Charles University in Prague

Faculty of Science

Study programme: Chemistry

Study branch: Organic Chemistry

Ondřej Palata

Synthesis of thiophenohelicenes and their physico-chemical properties

Syntéza thiofenohelicenů a jejich fyzikálně chemické vlastnosti

Diploma Thesis

Supervisor:

RNDr. Irena G. Stará, CSc.

Prague, 2013

Declaration:

Prohlašuji, že jsem tuto práci vypracoval samostatně a všechny použité zdroje byly řádně citovány. Tato práce nebyla využita jako závěrečná práce k získání jiného nebo obdobného druhu vysokoškolské kvalifikace.

V Praze, 17. 5. 2013

Ondřej Palata

Acknowledgement:

This Thesis was carried out under supervision of RNDr. Irena G. Stará, CSc. and RNDr. Ivo Starý, CSc., to whom special thanks are due. I would also like to thank Ing. Jiří Rybáček, Ph.D., Mgr. Andrej Jančařík, Serghei Chercheja, Ph.D., Bc. Václav Houska 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, RNDr. Lucie Bednárová, CSc. for measuring and interpretation of CD spectra, Doc. RNDr. Lubomír Pospíšil, CSc. for electrochemical measurements and interpretation, the members of the Department of Mass Spectroscopy for MS measurements and the members of the Analytical laboratory for measurement of optical rotation. Last but not least, I would like to thank my parents and all others who have supported me during my studies.

Abstract:

The objective of this Thesis was to prepare thiophenohelicenes by [2+2+2] cyclotrimerization of aromatic triynes, namely dithiopheno[5]helicene, dithiopheno[6]helicene and trithiopheno[6]helicene. The *Theoretical part* illustrates which heteroatoms can be embedded into helicene backbone and provides few representative syntheses of such heterohelicenes along with some examples of their utilization. The *Results and discussion* part and *Experimental part* deal with the synthesis of dithiopheno[5]helicene, dithiopheno[6]helicene and (dihydro)-trithiopheno[6]helicene from commercially available compounds by the [2+2+2] cyclotrimerization of corresponding aromatic triynes as the key step in the synthesis. The UV/Vis and fluorescence spectral analyses and electrochemical measurements of the dithiopheno[5]helicene and dithiopheno[6]helicene were performed. The enantiomers of configurationally stable dithiopheno[6]helicene were separated and CD spectra as well as optical rotation of each enantiomer were measured. A barrier of racemization for dithiopheno[6]helicene was also determined.

Úkolem této práce bylo připravit thiofenoheliceny pomocí [2+2+2] cyklotrimerizace aromatických triynů a to dithiofeno[5]helicen, dithiofeno[6]helicen a trithiofeno[6]helicen. *Teoretická část* popisuje, které heteroatomy mohou být součástí helikálního skeletu, uvádí několik ilustrativních syntéz takovýchto heterohelicenů a příklady jejich využití. Část *Výsledky a diskuze* a *Experimentální část* se zabývá syntézou dithiofeno[5]helicenu, dithiofeno[6]helicenu a (dihydro)trithiofeno[6]helicenu z komerčně dostupných látek, přičemž [2+2+2] cyklotrimerizace je v těchto syntézách klíčovým krokem. Byla změřena UV/Vis a fluorescenční spektra dithiofeno[5]helicenu a dithiofeno[6]helicenu a byly provedeny elektrochemické experimenty. Dále byly separovány enantiomery dithiofeno[6]helicenu a byla změřena jejich CD spektra, optická otáčivost a byla stanovena bariéra racemizace.

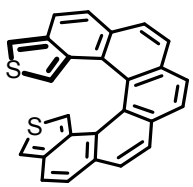
Table of contents

1. Introduction

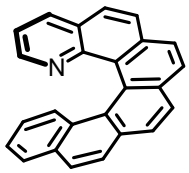
1.1 Helicenes

Helicenes are fascinating chiral molecules that have attracted great attention since their discovery.[1,2] Helicenes combine properties of π-conjugated systems with optical properties of chiral compounds. Helicenes in which one or more carbon atoms are formaly displaced by a heteroatom are called heterohelicenes. These heteroatoms can modify the helicene properties. The nature of the heteroatom is expressed by a prefix to the name of helicene. The most common heterohelicenes contain nitrogen[3], oxygen[4] or sulfur[5] atom or atoms (Figure 1). Heterohelicenes may also contain further heteroatoms such as silicon,[6] boron,[7] phosphorus,[8] germanium,[9] selenium or tellurium,[10] antimony[11] or combination of heteroatoms[12] (Figure 2).

