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Study program: Chemistry

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Syntéza a vlastnosti komplexních π-elektronových systémů s helikální chiralitou

Synthesis and properties of complex π-electron systems with helical chirality

Bachelor Thesis

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Prague, 2012

Declaration:

I declare that this thesis is my own independent work and that the results presented in the thesis are original, except as acknowledged in the text. I also declare that the text has not been submitted, either in whole or in part, for a degree at this or any other university.

Prague, 29. 8. 2012

Signature

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Abstract:

Planar shape-persistent macrocycles have been known for a long time and are routinely synthesized today. Non-planar 3D structures, however, still remain challenging synthetic targets in many cases. The objective of this Thesis was to develop a synthetic route to shape-persistent macrocycles containing dibenzo[5]helicene or its derivatives as structural units employing alkene and alkyne metathesis. The *Introduction* focuses on various methods of the macrocycle synthesis, on alkyne metathesis, and synthesis of helicenes is shortly reviewed as well. Then, the first part of *Results and discussion* describes the synthesis of 3,16-dichlorodibenzo[5]helicene and its derivatives. In the second part, the macrocycle synthesis from these dibenzohelicenes is discussed. The *Experimental part* provides a detailed description of performed experiments along with characterization of all new compounds prepared.

Planární rigidní makrocykly jsou známy už dlouhou dobu a jsou dnes rutinně připravovány. Neplanární 3D struktury však stále zůstávají syntetickou výzvou. Cílem této práce bylo vyvinout syntetický přístup k rigidním makrocyklům obsahujícím dibenzo[5]helicen nebo jeho deriváty jako strukturní jednotky a využít při tom metathesi alkenů a alkynů. *Úvod* se zaměřuje na rozličné metody syntézy rigidních makrocyklů, na metathesi alkynů a je zde také krátce diskutována syntéza helicenů. V první části kapitoly *Výsledky a diskuse* je popsána syntéza 3,16-dichlordibenzo[5]helicenu a jeho derivátů. Druhá část se zabývá syntézou makrocyklů z takto připravených dibenzohelicenů. *Experimentální část* detailně popisuje provedené experimenty a uvádí charakterizaci nově připravených látek.

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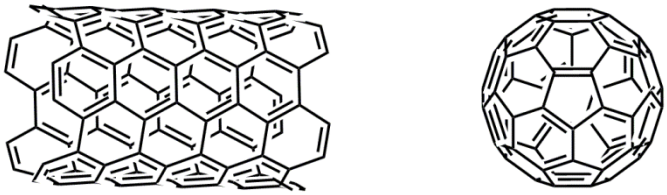
1. Introduction

1.1 Complex π-systems

An exact definition of *complex π-systems* probably does not exist. Usually this term is used for large π-conjugated organic molecules consisting mainly of a hydrocarbon framework modified with various hetero atoms or functional groups. Fullerene, carbon nanotubes or annulenes are examples of such systems (Figure 1).

Figure 1



nanotube fullerene

The rigidity of sp^2 or sp system allows the molecule to occupy smaller number of conformations compared to sp^3 ones, and therefore the molecule does not significantly change its shape in time compared to sp^3 systems. For this reason, the complex π-systems belong usually to so-called shape-persistent systems. This shape-persistence inspired many scientists to use π-conjugated systems as a "construction kit" for building various nanodevices. [(1)]

π-Systems do not only keep their geometrical shape but also, as a result of their geometrical stability, their electronic or optical properties remain relatively constant in time. Moreover, π-systems exhibit self-organization in solution or at the surface. [(2)] These unique properties make π-systems the ideal candidates for application in molecular electronics, optics, nanorobotics, molecular recognition, and many other fields. [(3)]

The central point of this Thesis was to synthesize conjugated macrocycles. Therefore further text will focus mainly on them.

1.2 Shape-persistent macrocycles

π-Conjugated macrocycles are often called shape-persistent macrocycles (SPMs) for the reasons explained above. Many of the features described in the previous paragraph are valid also for SPMs. The cyclic and repeating character of these molecules establishes also the base for interesting 2D and 3D nanostructures or host-guest complexes.

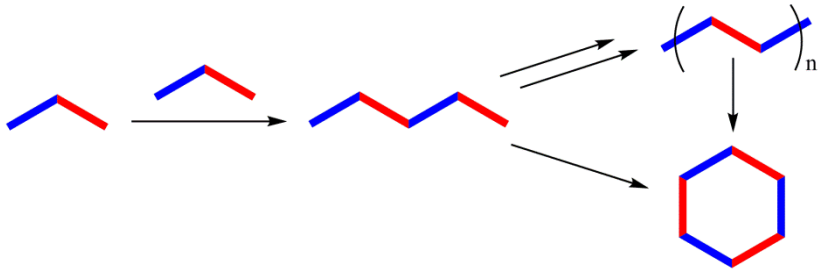
1.3 Strategies for the synthesis of shape-persistent macrocycles

1.3.1 General principles of macrocycle synthesis

Large macrocycles are usually synthesized by kinetically or thermodynamically controlled reactions. Both methods have some advantages and drawbacks but the thermodynamic control approach is increasing in popularity.

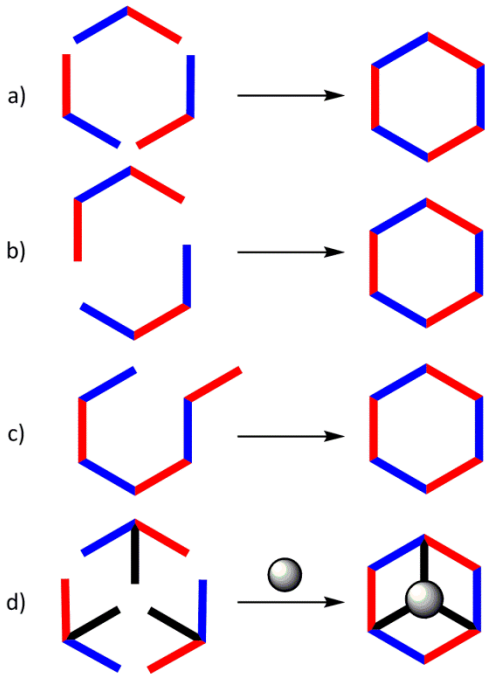
The formation of a macrocycle involves one or more steps. The example of the process is schematically demonstrated in Figure 2. Blue and red parts represent two different functional groups of the monomer which, after reaction with each other, give an oligomeric product. A cyclic product is formed when the two functional groups are parts of the same molecule.

Figure 2



The probability of formation of the cyclic product from short chains is low due to the high angle strain. The formation of large cycles is, on the other hand, limited by the low probability that the two ends of the same chain meet and react. In many cases, the formation of linear oligomers is a dominant process (so-called "overshooting") during the reaction and represents therefore a serious problem.

Figure 3



Although many interesting structures have been prepared by the kinetically controlled metal-catalyzed cross-couplings, these preparations often suffer from overshooting problems.

In the case of the thermodynamic control, the abundance of possible products depends on their relative Gibbs energies. The product with the lowest Gibbs energy will be formed predominantly. At first, kinetically controlled process occurs and then the overshot products are slowly transformed toward the most stable oligomer (Figure 2). Because the long linear oligomers are usually entropically disfavored, this method can be very effective for a preparation of medium-sized cycles in high yields.

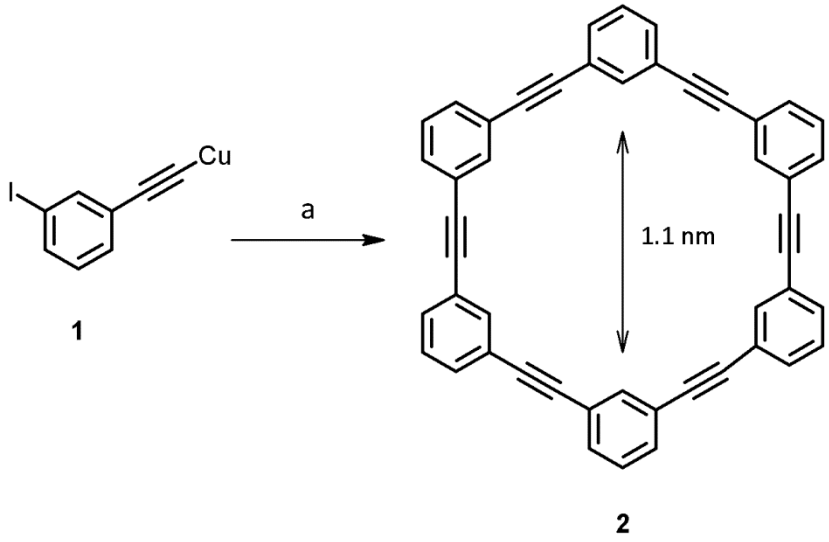
Several methods for macrocycle synthesis have been developed. They are schematically depicted in Figure 3. In the first case (a), cyclooligomerization is applicable to both kinetic and thermodynamic methods. However, in the case of kinetically controlled processes the yields are very low. On the other hand, the thermodynamically controlled cyclooligomerization is widely used providing more satisfactory outcomes. In order to increase yields of the kinetically controlled syntheses, bimolecular coupling (b) and intramolecular cyclization (c) were introduced. Despite the fact that more synthetic steps in the case of (b) and (c) than in the case (a) are required, the overall yield is often better compared to the simple cyclooligomerization. A very promising way of the macrocycle synthesis is a templated cyclization (d) taking advantage of a specific interaction between the template and the building blocks of a macrocycle.

1.3.2 Kinetic control in cross-coupling reactions

Cross-coupling reactions have occupied an important position among the methods of the macrocycle synthesis. As mentioned previously, they are usually kinetically controlled and therefore the synthetic route must be carefully considered in order to avoid formation of undesired by-products.

Various coupling reactions may be used, including Sonogashira, Suzuki-Miyaura, Heck or Glazer couplings. One of the first attempts to prepare the shape-persistent macrocycles was made by Staab and Neuhoeffer [4] using cyclooligomerization of the cooper salt of *m*-iodophenylacetylene **1** by Stephens-Castro reaction (Scheme 1, an arrow in the structure indicates the diameter of the macrocycle.). The macrocycle **2** was obtained in 4.6 % yield. This is an example of the overshooting problem where most of the starting material polymerizes and only a small portion hexamerizes into the desired macrocycle.

Scheme 1



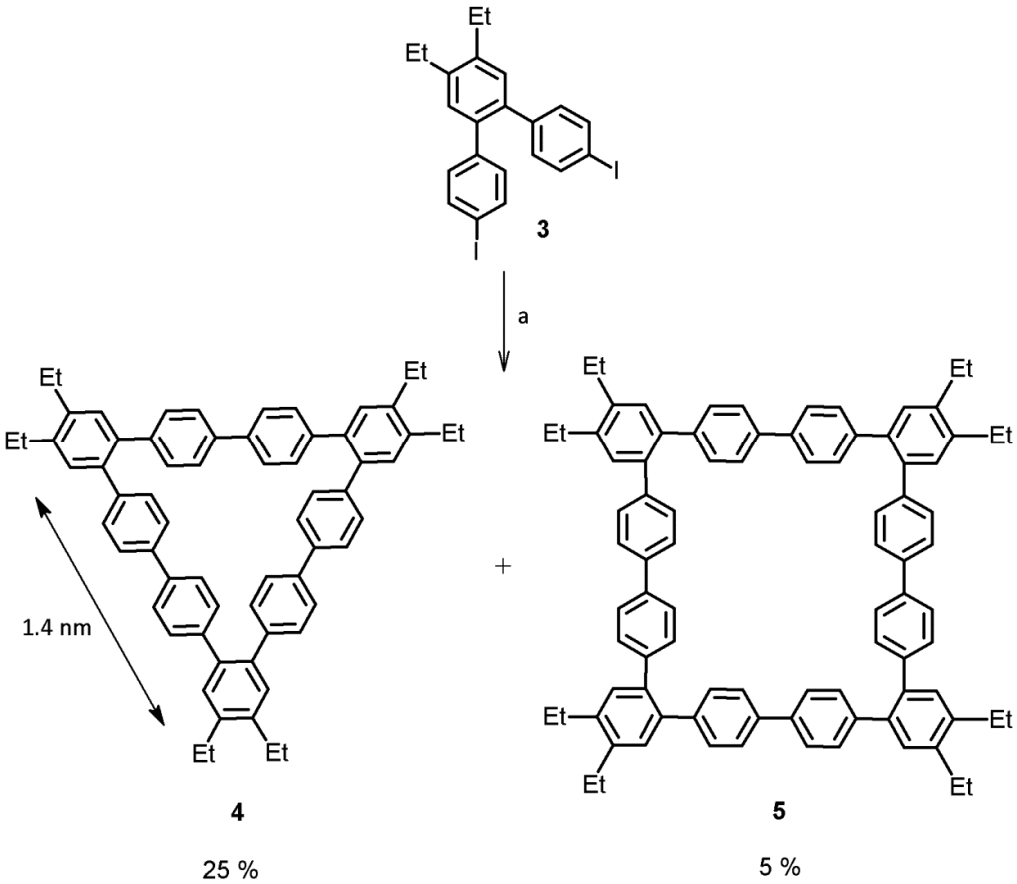
a) Pyridine, 4.6 %.

The cyclic oligophenylenes **4** and **5** were prepared by Iyoda and co-workers using the electron-transfer oxidation of Lipshutz cuprates in better yields (Scheme 2) [5] compared to the previous attempts (*i.e.* various $CuCl_2$-mediated couplings). [6] Although this example represents a successful utilization of cyclooligomerization, problems with overshooting called for more effective synthetic routes.

A significant improvement was achieved by the intramolecular ring closure of bifunctional oligomers. Compound **7**, a derivative of **2**, was prepared in 70 % yield by Sonogashira coupling of *m*-phenylethynylene oligomers under *pseudo*-high-dilution conditions by adding **6** to a palladium catalyst solution. [7] The yield is substantially higher than in the case of **2** (Scheme 3).

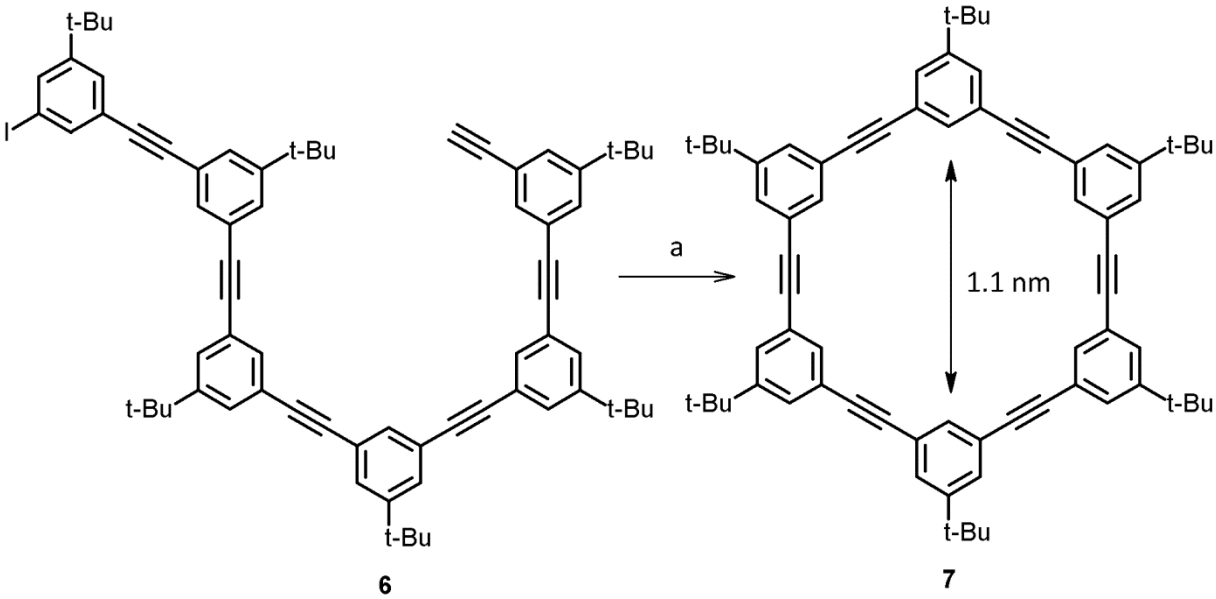
In spite of the dramatic improvement in yields of the cyclization step, the time-consuming preparation of the necessary intermediates makes a simple intramolecular cyclization of a limited use, unsuitable for the preparation of the larger systems. In order to overcome this disadvantage, many researchers investigated the possibility of a one-pot preparation of an intermediate followed by the unimolecular cyclization. In this case, the overall yield was usually better than in the case of the multi-step synthesis.

Scheme 2



a) 1. BuLi, THF, -78 °C; 2. CuCN; 3. 2,3,6,5-tetramethyl-1,4-benzoquinone.

Scheme 3

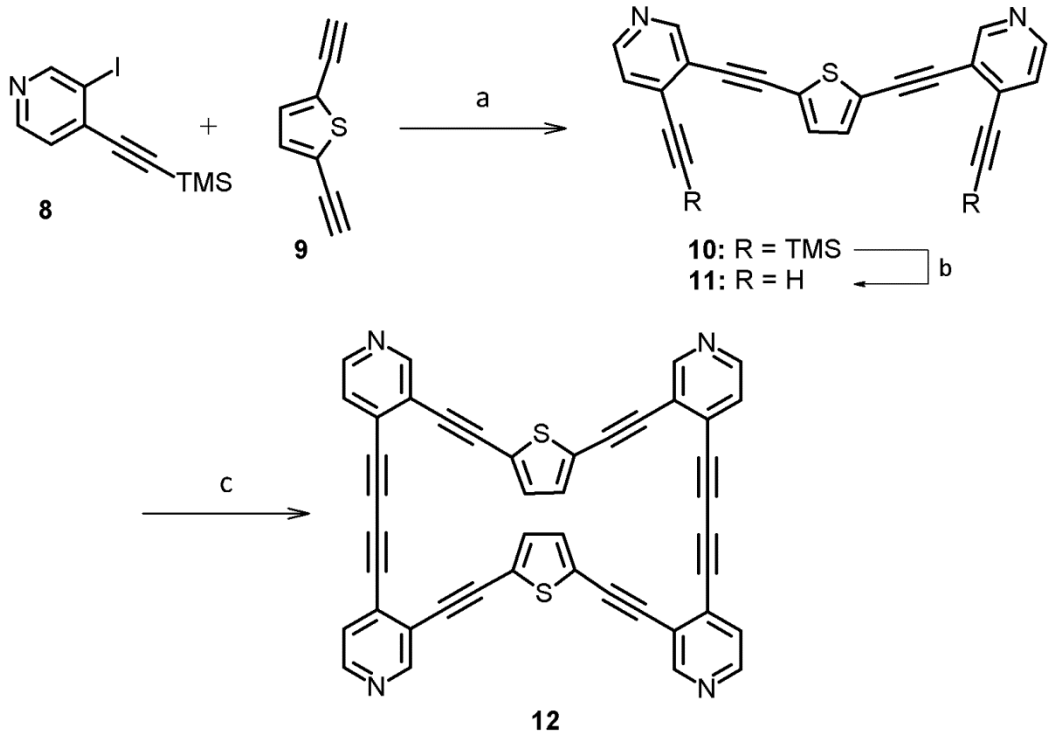


a) $Pd_2(dba)_3$, CuI, PPh_3, Et_3N, 70 %.

Baxter followed this approach and prepared the dehydroannulene-type macrocycle **12**.[8] Iodide **8** and diyne **9** were connected using Sonogashira coupling providing tetrayne

10. After deprotection of the terminal acetylenes, the resulting **11** was dimerized by Eglinghton – Galbraith coupling to give macrocycle **12** (Scheme 4).

Scheme 4



a) $PdCl_2(PPh_3)_2$, CuI, toluene, Et_3N, 20 °C, 54 %.
b) Bu_4NF, THF, H_2O, 20 °C, 88 %.
c) $Cu_2(OAc)_4 \cdot 2\ H_2O$, pyridine, 20 °C, 46 %.

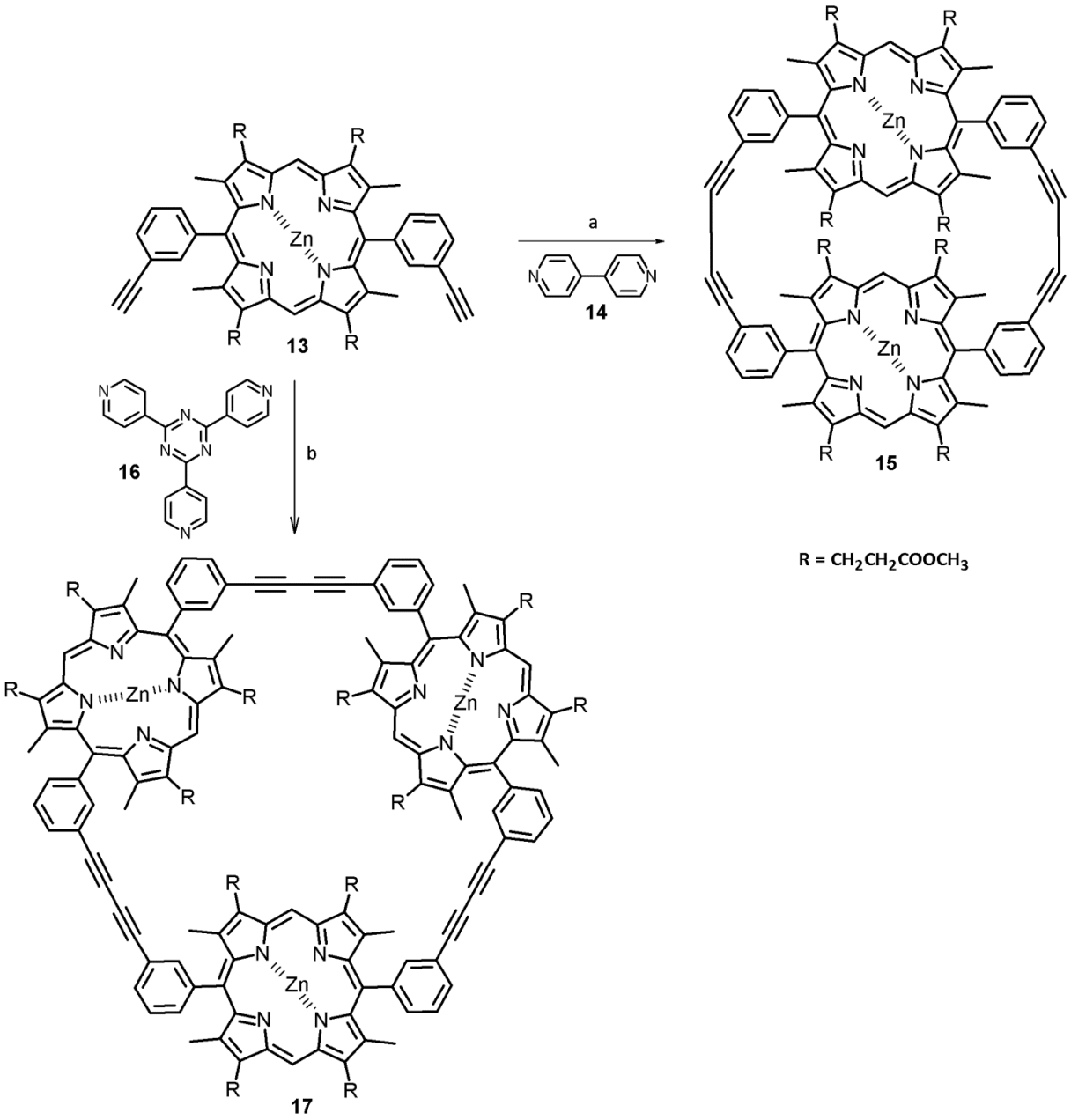
As already demonstrated, the one-pot cyclooligomerization is the easiest method of macrocycle synthesis. On the other hand, small yields make it unsuitable for preparation of the more complex macrocycles. As far as the intramolecular cyclization (or unimolecular cyclization) is concerned, the yields of the cyclization step are higher. However, a large number of synthetic steps and considerable amount of solvent, required for the cyclization step, are the obvious disadvantages of this approach. A very efficient compromise between these two discussed methods is therefore the templated cyclization.

The templated cyclization is performed under the high-dilution conditions. Monomer molecules are pre-organized by a specific interaction with the template into a complex resulting in high local concentration of the reacting functional groups, while the contact of neighboring complexes is kept to minimum. The groups subsequently react to give the desired product in high yield.

The template can be bound to the monomers covalently but it requires the additional synthetic steps. The noncovalent interactions of the template and monomers is therefore preferred. The reaction can be controlled by the careful choice of the template to give the cyclooligomers of different size.

The pioneering contributions in this field were made by Sanders and Anderson. [(9)] They used 4,4`-bipyridyl **14** and terpyridyl **16** as templates to specifically drive the oxidative coupling of bisacetylene **13** toward the formation of dimer **15** or trimer **17** depending on the choice of the template (Scheme 5). When no template was used, the reaction resulted in a mixture of macrocycles of different sizes.

Scheme 5



a) CuCl, TMEDA, DCM, air, 20 °C, 70 %.
b) CuCl, TMEDA, DCM, air, 20 °C, 50 %.

Since the synthesis of macrocycles using cross-coupling reactions in the cyclization step was not a subject of this Thesis, these methods were reviewed only briefly. More detailed information about the various possibilities of synthetic routes as well as detailed analysis of kinetics of the macrocycle formation can be found in several review articles. [3], [10]

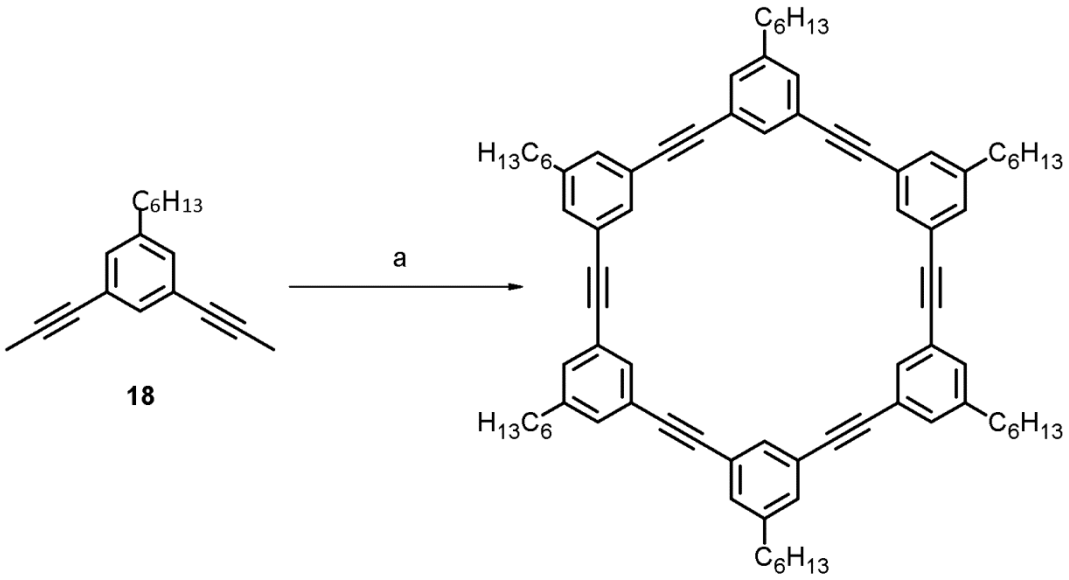
1.3.3 Metathesis as a route to shape-persistent macrocycles

For the reasons discussed in Chapter 1.3.5, metathesis can, under specific conditions, serve as an efficient method of the macrocycle synthesis by substantially reducing the

overshooting problems. Alkynes, alkenes or imines can all be used as starting materials. The following text reviews briefly the most important synthetic approaches in this field.

