PREPARATION AND CHARACTERIZATION OF NOVEL AZOCINNAMATES AND STEROIDAL AZO ETHERS

Abdullah Maamon Alhemyari

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PREPARATION AND CHARACTERIZATION OF NOVEL AZOCINNAMATES AND STEROIDAL AZO ETHERS

Abdullah Maamon Alhemyari

This thesis is submitted in partial fulfilment of the requirements for the degree of Master of Science Chemistry

Under the Supervision of Professor Thies Thiemann

April 2019
Declaration of Original Work

I, Abdullah Maamon Alhemyari, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this thesis entitled "Preparation and Characterization of Novel Azocinnamates and Steroidal Azo Ethers", hereby, solemnly declare that this thesis is my own original research work that has been done and prepared by me under the supervision of Professor Thies Thiemann, in the College of science at UAEU. This work has not previously been presented or published, or formed the basis for the award of any academic degree, diploma or a similar title at this or any other university. Any materials borrowed from other sources (whether published or unpublished) and relied upon or included in my thesis have been properly cited and acknowledged in accordance with appropriate academic conventions. I further declare that there is no potential conflict of interest with respect to the research, data collection, authorship, presentation and/or publication of this thesis.

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Abstract

This thesis is concerned with the synthesis of novel azo-cinnamates and of steroidal azo ethers and with the analysis of the spectroscopic and thermal properties of these materials. The compounds were identified as possible photoswitchable liquid crystals. The molecules were prepared by multi-step sequences, involving etherification, azo coupling and Appel-type reactions as the key steps in the case of the azo-cinnamates, and Finkelstejn reactions and Williamson-type etherification reactions as the major transformations in the case of the steroidal azo ethers. The preparation of the azo-cinnamates was a further example of an esterification reaction run under Appel-type conditions using BrCCl₃/PPh₃. The azo-cinnamates were shown to be photoswitchable under photoirradiation at \( \lambda = 350 \) nm, where the thermally stable trans-azo compounds isomerized photochemically to the cis-isomers. Subsequently, the energetically less stable cis-isomers isomerized thermally back to the trans-isomers. The azo-cinnamates were found to exhibit thermotropic liquid crystalline behavior as evidenced by differential scanning calorimetric analysis and by optical texture analysis under the polarization microscope of selected samples. Azocinnamates have been found to exhibit liquid crystalline behavior before, however, it is commonly accepted that in systems containing three (or more) aromatic rings, in the compounds that exhibit liquid crystalline (eg., nematic) behavior, the ring systems normally are positioned in close proximity to each other, preferably with less flexible linkers connecting them. In the presently studied compounds, however, the cinnamate unit is separated from the azobenzene substructure by flexible C9- and C11-alkyl chains, and so it is exciting to see that also these compounds exhibit (albeit in a narrow temperature range) thermotropic behavior.

Keywords: Azo cinnamates, steroidal azo compounds, photoswitching, liquid crystals, single X-ray crystal structure.
تحضير وتحليل ودراسة خصائص مركبات جديدة من سلالة الأزوسيناميت والازوكوليسترول

الملخص

في هذا البحث تم تحضير مركبات جديدة تصنف ضمن مجموعة (azo-cinnamates) و مجموعة (steroidal azo ethers) وتحليلها باستخدام أجهزة تحليل المركبات العضوية. وأيضا تم دراسة الخصائص الفيزيائية والحرارية لهذه المركبات. فقد تم تحضير هذه المركبات عن طريق العديد من التفاعلات الكيميائية من أهمها: تفاعلات تركيب الأزو وتفاعلات تركيب الأثير وتفاعلات الاسترة. تم تحليل جميع المركبات والتتأكد من نقاوتها بشكل دقيق. بعد دراسة الخصائص الفيزيائية والضوئية لهذه المواد باستخدام أجهزة تحليل الطيف الضوئي وجهاز الرنين المغناطيسي النووي وجدت أن هذه المركبات لها القدرة على التحول بين النظائر (النظير سي) والنظير ترانس) عند تعرضها للأشعة فوق البنفسجية أو حتى تعرضها للحرارة. وجدت أيضا بعد الانتهاء من دراسة الخصائص الحرارية لبعض هذه المواد باستخدام جهاز المجهر الحراري وجهاز المححر الحراري التفاضلي أن لها خصائص مشابهة لخصائص مركبات الكرستالات السائلة.

مفهوم البحث الرئيسي: الكرستالات السائلة، النظائر، تفاعلات تركيب الأثير، تفاعلات الاسترة.
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Dedication

To my beloved parents, brothers, sisters, hero supervisors, Al Hemyari family and great friends.
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<th>Description</th>
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<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimeter</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid crystal</td>
</tr>
<tr>
<td>POMHS</td>
<td>Polarizing optical microscope with a hot stage</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

1.1 Overview

In this work, novel photoswitching compounds will be prepared. Photoswitchable molecules are able to isomerize between at least two metastable forms through an external stimulus such as photoirradiation (Beharry, Sadowski, & Woolley, 2011). Originally, these types of molecules found interest in different areas of science such as in physics, chemistry and biology (Heckel & Mayer, 2010; Russew & Hecht, 2010; Szobota & Isacoff, 2010; Wyart et al., 2009). The extensive usage of photochromic molecules, i.e., molecules that change color upon photoirradiation, is due to the general, also commercial interest in two isomers of a molecule having fundamentally different physical and chemical properties, especially if the different isomers can be addressed separately. Photoswitchable molecules have a wide range of applications such as in photo-electric cells. They are also used in the generation of three-dimensional animations and images and in screen displays (in conjunction with liquid crystals) (Stranius & Börjesson, 2017).

Photoswitching molecules can be used as dopants in liquid crystalline hosts. Alternatively, photoswitching compounds can be liquid crystalline themselves. For the second category, most of molecules are based on an azobenzene as the photoswitching unit, but p-alkoxy substituted phenylbut-1,3-dien-4-ylbenzonitriles (1) (Davis, Mallia, & Das, 2003) (Figure 1) as well as the photoactive (-)-2-arylidene-p-menthane-3-one (2) unit in cholesteric polymeric LCs (Figure 2). (Brehmer, Lub, & Witte, 1998) have also been used as intrinsically photoactive liquid crystalline formulations (Davis et al., 2003).
Since their discovery by Reinitzer and Lehmann in 1888/1889, liquid crystals have gained ever-increasing interest, first with the excellent synthetic work of Vorländer and a first understanding of the different LC phases, then with detailed X-ray crystal structural analyses and the elucidation and classification of further mesophases such as of the smectic liquid crystals in the 1970s/1980s, and finally with the work on the application of LCs in electro-optical displays, starting with the investigations carried out at RCA, Princeton, on dynamic scattering displays in the late 1960 (Gray, 1998). The development of ever-new LC incorporating displays continues unabated.

Figure 1: 1,4-Diphenyl butadiene derivatives (1)

Figure 2: (-)-2-Arylidene-p-menthane-3-one on a polymer backbone (2)
The most important mesophases of thermotropic liquid crystals are the nematic, smectic A, smectic C and columnar discotic phases. Also, two important chiral phases exist: the cholesteric (chiral nematic) and the smectic C phase (Figure 3). In addition, a number of blue phases exist. Further new phases have been discovered over time.

Azobenzenes are the most commonly used photoswitchable LC materials. Thus, azobenzene derivatives have been utilized in photoresponsive functional devices in smart polymers (Kawai, Nakashima, & Irie, 2005), in molecular switches (Yasuda, Nakamura, Matsumoto, & Shigekawa, 2003), in data storage systems (Yager & Barrett, 2006) and as molecular “machines” in supramolecular organic chemistry (Beharry & Woolley, 2011; Broichhagen & Trauner, 2014; Goulet- Hanssens & Barrett, 2013). As such, azobenzene derivatives have received considerable experimental and theoretical attention.
1.2 Statement of the Problem

The idea was to prepare a series of $\text{p-alkoxyazobenzene-cinnamates}$ as potential photoswitchable guests (dopants) to be used in liquid crystal hosts. Also, it was to be examined, if it were possible to use $\text{p-alkoxyazobenzene-alkanols}$ shown in Scheme 1 to prepare $\text{p-alkoxyazobenzenealkyl cholesteryl ethers}$ as potential chiral dopants for liquid crystalline phases. Furthermore, it was to be determined whether these substances themselves would exhibit liquid crystalline behavior. In parallel, the photoswitching behavior of these materials was to be examined.

![Scheme 1: p-alkoxyazobenzene-cinnamates and p-alkoxyazobenzenealkyl cholesteryl ethers](image)

1.3 Azobenzene based liquid crystals

Azobenzenes can be found as important moieties in the structure of liquid crystals. Although the science of liquid crystals (LCs) has matured over the years, there is still interest in developing liquid crystalline material with enhanced properties as well as liquid crystalline devices that incorporate their formulations.
Azobenzene exists as two isomers: the $E$-isomer (or trans-isomer) and the $Z$-isomer (or cis-isomer) (Figure 4). The $E$-isomer is by 50 kJ mol$^{-1}$ more stable thermodynamically than the $Z$-form. Consequently, the different spatial arrangements of the different isomers lead to different physical and chemical properties (Ichimura, Oh, & Nakagawa, 2000).

Azobenzenes can be classified into three general types, depending on their photophysical response: azobenzenes which are unsubstituted and count as the parent compounds, aminoazobenzenes which are substituted with an electron donating group (NH$_2$) and pseudo-stilbenes which are known for their strongly asymmetric electron distribution (push/pull substitution). The reason behind the strongly asymmetric pattern of this third group of azobenzenes lies in the fact that they are substituted at 4 and 4′ by an electron donating group and an electron withdrawing group, respectively (Yager & Barrett, 2006).

The structure of $E$-azobenzene is not planar; the dihedral angle N,N,C,C is around 17.5°. In contrast, one of the phenyl rings of the $Z$ isomer occupies a plane tilted by 56° from the plane of the other ring (Figure 5). This leads to a great difference in the intramolecular distances between the phenyl groups in cis- and trans-
azobenzenes. Thus, the distances between the two carbon atoms in the 4-and 4’-positions are 9.0 and 5.0 Å for the E- and Z-isomer, respectively (Figure 5) (Hamon, Djedaini-Pillard, Barbot, & Len, 2009).

Figure 5: Geometrical structures of the E- and Z-isomer of azobenzene (Hamon, Djedaini-Pillard, Barbot, & Len, 2009)

The UV–visible absorption spectra of E-azobenzene are characterized by three major bands: (i) a band at $\lambda = 228$ nm originates from a $\pi-\pi^*$ transitions localized on the phenyl groups; (ii) a band at $\lambda = 318$ nm originates from symmetry-allowed $\pi-\pi^*$ transitions, from orbitals which are delocalized through the molecule including the two nitrogen atoms; and (iii) a band at $\lambda = 440$ nm originates from symmetry forbidden $n-\pi^*$ transitions occurring at the central nitrogen atoms (Figure 6). It is notable that the UV–visible absorption spectrum of the Z-isomer is quite different from that of the E-isomer, with a band at $\lambda = 260$ nm originating from symmetry-allowed $\pi-\pi^*$ transitions ($\lambda = 318$ nm for the E-isomer) (Y. Yang, Hughes, & Aprahamian, 2012). In addition, any substitution patterns on the azobenzene chromophores can affect the UV absorption bands, and this will be discussed in detail in the discussion part.
In this work, the photoisomerization of the synthesized compounds will be investigated. Photo-reversible switching between trans & cis isomers of the azo benzene derivatives can be performed by irradiation of the samples with light at various wavelengths (Figure 6) (Yin, Zhao, & Zhang, 2018). There are many previous studies which proposed the mechanism of the cis trans isomerization of 4,4'-substituted azobenzene derivatives. The first type is the rotation at the −N=N− bond through π-bond rupture, and the second type is an inversion of one or of both nitrogens through a linear hybridisation transition state, in which the double bond is retained. There are many differences between the two isomers such as absorption bands, redox potential, refractive index and the geometrical structure (these differences will be discussed further in the discussion part) (Yamaguchi et al., 2005).
1.4 Relevant Literature

Similar to our novel materials, compounds have been prepared by other researchers. Those types of compounds exhibit liquid crystalline behavior (LC). Figures 7, 8, 9, 10 below, show materials structurally similar to our novel, synthesized compounds. This includes a series of steroidal azo carbonates of type (3) and (6) (Figures 7 and 8) (Yang et al., 2013). When n= 0 in compound 3 “both cholesterol and azobenzene moieties are attached to each other by carbonate linkage”, there is an absence of a mesophase for the compound, while when n= 6, 11, the compounds exhibit mesomorphic phases, where the compounds show enantiotropic mesophases and chiral nematic phases (Figure 7).

![Figure 7: Cholesterol azo derivative (3)](image)

![Figure 8: Chiral azobenzene dopant (6)](image)
Compounds that are chiral azobenzenes can be used as a chiral dopant (guest) in liquid crystalline hosts. Upon the irradiation process, the trans form of azobenzene can stabilize the LC texture because of its rod-like shape, while the cis form destabilizes the texture by generating a disorder in the aligned system. The compound (6) shown in (Figure 8) was used as a chiral dopant in the nematic liquid crystalline 4-cyano-4’-pentylbiphenyl (5CB) (7) (Figure 10). The results proved that the cis form of the chiral dopant destroyed the short-range orientational order of the mesophase (Figure 10 C) (Wang & Li, 2012).

Figure 9: 4-Cyano-4’-pentylbiphenyl (5CB) (7)

Figure 10: POM image of the mixture achiral nematic LC host 5CB during cooling cycle at 38.9 °C (A: before UV irradiation, B: after UV irradiation, C: after the radiation was stopped) [from Wang & Li, 2012]
Azo-cinnamates shown in Figures 11 & 12 have been forwarded as liquid crystals by Selvarasu and Kannan (Selvarasu & Kannan, 2016). A series of these compounds, shown in Figure 11, exhibit nematic phases in the cooling cycle proceeding from the isotropic phase. In addition, with increasing carbon chain length, a focal conical texture characteristic of a Smectic-C mesophase started to appear. Also, for the compounds shown in Figure 12, nematic and smectic phases were recognized in the heating and cooling cycles.

