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Faculty of Science

Study programme: Chemistry
Study branch: Chemistry in Natural Science

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The synthesis of heterohelicenes by [2 + 2 + 2] cyclotrimerisation of alkynes

Syntéza heterohelicenů s využitím [2 + 2 + 2] cyklotrimerizace alkynů

Bachelor's Thesis

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Prague, 2011

Declaration:

This thesis describes my original work except where acknowledgement is made in the text. It is not substantially the same text as any work that has been, or is being submitted to any other university for any degree, diploma or any other qualification.

In Prague, 23. 5. 2011

Signature

Acknowledgement:

This thesis was carried out under supervision of RNDr. Ivo Starý, CSc. and RNDr. Irena G. Stará, CSc., to whom special thanks are due. I would also like to thank Ing. Jiří Rybáček, Ph.D. and other members of our group for their help and collaboration. Further, I am indebted to Ing. David Šaman, CSc. for measuring and interpretation of NMR spectra, RNDr. Pavel Fiedler, CSc. for measuring and interpretation of IR spectra, the members of the Department of Mass Spectroscopy for MS measurements, RNDr. Miroslav Gál, Ph.D. and Doc. RNDr. Lubomír Pospíšil, CSc. for CV measurements and interpretation. I would also like to thank Jan-Philip Meyer and Audrey Cassen. Last but not least, I would like to thank my parents and all others that have supported me during my studies.

Abstract:

The objective of this thesis was to investigate whether [2 + 2 + 2] cyclotrimerisation of aromatic triynes is a suitable method for preparation of helicenes containing sulfur. The thesis deals with the synthesis of dithia[5]helicene and thia[11]helicene. The aim of the theoretical part is to illustrate methods of synthesis of thiahelicenes that have already been prepared. It also describes the mechanism of the [2 + 2 + 2] cyclotrimerisation. The *Results and discussion* as well as the *Experimental part* focus on the synthesis of dithia[5]helicene and thia[11]helicene from the corresponding triyne and hexayne, respectively, as the key structures. A UV/Vis spectral analysis and cyclic voltammetry of the dithia[5]helicene was also peformed.

Úkolem této práce bylo zjistit, zda je [2 + 2 + 2] cyklotrimerizace aromatických triynů vhodná i pro syntézu helicenů obsahujících síru. Tato práce se zabývá syntézou dithia[5]helicenu a thia[11]helicenu. Teoretická část je zaměřena na metody přípravy již známých helicenů a také popisuje mechanismus [2 + 2 + 2] cyklotrimerizace. Část *Výsledky a diskuze* a *Experimentální část* se zabývá syntézou dithia[5]helicenu a thia[11]helicenu z odpovídajícího triynu, resp. hexaynu jako klíčových struktur. U dithia[5]helicenu bylo také změřeno UV/Vis spektrum a cyklická voltametrie.

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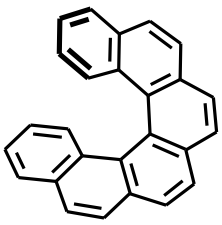
1. Introduction

1.1 Helicenes

Helicenes are polycyclic aromatic compounds that have all-*ortho*-fused aromatic rings. The first carbohelicene was intentionally synthetized in 1956 by Newman and Lednicer.[1] Helicenes are inherently chiral due to their helical shape caused by the steric interference of the terminal benzene rings. They can form two enantiomers. The enantiomeric forms are expressed by prefixes (*P*) or (*M*). Helicenes as π-conjugated systems have also interesting electronic properties. Combining the chiral and electronic properties makes them particularly attractive for example for their potencial use as organic field effect transistors (OFETs) or organic light-emitting diodes (OLEDs). From the practical point of view their solubility and stability in common organic solvents make them different from many other π-conjugated systems.

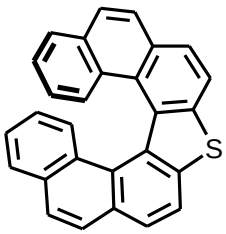
Number of fused cycles is indicated by the prefix in the name of the helicene compound, for example, *penta*helicene or simply [5]helicene. If the helicene structure is formed entirely by carbon atoms, they are called carbohelicenes (**1,** Figure 1). Another type of helicenes, where one or more carbon atoms are formally displaced by a heteroatom, is called heterohelicenes (**2,** Figure 1). The helicene-like compounds (**3,** Figure 1) have similar helical shape but contain, for example, an oxepine ring incorporated into the backbone.

Figure 1



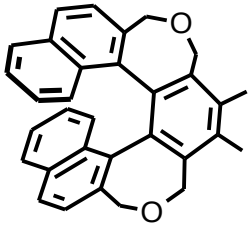
[6]carbohelicene

1



[7]heterohelicene

2



[7]helicene-like

3

1.2 Thiahelicenes

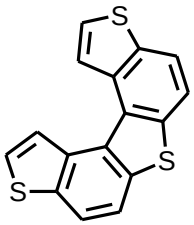
Although the chemistry of helicenes is dominated by carbohelicenes, there is a trend of the fusion of thiophene rings into the helicene skeleton to form thiahelicenes because of their possible interesting optoelectronic and photorefractive properties.[2,3] The first thiahelicene was prepared in 1971 by Wynberg.[4,5] Exchanging the carbons in the outer rim of the helicene for sulfur can bring a new advantage in the electronic properties of helicenes. One of them is that the α- and β- positions of the terminal thiophene ring can be easily substituted.

Note that this chapter deals only with thiahelicenes which have both benzene and thiophene rings and does not include oligothiophenes.[6]

1.2.1 Synthesis of thiahelicenes

The thiahelicenes that are formed by alternate thiophene and benzene rings are one of the types of thiahelicenes. The derivates with thiophene rings on both ends of the molecule (**4** – **7**, Figure 2) were synthesized by photocyclisation of 1,2-diheteroarylethylenes (stilbenes).

Figure 2



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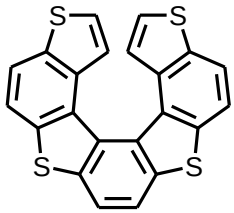

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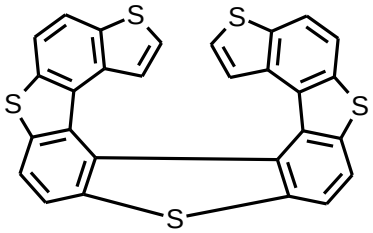

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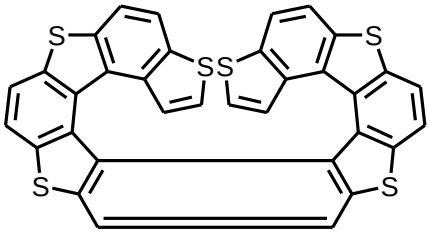
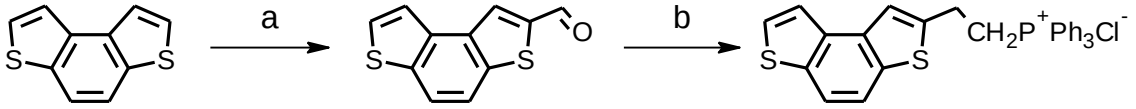


7

The common starting material for helicenes **4**-**7** was benzo[1,2-*b*:6,5-*b'*]bisthiophene **8** (Scheme 1).

Scheme 1

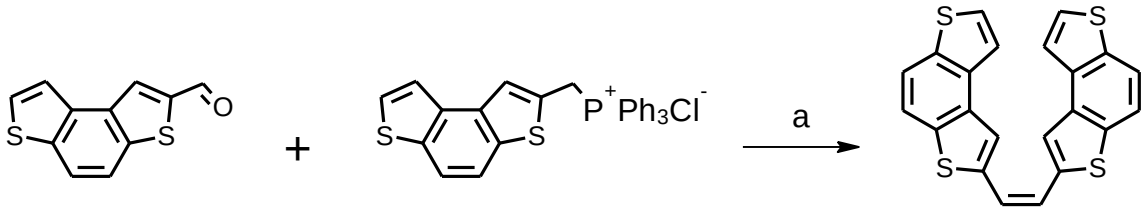


8 **9** **10**

a) $POCl_3$, PhN(Me)CHO, toluene, 69 %;
b) 1. $NaBH_4$, EtOH–THF, 2. $SOCl_2$, benzene–pyridine, 3. PPh_3, benzene.

Benzobisthiophene **8** was transformed into the corresponding carbaldehyde **9** by Vilsmeier reagent ($POCl_3$ and PhN(Me)CHO in boiling toluene). The carbaldehyde **9** was then reduced to alcohol, which was transformed into, first, chloride and subsequently the phosphonium salt **10**.[7] The stilbene derivative **11** needed for the preparation of the thia[7]helicene **5** was prepared by Wittig reaction of the 2-carbaldehyde **9** with the phosphonium salt **10** (Scheme 2).

Scheme 2

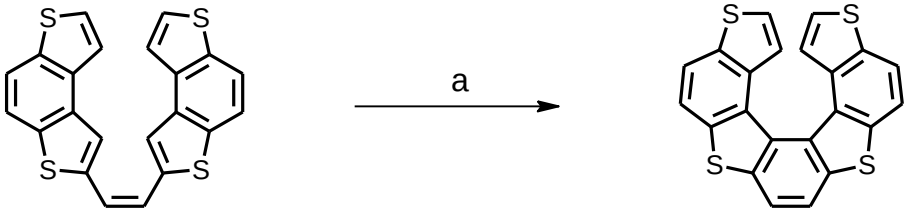


9 **10** **11**

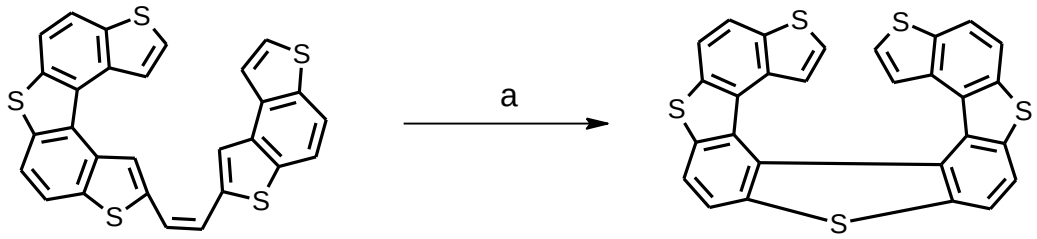
a) NaOMe, MeOH.

The photocyclisation reactions are described in Scheme 3. The derivatives **11** and **12** provided thia[7]helicene **5** and thia[9]helicene **6** in high yield.

Scheme 3



11 **5**

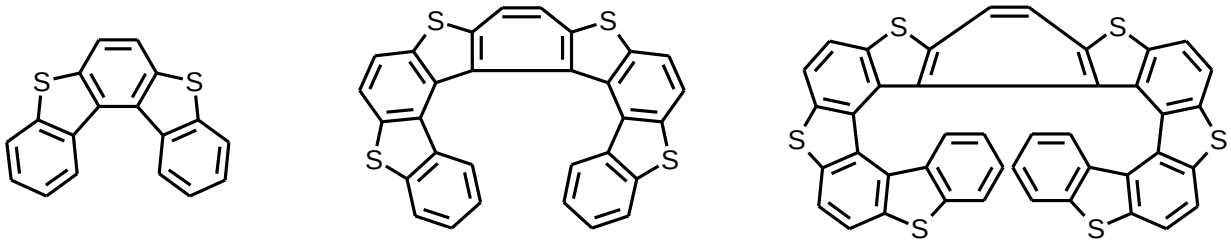


12 **6**

a) h*v*: 350 nm or visible light, 85 %.

Another group of thiahelicene derivatives have benzene rings on both ends (**13**-**15,** Figure 3).

Figure 3

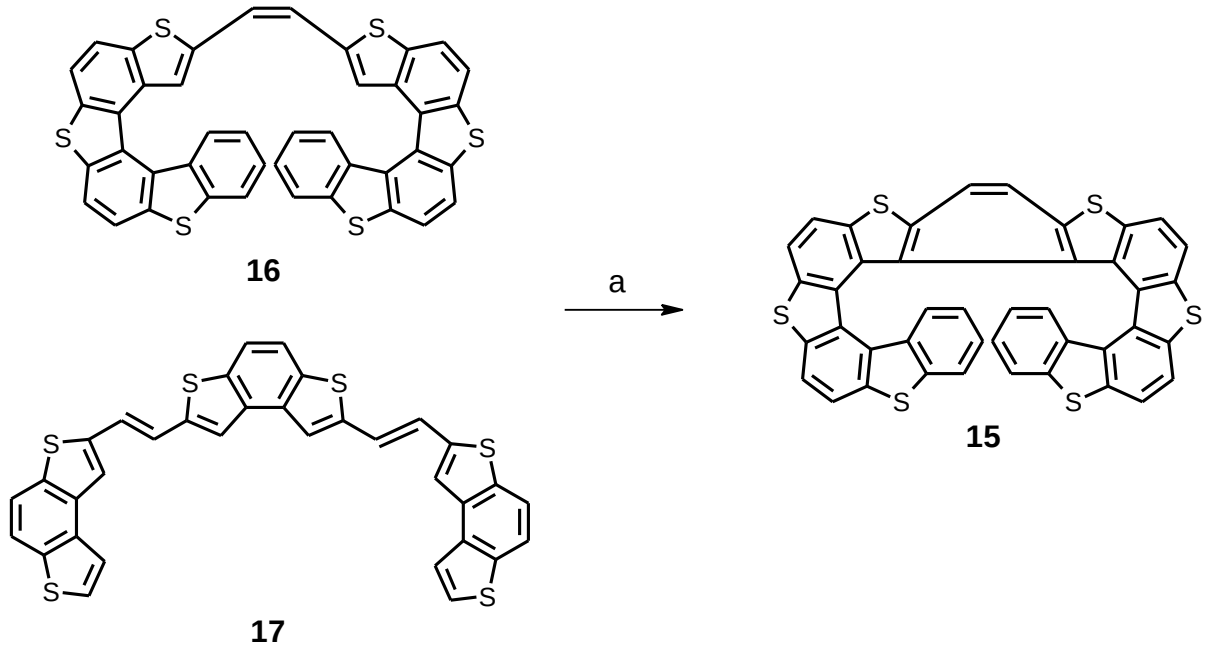


13 **14** **15**

The thiahelicenes **13**, **14** and **15** were prepared by was photocyclisation of 1,2-diheteroarylethylenes followed by *in situ* oxidation with iodine (Scheme 4).[8] The starting material for all these compounds was benzo[b]thiophene, which was lithiated in the acidic 2-position to prepare an important carbaldehyde intermediate. The desired stilbenoid precursors for the final photocyclisation are often prepared by Wittig-Horner or McMurry reactions or, more recently, using Suzuki coupling of

boronic esters.[9,10] The yields of the photocyclisations were 45 %. The symmetrical ethenes are advantageous because of the simplification of the synthesis. This photocyclisation did not form two geometrical isomers unlike often the similar preparation of carbohelicenes[11] because there is only one position available for the ring closure.