The first work concerning preparation of SPMs using alkyne metathesis was that of Bunz et al. (Scheme 6). [11] In this case, no effort to remove 2-butyne from the reaction mixture was made. Although the compound **19** was prepared only in 1 % yield, it was the starting point for the synthesis of many other SPMs and for the detailed study on principles underlining this interesting synthetic method.

Scheme 6

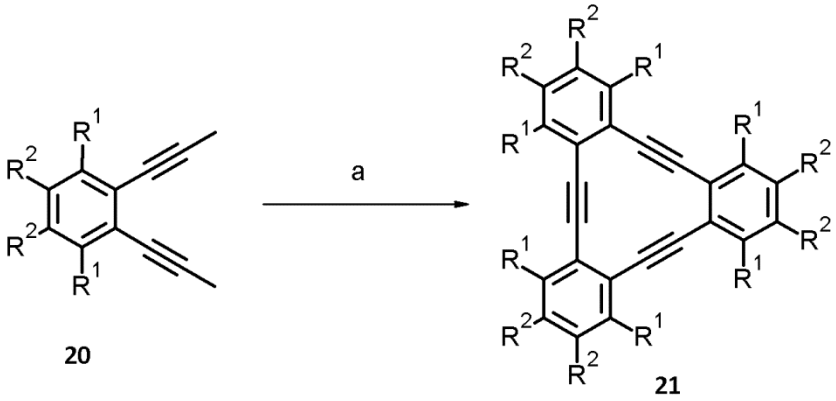


a) $[Mo(CO)_6]$, 4-chlorophenol, 1,2-dichlorobenzene, 150 °C, 1 %.

Since the macrocycle synthesis via metathesis is thermodynamically controlled (Chapter 1.3.4), it was necessary to decrease the reaction temperature. In order to accomplish that, a more active catalyst was needed. Another limitation of the previous synthetic efforts was an ineffective removal of the by-product, such as 2-butyne (Scheme 6). This problem could be solved by performing the reaction in a highly boiling solvent, such as 1,2,4-trichlorobenzene, while vacuum was applied. [12] Despite proceeding well on a small scale, the attempts to scale up were unsuccessful probably due to the inefficient removal of 2-butyne from the large volume of the solvent. Furthermore, a lot of the solvent was lost by evaporation under the vacuum-driven conditions.

The improvement in yield was brought by utilizing Schrock`s catalyst **28** (Figure 4). The compound **21** was prepared by Vollhardt and co-workers (Scheme 7). [13] While **20a** provided **21a** in 54 % yield, the sterically hindered **20c** gave no product.

Scheme 7



a: $R^1 = R^2 = H$ 54 %

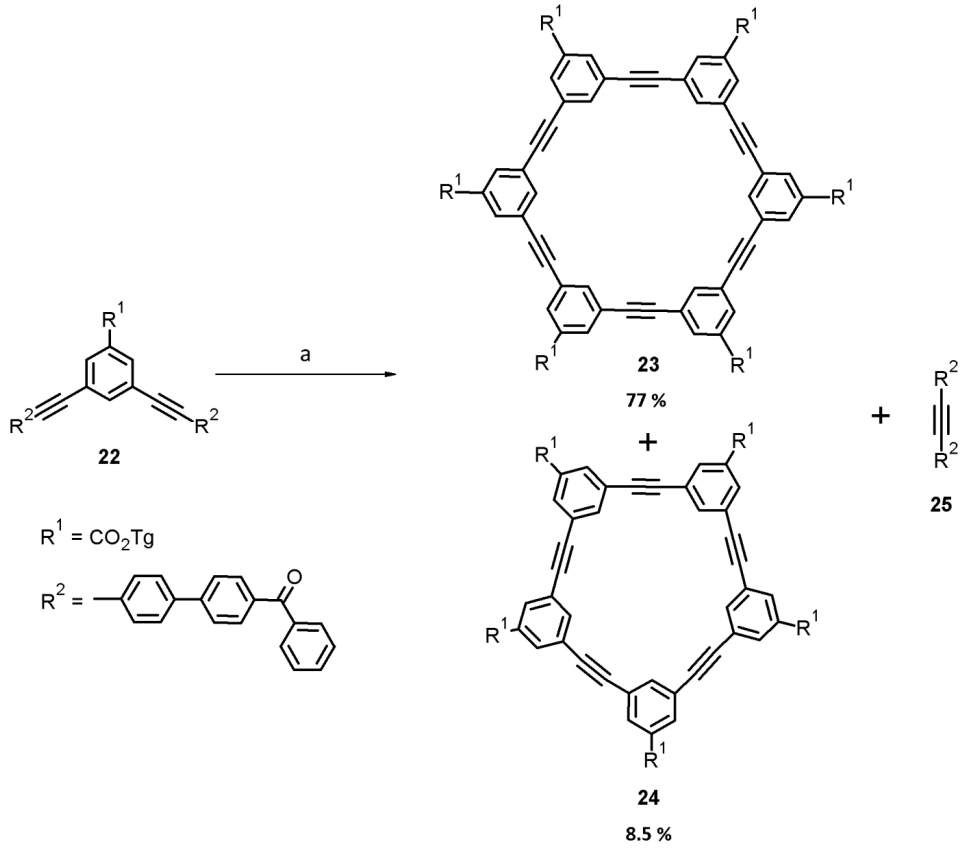
b: $R^1 = H$, $R^2 = OMe$ 28 %

c: $R^1 = R^2 = OMe$ 0 %

a) **28**, toluene, 80 °C.

These obstacles were solved by Zhang and Moore using molybdenum catalyst **33** (Scheme 10). In this approach, the equilibrium was shifted by the formation of an insoluble by-product **25** (Scheme 8). The procedure, performed at 30 °C, provided **23** in very good yield along with a minor product **24**. [12]

Scheme 8

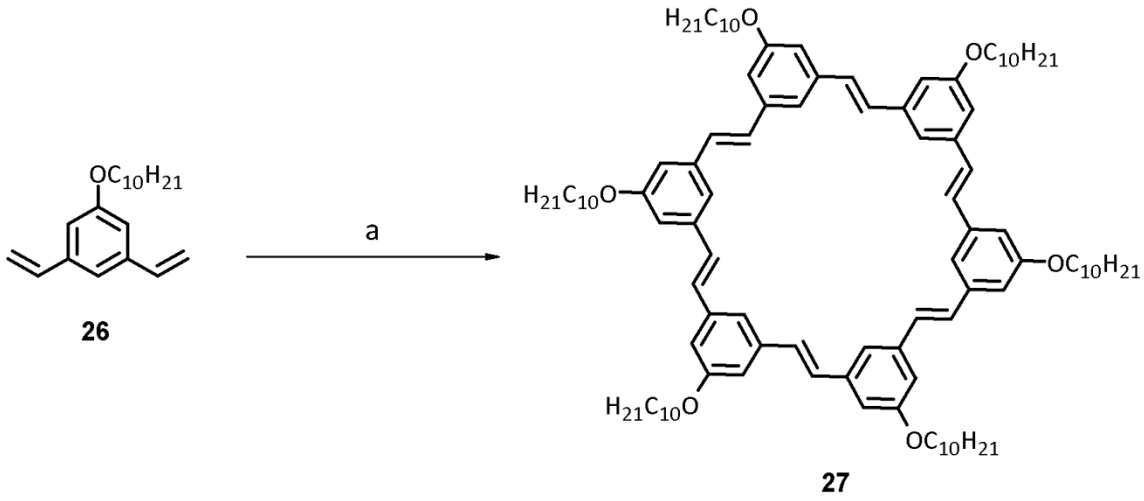


a) **33**, *p*-nitrophenol, CCl_4, 30 ° C.

As mentioned at the beginning of this Chapter, alkyne metathesis is not the only option for the synthesis of large cyclic molecules. Alkene metathesis has also been used by some researchers although much less work has been done in this field. However, alkene metathesis suffers from an essential deficiency as vinylene macrocycles can be arranged into a number of different E/Z-configurations. These oligomers differ only slightly in their relative Gibbs energies and therefore leading to the mixture of several products. Alkyne metathesis, by contrast, can generate the desired macrocycle selectively providing both starting material and catalyst have been chosen carefully. [3]

Despite the discussed difficulties, Jin and co-workers prepared arylene vinylene macrocycles using 2nd generation Grubb`s catalyst (Scheme 9). [14]

Scheme 9



a) Grubb`s 2nd generation catalyst, 1,2,4-trichlorobenzene, 35 °C, 64 %.

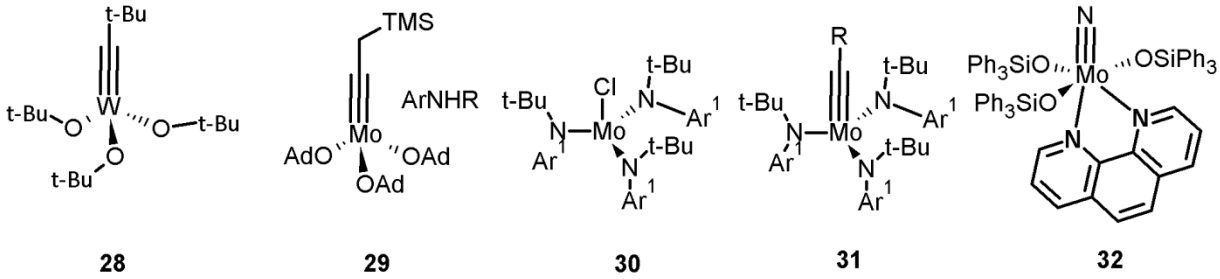
1.3.4 Catalysts for alkyne metathesis

While alkene metathesis has been studied for more than fifty years, the metathesis of alkynes (AM) significantly lags behind. A small number of catalytic systems has been used so far. The synthesis of AM catalysts requires often several steps and utilizing air and moisture sensitive compounds.

One of the first catalytic systems used for AM was a combination of $Mo(CO)_6$ and resorcinol at 160 °C. [15] Unfortunately, the high reaction temperature disqualified this system for purposes of thermodynamic control. However, the study of the reaction intermediates revealed the possible mechanism and opened the way to new, well defined catalysts. The system of $Mo(CO)_6$ and 4-chlorophenol was used to prepare the already discussed **19** in very low yield (Scheme 6). [11]

Modern catalysts used today are usually tungsten- or molybdenum-based alkylidyne or nitride complexes (Figure 4). Widely used tungsten catalyst **28** was utilized in the preparation of various natural products [3] or for the synthesis of **21** (Scheme 7). Molybdenum represents a much wider base for AM catalysts. Apart from $Mo(CO)_6$, various trialkoxymolybdenum(VI) alkylidynes with very promising features were prepared, such as the complex **29**, synthesized by Cummins and co-workers in a few steps. [16] This was the first, large scale preparation of an effective Mo-based AM catalyst working at ambient temperature.

Figure 4

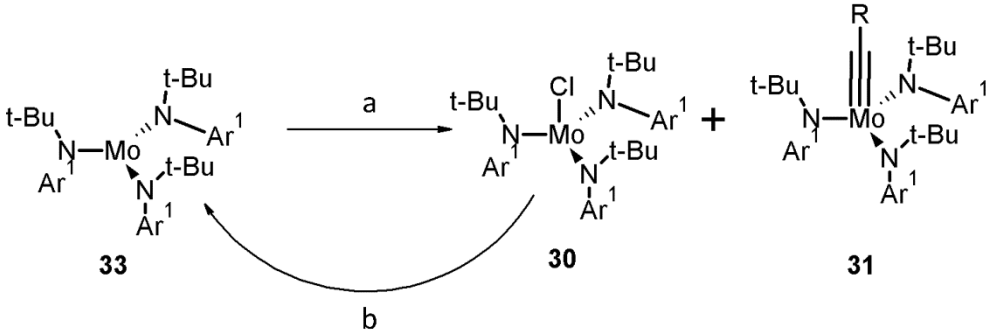


28 **29** **30** **31** **32**

Fürstner et al. found that the trisamido molybdenum complex **33** catalyzes alkyne metathesis in dichloromethane, while in pure hydrocarbon solvents was inactive (Scheme 10). The detailed study of the reaction showed that a mixture of **30** and **31**, where R depends on the used 1,1-dichloroalkane, is formed. Complex **31**, where R = Me or Et, turned out to be the catalytically active species. [17]

Moore and co-workers developed a reductive recycle strategy giving **31** in excellent yield. The addition of magnesium to the reaction mixture reduced the chloride **30** back to **33** and thus giving **31** in yield over 90 %. The subsequent hydrolysis of **31** with phenol provided an efficient catalyst working at 30 °C which is compatible even with thiophene derivatives deactivating previously prepared catalysts. [18]

Scheme 10

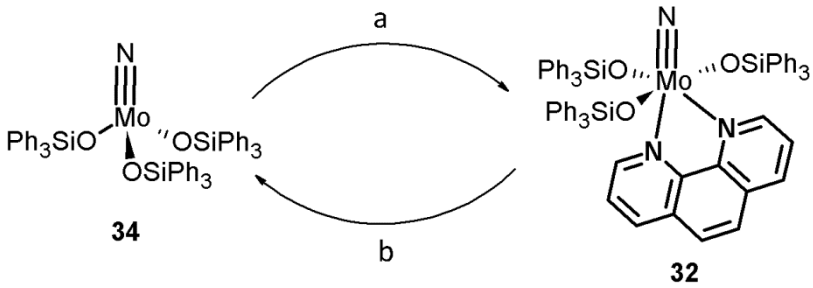


a) $RCHCl_2$, THF, 20 °C, > 90 %.
b) Mg, THF, 20 °C, 100 %.

The catalysts **28**-**31** tolerate a large scope of functional groups (*i.e.,* esters, ethers, silyl ethers, thioethers, sulfonates, amides, carbamates, ketones, acetals, epoxides, nitro groups, and trifluoromethyl groups in the case of **32**). The significant drawback, however, is their air and moisture sensitivity (except the complex **32**) which prevented the broader laboratory use of these AM catalysts. To overcome this limitation, Fürstner and his group investigated molybdenum nitrido complexes and found **32** to be an unusually stable precatalyst. [19]

Complex **34**, can be synthesized in two steps from Na_2MoO_4. The following treatment with 1,10-phenantroline gives an air and moisture stable compound **32**. Complex **34** can be regenerated from **32** by treatment with anhydrous $MnCl_2$ in toluene (Scheme 11).

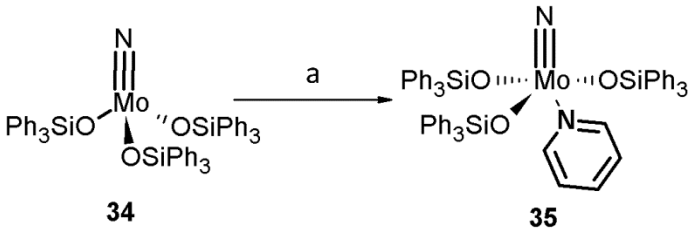
Scheme 11



a) 1,10-Phenantroline, toluene, 20 °C, 82 %.
b) $MnCl_2$, toluene, 80-100 °C.

The same group also prepared another catalytically active complex **35**, which is substantially less stable, but still can be weighed in air (Scheme 12). [20]

Scheme 12

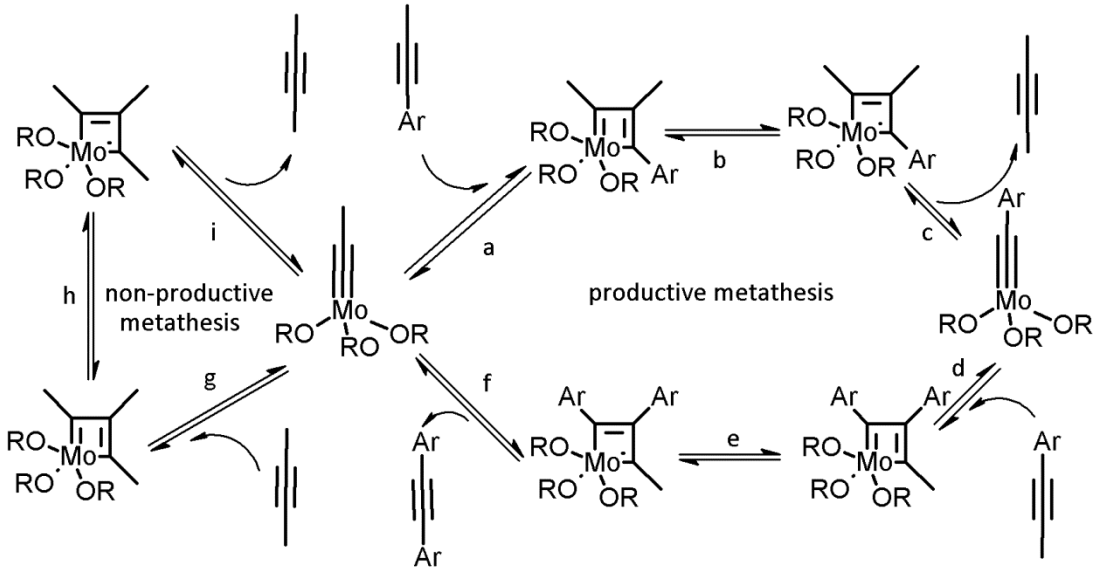


a) Pyridine, toluene, 20 °C, 81 %.

1.3.5 Mechanism of alkyne metathesis

Only the synthetic use of alkyne metathesis has been discussed so far in this Chapter. However, understanding its mechanism is crucial for the synthesis of (not only) SPMs. The reaction mechanism of AM was scrutinizingly studied by Zhang and Moore on the synthesis of arylene ethynylene macrocycles (Scheme 8). [21]

Scheme 13



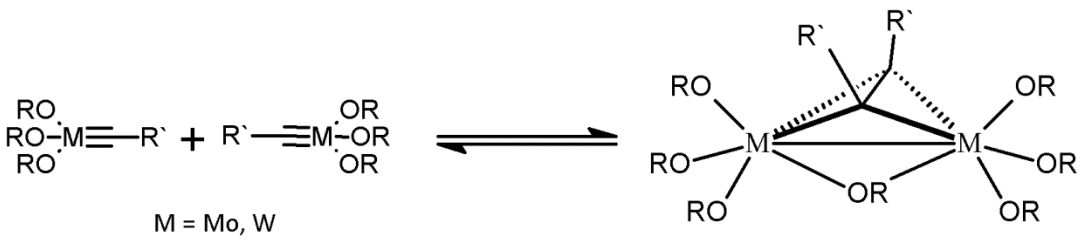
In order to confirm the thermodynamic fashion of the macrocycle formation in the preparation of **23** (Scheme 8), the scrambling experiment was performed. [22] The initial attempt at cross-metathesis of **23** with 3-hexyne was unsuccessful and revealed interesting facts concerning the mechanism. [21] When the experiment was repeated with diphenylacetylene, the reaction proceeded smoothly forming the open-chain oligomers as expected. It was therefore concluded that the electron-rich dialkylacetylenes are kinetically preferred by the molybdenum catalyst and the catalyst is consequently captured by the non-productive metathetic cycle. This effect was called *pseudo*-poisoning of the catalyst.

Scheme 13 shows the reaction mechanism of metathesis of propynylarene catalyzed by a molybdenum carbyne catalyst. The catalyst is quickly transformed into the active species by reaction with the starting compound. Two ways, in which the metathesis is directed, are possible. In the productive cycle, the starting compound reacts by [2+2] cycloaddition (step *a*) giving metallacyclobutadiene. Then, the system of double bonds is reorganized (step *b*), subsequently releasing 2-butyne and arylidyne catalyst (step *c*). This intermediate reacts again by [2+2] cycloaddition with the second equivalent of the propynylarene (step *d*) and the reaction sequence follows in the same fashion as in the first part (steps *e, f*) forming the desired diarylacetylene and recycling the starting catalyst. In the non-productive cycle, 2-butyne, initially formed in the step *c*, is involved in the whole catalytic cycle and therefore competitively inhibits the formation of the desired product (steps *g* – *i*). If 2-butyne is not efficiently removed during the reaction, the non-productive cycle prevails as a consequence of the kinetic preference for the electron-rich alkyl-substituted acetylenes.

The importance of the by-product removal is evident. The precipitation of the by-product, shown in Scheme 8, is one way to accomplish this task, the previously used approaches include, for instance, the vacuum-driven methods. Fürstner and co-workers utilized 5 Å molecular sieves added to the reaction mixture as a sorbent for 2-butyne. This protocol was used in the synthesis of various cyclic compounds, including SPMs, in high yield. [19]

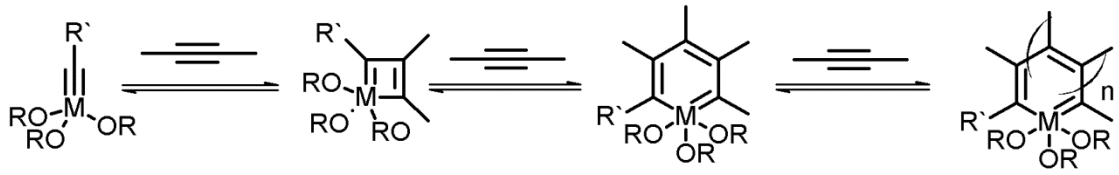
The catalyst *pseudo*-poisoning is not the only means of the metathesis inhibition, another one is the dimerization of the catalyst. Most tungsten and molybdenum catalysts were found in equilibrium with their dimers (Scheme 14). The character of R and R` substituents influences the position of the equilibrium. The choice of bulky electron withdrawing substituents, such as $(CF_3)_2MeC$ substituents, leads to the equilibrium shift toward the alkylidyne species. [3]

Scheme 14



Further way of a catalyst deactivation is the ring expansion showed in Scheme 15. Small alkyl-substituted by-products, such as 2-butyne, can repeatedly insert into the metal-carbon bond resulting in a formation of long vinyl alkylidynes which are unsuitable for further metathesis. [3]

Scheme 15

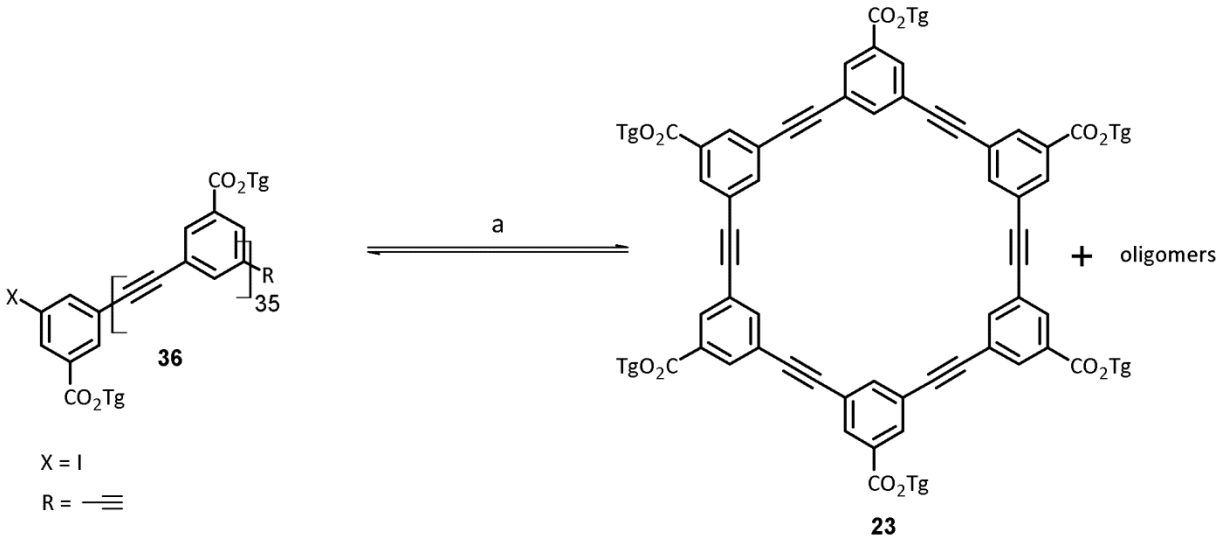


1.3.6 Thermodynamics of alkyne metathesis

The dynamic covalent chemistry (DCC) provided a very effective tool for the synthesis of various macrocyclic products. The basic feature of DCC methods is the use of the thermodynamic control over the reaction. The thermodynamically controlled approach requires the reaction used for cyclization to be reversible and the energies of the reacting bonds must be therefore almost the same on both sides of the equilibrium. If these conditions are satisfied, the distribution of the products is determined practically only by the relative Gibbs energies of the products. Accordingly, the most stable compound is formed as the major product. As discussed in Chapter 1.3.1, the undesired bonds, initially formed under kinetic control, cannot be transformed further and substantial amount of the monomer is consumed owing to the formation of by-products. In the case of the thermodynamically controlled processes, the overshot oligomers slowly change into the most stable ones. The chemical reactions fulfilling all these criteria are particularly imine, alkyne, and alkene metatheses.

The principles governing the macrocycle formation were demonstrated on the synthesis of phenylene ethynylene macrocycles performed by Zhang and Moore. [21] The phenylene ethynylene polymer **36** was subjected to alkyne metathesis conditions and the reaction mixture was then analyzed by gel permeation chromatography validating the formation of hexacyle **23** as a major product (Scheme 16).

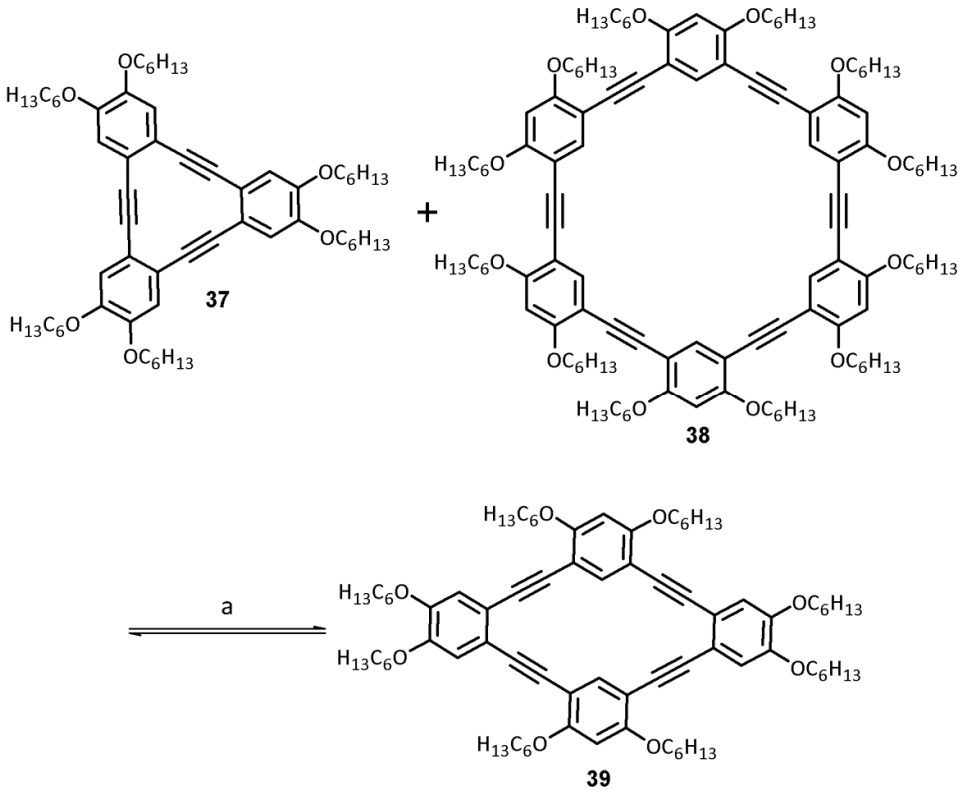
Scheme 16



a) **33**, *p*- nitrophenol, 1,2,4-trichlorobenzene, 30 °C.

In another experiment confirming the reversibility of the macrocycle formation, a 2 : 1 mixture of **37** and **38** were subjected to the metathesis conditions giving **39** as a major product, which was determined by field desorption mass spectrometry (Scheme 17). [22]

Scheme 17



a) **33**, *p*-nitrophenol, 1,2,4-trichlorobenzene, 30 °C.

