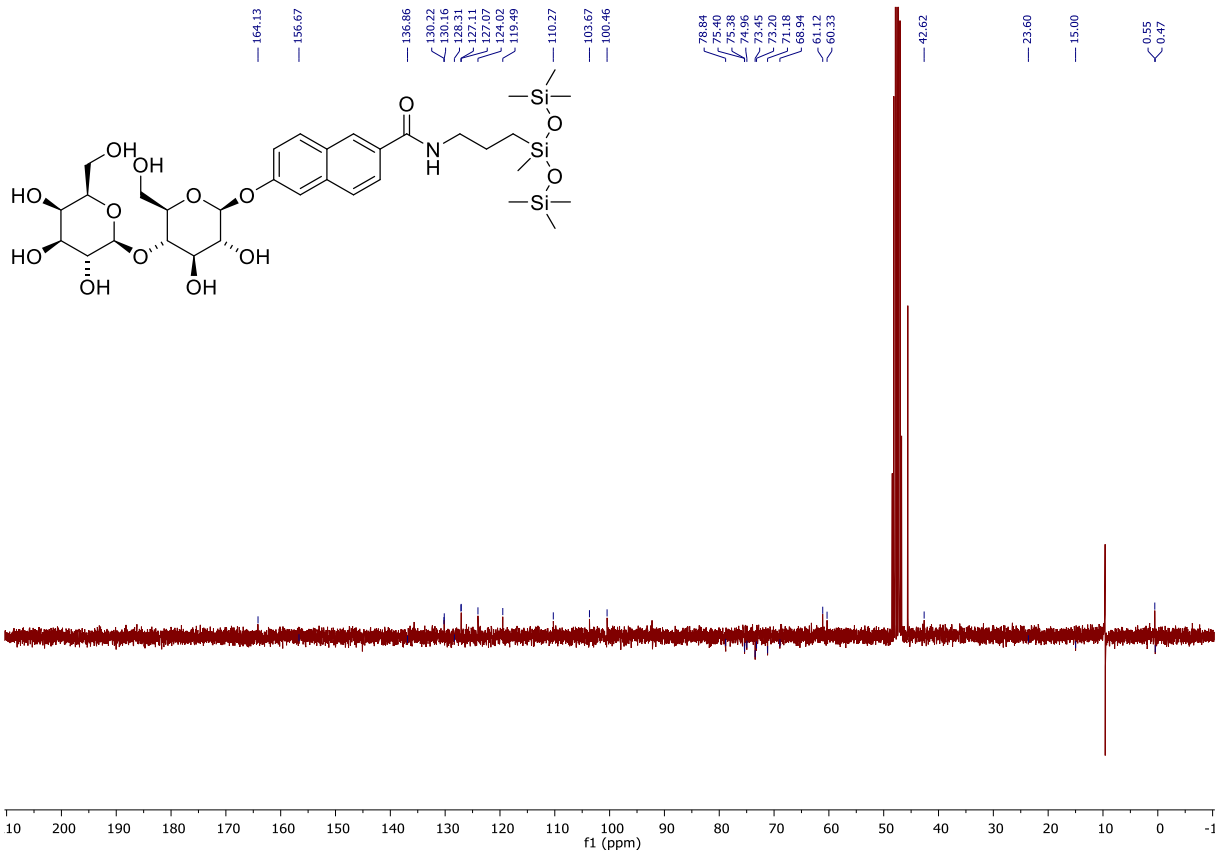


*Figure 126: ^{13}C NMR (300 MHz, MeOD-d_4) of surfactant **132b**.*