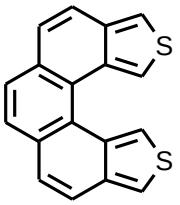
Scheme 4



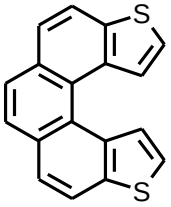
a) h*v*, I_2 (0.5 eq.), 50-60 °C, 2 h, 45 %.

Another type of thiahelicenes that were prepared by photocyclisation from the stilbenes are those having thiophene rings only on their ends. Examples of these structures **18** – **21** are showed in Figure 4.

Figure 4



18



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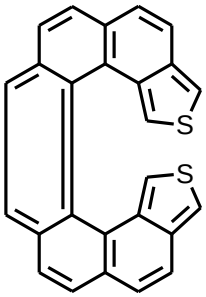

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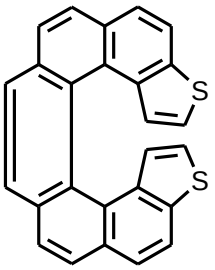
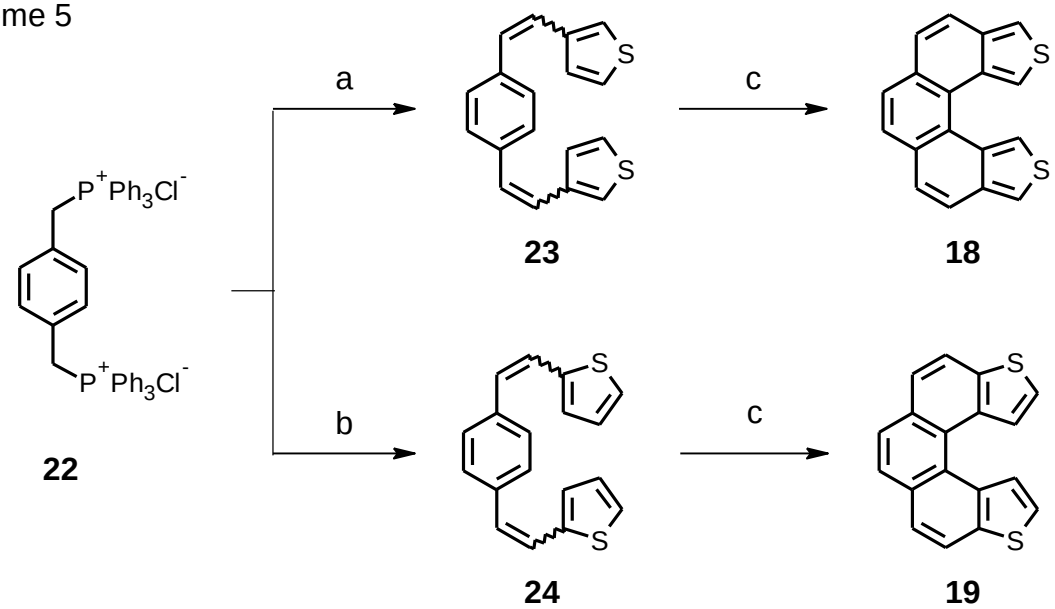


21

The synthesis of **18** or **19** begun by preparing the corresponding stilbenes **23** and **24** by Wittig reaction of the bisphosphonium salt **22** with the commercially availible 3- and 2-thiophene carbaldehydes, respectively (Scheme 5).[12] The bisphosphonium salt **22** was prepared from α,α'-dichloro-*p*-xylene and

Scheme 5

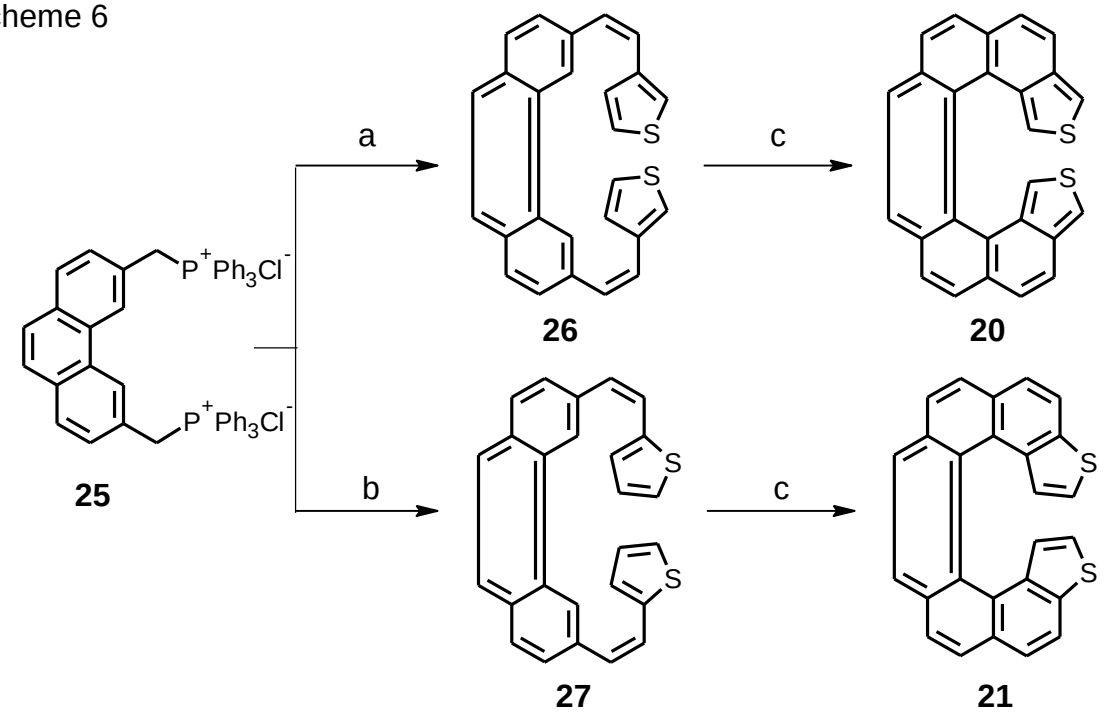


a) 3-Thiophene carbaldehyde, MeONa, MeOH, 74 %;
b) 2-thiophene carbaldehyde, MeONa, MeOH, 78 %;
c) h*v*, I_2, propylene oxide, toluene, 44 % for **18**, 60 % for **19**.

triphenylphosphine in refluxing DMF. The photocyclisation was done with 200 mg in 1 l of toluene with the stoichiometric amount of iodine and excess of propylene oxide. The thiahelicenes **18** and **19** were obtained in 44 % and 60 % yields, respectively. The relatively moderate yield of the compound **18** was probably due to the low solubility of stilbene **23** in toluene.

The similar synthetic approach was also used to prepare thiahelicenes **20** and **21**. The bisphosphonium salt **25** was subjected to the double Wittig reaction with either 2- or 3-thiophene carbaldehyde to obtain stilbenes **26** and **27** (Scheme 10) followed by photocyclisation to get **20** and **21** in 60 % and 40 % yields, respectively, under the same reaction conditions as for the compounds **18** and **19** (Scheme 6).

Scheme 6



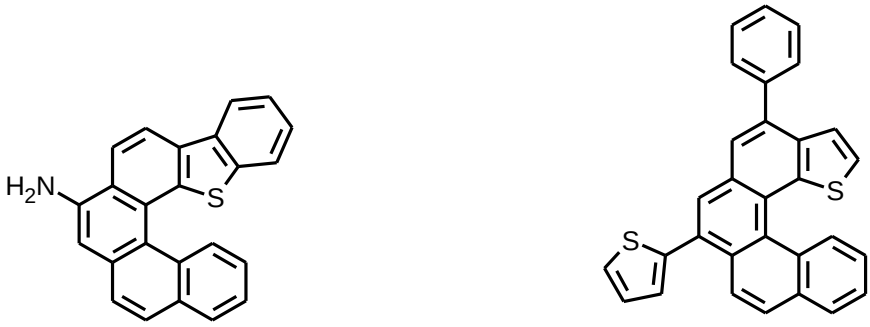
25 **26** **20** **27** **21**

a) 3-Thiophene carbaldehyde, MeONa, MeOH, 75 %;
b) 2-thiophene carbaldehyde, MeONa, MeOH, 60 %;
c) hν, I_2, propylene oxide, toluene, 60 % for **20**, 40 % for **21**.

All so far mentioned thiahelicenes have the sulfur atom in an outer helix position. To the best of our knowledge the preparation of thiahelicenes having the

sulfur atom in the inner helix position (such as **28** and **29**, Figure 5) have been reported only twice.[13,3]

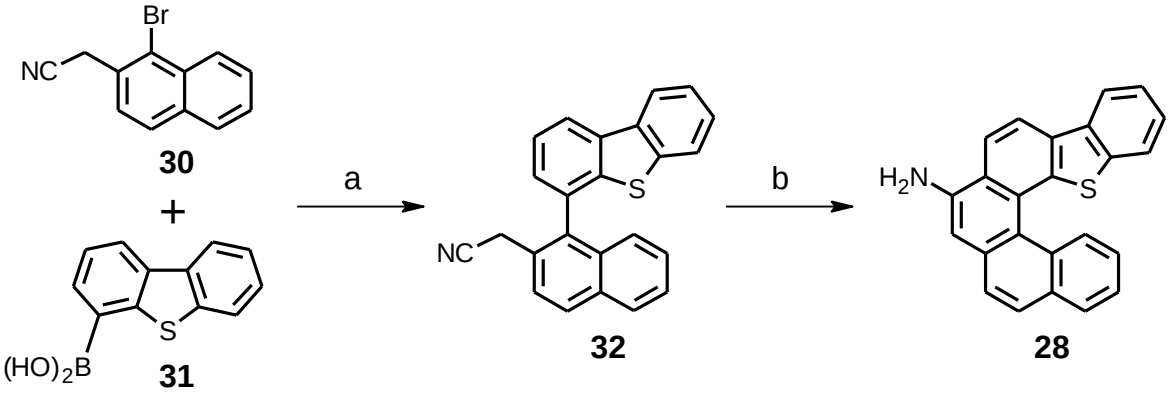
Figure 5



28 **29**

The aminothia[5]helicene **28** was prepared in two steps (Scheme 7).3 The first step was Suzuki cross-coupling of the bromonaphtalene derivative **30** and boronic acid **31** under treatment with Pd(II) catalyst and potassium carbonate in the refluxing mixture of toluene-ethanol-water. The nitrile **32** was heated in polyphosphoric acid at 80 °C for 48 h to give **28** in 36 % yield.

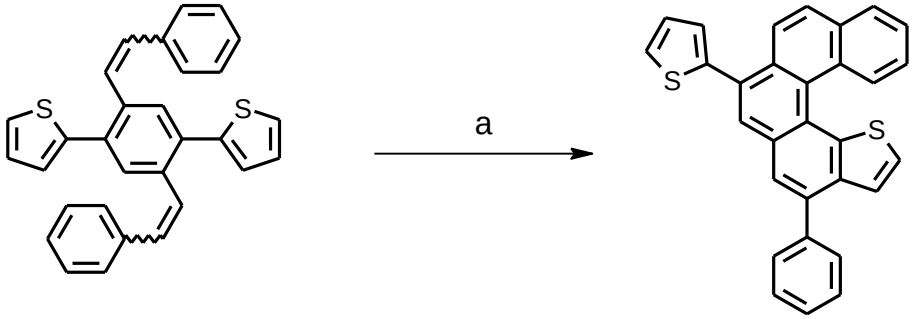
Scheme 7



a) $Pd(PPh_3)_2Cl_2$, K_2CO_3, toluene, ethanol, water, reflux, 68 %;
b) polyphosphoric acid, 80 °C, 48 h, 36 %.

The thiahelicene **29** was prepared from either *cis,cis* or *trans,trans* 2,5-dithienyl-1,4-distyrylbenzene **33** by irradiation in benzene with iodine for two weeks affording **29** in 20 % yield (Scheme 8).[13]

Scheme 8

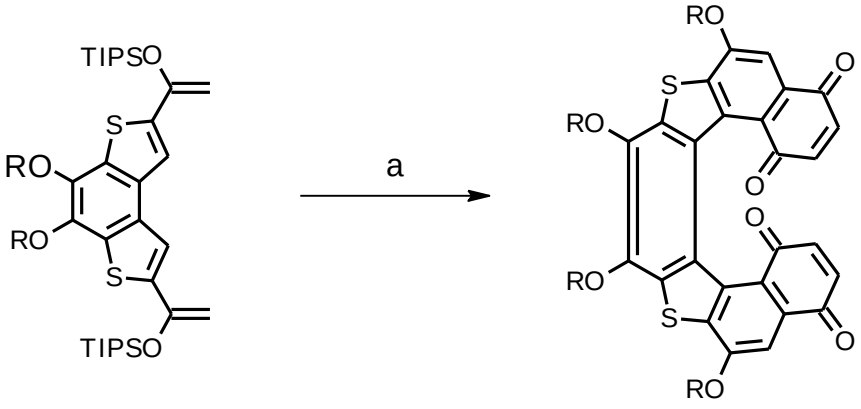


33 **29**

a) h*v*, I_2, benzene, 2 weeks, 20 %.

Besides the photocyclisation, Diels-Alder reaction of the electron rich bisvinylethers **34** with *p*-benzoquinone in large excess can be effectively used to prepare thiahelicenes **35** (Scheme 9).[14] This reaction provided the desired product **35** in quantitative yield. The clean product was separated only by trituration.