Further information concerning the detailed computational analysis as well as other experiments supporting the proposed mechanism can be found in the references. [21], [23]

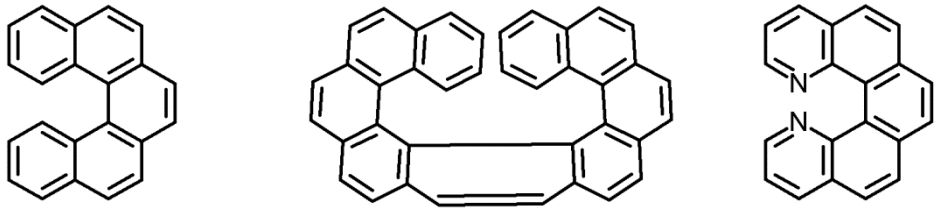
1.4 Helicenes

1.4.1 Synthesis and properties of helicenes

Helicenes are *ortho*-fused polyaromatic, spiral-like molecules. The first synthesis of helicenes [24] dates back to the beginning of the 20th century but a more widely applicable synthesis was developed by Newman and co-workers in 1956. [25] For many years, helicenes did not attract much attention because of their difficult synthesis and no industrial application. However, during the last two decades, the interest in the synthesis and study of helicenes dramatically increased. With the outbreak of molecular electronics, non-linear optics, and enantioselective catalysis, a new chance was given to these interesting molecules. Today, helicenes represent an important research target for the reasons mentioned above.

In Figure 5, the examples of carbo- and heterohelicenes (the number in brackets indicates the number of fused rings) [5]helicene **40**, [9]helicene **41**, and 1,14-diaza[5]helicene **42** are showed.

Figure 5

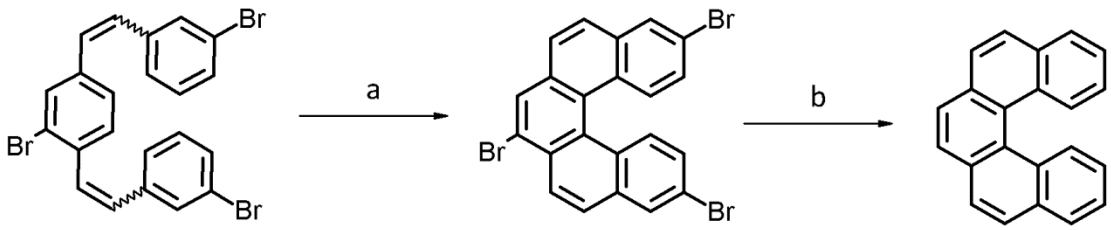


40 **41** **42**

The helical shape of helicenes is the source of their optical activity. Inherently chiral helicenes exhibit unusually high values of specific rotation. For example, the specific rotation of [11]helicene was measured to be $[\alpha]_D = 7142°$. [26] These properties make helicenes very attractive in enantioselective catalysis or as liquid crystals.

A lot of work has been done in the synthesis of helicenes since their original preparation. The first practical synthesis was published by Martin et al. using photodehydrocyclization of stilbene precursors. [27] The undesired linear by-products were formed during the reaction, however. Katz solved this problem by introducing bulky bromine atoms into the *m*-positions and at the central benzene ring of the starting phenyl compound **43.** He further improved the efficiency of the synthetic protocol by utilizing iodine as a mild oxidizing agent in the presence of propylene oxide as an HI scavenger (Scheme 18). [28]

Scheme 18

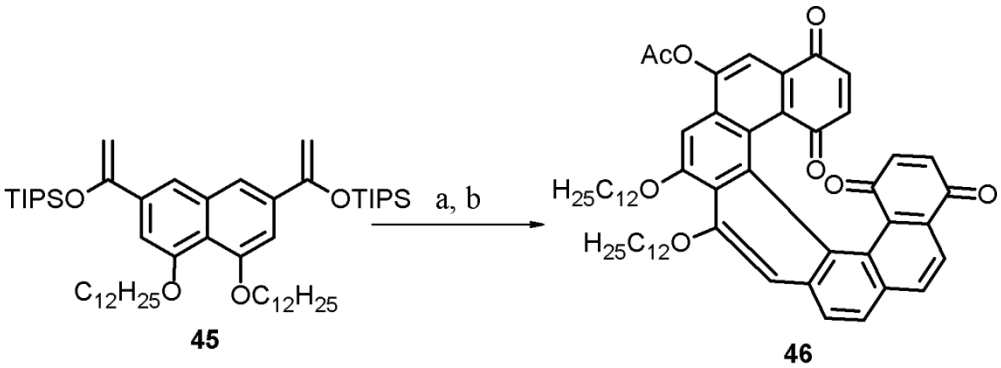


43 **44** **40**

a) h*v*, I_2, propylene oxide, benzene, 92 %.
b) 1. BuLi; 2. H_2O, 90 %.

The low concentration in the cyclization step, necessary for a successful preparation of **44** in high yield, is the limiting factor of this synthetic method. Therefore, Katz developed a different approach using Diels-Alder reaction of *p*-benzoquinone and divinyl ether **45** (Scheme 19). [29]

Scheme 19

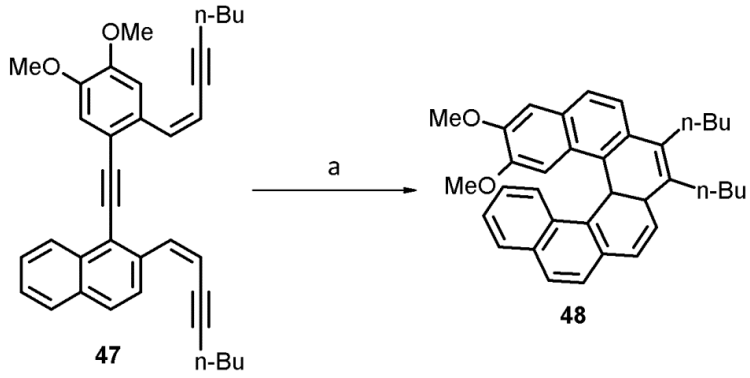


45 46

a) *p*-Benzoquinone, heptane, reflux.
b) Ac_2O, $Et_3N \cdot HF$, Et_3N, THF, 56 % (after 2 steps).

More recently, Starý, Stará et al. developed the efficient synthetic approach to various carbo- and heterohelicenes. This pioneering procedure, following the concept of atom economy, involves Ni^0 or Co^I mediated [2+2+2] cycloisomerization of aromatic triynes (Scheme 20). [30] The scope of this method is broad and allows the synthesis not only of helicenes but other helicene-like structures as well. Unlike the other methods, this procedure allows formation of three aromatic rings in a single step resulting in the rapid growth of molecule`s complexity. [31], [32], [33], [34], [35], [36]

Scheme 20

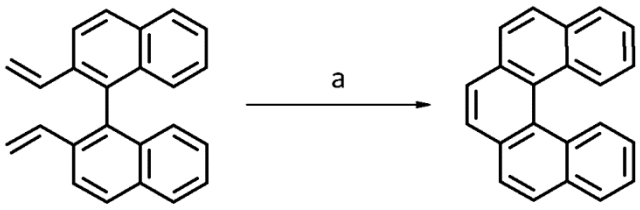


47 48

a) $[Ni(cod)_2]$, PPh_3, THF, 20 °C, 61 %.

Collins and co-workers utilized alkene metathesis as an elegant means of helicene synthesis (Scheme 21). [37]

Scheme 21



49 40

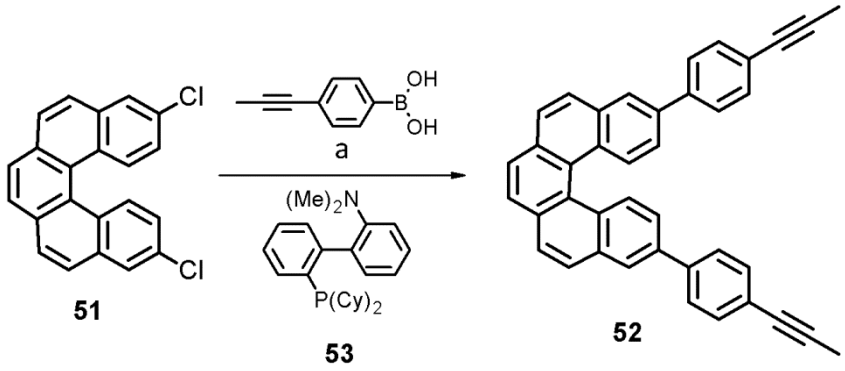
a) Grubb`s 2nd generation catalyst, DCM, microwave heating 100 °C, 88 %.

1.4.2 Helicenes as building blocks for shape-persistent macrocycles

Helicenes with their inherent chirality represent very interesting structures which can impart some of their features into various supramolecular systems.

Starý`s group studied palladium-catalyzed Suzuki-Miyaura coupling of pentahelicenes with several *p*-phenylboronic acids in the presence of the phosphine ligand **53** (Scheme 22). (38)

Scheme 22



a) $Pd(OAc)_2$, Cs_2CO_3, dioxane, 85 °C, 45 %.

Structures similar to **52** will be discussed later in Chapters 2 and 3 to be key intermediates in the synthesis of macrocycles, which is the topic of this Thesis.

2. Objectives

"There is a plenty of room at the bottom." stated Richard Feynman in one of his lectures in 1959, when he pointed out that learning to manipulate individual molecules and using their mechanical properties could bring totally new, unexpected applications. This moment is by many considered as a milestone in the history of nanotechnology. For obvious reasons, the field of nanotechnology soon attracted also the attention of chemists.

One of the important characteristics of nanotechnology is that it understands atoms and molecules as functional components of "molecular machines". During the 20th century we could see how various macroscopic machines and complicated electronic devices spread around the world and made our lives easier (but in many cases also much more painful). The "colonization of nanoworld" in this sense would be the same if not the greater technological revolution. Therefore, the preparation and study of the properties of nano-scaled molecules is one of the central interests of contemporary chemistry.

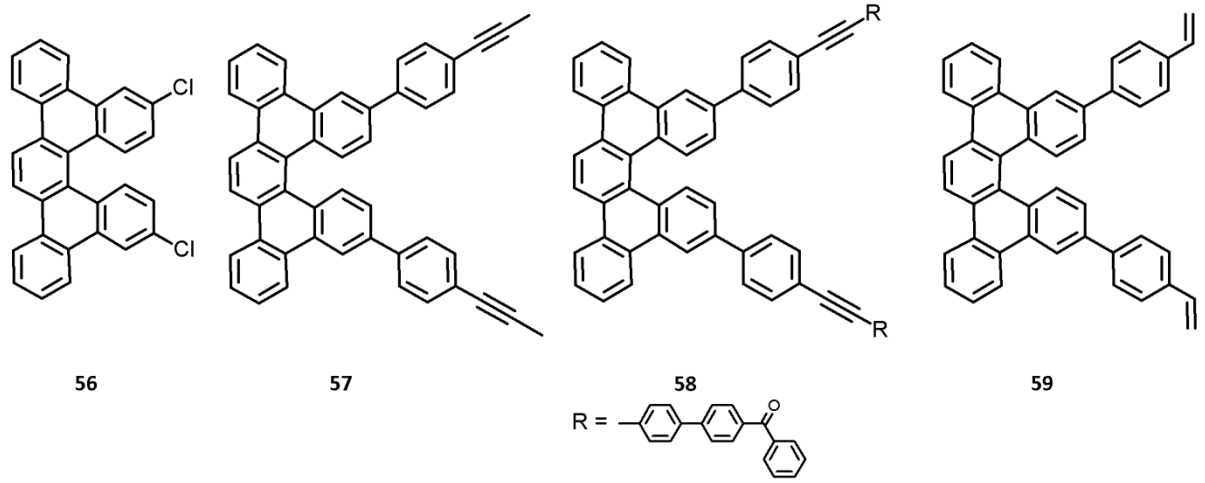
We believe that the shape-persistent macrocycles, which were in detail discussed in Chapters 1.2 and 1.3, as well as helicenes, described in Chapter 1.4, could contribute to this revolution and therefore we decided to combine their promising qualities into one molecule. This idea was based on the fact that many SPMs, prepared so far, are planar objects. Most machines and electronic devices, however, are 3D structures and thus the introduction of the helical moiety into the cyclic framework is an interesting innovation. Dibenzo[5]helicene was chosen as a basic structural unit of the macrocycles for its relatively simple synthesis.

Our previous attempts at the macrocycle synthesis via coupling reactions failed. Thus, inspired by Moore`s and Zhang`s application of precipitation driven metathesis to the synthesis of SPMs, [12] as well as the recent Fürstner`s results in molecular sieves promoted metatheses and the development of new generation catalysts, [19] metathesis was chosen as a hopeful means to prepare the target molecules. Accordingly, the goals of the Thesis were set.

The goals of the Thesis

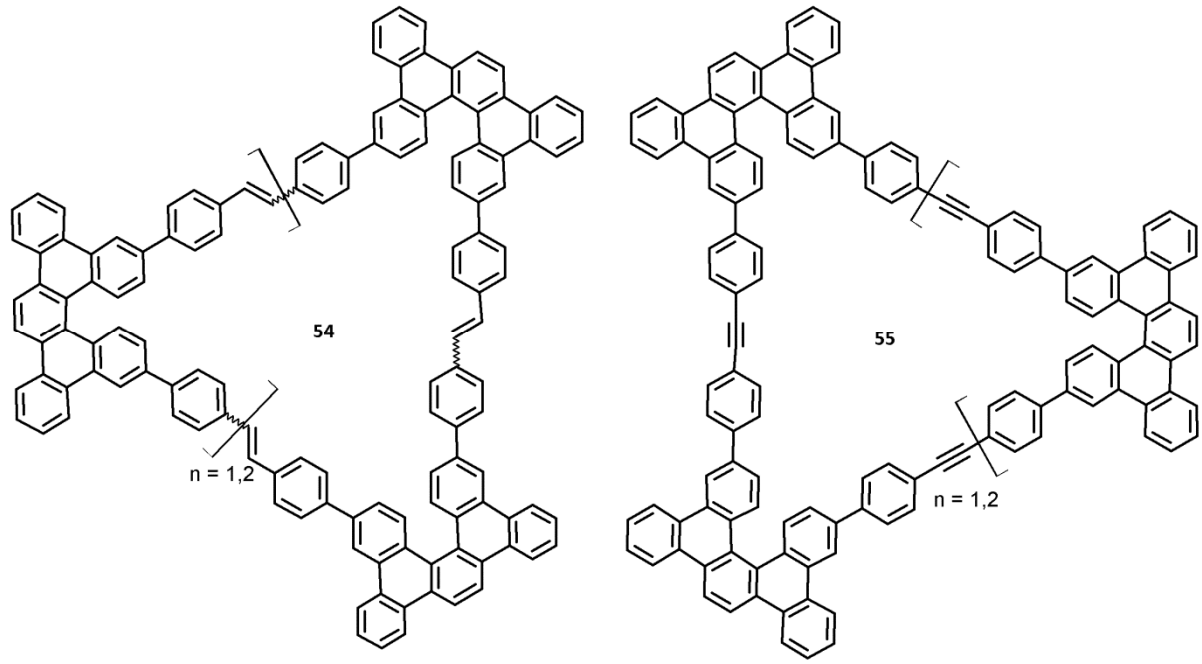
- To synthesize dichlorodibenzo[5]helicene **56** (Figure 6)
- To prepare dibenzo[5]helicene derivatives **57**, **58**, and **59** (Figure 6)
- To study the alkene and alkyne metathesis of **57**, **58** and **59** as a route to the target macrocycles **54** and **55** (Figure 7) - It follows from the geometry of pentahelicenes that either trimeric or tetrameric products come into consideration.

Figure 6



56 **57** **58** **59**

Figure 7



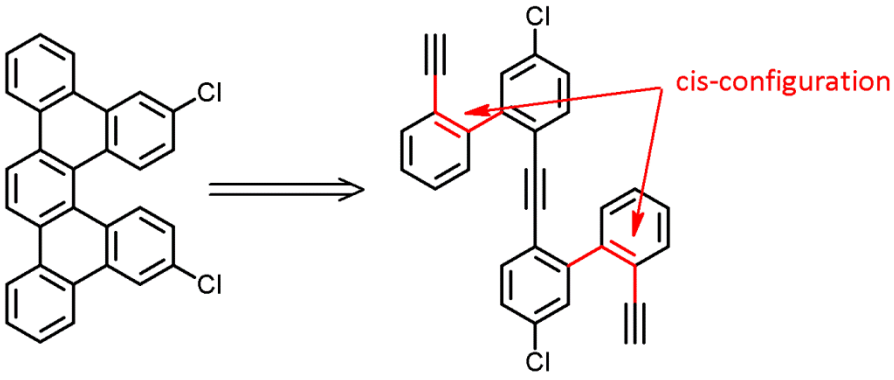
54 **55**

3. Results and discussion

3.1 Synthesis of 3,16-dichlorodibenzo[5]helicene

3,16-Dichlorodibenzo[5]helicene (DBH) **56** is a key component of the target macrocycles. On the basis of the previous research in our group, the cycloisomerization of triynes was chosen for the synthesis of the DBH. Unlike the synthesis of classical helicenes, where the problems with double bond configuration and stability of the corresponding dienetriynes were encountered (Chapter 1.4.1), [30] the synthesis of DBHs overcomes these difficulties by the incorporation of *cis*-configuration of the double bonds in the benzene ring (Scheme 23).

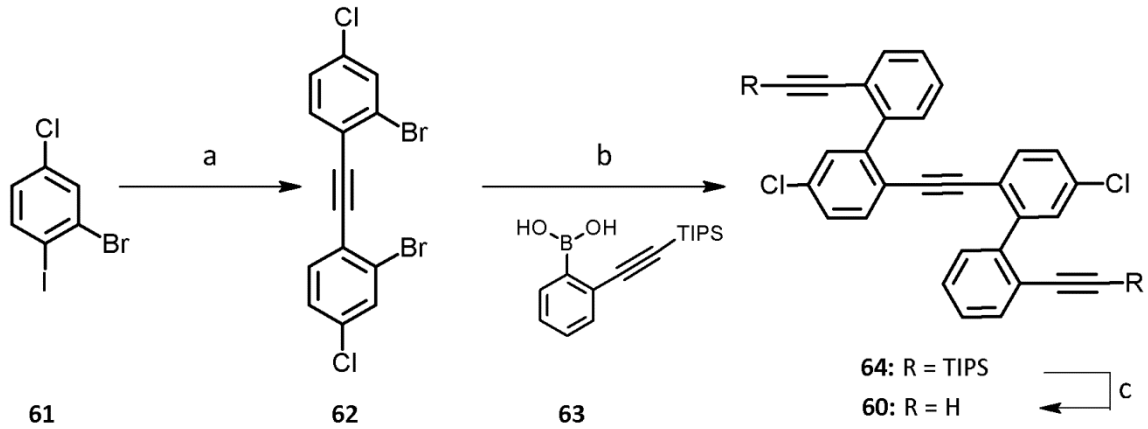
Scheme 23



56 **60**

The structure of the compound **56** suggests several possibilities of its preparation. The approach, developed in our group, is depicted in Schemes 24 and 25.

Scheme 24



61 **62** **63**

a) C_2H_2 (0.5 eq.), $Pd(PPh_3)_4$ (10 mol %), CuI (20 mol %), DIPA, 55 °C, 18 h, 82 %.
b) **63** (3.0 eq.), $Pd(PPh_3)_2Cl_2$ (10 mol %), K_2CO_3 (3.4 eq.), toluene : 1-propanol : water = 4 : 4 : 1, reflux, 3 h, 75 %.
c) TBAF (4.0 eq.), MeOH (25 eq.), THF, 20 °C, 2 h, 90 %.

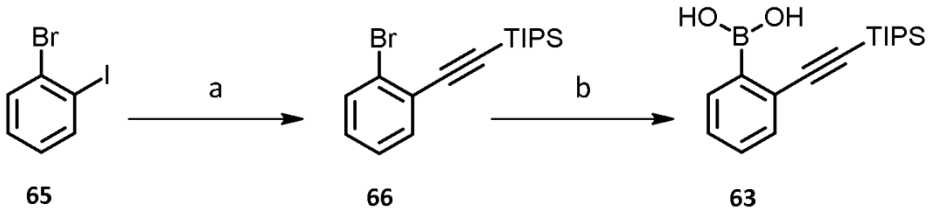
The first step of the synthesis of triyne **60** was Sonogashira coupling of **61** with gaseous acetylene which gave dibromide **62** in 82 % yield. A similar reaction was successfully applied in the previous syntheses of helicenes, [38] but the two additional halogens in the starting compound **61** turned out to cause unexpected problems. The developed procedure had to be followed very carefully in order to obtain reproducible results. Several factors significantly influenced the reaction yields. Increased temperature, high catalyst loading, and long reaction time, quite unusual for an iodine compound, were crucial for the reaction to run smoothly. Careful degassing of the reaction mixture played also an important role. To examine the influence of the apparatus arrangement on the reaction outcomes, the addition of a precisely measured amount of acetylene via a syringe through a septum was tried. In this case, the yield dropped to 55 %. Similar results were observed when a greased stopper was replaced by a stopper equipped with a Teflon gasket. It was concluded from these findings that even the smallest amount of air, getting into the apparatus, substantially decrease the yield. Lower yields were also observed if the concentration of the starting compound was too high as well as if the palladium loading was lower than 9 mol %. An ideal solvent for this reaction was diisopropylamine. The addition of other solvents (tetrahydrofuran or benzene) led to polymerization of the starting compound. The details of the procedure are described in Experimental section.

In the next step (**62** → **64**), Suzuki-Miyaura coupling was used to introduce the *o*-phenyleneethynyl moieties by reaction of dibromide **62** with boronic acid **63**. First, a mixture of ethanol, toluene and water was used as a solvent but ethanol was later replaced with 1-propanol in order to increase the reaction temperature and thus decrease the reaction time. Consequently, the yield increased from ca 50 % to 75 %.

In order to get triyne **60**, a standard deprotection of disilylated **64** with TBAF in anhydrous THF was performed but this procedure gave lower yields (40 – 69 %). The reaction mixture usually turned black immediately after the addition of TBAF and most of the starting compound **64** was probably polymerized. To overcome this obstacle, a modified procedure was utilized. Considering the mechanism of the deprotection, addition of a small amount of a proton source as methanol was assumed to prevent the polymerization. This assumption proved to be right and triyne **60** was thus prepared in 90 % yield. In addition, no chromatography was necessary as the pure product was simply precipitated from the reaction mixture by isopropanol.

Scheme 25 shows a preparation of the boronic acid **63**. [39]

Scheme 25



65 **66** **63**

a) TIPSA (1.05 eq.), $Pd(PPh_3)_2Cl_2$ (1 mol %), CuI (2 mol %), DIPA, 0 °C →20 °C, 15 h, 99 %.
b) 1. BuLi (1.3 eq.), THF, -78 °C, 75 min; 2. B(O-*i*-Pr)$_3$ (2.5 eq.), -78 °C → 20 °C, 2 h; 3. 1 M HCl, 20 °C, 1 h, 92 %.

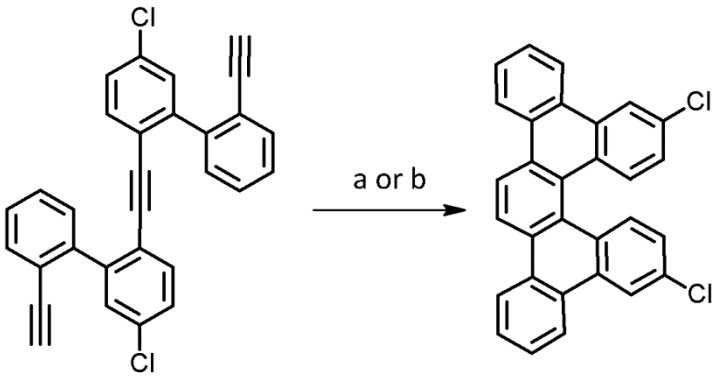
The compound **66** was prepared by Sonogashira coupling of 1-bromo-2-iodobenzene **65** and triisopropylsilylacetylene. At 20 °C, the reaction gave 97 % yield and it was necessary

to purify the product by column chromatography. When the temperature was kept at 0 °C, the completely pure product was obtained in 99 % yield.

Not only boronic acid **63** could be employed for the Suzuki-Miyaura reaction (Scheme 24). The corresponding pinacol ester of **63** was considered first. However, the difficulty to purify it was the reason why a more "risky" lithiation – borylation way was chosen. A standard procedure of lithiation with BuLi in THF at – 78 °C followed by addition of properly dried triisopropyl borate appeared to be very reliable. No special effort to cool the reaction mixture was necessary. It turned out, however, that the reaction period of the lithiation step plays a significant role. The addition of triisopropyl borate after just 20 minutes after the addition of BuLi gave approximately 85 % yield while the reaction period of 75 min gave 92 % yield.

The final cyclization could be achieved by several catalytic systems. Based on the experience with the synthesis of similar dibenzohelicenes, the system of $Ni(cod)_2$ and PPh_3 was the first choice. Later, trimerization with $CpCo(CO)_2$ was also successfully tried (Scheme 26).

Scheme 26



60 **56**

a) $Ni(cod)_2$ (20 mol %), PPh_3 (40 mol %), THF, 10 mg/mL, 20 °C, 15 min, 74 %.
b) $CpCo(CO)_2$ (15 mol %), THF, 10 mg/mL, flow reactor, 240 °C, 1 mL/min, 79 %.

It was observed that the concentration of triyne **60** in THF influences the outcomes of the reaction. The optimal concentration, where the amount of by-products was still low while keeping the reaction volume acceptable, was 10 mg/mL. At first, the reproducibility of the experiments with $Ni(cod)_2$ was low. In spite of a promising TLC analysis of the reaction mixture, showing that only one by-product was formed in a very low amount, the yields varied from 44 to 74 %. Interestingly, worse results were obtained when a larger amount of silica gel was used for the chromatography of the product. From these observations it was concluded that a substantial portion of the helicene was stuck at the silica gel. The elution of the column with solvents as tetrahydrofuran, chloroform or acetone released the product from the column. Unfortunately, it had no effect on the purification of the product. The attempts at crystallization of the helicene failed too. An alternative purification method was found. The crude reaction mixture was suspended in acetone and sonified for approximately 30 min. After decanting of the resulting solution, the procedure was repeated two more times. This way, a relatively pure dibenzohelicene **56** (according to TLC and NMR) was obtained in acceptable yield. As already discussed above, the problem of the separation of

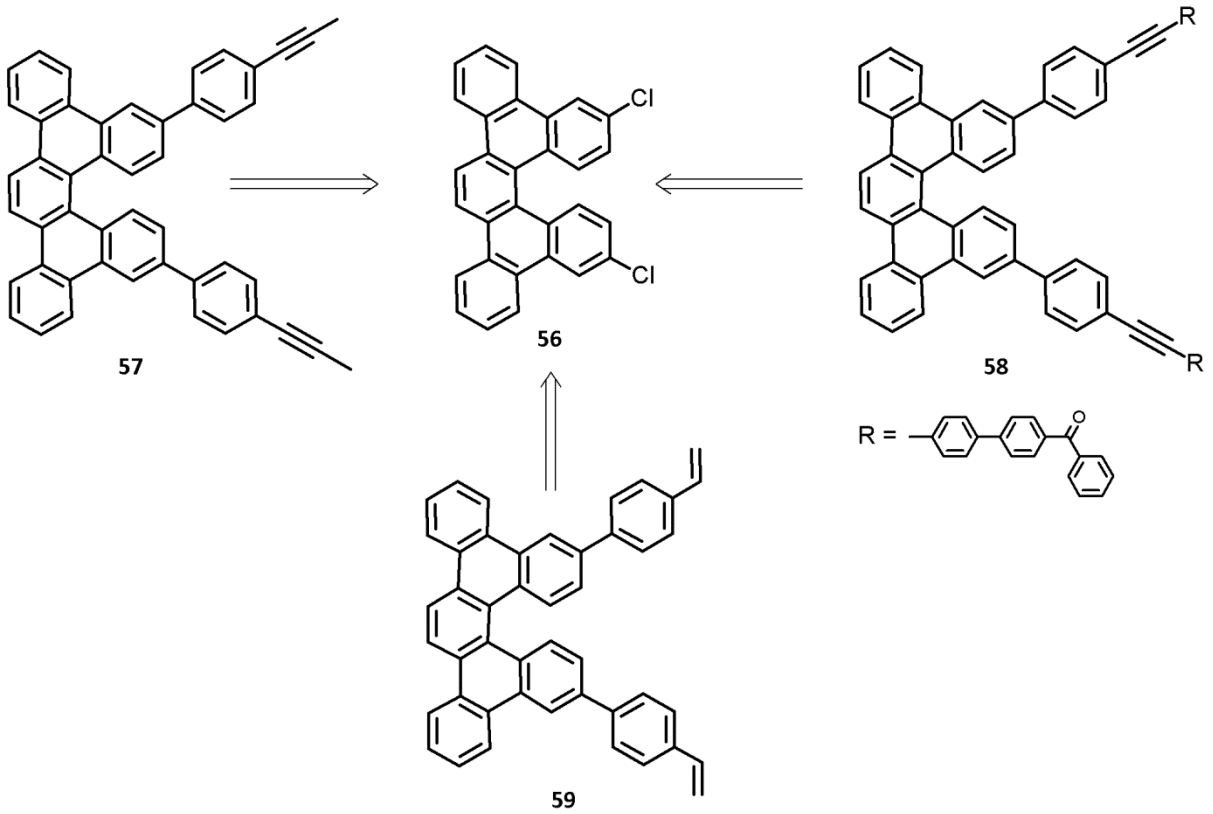
the product lies in its low solubility and consequent fixation on silica gel. Because the same problems with separation were encountered also later in the case of other compounds, it was necessary to find an eluent which would be both a good solvent for the product and lipophilic enough to achieve the separation on the column. After a survey of many solvent mixtures, the mixture of cyclohexane and toluene (7 : 2 in the case of **56**) was found to work very well and was applicable for the purification of many other conjugated compounds. Despite the substantially better results in purification, some portion of the product obviously could not be eluted even with the strongest eluents (a methanol – acetone mixture).