Figure 11: Cinnamate aldime derivative (4)

Figure 12: Cinnamate azo derivative (5)
1.5 Synthesis

As azobenzene have many applications, they are of great interest to scientists, especially to synthetic organic chemists. Azobenzenes can be synthesized in six main ways, which can be classified as: (i) oxidation of aromatic primary amines; (ii) reduction of aromatic compounds having a nitro group; (iii) coupling of primary arylamines with nitro compounds (Mills reaction); (iv) electrophilic reactions of diazonium salts; (v) oxidation of hydrazine derivatives; (vi) reduction of azoxybenzene derivatives (Hamon et al., 2009) (Figure 13) and (vii) other methods (Merino, 2011). In this work, we will choose a method analogous to that reported in a previous work (Yan, et al., 2012).

For specifically our targeted compounds, alkylation of nitrophenol with a 1,ω-haloalkanol is the first step in our synthetic route. To prepare the azobenzenes, the reduction of the nitro group to aniline is necessary. Under certain conditions, which we will describe later, in the experimental part, the diazotization step will occur in good yield. Thereafter, further alkylation of the hydroxyazobenzene intermediate with a haloalkane will be carried out to get the pen-ultimate building block of our synthesis. Finally, an esterification (in the case of the azocinnamates) and an etherification (in the case of the steroidal azo ether) will lead to the target compounds.
Figure 13: General preparations of azobenzene
1.6 Potential Contributions and Limitations of the Study

As the linker between the azobenzene and the cinnamate unit in the molecules is relatively long and flexible, it was predicted that the molecules would exhibit mesophases only with a relatively narrow temperature range, if at all. In the studies, it was seen, however, that the compounds analyzed have a rich thermal behavior, even exhibiting different crystal forms.

As a thermal hotplate – polarization microscope set-up was not available at the UAEU, the thermal measurements and texture analysis was carried out at the University of Hamburg, and only a limited investigation of the liquid crystalline behavior of the compounds could be performed. Here, it is believed that a more detailed study would be warranted. This is especially true for the use of the steroidal azobenzene ethers as chiral dopants, where a more complete study of hosts would be needed. Furthermore, although the photoswitching of the pure compounds was studied, the change of the alignment of the pure substances in the mesophase under photoirradiation could not be studied as could also not be studied the behavior of host phases under photoirradiation in presence of the here-synthesized compounds used as dopants.
Chapter 2: Methods

2.1 Research Design

The compounds shown in the thesis were synthesized, purified (using crystallization or column chromatography), and characterized by $^1$H NMR, $^{13}$C NMR, DEPT and/or INEPT techniques, LC-MS-MS, and IR spectroscopy. Selected compounds were analyzed by UV-VIS spectroscopy, and submitted to DSC thermal analysis and X-ray single crystal structural determination. Selected azo cinnamates were photoirradiated in an attempt to photo-isomerize the molecules. The progress of the photoreactions was followed by either UV-VIS or $^1$H NMR spectroscopy. Furthermore, a polarization microscope with a hot stage was used to look at the texture of some of the compounds.

Column chromatography was carried out on commercial 60 Å silica gel (230 – 400 mesh, Merck grade 9385, Sigma Aldrich) and on recycled silica gel (new research in our research group). Analytical thin layer chromatography (TLC) was carried out on TLC Alu foils from Fluka (with fluorescent indicator at $\lambda = 254$ nm). $^1$H NMR (at 400 MHz) and $^{13}$C NMR (at 100.5 MHz) spectra were taken on a Varian 400 MHz spectrometer. For some samples, a Bruker Avance 500 spectrometer with a working frequency of 500 MHz for $^1$H nuclei was used at NYU-AD. Furthermore, samples were also measured on a Varian 200 MHz NMR spectrometer ($^1$H at 200.0 MHz, $^{13}$C at 50.3 MHz). Infrared spectra were taken on a Thermo Nicolet Nexus 670 FT-IR spectrometer (solid samples as KBr pellets). UV-VIS spectroscopy was performed on UV-1800 (Shimadzu). X-ray crystal structural analysis was performed on single crystals of compounds xx, xx, and xx, utilizing a Bruker APEX DUO diffractometer.
with CCD area detector and monochromatic MoK\textalpha\ radiation ($\lambda = 0.71069$) (NYU-AD, Prof. Panče Naumov). For the photoirradiation, a Luzchem LZC 4V photoreactor was used with either 13 USHIO G8T5 lamps (7.2 W low pressure mercury arc lamp with a radiation peak at $\lambda = 253.7$ nm) or with 14 Hitachi FL8BL-B (0.75 W, UV irradiance 8.0 ($\mu$/cm)$^2$, with a radiation peak at $\lambda = 352$ nm). CH$_2$Cl$_2$ [Sigma Aldrich, purris. p.a., $\geq 99.9\%$ (GC)] and benzene were taken as solvents in the photoirradiation experiments. The thermal behavior was investigated using differential scanning calorimeter (DSC-60, Shimadzu) in the mechanical engineering at UAEU (Prof. Dr. Abdel-Hamid Mourad). The masses of the synthesized compounds were measured using an LC-MS-MS 8060 (Shimadzu, with Dr. Iltaf Khan). Textures of selected samples were investigated using an Olympus BH polarization microscope with a Mettler-Toledo hotstage.
2.2 Experimental

General: $^1$H and $^{13}$C NMR spectra were recorded with a Varian 400 NMR ($^1$H at 395.7 MHz, $^{13}$C at 100.5 MHz) and a Varian 200 MHz NMR spectrometer ($^1$H at 200.0 MHz, $^{13}$C at 50.3 MHz). The chemical shifts are relative to TMS (solvent CDCl$_3$, unless otherwise noted). Infrared spectra were taken on a Thermo Nicolet Nexus 670 FT-IR spectrometer (solid samples as KBr pellets). Column chromatography was carried out on silica gel with Sigma Aldrich 60 Å (230 – 400 mesh, Merck grade 9385). TLC was performed on TLC foils (Silica gel on TLC alu foils, Fluka 60778-25EA).

2.2.1 First pathway

The compounds, which are prepared in this section, will follow the synthetic route shown in Figure 14.

Figure 14: Synthetic route of the preparation of the alkoxy azobenzene derivatives
9-(4-Nitrophenoxy)nonan-1-ol (9):

A mixture of 4-nitrophenol (8) (8.6 g, 62 mmol), 11-bromo-1-nonanol (14 g, 62 mmol) and potassium carbonate (8.8 g, 62 mmol) was dissolved in dimethylformamide (DMF, 50 mL). The resulting solution was heated to 120 °C and left until the reaction finished. After that, the reaction mixture was cooled down to room temperature. Then, distilled water (200 mL) was added to the mixture. A yellow precipitate was formed. The precipitate was collected and extracted with ethyl acetate (70 mL). The ethyl acetate solution was washed with water (100 mL) and dried over magnesium sulfate (MgSO₄). The organic phase (ethyl acetate) was filtered and evaporated in vacuo using a rotary evaporator to obtain comp. 9 as a solid (12.9 g, 74%).

δ_H (400 MHz, CDCl₃) 1.27-1.52 (12H, m, CH₂), 1.78 (2H, m, CH₂), 3.58 (2H, t, OCH₂), 4.00 (2H, t, OCH₂), 6.89 (2H, d, CH), 8.14 (2H, d, CH); δ_C (100.5 MHz, CDCl₃) 25.7 (CH₂), 25.9 (CH₂), 28.9 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 32.7 (CH₂), 62.8 (OCH₂), 68.8 (OCH₂), 114.4 (CH), 125.9 (CH), 141.2 (CH), 164.2 (CH). IR _υ_ (KBr, cm⁻¹): 3021, 2918, 2850, 1608, 1590, 1517, 1473, 1396, 1367, 1242, 1070, 1009, 821, 763.

9-(4-Aminophenoxy)nonan-1-ol (10):

9-(4-Nitrophenoxy)nonan-1-ol (9) (12.9 g, 46 mmol) was dissolved in tetrahydrofuran (THF, 80 mL). Then, palladium on carbon (2.4 g, 10 w% Pd/C) was added to the resulting solution. After that, hydrogen gas was added using a balloon. The reaction mixture was stirred, until the reaction finished (typically, 72 h). After the reaction finished, the reaction mixture was filtered over Celite (5 g) to remove the
Pd/C. Then, the solvent was removed in vacuo using a rotary evaporator to obtain 10 as a solid (8.25 g, 72%).

δ_\text{H} (400 MHz, CDCl_3) 1.31-1.56 (12H, m, CH_2), 1.72 (2H, m, CH_2), 3.61 (2H, t, OCH_2), 3.86 (2H, t, OCH_2), 6.63 (2H, d, CH), 6.73 (2H, d, CH); δ_\text{C} (100.5 MHz, CDCl_3) 25.7 (CH_2), 26.0 (CH_2), 29.3 (CH_2) 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 32.8 (CH_2), 62.0 (OCH_2), 68.6 (OCH_2), 115.6 (CH), 116.4 (CH), 139.7 (CH), 152.3 (CH). IR υ (KBr, cm⁻¹): 3526, 3113, 3089, 2918, 2850, 1604, 1592, 1501, 1472, 1346, 1307, 1261, 1184, 1116, 1047, 1006, 857, 753, 660.

4-((4-((9-Hydroxy)nonyl)oxy)phenyl)diazenyl phenol (11): (10) (8.25 g, 32.9 mmol) was dissolved in hydrochloric acid (160 mL, 1 M), and the resulting solution was cooled to 0 °C. With stirring, a solution of sodium nitrite (2.27 g, 32.9 mmol) in water (18 mL) was added dropwise to the solution to produce the diazonium salt. Then, a mixture of phenol (3.1 g, 32.9 mmol) and sodium hydroxide (1.3 g, 32.9 mmol) in water (18 mL) was added slowly to the solution, at 0 °C. An aqueous solution of potassium carbonate was added to the mixture to give pH = 8, and then a yellow solid precipitated. The reacting mixture was stirred further at 0 °C and left, until the reaction finished. After the reaction finished, hydrochloric acid (1 M) was added to the reacting mixture to give pH = 4. The yellow solid precipitate was collected and washed with water. The crude product was re-crystallized from ethanol to give 11 as a solid (5.18 g, 45.6%).

δ_\text{H} (400 MHz, DMSO) 1.23-1.37 (16H, m, CH_2), 1.69 (2H, m, CH_2), 3.34 (2H, t, OCH_2), 4.01 (2H, t, OCH_2), 6.89 (2H, d, CH), 7.04 (2H, d, CH), 7.71 (2H, d, CH), 7.76 (2H, d, CH); δ_\text{C} (100.5 MHz, DMSO) 25.9 (CH_2), 26.1 (CH_2), 29.0 (CH_2), 29.0
(CH₂), 29.2 (CH₂), 29.3 (CH₂) 29.3 (CH₂), 29.5 (CH₂), 32.9 (CH₂), 61.2 (OCH₂), 68.3 (OCH₂), 115.3 (CH), 116.2 (CH), 124.4 (CH), 124.8 (CH), 145.6 (CH), 146.5 (CH) 160.6 (CH), 161.1 (CH). IR υ (KBr, cm⁻¹): 3370, 2938, 2853, 1593, 1562, 1503, 1471, 1257, 1145, 1020, 846.

9-(4-((4-(Hexyloxy)phenyl)diazenyl)phenoxy)nonan-1-ol (12):

A mixture of (11) (5.18 g, 15 mmol), 1-bromohexane (2.39 g, 15 mmol) and potassium carbonate (2.07 g, 15 mmol) was dissolved in dimethylformamide (13 mL). The resulting solution was heated at 120 °C and left it until the reaction finished. After that, the mixture cooled to room temperature. Then, distilled water (100 mL) was added to the mixture, and a yellow precipitate formed. The precipitate was collected and extracted with ethyl acetate (100 mL). The ethyl acetate solution was washed with water and dried over magnesium sulfate (MgSO₄). The organic phase (ethyl acetate) was filtered from the sulfate (MgSO₄) and evaporated in vacuo using the rotary evaporator to obtain 12 as a solid (5.2 g, 62%).

δH (400 MHz, CDCl₃) 0.91 (3H, t, CH₃), 1.34-1.56 (24H, m, CH₂), 1.80 (2H, m, CH₂), 3.63 (2H, t, OCH₂), 4.02 (4H, t, OCH₂), 6.98 (4H, d, CH), 7.86 (4H, d, CH); δC (100.5 MHz, CDCl₃) 1.1 (CH₃), 22.6 (CH₂), 25.7 (CH₂), 25.9 (CH₂), 26.0 (CH₂), 26.1 (CH₂), 29.0 (CH₂), 29.0 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.3 (CH₂) 29.3 (CH₂), 29.5 (CH₂), 32.9 (CH₂), 63.0 (OCH₂), 68.3 (OCH₂), 68.3 (OCH₂), 114.6 (CH), 124.3 (CH), 146.9 (CH) 161.1 (CH). IR υ (KBr, cm⁻¹): 3349, 2934, 2850, 1602, 1581, 1497, 1474, 1247, 1150, 1027, 843, 555.
9-((4-(Heptyloxy)phenyl)diazenyl)phenoxy)nonan-1-ol (13):

A mixture of 11 (3 g, 8.42 mmol), 1-bromoheptane (1.8 g, 10.1 mmol) and potassium carbonate (1.3 g, 10.1 mmol) was dissolved in dimethylformamide (DMF, 12 mL). The resulting solution was heated at 120 °C, and it was left it until the reaction finished. After that, the mixture was cooled to room temperature. Then, distilled water (70 mL) was added to the mixture, and a yellow precipitate formed. The precipitate was collected and extracted with ethyl acetate (100 mL). The ethyl acetate solution was washed with water and dried over magnesium sulfate (MgSO₄). The organic phase (ethyl acetate) was filtered from the sulfate (MgSO₄) and evaporated in vacuo using the rotary evaporator to obtain 13 as a solid (2.1 g, 56.5%).