Scheme 9



34 **35**

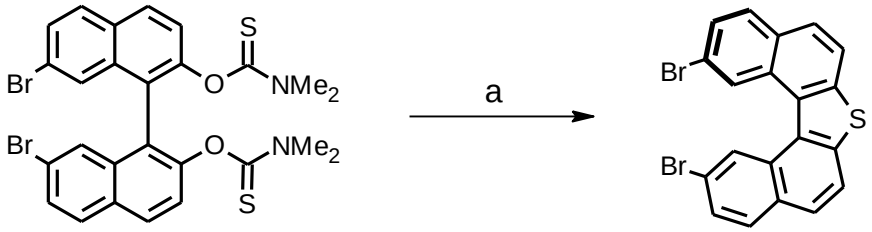
R = $C_{12}H_{25}$

a) 1. *p*-Benzoquinone, heptane, 95 %, 2. CsF, $C_{12}H_{25}I$, DMF, 91 %.

Furthermore, the Newman-Kwart rearrangement can be used for the preparation of thiahelicene by introduction of a thiophene ring in the final step of the

synthesis. This method was used to prepare the thia[5]helicene derivative **36** from the carbamoyl derivative **37** prepared from the BINOL precursor (Scheme 10)[15]. The rearrangement was carried out by heating at 285 °C for 45 minutes and afforded the product in 36 % yield.

Scheme 10



37 **36**

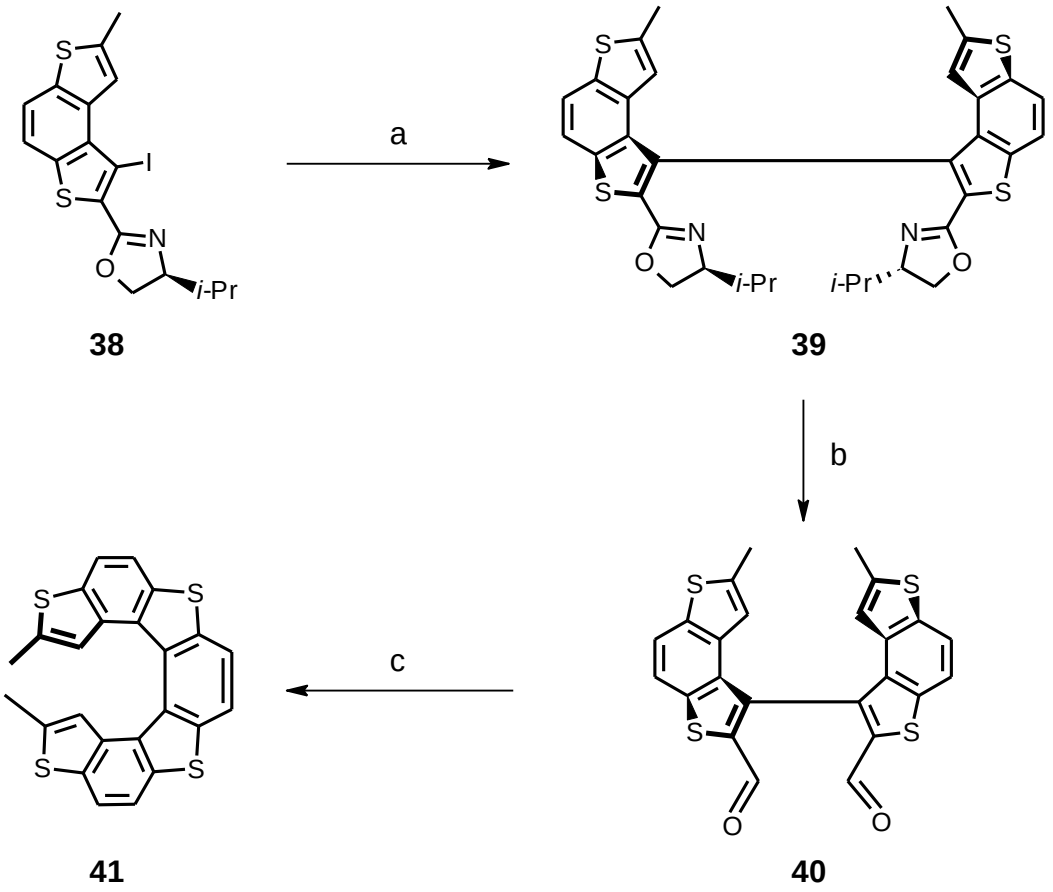
a) 285 °C, 45 min., 36 %.

1.2.1 Preparation of nonracemic thiahelicenes

The thiahelicenes as inherently chiral compounds can be prepared in an enantiopure form. The use of a pendant chiral auxiliary at the terminal thiophene unit resulted after photocyclisation in modest diastereoselectivity.[16] The more effective way how to prepare enantiopure thiahelicenes is enzymatic resolution exploiting lipase-catalysed transesterification. For example, thia[7]helicene diol when treated with *Pseudomonas cepacia*[17] and vinyl acetate in dichloromethane in the presence of molecular sieves at room temperature for 25 h led to 98 % ee and 45 % yield.

The asymmetric synthesis other than photocyclisation uses metal mediated coupling reaction.[18] First, the iodo-precursor **38** substituted with a chiral oxazoline moiety was treated with activated copper in dimethylformamide to give **39** as a mixture of diastereomers in a ratio of 2 : 1 (Scheme 11). The diastereomers of **39** were separated by chromatography and the chiral auxiliaries were transformed into aldehyde groups of **40**. The enantiopure helicene **41** was prepared by McMurry coupling of dialdehyde **40** in 52 % yield.

Scheme 11



38 **39** **40** **41**

a) Cu, DMF, 100 °C, 1 h, 99 %, 2:1 ratio of diastereomers;
b) 1. TFA, Na_2SO_4, 2. Ac_2O, pyridine, 3. $LiAlH_4$, 86 %;
c) 1. PCC, DCM, 2. $TiCl_3$-$DME_{1.5}$, Zn-Cu, 52 % (99 % ee).

Moreover, nonracemic thiahelicenes can be prepared by separation of enantiomers using a chiral stationary phase in HPLC[19] or a pendant chiral auxiliary in the diastereomers separation by column chromatography.[14]

1.2.2. Utilisation of thiahelicenes

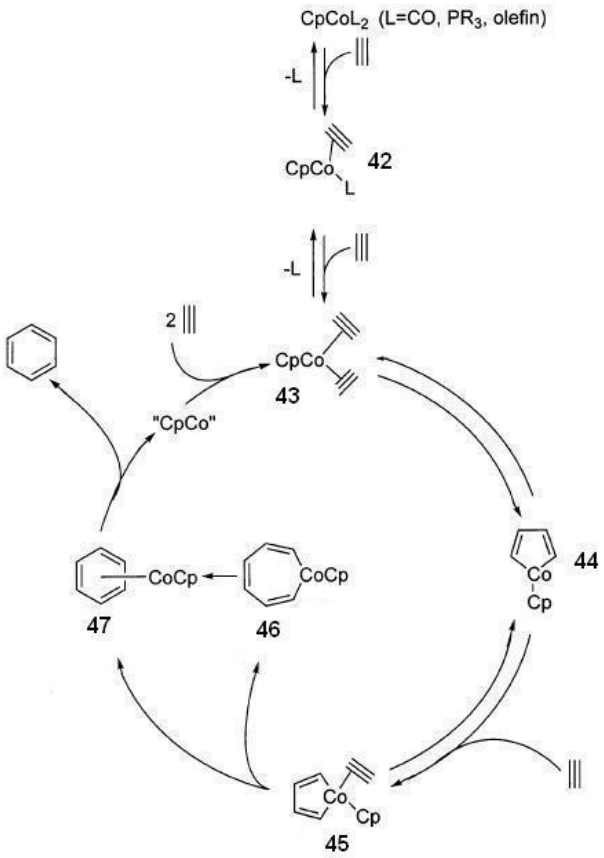
Due to their stable polyconjugated helical framework and the presence of heteroatoms, heterohelicenes are very promising structures. They could be used as chiral ligands for various enantioselective reactions or as organocatalysts. For example, highly enantioselective addition of *i*-Pr_2Zn to pyrimidine-5-carbaldehyde done in the presence of tetrathia[7]helicene provided a product with 99 % ee.[20] Thiahelicenes have also high electron afinity[12] and high thermal stability and could serve as materials for organic light-emitting diodes. They might have a potential to be used as new non-linear optical materials[21] or to exhibit an interesting interaction with DNA.[22]

1.3 [2+2+2] Cyclotrimerisation for the helicene synthesis

[2+2+2] Cyclotrimerisation is a highly exothermic reaction in which three alkynes react and form a benzene ring.[23] The first cyclotrimerisation was done in 1886 when Berthelot prepared benzene from acetylene.[24] It has been found that the cyclotrimerisation reaction can be catalysed by transition metals such as Co, Rh, Ni or Cu.

One of the catalysts successfully used for this reaction is cyclopentadienylcobalt dicarbonyl $CpCo(CO)_2$. The assumed mechanism of this catalysis[25] is described in Scheme 12.

Scheme 12



First two acetylenes sequentially displace carbonyl(s) to form the complexes **42** and **43**, respectively. The oxidative coupling of the alkyne ligands in **43** generates the cobaltocyclopentadiene **44**, which is coordinatively unsaturated. This complex **44** coordinates to the third acetylene to form **45**, which is transformed into η^4-benzene complex **47**. This last step could involve formation of cobaltocycloheptatriene **46** that can undergo the reductive elimination to give **47**. The cycle is completed by the decomplexation of arene and coordination of two acetylenes to the cobalt species. There is an experimental evidence for the intermediates **45** and **47**.[26]

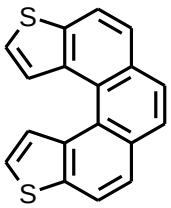
In the group of Dr. Ivo Starý at the IOCB AS CR the [2+2+2] cyclotrimerisation of aromatic triynes catalysed by Co(I) and Ni(0) complexes has been used to prepare helicenes and their congeners. They have successfully used this methodology to prepare various helicenes such as substituted 2-aza[6]helicene,[27] [11]anthrahelicene,[28] [7]helicene[29] and [7]helicene-like compounds.[30]

2. Objectives

The objectives of this thesis have been:

- to prove that intramolecular [2+2+2] cyclotrimerisation catalysed by transition metals is a suitable method also for the synthesis of S-containing helicenes
- to prepare dithia[5]helicene **19** and thia[11]helicene **48** (Figure 6)
- to perform spectral characterisation of dithia[5]helicene **19** (including UV/Vis, fluorescence and cyclic voltammetry)

Figure 6



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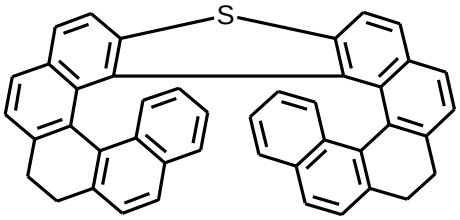