In order to investigate also the other catalytic systems, $CpCo(CO)_2$, commonly used for alkyne trimerization, was tried. According to previous results in our group, cyclotrimerization under classical Vollhardt's conditions at 140 °C promoted by halogen lamp irradiation utilized in the synthesis of other helicenes [30] did not work very well for dibenzohelicenes. Therefore, a flow reactor with a heated capillary was tried for the cycloisomerization with $CpCo(CO)_2$. The first experiment (10 mol % of $CpCo(CO)_2$, THF, 10 mg/mL, 240 °C, 1 mL/min) showed an excellent outcome according to TLC. No by-products were observed but there was not a full conversion of the starting triyne. Based on this initial trial, optimization of the reaction conditions was performed (estimated by TLC). The conditions were the same as in the case of the first experiment except for the temperature, which was varied. TLC analysis of the resulting reaction mixture showed that at 250 °C, the conversion was full with a minor content of by-products (which could be seen only in UV, the analysis with phosphomolybdic acid did not show any by-products). At 270 °C, the amount of by-products increased (but was still analyzable only by UV). In order to avoid the formation of any by-products, the catalyst loading was increased to 15 mol % and the temperature decreased to 240 °C. These conditions gave a completely pure product, while keeping the full conversion of the starting material. A large scale preparation was done by the optimized procedure giving the helicene derivative **56** in 79 %, which was the highest yield so far. The compound was purified by chromatography but the separation of the remaining catalyst was unfortunately impossible. The product was pure according to both TLC and ^{1}H-NMR but its color clearly indicated the traces of the catalyst. Therefore the sonication method had to be applied for the purification.

3.2 Synthesis of dibenzo[5]helicene derivatives

As discussed in Chapter 2, the dibenzohelicene moiety, contained in the proposed macrocycles, might be incorporated by means of metathesis. Thus, the corresponding starting compounds **57**, **58**, and **59** had to be synthesized. Their structure suggests the possible ways of the synthesis (Scheme 27, Scheme 22):

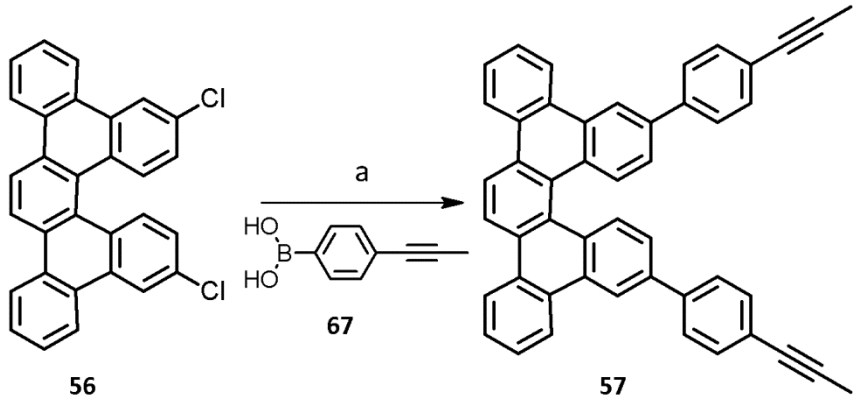
Scheme 27



Based on the previous results in our group, Suzuki-Miyaura coupling was chosen as a suitable reaction for this purpose. [38]

The synthesis of the dipropynyl derivative **57** was first attempted (Scheme 28). The initial experiment, following the published procedure, used palladium acetate (40 mol %) and DavePhos (80 mol %) as a catalytic system with cesium carbonate (5 eq.) in anhydrous dioxane. TLC showed only small conversion of the starting material after 18 h. Therefore, the catalyst loading was further increased to 80 mol % of palladium and 160 mol % of DavePhos which gave 32 % yield after 45 h of reaction time. However, the chromatography (cyclohexane : toluene = 7 : 2) of the crude product was very difficult due to a number of by-products and a total purification of **57** was never achieved by this protocol. The reason for this may have been a low quality of boronic acid **67** (Scheme 30) which tended to decompose at room temperature.

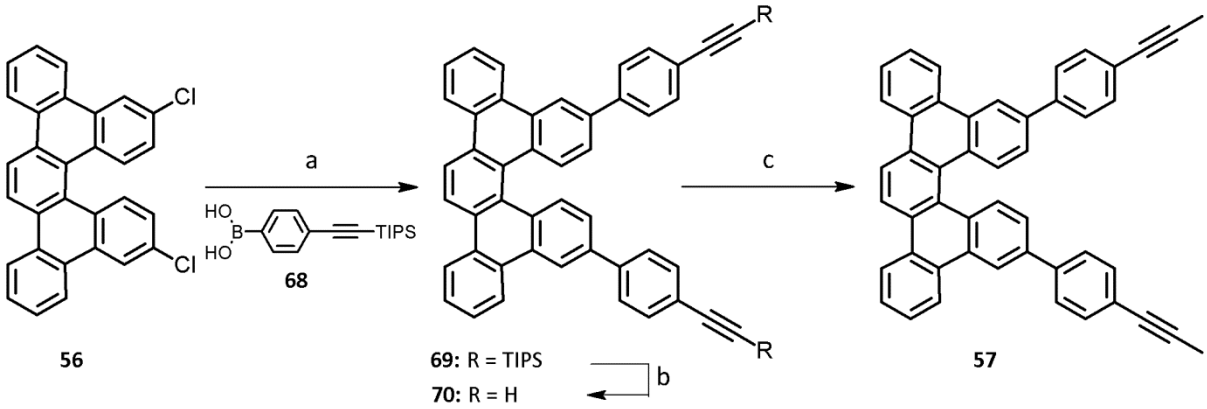
Scheme 28



a) **67** (5 eq.), $Pd(OAc)_2$ (80 mol %), DavePhos (160 mol %), Cs_2CO_3 (5 eq.), dioxane, 85 °C, 45 h, 32 %.

In order to search for a more efficient synthesis of **57**, a stepwise approach was tried. Instead of the direct introduction of the 4-propynylphenyl groups, triisopropylsilylethynylphenyl groups were introduced, followed by a deprotection step and subsequent methylation (Scheme 29).

Scheme 29



a) **68** (6 eq.), $Pd(OAc)_2$ (80 mol %), DavePhos (160 mol %), Cs_2CO_3 (5 eq.), dioxane, 85 °C, 16 h, 87 %.
b) TBAF (9 eq.), MeOH (25 eq.), THF, 20 °C, 1 h, 91 %.
c) 1. BuLi (3 eq.), THF, -40 °C, 10 min; 2. MeI (6 eq.), 20 °C, 2 h; 3. BuLi (3 eq.), THF, -40 °C, 10 min; 4. MeI (6 eq.), 20 °C, 2 h, 28 %.

The preparation of disilylated derivative **69** was first tried with 10 mol % of $Pd(OAc)_2$ leading to only small conversion, similarly as in the case of **57**. To achieve the full conversion of **56**, the catalyst loading was increased and the reaction was complete after 16 h, giving 87 %. Unlike the compound **57**, in this case a mixture of hexane and acetone (95 : 5) worked well for the separation of the product, in accordance with the present triisopropylsilyl groups which made the compound well soluble even in hexane.

Deprotection of **69**, performed with TBAF in anhydrous THF, led to polymerization and therefore, the modified procedure using methanol had to be applied again with excellent results. Unfortunately, the polymerization was also observed during the work-up.

To avoid this, the reaction mixture was quenched by addition of a further portion of methanol and subsequently filtered through a short pad of silica gel using chloroform with 1 % of triethylamine to remove the remaining TBAF. By this procedure, no decomposition or polymerization were observed (monitored by TLC).

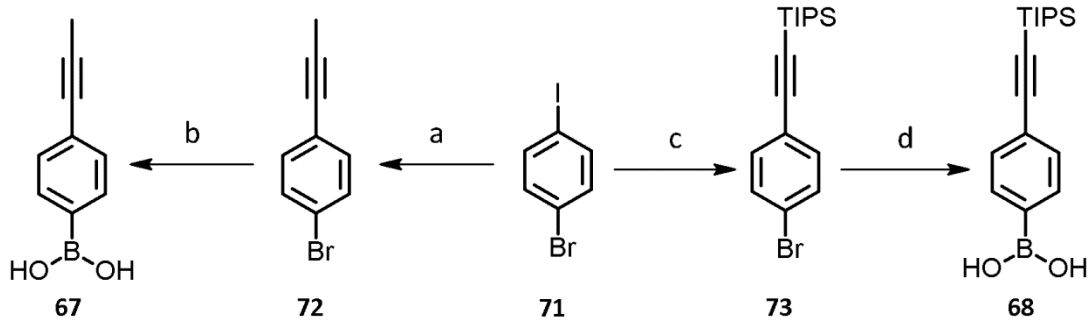
Although the final methylation seemed to be an easy task, the opposite was true. A treatment of desilylated diyne **70** with BuLi in THF at -20 °C followed by addition of MeI at 20 °C resulted in an extensive polymerization. When the temperature was kept at -40 °C, very little polymerization was observed and the analysis by TLC showed a spot to spot reaction. ^{1}H-NMR of the isolated compound showed that the obtained material actually contained a mixture of mono- and dimethylated products. The material was therefore submitted to the same reaction conditions again, this time finally giving the expected **57** in 28 %.

Before the discussion of the successful synthesis of **57**, the synthesis of boronic acids **67** and **68** will be described here (Scheme 30).

The preparation of **67** was based on the same protocol which was used in the case of **63**. [39] 4-Propynylbromobenzene **72** was prepared by Sonogashira reaction of 4-bromo-1-iodobenzene **71** and gaseous 1-propyne. Propyne was simply bubbled into the reaction mixture. Only a small amount of by-products was observed on TLC giving **71** in 93 % yield. The compound **72** was further borylated by a standard procedure, described earlier in the text, leading to 52 % yield of **67**. It should be noted that if stored in the air and at room temperature, the boronic acid decomposed with time and changed from a colorless to pink solid. The decomposition could also be seen on TLC.

The boronic acid **68** was prepared by the same reaction sequence. [40] Bromide **73** was prepared from **71** by Sonogashira coupling in 97 % yield. The standard borylation then afforded **68** in 81 % yield. Unlike **67**, this boronic acid was stable.

Scheme 30



67 **72** **71** **73** **68**

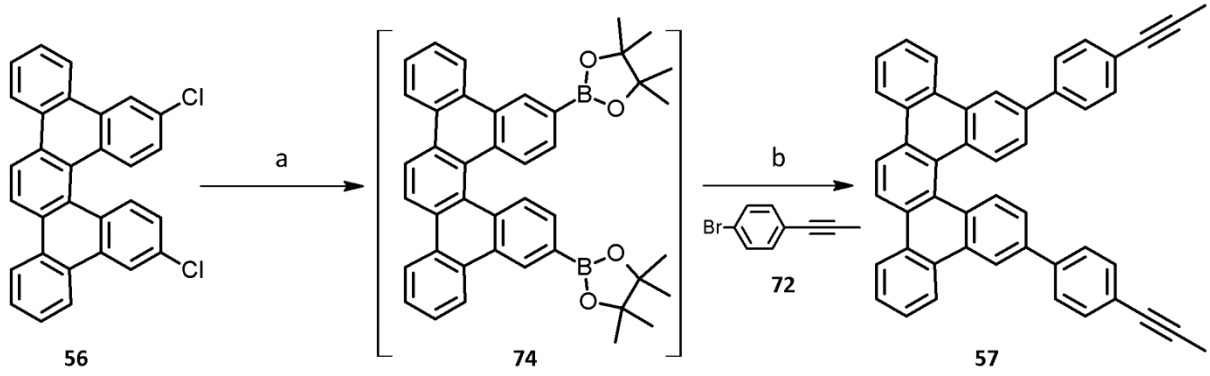
a) Bubbling with propyne, $Pd(PPh_3)_2Cl_2$ (2 mol %), CuI (4 mol %), DIPA, 20 °C, 3 h, 93 %.
b) 1. BuLi (1.3 eq.), THF, -78 °C, 50 min; 2. B(O-*i*-Pr)$_3$ (2 eq.), -78 °C, 1 h → 20 °C, 1 h; 3. 1 M HCl, 20 °C, 10 min, 52 %.
c) TIPSA (1.05 eq.), $Pd(PPh_3)_2Cl_2$ (2 mol %), CuI (4 mol %), DIPA, 0 °C → 20 °C, 20 h, 97 %.
d) 1. BuLi (1.3 eq.), THF, -78 °C, 30 min; 2. B(O-*i*-Pr)$_3$ (2 eq.), -78 °C, 50 min → 20 °C, 2 h; 3. 1 M HCl, 20 °C, 2 h, 81 %.

The ^{1}H-NMR analysis showed that all three boronic acids **63**, **67**, and **68**, if properly dried, contained a variable amount of its anhydrides. **63** consisted practically of only its anhydride, for instance. Recrystallization from an acetone-water mixture provided crystalline

63 with a ^{1}H-NMR spectrum showing no anhydride content. The anhydride content had no effect on the Suzuki-Miyaura reaction, however.

Since all the previous attempts at the synthesis of **57** gave poor yields along with an unsatisfactory purity, limiting its use for subsequent metathesis, another synthetic route was sought. Although the Suzuki-Miyaura reaction of aryl chlorides and boronic acids is well established today, the instability of the boronic acid **67** made the reaction inefficient. On the other hand, Suzuki-Miyaura reaction offers also the opposite means of 4-propynylphenyl groups introduction. Inspired by the Buchwald`s protocol for the palladium-catalyzed borylation of aryl chlorides and their subsequent reaction with arylhalides, [41] the preparation of dibenzo[5]helicene pinacol boronate **74** followed by the Suzuki-Miyaura reaction with a corresponding aryl bromide was considered as the last chance for a reliable synthesis of **57** (Scheme 31). First, preparation of **74** was attempted. The TLC analysis showed a complete conversion of the starting helicene within one hour but purification of the product by column chromatography caused its decomposition. ^{1}H-NMR analysis then proved the formation of **74** along with a minor content of decomposition products. Based on these findings, the one-pot procedure was employed. Helicene **56** was first treated with bis(pinacolato)diboron, catalyzed by $Pd(OAc)_2$, XPhos, and potassium acetate in boiling dioxane. After two hours, bromide **72** dissolved in dioxane was added, followed by the addition of 5 M aqueous K_3PO_4. After next two hours, the reaction was completed with a full conversion of helicene **56** to **57** in 74 % yield. Additionally, the purification by column chromatography using a cyclohexane – toluene mixture afforded a practically pure compound **57** with only minor impurities (according to TLC in UV). A completely pure product could be obtained by recrystallization from hot toluene.

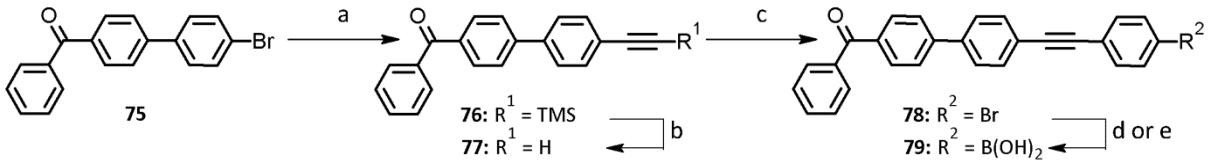
Scheme 31



a) $B_2(pin)_2$ (2.3 eq.), $Pd(OAc)_2$ (10 mol %), XPhos (40 mol %), AcOK (5.6 eq.), dioxane, reflux, 2.5 h.
b) **72** (4 eq.), 5 M K_3PO4 (aq.) (12.5 eq.), reflux, 2 h, 74 % (after 2 steps).

In order to prepare **58**, an approach similar to that described in Scheme 28 was considered at first. In accordance with this, the corresponding boronic acid **79** had to be synthesized. An attempt at the synthesis of this acid is depicted in Scheme 32.

Scheme 32



a) TMSA (1.5 eq.), $Pd(PPh_3)_4$ (2 mol %), CuI (4 mol %), DIPA : THF = 1 : 1 , 50 °C, 18 h, 99 %.
b) K_2CO_3 (3.2 eq.), MeOH : THF = 1 : 2.3, 20 °C, 2 h 45 min, 99 %.
c) 4-Bromo-1-iodobenzene (2 eq.), $Pd(PPh_3)_4$ (5 mol %), CuI (8.8 mol %), DIPA : toluene = 2 : 1, 20 °C, 2 h, 80 %.
d) 1. BuLi (1.3 eq.), THF, ca -120 °C, 2 h; 2. $B(O\text{-}i\text{-}Pr)_3$ (2 eq.), -120 °C, 1 h → 20 °C, 2 h; 3. 1 M HCl, 20 °C, 2 h, 0 %.
e) $Pd_2(dba)_3$, (20 mol %), Xphos (40 mol %), $B_2(pin)_2$ (3 eq.), AcOK (3 eq.), dioxane, 110 °C, a mixture of products.

In the first step, 4,4'-bromobenzoylbiphenyl **75** reacted with trimethylsilylacetylene in Sonogashira reaction to give the silylated derivative **76** in quantitative yield. [42] The following deprotection of **76** with K_2CO_3 in a methanol – tetrahydrofuran mixture gave quantitatively the terminal acetylene **77**. [42] A subsequent Sonogashira coupling, however, represented a problem during the first experiments. Although the conversion of the starting compound **77** was apparently 100 % after two hours (according to TLC), there were no major spots observed except that on the start, even if the TLC plate was developed with the strongest eluents (THF, chloroform). Fortunately, mass spectrometry of the evaporated reaction mixture proved the formation of the desired bromide **78**. It was therefore concluded, that the product must be very badly soluble and that it was filtered along with the precipitated diisopropylammonium iodide. To prove that conclusion, the experiment was repeated and the resulting mixture, diluted with a large amount of chloroform, was washed with a solution of ammonium chloride and water to make sure that all the ammonium salt was removed. This procedure worked well and, after evaporation of the solvent, the crude **78** was obtained. A subsequent recrystallization from boiling toluene gave the pure product.

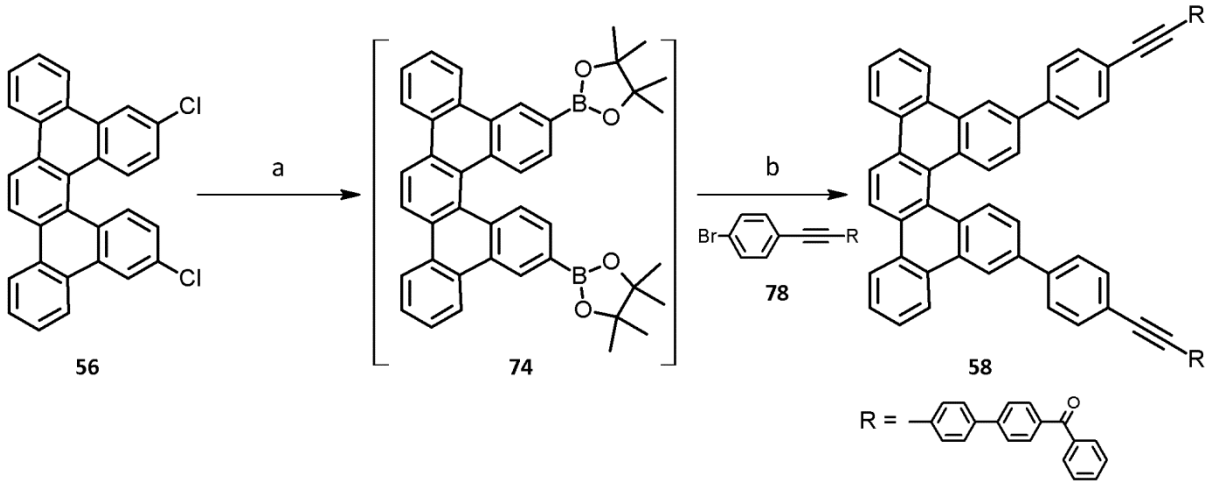
Since bromide **78** was very badly soluble in all common solvents at room temperature, it was obvious that its transformation to boronic acid **79** would be a problem. Nevertheless, two experiments were done. In the first one, a classical lithiation – borylation protocol, successfully employed in the preparations of **63**, **67**, and **68**, was applied. The only difference was that the reaction was performed between –130 and –110 °C (it was difficult to keep the temperature stable), hoping that the carbonyl group would not react at such a low temperature. A change of color was observed, similarly as in the cases of other lithiations, but the starting compound was still in a form of suspension. It was clear that this was not the right way to get **79**.

While the compound **78** was found inconvenient for reactions at low temperatures, this would not have to be true for reactions at high temperatures. It was previously observed that **78** dissolves moderately in boiling toluene as well as in chloroform. Buchwald`s borylation was therefore tried.[37] The compound **78** was heated with a catalyst in dioxane to 110 °C. The starting material dissolved in the solvent but the analysis of the reaction mixture by TLC showed that the solubility of the product is still very low. Several products could be seen on the TLC and therefore the material would be probably very difficult to purify. Since

in the meantime the preparation of **57** was successfully developed, the preparation of **79** or its pinacol ester was eventually abandoned.

The protocol for the synthesis of dipropynyl derivative **57** was applied for the synthesis of dimethanone **58**. The conditions were the same as in the case of **57**. The only difference was that bromide **78** was added as a solid due to its insolubility in cold dioxane. The reaction is summarized in Scheme 33.

Scheme 33

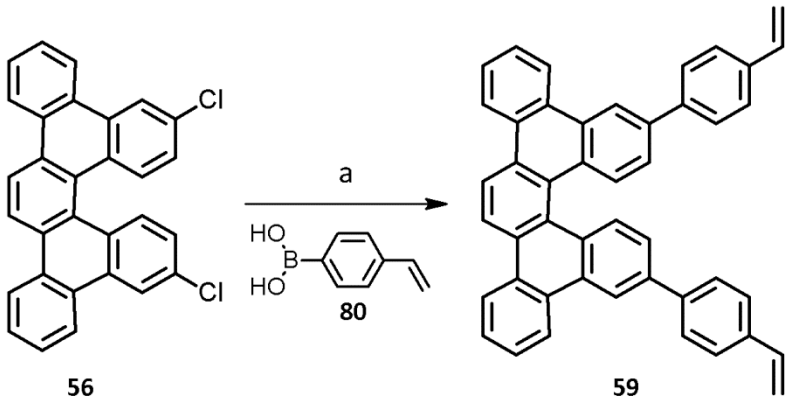


a) $B_2(pin)_2$ (2.4 eq.), $Pd(OAc)_2$ (10 mol %), XPhos (40 mol %), AcOK (5.6 eq.), dioxane, reflux, 1.5 h.
b) **78** (3 eq.), 5 M K_3PO_4 (aq.) (12.5 eq.), reflux, 1 h 40 min, mixture of products (after 2 steps).

The progress of the reaction was monitored by TLC, showing the complete consumption of pinacol boronate **74** after 1 h 40 min after the addition of **78**. Several compounds with strong green fluorescence were formed. The attempts at chromatographic separation of **58** failed and only few fractions containing a mixture of various compounds were obtained. The high resolution mass spectrometry analysis found dimethanone **58** in the first fraction. Unfortunately, further trials to purify the mixture by crystallization were also unsuccessful.

The divinyl compound **59**, necessary for the alkene metathesis, was prepared according to the Scheme 34.

Scheme 34



a) **80** (5 eq.), $Pd(OAc)_2$ (50 mol %), XPhos (100 mol %), K_3PO_4 (10 eq.), dioxane, water (2 eq.), reflux, 3 h, 56 %.

In the initial experiment, based on our previous research, [38] palladium acetate (80 mol %), DavePhos (160 mol %), and cesium carbonate (5 eq.) in anhydrous dioxane were tested. The reaction period was 16 hours at 85 °C and gave the yield only 41 % of **59**. After the introduction of the Buchwald`s procedure, however, the results were a way better. Cesium carbonate was replaced with potassium phosphate, water was added and the reaction temperature was increased to reflux. Under these conditions, the reaction not only proceeded comparably faster but it also gave less by-products and a better yield. Chromatography using cyclohexane-toluene mixture gave the product containing only small content of impurities (visible on TLC in UV). Recrystallization from hot toluene gave the pure **59** in 56 %.

As described in the previous paragraphs, the dipropynyl compound **57** and divinyl derivative **59** were successfully synthesized in good yields and excellent purity and could be used for the subsequent metathesis. Unfortunately, dimethanone **58** was difficult to purify and its preparation was therefore not successful although its formation was proved by the HR-MS analysis.

It could be clearly seen how the solubility of the compounds was influenced by its geometrical and chemical properties. The first solubility problem was encountered in the case of triyne **60** but the developed purification procedure made it possible to avoid a column chromatography. In the case of 3,16-dichlorodibenzo[5]helicene **56**, this was not possible. The subsequent introduction of 4-propynylphenyl and 4-vinylphenyl groups to the molecule substantially increased the solubility again, supposedly by a spatial extension of the molecule. In the case of dimethanone **58**, however, the large conjugated molecules did not separate well, despite being more soluble than dichlorohelicene **56**, for instance.

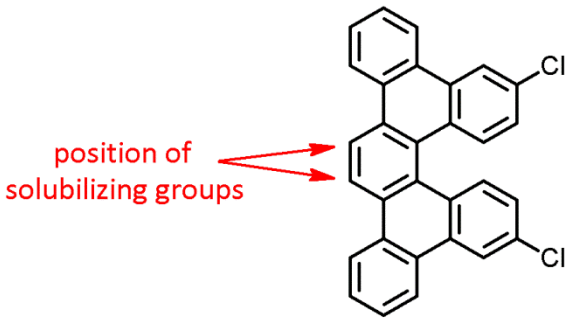
3.3 Solubilization of 3,16-dichlorodibenzo[5]helicene

As will be discussed in Chapter 3.4, alkene metathesis of the divinyl derivative **59** led to a mixture of highly insoluble oligomers, in which case any kind of separation was practically impossible. Although this could be expected, based on both already described solubility tendencies and published experimental results in the field of SPMs, it was important to try to prepare the molecules without any kind of substitution for the purposes

of a further research. As this turned out to be an unfeasible task, the preparation of solubilized DBH was started.