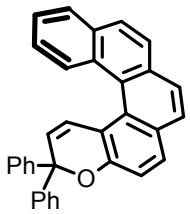
Figure 1



1

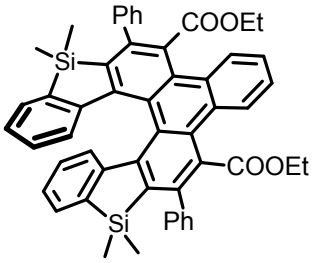


2

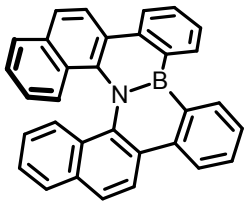


3

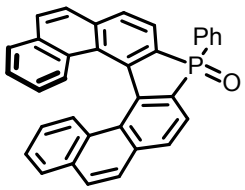
Figure 2



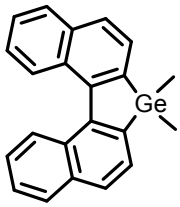
4



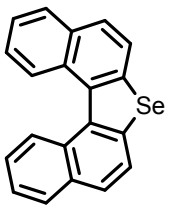
5



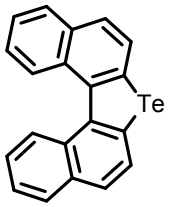
6



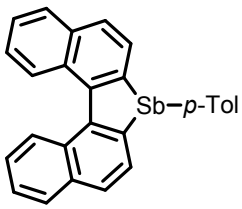
7



8



9



10

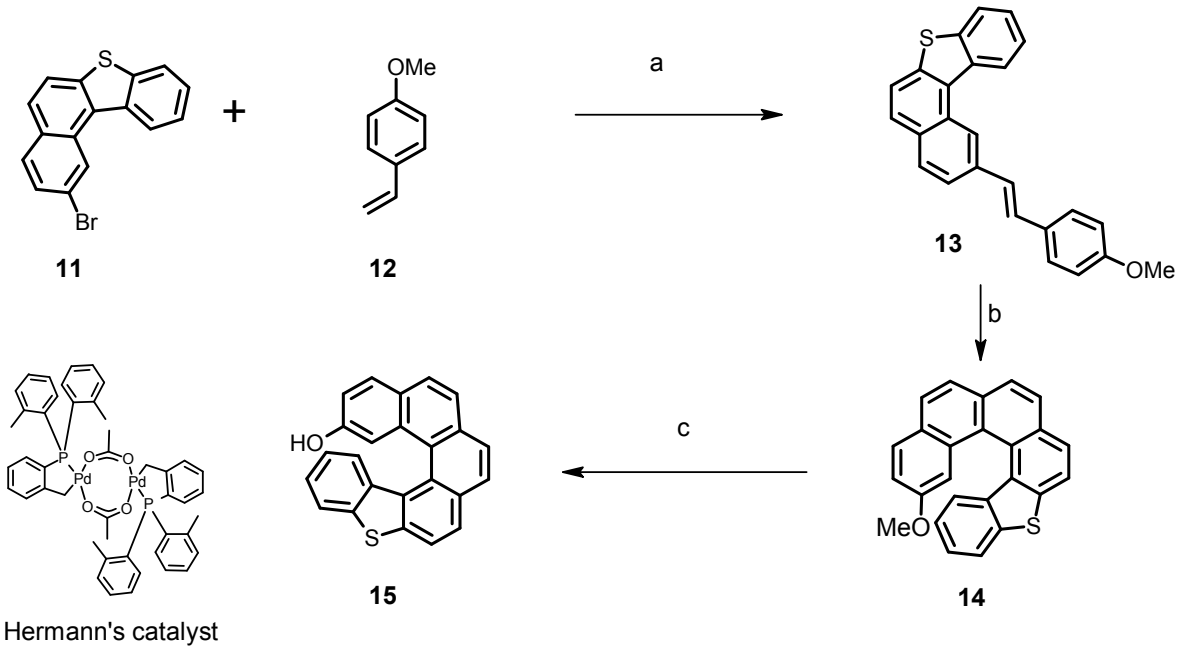
1.2 Thiahelicenes

Helicenes containing one or more sulfur atom(s) are called thiahelicenes. Thiophenohelicenes are special class of thiahelicenes formally formed by condensing thiophene(s) and carbohelicene. More on thiahelicenes can be found in my Bachleor's Thesis. In this Chapter, there will be shown a recent example of the synthesis of thiahelicene containing both benzene and thiophene rings (**15**, Scheme 1) and the rest of the Chapter will deal with helicenes containing only thiophene rings *i.e.* oligothiophenes.