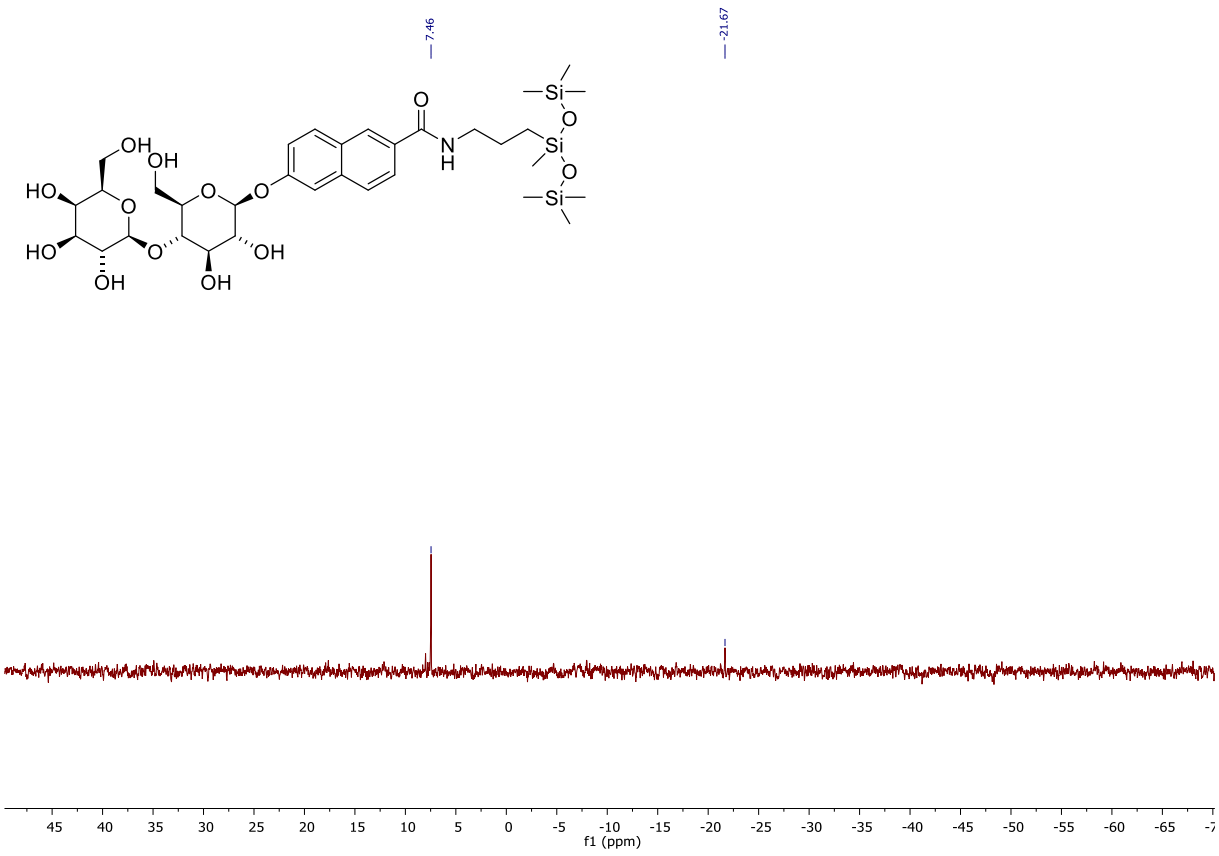


*Figure 127: ^{29}Si NMR (300 MHz, MeOD-d_4) of surfactant **132b**.*

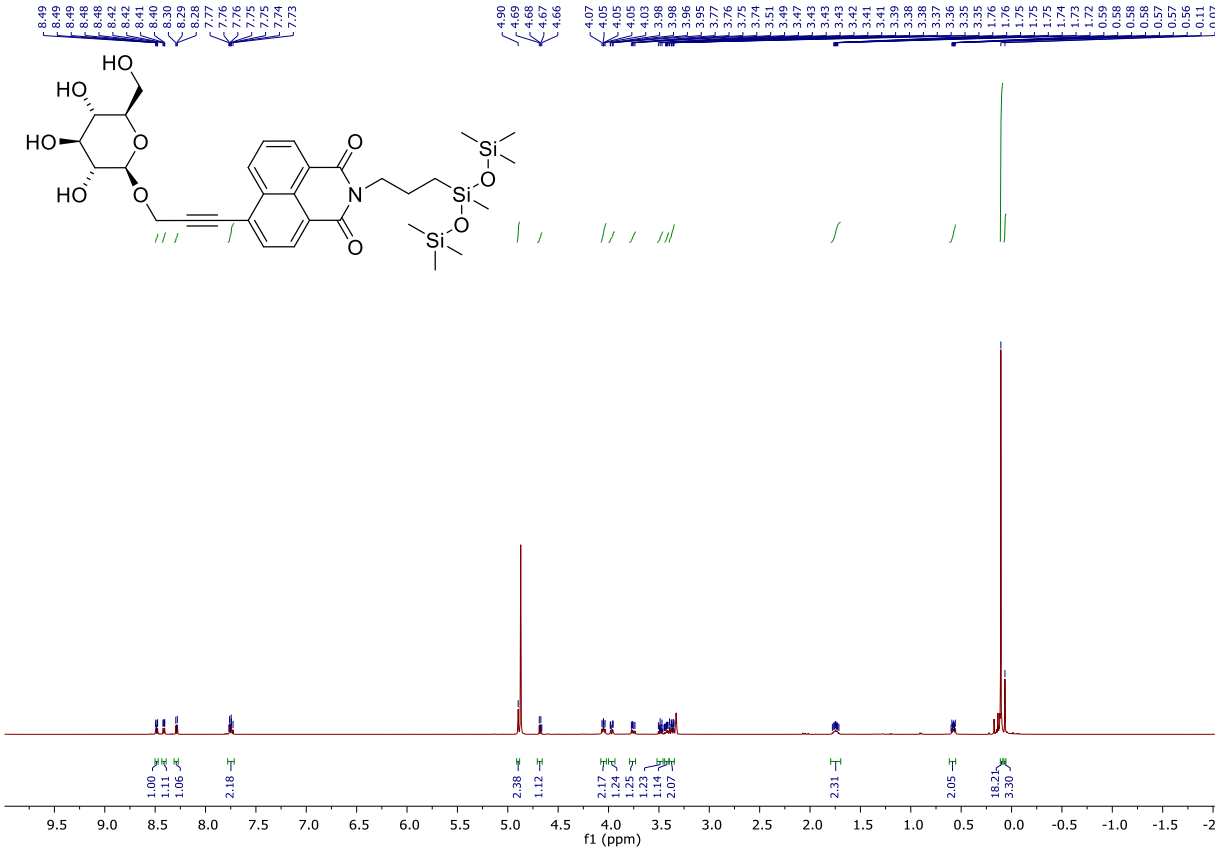