δH (400 MHz, CDCl₃) 0.89 (3H, t, CH₃), 1.29-1.58 (24H, m, CH₂), 1.80 (2H, m, CH₂), 3.64 (2H, t, OCH₂), 4.02 (4H, t, OCH₂), 6.98 (4H, d, CH), 7.85 (4H, d, CH);
δC (100.5 MHz, CDCl₃) 14.1 (CH₃), 22.6 (CH₂), 25.7 (CH₂), 25.9 (CH₂), 29.1 (CH₂), 29.2 (CH₂), 29.2 (CH₂), 29.3 (CH₂) 29.3 (CH₂), 29.5 (CH₂), 31.8 (CH₂), 32.8 (CH₂), 63.1 (OCH₂), 68.3 (OCH₂), 68.3 (OCH₂), 114.6 (CH), 124.3 (CH), 146.9 (CH) 161.1 (CH). IR υ (KBr, cm⁻¹): 3351, 2935, 2850, 1602, 1581, 1497, 1250, 1151, 1021, 843, 559.

11-(4-Nitrophenoxy)undecan-1-ol (14):

A mixture of 4-nitrophenol (8) (6.68 g, 48 mmol), 11-bromo-1-nonanol (12.06 g, 48 mmol) and potassium carbonate (6.66 g, 48 mmol) was dissolved in dimethylformamide (DMF, 40 mL). The resulting solution was heated at 120 °C and left until the reaction finished. After that, the mixture was cooled to room temperature. Then, distilled water (200 mL) was added to the mixture and a yellow precipitate
formed. The precipitate was collected and extracted with ethyl acetate (100 mL). The ethyl acetate solution was washed with water and dried over magnesium sulfate (MgSO₄). The organic phase (ethyl acetate) was filtered from the sulfate (MgSO₄) and evaporated in vacuo using the rotary evaporator to obtain 14 as a solid (13.0 g, 92.5%).

δₜ (400 MHz, CDCl₃) 1.27-1.82 (18H, m, CH₂), 3.61 (2H, t, OCH₂), 4.01 (2H, t, OCH₂), 6.91 (2H, d, CH), 8.17 (2H, d, CH); δc (100.5 MHz, CDCl₃) 25.7 (CH₂), 25.9 (CH₂), 28.9 (CH₂), 29.2 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 32.7 (CH₂), 62.8 (OCH₂), 68.8 (OCH₂), 114.4 (CH), 125.9 (CH), 141.2 (CH), 164.2 (CH). IR ν (KBr, cm⁻¹): 3088, 2917, 2849, 1604, 1591, 1500, 1471, 1345, 1306, 1260, 1183, 1005, 856, 753.

11-(4-Aminophenoxy)undecan-1-ol (15):

14 (13 g, 42 mmol) was dissolved in tetrahydrofuran (THF, 80 mL), then palladium on carbon (Pd/C 10 w%, 2.2 g) was added to the resulting solution. After that, hydrogen gas was added using a balloon. The reaction mixture was stirred at room temperature until the reaction finished (72 h). After the reaction finished, the reaction mixture was filtered over Celite to remove the Pd/C. Then, the solvent was removed using a rotary evaporator to obtain 15 as a solid (9.5 g, 81%).

δₜ (400 MHz, CDCl₃) 1.26-1.72 (18H, m, CH₂), 3.61 (2H, t, OCH₂), 3.84 (2H, t, OCH₂), 6.61 (2H, d, CH), 6.71 (2H, d, CH); δc (100.5 MHz, CDCl₃) 25.7 (CH₂), 25.9 (CH₂), 28.9 (CH₂), 29.2 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 32.7 (CH₂), 62.8 (OCH₂), 68.8 (OCH₂), 115.6 (CH), 116.4 (CH), 141.2 (CH), 164.2
(CH). IR ν (KBr, cm⁻¹): 3526, 3113, 3089, 2918, 2850, 1604, 1592, 1501, 1472, 1346, 1307, 1261, 1184, 1116, 1047, 1006, 857, 753, 660.

4-((4-((11-Hydroxyundecyl)oxy)phenyl)diazenyl)phenol (16):

15 (3.18 g, 11.39 mmol) was dissolved in hydrochloric acid (1 M, 160 mL), and the resulting solution was cooled at 0 °C. With stirred, a solution of sodium nitrite (0.79 g, 11.39 mmol) in water (10 mL) was added dropwise into the solution to produce diazonium salt. A mixture of phenol (1.07 g, 11.39 mmol) and sodium hydroxide (0.46 g, 11.39 mmol) in water (10 mL) was added to the solution slowly at 0 °C. An aqueous solution of potassium carbonate was added to the mixture to give pH = 8, and then a yellow solid precipitated. The reacting mixture was stirred at 0 °C and leave it until the reaction finish. After reaction finished, hydrochloric acid (1 M) was added to the reacting mixture to give pH = 4. The yellow solid precipitation was collected and washed with water. The crude product was re-crystallized from ethanol to give comp. 16 (2.1 g).

δ_H (400 MHz, DMSO): 1.22-1.71 (18H, m, CH₂), 3.34 (2H, t, OCH₂), 4.01 (2H, t, OCH₂), 6.89 (2H, d, CH), 7.04 (2H, d, CH), 7.71 (2H, d, CH), 7.76 (2H, d, CH), 10.20 (OH); δ_C (100.5 MHz, DMSO): 25.9 (CH₂), 25.9 (CH₂), 29.0 (CH₂), 29.2 (CH₂), 29.4 (CH₂) 29.4 (CH₂), 29.5 (CH₂), 33.0 (CH₂), 61.2 (OCH₂), 68.3 (OCH₂), 115.3 (CH), 116.3 (CH), 124.4 (CH), 124.8 (CH), 145.6 (CH), 146.5 (CH) 160.7 (CH), 161.1 (CH). IR ν (KBr, cm⁻¹): 3411, 2918, 2849, 1696, 1682, 1500, 1470, 1242, 1145, 1015, 845, 549.
11-(4-((4-(Hexyloxy)phenyl)diazenyl)phenoxy)undecan-1-ol (17):

A mixture of 16 (1.68 g, 4.37 mmol), 1-bromohexane (0.86 g, 5.23 mmol) and potassium carbonate (0.72 g, 5.23 mmol) was dissolved in dimethylformamide (DMF, 8 mL). The resulting solution was heated at 120 °C and left until the reaction finished. After that, the mixture was cooled to room temperature. Thereafter, distilled water (70 mL) was added to the mixture, and a yellow precipitate formed. The precipitate was collected and extracted with ethyl acetate (100 mL). The ethyl acetate solution was washed with water and dried over magnesium sulfate (MgSO₄). The organic phase (ethyl acetate) was filtered from the sulfate (MgSO₄) and evaporated in vacuo using the rotary evaporator to obtain 17 as a solid (0.49 g).

δ_H (400 MHz, CDCl₃): 0.91 (3H, t, CH₃), 1.3-1.82 (26H, m, CH₂), 3.64 (2H, t, OCH₂), 4.03 (4H, t, OCH₂), 6.98 (4H, d, CH), 7.86 (4H, d, CH); δ_C (100.5 MHz, CDCl₃): 14.1 (CH₃), 22.6 (CH₂), 25.7 (CH₂), 25.7 (CH₂), 26.0 (CH₂), 29.2 (CH₂), 29.2 (CH₂), 29.4 (CH₂), 29.4 (CH₂), 29.5 (CH₂) 29.5 (CH₂), 29.6 (CH₂), 31.6 (CH₂), 32.8 (CH₂), 63.1 (OCH₂), 68.3 (OCH₂), 68.3 (OCH₂), 114.6 (CH), 124.3 (CH), 146.8 (CH) 161.2 (CH). IR ν (KBr, cm⁻¹): 3350, 2955, 2919, 2849, 1602, 1681, 1498, 1473, 1394, 1248, 1151, 1025, 843, 554.

11-(4-((3-prooxyphenyl)diazenyl)phenoxy)undecan-1-ol (18):

A mixture of (16) (0.65 g, 1.7 mmol), 1-bromo-propane (0.67 g, 2.03 mmol) and potassium carbonate (0.28 g, 2.03 mmol) was dissolved in dimethylformamidem (DMF, 5 mL). The resulting solution was heated at 120 °C and left until the reaction finished. After that, it was cooled down to room temperature. Then, distilled water (100 mL) was added to the mixture, and a yellow precipitate was formed.
precipitate was collected and extracted with ethyl acetate (100 mL). The ethyl acetate solution was washed with water and dried over magnesium sulfate (MgSO₄). The organic phase (ethyl acetate) was filtered from the sulfate (MgSO₄) and evaporated in vacuo using the rotary evaporator to obtain 18 as a solid (0.39 g).

δ_H (400 MHz, CDCl₃): 0.91 (3H, t, CH₃), 1.3-1.82 (26H, m, CH₂), 3.64 (2H, t, OCH₂), 4.03 (4H, t, OCH₂), 6.98 (4H, d, CH), 7.86 (4H, d, CH); δ_C (100.5 MHz, CDCl₃): 13.9 (CH₃), 19.2 (CH₂), 25.7 (CH₂), 26.0 (CH₂), 29.1 (CH₂), 29.3 (CH₂) 29.3 (CH₂), 29.5 (CH₂), 31.2 (CH₂), 32.8 (CH₂), 63.1 (OCH₂), 68.1 (OCH₂), 68.4 (OCH₂), 114.8 (CH), 124.8 (CH), 145.8 (CH) 161.7 (CH). IR υ (KBr, cm⁻¹): 3353, 2958, 1918, 2849, 1602, 1581, 1497, 1243, 1150, 844, 554.

11-(4-((4-Butoxyphenyl)diazenyl)phenoxy)undecan-1-ol (19):

A mixture of 16 (1.57 g, 4.08 mmol), 1-bromo-butane (0.67 g, 4.88 mmol) and potassium carbonate (0.67 g, 4.88 mmol) was dissolved in Dimethylformamide (DMF, 7mL). The resulting solution was heated at 120 °C and left, until the reaction finished. After that, the reaction mixture was cooled to room temperature. Then, distilled water (60 mL) was added to the mixture, and a yellow precipitate formed. The precipitate was collected and extracted with ethyl acetate (100 mL). The ethyl acetate solution was washed with water and dried over magnesium sulfate (MgSO₄). The organic phase (ethyl acetate) was filtered from the sulfate (MgSO₄) and evaporated in vacuo using the rotary evaporator to obtain 19 as a solid (0.97 g).

δ_H (400 MHz, CDCl₃): 1.06 (3H, t, CH₃), 1.26-1.87 (20H, m, CH₂), 3.64 (2H, t, OCH₂), 4.04 (4H, t, OCH₂), 6.99 (4H, d, CH), 7.94 (4H, d, CH); δ_C (100.5 MHz, CDCl₃): 10.5 (CH₃), 22.5 (CH₂), 25.7 (CH₂), 26.0 (CH₂), 29.2 (CH₂), 29.4 (CH₂) 29.4
(CH\textsubscript{2}), 29.4 (CH\textsubscript{2}), 29.5 (CH\textsubscript{2}), 29.5 (CH\textsubscript{2}), 29.6 (CH\textsubscript{2}), 32.8 (CH\textsubscript{2}), 63.1 (OCH\textsubscript{2}), 68.4 (OCH\textsubscript{2}), 69.9 (OCH\textsubscript{2}), 114.8 (CH), 124.7 (CH), 146 (CH) 161.6 (CH). IR \(\nu\) (KBr, cm\textsuperscript{-1}): 3350, 2958, 2918, 2849, 1602, 1581, 1497, 1243, 1150, 844, 554.

11-((4-((4-(Octyloxy)phenyl)diazenyl)phenoxy)undecan-1-ol (20):

A mixture of 16 (0.8 g, 2.08 mmol), 1-bromo-octane (0.48 g, 2.49 mmol) and potassium carbonate (0.34 g, 2.49 mmol) was dissolved in dimethylformamide (DMF, 6 mL). The resulting solution was heated at 120 °C and left until the reaction finished. After that, the mixture was cooled down to room temperature. Then, distilled water (50 mL) was added to the mixture, and a yellow precipitate formed. The precipitate was collected and extracted with ethyl acetate (100 mL). The ethyl acetate solution was washed with water and dried over magnesium sulfate (MgSO\textsubscript{4}). The organic phase (ethyl acetate) was filtered from the sulfate (MgSO\textsubscript{4}) and evaporated \textit{in vacuo} using the rotary evaporator to obtain 20 as a solid (0.64 g).

\(\delta\text{H} \) (400 MHz, CDCl\textsubscript{3}): 0.88 (3H, t, CH\textsubscript{3}), 1.24-1.84 (30H, m, CH\textsubscript{2}), 3.63 (2H, t, OCH\textsubscript{2}), 4.02 (4H, t, OCH\textsubscript{2}), 6.98 (4H, d, CH), 7.87 (4H, d, CH); \(\delta\text{C} \) (100.5 MHz, CDCl\textsubscript{3}): 14.1 (CH\textsubscript{3}), 22.7 (CH\textsubscript{2}), 25.7 (CH\textsubscript{2}), 26.0 (CH\textsubscript{2}), 26.0 (CH\textsubscript{2}), 29.2 (CH\textsubscript{2}), 29.2 (CH\textsubscript{2}), 29.4 (CH\textsubscript{2}), 29.4 (CH\textsubscript{2}), 29.5 (CH\textsubscript{2}), 29.5 (CH\textsubscript{2}), 29.6 (CH\textsubscript{2}), 31.8 (CH\textsubscript{2}), 32.8 (CH\textsubscript{2}), 63.1 (OCH\textsubscript{2}), 68.3 (OCH\textsubscript{2}), 68.3 (OCH\textsubscript{2}), 114.7 (CH), 124.4 (CH), 146.7 (CH) 161.2 (CH). IR \(\nu\) (KBr, cm\textsuperscript{-1}): 33549, 2954, 2919, 2849, 1602, 1681, 1498, 1473, 1248, 1151, 843, 554.
2.2.2 Second pathway

The following preparations were carried out according to Figure 15.

![Figure 15: Appel-type esterification reaction in order to synthesis azo cinnamates](image)

9-((E)-(4-(Hexyloxy)phenyl)diazenyl)phenoxy)nonyl cinnamate (21):

To a solution of triphenylphosphine (PPh₃, 970 mg, 3.70 mmol) in dry CH₂Cl₂ (15 mL) was added dropwise bromotrichloromethane (BrCCl₃, 720 mg, 3.63 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, cinnamic acid (460 mg, 3.1 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, 12 (619 mg, 1.4 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH₂Cl₂) to give 21 (660 mg, 82%) as a yellow solid.