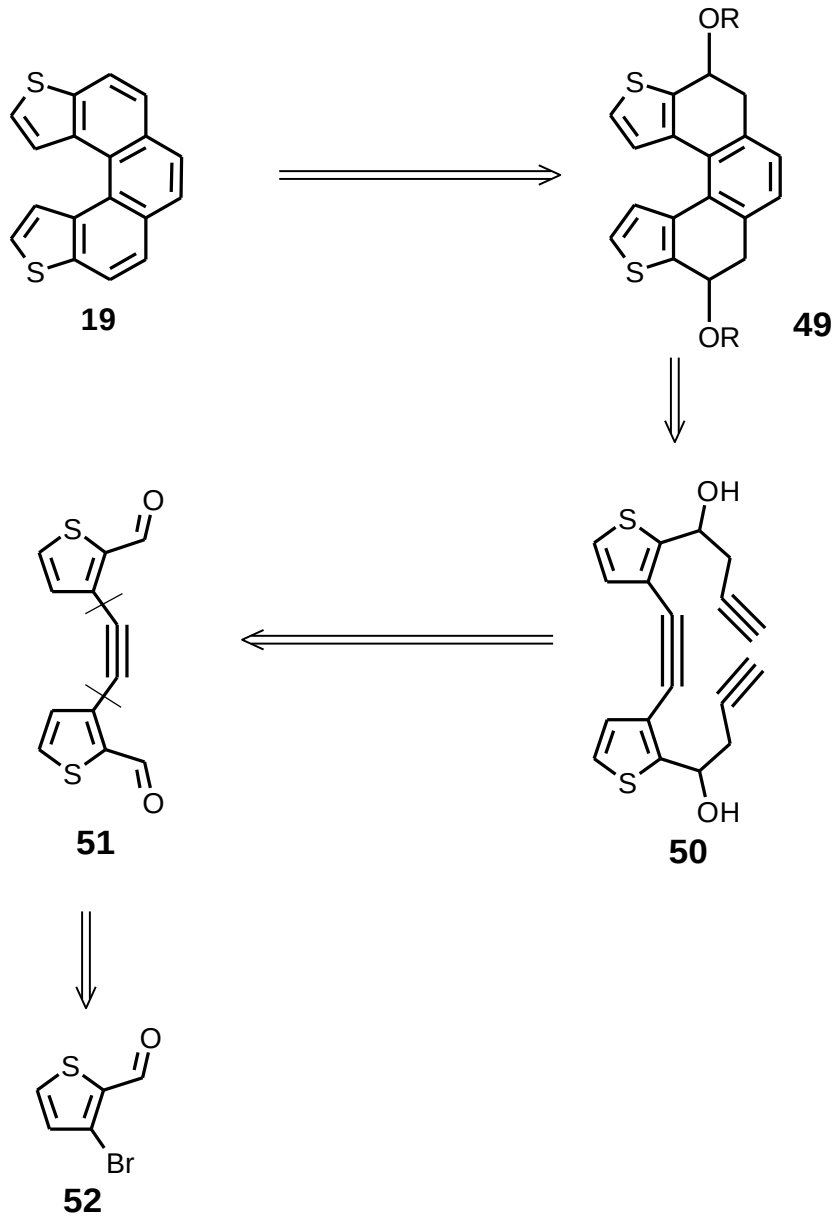
48

3. Results and discussion

3.1 Synthesis of dithia[5]helicene

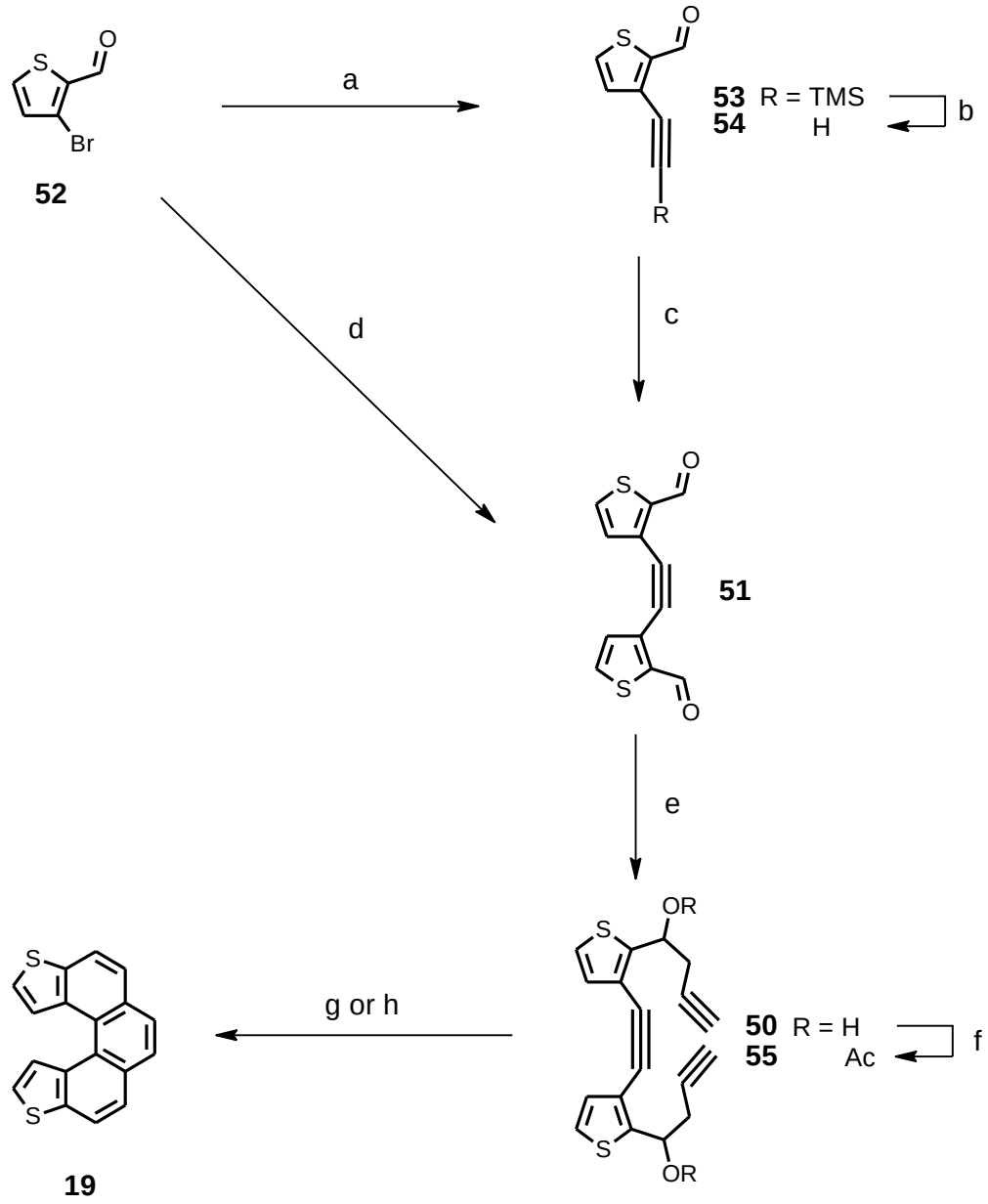
My objective was to prepare dithia[5]helicene **19**. A retrosynthetic analysis revealed that the crucial steps are: elimination leading to the fully aromatic product (**49** → **19**), double addition of an organometallic reagent to carbonyl groups (**51** → **50**) and the double Sonogashira coupling of the bromothiophene derivative with acetylene (**52** → **51**) (Scheme 13).

Scheme 13



The starting material for the desired dithia[5]helicene **19** was 3-bromothiophene-2-carbaldehyde **52** (Scheme 14).

Scheme 14



a) TMS-acetylene (2 eq.), $Pd(PPh_3)_4$ (5 mol %), CuI (10 mol %), *i*-Pr_2EtN (2.5 eq.), toluene, rt, 1.5 h, 70 %;
b) NaOMe (3.5 eq.), MeOH-THF (1:1), rt, 20 min, 75 %;
c) **52** (1 eq.), **54** (1.2 eq.), $Pd(PPh_3)_4$ (5 mol %), CuI (10 mol %), *i*-Pr_2EtN (2.5 eq.), toluene, rt, 1 h, 30 %;
d) acetylene (0.7 eq.), $Pd(PPh_3)_4$ (5 mol %), CuI (10 mol %), *i*-Pr_2EtN (2.5 eq.), toluene, rt, 1 h, 33 %;
e) propargylbromide (9.5 eq), Ga (2.2 eq.), In (30 mol %), THF, 5 °C, 1.5 h, then **51** (1 eq.), rt, 1 h 43 %;
f) Ac_2O (100 eq.), DMAP (20 mol %), pyridine, 25 min, rt, 78 %;
g) $CpCo(CO_2)$ (1 eq.), PPh_3 (4 eq.), decane, halogen lamp, 140 °C, 20 min, 86 %;
h) $CpCo(CO_2)$ (1 eq.), THF, flow reactor, 250 °C, 100 atm, 16 min, 92 %.

Based on our previous experience that a sequence of (trimethylsilyl)acetylene coupling – trimethylsilyl group deprotection is usually a reliable way to introduce an acetylene moiety, the Sonogashira coupling with bromocarbaldehyde **52** was carried out under catalysis by $Pd(PPh_3)_4$ and CuI in toluene and in the presence of 2.5 equivalents of diisopropylethylamine as a base. The reaction provided the trimethylsilylated derivative **53** in 70 % yield. The following step, desilylation (**53** → **54**) by excess of NaOMe in 1:1 mixture of methanol-THF proceeded in 75 % yield. After the desilylation, a coupling of acetylene **54** and bromide **52** was done under the same conditions as those with the (trimethylsilyl)acetylene. The low 30 % yield of the second coupling is probably caused by the instability of the terminal acetylene **54** in the basic environment. The overall yield of this route was only 16 %.

Therefore, the procedure that can directly provide the symmetric product **51** was examined. This procedure involves the double Sonogashira coupling of bromide **52** with gaseous acetylene. As it has been found earlier in our group, this method is very efficient, however, it is not as general as the stepwise procedure already mentioned since they were many cases when this method completely failed. Unfortunately, the critical appraisal of the scope and limitation of this reaction is still lacking. The reaction of **52** with acetylene in toluene catalysed by $Pd(PPh_3)_4$, CuI and in the presence of 2.5 equivalents of diisopropylethylamine was done with a little larger than calculated stoichiometric amount of acetylene in order to avoid oligomerisation. The dialdehyde **51** was unstable on silica gel so the deactivated silica gel by triethylamine (1 %) for the flash chromatography was used to obtain the product in 33 % yield.

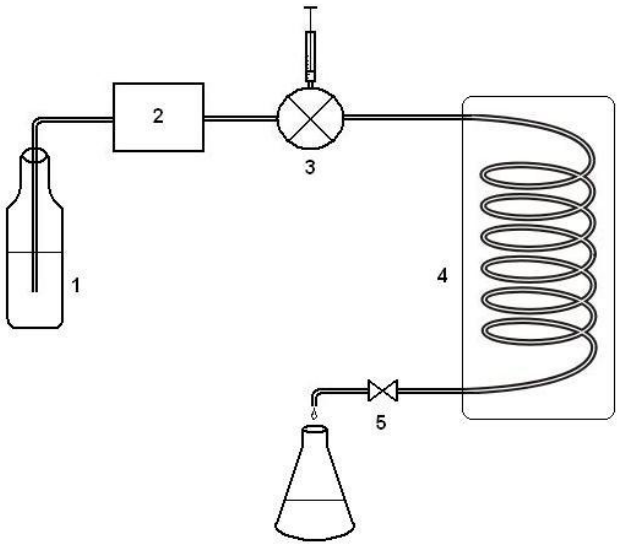
The next step of the synthesis was the indium catalysed nucleophilic propargylation of the dialdehyde **51** by means of propargylbromide with a stoichiometric amount of gallium in tetrahydrofuran. This reaction led to the desired product **50** as a mixture of two diastereomers in 43 % yield (according to the ^{1}H NMR spectrum**)** and byproduct in ratio of 1:1 (according to their mass). The ^{1}H NMR

analysis showed that the byproduct is in fact a complex mixture of compounds having aromatic protons.

The subsequent [2 + 2 + 2] cyclotrimerisation did not work with diol **50**. Therefore, diol **50** was transformed into the diacetoxy derivative **55** by a large excess of acetanhydride in pyridine catalysed by 4-(dimethylamino)pyridine. The reaction provided **55** as a mixture of two diastereomers in 78 % yield (according to the ^{1}H NMR spectrum**)**. The cycloisomerisation was then done using two procedures. First attempt was done by the irradiation of the decane solution of **55** by a halogen lamp in the presence of the commercially available $CpCo(CO)_2$ reagent with triphenylphosphine at 140 °C. The product **19** was obtained in 86 % yield. The triphenylphosphine was used to stabilise the active species of CpCo in the solution.

For the second attempt a flow reactor was used (Figure 7). The flow reactor consists of a pump, a section where the capillary is heated to the required temperature and a back pressure pump to build up the pressure. The internal diameter of the capillary is 1 mm and its length is 10 m, which corresponds to the

Figure 7

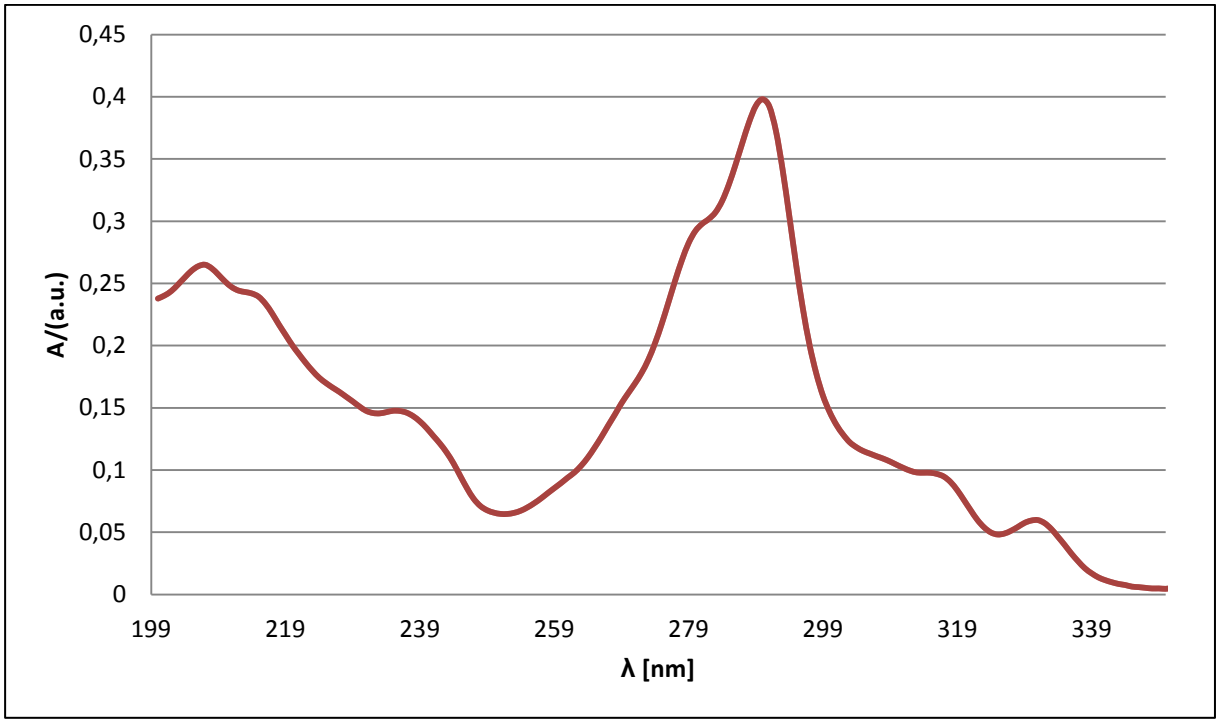


1. Solvent reservoir, 2. HPLC pump, 3. injection valve, 4. heated capillary, 5. back pressure valve.

total volume of 8 ml. It is possible to set the pressure, temperature and flow rate with this instrument. The [2 + 2 + 2] cyclotrimerisation was carried out in tetrahydrofuran with $CpCo(CO)_2$ at 250 °C and 100 atm for 16 minutes and afforded the product **19** in 92 % yield. These conditions were used since they had successfully been applied in the preparation of the similar carbohelicenes. Within both procedures the [2 + 2 + 2] cyclotrimerisation was immediately followed by the *in situ* elimination of acetic acid, *i.e.* the diacetoxyl derivate of tetrahydrodithia[5]helicene **49** was never observed, and only the fully aromatic dithia[5]helicene **19** was detected. The use of the flow reactor seemed to be more efficient because of the easier and faster experimental procedure.

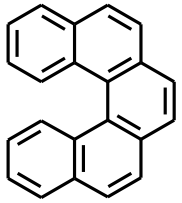
The further objective was the spectral characterisation of dithia[5]helicene **19**. Therefore, the UV/Vis absorption spectra were recorded (Figure 8). At the same time an attempt to measure the fluorescence spectra of compound **19** was done. However, its acetonitrile solution did not provide any spectrum.