*Figure 128: ^{1}H NMR (500 MHz, MeOD-d_4) of surfactant **131a**.*

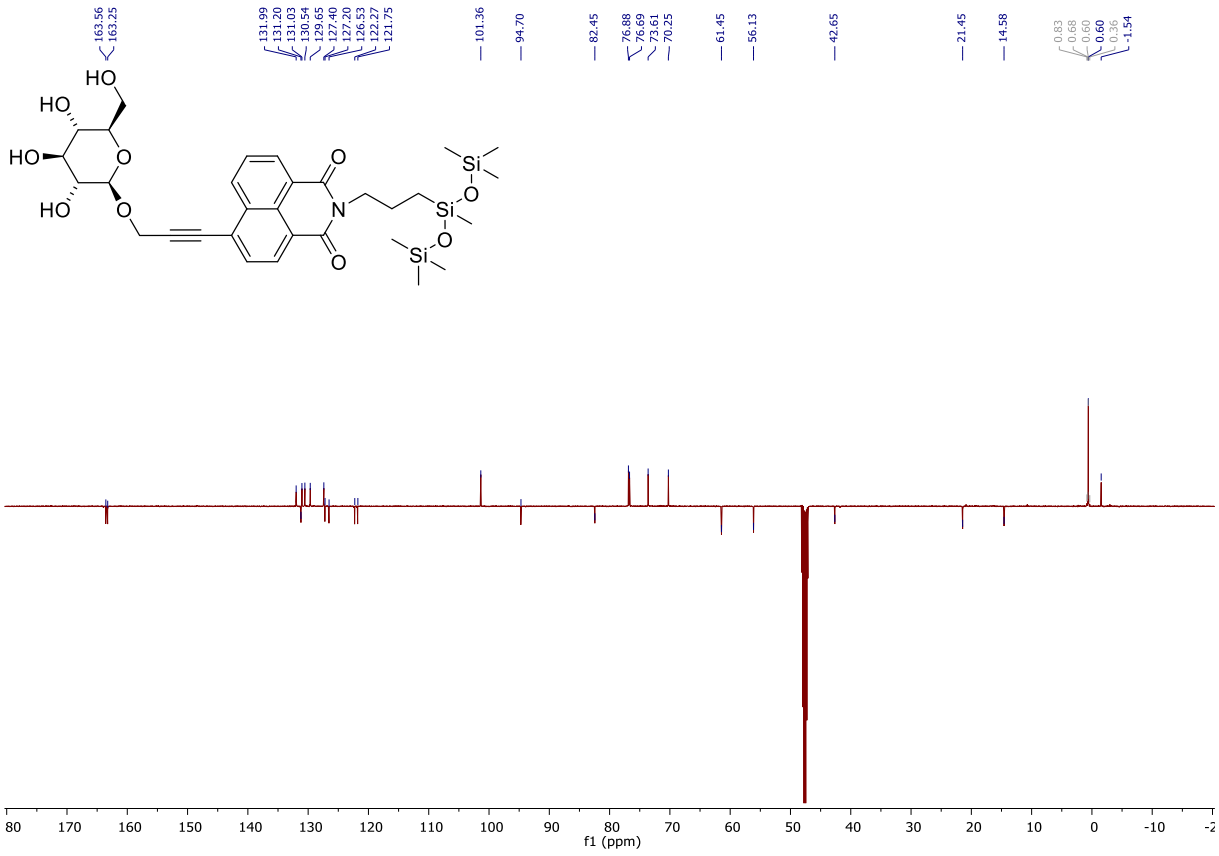