δ_H (400 MHz, CDCl₃) 0.92 (3H, t, CH₃), 1.34-1.84 (22H, m, CH₂), 4.02 (4H, t, OCH₂), 4.21 (2H, t, OCH₂), 6.45 (1H, d, CH), 6.98 (4H, d, CH), 7.38 (3H, t, CH), 7.54 (2H, d, CH), 7.69 (1H, d, CH) 7.86 (4H, d, CH); δ_C (100.5 MHz, CDCl₃) 14.1 (CH₃), 22.6 (CH₂), 25.7 (CH₂), 26.0 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.2 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 31.6 (CH₂), 64.7 (OCH₂), 68.3 (OCH₂), 68.3 (OCH₂), 114.6 (CH), 118.2 (CH), 124.3 (CH), 128.0 (CH), 128.9 (CH), 130.2
(CH), 134.4 (CH), 144.6 (CH), 146.9 (CH), 161.1 (CH), 167.1 (C=O). \( \nu \) IR (KBr, cm\(^{-1}\))): 2921, 2852, 1709, 1637, 1603, 1579, 1500, 1473, 1331, 1311, 1245, 1179, 1146, 1027, 844. Mass found: 571 (M\(^+\)).

(E)-9-((E)-(4-(Hexyloxy)phenyl)diazenylphenoxy)nonyl3-(4-methoxyphenyl)acrylate (22):

To a solution of triphenylphosphine (PPh\(_3\), 1.15 g, 4.39 mmol) in dry \( \text{CH}_2\text{Cl}_2 \) (15 mL) was added dropwise bromotrichloromethane (BrCCl\(_3\), 855 mg, 4.31 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, 3-(4-methoxyphenyl) acrylic acid (655 mg, 3.68 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, (12) (735 mg, 1.67 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH\(_2\)Cl\(_2\)) to give 22 (815 mg, 81.5 %) as a yellow solid.

\( \delta \)\text{H} (400 MHz, CDCl\(_3\)) 0.91 (3H, t, CH\(_3\)), 1.36-1.84 (22H, m, CH\(_2\)), 3.82 (3H, t, OCH\(_3\)), 4.02 (4H, t, OCH\(_2\)), 4.19 (2H, t, OCH\(_2\)), 6.31 (1H, d, CH), 6.89 (2H, d, CH), 6.98 (4H, d, CH), 7.47 (2H, d, CH), 7.64 (1H, d, CH), 7.86 (4H, d, CH); \( \delta \)\text{C} (100.5 MHz, CDCl\(_3\)) 14.0 (CH\(_3\)), 22.6 (CH\(_2\)), 25.7 (CH\(_2\)), 26.0 (CH\(_2\)), 28.7 (CH\(_2\)), 29.1 (CH\(_2\)), 29.2 (CH\(_2\)), 29.2 (CH\(_2\)), 29.3 (CH\(_2\)), 29.4 (CH\(_2\)), 31.6 (CH\(_2\)), 55.4 (OCH\(_2\)), 64.5 (OCH\(_2\)), 68.3 (OCH\(_2\)), 68.3 (OCH\(_2\)), 114.3 (CH), 114.7 (CH), 115.7 (CH), 124.5 (CH), 127.1 (CH), 129.7 (CH), 144.2 (CH), 146.4 (CH), 161.3 (CH), 161.3 (CH), 167.4 (C=O). \( \nu \) IR (KBr, cm\(^{-1}\))): 2936, 2856, 1703, 1634, 1602, 1581, 1514, 1497, 1474, 1243, 1176, 1150, 1025, 843. Mass found: 601 (M\(^+\)).
(E)-9-((E)-(4-(Hexyloxy)phenyl)diazenyl)phenoxy)nonyl-3-(3,4-dimethoxy phenyl)acrylate (23):

To a solution of triphenylphosphine (PPh₃, 970 mg, 3.70 mmol) in dry CH₂Cl₂ (15 mL) was added dropwise bromotrichloromethane (BrCCl₃, 720 mg, 3.63 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, 3-(3,4-dimethoxyphenyl) acrylic acid (640 mg, 3.27 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, (12) (600 mg, 1.36 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH₂Cl₂) to give 23 (853 mg, 99%) as a yellow solid.

δH (400 MHz, CDCl₃) 0.89 (3H, t, CH₃), 1.29-1.84 (22H, m, CH₂), 3.91 (6H, s, OCH₃), 4.02 (4H, t, OCH₂), 4.19 (2H, t, OCH₂), 6.31 (1H, d, CH), 6.85 (1H, d, CH), 6.98 (4H, d, CH), 7.05 (1H, d, CH), 7.10 (1H, dd, CH), 7.62 (1H, d, CH), 7.87 (4H, d, CH); δC (100.5 MHz, CDCl₃) 14.1 (CH₃), 22.6 (CH₂), 26.0 (CH₂), 28.8 (CH₂), 29.1 (CH₂), 29.2 (CH₂) 29.2 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 31.8 (CH₂), 55.9 (OCH₃), 56.0 (OCH₃), 64.6 (OCH₂), 68.3 (OCH₂), 68.3 (OCH₂), 109.4 (CH), 110.9 (CH), 114.7 (CH), 115.9 (CH), 122.6 (CH), 124.4 (CH), 127.4 (CH), 144.5 (CH), 146.6 (CH), 149.1 (CH), 151.0 (CH), 161.2 (CH), 161.3 (CH), 161.3 (CH), 167.4 (C=O). ν IR (KBr, cm⁻¹): 2921, 2853, 1703, 1630, 1600, 1579, 1514, 1500, 1473, 1254, 1137, 1023, 842. Mass found: 631 (M⁺).
(E)-9-((E)-4-(Hexyloxy)phenyl)diazenyl)phenoxy)nonyl 3-(4-(heptyloxy)phenyl)acrylate (24):

To a solution of triphenylphosphine (PPh₃, 810 mg, 3.09 mmol) in dry CH₂Cl₂ (15 mL) was added dropwise bromotrichloromethane (BrCCl₃, 600 mg, 3.03 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, 3-(4-(heptyloxy)phenyl)acrylic acid (670 mg, 2.56 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, (12) (500 mg, 1.38 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH₂Cl₂) to give (24) (587 mg, 52%) as a yellow solid.

δ_H (400 MHz, CDCl₃) 0.87 (6H, t, CH₃), 1.28-1.81 (32H, m, CH₂), 3.95 (2H, t, OCH₂), 4.01 (4H, t, OCH₂), 4.17 (2H, d, CH), 6.28 (1H, d, CH), 6.86 (2H, d, CH), 6.97 (4H, d, CH), 7.44 (2H, d, CH), 7.61 (1H, d, CH), 7.88 (4H, d, CH); δ_C (100.5 MHz, CDCl₃) 14.0 (CH₃), 14.1 (CH₃), 22.6 (CH₂), 25.7 (CH₂), 25.9 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.0 (CH₂), 29.1 (CH₂) 29.2 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 31.6 (CH₂), 31.7 (CH₂), 64.5 (OCH₂), 68.1 (OCH₂), 68.3 (OCH₂), 68.3 (OCH₂), 114.6 (CH), 114.7 (CH), 114.7 (CH), 115.5 (CH), 124.4 (CH), 124.4 (CH), 124.5 (CH), 126.9 (CH), 129.7 (CH), 144.3 (CH), 160.9 (CH), 167.5 (C=O). v IR (KBr, cm⁻¹): 2921, 2854, 1708, 1632, 1603, 1578, 1510, 1474, 1249, 1171, 1145, 1023, 840. Mass found: 685 (M⁺).
(E)-9-(4-((E)-(4-(Hexyloxy)phenyl)diazenyl)phenoxy)nonyl 3-(4-bromophenyl)acrylate (25):

To a solution of triphenylphosphine (PPh3, 970 mg, 3.70 mmol) in dry CH2Cl2 (15 mL) was added dropwise bromotrichloromethane (BrCCl3, 720 mg, 3.63 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, 3-(4-bromophenyl)acrylic acid (694.77 mg, 3.06 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, (12) (608 mg, 1.38 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH2Cl2) to give (25) (890 mg, 94%) as a yellow solid.

δH (400 MHz, CDCl3) 0.89 (3H, t, CH3), 1.34-1.83 (22H, m, CH2), 4.00 (4H, t, OCH2), 4.17 (2H, t, OCH2), 6.41 (1H, d, CH), 6.96 (4H, d, CH), 7.36 (2H, d, CH), 7.49 (2H, d, CH), 7.59 (1H, d, CH), 7.85 (4H, d, CH); δC (100.5 MHz, CDCl3) 14.0 (CH3), 23.0 (CH2), 25.7 (CH2), 25.9 (CH2), 26.0 (CH2), 28.7 (CH2), 29.1 (CH2), 29.2 (CH2) 29.3 (CH2), 29.4 (CH2), 31.6 (CH2), 64.8 (OCH2), 68.3 (OCH2), 68.3 (OCH2), 68.3 (OCH2), 114.7 (CH), 118.9 (CH), 124.4 (CH), 124.5 (CH), 124.5 (CH), 129.4 (CH), 132.1 (CH), 133.3 (CH), 143.2 (CH), 146.3 (CH), 146.3 (CH), 146.4 (CH), 161.3 (CH), 161.4 (CH), 161.4 (CH), 166.8 (C=O). ν IR (KBr, cm⁻¹): 2924, 2850, 1706, 1599, 1583, 1501, 1474, 1330, 1315, 1252, 1147, 1022, 841, 548. Mass found: 649 (M⁺).
(E)-9-((E)-(4-(Hexyloxy)phenyl)diazenyl)phenoxy)nonyl 3-(anthracen-9-yl)acrylate (26):

To a solution of triphenylphosphine (PPh₃, 970 mg, 3.70 mmol) in dry CH₂Cl₂ (15 mL) was added dropwise bromotrichloromethane (BrCCl₃, 720 mg, 3.63 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, 3-(anthracen-9-yl)acrylic acid (770 mg, 3.10 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, 12 (608 mg, 1.38 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH₂Cl₂) to give (26) (870 mg, 94%) as a yellow solid.

δₜH (400 MHz, CDCl₃) 0.83 (3H, t, CH₃), 1.24-1.76 (22H, m, CH₂), 3.93 (4H, t, OCH₂), 4.24 (2H, t, OCH₂), 6.35 (1H, d, CH), 6.98 (4H, d, CH), 7.91 (4H, dd, CH), 8.00 (2H, d, CH), 8.22 (2H, d, CH) 8.44 (1H, s, CH), 8.62 (1H, d, CH); δC (100.5 MHz, CDCl₃) 14.1 (CH₃), 22.6 (CH₂), 25.7 (CH₂), 26.0 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.2 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.3 (CH₂), 29.5 (CH₂), 31.6 (CH₂), 65.0 (OCH₂), 68.2 (OCH₂), 68.3 (OCH₂), 114.6 (CH), 124.3 (CH), 125.2 (CH), 125.4 (CH), 126.3 (CH), 127.2 (CH), 128.2 (CH), 128.8 (CH), 129.3 (CH), 129.3 (CH), 131.2 (CH), 141.9 (CH), 146.8 (CH), 161.1 (CH), 161.6 (CH), 166.6 (C=O). ν IR (KBr, cm⁻¹): 2935, 2851, 1707, 1601, 1580, 1500, 1472, 1311, 1266, 1246, 1178, 1145, 1017, 843, 730. Mass found: 671 (M⁺).
9-((4-((E)-(4-(Hexyloxy)phenyl)diazenyl)phenoxy)nonyl cinnamate (27):

To a solution of triphenylphosphine (PPh$_3$, 970 mg, 3.70 mmol) in dry CH$_2$Cl$_2$ (15 mL) was added dropwise bromotrichloromethane (BrCCl$_3$, 720 mg, 3.63 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, cinnamic acid (450 mg, 3.04 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, 13 (588 mg, 1.30 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH$_2$Cl$_2$) to give 27 (630 mg, 83%) as a yellow solid.

δ$_H$ (400 MHz, CDCl$_3$) 0.89 (3H, t, CH$_3$), 1.31-1.83 (24H, m, CH$_2$), 4.02 (4H, t, OCH$_2$), 4.10 (2H, t, OCH$_2$), 6.44 (1H, d, CH), 6.98 (4H, d, CH), 7.37 (3H, t, CH), 7.52 (2H, d, CH), 7.68 (1H, d, CH) 7.93 (4H, d, CH); δ$_C$ (100.5 MHz, CDCl$_3$) 14.1 (CH$_3$), 22.6 (CH$_2$), 25.9 (CH$_2$), 26.0 (CH$_2$), 28.7 (CH$_2$), 29.1 (CH$_2$), 29.2 (CH$_2$), 29.2 (CH$_2$) 29.2 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 31.8 (CH$_2$), 64.7 (OCH$_2$), 68.3 (OCH$_2$), 68.4 (OCH$_2$), 114.8 (CH), 118.2 (CH), 124.7 (CH), 124.7 (CH), 128.0 (CH), 128.9 (CH), 130.2 (CH), 144.4 (CH), 144.6 (CH), 167.1 (C=O). ν IR (KBr, cm$^{-1}$): 2937, 2852, 1709, 1642, 1599, 1504, 1473, 1332, 1314, 1258, 1204, 1192, 1147, 846. Mass found: 585 (M$^+$).

9-((4-((4-(Hexyloxy)phenyl)diazenyl)phenoxy)nonyl 3-(4-bromophenyl)acrylate (28):

To a solution of triphenylphosphine (PPh$_3$, 970 mg, 3.70 mmol) in dry CH$_2$Cl$_2$ (15 mL) was added dropwise bromotrichloromethane (BrCCl$_3$, 720 mg, 3.63 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-
brown. Thereafter, 3-(4-bromophenyl)acrylic acid (705 mg, 3.10 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, 13 (608 mg, 1.38 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH₂Cl₂) to give (28) (653 mg, 77%) as a yellow solid.