There were a few alternatives of the solubilizing group positioning. In order to make the introduction of the groups as easy as possible and also with respect to our future research plans, the groups were introduced as depicted in Figure 8.

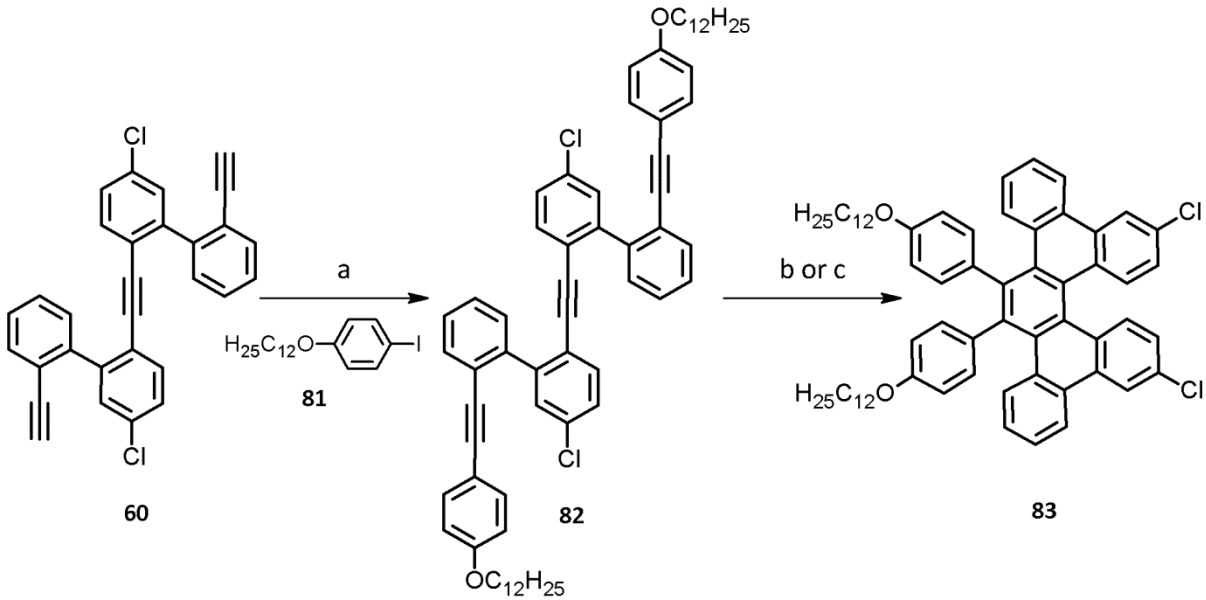
Figure 8



56

Since at that time a large amount of triyne **60** was at disposal, it was used as a starting compound for the introduction of solubilizing groups by reliable Sonogashira coupling with aryl iodides. As described in Chapter 1, long alkyl chains are commonly used to make the desired compound well soluble. Inspired by this fact, the first experiments focused on the preparation of the substituted helicene **83** (Scheme 35).

Scheme 35



a) **81** (2.2 eq.), $Pd(PPh_3)_2Cl_2$ (10 mol %), CuI (20 mol %), DIPA : toluene = 2 : 1, 50 °C, 1 h, 89 %.

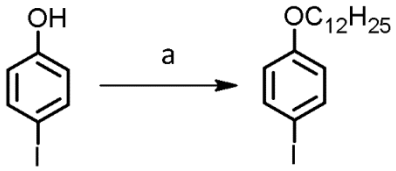
b) $Ni(cod)_2$ (100 mol %), PPh_3 (200 mol %), THF, 10 mg/mL, 20 °C, 15 min, a mixture of products.

c) $CpCo(CO)_2$ (15 mol %), THF, 10 mg/mL, flow reactor, 240 °C, 1 mL/min, a mixture of products.

The arylated triyne **82** was prepared by a smooth Sonogashira reaction of triyne **60** and iodide **81**. Contrary to expectation, the solubility of **82** was even lower than that of **60**, bringing about the same problems with purification. Although **82** was easy to chromatograph on a small scale (30 mg), the chromatography did not work well on the larger scale (800 mg). Since the product was not accompanied by any by-products, crystallization from 2-propanol was eventually used for the large scale preparation of this compound.

Aryl iodide **81** was synthesized according to Scheme 36. [43] In the initial experiment, the mixture was heated to 150 °C and an excess of 1-bromododecane was used, but due to the troublesome separation of the product from the alkyl bromide, the excess of phenol was used in the next experiment and the temperature was also decreased to 100 °C.

Scheme 36



84 **81**

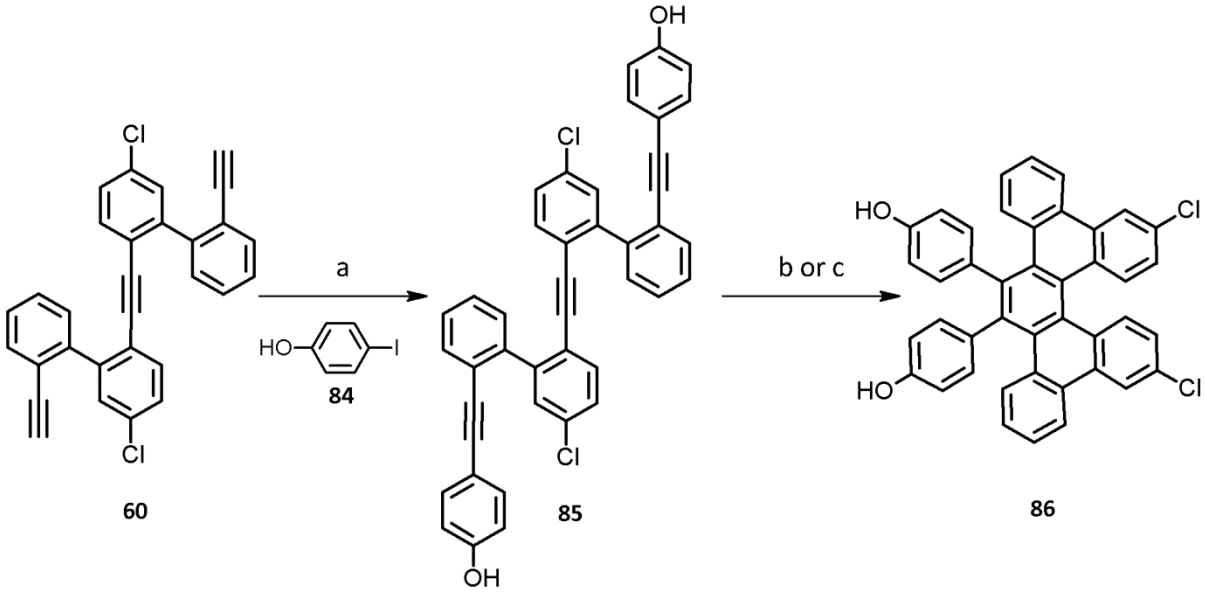
a) 1-Bromododecane (0.95 eq.), K_2CO_3 (2 eq.), NaI (5 mol %), DMF, 100 °C, 20 h, 82 %.

In the case of our previous trimerization of tolyl-substituted triynes similar to **82**, the reaction was much slower and gave poorer yields compared to triyne **60**. The first attempt to trimerize **82** was tried using $Ni(cod)_2 – PCy_3$ system as well as $Ni(cod)_2 – PPh_3$ (Scheme 35). The catalyst loading was 20, 60 or 100 mol %, with the double amount of phosphine. The TLC analysis of the reaction mixture showed the formation of two products and their ratio estimated by TLC varied only slowly with the catalytic system. The chromatographic separation was easy, using hexane : tetrahydrofuran = 200 : 1, and confirmed that the introduction of the alkyl chains strongly influenced the product`s solubility. The analysis by HR-MS proved the formation of the desired product. The analysis by ^{1}H-NMR, however, showed a mixture of compounds, despite a single-spot appearance on TLC.

Owing to these results, trimerization using 20 mol % of $CpCo(CO)_2$ in a flow reactor was tried (Scheme 35). Although the amount of the by-products was smaller (according to TLC), the ^{1}H-NMR analysis of the isolated product showed the same mixture again. In order to figure out the composition of the isolated material, both analytical and preparative HPLC were performed. However, the analysis showed only a single peak leading to the conclusion that the separation of the products is beyond reach of any method at disposal and the preparation of dodecyloxophenyl substituted helicene **83** was given up.

Instead, inspired by a successful preparation of hydroxyphenyl substituted dibenzohelicenes in our group, a different approach was chosen (Scheme 37). First, the hydroxy-substituted helicene could be prepared and then alkylated with dodecylbromide.

Scheme 37



a) **84** (2.05 eq.), $Pd(PPh_3)_2Cl_2$ (5 mol %), CuI (10 mol %), DIPA : toluene = 1 : 2, 40 °C, 2 h, 81 %.
b) $Ni(cod)_2$ (100 mol %), PPh_3 (200 mol %), THF, 10 mg/mL, 20 °C, 1 h, 17 %.
c) $CpCo(CO)_2$ (10 mol %), THF, 10 mg/mL, flow reactor, 250 °C, 1 mL/min, 0 %.

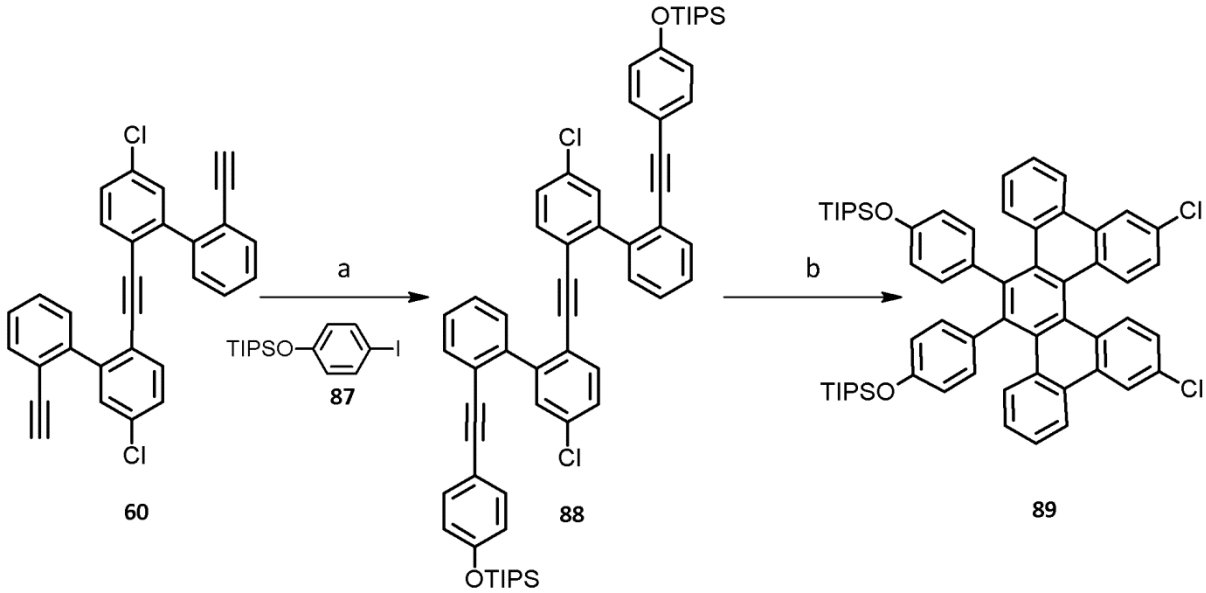
Hydroxyphenyl triyne **85** was prepared by a Sonogashira coupling of triyne **60** and 4-iodophenol **84**. The TLC analysis of the reaction mixture was complicated by the strong affinity of the hydroxy groups to silica gel in the presence of DIPA. For this reason, isopropanol had to be used in the eluent to weaken the interaction of the product with the sorbent. A strange behavior of **85** was also observed during the aqueous work-up. Since the pure compound dissolved well in chloroform, dichloromethane, ethyl acetate, benzene etc., benzene was used for work-up in the next experiment. In this case, however, the product did not dissolve either in organic or aqueous phase. In another experiment, when ethyl acetate was used, the product dissolved perfectly. It was found that this strange behavior disappears when the aqueous phase is gently acidified with 1 M HCl to transfer all DIPA into the aqueous phase. Chromatography of the compound was for obvious reasons impossible and crystallization also did not work well. Eventually, a sonication technique, applied in the case of dichlorohelicene **56,** turned out to be a successful purification method providing **85** in 81 % yield.

Trimerization of hydroxyphenyl triyne **85** was first performed with $Ni(cod)_2$ – PCy_3 system since it worked slightly better in the case of dodecyloxyphenyl triyne **82**. This time, however, no reaction was observed, supposedly due to a reaction of the hydroxyl groups with tricyclohexylphosphine. On the other hand, the $Ni(cod)_2$ – PPh_3 system worked and TLC showed the formation of two products. 20 mol % of $Ni(cod)_2$ was used first but the conversion of the starting compound was very low. In another experiment, 100 mol % gave a 17 % yield after the separation by chromatography. Trimerization was also tried with 10 mol % of $CpCo(CO)_2$ in a flow reactor but with no positive results.

Despite the previous success in the preparation of **86**, the obtained yield was unacceptable and therefore another approach was evaluated. Based on the observation that

compounds containing triisopropylsilyl groups were well soluble in non-polar solvents, a modified strategy was designed (Scheme 38).

Scheme 38



a) **87** (2.1 eq.), $Pd(PPh_3)_4$, (20 mol %), CuI (40 mol %), DIPA, 20 °C, 20 h, 91 %.
b) $Ni(cod)_2$ (100 mol %), PCy_3 (200 mol %), THF, 10 mg/mL, 20 °C, 20 h, 19 %.

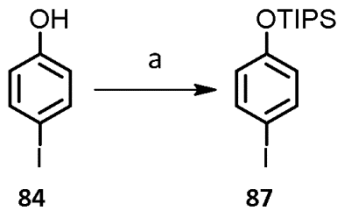
The preparation of the silylated hydroxyphenyl triyne **88** was carried out under different reaction conditions, compared to previous preparations of the dodecyloxyphenyl triyne **82** and hydroxyphenyl triyne **85**. The reaction catalyzed by $Pd(PPh_3)_2Cl_2$ led to the formation of a substantial amount of a by-product at either elevated or room temperature. On the basis of the previous experience with the preparation of dibromide **62**, bis(triphenylphosphine)palladium chloride was replaced with a high loading of $Pd(PPh_3)_4$ with pure DIPA as a solvent. A properly greased stopper was used instead of a septum and the reaction mixture was very carefully degassed. For purification, only crystallization from ethyl acetate was necessary to get totally pure **88** in excellent yield.

Trimerization of **88** was carried out using $Ni(cod)_2$ and either PPh_3 or PCy_3, slightly favoring PCy_3 according to TLC. The reaction proceeded with only one by-product formed and the conversion of the starting material was approximately 50 % (based on TLC) but it could be recovered by means of chromatography. The product was very easily chromatographed and the ^{1}H-NMR spectrum showed a high purity of the product. Catalysis by cobalt was not tried because at the time of the experiments, the flow reactor was out of order.

The poor outcomes of the reaction are difficult to explain. In our previous experiments, the trimerization of phenyl substituted triynes bearing donor substituents, similarly as **82**, **85**, and **88**, gave low yields or complex mixtures of products. Therefore the electron rich, sterically hindered substrates are probably not suitable substrates for the DBH synthesis.

To obtain **87**, iodophenol was treated with TIPSCl in the presence of imidazole in anhydrous dichloromethane. [(44)] The reaction was carried out at room temperature and was completed after 15 hours (Scheme 39).

Scheme 39



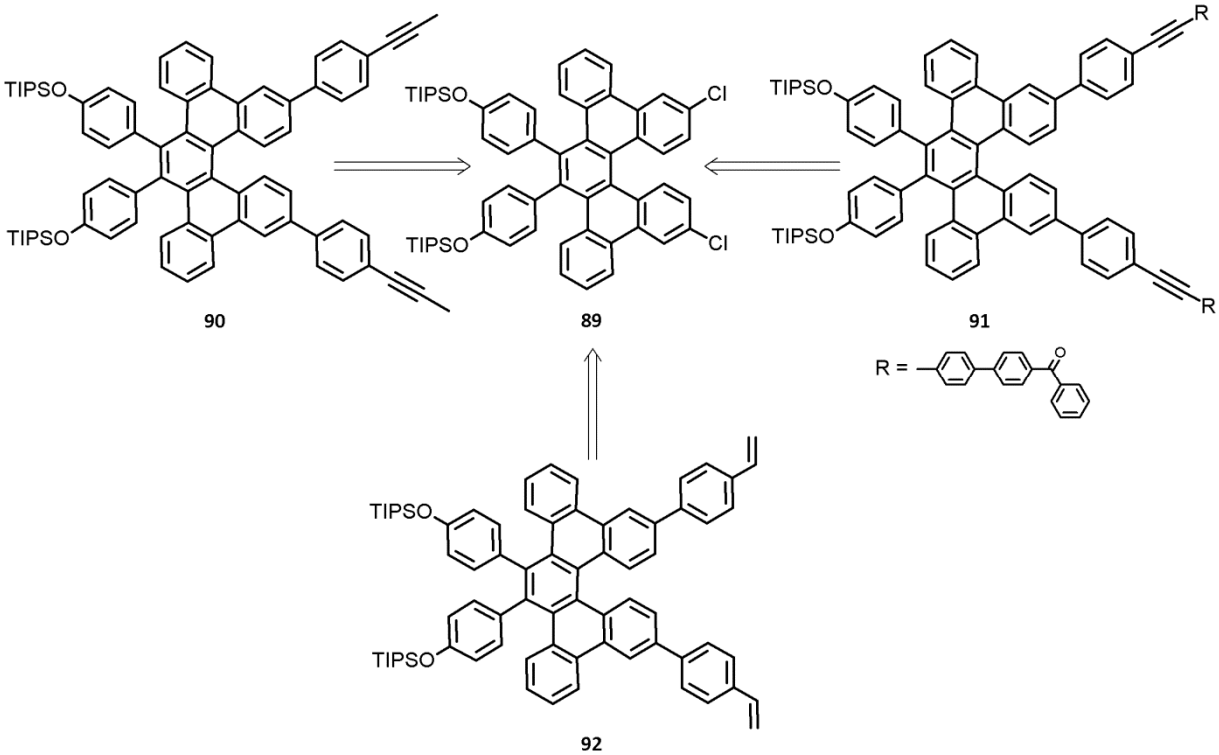
a) TIPSCl (1.2 eq.), imidazole (2.5 eq.), DCM, 20 °C, 15 h, 97 %.

Despite the low yields of products, two DBH derivatives were prepared. The triisopropylsiloxyphenyl triyne **88** was for obvious reasons chosen as a starting compound for further Suzuki-Miyaura reactions. Trimerization of dodecyloxyphenyl triyne **82** and triisopropylsiloxyphenyl triyne **88** is still a subject of ongoing research in order to identify the nature of the formed by-products and, if possible, to suggest an appropriate solution.

3.4 Synthesis of solubilized 3,16-dichlorodibenzo[5]helicene derivatives

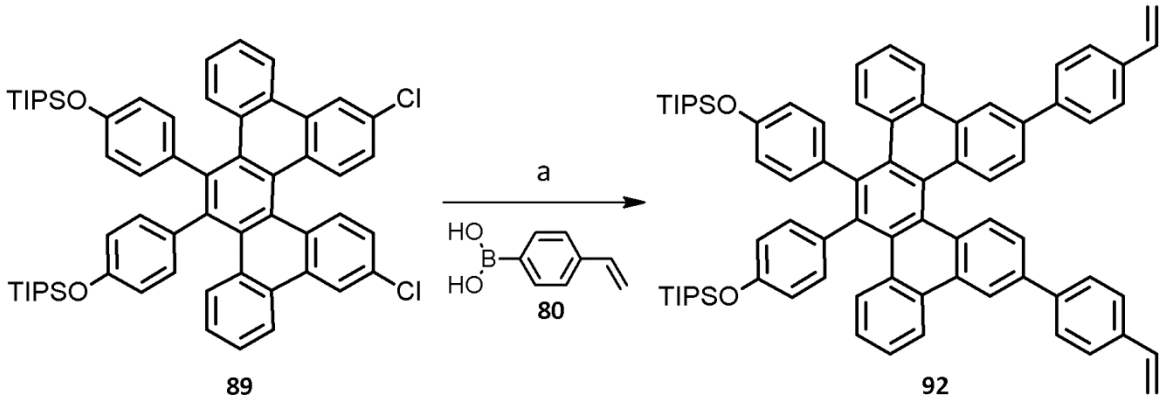
In analogy with the preparation of **57**, **58**, and **59**, the preparation of solubilized compounds **90**, **91**, and **92** was studied. Scheme 40 depicts their structure and way of their syntheses.

Scheme 40



The triisopropylsiloxy divinyl helicene **92** was prepared in 44 % yield using a methodology developed for the synthesis of the nonsubstituted diene **59**. The reaction conditions are shown in Scheme 41. As expected, the solubility of the prepared helicene **92** was excellent.

Scheme 41



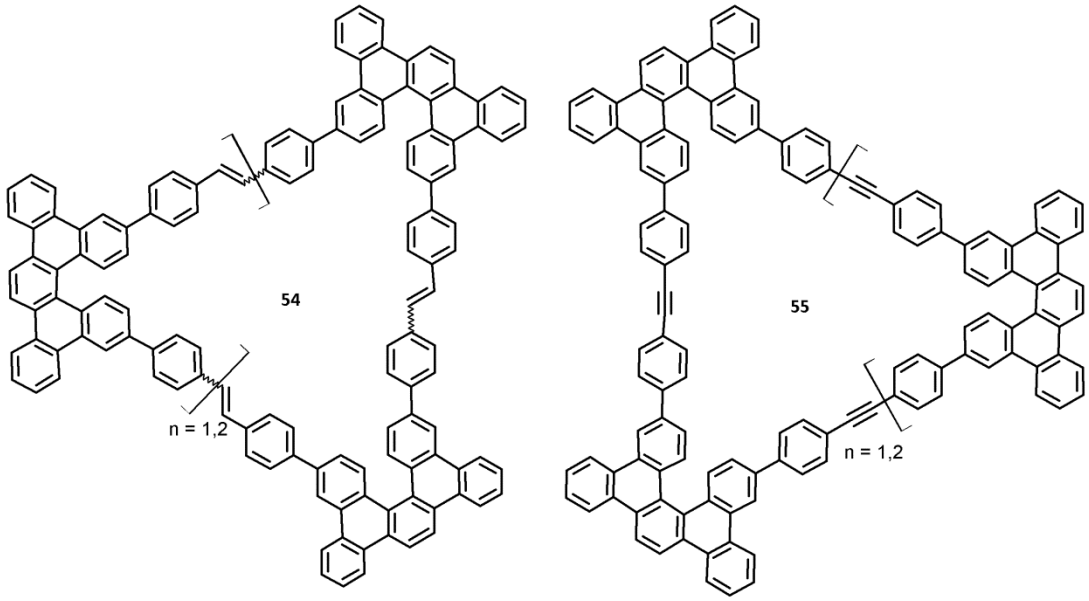
a) **80** (5 eq.), $Pd(OAc)_2$ (50 mol %), XPhos (100 mol %), 5 M K_3PO_4 (aq.) (15 eq.), dioxane, 95 °C, 10 h, 44 %.

The preparation of the solubilized helicenes **90** and **91** is a subject of the current research.

3.5 Metathesis of dibenzo[5]helicene derivatives

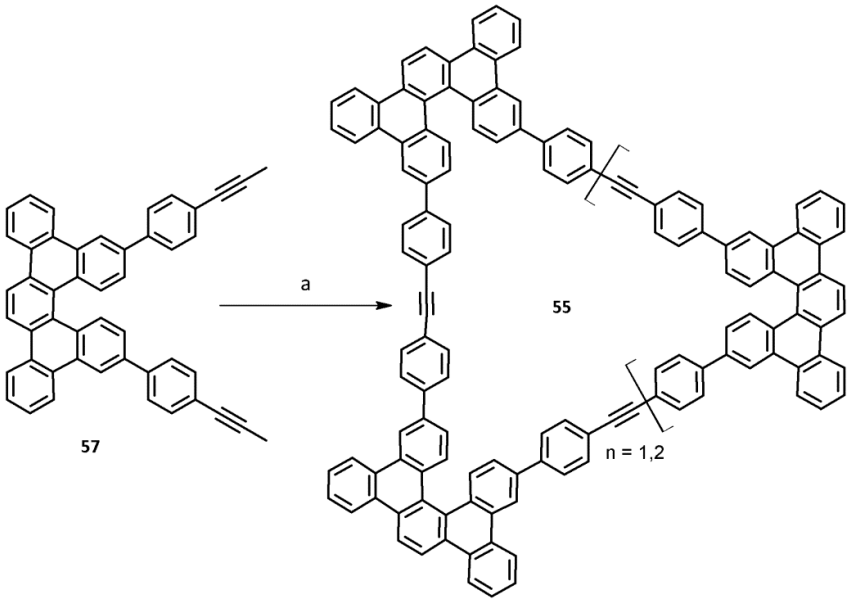
After the successful preparation of compounds **57** and **59**, their metathesis came in order. The target molecules are shown again in Figure 9.

Figure 9



As discussed in Chapter 1.3.4, there is a broad choice of possible alkyne metathesis catalysts. However, only few of them are commercially available. The nitride complex **35** (Scheme 12) was initially chosen as a catalyst. Based on the Fürstner`s protocol, [20] metathesis of dipropynyl helicene **57** was first performed to investigate if the trimer **55** (or the corresponding tetramer) would be formed (Scheme 42).

Scheme 42



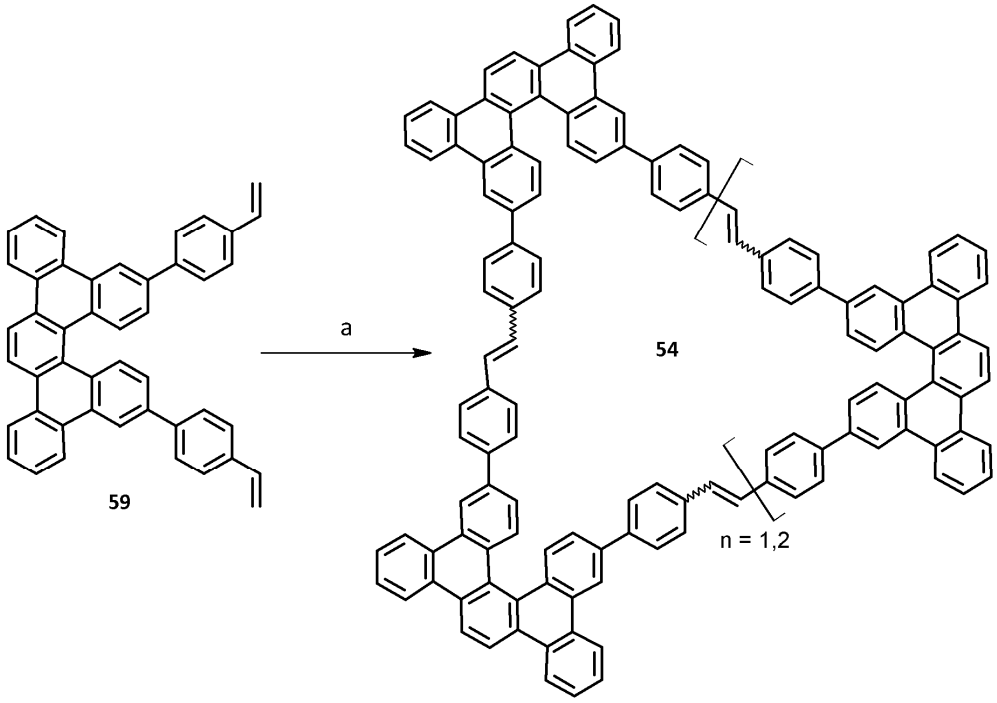
a) **35** (10 mol %), molecular sieves 5 Å (1000 mg/mmol of **57**), toluene, 80 °C, 18 h, 0 %.