*Figure 129: ^{13}C NMR (500 MHz, MeOD-d$_4$) of surfactant **131a**.*

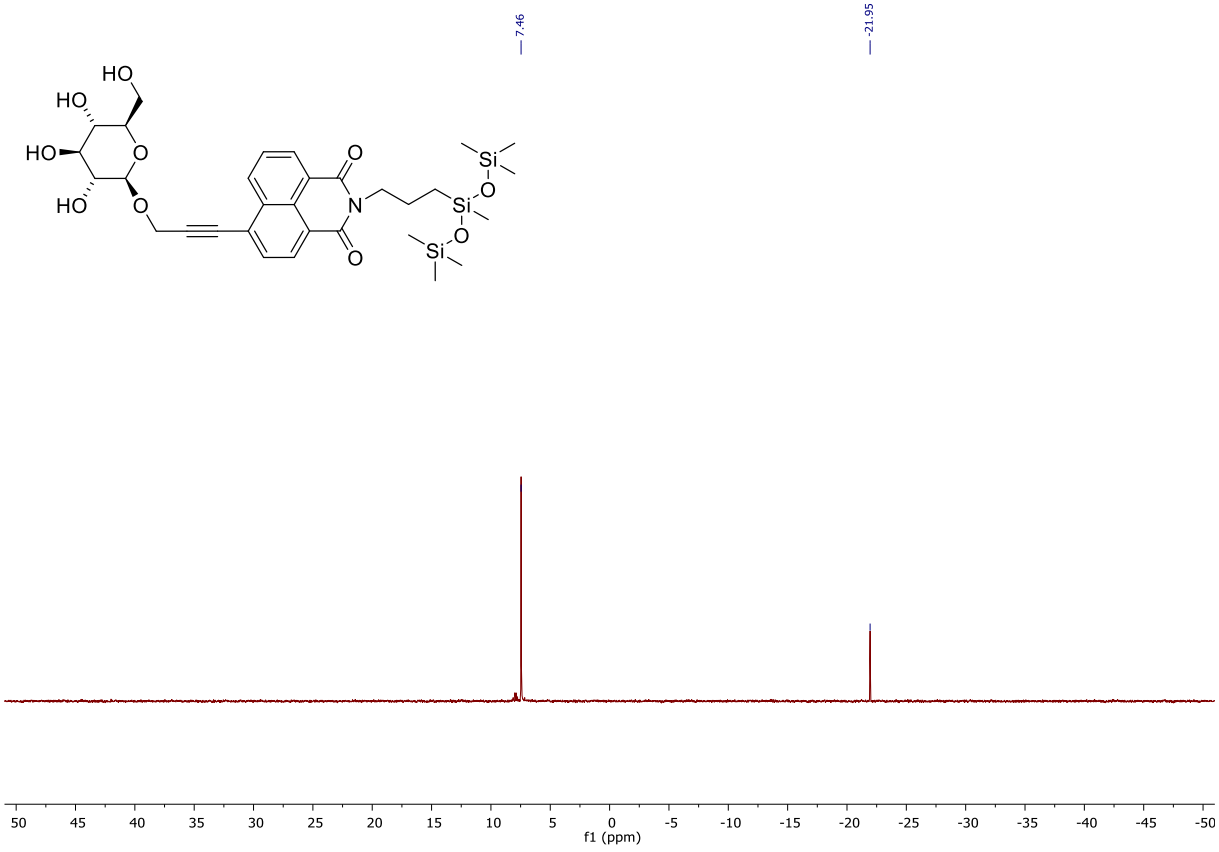


*Figure 130: ^{29}Si NMR (500 MHz, MeOD-d$_4$) of surfactant **131a**.*

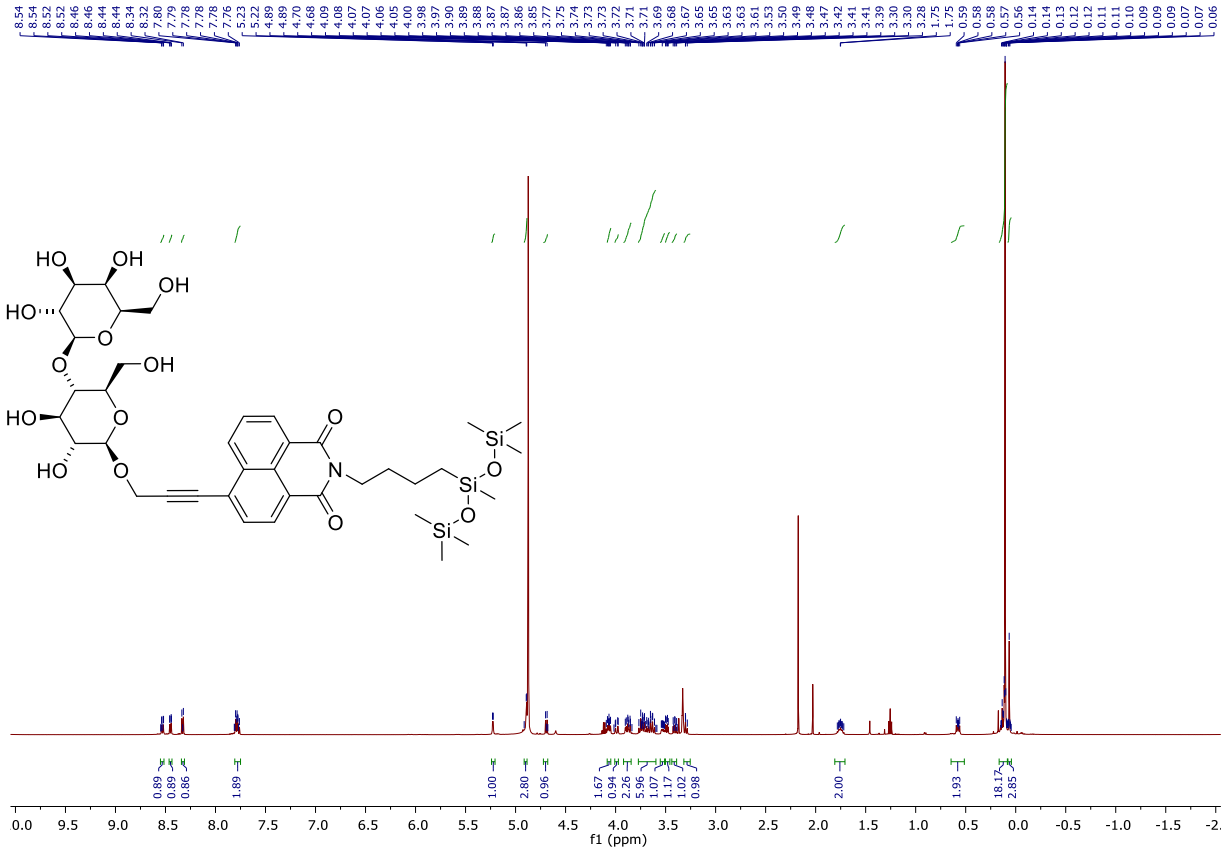


*Figure 131: ^{1}H NMR (500 