Figure 8



The last objection regarding the dithia[5]helicene **19** was to study its electrochemical behaviour. Thus, the cyclic voltametry was performed and compared to that of [5]helicene **56** (Figure 9). Experimental estimation of the reduction and oxidation

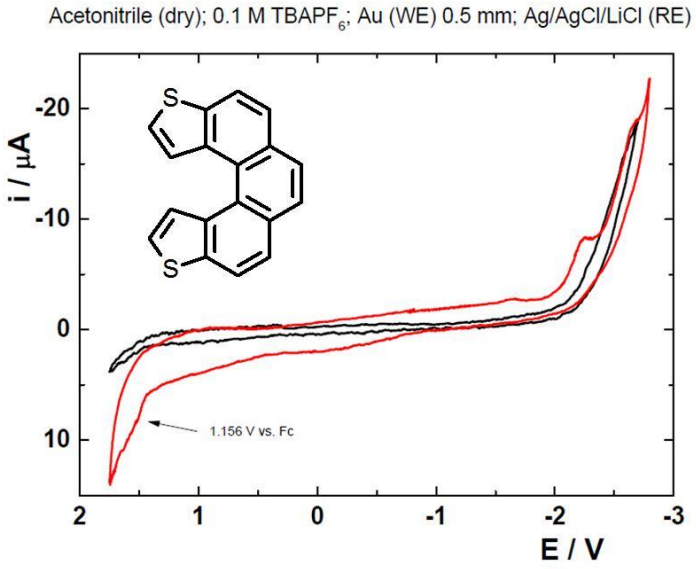
Figure 9



56

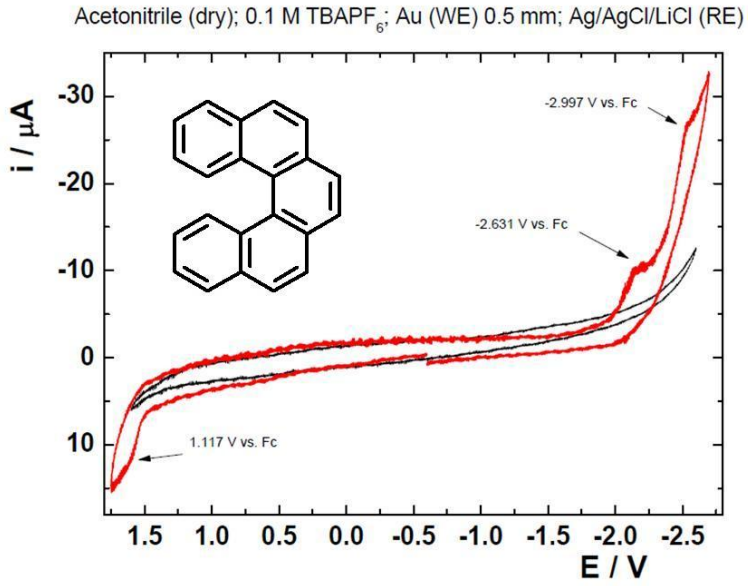
potentials was made by measuring the current-voltage curves on an inert gold electrode in the acetonitrile solutions of dithia[5]helicene **19** and [5]helicene **56**. The cyclic voltammograms of both compounds (Figure 10 and Figure 11) are very similar even though some small differences in both the shape of cyclic voltammograms and the values of the reduction potentials are observed. The voltammetric data show that dithia[5]helicene **19** as well as [5]helicene **56** can accept another two or three electrons at considerably more negative potentials. However, these subsequent electron transfer steps are irreversible as can be seen on the cyclic voltammograms.

Figure 10



The cyclic voltammetry of 0.56 mM solution of dithia[5]helicene **19** in 0.1 M tetrabutyl-ammonium hexafluorophosphate in acetonitrile at the scan rate of 0.5 V/s (red curve), baseline (black curve).

Figure 11

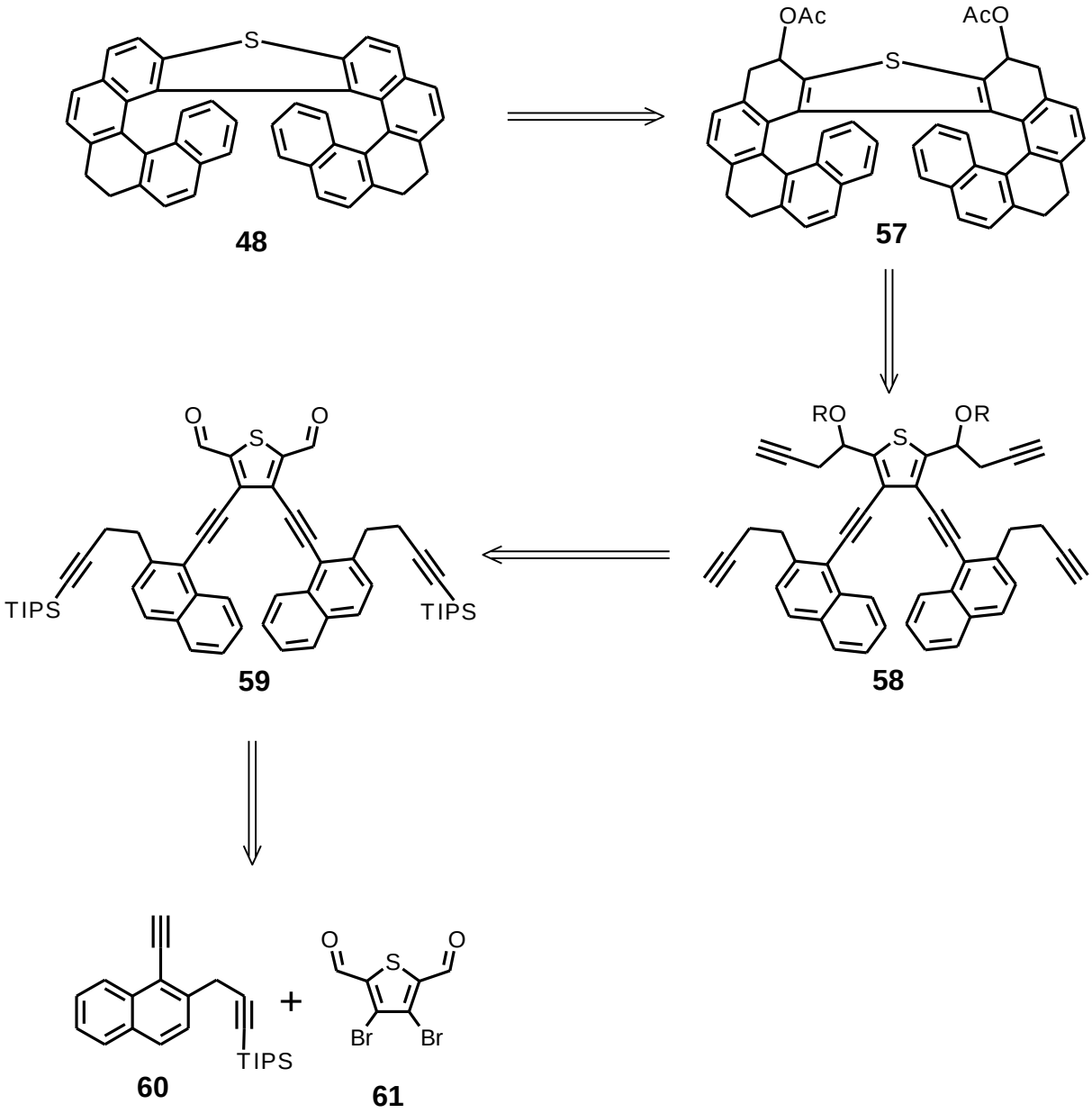


The cyclic voltammetry of 0.67 mM solution of [5]helicene **56** in 0.1 M tetrabutyl-ammonium hexafluorophosphate in acetonitrile at the scan rate of 0.5 V/s (red curve), baseline (black curve).

3.2 Synthesis of thia[11]helicene

From the retrosynthetic analysis of the preparation of the thia[11]helicene **48** emerged that the key to success are the following steps (Scheme 15): The double [2+2+2] cyclotrimerisation of the hexayne (**58** → **57**), elimination (**57** → **48**), double addition of an organometallic reagent to carbonyl groups (**59** → **58**) and double Sonogashira coupling of the dibromothiophene derivative **61** with diyne **60**.

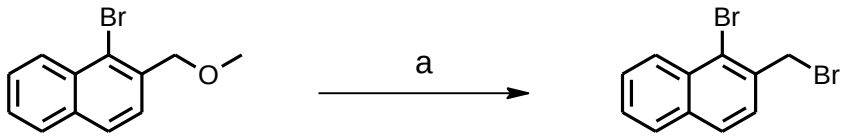
Scheme 15



The starting materials for the synthesis of thia[11]helicene **48** were diyne **60** and dibromide **61**. The diyne **60** was prepared by a known procedure[31] from 1-

bromo-2-(bromomethyl)naphthalene **63** in overall 45 % yield. The naphthalene dibromide **63** was prepared by reaction of 1-bromo-2-(methoxymethyl)naphthalene **62** with hydrogen bromide in acetic acid in 87 % yield (Scheme 16).

Scheme 16



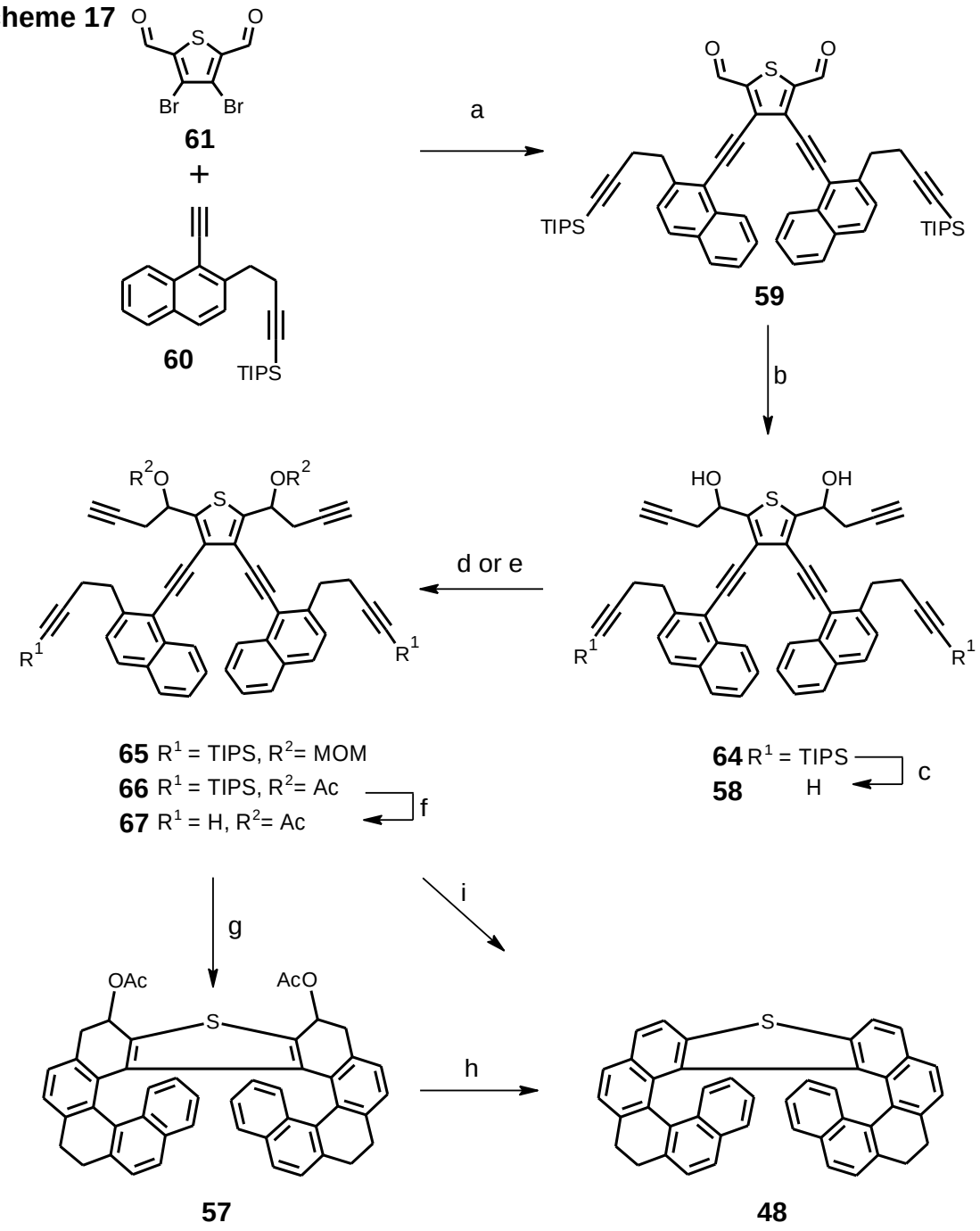
62 **63**

a) HBr (7 eq.), AcOH, rt., 2 h, 87 %.

Being inspired by the reaction of the similar thiophene monobromide **52**, the double Sonogashira coupling of the diyne **60** and dibromide **61** was carried out under catalysis by $Pd(PPh_3)_2Cl_2$ and CuI in the presence of 2.5 equivalents of diisopropylethylamine in toluene (Scheme 17). The product **59** could not be separated by normal-phase silica gel chromatography, because the byproducts had the very similar retention factors, so chromatography on a C18 reverse phase was used. Unfortunately, this reaction provided the product **59** only in 16 % yield while the starting material **61** was recovered in 65 % yield. Therefore, other conditions were tested. First, the reaction was carried out under the same condition except for $Pd(PPh_3)_4$, which was used instead of $Pd(PPh_3)_2Cl_2$. However, this reaction afforded the product **59** only in 10 % yield. Then toluene as a solvent was replaced by tetrahydrofuran. Unfortunately, this change did not lead to the desired product **59** at all. Finally, it was found that the best results in this double Sonogashira coupling were obtained using a catalytic system of $Pd(PPh_3)_2Cl_2$ and CuI in triethylamine as a solvent when the dialdehyde **59** arose in 50 % yield.

The next step of the synthesis was the indium catalysed nucleophilic propargylation of the dialdehyde **59** by means of organogallium prepared from propargylbromide and a stoichiometric amount of gallium in tetrahydrofuran.[32] This reaction afforded the diol **64** in 86 % yield.