Unfortunately, TLC analysis did not show any changes in the composition of the reaction mixture although the original procedure was carefully followed. Based on these observations, the quality of the catalyst was examined by ^{1}H-NMR, revealing its decomposition.

Because of the problems with the quality of the commercially available catalyst, it had to be prepared. [19] That, on the other hand, opened the way to the new generation of Fürstner`s catalyst **32** (Figure 4) since both **32** and **35** can be prepared from the same intermediate. The preparation of the catalyst is still in progress.

Scheme 45 shows the preparation of the macrocycle **54**. On the basis of the published preparation of arylenevinylene macrocycles, [14] the 2nd generation Grubb`s catalyst was used for the purpose of the synthesis.

Scheme 45



a) 2nd generation Grubb`s catalyst (10 mol %), 1,2,4-trichlorobenzene, 35 °C, 17 h, an unknown yield.

Shortly after the addition of divinyl helicene **59** to the catalyst solution, a dark green precipitate formed. The TLC analysis after 17 hours showed total conversion of **59**, however, all the material remained at the start of the TLC plate even if eluted by strong eluents (chloroform, tetrahydrofuran, toluene). The mixture was analyzed by MALDI-MS (Figure 11) revealing the formation of the linear dimer **98** (1136.4248 m/z) (Figure 10), trimer **98** (1692.6345 m/z) and a weak signal of the cyclic trimer **54** (1662.5830 m/z) (Figure 11 and 12).

Figure 10

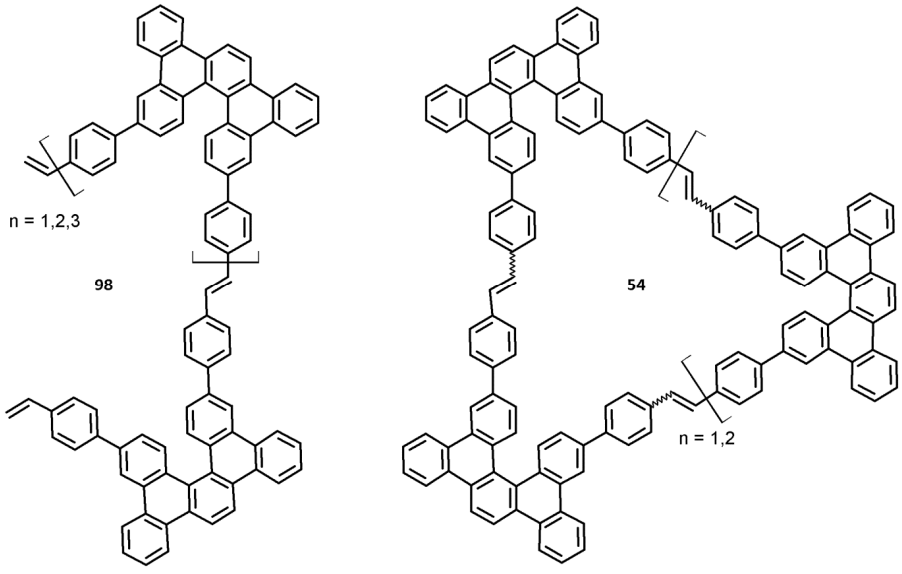
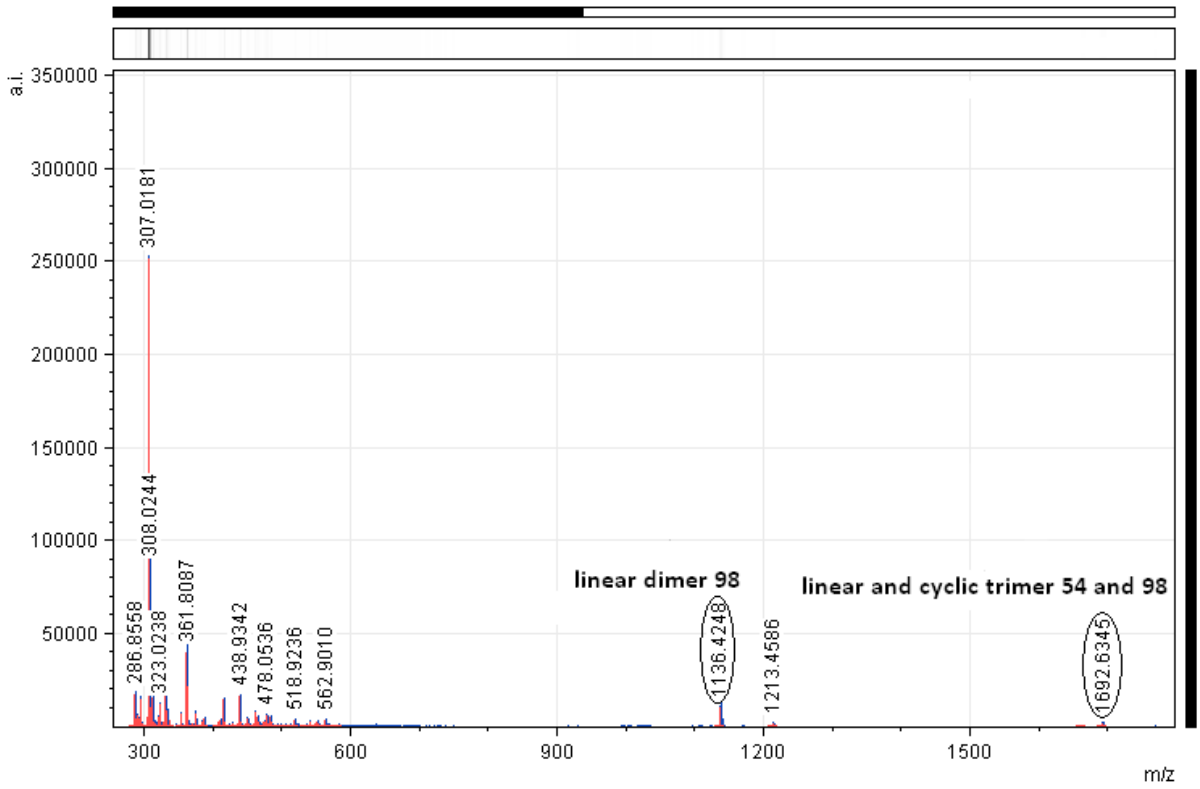
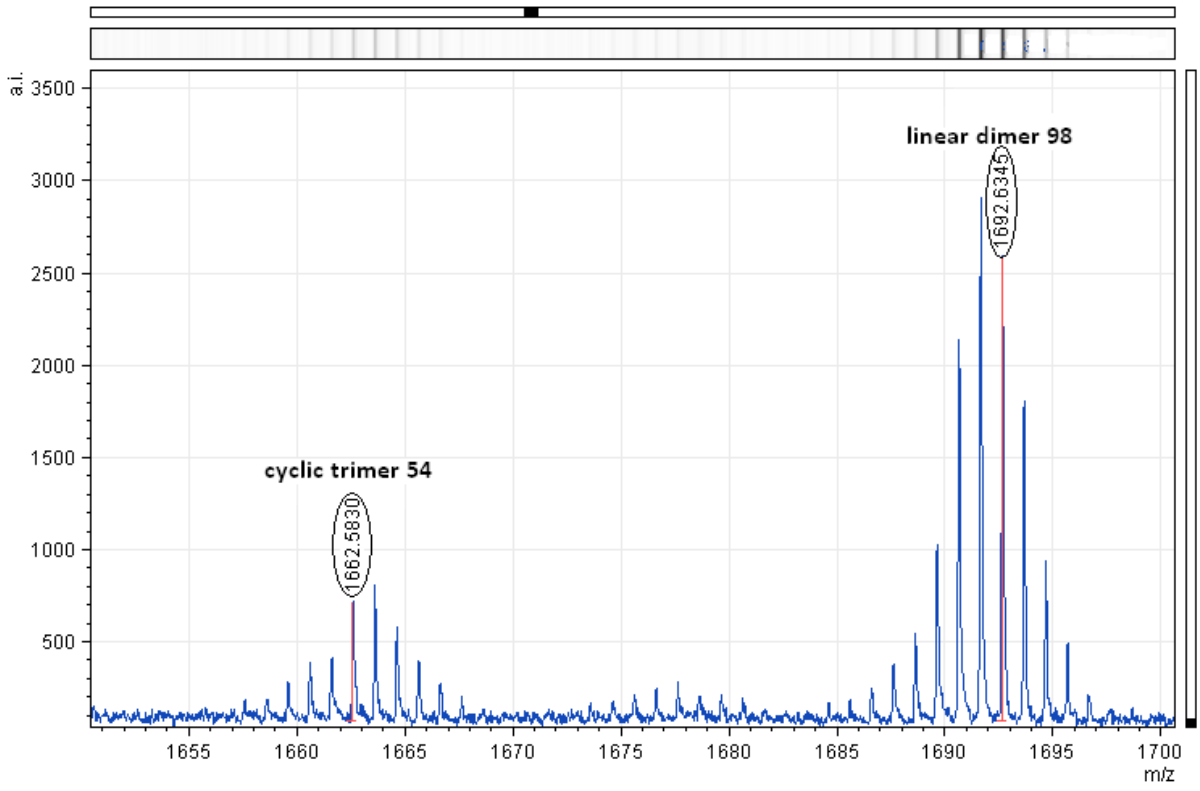


Figure11



The zoomed spectrum of the desired macrocycle **54** is shown in Figure 12.

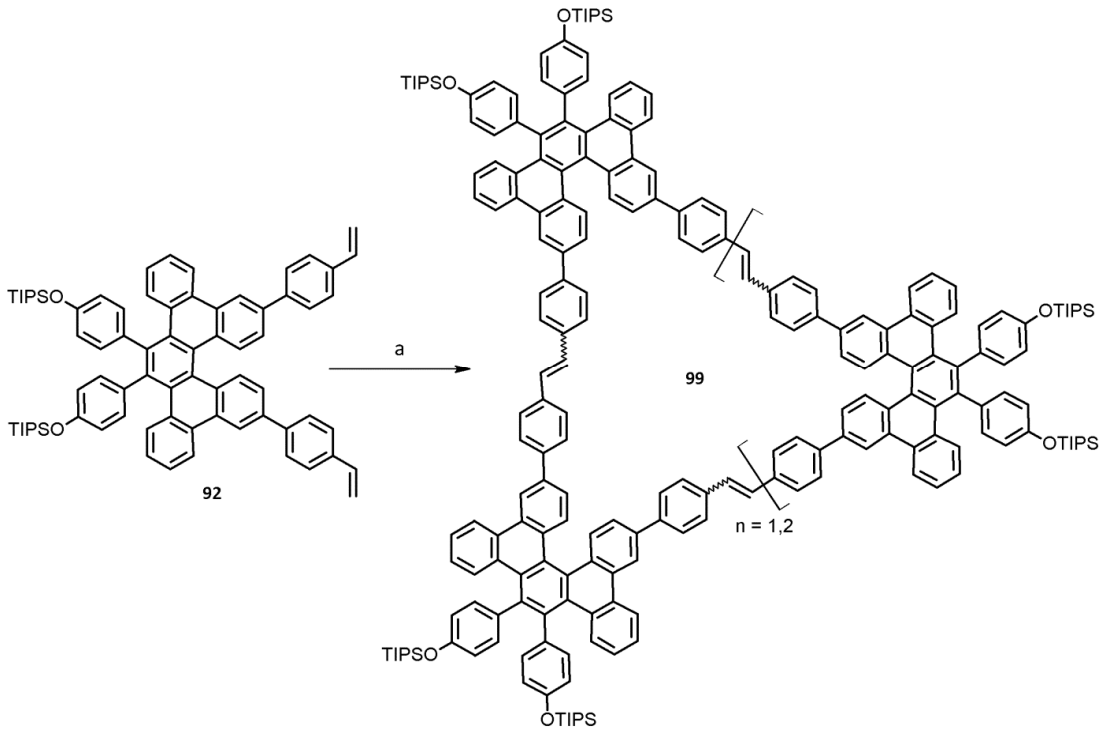
Figure 12



Due to the insolubility of the obtained material, the separation of the desired trimer **54**, as well as the liner oligomers, was unfeasible. Furthermore, it follows from the discussion in Chapters 1.3.5 and 1.3.6 that the solubility of the metathetic products is crucial for the thermodynamic control of the reaction. For this reason, the preparation of the solubilized DBH derivatives was started (Chapter 3.3).

After the successful preparation of the solubilized divinyl helicene **92**, it was subjected to the similar reaction conditions as the divinyl helicene **59** (only DCM instead of 1,2,4-trichlorobenzene was used) shortly leading to a green-yellow fluorescent solution (Scheme 46). The TLC analysis after 20 h showed that some part of the material was stuck at the start, while a smaller portion formed two badly separated spots. The mixture was separated by a preparative TLC and the individual fractions were analyzed by mass spectrometry.

Scheme 46



a) 2nd generation Grubb`s catalyst (10 mol %), DCM, 35 °C, 20 h, an unknown yield.

The possible products are depicted in Figure 13 while the mass spectrum is shown in Figures 14 and 15. The MALDI analysis not only proved the formation of the desired trimeric compound **99**, but it also showed the distribution of the linear oligomers **100**, as well as the monomer **92** (Figure 14 and 15). The monoisotopic mass 1078.5540 m/z corresponds to the unreacted monomer **92**, the mass 2129.0768 m/z corresponds to the linear dimer **100**, the mass 3151.5682 m/z to the cyclic trimer and the mass 3179.5995 m/z to the linear trimer **100**. Although MALDI, as any other MS method, is not designed to quantify the content of the measured compounds, it can be approximately concluded that the amount of the trimeric compounds is of the same order. The presence of the unreacted monomer **92** also

suggests that a more efficient method of ethylene removal (which is formed as a by-product of the reaction) might substantially increase the conversion of the starting material.

Figure 13

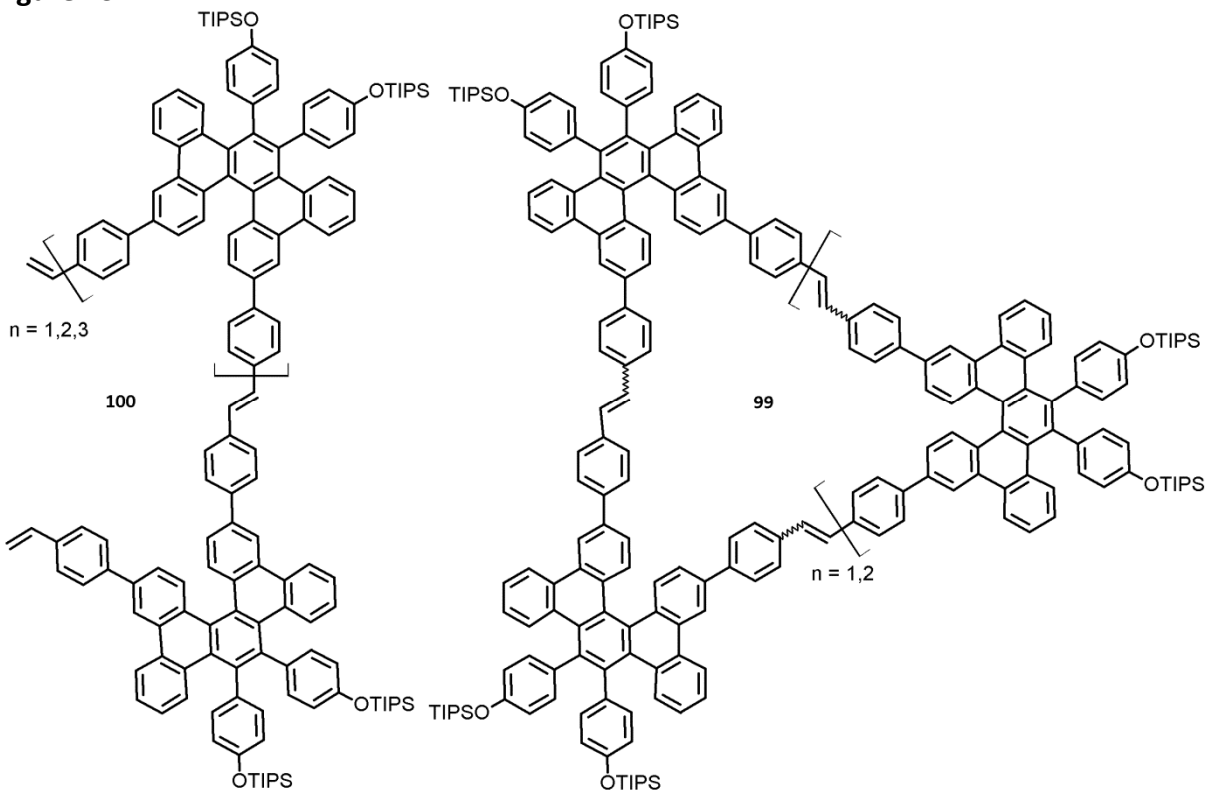


Figure 14

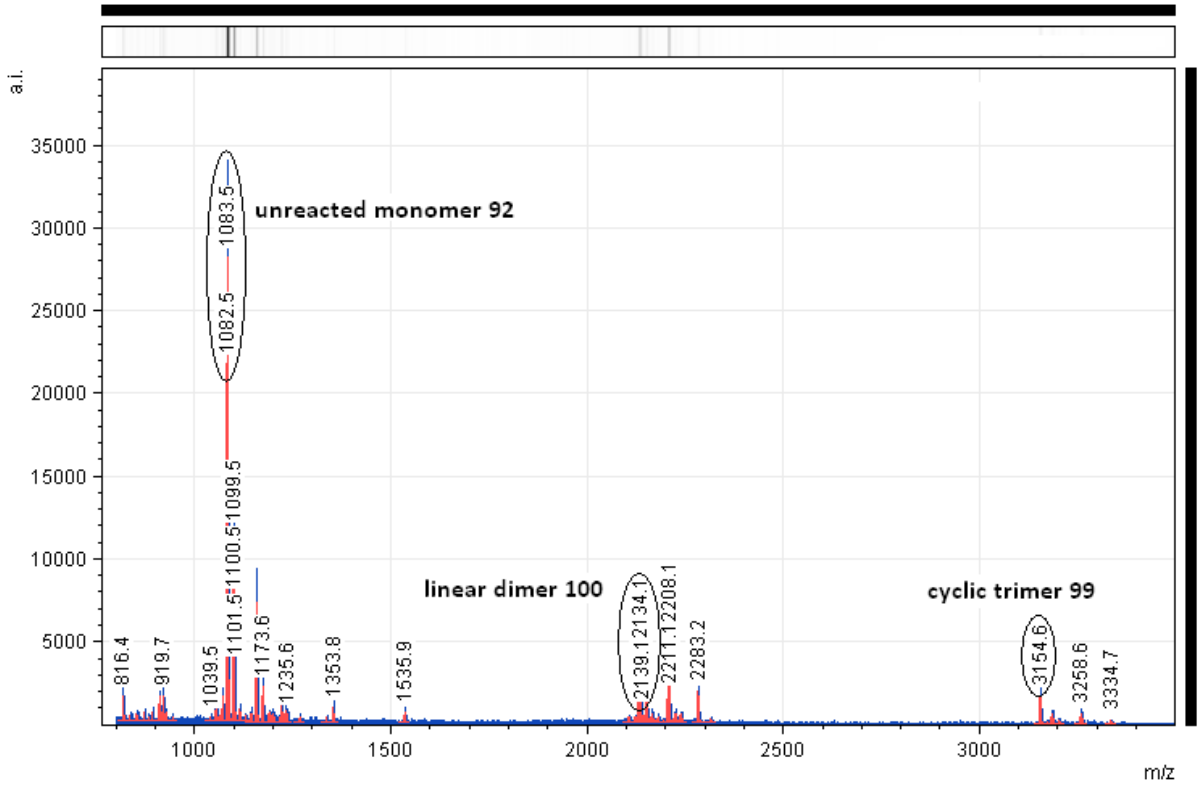
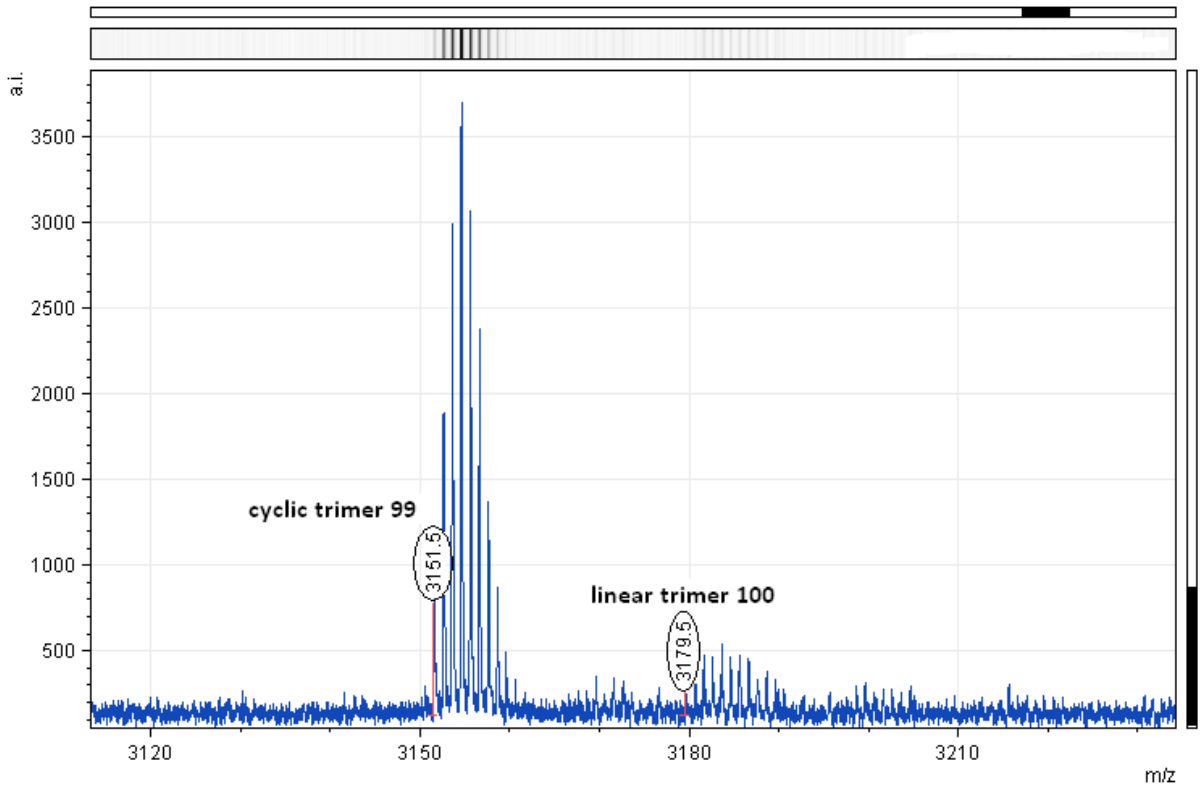


Figure 15



Since the preparative TLC was able to separate the products at least partially, the possibility of an efficient HPLC separation of the desired products is still open and under investigation.

4. Conclusion and outlooks

3,16-Dichlorodibenzo[5]helicene **56** was successfully synthesized in good yield as well as its propynyl and divinyl derivatives **57** and **59**. Although the dimethanone compound **58** was formed (proved by HR-MS) during its synthesis, it was impossible to separate it from the reaction mixture and the preparation of this compound was therefore unsuccessful.

In many cases, solubility problems were encountered, making the separation of the target compounds difficult or even impossible. Although the suitable chromatography conditions were finally found in some cases, the introduction of solubilizing groups was studied to overcome this obstacle. Dodecyloxyphenyl groups, first chosen for this purpose, turned out to be incompatible with the trimerization conditions, however. On the other hand, hydroxyphenyl- as well as triisopropylsiloxyphenyl-substituted helicenes were prepared, despite lower yields of their synthesis. The solubilization concept proved to work well, making the separation of the desired compounds more efficient.

The alkene metathesis of **59** afforded an insoluble oligomeric product and only minor amount of the target arylenevinylene macrocycle **54**. The solubilized divinyl helicene **92** was subjected to the similar metathesis conditions. The product was perfectly soluble in common polar solvents and MALDI-MS showed substantially bigger content of the desired macrocycle **99**. However, it also showed substantial amount of the unreacted monomer **92**.

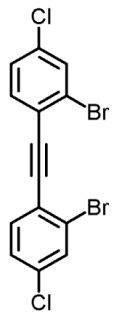
The alkyne metathesis was tried but due to the low quality of the commercial catalyst, the synthesis of the air stable precatalyst **32** was started.

Based on the discussed findings, the next steps will be the preparation of the alkyne metathesis catalyst and its application in metathesis of the dipropynyl compound **57** and the solubilized derivatives **90** and **91**. The study on trimerization of solubilized triynes will be continued and triynes with electron-withdrawing substituents will be explored. If this approach is found to be unfeasible, the solubilizing groups will be placed in different positions of helicene, thus leaving the free terminal acetylenes for the trimerization (as in the case of **56**).

5. Experimental part

General: Unless otherwise noted, all reactions were carried out under argon in an oven-dried glassware. The solvents used for reactions were distilled from drying agents indicated and were transferred under argon: THF, 1,4-dioxane (Na/benzophenone); toluene (Na); DIPA, DCM (CaH_2). Chromatography was performed either classically or using HPFC Biotage Isolera One system, using Fluka silica gel 60 (0.040 – 0.063 mm) or Merck silica gel 60 (0,015-0,040 mm), if noted. For TLC analysis, Merck silica gel 60 F_{254}, or Merck silica gel 60 RP-18 F_{254} -coated aluminium sheets were used. The spots were detected both in UV and by the solution of $Ce(SO_4)_2.4\ H_2O$ (1 %) and $H_3P(Mo_3O_{10})_4$ (2 %) in 10 % sulfuric acid (10 %). All starting materials were used as purchased (Sigma Aldrich, Alfa Aesar, Strem Chemicals), unless otherwise indicated. The standard EI spectra were recorded in the positive ion mode. The ^{1}H-NMR spectra were measured at 400.13 or 600.13 MHz, the ^{13}C-NMR spectra at 100.61 or 150.90 MHz in $CDCl_3$, $(CD_3)_2CO$ or CD_2Cl_2, with tetramethylsilane or solvent peaks as an internal standard. The chemical shifts are given in δ-scale, coupling constants J are given in Hz. The IR spectra were measured in $CHCl_3$ or in KBr tablet in the range 400 – 3800 cm^{-1} using Nicolet 6700 system. GC-MS analysis was performed on Agilent 5975C series with DB-5MS (JW & Scientific) column at temperature gradient from 60 °C to 320 °C. The spray temperature was 320 °C with 10 : 1 split. The column length was 30 m, internal diameter was 0.25 mm, and film thickness was 0.25 µm. Helium was used as carrying gas at 1 mL/min flow rate. The MS used quadrupole analyzer which operated at 150 °C. The EI mass spectra were determined at an ionizing voltage of 70 eV, the m/z values are given along with their relative intensities (%). The TOF EI spectra were measured using an orthogonal acceleration time-of-flight mass spectrometer GCT Premier (Waters). The sample was dissolved in chloroform, loaded into a quartz cup of the direct probe and inserted into the ion source. The source temperature was 220 °C. For exact mass measurement, the spectra were internally calibrated using perfluorotri-*n*-butylamine (Heptacosa). The ESI mass spectra were recorded using ZQ micromass mass spectrometer (Waters) equipped with an ESCi multi-mode ion source and controlled by MassLynx software. Methanol was used as solvent. Accurate mass measurements were obtained by the EI, TOF EI, CI or APCI MS. The CI mass spectra were determined at an ionizing voltage of 70 eV and recorded using CTC Premiere (Waters) with TOF analyzer. The source temperature was 130 °C and the carrying gas was methane.