δ_H (400 MHz, CDCl₃) 0.89 (3H, t, CH₃), 1.29-1.85 (24H, m, CH₂), 3.83 (3H, t, OCH₃), 4.02 (4H, t, OCH₂), 4.18 (2H, t, OCH₂), 6.31 (1H, d, CH), 6.89 (2H, d, CH), 6.98 (4H, d, CH), 7.47 (2H, d, CH), 7.63 (1H, d, CH), 7.88 (4H, d, CH); δ_C (100.5 MHz, CDCl₃) 14.1 (CH₃), 22.6 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.1 (CH₂), 29.2 (CH₂), 29.2 (CH₂), 29.3 (CH₂) 29.4 (CH₂), 31.8 (CH₂), 55.4 (OCH₂), 64.5 (OCH₂), 68.3 (OCH₂), 68.3 (OCH₂), 114.3 (CH), 114.7 (CH), 115.7 (CH), 124.5 (CH), 127.2 (CH), 129.7 (CH), 144.2 (CH), 146.5 (CH), 161.3 (CH), 161.3 (CH), 167.5 (C=O), ν IR (KBr, cm⁻¹): 2935, 2856, 1703, 1633, 1602, 1580, 1514, 1497, 1474, 1246, 1176, 1149, 1021, 842. Mass found: 615 (M⁺).

(E)-9-((E)-(4-((Heptyloxy)phenyl)diazenyl)phenoxy)nonyl 3-(3,4-dimethoxyphenyl)acrylate (29):

To a solution of triphenylphosphine (PPh₃, 970 mg, 3.70 mmol) in dry CH₂Cl₂ (15 mL) was added dropwise bromotrichloromethane (BrCCl₃, 720 mg, 3.63 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, 3-(3,4-dimethoxyphenyl) acrylic acid (640 mg, 3.08 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, 13 (606 mg, 1.34 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH₂Cl₂) to give 29 (692 mg, 80%) as a yellow solid.
δ_H (400 MHz, CDCl_3) 0.89 (3H, t, CH_3), 1.29-1.84 (22H, m, CH_2), 3.91 (6H, s, OCH_3), 4.02 (4H, t, OCH_2), 4.19 (2H, t, OCH_2), 6.31 (1H, d, CH), 6.85 (1H, d, CH), 6.98 (4H, d, CH), 7.05 (1H, d, CH), 7.20 (1H, dd, CH), 7.62 (1H, d, CH), 7.87 (4H, d, CH); δ_C (100.5 MHz, CDCl_3) 14.1 (CH_3), 22.6 (CH_2), 26.0 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.2 (CH_2) 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 55.9 (OCH_3), 56.0 (OCH_3), 64.6 (OCH_2), 68.2 (OCH_2), 68.3 (OCH_2), 109.4 (CH), 110.9 (CH), 114.7 (CH), 115.9 (CH), 122.6 (CH), 124.4 (CH), 124.4 (CH), 144.5 (CH), 146.6 (CH), 149.1 (CH), 151.0 (CH), 161.1 (CH), 161.2 (CH), 161.3 (CH), 167.4 (C=O). ν IR (KBr, cm⁻¹): 2921, 2853, 1703, 1630, 1600, 1579, 1514, 1500, 1473, 1254, 1137, 1023, 842. Mass found: 645 (M⁺).

(E)-11-(4-((E)-(4-(Hexyloxy)phenyl)diazenyl)phenoxy)undecyl 3-(4-methoxyphenyl)acrylate (30):

To a solution of triphenylphosphine (PPh_3, 770 mg, 2.94 mmol) in dry CH_2Cl_2 (15 mL) was added dropwise bromotrichloromethane (BrCCl_3, 570 mg, 2.87 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, 3-(4-methoxyphenyl)acrylic acid (440 mg, 2.47 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, 17 (520 mg, 1.11 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH_2Cl_2) to give (30) (550 mg, 79%) as a yellow solid.

δ_H (400 MHz, CDCl_3): 0.90 (3H, t, CH_3), 1.31-1.82 (26H, m, CH_2), 3.82 (3H, s, OCH_3), 4.02 (4H, t, OCH_2), 4.19 (2H, t, OCH_2), 6.31 (1H, d, CH), 6.89 (2H, d, CH), 6.98 (4H, d, CH), 7.47 (2H, d, CH), 7.63 (1H, d, CH), 7.86 (4H, d, CH); δ_C (100.5 MHz, CDCl_3): 11.0 (CH_3), 14.1 (CH_2), 14.1 (CH_2), 22.6 (CH_2), 23.0 (CH_2), 23.7
(CH$_2$), 25.7 (CH$_2$), 26.0 (CH$_2$), 26.0 (CH$_2$), 28.8 (CH$_2$), 28.9 (CH$_2$), 29.2 (CH$_2$), 29.2 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$) 29.5 (CH$_2$), 29.5 (CH$_2$), 30.3 (CH$_2$), 31.6 (CH$_2$), 38.7 (CH$_2$), 55.4 (OCH$_2$), 64.6 (OCH$_2$), 68.1 (OCH$_2$), 68.3 (OCH$_2$), 114.3 (CH), 114.6 (CH), 115.7 (CH), 124.3 (CH), 127.2 (CH), 128.8 (CH), 129.7 (CH), 130.9 (CH), 132.4 (CH), 144.2 (CH), 146.9 (CH), 161.1 (CH), 161.3 (CH), 167.4 (CH), 167.8 (C=O). $\nu$ IR (KBr, cm$^{-1}$): 2935, 2856, 1703, 1633, 1602, 1580, 1514, 1497, 1474, 1246, 1176, 1149, 1021, 842. Mass found: 629 (M$^+$).

(E)-11-((E)-(4-propoxyphenyl)diazonetyl)phenoxy)undecyl 3-(4-methoxyphenyl)acrylate (31):

To a solution of triphenylphosphine (PPh$_3$, 900 mg, 3.43 mmol) in dry CH$_2$Cl$_2$ (15 mL) was added dropwise bromotrichloromethane (BrCCl$_3$, 670 mg, 3.38 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, 3-(4-methoxyphenyl)acrylic acid (500 mg, 2.81 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, 18 (454 mg, 1.07 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH$_2$Cl$_2$) to give 31 (435 mg, 69%) as a yellow solid.

$\delta$$_H$ (400 MHz, CDCl$_3$) 0.99 (3H, t, CH$_3$), 1.36-1.84 (22H, m, CH$_2$), 3.82 (3H, s, OCH$_3$), 4.02 (4H, t, OCH$_2$), 4.18 (2H, t, OCH$_2$), 6.31 (1H, d, CH), 6.89 (2H, d, CH), 6.98 (4H, d, CH), 7.47 (2H, d, CH), 7.64 (1H, d, CH), 7.86 (4H, d, CH); $\delta$$_C$ (100.5 MHz, CDCl$_3$) 13.8 (CH$_3$), 19.2 (CH$_2$), 25.9 (CH$_2$), 25.9 (CH$_2$), 28.7 (CH$_2$), 29.1 (CH$_2$), 29.2 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 31.2 (CH$_2$), 55.4 (OCH$_2$), 64.5 (OCH$_2$), 68.0 (OCH$_2$), 68.3 (OCH$_2$), 114.3 (CH), 114.6 (CH), 115.7 (CH), 124.3 (CH), 127.2 (CH), 129.7 (CH), 144.2 (CH), 146.8 (CH), 161.1 (CH), 161.2 (CH), 161.3 (CH), 167.5 (CH).
(C=O). \( \nu \) IR (KBr, cm\(^{-1}\)): 2935.68, 2856.85, 1712.37, 1603.08, 1580.67, 1513.29, 1497.38, 1289.84, 1246.28, 1177.48, 1149.98, 1025.57, 983.77, 843.32. Mass found: 587 (M\(^+\)).

(E)-11-(4-((E)-(4-Butoxyphenyl)diazenyl)phenoxy)undecyl 3-(3,4-dimethoxyphenyl)acrylate (32):

To a solution of triphenylphosphine (PPh\(_3\), 900 mg, 3.43 mmol) in dry CH\(_2\)Cl\(_2\) (15 mL) was added dropwise bromotrichloromethane (BrCCl\(_3\), 670 mg, 3.37 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, 3-(3,4-dimethoxyphenyl)acrylic acid (530 mg, 2.55 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, 19 (457 mg, 1.04 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH\(_2\)Cl\(_2\)) to give (32) (510 mg, 78\%) as a yellow solid.

\( \delta \)\( _H \) (400 MHz, CDCl\(_3\)): 0.98 (3H, t, CH\(_3\)), 1.31-1.83 (22H, m, CH\(_2\)), 3.90 (6H, s, OCH\(_3\)), 4.02 (4H, t, OCH\(_2\)), 4.18 (2H, t, OCH\(_2\)), 6.31 (1H, d, CH), 6.85 (1H, d, CH), 6.98 (4H, d, CH), 7.05 (1H, dd, CH), 7.09 (1H, dd, CH), 7.62 (1H, d, CH), 7.86 (4H, d, CH); \( \delta \)\( _C \) (100.5 MHz, CDCl\(_3\)): 13.8 (CH\(_3\)), 19.2 (CH\(_2\)), 25.9 (CH\(_2\)), 26.0 (CH\(_2\)), 28.7 (CH\(_2\)), 29.1 (CH\(_2\)), 29.2 (CH\(_2\)) 29.3 (CH\(_2\)), 29.4 (CH\(_2\)), 29.5 (CH\(_2\)), 29.5 (CH\(_2\)), 31.2 (CH\(_2\)), 55.8 (OCH\(_3\)), 55.9 (OCH\(_3\)), 64.6 (OCH\(_2\)), 68.0 (OCH\(_2\)), 68.3 (OCH\(_2\)), 109.3 (CH), 109.4 (CH), 110.9 (CH), 114.6 (CH), 114.7 (CH), 115.9 (CH), 122.6 (CH), 124.4 (CH), 124.4 (CH), 124.5 (CH), 127.3 (CH), 144.4 (CH), 149.1 (CH), 150.9 (CH), 161.3 (CH), 167.3 (C=O); \( \nu \) IR (KBr, cm\(^{-1}\)): 2924, 2853, 1710, 1634, 1600, 1579, 1510, 1499, 1472, 1262, 1243, 1171, 1140, 1027, 847. Mass found: 631 (M\(^+\)).
(E)-11-(4-((E)-(4-butoxyphenyl)diazenyl)phenoxy)undecyl 3-(4-(tetradecyloxy)phenyl)acrylate (33):

To a solution of triphenylphosphine (PPh₃, 740 mg, 2.82 mmol) in dry CH₂Cl₂ (15 mL) was added dropwise bromotrichloromethane (BrCCl₃, 550 mg, 2.77 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, 3-(4-tetradecyloxyphenyl)acrylic acid (835 mg, 2.32 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, (19) (400 mg, 0.91 mmol) was added, and the mixture was stirred at reflux for an additional 14 h. The cooled solution was submitted directly to column chromatography on silica gel (CH₂Cl₂-hexane 4:1) to give 33 (485 mg, 68%) as a yellow solid.

δH (400 MHz, CDCl₃): 0.88 (3H, t, CH₃), 0.99 (3H, t, CH₃), 1.25-1.84 (46H, m, CH₂), 3.97 (2H, t, OCH₂), 4.03 (4H, t, OCH₂), 4.18 (2H, t, OCH₂), 6.30 (1H, d, CH), 6.88 (2H, d, CH), 6.98 (4H, d, CH), 7.46 (2H, d, CH), 7.63 (1H, d, CH), 7.87 (4H, d, CH);

δC (100.5 MHz, CDCl₃): 13.8 (CH₃), 14.1 (CH₃), 19.2 (CH₃), 22.7 (CH₂), 25.9 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.1 (CH₂), 29.1 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 31.2 (CH₂), 31.9 (CH₂), 64.5 (OCH₂), 67.9 (OCH₂), 68.1 (OCH₂), 68.3 (OCH₂), 114.6 (CH), 114.6 (CH), 114.7 (CH), 115.4 (CH), 124.3 (CH), 126.8 (CH), 129.6 (CH), 144.3 (CH), 146.6 (CH), 160.9 (CH), 161.2 (CH), 167.5 (C=O); ν IR (KBr, cm⁻¹): 2919, 2850, 1709, 1633, 1602, 1580, 1511, 1473, 1280, 1244, 1177, 1039, 984, 843. Mass found: 783 (M⁺).
11-(4-((E)-(4-(Octyloxy)phenyl)diazenyl)phenoxy)undecyl cinnamate (34):

To a solution of triphenylphosphine (PPh₃, 970 mg, 3.70 mmol) in dry CH₂Cl₂ (15 mL) was added dropwise bromotrichloromethane (BrCCl₃, 720 mg, 3.63 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, cinnamic acid (450 mg, 3.04 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, 20 (610 mg, 1.23 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH₂Cl₂) to give 34 (655 mg, 85%) as a yellow solid.

δ_H (400 MHz, CDCl₃): 0.89 (3H, t, CH₃), 1.29-1.84 (30H, m, CH₂), 4.02 (4H, t, OCH₂), 4.22 (2H, t, OCH₂), 6.44 (1H, d, CH), 6.98 (4H, d, CH), 7.38 (3H, t, CH), 7.52 (2H, d, CH), 7.68 (1H, d, CH) 7.86 (4H, d, CH); δ_C (100.5 MHz, CDCl₃): 14.1 (CH₃), 22.6 (CH₂), 25.9 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.1 (CH₂), 29.2 (CH₂), 29.2 (CH₂) 29.2 (CH₂), 29.3 (CH₂), 29.3 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 31.8 (CH₂), 64.7 (OCH₂), 68.2 (OCH₂), 68.3 (OCH₂), 114.6 (CH), 118.2 (CH), 124.3 (CH), 128.0 (CH), 128.8 (CH), 130.2 (CH), 134.4 (CH), 144.5 (CH), 161.2 (CH), 167.1 (C=O); ν IR (KBr, cm⁻¹): 2918, 2849, 1712, 1602, 1579, 1498, 1473, 1309, 1244, 1146, 1107, 1040, 846. Mass found: 627 (M⁺).

(E)-11-(4-((E)-(4-(Octyloxy)phenyl)diazenyl)phenoxy)undecyl 3-(4-methoxyphenyl)acrylate (35):

To a solution of triphenylphosphine (PPh₃, 970 mg, 3.70 mmol) in dry CH₂Cl₂ (15 mL) was added dropwise bromotrichloromethane (BrCCl₃, 720 mg, 3.63 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-
brown. Thereafter, 3-(4-methoxyphenyl)acrylic acid (530 mg, 3.00 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, 20 (600 mg, 1.21 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The cooled solution was submitted directly to column chromatography on silica gel (CH₂Cl₂) to give 35 (625 mg, 78.5%) as a yellow solid.