Scheme 17



a) **60** (2.1 eq), $Pd(PPh_3)_2Cl_2$ (10 mol %), CuI (20 mol %), Et_3N, 1 h, rt, 50 %;
b) In (10 mol %), Ga (2.2 eq.), propargylbromide (9.4 eq.), THF, 5 °C, 1 h, then **59** (1 eq.), rt, 1 h, 86 %;
c) TBAF (3 eq.), THF, 1 h, rt, 95 %;
d) chloromethyl methyl ether (12.2 eq.), *i*-Pr_2EtN (12.5 eq.), DCM, rt, 15 hod, 14 % for **65**;
e) Ac_2O (100 eq.), DMAP (20 mol %), pyridine, rt, 20 min, 88 % for **66**;
f) TBAF (3 eq.), THF, 1 h, rt, 64 %.;
g) $CpCo(CO_2)$ (2.1 eq.), PPh_3 (4 eq.), decane, halogen lamp, 140 °C, 25 min., <67 %;
h) TsOH (15 eq.), benzene, 30 min., 80 °C, microwave oven, <57 %;
i) $CpCo(CO_2)$ (1 eq.), THF, flow reactor, 250 °C, 100 atm, 16 min., <50 %.

Prior to the cyclotrimerisation, the triisopropylsilyl group deprotection of **64** was tested in a small scale, affording the terminal hexayne **58** (R = H) in 95 % yield. The reaction was done by 3 equivalents of tetra-*n*-butylammonium fluoride in tetrahydrofuran and the progress of the reaction was monitored by TLC. Unfortunately, the [2 + 2 + 2] cyclotrimerisation did not work with the diol **58**. Therefore, the silylated diol **64** was transformed into the methoxymethyl derivative **65** (MOM derivative) by reaction with 12 equivalents of chloromethyl methyl ether and 12.5 equivalents of diisopropylethylamine in dichloromethane. The reaction led to two products. The inspection of the ^{1}H NMR spectrum revealed that one product was the desired methoxymethyl derivative **65** whereas the other one had only one methoxymethyl group. After flash chromatography the desired di-MOM derivative was obtained in 14 % yield. The experiment was repeated at 40 °C but this attempt led to the complete decomposition of the starting materials. Therefore the silylated diol **64** was transformed into the acetoxy derivative **66** by a large excess of acetanhydride in pyridine catalysed by 4-(dimethylamino)pyridine. The reaction provided the diacetate **66** in 88 % yield. Its desilylation under the same conditions as for the diol **64** led to the acetoxy derivative **67** in 64 % yield.

The acetoxy derivative **67** was subjected to the [2 + 2 + 2] cyclotrimerisation. Similarly as in the case of the dithia[5]helicene **19**, the cyclotrimerisation by means of Co(I) was pursued using several procedures. First, the decane solution of **67** was irradiated by the halogen lamp using the classical Vollhardt's conditions in the presence of $CpCo(CO)_2$ reagent with triphenylphosphine at 140 °C. After irradiation, the triphenylphosphine was separated by flash chromatography on silica gel. According to ^{1}H NMR, the remaining mixture contained probably the helicene acetoxy derivative **57** (<67 % yield). In order to carry out the subsequent preparation of the thia[11]helicene **48,** this mixture was heated at 80 °C in a microwave oven for 30 minutes with 15 equivalents of *p*-toluenesulfonic acid in benzene which led to unclean product **48** in <57 % yield.

For another attempt to get compound **48** a flow reactor was used. The [2 + 2 + 2] cyclotrimerisation was carried out in tetrahydrofuran with $CpCo(CO)_2$ at 250 °C and 100 atm for 16 minutes. Both procedures afforded the unclean product **48** whose molecular composition was confirmed by high resolution mass spectrometry. Unfortunately, it has not yet been possible to purify the desired product **48** by flash chromatography on either normal or reverse phase or by preparative TLC. The further attempt to obtain the clean thia[11]helicene **48** is under way.

4. Conclusion

It was proven that the intramolecular [2+2+2] cyclotrimerisation catalysed by transition metals is a suitable method also for the synthesis of S-containing helicenes. Dithia[5]helicene **19** was prepared and fully characterised. Thia[11]helicene **48** was also prepared but it was characterised only by HR MS due to difficulties during its purification.

The UV/Vis characterisation of the dithia[5]helicene **19** was performed. The cyclic voltammogram was similar to that of carbo[5]helicene **56**.

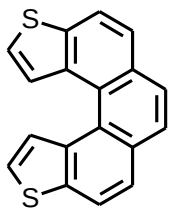
5. Experimental part

General: The ^{1}H NMR spectra were measured at 400.13 MHz, 499.88 MHz, and 600.13 MHz, the ^{13}C NMR spectra at 100.61 MHz, 125.71 MHz and 150.90 MHz in $CDCl_3$ with TMS as an internal standard. The chemical shifts are given in δ-scale, the coupling constants *J* are given in Hz. The HMBC experiments were set up for J_{C-H} = 5 Hz. For the correct assignment of both the ^{1}H and ^{13}C NMR spectra of key compounds, COSY, HMQC and HMBC experiments were performed. The IR spectra were measured in $CHCl_3$. The EI mass spectra were determined at an ionising voltage of 70 eV, the *m/z* values are given along with their relative intensities (%). The standard EI spectra were recorded in the positive ion mode. 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 or TOF EI MS. The CI mass spectra were determined at an ionising voltage of 70 eV and recorded using CTC Premiere (Waters) with TOF analyser. The source temperature was 130 °C and the carrying gas was methane. The commercially available catalysts and reagent grade materials (such as $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, CuI, $CpCo(CO)_2$, DMAP) were used as received. If mentioned, the solvents were degassed by three freeze-pump-thaw cycles and distilled before use otherwise they were used as received. TLC was performed on Silica gel 60 F_{254}-coated aluminium sheets (Merck) and spots were detected by the solution of $Ce(SO_4)_2$. 4 H_2O (1%) and $H_3P(Mo_3O_{10})_4$ (2%) in sulfuric acid (10%) or by the solution of 2,4-dinitrophenylhydrazine (3.3 %) with sulfuric acid (30 %) in aqeous ethanol (68 vol %). The flash chromatography was performed on Silica gel 60 (0.040-0.063 mm, Fluka) or on Biotage® KP-C18-HS SNAP cartridges

using the Isolera One HPFC system (Biotage, Inc.). Biotage Initiator EXP EU (300 W power) was used for reactions carried out in microwave oven. The 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 analysator which operated at 150 °C. The UV/Vis spectra were measured with UV-Vis-NIR spectrophotometer Varian Cary 5000 in 1 mm cell by a single beam method using correction of absorbance by a blank sample.

The electrochemical measurements were done using an electrochemical system for cyclic voltammetry. It consisted of a fast rise-time potentiostat interfaced to a personal computer via an IEEE–interface card (PC–Lab, AdvanTech Model PCL–848) and a data acquisition card (PCL–818) using 12–bit precision. A three-electrode electrochemical cell was used. The reference electrode (RE), Ag|AgCl|1M LiCl, was separated from the test solution by a salt bridge. The half-wave potential of ferrocene against it was +0.469 V. The gold working electrode (WE) was sealed Au wire (Goodfellow) exposed to the solution as a disc with a diameter 0.5 mm. Au electrode was mirror-polished on a polishing cloth with alumina suspension and three grades diamond pastes. The counter electrode (CE) was cylindrical platinum wire. Tetrabutylammonium hexafluorophosphate (TBAPF6), used as a supporting electrolyte, was obtained from Sigma-Aldrich (electrochemical grade). Acetonitrile (dry, Sigma-Aldrich) was treated with activated molecular sieves 3 Å (Lachema, Brno) to further decrease the water content as low as possible (usually below 20 ppm). Oxygen was removed from the solution by purging with argon (Messer, min 99.998 Vol %) prior to the each measurement.

Phenanthro[3,4-*b*:6,5-*b'*]bisthiophene 19



Method A (flow reactor): The flow reactor was heated up to 250 °C with THF flowing at 0.5 ml/min rate and at pressure of 100 atm. Triyne **55** (10 mg, 0.02 mmol) was dissolved in 2 ml of THF and $CpCo(CO)_2$ (3 µl, 0.02 mmol, 1 eq.) was added. The reaction mixture was then injected into the flow reactor using a 2 ml sample loop. The residence time in the heated capillary was 16 min. The effluent on an output was collected and evaporated to dryness. Then the residue was dissolved with small amount of DCM, filtered through a short pad of silica gel and eluted with DCM (20 ml). The solvent was removed *in vacuo.* The product was purified by flash chromatography (hexane-EtOAc 100:0 to 80 : 20) to give **19** (6.5 mg, 92 %) as a colorless oil.

Method B (halogen lamp): Triphenylphosphine (51 mg, 0.20 mmol, 4 eq.) was dissolved in decane (4 ml, anhydrous, degased) in a Schlenk flask under argon. The solution was hearted in an oil bath to 90 °C and triyne **55** (20 mg, 0.049 mmol) was added in THF (100 µl). The reaction mixture was removed from the oil bath and was irradiated with a halogen lamp until the solution reached 100 °C. Then $CpCo(CO)_2$ (7 µl, 0.049 mmol, 1 eq.) was added in THF (100 µl). The reaction mixture was irradiated at 140 °C for 20 min. The mixture cooled down to room temperature, filtered through a short pad of silica gel and eluted with DCM (20 ml). The solvents were removed *in vacuo*. The product was purified with flash chromatography on silica gel (hexane-EtOAc 100:0 to 80 : 20) to give **19** (12 mg, 86 %) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): 7.51 (2 H, dd, J = 5.5, 0.5), 7.86 (2 H, s), 7.87 (2 H, bd, J = 8.4), 8.00 (2 H, dd, J = 5.5, 0.8), 8.10 (2 H, dd, J = 8.4, 0.9).

^{13}C NMR (150 MHz, $CDCl_3$): 121.66 (d), 123.84 (d), 124.79 (d), 125.87 (s), 126.20 (d), 127.16 (d), 130.82 (s), 135.51 (s), 139.33 (s).

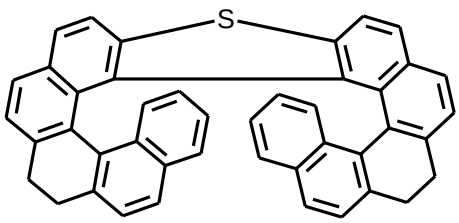
IR ($CHCl_3$): 3098 vw, 3058 w, 1635 vw, 1611 vw, 1592 vw, 1570 vw, 1438 w, 1403 w, 1389 w, 1340 w, 1307 w, 1260 vw, 1244 vw, 1182 w, 1158 w, 1147 vw, 1120 w, 1097 w, 1084 vw, 1065 w, 1038 vw, 838 vs, 697 vs cm^{-1}.

UV/Vis (acetonitrile): λ_{max} (log ε) 207 nm (4.22), 290 nm (4.40).

TOF EI MS: 290 ($M^{+\bullet}$, 100), 288 (53), 278 (32), 277 (78), 263 (6), 262 (38), 261 (7), 244 (18), 243 (16), 185 (12), 183 (36), 152 (10), 149 (25), 144 (13), 111 (11), 97 (15), 83 (15), 69 (15), 57 (18), 55 (13).

TOF HR EI MS: calculated for $C_{18}H_{10}S_2$ 290.0224, found 290.0218.

1,2,12,13-Tetrahydrodipentaheliceno[2,1-*b*:1',2'-*d*]thiophene 48



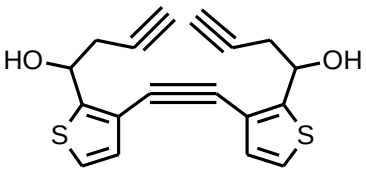
Method A (flow reactor): The flow reactor was heated up to 250 °C with THF flowing at 0.5 ml/min rate and at pressure of 100 atm. Hexayne **67** (9 mg, 0.01 mmol) was dissolved in 2 ml of THF and $CpCo(CO)_2$ (2 µl, 0.01 mmol, 1 eq.) was added. The reaction mixture was then injected into the flow reactor using a 2 ml sample loop. The residence time in the heated capillary was 16 minutes. The effluent on an output was collected and evaporated to dryness. Then the residue was dissolved with small amount of DCM, filtered through a short pad of silica gel and eluted with DCM (20 ml). The solvents were removed *in vacuo.* A flash chromatography was performed on silica gel (hexane-EtOAc 100:0 to 80 : 20) to get the crude product **48** (8 mg, <50 %). Due to difficulties with purifying the product **48**, it was characterised only by HR EI MS.

Method A (microwave reactor): A Schlenk flask was charged with TsOH (16.4 mg, 0.0952 mmol, 15 eq.) under argon. Then compound **57** (4.5 mg, 0,006 mmol) was added in benzene (2 ml). The reaction mixture was heated in a microwave oven at 80 °C for 30 min. The reaction mixture was filtered through a short pad of silica gel and eluted with DCM (15 ml). Flash chromatography was performed on silica gel (hexane-EtOAc 100:0 to 80 : 20) to get the crude product **48** (6.4 mg, <57 %). Due to difficulties with purifying the product **48**, it was characterised only by HR EI MS.

TOF EI MS: 588 ($M^{+\bullet}$, 100), 586 (12), 584 (4), 430 (4), 294 (12), 276 (10).

TOF HR EI MS: calculated for $C_{44}H_{28}S$ 588.1912, found 588.1918.

1,1'-(Ethyne-1,2-diyldithiene-3,2-diyl)bisbut-3-yn-1-ol 50



A Schlenk flask was charged with Ga (44 mg, 0.63 mmol, 2.2 eq.), In (10 mg, 0.087 mmol, 30 mol %) and THF (1.5 ml, distilled from Na/benzophenone) under argon. The reaction mixture was cooled to 5 °C and propargylbromide (300 µl, 2.70 mmol, 9.5 eq., 80 % solution in toluene) was added. Then it was stirred at 5 °C for 1.5 h (until the In and Ga were dissolved). The reaction mixture was warmed to room temperature and a solution of **51** (70 mg, 0.28 mmol) in THF (2 ml, distilled from Na/benzophenone) was added and the reaction was stirred at room temperature for 1 h. The reaction was quenched with water (10 ml) and the aqueous layer was extracted with DCM (3 x 20 ml). The combined organic portions were dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-EtOAc 80:20 to 70 : 30) to give **50** (40 mg, 43 %) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): 2.14 (2 H, t, J = 2.6), 2.78 (2 H, ddd, J = 2.6, 7.7, 16.8), 2.89 (2 H, ddd, J = 2.6, 4.8, 16.8), 5.40 (1 H, bdd, J = 4.8, 7.7), 5.42 (1 H, bdd, J = 4.8, 7.7), 7.07.(2 H, dd, J = 0.6, 5.1), 7.23 (2 H, bd, J = 5.1).