1,1'-Ethyne-1,2-diylbis(2-bromo-4-chlorobenzene) (62)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with 2-bromo-4-chloro-1-iodobenzene (7.03 g, 8.44 mmol), $Pd(PPh_3)_4$ (2.56 g, 2.21 mmol, 10 mol %), and CuI (0.84 g, 4.42 mmol, 20 mol %), sealed with a greased stopper and backfilled with argon. Diisopropylamine was added via syringe (336 mL). The mixture was degassed three times using a freeze-thaw-pump cycle and left sealed to warm to room temperature under vacuum. Then, the Schlenk flask with a closed stopcock was connected to a balloon filled with acetylene. The connecting pipes were evacuated and refilled with acetylene from the balloon, the Schlenk flask was briefly connected to the balloon (2 s) and the stopcock was closed again. The mixture was heated to 55 °C for 18 h. After this period, the white precipitate was filtered off and the solvent was removed *in vacuo*. The obtained yellowish substance was subsequently chromatographed on silica gel (hexane) providing a white crystalline compound (3.64 g, 82 %).[1]

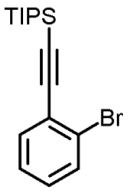
^{1}H NMR (400 MHz, $CDCl_3$): 7.30 (1 H, dd, *J* = 8.4, 2.1), 7.52 (1 H, d, *J* = 8.3), 7.65 (1 H, d, *J* = 2.0).

^{13}C NMR (100 MHz, $CDCl_3$): 92.17 (s), 123.47 (s), 125.93 (s), 127.57 (s), 132.42 (s), 134.07 (s), 135.17 (s).

IR ($CHCl_3$): 3092 vw, 3066 vw, 2224 vvw, 1585, 1578 vw, 1545 w, 1483 vs, 1461 w, 1378 w, 1366 w, 1262 w, 1138 w, 1098 s, 1047 m, 1042 w, 871 m, 860 w, 823 m, 714 w, 653 vw, 564 w, 537 w, 445 w.

TOF HR CI MS: calcd. for $C_{14}H_7Cl_2Br_2$ 402.8292, found 402.8298.

[(2-Bromophenyl)ethynyl][tris(1-methylethyl)]silane (66)

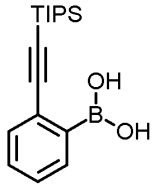


An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with 2-bromo-1-iodobenzene (20.0 g, 70.7 mmol), $Pd(PPh_3)_2Cl_2$ (0.992 g, 1.41 mmol, 2 mol %), and CuI (0.539 g, 2.83 mmol, 4 mol %), capped with a septum and then evacuated and backfilled with argon. Diisopropylamine was added via syringe (350 mL). The septum was replaced with a glass stopper and the mixture was degassed three times using a freeze-thaw-pump cycle. The Schlenk flask was immersed in a water/ice bath, the stopper was replaced with a septum again and TIPSA (16.6 mL, 74.2 mmol, 1.05 eq.) was added via syringe. The mixture was stirred at 0 °C for ca 2 h and then left stirred at room temperature? for 18 h. Then, the white precipitate was filtered off and the solvent was removed *in vacuo*. The obtained yellowish oil was purified by flash chromatography on silica gel (hexane) providing a colorless oil (23.9 g, 99 %).

[1] The stopcock and the stopper had to be properly greased to avoid penetration of the air into the tube. During the degassing process, all solvent had to freeze. The amount of solvent was V(DIPA) = V(Schl.tube+stir. bar) – V(C_2H_2, = 1 atm, T = 298 K). The acetylene had to be added quickly (within 1 – 2 s) to avoid additional dissolving in the mixture. The yield substantially depended on following this procedure!

The measured ^{1}H-NMR spectrum was in agreement with the published data. [39]

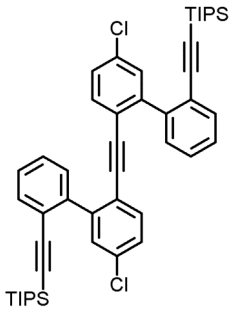
(2-{[Tris(1-methylethyl)silyl]ethynyl}phenyl)boronic acid (63)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with **66** (42.9 g, 127 mmol), THF (860 mL) was added and the resulting solution was cooled to –78 °C in an acetone/CO_2 bath. The solution of *n*-BuLi (1.6 M in hexanes, 103 mL, 165 mmol, 1.3 eq.) was added slowly. The resulting yellow-orange mixture was stirred for 75 min and then triisopropyl borate (15.3 mL, 66.7 mmol, 2.5 eq.)[2] was added in portions. The color of the mixture turned from yellow to colorless. The mixture was allowed to reach room temperature, while the color turned gradually to orange again. The solution was stirred for additional 20 h. Then, 1 M HCl (100 mL) was added and the mixture was stirred for 3 h. The mixture was extracted with diethyl ether (3 x 150 mL), the combined extracts were washed with brine (1 x) and dried over anhydrous $MgSO_4$. The solvents were removed by rotavap and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 95 : 5 to 50 : 50). **63** was obtained as a colorless oil which solidified in a fridge (35.5 g, 92 %).

The measured ^{1}H-NMR spectrum was in agreement with the published data. [39]

{Ethyne-1,2-diylbis[(5'-chlorobiphenyl-2',2-diyl)ethyne-2,1-diyl]}bis[tris(1-methylethyl)-silane] (64)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with **62** (3.66 g, 10.9 mmol), $Pd(PPh_3)_2Cl_2$ (0.762 g, 1.08 mmol, 10 mol %), and K_2CO_3 (5.10 g, 36.9 mmol, 3.4 eq.), capped with a rubber septum, evacuated and backfilled with argon. 1-Propanol (100 mL) and water (26 mL) were added. Another Schlenk flask was charged with **63** (9.84 g, 32.6 mmol, 3.0 eq.) and toluene (100 mL) was added. Both mixtures were vigorously bubbled with argon for ca 10 min, then the solution of **63** was added via cannula to the flask containing **62** and the resulting mixture was bubbled with argon for another 15 min. The mixture was then vigorously stirred and refluxed (120 °C oil bath) for 3 h. The resulting black solution was filtered through a short pad of silica (DCM) and then purified by chromatography (hexane-toluene 100 : 0 to 20 : 1). The compound **64** was obtained in the form of brown resin (6.17 g, 75 %).

^{1}H NMR (400 MHz, $CDCl_3$): 7.09 (1 H, d, *J* = 8.3 Hz), 7.17 (1 H, dd, *J* = 8.3, 2.2), 7.21 – 7.24 (1 H, m), 7.23 – 7.36 (2 H, m), 7.40 (1 H, d, *J* = 2.0 Hz), 7.58 – 7.54 (1 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): 11.18, 18.50, 91.59, 94.52, 105.43, 121.13, 122.73, 127.33, 127.58, 127.61, 129.88, 130.30, 132.94, 133.31, 133.50, 141.66, 144.04.

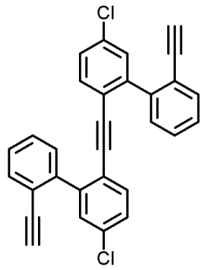
IR ($CHCl_3$): 3094 vw, 3065 w, 3065 w, 2959 s, 2944 vs, 2926 s, 2892 s, 2866 vs, 1598 w, 1587 w, 1568 vvw, 1549 w, 1499 m, 1471 s, 1463 s, sh, 1445 m, 1397 m, 1385 w, 1367 w, 1289 w,

[2] Dried by 3 Å molecular sieves for 24 h.

1263 vw, 1245 w, 1159 vw, 1105 w, 1093 m, 1074 w, 1046 w, 996 m, 950 w, 909 vw, 884 s, 825 m, 802 w, 697 w, 697 w, 678 s, 662 s, 641 m, 462 w, 417 w.

TOF HR ESI MS: calcd. for $C_{48}H_{56}Cl_2NaSi_2$ 781.3189, found 781.3193.

2,2'-Ethyne-1,2-diylbis(5-chloro-2'-ethynylbiphenyl) (60)



64 (6.58 g, 8.65 mmol) was dissolved in THF (800 mL) in an oven-dried Schlenk flask equipped with a magnetic stirring bar and rubber septum. Methanol (8.6 mL, 213 mmol, 25 eq.) was added. Another Schlenk flask was charged with TBAF (9.05 g, 34.6 mmol, 4.0 eq.) and TBAF was shortly dried under vacuum for several minutes. Then, THF (80 mL) was added. The resulting solution was added slowly to the stirred solution of **64**. The solution darkened a little bit, but the color still remained yellow. After 2 h, the reaction was quenched with methanol (50 mL), left stirred for another 15 min and the mixture was then filtered through a short pad of silica gel using cold chloroform. The solvent was evaporated *in vacuo* to provide a brown viscous liquid. Isopropanol (100 mL) was added and the mixture was concentrated *in vacuo*. A fine precipitate formed. The mother liquid was removed by suction, the obtained white solid rinsed twice with acetone and dried *in vacuo* to give **60** as white fine powder (3.48 g, 90 %).

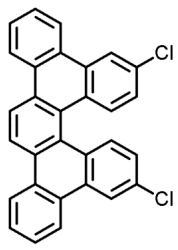
^{1}H NMR (400 MHz, $CDCl_3$): 2.97 (1 H, s), 7.14 (1 H, d, *J* = 8.3), 7.23 (1 H, dd, *J* = 8.3, 2.2), 7.29 (1 H, t, *J* = 3.8), 7.34 (2 H, dd, *J* = 5.3, 3.8), 7.40 (1 H, d, *J* = 2.1), 7.56 – 7.63 (1 H, m).

C^{13} NMR (100 MHz, $CDCl_3$): 80.67, 82.24, 91.56, 121.06, 121.36, 127.61, 127.78, 128.20, 130.09, 130.22, 133.14, 133.35, 133.55, 141.85, 143.62.

IR ($CHCl_3$): 3308 vs, 3095 vw, 3067 w, 2219 vw, 2108 vw, 1599 w, 1588 m, 1588 m, 1565 vw, 1548 w, 1501 s, 1472 vs, 1443 m, 1397 m, 1289 w, 1265 vw, 1247 w, 1162 vw, 1093 s, 1046 w, , 951 w, 984 vw, 867 m, 825 vs, 687 vw, 660 s, 621 s, 600, w, 589 w, 573 w, 532 w, sh, 540 w, 455 vw.

TOF HR EI MS: calcd. for $C_{30}H_{16}Cl_2$ 446.0629, found 446.0623.

3,16-Dichlorodibenzo[5]helicene (56)



A procedure using Ni(cod)$_2$ – PPh$_3$:

An oven-dried Schlenk flask equipped with a magnetic stirring bare was in glove box charged with $Ni(cod)_2$ (123 mg, 0.447 mmol, 20 mol %), PPh_3 (235 mg, 0.894 mmol, 40 mol %), and sealed with a rubber septum. Another Schlenk flask was charged with **60** (1.00 g, 2.24 mmol) and closed by a rubber septum, also in a glove box.[3] THF (60 mL to the first flask, 40 mL to the second one) was added by a syringe.[4] The solution of the catalyst was stirred for ca 5 min and then the solution of **60** was transferred via cannula to the flask containing

[3] The Schlenk flask was charged with **60** in the air, evacuated in the exchange chamber of the glovebox and closed with the glovebox by a rubber septum.

[4] A great care was taken to avoid any contact with air.

the catalyst. The mixture was stirred for ca 10 min. The resulting brown solution was quenched with acetone (ca 50 mL), evaporated with a spoonful of silica gel and chromatographed on silica gel (cyclohexane-toluene 7 : 2). The compound **56** was obtained as a white solid (0.676 g, 68 %).

A procedure using $CpCo(CO)_2$:
An oven-dried Schlenk flask was charged with **56** (370 mg, 0.827 mmol), capped with a rubber septum, evacuated, and backfilled with argon. THF (18 mL) was added via syringe, followed by the addition of $CpCo(CO)_2$ (22.3 mg, 0.124 mmol, 15 mol %). The solution was heated in a flow reactor to 240 °C with flow of 1 mL/min. The obtained yellow solution was evaporated with silica gel and chromatographed on silica gel (cyclohexane – toluene 7 : 2) to obtain **56** in acceptable purity as a beige powder (293 mg, 79 %).

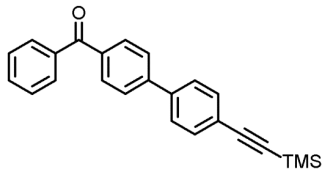
^{1}H NMR (400 MHz, $CDCl_3$): 7.16 (1 H, dd, *J* = 8.9, 2.2), 7.71 – 7.81 (2 H, m), 8.14 (1 H, d, *J* = 8.9), 8.53 (1 H, d, *J* = 2.2), 8.58 – 8.63 (1 H, m), 8.63 – 8.70 (1 H, m).

^{13}C NMR (150 MHz, $CDCl_3$): 122.07 (d), 123.28 (d) (2 C) , 123.76 (d), 125.72 (d), 126.84 (s), 127.63 (d), 128.18 (d), 129.05 (s), 129.28 (s), 129.75 (s), 130.37 (s), 131.40 (s), 132.01 (d), 133.00 (s).

IR ($CHCl_3$): 3105 vw, 3074 w, 2958 w, 2927 m, 2870 w, 2856 w, 1737 w, 1727 w, 1600 s, 1590 w, 1566 w, 1537 w, 1493 s, 1475 m, 1442 s, 1396 m, 1385 m.

TOF HR EI MS: calcd. for $C_{30}H_{16}Cl_2$ 446.0629, found 446.0627.

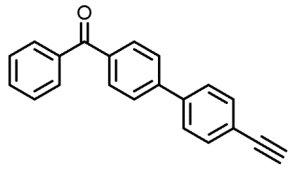
Phenyl{4'-[(trimethylsilyl)ethynyl]biphenyl-4-yl}methanone (76)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with 4-benzoyl-4'-bromobiphenyl (2.0 g, 5.93 mmol), $Pd(PPh_3)_4$ (137 mg, 0.119 mmol, 2 mol %), and CuI (45.0 mg, 0.237 mmol, 4 mol %), closed with a stopper, evacuated and backfilled with argon. THF (29 mL) and diisopropylamine (26 mL) were added via syringe. The mixture was degassed three times using a freeze-thaw cycle and after warming to room temperature, TMSA (1.3 mL, 8.89 mmol, 1.5 eq.) was added via syringe. The mixture was stirred at 55 °C for 18 h. The solvent was removed *in vacuo*, the residue was dissolved in dichloromethane (ca 20 mL) and the solution was filtered through a short pad of silica (DCM). The solvent was removed and the residue was chromatographed on silica gel (hexane-AcOEt 100 : 0 to 80 : 20) to provide **76** as light brown solid (2.10 g, 100 %).

The measured ^{1}H-NMR spectrum was in agreement with the published data. [42]

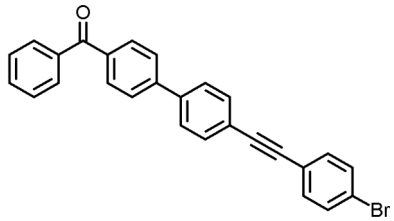
(4'-Ethynylbiphenyl-4-yl)(phenyl)methanone (77)



A flask equipped with a magnetic stirring bar was charged with **76** (2.19 mg, 6.18 mmol) and K_2CO_3 (2.70 g, 19.5 mmol, 3.2 eq.). THF (22 mL) and methanol (51 mL) were added. The mixture was stirred under argon for 3 h. Then, water (ca 100 mL) was added resulting in a formation of a precipitate which was filtered by suction, rinsed with water (2 x) and dried *in vacuo* to afford **77** as white crystals (1.72 g, 99 %).

The measured ^{1}H-NMR spectrum was in agreement with the published data. [42]

{4'-[(4-Bromophenyl)ethynyl]biphenyl-4-yl}(phenyl)methanone (78)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with **77** (300 mg, 1.06 mmol), $Pd(PPh_3)_4$ (61 mg, 0.053 mmol, 5 mol %), CuI (18 mg, 0.094 mmol, 9 mol %), and *p*-bromoiodobenzene (600 mg, 2.13 mmol, 2.0 eq.). DIPA (15 mL) and toluene (8 mL) were added. The mixture was degassed three times using the freeze-pump-thaw cycle. The solution was stirred under argon for 2 h. After this period, chloroform (ca 150 mL) was added into the mixture and the resulting suspension was poured into a separatory funnel filled with a saturated solution of NH_4Cl (500 mL). The mixture was extracted with chloroform (3 x 100 mL) and the combined extracts were dried over anhydrous $MgSO_4$. The solution was evaporated, the solid was suspended in toluene (100 mL) and shortly refluxed for 5 min. After cooling down, the formed pearly crystals were separated by suction and dried *in vacuo* to give **78** (371 mg, 80 %).

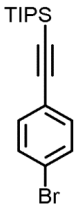
^{1}H NMR (600 MHz, $CDCl_3$): 7.41 – 7.44 (1 H, m), 7.49 – 7.52 (1 H, m), 7.50 – 7.53 (1 H, m), 7.59 – 7.62 (1 H, m), 7.62 – 7.64 (1 H, m), 7.65 – 7.67 (1 H, m), 7.71 – 7.74 (1 H, m), 7.83 – 7.85 (1 H, m), 7.90 – 7.92 (1 H, m).

^{13}C NMR (150 MHz, $CDCl_3$): 32.46 (d), 12.34 (d), 89.57 (s), 90.16 (s), 122.09 (s), 122.67 (s), 122.83 (s), 126.84 (d), 127.25 (s), 130.00 (d), 130.79 (d), 131.67 (d), 132.18 (d), 133.04 (d), 136.58 (s), 137.65 (s), 139.87 (s), 144.18 (s), 196.25 (s).

IR (KBr): 551 w, 663 m, 832 s, 941 m, 1009 m, 1097 w, 1180 w, 1284 w, 1325 w, 1394 m, 1394 w, 1471 w, 1480 w, 1544 w, 1567 w, 1580 w, 1597 m.

TOF HR EI MS: calcd. for $C_{30}H_{16}Cl_2$ 436.0463, found 436.0469.

[(4-Bromophenyl)ethynyl][tris(1-methylethyl)]silane (73)

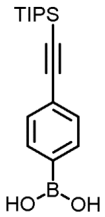


An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with *p*-bromoiodobenzene (2.00 g, 7.07 mmol), $Pd(PPh_3)_2Cl_2$ (99.0 mg, 0.141 mmol, 2 mol %), and CuI (54.0 mg, 0.283 mmol, 4 mol %), sealed with a stopper, evacuated and backfilled with argon. Diisopropylamine was added via syringe (20 mL), the mixture was degassed three times using freeze-pump-thaw cycle and subsequently

immersed in a water-ice bath. The triisopropylsilylacetylene (0.933 mL, 7.42 mmol, 1.05 eq.) was added. The mixture was gradually warmed to a room temperature and stirred for 20 h. The precipitate was filtered off by suction and rinsed with DIPA (4 x). The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane) to obtain **73** as a pale yellow liquid (2.15 mg, 97 %).

The measured ^{1}H-NMR spectrum was in agreement with the published data. [40]

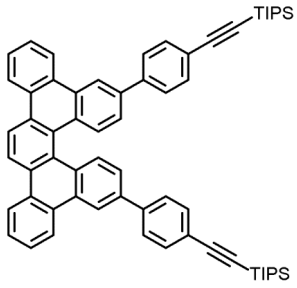
(4-{[Tris(1-methylethyl)silyl]ethynyl}phenyl)boronic acid (78)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with **73** (5.30 g, 15.7 mmol), THF (106 mL) was added, and the solution was cooled to –78 °C in an acetone-CO_2 bath. The solution of *n*-BuLi (1.6 M in hexanes, 12.8 mL, 20.4 mmol, 1.3 eq.) was added dropwise, keeping the temperature around –78 °C. The yellow-brown mixture was stirred for 30 min and then triisopropyl borate (9.06 mL, 39.3 mmol, 2.5 eq.) was added dropwise. The color of the mixture turned from yellow to colorless. The solution was allowed to reach room temperature, turning white. The mixture was stirred for 2 h, subsequently 1 M HCl (ca 50 mL) was added and the mixture was stirred for additional 3 h. The solution was then extracted with diethyl ether (4 x 50 mL), the combined extracts were washed with brine (1 x) and dried over anhydrous $MgSO_4$. The solvents were removed by rotavap and the residue was purified by flash chromatography on silica gel (hexane-AcOEt 9 : 1 to 4 : 6). **78** was obtained as a white amorphous solid (3.50 g, 74 %).

The measured ^{1}H-NMR spectrum was in agreement with the published data. [40]

3,16-Bis[4-(triisopropylsilylethyn-1-yl)phenyl]dibenzo[5]helicene (69)

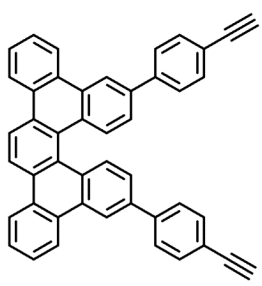


An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with **56** (300 mg, 0.671 mmol), **78** (1.01 g, 3.35 mmol, 5 eq.), $Pd(OAc)_2$ (120 mg, 0,537 mmol, 80 mol %), Cs_2CO_3 (1090 mg, 3.35 mmol, 5 eq.), and DavePhos (422 mg, 1.07 mmol, 160 mol %). The Schlenk flask was sealed with a glass stopper, evacuated and backfilled with argon. Dioxane (21 mL) was added via syringe and the mixture was bubbled with argon for 15 min. The reaction mixture was heated to 85° C for 17 h. After this period, the salts were removed by filtration through a paper filter (DCM) and the solvent was removed *in vacuo*. The residue was chromatographed on silica gel (hexane-acetone 95 : 5). The compound **69** was obtained as a yellow resin (498 mg, 83 %).

^{1}H NMR (400 MHz, $CDCl_3$): 1.16 (21 H, s), 7.48 – 7.44 (1 H, m), 7.60 (2 H, d, *J* = 8.1 Hz), 7.81 – 7.69 (4 H, m), 8.38 (1 H, d, *J* = 8.6), 8.80 – 8.66 (4 H, m).

TOF HR EI MS: calcd. for $C_{64}H_{66}Si_2$ 890.4703, found 890.4730.

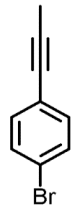
3,16-Bis[4-(ethyn-1-yl)phenyl]dibenzo[5]helicene (70)



69 (22.0 mg, 0.025 mmol) was dissolved in THF (2 mL) in an oven-dried Schlenk flask equipped with a magnetic stirring bar and rubber septum. Methanol (22.0 µL, 0.607 mmol, 25 eq.) was added . Another Schlenk flask was charged with TBAF (59 mg, 0.224 mmol, 9.1 eq.) and TBAF was shortly dried under vacuum for several minutes. Then, THF (0.2 mL) was added. The resulting solution was added slowly to the stirred solution of **69**. After 1 h, the reaction was quenched with methanol (0.5 mL), the solution was diluted with chloroform (20 mL, with 1 % Et_3N), and filtered through a short pad of silica gel (DCM). The solvent was evaporated *in vacuo* and subsequently chromatographed on silica gel (cyclohexane-toluene 7 : 2) to provide **70** as a yellow resin (13 mg, 91 %).

^{1}H NMR (400 MHz, $CDCl_3$): 3.17 (1 H, s), 7.43 (1 H, d, *J* = 8.6), 7.46 (2 H, d, *J* = 8.1), 7.62 (2 H, d, *J* = 8.0), 7.74 – 7.77 (4 H, m), 8.36 (1 H, d, *J* = 8.5), 8.73 (4 H, dd, *J* = 35.0, 6.0).

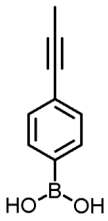
1-Bromo-4-prop-1-yn-1-ylbenzene (72)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with *p*-bromoiodobenzene (5.00 g, 17.7 mmol), $Pd(PPh_3)_2]Cl_2$ (248 mg, 0.354 mmol, 2.0 mol %) and CuI (135 mg, 0.707 mmol, 4.0 mol %), DIPA (100 mL) was added via syringe and the mixture was degassed three times using a freeze-thaw-pump cycle. Propyne was bubbled through the stirred mixture. After 2 h, the formed precipitate was removed by suction, rinsed with DIPA (3 x), the solution was evaporated *in vacuo* and subsequently purified by flash chromatography on silica gel (hexane). **72** was obtained as a colorless liquid (3.21 g, 93 %).

The measured ^{1}H-NMR spectrum was in agreement with the published data. [39]

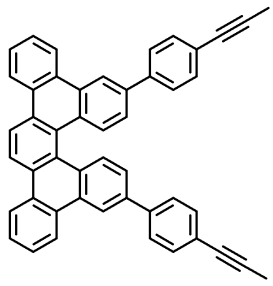
(4-Prop-1-yn-1-ylphenyl)boronic acid (67)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with **72** (2.61 g, 13.5 mmol), THF (85 mL) was added, and the solution was cooled to –78 °C in an acetone-CO_2 bath. The solution of *n*-BuLi (1.6 M in hexanes, 10.9 mL, 17.5 mmol, 1.3 eq.) was added dropwise, keeping the temperature around –78 °C. The yellow mixture was stirred for 50 min and then triisopropyl borate (0.24 mL, 1.05 mmol, 2.0 eq.) was added dropwise and stirred for additional 50 min. The solution turned turbid. The mixture was allowed to reach room temperature and the mixture was left stirred for 20 h. 1 M HCl (10 mL) was then added and the mixture was stirred for 3 h. The resulting mixture was extracted with diethyl ether (3 x 20 mL), the combined extracts were washed with brine (1 x) and dried over anhydrous $MgSO_4$. The solvents were removed by rotavap and the residue was purified by flash chromatography on silica gel (hexane-acetone 7 : 3 to 1 : 1). **67** was obtained as a colorless waxy solid (1.13 g, 52 %).

The measured ^{1}H-NMR spectrum was in agreement with the published data. [39]

3,16-Bis[4-(prop-1-yn-1-yl)phenyl]dibenzo[5]helicene (57)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with a 3,16-dichlorodibenzo[5]helicene[5] **56** (100 mg, 0.224 mmol), $B_2(pin)_2$ (131 mg, 0.514 mmol, 2.3 eq.), $Pd(OAc)_2$ (5.00 mg, 0.022 mmol, 10 mol %), XPhos (43.0 mg, 0.089 mmol, 40 mol %), AcOK (123 mg, 1.25 mmol, 5.6 eq.). The Schlenk flask was capped with a rubber septum and dioxane (2.5 mL) was added via syringe. The mixture was bubbled with argon for 10 min and then heated to reflux.[6] After 2.5 h, **72** (174 mg, 0.894, 4.0 eq.) dissolved in dioxane (1.1 mL) was added and the mixture was refluxed for additional 2 h. Then, the mixture was cooled down, diluted with water, and extracted with chloroform (3 x 20 mL), washed with brine (1 x 20 mL) and dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo* and the crude product was chromatographed on silica gel (cyclohexane-toluene 7 : 2)[7] to provide the pure product as yellow solid (100 mg, 74 %). The product could be further recrystallized from boiling toluene to give **57** as pale yellow needles.

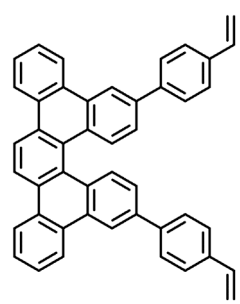
^{1}H NMR (400 MHz, $CDCl_3$): 2.11 (3 H, s), 7.39 (1 H, dd, *J* = 8.6, 1.9), 7.50 – 7.53 (2 H, m), 7.70 – 7.74 (2 H, m), 8.30 (1 H, d, *J* = 8.6), 8.58 (1 H, s), 8.59 – 8.62 (1 H, m).