δ_H (400 MHz, CDCl₃): 0.88 (3H, t, CH₃), 1.24-1.84 (24H, m, CH₂), 3.83 (3H, s, OCH₃), 4.02 (4H, t, OCH₂), 4.18 (2H, t, OCH₂), 6.31 (1H, d, CH), 6.89 (2H, d, CH), 6.98 (4H, d, CH), 7.47 (2H, d, CH), 7.63 (1H, d, CH), 7.86 (4H, d, CH); δ_C (100.5 MHz, CDCl₃): 14.1 (CH₃), 22.6 (CH₂), 25.9 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.2 (CH₂), 29.2 (CH₂), 29.2 (CH₂) 29.3 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 31.8 (CH₂), 55.3 (OCH₂), 68.2 (OCH₂), 68.2 (OCH₂), 68.3 (OCH₂), 114.2 (CH), 114.6 (CH), 115.7 (CH), 124.3 (CH), 127.1 (CH), 129.6 (CH), 144.2 (CH), 146.7 (CH), 161.1 (CH), 161.2 (CH), 167.4 (C=O); v _IR (KBr, cm⁻¹): 2029, 2851, 1702, 1632, 1580, 1514, 1496, 1473, 1289, 1243, 117, 1027, 842. Mass found: 657 (M⁺).

(E)-11-(4-((E)-(4-(Octyloxy)phenyl)diazenyl)phenoxy)undecyl 3-(3,4-dimethoxyphenyl)acrylate (36):

To a solution of triphenylphosphine (PPh₃, 970 mg, 3.70 mmol) in dry CH₂Cl₂ (15 mL) was added dropwise bromotrichloromethane (BrCCl₃, 720 mg, 3.63 mmol) and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, 3-(3,4-dimethoxyphenyl)acrylic acid (630 mg, 3.03 mmol) was added, and the mixture was stirred at reflux temperature for 30 min. Then, 20 (610 mg, 1.23 mmol) was added, and the mixture was stirred at reflux for an additional 14h. The
cooled solution was submitted directly to column chromatography on silica gel (CH₂Cl₂) to give \textbf{36} (660 mg, 78\%) as a yellow solid.

δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}): 0.89 (3H, t, CH\textsubscript{3}), 1.29-1.84 (22H, m, CH\textsubscript{2}), 3.91 (6H, s, OCH\textsubscript{3}), 4.02 (4H, t, OCH\textsubscript{2}), 4.19 (2H, t, OCH\textsubscript{2}), 6.31 (1H, d, CH), 6.85 (1H, d, CH), 6.98 (4H, d, CH), 7.05 (1H, dd, CH), 7.09 (1H, dd, CH), 7.62 (1H, d, CH), 7.86 (4H, d, CH); δ\textsubscript{C} (100.5 MHz, CDCl\textsubscript{3}): 10.5 (CH\textsubscript{3}), 22.5 (CH\textsubscript{2}), 25.9 (CH\textsubscript{2}), 26.0 (CH\textsubscript{2}), 28.7 (CH\textsubscript{2}), 29.2 (CH\textsubscript{2}) 29.2 (CH\textsubscript{2}), 29.3 (CH\textsubscript{2}), 29.5 (CH\textsubscript{2}), 29.5 (CH\textsubscript{2}), 55.8 (OCH\textsubscript{3}), 55.9 (OCH\textsubscript{3}), 64.6 (OCH\textsubscript{2}), 68.2 (OCH\textsubscript{2}), 69.7 (OCH\textsubscript{2}), 109.3 (CH), 110.9 (CH), 114.6 (CH), 115.9 (CH), 122.6 (CH), 124.3 (CH), 127.3 (CH), 144.4 (CH), 146.7 (CH), 149.1 (CH), 150.9 (CH), 161.1 (CH), 161.1 (CH), 167.3 (C=O); ν IR (KBr, cm\textsuperscript{-1}): 2918, 2848, 1698, 1601, 1580, 1515, 1499, 1472, 1268, 1247, 1140, 1023, 847. Mass found: 687 (M\textsuperscript{+}).
2.2.3 Third path-way

The synthetic route shown in scheme 2 will be used in order to synthesis the steroidal azo ethers.

Scheme 2: synthesis of steroidal azo ethers
To a solution of triphenylphosphine (PPh₃, 2.7 g, 10.4 mmol) in dry CH₂Cl₂ (20 mL) was added dropwise tetrachloromethane (CCl₄, 1.6 g, 11.1 mmol), and the resulting solution was stirred at rt for 25 min, during which it turned yellow-brown. Thereafter, 12 (3.3 g, 7.4 mmol) was added, and the mixture was stirred at room temperature for 14 h. The solution was submitted directly to column chromatography on silica gel (CH₂Cl₂) to give (1.3 g, 82%) as a yellow solid.

δH (400 MHz, CDCl₃): 0.92 (3H, t, CH₃), 1.35-1.84 (22H, m, CH₂), 3.53 (2H, t, OCH₂), 4.03 (4H, t, OCH₂), 6.98 (4H, d, CH), 7.86 (4H, d, CH); δC (100.5 MHz, CDCl₃): 14.0 (CH₃), 22.5 (CH₂), 25.6 (CH₂), 25.9 (CH₂), 26.8 (CH₂), 28.8 (CH₂), 29.1 (CH₂), 29.2 (CH₂) 29.3 (CH₂), 31.5 (CH₂), 32.6 (CH₂), 45.1 (CH₂), 68.2 (OCH₂), 68.3 (OCH₂), 114.6 (CH), 124.2 (CH), 146.9 (CH), 146.9 (CH), 161.1 (CH), 161.1 (CH); IR ν (KBr, cm⁻¹): 2935, 2852, 1602, 1579, 1499, 1472, 1316, 1244, 1143, 1107, 1017, 842, 723, 556.

(E)-1-(4-((9-Chlorononyl)oxy)phenyl)-2-(4-(hexyloxy)phenyl)diazene (37):

A mixture of 37 (2.6 g, 5.6 mmol) and sodium iodide (NaI, 1.7 g, 11.3 mmol) was dissolved in dry acetone (20 mL). The mixture was stirred at reflux temperature for 48 h. Thereafter, an excess of water was added to the resulting solution dropwise and then a yellow precipitate was formed. The precipitate was filtered off and dried to give 38 as a solid (1.9 g, 67%).

δH (400 MHz, CDCl₃): 0.92 (3H, t, CH₃), 1.34-1.86 (22H, m, CH₂), 3.19 (2H, t, OCH₂), 4.02 (4H, t, OCH₂), 6.98 (4H, d, CH), 7.86 (4H, d, CH); δC (100.5 MHz, CDCl₃): 14.0 (CH₃), 22.6 (CH₂), 25.7 (CH₂), 25.9 (CH₂), 26.8 (CH₂), 28.4 (CH₂), 28.8
(CH₂), 29.1 (CH₂), 29.2 (CH₂), 29.3 (CH₂) 29.3 (CH₂), 30.4 (CH₂), 31.5 (CH₂), 32.6 (CH₂), 45.1 (CH₂), 68.2 (OCH₂), 68.3 (OCH₂), 114.6 (CH), 124.2 (CH), 146.8 (CH), 146.9 (CH), 161.1 (CH), 161.1 (CH);

IR ν (KBr, cm⁻¹): 2930, 2851, 1600, 1579, 1450, 1322, 1243, 1145, 1016, 844.

(E)-1-(4-((9-((10,13-Dimethyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)nonyl)-oxy)phenyl)-2-(4-(hexyloxy)phenyl)diazene (39):

Sodium hydride (NaH, 220 mg, 9.1 mmol) was added to dry THF (9 mL) and the resulting suspension was stirred for 10 min. Then, cholesterol (530 mg, 1.3 mmol) was added slowly to the solution. After 10 min, 38 (500 mg, 0.91 mmol) was added to the solution, and the reaction mixture was stirred for 48 h at 55 °C. Thereafter, water (20 mL) was added dropwise and the mixture was extracted with chloroform (3 X 25 mL). The organic phase was dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was submitted to column chromatography on silica gel (CH₂Cl₂ 1:4 hexane) to give 39 (97 mg, 13%) as a yellow solid.

δH (400 MHz, CDCl₃): 0.66 (3H, s, CH₃), 0.82-2.37 (63H, m), 3.12 (1H, m, CH), 3.44 (2H, t, OCH₂), 4.02 (4H, t, OCH₂), 5.34 (1H, m, CH), 6.98 (4H, d, CH), 7.85 (4H, d, CH); δC (100.5 MHz, CDCl₃): 11.8 (CH₃), 14.0 (CH₃), 18.7 (CH₃), 19.3 (CH₃), 21.0 (CH₂), 22.5 (CH₂), 22.6 (CH₃), 22.8 (CH₃), 23.8 (CH₂), 24.2 (CH₂), 25.7 (CH₂), 25.9 (CH₂), 26.1 (CH₂), 28.0 (CH), 28.2 (CH₂), 28.4 (CH₂), 29.1 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.7 (CH₂), 30.1 (CH₂), 31.5 (CH₂), 31.8 (CH), 31.9 (CH₂), 35.7 (CH), 36.1 (CH₂), 36.8 (C), 37.2 (CH₂), 39.2 (CH₂), 39.5 (CH₂), 39.7 (CH₂), 42.2 (C), 50.1 (CH), 56.1 (CH), 56.7 (CH₂), 68.1 (CH₂), 68.2 (CH₂), 68.2 (CH₂), 78.9 (CH), 114.6 (CH), 121.3 (CH), 124.2 (CH), 141.1 (C), 146.8 (C), 161.1
(C); IR \( \nu \) (KBr, cm\(^{-1}\)): 2931, 2852, 1600, 1579, 1499, 1473, 1250, 1144, 1101, 841. Mass Found: 810 (M\(^+\)).

(E)-1-(4-((11-Chloroundecyl)oxy)phenyl)-2-(4-(hexyloxy)phenyl)diazene (40):

To a solution of triphenylphosphine (PPh\(_3\), 1.34 g, 5.1 mmol) in dry CH\(_2\)Cl\(_2\) (10 mL) was added dropwise tetrachloromethane (CCl\(_4\), 0.8 g, 5.4 mmol) and the resulting solution was stirred at room temperature for 25 min, during which it turned yellow-brown. Thereafter, 17 (1.7 g, 3.6 mmol) was added, and the mixture was stirred at room temperature for 14 h. The solution was submitted directly to column chromatography on silica gel (CH\(_2\)Cl\(_2\)) to give 40 (1.2 g, 72%) as a yellow solid.

\( \delta_H \) (400 MHz, CDCl\(_3\)): 0.91 (3H, t, CH\(_3\)), 1.30-1.84 (26H, m, CH\(_2\)), 3.53 (2H, t, OCH\(_2\)), 4.02 (4H, t, OCH\(_2\)), 6.98 (4H, d, CH), 7.86 (4H, d, CH); \( \delta_C \) (100.5 MHz, CDCl\(_3\)): 14.06 (CH\(_3\)), 22.61 (CH\(_2\)), 25.70 (CH\(_2\)), 25.98 (CH\(_2\)), 26.01 (CH\(_2\)), 26.85 (CH\(_2\)), 26.88 (CH\(_2\)), 28.88 (CH\(_2\)), 29.17 (CH\(_2\)), 29.27 (CH\(_2\)) 29.37 (CH\(_2\)), 29.44 (CH\(_2\)), 32.61 (CH\(_2\)), 45.20 (CH\(_2\)), 68.23 (OCH\(_2\)), 68.29 (OCH\(_2\)), 114.61 (CH), 124.27 (CH), 146.86 (CH), 146.88 (CH), 161.09 (CH), 161.13 (CH); IR \( \nu \) (KBr, cm\(^{-1}\)): 2935, 2854, 1602, 1581, 1498, 1474, 1316, 1247, 1150, 1108, 1027, 843.

(E)-1-(4-(Hexyloxy)phenyl)-2-(4-((11-iodoundecyl)oxy)phenyl)diazene (41):

A mixture of 40 (0.4 g, 0.86 mmol) and sodium iodide (0.98 g, 6.6 mmol) was dissolved in 8 ml dry acetone. The mixture was stirred at reflux temperature for 48 h. Thereafter, an excess of water was added to the resulting solution dropwise, and then a yellow precipitate was formed. The precipitate was filtered off and dried to give 41 as a yellow solid (0.3 g, 69%).
δ_H (400 MHz, CDCl_3): 0.91 (3H, t, CH_3), 1.29-1.84 (26H, m, CH_2), 3.19 (2H, t, OCH_2), 4.03 (4H, t, OCH_2), 6.98 (4H, d, CH), 7.85 (4H, d, CH); δ_C (100.5 MHz, CDCl_3): 14.0 (CH_3), 22.6 (CH_2), 25.7 (CH_2), 25.9 (CH_2), 26.0 (CH_2), 26.8 (CH_2), 28.4 (CH_2), 29.1 (CH_2), 29.2 (CH_2) 29.3 (CH_2), 30.4 (CH_2), 31.5 (CH_2), 33.5 (CH_2), 68.2 (OCH_2), 68.3 (OCH_2), 114.6 (CH), 124.2 (CH), 146.8 (CH), 146.8 (CH), 161.0 (CH), 161.1 (CH); IR υ (KBr, cm^-1): 2935, 2851, 1602, 1580, 1500, 1471, 1246, 1147, 1016, 844.

(E)-1-(4-((11-((10,13-Dimethyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)undecyl)oxy)phenyl)-2-(4-(hexyloxy)phenyl)diazene (42):

Sodium hydride (NaH, 173 mg, 7.2 mmol) was added to dry THF (5 mL), and the resulting suspension was stirred for 10 min at rt. Then, cholesterol (464 mg, 1.2 mmol) was added slowly to the solution. After 10 min, 41 (280 mg, 0.483 mmol) was added to the resulting solution, and the reaction mixture was stirred for 48 h at 55 °C. Thereafter, water (20 mL) was added dropwise and the mixture was extracted with chloroform (3 X 25 mL). The organic phase was dried over anhydrous MgSO_4 and concentrated in vacuo. The residue was submitted directly to column chromatography on silica gel (CH_2Cl_2 1:4 C_6H_{14}) to give 42 (60 mg, 16%) as a yellow solid.