MHz, MeOD-d$_4$) of surfactant **131b**.*

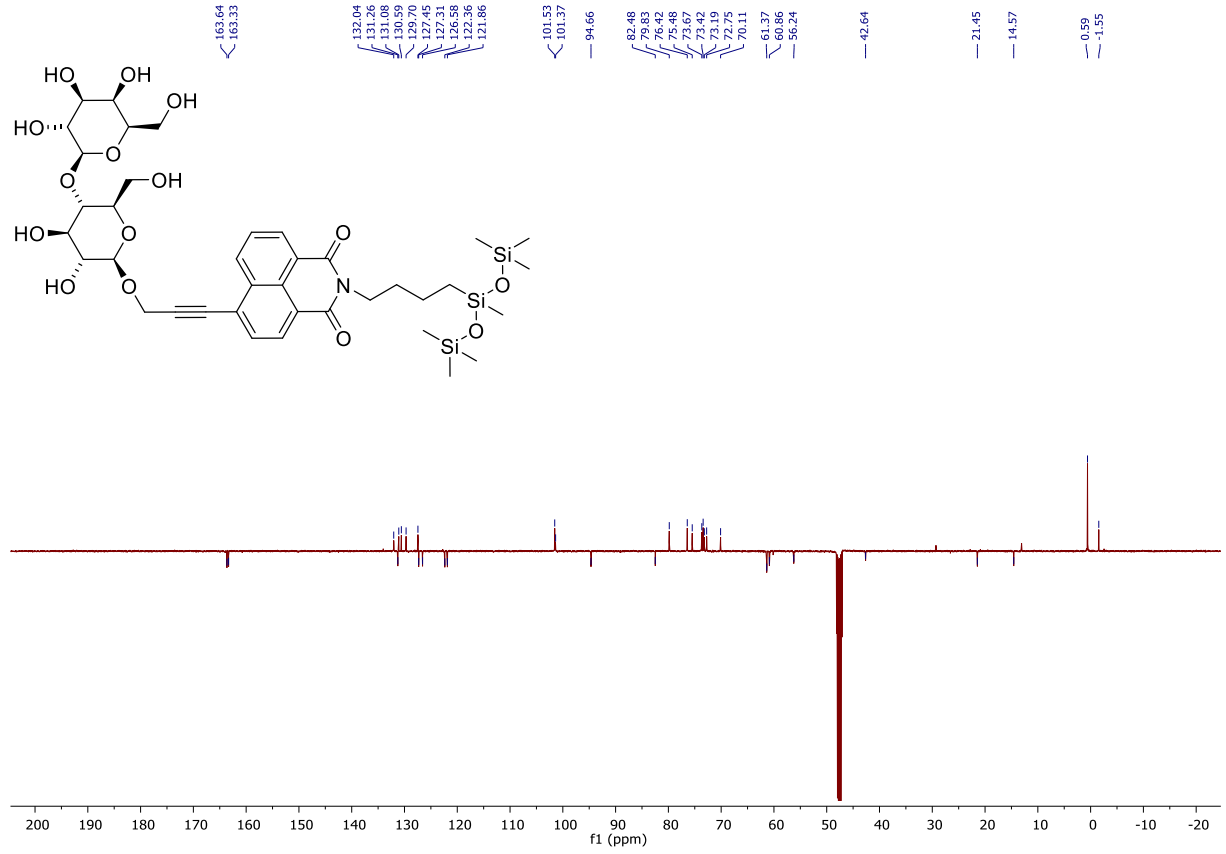


*Figure 132: ^{13}C NMR (500 MHz, MeOD-d$_4$) of surfactant **131b**.*