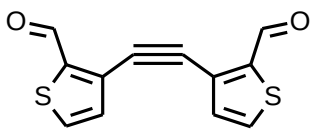
^{13}C NMR (150 MHz, $CDCl_3$): 28.89 (t), 28.97 (t), 68.14 (d), 68.16 (d), 71.71 (d), 71.75 (d), 79.82 (s), 79.88 (s), 86.82 (s), 86.85 (s), 118.62 (s), 118.64 (s), 124.06 (d), 129.65 (d), 149.03 (s), 149.05 (s).

IR ($CHCl_3$): 3597 m, 3308 vs, 3116 vw, 3090 vw, 2209 vw, 2122 vw, 1547 vw, 1422 w, 1375 w, 1366 w, 1066 m, 1048 m, 882w, 839w , 648 s, 529 w cm^{-1}.

TOF ESI MS: 349 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{18}H_{14}O_2NaS_2$ 349.0327, found 349.0327.

3,3'-Ethyne-1,2-diyldithiophene-2-carbaldehyde 51



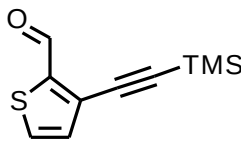
Method A (direct): A Schlenk flask was charged with **52** (161 mg, 0.843 mmol), $Pd(PPh_3)_4$ (49 mg, 0.042 mmol, 5 mol %) and CuI (16 mg, 0.084 mmol, 10 mol %) under argon. Then toluene (4 ml, distilled from Na, degassed) and *i*-Pr_2EtN (370 µl, 2.11 mmol, 2.5 eq., distilled from CaH_2, degassed) was added. The reaction mixture was frozen in liquid nitrogen bath and degassed. Then it was taken out of the bath and when the temperature of the mixture was approximately -30 °C, the flask was evacuated and re-filled with gaseous acetylene (14.5 ml, 0.59 mmol, 0.7 eq.) from a balloon and sealed. The reaction mixture was stirred for 1 h at room temperature. Then it was filtered through a short pad of silica gel, eluted with toluene (25 ml) and the solvents were removed *in vacuo.* The product was purified by flash chromatography (hexane-EtOAc-Et_3N 89 : 10 : 1) to give **51** (70.8 mg, 33 %) as a amorphous solid.

Method B (stepwise): A Schlenk flask was charged with **52** (50 mg, 0.26 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol, 5 mol %), CuI (5 mg, 0.026 mmol, 10 mol %), **54** (47 mg, 0.31 mmol, 1.2 eq.) and toluene (5 ml, distilled from Na, degassed) was added under argon. Then *i*-Pr_2EtN (120 µl, 0.64 mmol, 2.5 eq., distilled from CaH_2, degassed) was added. The reaction mixture was stirred at room temperature for 1 h. Then it was filtered through a short pad of silica gel and eluted with DCM (30 ml). The product was purified by flash chromatography on silica gel (hexane-DCM 50:50 to 0:100) to give **51** (20 mg, 30 %) as a amorphous solid.

TOF CI MS: 275 ($[M+C_2H_5]^+$), 247 ($[M+H]^+$).

TOF HR CI MS: calculated for $C_{12}H_6O_2S_2$ 246.9887, found 246.9880.

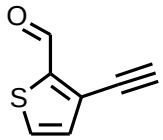
3-[(Trimethylsilyl)ethynyl]thiophene-2-carbaldehyde 53



A Schlenk flask was charged with **52** (65 mg, 0.34 mmol), $Pd(PPh_3)_4$ (18 mg, 0.017 mmol, 5 mol %), CuI (6.5 mg,

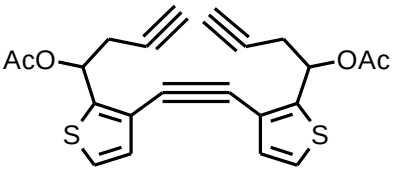
0.034 mmol, 10 mol %) under argon and toluene (5 ml, distilled from Na, degassed) was added. Then *i*-Pr_2EtN (160 µl, 0.85 mmol, 2.5 eq., distilled from CaH_2, degassed) and TMS-acetylene (100 µl, 0.068 mmol, 2.0 eq.) were added. The reaction mixture was stirred at room temperature for 1.5 h. Then it was filtered through a short pad of silica gel and eluted with DCM (30 ml). The product was purified by flash chromatography on silica gel (hexane) to give **53** (50 mg, 70 %) as an oil. The ^{1}H NMR spectrum was in accordance with the literature.[33]

3-Ethynylthiophene-2-carbaldehyde 54



Compound **53** was dissolved in a mixture of THF and methanol (1 : 1, 3 ml) in a Schlenk flask under argon. Then NaOMe (0.4 ml, 0.8 mmol, 3.5 eq., prepared by dissolving Na (50 mg, 2.2 mmol) in methanol (1 ml)) was added. The reaction mixture was stirred at room temperature for 20 min and then water (10 ml) was added. The reaction mixture was extracted with Et_2O (3 x 20 ml), the combined organic portions were dried over anhydrous $MgSO_4$ and evaporated *in vacuo* to give **54** (24.6 mg, 75 %) as a brown oil. The ^{1}H NMR spectrum was in accordance with the literature.[34]

Ethyne-1,2-diylbis(thiene-3,2-diylbut-1-yne-4,4-diyl) diacetate 55



Diol **50** (40 mg, 0.12 mmol) was dissolved in pyridine (2 ml), then Ac_2O (1.4 ml, 12 mmol, 100 eq.) and DMAP (2.5 mg, 0.025 mmol, 20 mol %) were added. The reaction mixture was stirred at room temperature for 25 min. Then the mixture was co-evaporated with toluene (2 x 10 ml) to remove Ac_2O. The product was purified by flash chromatography (hexane-EtOAc 100:0 to 90 : 10) to give **55** (39 mg, 78 %) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): 2.04 (1 H, t, *J* = 2.7), 2.05 (1 H, t, *J* = 2.7), 2.126 (1 H, s), 2.128 (1 H, s), 2.91 (1 H, ddd, *J* = 16.9, 6.2, 2.7), 2.92 (1 H, ddd, *J* = 16.9,

6.2, 2.7), 2.94 (1 H, ddd, *J* = 16.9, 6.2, 2.7), 2.96 (1 H, ddd, *J* = 16.9, 6.2, 2.7), 6.46 (1 H, t, *J* = 6.2), 6.48 (1 H, t, *J* = 6.2), 7.10 (2 H, d, *J* = 5.2), 7.25 (2 H, dd, *J* = 5.2, 0.3).

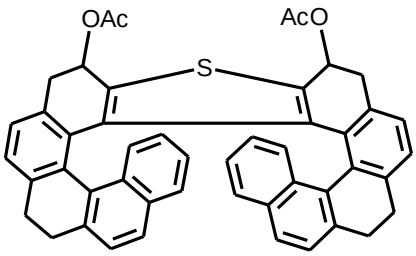
^{13}C NMR (150 MHz, $CDCl_3$): 20.91 (q), 26.28 (t), 26.29 (t), 68.61 (d), 68.71 (d), 71.31 (d), 78.75 (s), 78.78 (s), 86.72 (s), 86.76 (s), 120.31 (s), 120.33 (s), 124.64 (d), 129.78 (d), 129.79 (d), 144.37 (s), 144.39 (s), 169.55 (s), 169.56 (s).

IR ($CHCl_3$): 3309 m, 3116 vw, 3092 vw, 2957 w, 2927 w, 2856 w, 2212 vvw, 2125 vw, 1743 s, 1549 vw, 1427 w, 1372 m, 1234 vs, 1172 w, 1043 m, 978 w, 883 w, 841 w, 651 m, 640 m, 606 w, 525 w cm^{-1}.

TOF ESI MS: 433 ($[M+Na]^+$).

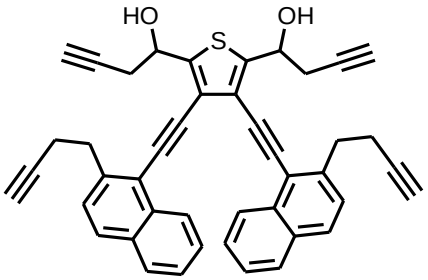
HR ESI MS: calculated for $C_{22}H_{18}O_4NaS_2$ 433.0539, found 433.0537.

1,2,5,6,8,9,12,13-Octahydrodipentaheliceno[2,1-*b*:1',2'-*d*]thiene-6,8-diyl diacetate 57



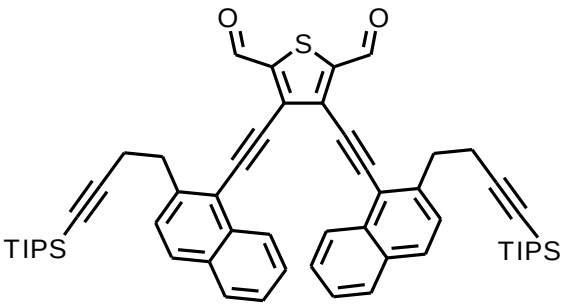
Triphenylphosphine (30 mg, 0.11 mmol, 4 eq.) was dissolved in decane (4 ml, anhydrous, degased) in a Schlenk flask under argon. The solution was heated in an oil bath to 90 °C and triyne **55** (20.4 mg, 0.0288 mmol) was added in THF (100 µl). The reaction mixture was removed from the oil bath and it was irradiated with a halogen lamp until the solution reached 100 °C. Then $CpCo(CO)_2$ (8 µl, 0.06 mmol, 2.1 eq) was added in THF (100 µl). The reaction mixture was irradiated at 140 °C for 20 min. The mixture was cooled down to room temperature, filtered through a short pad of silica gel and eluted with DCM (20 ml). The solvents were removed *in vacuo*. Flash chromatography was performed on silica gel (hexane-EtOAc 100:0 to 80 : 20) to get the crude product **57** (13.7 mg, <67 %). Due to the difficulties with purifying the product **57** and its instability, it was not characterised and used further without purification.

1,1'-{3,4-Bis[(2-but-3-yn-1-ylnaphthalen-1-yl)ethynyl]thiene-2,5-diyl}bisbut-3-yn-1-ol 58



A Schlenk flask was charged with TBAF (30 mg, 0.96 mmol, 3 eq.). A solution of diol **64** (30 mg, 0.032 mmol) in THF (2 ml, distilled from Na/benzophenone) was added. The reaction mixture was stirred at room temperature for 30 min and then filtered through a short pad of silica gel, eluted with THF (30 ml) and the solvent was removed *in vacuo* at room temperature. The product was purified by flash chromatography on silica gel (hexane-EtOAc 80:100 to 65 : 35) to give hexayne **58** (19.4 mg, 95 %) as an oil.

3,4-Bis[(2-{4-[tris(1-methylethyl)silyl]but-3-yn-1-yl}naphthalen-1-yl)ethynyl]thiophene-2,5-dicarbaldehyde 59



A Schlenk flask was charged with **61** (256 mg, 0.860 mmol), $Pd(PPh_3)_2Cl_2$ (61 mg, 0.087 mmol, 10 mol %) and CuI (33 mg, 0.17 mmol, 20 mol %) under argon. Then a solution of diyne **60** (650 mg, 1.81 mmol, 2.1 eq.) in Et_3N (25 ml, distilled from CaH_2, degassed) was added. The reaction mixture was stirred at room temperature for 1 h. Then it was filtered through a short pad of silica gel, eluted with DCM (30 ml) and the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane-EtOAc 90:10 to 50:50). Further purification was achieved by flash chromatography on reverse phase silica gel C18 (acetonitrile-EtOAc 100:0 to 50:50) to give dialdehyde **59** (375 mg, 50 %) as a yellow powder.

M.p.: 188 – 191 °C (acetonitrile-EtOAc 1:1).

^{1}H NMR (600 MHz, $CDCl_3$): 0.90 - 0.96 (42 H, m), 2.62 (4 H, t, *J* = 7.2), 3.24 (4 H, t, *J* = 7.1), 6.93 (2 H, ddd, *J* = 8.4, 6.8, 1.4), 7.33 (2 H, ddd, *J* = 8.1, 6.8, 1.2), 7.49 (2 H, d, *J* = 8.4), 7.79 (2 H, ddt, *J* = 8.1, 1.4, 0.6, 0.6), 7.84 (2 H, bdt, *J* = 8.4, 0.7, 0.7), 8.36 (2 H, ddt, *J* = 8.4, 1.2, 0.8, 0.8), 10.46 (2 H, s).

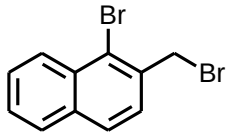
^{13}C NMR (150 MHz, $CDCl_3$): 11.17 (d), 18.50 (q), 21.17 (t), 34.60 (t), 81.86 (s), 88.65 (s), 96.36 (s), 107.04 (s), 117.31 (s), 125.79 (d), 125.79 (d), 127.28 (d), 127.28 (d), 128.11 (d), 130.01 (d), 131.77 (s), 133.08 (s), 133.42 (s), 143.31 (s), 146.94 (s), 183.03 (d).

IR ($CHCl_3$): 3059 w, 2959 m, 2944 s, 2892 m, 2866 s, 2197 w, 2171 w, 1930 w, 1683 vs, 1672 s, sh, 1620 vw, 1593 w, 1568 vw, 1508 w, 1463 m, 1388 w, 1366 w, 1349 vw, 1255 vw, 1027 vw, 996 w, 884 m, 868 w, 818 m, 679 m, 660 m, 618 w cm^{-1}.

TOF EI MS: 857 ($M^{+\bullet}$, 5), 856 (8), 815 (24), 814 (71), 813 (100), 771 (5), 655 (5), 639 (6), 604 (5), 509 (4), 413 (4), 129 (4), 115 (20), 87 (23), 73 (19), 59 (22).

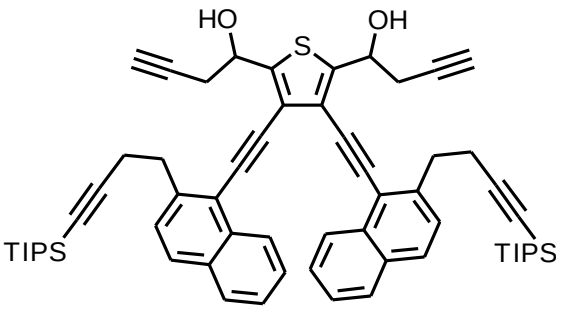
TOF HR EI MS: calculated for $C_{56}H_{64}O_2Si_2S$ 856.4166, found 856.4163.