δ_H (400 MHz, CDCl_3) 0.66 (3H, s, CH_3), 0.85-2.37 (67H, m), 3.11 (1H, m, CH), 3.44 (2H, t, OCH_2), 4.02 (4H, t, OCH_2), 5.34 (1H, m, CH), 6.98 (4H, d, CH), 7.86 (4H, d, CH); δ_C (100 MHz, CDCl_3): 11.8 (CH_3), 14.0 (CH_3), 18.7 (CH_3), 19.3 (CH_3), 21.0 (CH_2), 22.5 (CH_2), 22.6 (CH_3), 22.8 (CH_3), 23.8 (CH_2), 24.2 (CH_2), 25.7 (CH_2), 25.9 (CH_2), 26.0 (CH_2), 26.1 (CH_2), 28.0 (CH), 28.2 (CH_2), 28.4 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 30.1 (CH_2), 31.5 (CH_2), 31.8
(CH), 31.9 (CH₂), 35.7 (CH₂), 36.1 (CH₂), 36.8 (C), 37.2 (CH₂), 39.2 (CH₂), 39.5 (CH₂), 39.7 (CH₂), 42.2 (C), 50.1 (CH), 56.1 (CH), 56.7 (CH₂), 68.1 (CH₂), 68.2 (CH₂), 68.2 (CH₂), 78.9 (CH), 114.6 (CH), 121.3 (CH), 124.2 (CH), 141.1 (C), 146.8 (C), 161.1 (C); IR (KBr, cm⁻¹): 2932, 2851, 1601, 1579, 1499, 1473, 1249, 1144, 1100, 1029, 840. Mass Found: 838 (M⁺).
Chapter 3: Results and Discussion

3.1 Synthesis of the target compounds

The reactions start from commercially available 4-nitrophenol (8), which is subjected to a Williamson ether synthesis with various commercially available ω-bromoalkan-1-ols. With the relatively acidic phenol system, K$_2$CO$_3$ can be used as a base. Some of the products could be gained by simple extraction, some of the products needed to be purified by column chromatography on silica gel. Next, the nitro group in (9 & 14) was to be reduced. There are various ways on how to reduce nitrobenzenes to anilines such as with low valent metals in acidic medium such as with zinc or tin(II). (Faul & Thiel, 2005) Further, a reduction with samarium is possible. (Basu, Becker, & Banik, 2000) Efficient, however, is the hydrogenation of nitrobenzenes over metal catalysts as little solid wastes are created as side products. Typical metal catalysts for this reaction are Raney Nickel, (Allen & VanAllan, 2003) finely divided nickel on solid, (Mazaheri & Kalbasi, 2015) also in form of Urushibara nickel, as well as platinum oxide PtO$_2$. Furthermore, palladium on carbon is a popular hydrogenation catalyst. The hydrogenation of compounds (9 & 14) over 10w% Pd/C in THF using a hydrogen balloon was successful and the anilines (10 & 15) were produced almost quantitatively, where there was no need for extensive purification. Because of safety concerns, later NaBH$_4$–acetic acid was used as an internal hydrogen source. These reactions, however, were very slow to complete. No water was added to the medium so that every mole NaBH$_4$ only produced ½ mole H$_2$, the other product being borane (BH$_3$), which is in equilibrium with diborane (B$_2$H$_6$). It is known that decaborane (B$_{10}$H$_{14}$) in acetic acid also hydrogenates nitrobenzenes to anilines, so perhaps in the present case the scale of the reaction was a hindrance with the reaction conditions used.
It is known that the addition of $\text{H}_2\text{O}$ to $\text{B}_2\text{H}_6$ produces hydrogen, also, but the addition of $\text{H}_2\text{O}$ was not tried. Instead, the direct hydrogenation of the nitrobenzenes to anilines was continued. Next, the obtained anilines were subjected to a diazotization ($\text{NaNO}_2, \text{HCl}$) in the presence of phenol to give diazobenzenes (11 & 16). This reaction proved to be tricky and the reaction yields were variable. The diazobenzenes (11 & 16) were alkylated at the phenol OH using $\text{K}_2\text{CO}_3$ as base. The base is not strong enough to also deprotonate the alcohol function in (11 & 16), so that the alkylation proceeds at the phenolic OH, only, although the reaction temperature needed is quite high (120 °C).

For the preparation of azo-cinnamates (21-36), the final step is an esterification reaction. Normally, this would proceed via an acyl halide, i.e., via a cinnamoyl halide. We had only little thionyl chloride left, which we used to prepare cinnamoyl chloride (Figures 16&17). (Becker, Berger, & Domschke, 1996) No other chlorinating or brominating agent was available ($\text{PBr}_3, \text{PCl}_3, \text{PCl}_5, \text{POCl}_3$ or $\text{SO}_2\text{Cl}_2$). Also, it was evident when preparing cinnamoyl chloride that the preparation and especially the distillation of the prepared acid halides would be difficult. So, we decided to generate acyl halides in situ, via Appel reaction. Here, we used triphenylphosphine–bromotrichloromethane ($\text{PPh}_3\text{-BrCCl}_3$) instead of triphenylphosphine–tetrachlorocarbon ($\text{PPh}_3\text{-CCl}_4$) or triphenylphosphine–tetrabromomethane ($\text{PPh}_3\text{-CBr}_4$) to produce the acid halide which is most likely a mixture of chloride and bromide. The reasons behind this has to do with the fact that tetrachlorocarbon is an ozone depletory and therefore should not be used at an academic institution. Bromotrichlorocarbon is significantly more polar and so does not present such a grave environmental hazard.
Figure 16: Preparation of the cinnamoyl chloride (44) started from (43)

Figure 17: $^{13}$C of both cinnamic acid & cinnamoyl chloride, respectively
There are many common ways that can be used to prepare cinnamic acid derivatives such as Heck reaction (Carmichael, Earle, Holbrey, McCormac, & Seddon, 1999), Perkin reaction (John, n.d.) and Knoevenagel reactions (Pal & Sarkar, 2014). Nevertheless, the Wittig reaction is used extensively to prepare cinnamic acid derivatives. In this work, the different cinnamic acids that have been used to synthesize our azo-cinnamate compounds were obtained through previous work reacting different, substituted benzaldehydes with ethoxymethyldenetriphenylphosphorane (1.3eq) at 70 °C in 10w% aq. NaOH solution to form sodium cinnamates. After that, upon neutralization of the aqueous solutions with 15w% aq. HCl, the cinnamic acids were obtained by filtration and air-drying of the solids (Figure 18) (Thiemann et al., 2016).

![Wittig Reaction Diagram](image)

**Figure 18**: General way of substituted cinnamic acid preparation
The preparation of azobenzene-alkyl-cholesterol was a little tricky, also. The coupling reaction of the alkoxy-azobenzene with the cholesterol needed two intermediate steps for the conversion of the hydroxy group in the alkoxy-azobenzene to a halo group (first Cl, then I by Finkelstein reaction). This way was more efficient than the conversion of the hydroxy group to a halo group (Cl then I) in the cholesterol. 3-Chloro-3-deoxycholesterol was prepared by Appel reaction without problem (Figure 19a). However, the Finkelstein reaction to convert it to the iodo-derivative did not work (Figure 19b).

Figure 19: Synthesis of: a) cholesteryl chloride, b) cholesteryl iodide
Also, the direct coupling of the 3-chloro-3-deoxycholesterol with the hydroxyalkoxybenzene did not proceed well (Figure 20).

![Figure 20: The reaction of the cholesterol chloride with the alkoxyazobenzene does not succeed](image)

Nevertheless, it was possible to link the cholesterol as the alcohol component to the iodo derivative (38&41) by Williamson-type synthesis with NaH as base in dry THF to get the target compounds (39&42). Here, alkenes (45) & (46) was found as a by-product (Figure 21), suggesting a competing E2-elimination pathway. The by-product could be separated easily using column chromatography. The $^1$H and $^{13}$C-NMR of the alkene is shown in Figure 22.

![Figure 21: Alkene (44) & (45) as side-product in the coupling of the alkoxyazobenzene with the cholesterol {44 when (n=11, m=5), 45 when(n=9, m=5)}](image)
Figure 22: $^1$H NMR & $^{13}$C NMR of compound (44)
3.2 Photochemical behavior of azobenzene cinnamates

UV spectroscopy is an important field to identify electronic transitions in compounds, especially in organic compounds which have a chromophore in their structures. Also it is a powerful tool to obtain information on the photo-behavior of the materials. In this chapter, I will discuss the UV spectra of our synthesized compounds. Also, I will discuss the photoisomerization experiments that were carried out.

Table 1 shows the absorption bands of the synthesized azocinnamates, showing an absorption band for the trans-cinnamate moiety ($\lambda_{\text{max}1}$ and $\lambda_{\text{max}2}$), the trans form of the azobenzene moiety ($\lambda_{\text{max}3}$) and the cis form of the azobenzene moiety. The results obtained show that the $\lambda_{\text{max}}$ for the -C=C- depends strongly on the substitution pattern of the cinnamate unit. This again determines how well the bands of the -C=C- moiety and the –N=N- moiety are separated from each other.

Table 1: $\lambda_{\text{max}}$ of the azo-cinnamates

<table>
<thead>
<tr>
<th>Compound name</th>
<th>$\lambda_{\text{max}1}$ (nm)</th>
<th>$\lambda_{\text{max}2}$ (nm)</th>
<th>$\lambda_{\text{max}3}$ (nm)</th>
<th>Compound name</th>
<th>$\lambda_{\text{max}1}$ (nm)</th>
<th>$\lambda_{\text{max}2}$ (nm)</th>
<th>$\lambda_{\text{max}3}$ (nm)</th>
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As mentioned above, the cinnamate chromophore has a UV absorption at different wavelengths than the azobenzene chromophore. The different substitution pattern on the cinnamate moiety changes the position of \( \lambda_{\text{max}} \) and sometimes shifts the absorption band towards higher wavelength, causing overlap with the azobenzene absorption band. This shift, in some cases, means that we can no longer selectively irradiate the azo moiety without affecting the double bond of the cinnamate. This means that upon irradiation, \((E-Z)\) isomerization of the double bond would also happen. A theoretical calculation has been done to show the effect of the substitution patterns on the absorption band of the cinnamate moiety. Those calculations were done using Gaussian 03W program and the compounds were modeled in the gas phase.

The geometry of the compounds was optimized using B3LYP hybrid functional and 6-31G(d) basis set. The estimated UV-absorption bands showed a closely similar pattern to what we have observed practically. The Figures 23-25 show the absorption bands of cinnamates with different substitution patterns. The reason behind this differences in the number of bands is the symmetry of the cinnamate moiety. The compounds 49, 50, 51 have maximum absorption at different wavelength in the gas phase (Compd. 49: \( \lambda_{\text{max}} = 277 \text{ nm} \) [pract. 275 nm]), (Compd. 50: \( \lambda_{\text{max}} = 300 \text{ nm} \) [pract. 310 nm]) and (Compd. 51: \( \lambda_{\text{max}1} = 282 \text{ nm} \) [pract. 295 nm], \( \lambda_{\text{max}2} = 329 \text{ nm} \) [pract. 325 nm]) respectively. Previous work found the maximum absorption of compound 50 experimentally in two further solvents, cyclohexane and methanol at \( \lambda_{\text{max}} = 290 \text{ nm} \), and 308 nm, respectively, indicating some solvent dependency in the absorption (Peperstraete et al., 2016).
Figure 23: UV-absorption band of the Methyl Cinnamate (49)

Figure 24: UV-absorption band of the (E)-methyl 3-(4-methoxyphenyl)acrylate (50)
Figure 25: UV-absorption band of (E)-methyl 3-(3,4-dimethoxyphenyl)acrylate (51)
3.2.1 Photoisomerization experiment

The main idea was to trigger only the azo group in the synthesized azo-cinnamates while leaving the (trans-)-C=C- of the cinnamate unit untouched by irradiating the molecules at $\lambda = 350$ nm. In addition, the thermal isomerization backward from the cis-azo isomer to the trans-azo isomer was also to be part of the investigation. In the last decades, similar experiments have been done with photoswitching materials. For the azobenzenes, there are two proposed mechanisms for the photoisomerization of the azo functionality, which are an inversion ($n-\pi^*$) and a rotational ($\pi-\pi^*$) mechanism as shown in Figure 26.

![Figure 26: Established photoisomerization mechanisms of the azobenzene moiety](image)
In the rotation mechanism, the cis-trans isomerization is going through a π-bond rupture so that the transition state no longer has a planar structure and C-N-N-C exhibits no linearity (Figure 27), while the inversion mechanism proceeds through a transition state with linear hybridization in which the double bond is retained. In this case, the intermediate has a semi-linear geometry as shown in Figure 26. The energy needed for the rotation mechanism to proceed is higher than for the inversion (Figure 21) (Tamai & Miyasaka, 2000; Yang et al., 2013).

Figure 27: Mechanism of both inversion and rotational isomerization
3.2.2 Photoisomerization followed by UV spectroscopy

Azobenzene is the most common example of a photoswitching compound. The UV spectrum of the azobenzene shows the n-π* transition peak in the visible region with a low intensity peak as compared to the π-π* peak. The π-π* peak appears in the ultraviolet region. The substitution pattern in the 4 and 4’ positions of the azobenzene affects the optical properties as well as the absorption bands. Adding to the structure another chromophore such as a cinnamate unit might also affect the absorption band of the whole compound.

The maximum absorption of the -C=C-(CO)Ph band of the cinnamate can be shifted to shorter wavelengths with a different intensity depending on the substitution patterns. Photoisomerization experiments were performed for our synthesized compounds, which have different substitution patterns on the cinnamate with different chain lengths connecting cinnamate and azobenzene moiety. In the photoisomerization experiments, the sample concentrations were the same for all compounds (1.0*10^−5 mol/L) in order to have an idea about the isomerization time. The experiments were followed using UV spectroscopy and 1H NMR spectroscopy. The Figures below (Figures 28, 29, 30, 31, 32) show the change of the UV spectra of the compounds during trans-cis isomerization (Figures a) and thermal cis-trans conversion (Figures b).
For all Figures 28-32, the Y-axis represents the absorbance while the X-axis represents the wavelength in nm. During the irradiation, the compound 26 took the shortest time (30 s) to reach the maximum conversion from trans to cis form (photostationary phase), while compounds 33, 34, and 35 took 35 s. The slowest compound is 32, taking 40 s to reach the photostationary phase.