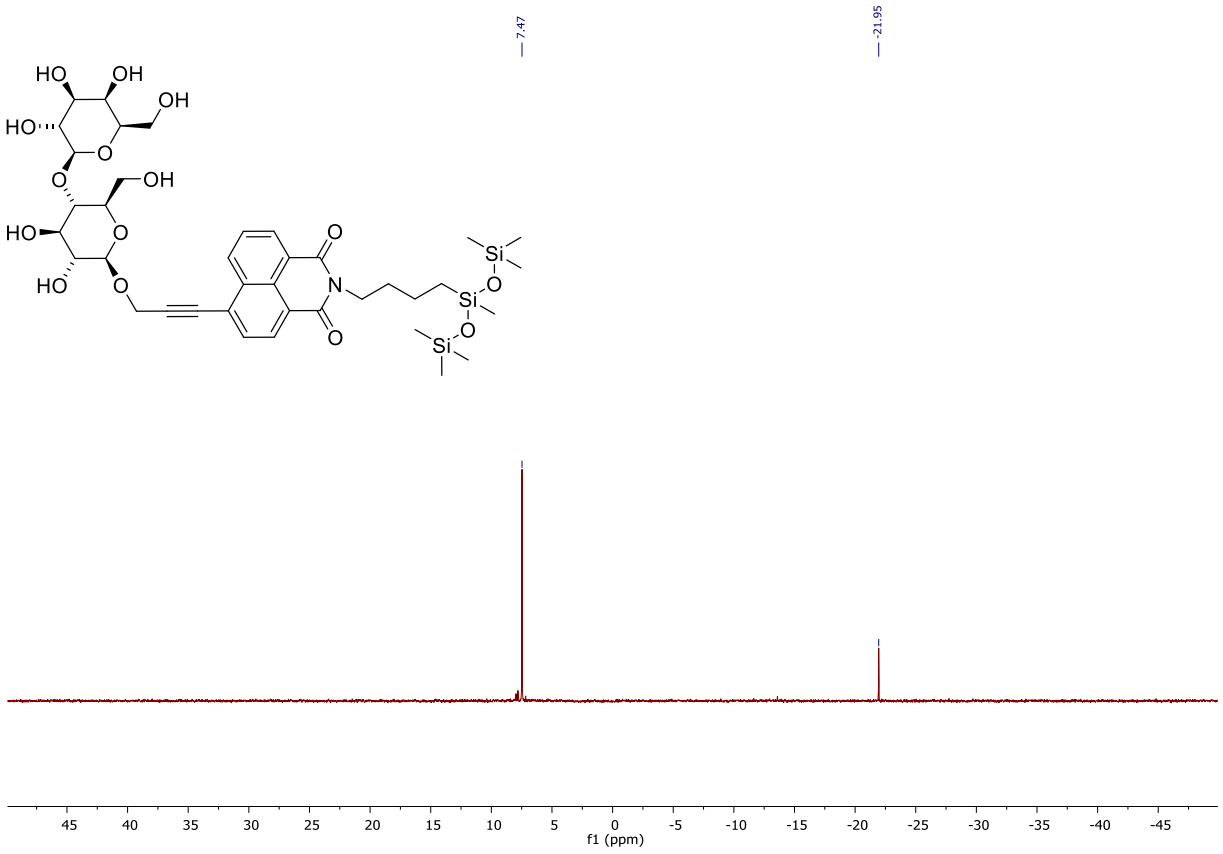


*Figure 133: ^{29}Si NMR (500 MHz, MeOD-d_4) of surfactant **131b**.*