1-Bromo-2-(bromomethyl)naphthalene 63



Compound **62** (3.22 g, 12.8 mmol) was dissolved in acetic acid (16 ml). Then hydrogen bromide (16 ml, 89.8 mmol, 7 eq., 33 % w solution in acetic acid,) was added. The mixture was stirred for 2 h at the room temperature. Then it was concentrated *in vacuo* and the residue was evaporated from toluene (2 x 20 ml). The product was crystallized from heptanes to give dibromide **63** (3.33 g, 87 %) as the light brown crystals. The ^{1}H NMR spectrum was in accordance with the literature.[35]

1,1'-{3,4-Bis[(2-{4-[tris(1-methylethyl)silyl]but-3-yn-1-yl}naphthalen-1-yl)ethynyl]thiene-2,5-diyl}bisprop-2-yn-1-ol 64



A Schlenk flask was charged with Ga (53 mg, 0.76 mmol, 2.2 eq.), In (12.5 mg, 0.109 mmol, 10 mol %) and THF (5 ml, distilled from Na/benzophenone) under argon. The reaction mixture was cooled to 5 °C and propargylbromide (320 µl, 3.59 mmol, 9.4 eq., 80 % solution in toluene) was added. Then it was stirred at 5 °C for 1 h (until the In and Ga were not dissolved). The reaction mixture was warmed to room temperature and a solution of **59** (260 mg, 0.303 mmol) in THF (7 ml, distilled from Na/benzophenone) was added and the reaction was stirred at room temperature for 1 h. The reaction was quenched with water (20 ml) and the aqueous layer was extracted with DCM (3 x 30 ml). The combined organic portions were dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (DCM-EtOAc 100:0 to 90 : 10) to give diol **64** (245 mg, 86 %) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): 0.92-1.00 (42 H, m), 2.19 (2 H, t, *J* = 2.6), 2.63 (4 H, t, *J* = 7.2), 2.80 (2 H, bd, *J* = 3.0), 2.86 (2 H, ddd, *J* = 16.9, 7.6, 2.6), 3.04 (2 H, ddd, *J* = 16.9, 4.6, 2.6), 3.23 (4 H, t, *J* = 7.2), 5.53 (2 H, ddd, *J* = 7.6, 4.6, 3.0), 6.88 (2H, ddd, *J* = 8.4, 6.9, 1.3), 7.28 (2 H, ddd, *J* = 8.1, 6.9, 1.2), 7.47 (2 H, d, *J* = 8.4), 7.75 (2 H, bdd, *J* = 8.4, 0.8), 7.75 (2 H, ddt, *J* = 8.1, 1.3, 0.8, 0.8), 8.39 (2 H, dq, *J* = 8.4, 0.9, 0.9, 0.9).

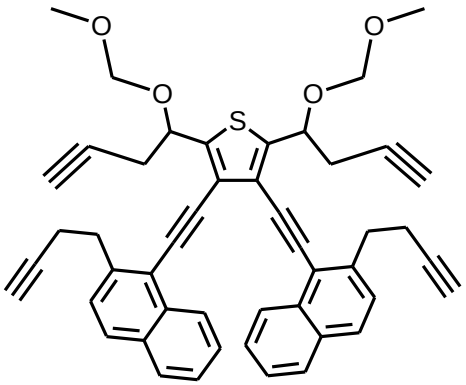
^{13}C NMR (150 MHz, $CDCl_3$): 11.21 (d), 18.53 (d), 21.10 (t), 28.97 (t), 34.54 (t), 68.55 (d), 72.11 (d), 79.48 (s), 81.45 (s), 90.92 (s), 92.12 (s), 107.74 (s), 118.57 (s), 121.01 (s), 125.75 (d), 126.17 (d), 126.82 (d), 127.45 (d), 127.83 (d), 128.66 (d), 131.78 (s), 133.40 (s), 141.89 (s), 147.31 (s).

IR ($CHCl_3$): 3596 w, br, 3308 m, 3059 w, 2959 s, 2944 vs, 2929 vs, 2893 m, 2866 vs, 2200 vw, sh, 2170 w, 2124 vw, 1619 vw, 1593 w, 1568 vw, 1508 w, 1464 m, 1429 w, 1383 w, 1367 w, 1064 m, 1044 m, 1027 w, 996 w, 884 m, 867 w, 817 m, 678 m, 660 s, 639 m, sh, 618 w, sh

ESI MS: 960 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{62}H_{72}O_2NaSSi_2$ 959.4684, found 959.4681.

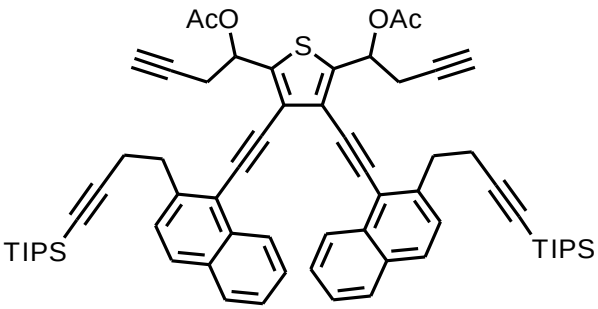
3,4-Bis[(2-but-3-yn-1-ylnaphthalen-1-yl)ethynyl]-2,5-bis[1-(methoxymethoxy)-but-3-yn-1-yl]thiophene 65



Diol **64** (30 mg, 0.032 mmol) was dissolved in DCM (3 ml, absolute) in a Schlenk flask under argon. The solution was cooled down to 0 °C and *i*-Pr_2EtN (16 µl, 0.080 mmol, 2.5 eq., distilled from CaH_2, degassed) was added. Then chloromethyl methyl ether (6 µ, 0.07 mmol, 2.2 eq) was added. The reaction mixture was stirred at room temperature for 2 h with no reaction according to TLC. Additional *i*-Pr_2EtN (64 µl, 0.32 mmol, 10 eq., distilled from CaH_2, degassed) was added followed by an addition of chloromethyl methyl ether (27 µl, 0.32 mmol, 10 eq.). The reaction mixture was stirred for 15 h at room temperature. The product was purified by flash chromatography (hexane-EtOAc 100:0 to 90 : 10) to give MOM derivative **65** (4.5 mg, 14 %) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$): 0.97 - 1.0 (42 H, m), 2.12 - 2.15 (2 H, m), 2.66 (4 H, t, *J* = 16.0), 2.93 - 2,95 (4 H, m), 3.26 (4 H, t, *J* = 16.0), 3.50 (6 H, s), 4.77 (2 H, d, *J* = 8.0), 4.85 (2 H, d, *J* = 8.0), 5.51 (2 H, t, *J* = 4.0), 6.92 (2 H, t, *J* = 16.0), 7.32 – 7.34 (2 H, m), 7.52 (2 H, d, *J* = 8.0), 7.77 (4 H, d, *J* = 8.0), 8.45 (2 H, d, *J* = 8.0).

{3,4-Bis[(2-{4-[tris(1-methylethyl)silyl]but-3-yn-1-yl}naphthalen-1-yl)ethynyl]thiene-2,5-diyl}diprop-1-yne-3,3-diyl diacetate 66



Diol **64** (125 mg, 0.133 mmol) was dissolved in pyridine (1 ml). Ac_2O (1.5 ml, 13.3 mmol, 100 eq.) and DMAP (2.7 mg, 0.027 mmol, 20 mol %) were added. The reaction mixture was stirred at room temperature for 20 min. Then the mixture was co-evaporated with toluene (2 x 10 ml) to remove Ac_2O. The product was purified by flash chromatography (hexane-EtOAc 100:0 to 90 : 10) to give diacetate **66** (120 mg, 88 %) as an yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): 0.9 – 0.98 (42 H, m), 2.10 (2 H, t, *J* = 2.6), 2.18 (6H, s), 2.65 (4 H, dt, *J* = 7.0, 7.0, 1.0), 2.99 (4 H, ddd, *J* = 17.0, 6.5, 2.7), 3.04 (1 H, ddd, *J* = 17.0, 5.8, 2.6), 3.25 (4 H, t, *J* = 6.9), 6.52 (2 H, dd, *J* = 6.8, 5.8), 6.87 (2 H, ddd, *J* = 8.4, 6.9, 1.3), 7.27 (2 H, ddd, *J* = 8.0, 6.9, 1.1), 7.50 (2 H, d, *J* = 8.4), 7.74 (2 H, dd, *J* = 8.4, 0.7), 7.74 (2 H, ddt, *J* = 8.0, 1.3, 0.8, 0.8), 8.42 (2 H, dq, *J* = 8.4, 1.0, 1.0, 1.0).

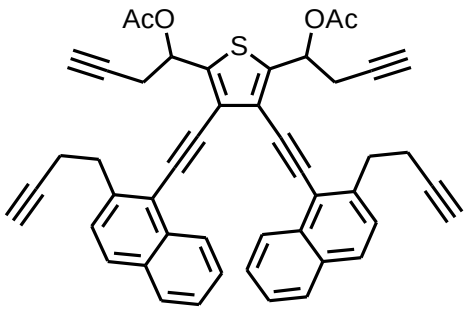
^{13}C NMR (150 MHz, $CDCl_3$): 11.22 (d), 18.53 (q), 20.90 (q), 21.04 (t), 26.23 (t), 34.34 (t), 68.90 (d), 71.75 (d), 78.39 (s), 81.36 (s), 90.55 (s), 92.50 (s), 107.89 (s), 118.40 (s), 122.83 (s), 125.71 (d), 126.27 (d), 126.78 (d), 127.66 (d), 127.78 (d), 128.63 (d), 131.74 (s), 133.50 (s), 142.20 (s), 142.80 (s), 169.41 (s).

IR ($CHCl_3$): 3310 m, 3059 w, 2951 s, 2943 vs, 2928 vs, 2894 m, 2865 vs, 2202 vw, 2170 m, 2127 vw, 1746 s, 1620 vw, 1593 w, 1568 vw, 1508 w, 1494 vw, 1464 m, 1430 w, 1383 m, 1372 m, 1343 vw, 1261 w, sh, 1230 vs, 1078 w, 1043 m, 1027 m, 997 m, 884 m, 867 w, 817 m, 678 m, 660 s, 639 m, 618 m,

TOF ESI MS: 1061 ($[M+K]^+$), 1044 ($[M+Na]^+$).

TOF HR ESI: calculated for $C_{66}H_{76}O_4NaSSi_2$ 1043.4895, found 1043.4894.

{3,4-Bis[(2-but-3-yn-1-ylnaphthalen-1-yl)ethynyl]thiene-2,5-diyl}diprop-1-yne-3,3-diyl diacetate 67



A Schlenk flask was charged with TBAF (76 mg, 0.24 mmol, 3 eq.). A solution of **66** (75 mg, 0.073 mmol) in THF (3 ml, distilled from Na/benzophenone) was added. The reaction mixture was stirred at room temperature for 1 h and then it was filtered through a short pad of silica gel, eluted with THF (30 ml) and the solvents were removed *in vacuo* at room temperature. The product was purified by flash chromatography (hexane-EtOAc 100:0 to 80 : 20) to give hexayne **67** (30 mg, 64 %) as an orange oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.88 (2 H, bt, *J* = 2.5), 2.11 (1 H, t, *J* = 2.6), 2.18 (6 H,s), 2.57 (4 H, dt, *J* = 7.2, 7.2, 2.5), 2.96 - 3.08 (4 H, m), 3.25 (4 H, t, *J* = 7.2), 6.55 (2 H, t, *J* = 6.4), 6.88 (2 H, bdd, *J* = 8.6, 7.0), 7.29 (2 H, bdd, *J* = 8.0, 7.0), 7.42 (2 H, *J* = 8.5), 7.75 (2 H, bd, *J* = 8.0), 7.79 (2 H, bd, *J* = 8.5), 8.43 (2 H, bd, *J* = 8.6).

^{13}C NMR (150 MHz, $CDCl_3$): 19.68 (t), 20.92 (q), 26.28 (t), 34.13 (t), 68.86 (d), 69.23 (d), 71.78 (d), 78.45 (s), 83.57 (s), 90.59 (s), 92.32 (s), 118.66 (s), 122.84 (s), 125.84 (d), 126.33 (d), 126.91 (d), 127.11 (d), 127.83 (d), 128.88 (d), 131.75 (s), 133.50 (s), 141.79 (s), 143.00 (s), 169.44 (s).

IR: 3309 s, 3059 w, 2202 vw, 2118 vw, 1746 s, 1711 m, 1621 vw, 1593 w, 1568 vw, 1508 w, 1508 w, 1462 w, 1431 w, 1431 w, 1372 m, 1262 m, sh, 1229 vs, 1146 vw, 1058 m, 1046 m, 1028 m, 868 w, 820 m, 640 s cm^{-1}.

TOF ESI MS: 731 ($[M+Na]^+$).

HR ESI MS: calculated for $C_{48}H_{36}O_4NaS$ 731.2227, found 731.2225.

6. Abbreviations

bd	broad doublet
bq	broad quartet
BINOL	1,1'-bi-2-naphthol
CI	chemical ionisation
COSY	correlation spectroscopy
CV	cyclic voltammetry
DCM	dichloromethane
dd	doublet of doublets
DMAP	4-(dimethylamino)pyridine
DMF	dimethylformamide
dq	doublet of quartets
dt	doublet of triplets
EI	electron ionisation
ESI	electrospray ionisation
HMBC	heteronuclear multiple bond correlation
HMQC	heteronuclear multiple quantum coherence
HPFC	high performance flash chromatography
HPLC	high performance liquid chromatography
HR	high resolution

IR	infrared spectroscopy
m	multiplet, medium intensity
MOM	methoxymethyl
M.p.	melting point
MS	mass spectrometry
NMR	nuclear magnetic resonance
PCC	pyridinium chlorochromate
q	quartet
rt	room temperature
s	singlet, strong intensity
TBAF	tetra-*n*-butylammonium fluoride
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
TOF	time of flight analyser
UV/Vis	ultraviolet/visible spectroscopy
vs	very strong intensity
vw	very weak intensity
w	weak intensity

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