The results proved that the isomerization time depends on the terminal substitution and different carbon chains linked between the moieties. For all compounds (26, 32, 33, 34, 35), with increasing the radiation time, the absorption peak around 358 nm starts to decrease (trans form) while the peak around 450 nm increases (cis form). Those changes are representing the trans to cis isomerization of the azo group (figures 28a-32a). There are small changes with the -C=C- bands, but those are not indicating a E-Z isomerization. Those changes are due to a temperature change (mostly due to the heat dissipation from the instrument), different concentrations of oxygen in the samples and an instable baseline of long measurement times. NMR data proved that the cinnamate E-Z isomerization did not happen and this will be discussed in the next subchapter. Figures b exhibiting the conversion from cis to trans form thermally show that there is a difference in the kinetics of the cis to trans isomerization of the azo cinnmates, again depending on the substitution pattern of the cinnamates.
Figure 28: UV spectra of: a) during irradiation 350 nm, b) backward thermally of compound 26
Figure 29: UV spectra of: a) during irradiation 350 nm, b) backward thermally of compound 32
Figure 30: UV spectra of: a) during irradiation 350 nm,
b) backward thermally of compound 33
Figure 31: UV spectra of: a) during irradiation 350 nm, b) backward thermally of compound 34
Figure 32: UV spectra of: a) during irradiation 350 nm, 
b) backward thermally of compound 35
3.2.3 Photoisomerization followed by NMR spectroscopy

The photoisomerization experiments of compounds 26, 33, 34 and 35 were followed using $^1$H NMR spectroscopy. For compound 26, the NMR peaks which are related to the cis form start to show after 7 min of radiation. With increasing irradiation time, the trans-cis isomerization keeps increasing until 15 min have passed, as shown in the Figure 33. Also, from the NMR data we can conclude that the $E$-$Z$ isomerization of the -C=C- of the cinnamate moiety is not happening because the protons of the Cis form do not appear at $\delta_H$ around 5.9 ppm. (Fukuda et al., 2016)

![Figure 33: $^1$H NMR of compound 26 during irradiation](image)
The $^1$H NMR spectra in the (Figure 34) below shows the thermal isomerization of the compound $26$. As expected, the spectra show that the compound starts to isomerize back thermally to the trans form with increasing time in absence of irradiation. It seems that even after 25 hrs, the conversion is not totally complete.

Figure 34: $^1$H NMR of compound $26$ during cis to trans isomerize thermally
The Figures 35 and 36 below shows the trans-cis isomerization of 34 during photoirradiation. It appears that compound 34 exhibits the same kinetics as compound 26 for both processes, the photochemical trans-cis isomerization and the thermal cis-trans isomerization.

Figure 35: $^1$H NMR of compound 34 during irradiation
Figure 36: $^1$H NMR of compound 34 during cis to trans isomerize thermally
Compound 35 exhibits similar behavior as compared to the compounds 26 and 34 during the photo-irradiation process, but E-Z isomerization of -C=C- of the cinnamate moiety also occurred on a very small scale. The reason behind this isomerization is that the absorption band of the -C=C- (λ_max 312 nm) is much closer to the irradiation region as compared with compounds 26 and 35 (λ_max 259 nm and (λ_max 280 nm, respectively). This convergence might be effected further by the irradiation with the time of irradiation. It seems that the E-Z isomerization of the cinnamate moiety does not occur immediately as shown in the Figure 37. After 5 min irradiation there is no peak evident for the cis form, while after 25 min small peaks started to appear. From the integration, the ratio between the Z to E forms are 10:90.

Figure 37: \(^1\)H NMR of compound 35 during irradiation
As the E-Z isomerization of the -C=C- moiety is not a thermally reversible process and, as we expected, the peaks related to the cis form do not decrease with time (in absence of irradiation), while the cis-trans isomerization of the azo group is thermally a reversible process, and so the intensity of the peaks related to the cis form of the azo group of compound 35 started to decrease with time in absence of irradiation (Figure 38).

Figure 38: $^1$H NMR of compound 35 during cis to trans isomerize thermally
The $^1$H NMR spectra in the (Figure 39) below, proves that compound 33 exhibits a behavior similar to compound 35, because the absorption band of the -C=C- of the cinnamate unit of compound 33 is with 312 nm is similarly close to the $\lambda_{\text{max}}$ of the azo group. The ratio between the Z to E forms after 20 min. photoirradiation in this case is 20:80.

Figure 39: $^1$H NMR of compound 35 during irradiation
3.3 X-ray crystal structure

3.3.1 X-ray crystal structure of azocinnamate 29

A single crystal of compound 29 was grown by slow evaporation a solution of the compound in methanol & dichloromethane (DCM) (1:3) at room temperature. The crystals were measured using a Bruker APEX DUO diffractometer with CCD area detector and monochromatic MoKα radiation (λ= 0.71069) (NYU-AD, Prof. Panče Naumov). Figure 40 shows the shape of the molecule, which exhibits for the most part a linear and rod like structure. At the tail-end, however, there is a kink. It can be seen that this kink is due to the interactions that holds the molecules together. In fact, the stacking of the molecules in the crystal is quite interesting. Interaction between two stacked molecules is mostly at both ends of the molecules by C-H…π interaction.

Figure 40: Structure with atomic labels & phenyl rings labels (R1-3)
The Figure 41, show how the molecules stack over each other within layers. As shown, specific short contacts between molecules are only through C-H…pi interactions. It would be expected that the interactions is weak which can give the molecules more possibility to move against each other when given the energy through heating. On the other hand, the packing of the relatively long rod-like molecules would indicate an initial movement of the molecules in the direction of their long axis, which may mean that a liquid crystalline nematic state, even though perhaps only over a short temperature range, could be expected.

Figure 41: The C-H…pi interaction showed by blue cyan
3.3.2 X-ray crystal structure of 9-(4-Nitrophenoxy)nonan-1-ol (9)

Figure 42 below shows the crystal structure of one of the intermediates. Molecule 9 exhibits for the most part a linear and rod like structure. Single crystals from dichloromethane – methanol (3:1).

Figure 42: ORTEP drawing of the single crystal structure of compound 9
3.4 Thermal analyses

One of the instruments used to identify phase transitions is the differential scanning calorimeter (DSC). The Figures 43-48 below show the DSC measurements for azo-cinnamates 24-27 and 35, 36. For all compounds, two cycles were run. The lower trace is the heating phase, the upper trace shows the cooling phase. All compounds show more than one transition in the cooling phase except for anthryl-substituted compound 26 (Figure 44). It would be not expected that the anthryl compound would show a mesophase. Later, this was confirmed, when compound 26 was viewed under a polarization microscope. Some of the compounds show a transition in addition to the transition from the solid (crystalline) phase to the isotropic phase. Some of these transitions shown in the heating cycle (eg., figure 48) would be expected to be crystal to crystal transformations as was shown for compound 24 under the polarization microscope. In the cooling cycle, many compounds exhibit a transition before the crystallization sets in. In the DSC of compound 24, this transition is at around 111 °C. These transitions are from the isotropic state to the nematic phase. The series of compounds that have a 3,4-dimethoxycinnamate substituent show thermally a relatively strong signal in the cooling cycle; these substances such as 36, as viewed under the optical polarization microscope show both a nematic and a smectic A phase (albeit for 36 with a narrow temperature of 3 °C [74-71 °C]) upon rapid cooling. Contact of 24 with cholesteryl esters led to the induction of a cholesteric phase (Figure 53).

Steroidal azo ether 42 shows a reentrant chiral nematic (cholesteric) phase at around 120 °C. A contact with PCH-7 at 122 °C showed a chiral nematic phase, where the helical pitch decreases with increasing concentration of 42.
Figure 43: DSC thermogram of compound 25

Figure 44: DSC thermogram of compound 26
Figure 45: DSC thermogram of compound 27

Figure 46: DSC thermogram of compound 35
Figure 47: DSC thermogram of compound 36

Figure 48: DSC thermogram of the compound 24
3.4.1 Thermotropic behavior of compound 24

Upon heating, the substance was found to melt at 114-115 °C. Cooling from 130 °C gave needles at 115.5 °C. Rapid cooling showed a nematic phase at 112.7 °C. Further cooling gave the previously noted needles at 104 °C. Reheating brought about a nematic to isotropic transition at 113.5 °C (Figure 49). It was found that there was a crystal to crystal transformation (fanshape crystals to small rhombic crystals) at 89.9 – 92.2 °C (Figure 50). This transformation seems to correspond to the signal seen at about 83 °C in the DSC heating cycle for the compound. At 102.3 °C – 104 °C, the small rhombic crystals changed to the previously observed needles (Figure 51). A contact with 4-heptylcyano-phenylcyclohexane (PCH-7) induced a smectic phase (SmA) (Figure 52). The contact showed a higher isotropic point than PCH-7 alone. A contact with cholesteryl esters induced a cholesteric phase, where pitch of the helix was only slightly temperature dependent.

Figure 49: Nematic phase of compound 24 at 112.7 °C (Schlieren texture), 1st cycle, cooling
Figure 50: Change of fan-shape crystals to smaller crystals at 89.9-92.2 °C of compound 24

Figure 51: Needle shape of crystal of compound 24
Figure 52: Contact with PCH-7: induction of a SmA phase (at 90 °C of compound 24, picture taken under quick cooling)

Figure 53: Contact with cholesteryl esters: induction of a cholesteric phase of compound 24
3.4.2 Thermotropic behavior of compound 42

The compound **42** which is one the series of the Cholesteryl azo ethers, exhibit thermotropic behavior. The results of the POMHS show a chiral nematic mesophase during the cooling cycle. When the (PCH-7) was added to the texture as a dopant, the helical pitch was increased (Figure 54).

Figure 54: Chiral helical phase with large pitch at upper left hand corner (PCH-7) transforming into helical phase with smaller pitch as you go downwards (increasing the conc. of **42**)
Chapter 4: Conclusion

In conclusion, the target compounds could be synthesized successfully. The synthesized compounds have been characterized by $^1$H NMR, $^{13}$C NMR, DEPT, IR-spectroscopy, LC-MS-MS and UV-spectroscopy. Key steps en route to the target compounds were diazotization, Appel-type esterification and Williamson etherification.

The photoswitching behavior of the compounds was investigated using UV-spectroscopy and $^1$H NMR spectroscopy. It could be seen that cis-trans isomerization of the azo functionality could be triggered selectively in the presence of a cinnamate function. In some cases, substitution patterns on the cinnamate moiety changed the position of $\lambda_{\text{max}}$ of the cinnamate moiety and sometimes shifted the absorption band towards higher wavelength, causing an overlap with the azobenzene absorption band, which affected the selectivity of the trans-cis isomerization of the azo moiety. The time for the thermal reversion after photoirradiation was dependent on the structure of the compound, i.e., the substitution pattern of the cinnamate and the chain lengths within the compounds.

The thermal behavior of the compounds was investigated using differential scanning calorimeter “DSC”, and the DSC results showed more than one transition for all azo-cinnamate compounds in the cooling phase except for compound 26. Also, the textural changes were investigated using a polarized light microscope with a hot stage. These results indicate that most of the azo-cinnamates compounds could exhibit thermotropic behavior.
From the optical microscopy analysis, it can be said that apart from anthryl compound 26, the azo-cinnamates show an isotropic to nematic transition upon cooling. The 3,4-dimethoxycinnamates show an additional smectic A phase as could be evidenced by the behavior of compound 36. Contacts with PCH-7 led in certain cases to the induction of a smectic A phase also in those compounds that only showed a nematic phase in their pure state, such as compound 24. Cholesteryl azo ether 42 showed a reentrant chiral nematic phase.
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Appendix

Figure 55: $^1$H, $^{13}$C NMR of compound 12

Figure 56: $^1$H, $^{13}$C NMR of compound 13
Figure 57: $^1$H, $^{13}$C NMR of compound 17

Figure 58: $^1$H, $^{13}$C NMR of compound 18
Figure 59: $^1$H, $^{13}$C NMR of compound 19

Figure 60: $^1$H, $^{13}$C NMR of compound 20
Figure 61: $^1$H, $^{13}$C NMR of compound 21

Figure 62: $^1$H, $^{13}$C NMR of compound 22
Figure 63: $^1$H, $^{13}$C NMR of compound 23

Figure 64: $^1$H, $^{13}$C of NMR compound 24
Figure 65: $^1$H, $^{13}$C NMR of compound 25

Figure 66: $^1$H, $^{13}$C NMR of compound 26
Figure 67: $^1$H, $^{13}$C NMR of compound 27

Figure 68: $^1$H, $^{13}$C NMR of compound 28
Figure 69: $^1$H, $^{13}$C NMR of compound 29

Figure 70: $^1$H, $^{13}$C NMR of compound 30
Figure 71: $^1$H, $^{13}$C NMR of compound 31

Figure 72: $^1$H, $^{13}$C NMR of compound 32
Figure 73: $^1$H, $^{13}$C NMR of compound 33

Figure 74: $^1$H, $^{13}$C NMR of compound 34
Figure 75: $^1\text{H}, ^{13}\text{C}$ NMR of compound 35

Figure 76: $^1\text{H}, ^{13}\text{C}$ NMR of compound 36
Figure 77: $^1$H, $^{13}$C NMR of compound 37

Figure 78: $^1$H, $^{13}$C NMR of compound 38
Figure 79: $^1$H, $^{13}$C NMR of compound 39

Figure 80: DEPT NMR of compound 39
Table 2: list of the $^{13}$C peaks of the DEPT NMR of compound 39

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<td>19.38 (CH$_3$)</td>
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<td>124.27(CH)</td>
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Figure 81: $^1$H, $^{13}$C NMR of compound 40

Figure 82: $^1$H, $^{13}$C NMR of compound 41
Figure 83: $^1$H, $^{13}$C NMR of compound 42