^{13}C NMR (150 MHz, $CDCl_3$): 4.45 (q), 86.79 (s), 79.65 (s), 121.50 (d), 121.83 (d), 123.16 (s), 123.18 (d), 123.76 (d), 124.04 (d), 126.94 (d), 127.31 (d), 127.39 (s), 127.60 (d), 129.02 (s), 129.75 (s), 130.19 (s), 130.31 (s), 130.35 (s), 131.28 (d), 132.00 (d), 138.53 (s), 139.84 (s).

IR ($CHCl_3$): 2960 w, 2854 w, 2160 w, 2147 w, 1610 m, 1517 w, 1466 – 1422 w, 1447 m, 1392 m, 1293 w, 1308 – 1262 m, 1262 m, 1118 – 1047 w, 1030 m, 946 w, 860 – 886 w, 829 vs, 536 w.

TOF HR EI MS: calcd. for $C_{48}H_{30}$ 606.2348, found 606.2365.

3,16-Bis[4-vinylphenyl]dibenzo[5]helicene (57)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with **56** (100 mg, 0.224 mmol), 4-vinylbenzeneboronic acid (165 mg, 1.12 mmol, 5.0 eq.), $Pd(OAc)_2$ (25.0 mg, 0.112 mmol, 50 mol %), XPhos (107 mg, 0.224 mmol, 100 mol %), K_3PO_4 (475 mg, 2.24 mmol, 10.0 eq.), capped with a rubber septum, evacuated, and backfilled with argon. Dioxane (10 mL) was added via syringe and the mixture was bubbled with argon for 15 min. The reaction mixture was heated to reflux[6] for 6 h. After this period, the mixture was cooled down, diluted with water and extracted with chloroform (3 x 20 mL), washed with brine (1 x) and dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo* and the crude product was chromatographed on silica gel[8] (cyclohexane-toluene 8 : 2) to provide the pure product **69** as a yellow resin (498 mg, 83 %).

[5] Or its corresponding solubilized derivative.
[6] The temperature of the bath was 110 °C.
[7] Merck, 60 (0.015 – 0.040 mm).

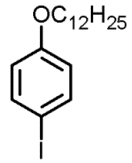
^{1}H NMR (400 MHz, $CDCl_3$): 5.31 (1 H, d, *J* = 11.2), 5.84 (1 H, d, *J* = 17.6), 6.80 (1 H, dd, *J* = 17.6, 10.9), 7.46 – 7.59 (3 H, m), 7.74 – 7.81 (4 H, m), 8.40 (1 H, d, *J* = 8.6), 8.75 (4 H, dt, *J* = 9.4, 2.5).

^{13}C NMR (100 MHz, $CDCl_3$): 77.98, 83.58, 121.19, 121.71, 121.94, 123.19, 123.80, 124.06, 127.05, 127.39, 127.70, 129.78, 130.28, 130.37, 130.46, 131.35, 132.66, 138.32, 141.18.

IR ($CHCl_3$): 3069 w, 3036 w, 3013 w, 3013 m, 1629 w, 1611 w, 1518 m, 1411 w, 1298 w, 1279 w, 1252 w, 1186 w, 1128 w, 1030 w, 1022 w, 946 w, 826 vs, 649 w, 641 w, 547 w.

HR APCI MS: calcd. for $C_{46}H_{31}$ 583.2420, found 583.2415.

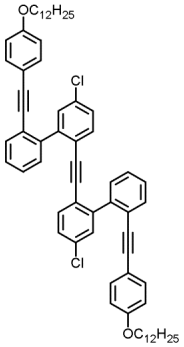
1-Dodecyloxy-4-iodobenzene (81)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with 4-iodophenol (556 mg, 2.528 mmol), K_2CO_3 (699 mg, 5.05 mmol, 2.0 eq.) was capped with a rubber septum, evacuated, and backfilled with argon, then DMF was added (5 mL). 1-Bromododecane was added via syringe (600 mg, 2.41 mmol, 0.95 eq.) and the mixture was stirred at 100 °C for 20 h. The reaction mixture was cooled down and filtered through a short pad of celite (DCM). After evaporation of the solvents, the crude mixture was purified by flash chromatography on silica gel (cyclohexane) to provide **81** as a white solid (768 mg, 82 %). The compound could be further recrystallized from isopropanol to give **81** in a form of white needles.

The measured ^{1}H-NMR spectrum was in agreement with the published data. [43]

2,2'-Ethyne-1,2-diylbis(5-chloro-2'-{[4-(dodecyloxy)phenyl]ethynyl}biphenyl) (82)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with **60** (16.0 mg, 0.034 mmol), $Pd(PPh_3)_2Cl_2$ (2.40 mg, 0.003 mmol, 10 mol %), CuI (1.30 mg, 0.007 mmol, 20 mol %), **81** (25.0 mg, 0.074 mmol, 2.2 eq.). DIPA (71 µL), and toluene (1 mL) were added. The mixture was degassed three times using a freeze-pump-thaw cycle. The solution was stirred under argon at 50 °C for 2 h. After this period, the mixture was extracted with diethyl ether (3 x 20 mL) and the combined extracts were dried over anhydrous $MgSO_4$. The solution was evaporated and the remaining solid was recrystallized from isopropanol to give **82** as white crystals. (29 mg, 89 %).

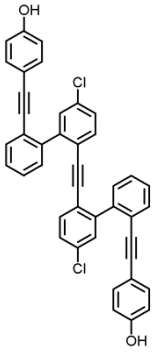
^{1}H NMR (400 MHz, $CDCl_3$): 0.88 (3 H, t, *J* = 6.8), 1.28 (16 H, d, *J* = 15.6), 1.47 – 1.37 (2 H m), 1.80 – 1.70 (2 H, m), 3.91 (2 H, t, *J* = 6.6), 6.76 (2 H, d, *J* = 8.8), 7.20 – 7.14 (3 H, m), 7.23 (1 H, dd, *J* = 8.3, 2.1), 7.28 (1 H, dd, *J* = 8.7, 1.3), 7.34 (2 H, ddd, *J* = 6.7, 3.7, 2.5), 7.54 (1 H, d, *J* = 2.1), 7.58 (1 H, dd, *J* = 5.8, 2.8).

^{13}C NMR (100 MHz, CD_2Cl_2): 14.48, 23.30, 26.58, 29.79, 29.96, 29.98, 30.18, 30.21, 30.25, 30.27, 32.54, 68.74, 87.63, 92.24, 93.78, 115.06, 115.43, 121.81, 123.43, 128.06, 128.10, 128.58, 130.67, 131.10, 132.48, 133.34, 133.98, 134.03, 141.56, 144.68, 159.98.

IR ($CHCl_3$): 3065 w, 2970 m, 2928 s, 2856 m, 2216 w, 1598 m, 1548 w, 1470 m, 1440 w, 1396 w, 1248 ms, 1175 m, 1148 w, 1094 w, 1045 w, 870 w, 825 m.

HR MALDI MS: calcd. for $C_{66}H_{72}Cl_2O_2$ 966.4904, found 966.4888.

4,4'-{Ethyne-1,2-diylbis[(5'-chlorobiphenyl-2',2-diyl)ethyne-2,1-diyl]}diphenol (85)



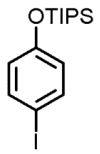
An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with **60** (300 mg, 0.671 mmol), $Pd(PPh_3)_2Cl_2$ (24.0 mg, 0.034 mmol, 5.0 mol %), CuI (13.0 mg, 0.067 mmol, 10 mol %), and 4-iodophenol (302 mg, 1.37 mmol, 2.1 eq.). DIPA (10 mL) and toluene (18 mL) were added. The mixture was degassed three times using a freeze-pump-thaw cycle. The solution was stirred under argon at 40 °C for 2 h. After this period, the mixture was diluted with benzene (150 mL) and washed with saturated solution of NH_4Cl (50 mL) and with water (50 mL). The resulting suspension of the product in the organic phase was filtered off by suction and rinsed with benzene (10 mL). The obtained solid was suspended in toluene (20 mL) and sonicated for 20 min. Toluene was decanted from the solid and the sonication process was repeated twice more. Subsequently the solid was removed by suction and dried *in vacuo* to yield **85** as a beige powder (344 mg, 81 %).

^{1}H NMR (400 MHz, $CDCl_3$): 6.78 (2 H, d, *J* = 8.7) 7.12 (2 H, d, *J* = 8.7), 7.31 (1 H, d, *J* = 8.3), 7.47 – 7.36 (4 H, m), 7.56 (1 H, d, *J* = 2.0), 7.62 (1 H, d, *J* = 6.9), 8.74 (1 H, s).

IR ($CHCl_3$): 3541 w, 3426 w, 3097 w, 3058 w, 3231 w, 2214 w, 1606 m, 1593 m, 1512 s, 1545 w, 1471 m, 1444 m, 1397 m, 1362 w, 1287 w, 1263 m, 1231 s, 1172 m, 1160 m, 1130 w, 1096 m, 1017 m, 945 w, 873 m, 830 s, 755 m, 669 m, 649 w, 579 m, 544 w, 454 w.

TOF HR ESI MS: calcd. for $C_{42}H_{24}O_2Cl_2Na$ 653.1045, found 653.1037.

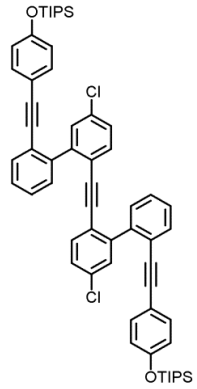
4-Triisopropylsilyloxy-1-iodobenzene (87)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with 4-iodophenol (350 mg, 1.59 mmol) and imidazole (271 mg, 3.98 mmol, 2.5 eq.) was capped with a rubber septum, evacuated, and backfilled with argon. DCM was added (18 mL) and then TIPSCl (408 µL, 1.91 mmol, 1.2 eq.) added via syringe, and the mixture was stirred at room temperature for 15 h. After evaporation of the solvents, the crude mixture was purified by flash chromatography on silica gel (hexane) to provide **87** as a colorless liquid (579 mg, 97 %).

The measured ^{1}H-NMR spectrum was in agreement with the published data. [44]

{Ethyne-1,2-diylbis[(5'-chlorobiphenyl-2',2-diyl)ethyne-2,1-diylbenzene-4,1-diyloxy]}bis[tris(1-methylethyl)silane] (88)



An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with **60** (209 mg, 0.467 mmol), $Pd(PPh_3)_4$ (113 mg, 0.098 mmol, 21 mol %), CuI (37.0 mg, 0.196 mmol, 42 mol %), and **87** (369 mg, 0.981 mmol, 2.1 eq.) was capped with a rubber septum, evacuated, and backfilled with argon. DIPA (21 mL) was added via syringe and the mixture was degassed three times using a freeze-pump-thaw cycle. The solution was stirred under argon at room temperature for ca 20 h. After this period, the mixture was diluted with chloroform (ca 10 mL), and washed with saturated solution of NH_4Cl (3 x 50 mL), with water (1 x 50 mL), and with brine (1 x 50 mL). The obtained solution was dried over anhydrous $MgSO_4$ and evaporated. The crude compound was dissolved in AcOEt (ca 150 mL), concentrated to 1/3 of its volume and left to crystallize. The formed precipitate was removed by suction, rinsed with AcOEt (3 x 10 mL), and dried *in vacuo* to afford **88** as a white powder (400 mg, 91 %).

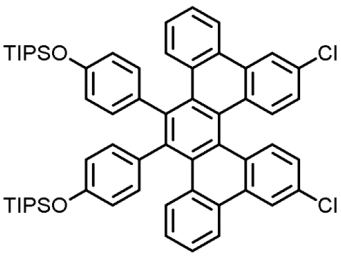
^{1}H NMR (400 MHz, $(CD_3)_2CO$): 1.10 (18 H, d, *J* = 7.3), 1.29 (3 H, dt, *J*= 14.9, 7.4), 6.87 (2 H, d, *J*= 8.7), 7.17 (2 H, d, *J*= 8.7), 7.30 (1 H, d, *J*= 8.3), 7.48 – 7.37 (4 H, m), 7.56 (1 H, d, *J*= 2.0), 7.63 (1 H, d, *J*= 6.9).

^{13}C NMR (100 MHz, $CDCl_3$): 12.66, 17.87, 87.35, 91.72, 93.29, 115.64, 119.91, 121.21, 122.84, 127.27, 127.42, 127.79, 130.13, 130.53, 131.97, 132.83, 133.29, 133.42, 140.92, 143.94, 156.33.

IR ($CHCl_3$): 3541 w, 3426 w, 3231 w, 3097 w, 3058 w, 2214 w, 1606 m, 1593 m, 1545 w, 1512 s, 1471 m, 1444 m, 1397 m, 1362 w, 1287 w, 1263 m, 1231 s, 1172 m, 1160 m, 1130 w, 1096 m, 1017 m, 945 w, 873 m, 830 s, 755 m, 669 m, 649 w, 579 m, 544 w, 454 w.

TOF HR ESI MS: calcd. for $C_{60}H_{65}O_2Cl_2Si_2$ 943.3894, found 943.3894.

3,16-Dichloro-9,10-bis[4-(triisopropylsilyloxy)phenyl]dibenzo[5]helicene (89)

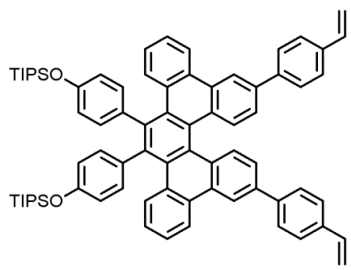


An oven-dried Schlenk flask equipped with a magnetic stirring bar was in glove box charged with $Ni(cod)_2$ (150 mg, 0.159 mmol, 50 mol %), PCy_3 (45 mg, 0.079 mmol, 100 mol %), and sealed with a rubber septum. Another vial was charged with **88** (150 mg, 0.159 mmol) and closed by a rubber septum, also in a glove box.[3] THF (4 mL to the first flask, 6 mL to the second one) was added by a syringe.[4] The solution of the catalyst was stirred for ca 5 min and then the solution of **88** was transferred via a cannula to the flask containing the catalyst. The mixture was stirred at room temperature for ca 20 h. The resulting brown solution was quenched with acetone (ca 2 mL), evaporated, and the residue was chromatographed on silica gel[8] (cyclohexane). The compound **89** was obtained as a pale yellow resin (28 mg, 19 %).

^{1}H NMR (400 MHz, $CDCl_3$): 1.19 – 1.07 (18 H, m), 1.34 – 1.20 (3 H, m), 6.66 (1 H, dd, *J* = 8.3, 2.5,), 6.74 (2 H, ddd, *J* = 8.0, 4.1, 2.3), 6.91 (1 H, dd, J = 8.3, 2.1), 7.05 (1 H, t, *J* = 7.8), 7.15 (1 H, dd, *J* = 8.9, 2.1), 7.51 – 7.45 (2 H, m), 7.99 (1 H, d, *J* = 8.9), 8.47 – 8.39 (2 H, m).

TOF HR ESI MS: calcd. for $C_{60}H_{64}O_2Cl_2NaSi_2$ 965.3714, found 965.3711.

3,16-Bis[4-vinylphenyl]-9,10-bis[4-(triisopropylsilyloxy)phenyl]dibenzo[5]helicene (92)

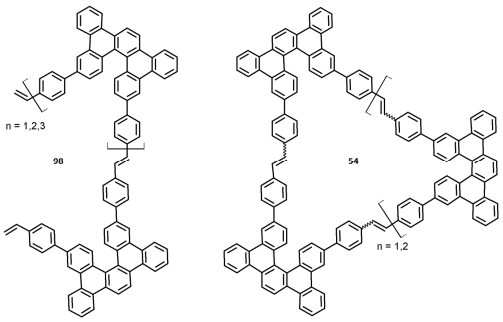


An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with **89** (14 mg, 0.02 mmol), 4-vinylbenzeneboronic acid (10 mg, 0.07 mmol, 4.6 eq.), $Pd(OAc)_2$ (0.5 mg, 0.002 mmol, 15 mol %), XPhos (4.2 mg, 0.009 mmol, 60 mol %), and capped with a rubber septum. 5 M aqueous solution of K_3PO_4 (44 µL, 0.22 mmol, 15 eq.) and dioxane (1 mL) were added, and the resulting solution was bubbled with argon for 15 min. The reaction mixture was heated to reflux[6] for 10 h. After this period, the mixture was cooled down, diluted with DCM (2 mL), and extracted with DCM (3 x 15 mL), washed with brine (1 x 15 mL), and dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo* and the crude product was chromatographed on silica gel[8] (cyclohexane-toluene 8 : 2) to provide the pure product. The compound **92** was obtained as a yellow-green fluorescent resin (7 mg, 44 %).

^{1}H NMR (400 MHz, $CDCl_3$): 1.23 – 1.07 (18 H, m), 1.37 – 1.26 (3 H, m), 5.23 – 5.14 (1 H, m), 5.74 – 5.62 (1 H, m), 6.62 (1 H, dd, *J* = 17.6, 11.0), 6.94 – 6.70 (3 H, m), 7.20 – 6.99 (5 H, m), 7.61 (2 H, t, *J* = 7.5), 7.68 (2 H, t, *J* = 8.5), 8.15 (1 H d, *J* = 8.7), 8.94 (1 H, d, *J* = 7.7), 9.03 (1 H, d, *J* = 1.7).

TOF HR ESI MS: calcd. for $C_{42}H_{24}O_2Cl_2Na$ 653.1045, found 653.1037.

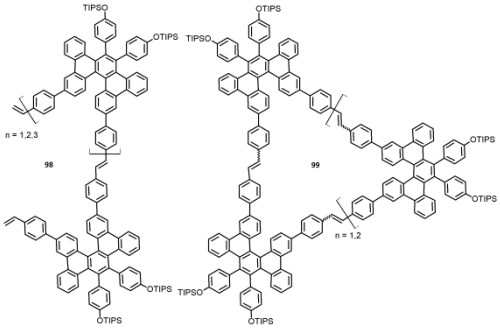
Macrocycle 54



An oven-dried Schlenk flask was charged in glove box with **58** (28 mg, 0.048 mmol) and the 2nd generation Grubb`s catalyst (4.1 mg, 0.005 mmol, 10 mol %). 1,2,4-Trichlorobenzene (1 mL) was added via syringe, the flask was capped with a Teflon stopper, and the solution was heated to 35 °C. After 17 h, the resulting dark-green fluorescent precipitate was removed by suction, rinsed with with DCM (3 x 10 mL) and dried *in vacuo* to provide product (21 mg).

HR MALDI MS: calcd. for $C_{90}H_{56}$ 1136.4382, found 1136.4377.

Macrocycle 100



An oven-dried Schlenk flask was charged in glove box with **92** (7 mg, 0.006 mmol) and the 2nd generation Grubb`s catalyst (1.1 mg, 0.001 mmol, 20 mol %). DCM (0.3 mL) was added via syringe, the flask was capped with a Teflon stopper, and the solution was heated to 37 °C. After 20 h, the resulting dark-green fluorescent solution was diluted with DCM (1 mL) and filtered through a short pad of silica gel (DCM).[7] The solution was loaded on a preparative TLC plate and evolved with the mixture of hexane – THF (1 : 1). The individual spots were extracted with chloroform (2 x 5 mL) and submitted to MALDI analysis.

TOF HR ESI MS: calcd. for $C_{222}H_{222}O_6Si_6$ for 3151.5682, found 3151.5677.

6. List of abbreviations

^{1}H-NMR	proton nuclear magnetic resonance
2D	two dimensional
3D	three dimensional
Ac	acetyl
Ad	adamantyl
AM	alkyne metathesis
Ar[1]	3,5-dimethylphenyl
i-Pr	isopropyl
pin	pinacol
Bu	butyl
calcd.	calculated
cod	cyclooctadienyl
Cp	cyclopentadienyl
DavePhos	2-dicyclohexylphosphino-2`-(*N*,*N*-dimethylamino)biphenyl
DBH	dibenzo[5]helicene
DCC	dynamic covalent chemistry
DCM	dichloromethane
DIPA	diisopropylamine
DMF	dimethylformamide
Et	ethyl
GC-MS	gas chromatography – mass spectrometry
Grubbs 2nd gen.	(1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium
HPLC	high performance liquid chromatography
HR-MS	high resolution mass spectrometry
IR	infrared spectrometry
m	medium (infrared spectrometry)
MALDI-MS	matrix-assisted laser desorption-ionization – mass spectrometry
Me	methyl
NMR	nuclear magnetic resonance
Cy	cyclohexyl
Ph	phenyl
s	strong (infrared spectrometry)
SPMs	shape-persistent macrocycles
t-Bu	*tert*-butyl
Tg	-$(CH_2CH_2O)_3CH_3$
THF	tetrahydrofuran
TIPSA	(triisopropylsilyl)acetylene
TIPSCl	triisopropylsilyl chloride
TLC	thin-layer chromatography
TMEDA	tetramethylethylenediamine
TMS	trimethylsilyl
TMSA	(trimethylsilyl)acetylene
UV	ultraviolet
vs	very strong (infrared spectrometry)

vw	very weak (infrared spectrometry)
w	weak (infrared spectrometry)
XPhos	2-dicyclohexylphosphino-2`,4`,6`-triisopropylbiphenyl

7. References

1. J. F. Morin, Y. Shirai, J. M. Tour, *Org. Lett.* **2006**, *8,* 1713.
2. K. Nakao, M. Nishimura, T. Tamachi, Y. Kuwatani, H. Miyasaka, T. Nishinaga, M. Iyoda, *J. Am. Chem. Soc.* **2006,** *128,* 16740.
3. M. Iyoda, J. Yamakawa, M. J. Rahman, *Angew. Chem. Int. Ed.* **2011**, *50,* 10522.
4. H. A. Staab, K. Neunhoeffer*, Synthesis* **1974**, 424.
5. M. Iyoda, M. J. Rahman, A. Matsumoto, M. Wu, Y. Kuwatani, K. Nakao, Y. Miyake, *Chem. Lett.* **2005**, *34,* 1474.
6. H. Meyer, H. A. Staab, *Justus Liebigs Ann. Chem.* **1969**, *724,* 30.
7. J. Zhang, D. J. Pesak, J. L. Ludwick, J. S. Moore, *J. Am. Chem. Soc.* **1994,** *116,* 4227.
8. P. N. W. Baxter, *J. Org. Chem.* **2004**, *69,* 1813.
9. H. L. Anderson, J. K. M. Sanders, *Angew. Chem. Int. Ed.* **1990**, *29,* 1400.
10. W. Zhang, J. S. Moore, *Angew. Chem. Int. Ed.* **2006**, *45,* 4416.
11. P. H. Ge, W. Fu, W. A. Herrmann, E. Herdtweck, C. Campana, R. D. Adams, U. H. F. Bunz, *Angew. Chem. Int. Ed.* **2000**, *39,* 3607.
12. W. Zhang, J. Moore, *J. Am. Chem. Soc.* **2004**, *126,* 12796.
13. O. Š. Miljanić, K. P. C. Vollhardt, G. D. Whitener, *Synlett* **2003**, 29.
14. Y. Jin, A. Zhang, Y. Huanga, W. Zhang, *Chem. Commun.* **2010**, *46,* 8258.
15. A. Mortreux, M. Blanchard, *J. Chem. Soc., Chem. Commun.* **1974**, 786.
16. Y.-C. Tsay, P. L. Diaconescu, C. C. Cummins, *Organometallics* **2000**, *19,* 5260.
17. A. Fürstner, C. Mathes, C. W. Lehmann, *Chem. Eur. J.* **2001**, *7*, 5299.
18. W. Zhang, S. Kraft, J. Moore, *J. Am. Chem. Soc.* **2004**, *126,* 329.
19. J. Heppekausen, R. Stade, R. Goddard, A. Fürstner, *J. Am. Chem. Soc.* **2010,** *132,* 11045**.**
20. M. Bindl, R. Stade, E. K. Heilmann, A. Picot, R. Goddard, A Fürstner, *J. Am. Chem. Soc.* **2009**, *131*, 9468.
21. W. Zhang, J. Moore, *J. Am. Chem. Soc.* **2005**, *127,* 11863.
22. W. Zhang, S. M. Brombosz, J. L. Mendoza, J. Moore, *J. Org. Chem.* **2005**, *70,* 10198.
23. M. Mammen, E. I. Shakhnovich, J. M. Deutch, G. M. Whitesides, *J. Org. Chem.* **1998**, *63,* 3821.
24. J. Meisenheimer, K. Witte, *BDCGAS* **1903**, 36, 4153.
25. a) M. S. Newman, W. B. Luts, D. Lednicer, *J. Am. Chem. Soc.* **1955**, *77,* 3420.
    b) M. S. Newman, D. Lednicer, *J. Am. Chem. Soc.* **1956**, *78,* 4765.
26. P. Sehnal, I. G. Stará, D. Šaman, M. Tichý, J. Míšek, J. Cvačka, L. Rulíšek, J. Chocholoušová, J. Vacek, G. Goryl, M. Szymonski, I. Císařová, I. Starý, *Proc. Natl. Acad. Sci. USA* **2009**, *32,* 13169.
27. M. Flammang-Barbieux, J. Nasielski, R. H. Martin, *Tetrahedron Lett.* **1967**, 743.
28. L. B. Liu, T. J. Katz, *Tetrahedron Lett.* **1991**, *32,* 6831.
29. N. D. Willmore, L. B. Liu, T. J. Katz, *Angew. Chem. Int. Ed.* **1992**, *31,* 1093.
30. F. Teplý, I. G. Stará, I. Starý, A. Kollárovič, D. Šaman, L. Rulíšek, P. Fiedler, *J. Am. Chem. Soc.* **2002**, *124,* 9175.
31. J. Žádný, A. Jančařík, A. Andronova, M. Šámal, J. Chocholoušová, J. Vacek, R. Pohl, D. Šaman, I. Císařová, I. G. Stará, I. Starý, *Angew. Chem. Int. Ed.* **2012**, *51,* 5851.
32. J. Rybáček, G. Huerta-Angeles, A. Kollárovič, I. G. Stará, I. Starý, P. Rahe, M. Nimmrich, A. Kuhnle, *Eur. J. Org. Chem.* **2011**, 853.

33. O. Songis, J. Míšek, M. B. Schmid, A. Kollárovič, I. G. Stará, D. Šaman, I. Císařová, I. Starý, *J. Org. Chem.* **2010**, *75,* 6889.
34. P. Sehnal, Z. Krausová, F. Teplý, I. G. Stará, I. Starý, L. Rulíšek, D. Šaman, I. Císařová, *J. Org. Chem.* **2008**, *73,* 2074.
35. J. Míšek, F. Teplý, I. G. Stará, M. Tichý, D. Šaman, I. Císařová, P. Vojtíšek, I. Starý, *Angew. Chem. Int. Ed.* **2008**, *47,* 3188.
36. F. Teplý, I. G. Stará, I. Starý, A. Kollárovič, D. Šaman, S. Vyskočil, P. Fiedler, *J. Org. Chem.* **2003**, *68,* 5193.
37. S. K. Collins, A. Grandbois, M. P. Vachon, J. Côté, *Angew. Chem. Int. Ed.* **2006**, *45,* 2923.
38. O. Songis, J. Míšek, M. B. Schmid, A. Kollárovič, I. G. Stará, D. Šaman, I. Císařová, I. Starý, *J. Org. Chem.* **2010**, *75,* 6889.
39. T. Ide, S. Sakamoto, D. Takeuchi, K. Osakada, S. Machida, *J. Org. Chem.* **2012**, *77*, 4837.
40. A. Godt , Ö. Ünsal, M. Roos, *J. Org. Chem.* **2000**, *65*, 2837
41. K. L. Billingsley, T. E. Barder, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2007**, *46*, 5359.
42. C. Zhang, Q. Wang, H. Long, W. Zhang, *J. Am. Chem. Soc.*, **2011**, *133* , 20995
43. H. Yamanishi, I. Tomita, K. Ohta, T. Endo, *Mol.Cryst.Liq.Cryst.*, **2006**, *169*, 47
44. F. Mitzel, S. F. Gerald, A. Beeby, R. Faust, *Chem. Eur. J.* **2003**, *9*, 1233