There have been many different methods developed during the last 20 years for helicene synthesis, but photocyclization of stilbene type precursors has been still widely used. The photocyclization was a key step also in the recently published preparation of thia[6]helicene **15** bearing a hydroxy group (Scheme 1)[13].

First, the heterocyclic bromide **11** underwent Mizoroki–Heck coupling with 4-methoxystyrene **12**. The reaction gave diarylethene **13** which was photocyclized in a diluted toluene solution in the presence of the stoichiometric amount of iodine. This reaction provided exclusively the methoxy derivative of thiahexahelicene **14** and no other regioisomer was isolated. Then the methoxy group was transformed to a hydroxy group by treatment of compound **14** with a boron tribromide solution in dichloromethane. These four steps gave the desired product **15** in an overall 55 % yield.

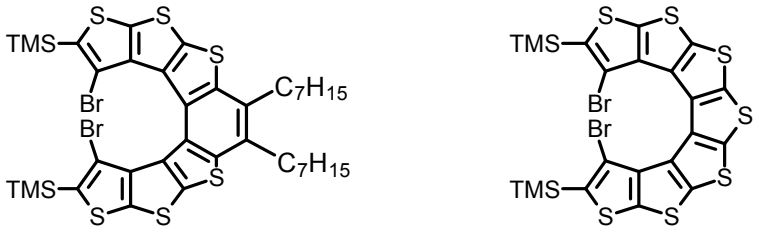
Scheme 1



a) **12** (1.5 eq.), Hermann's catalyst (1 mol%), NaOAc (1.1 eq.), DMA, 140 °C, 48 h, 78 %; b) I_2 (1.125 eq., 0.45 mmol/dm^3), propylene oxide (1 eq.), hv, toluene, 3 h, 75 %; c) BBr_3, DCM, 95 %.

As far as helical oligothiophenes are concerned, the first oligothiophene (**17**, Figure 3) was synthesized in 2000 (Scheme 2).[14] The starting material for this synthesis was 3,4-dibromothiophene **18** which was transformed into 4,4'-dibromo-

Figure 3

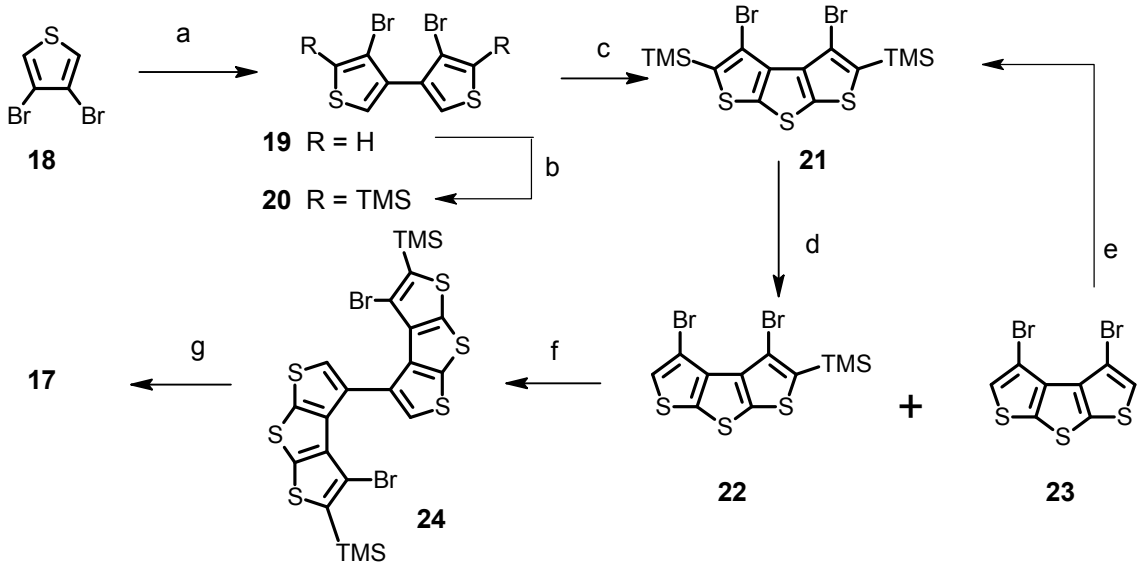


3,3'-bithienyl **19** by a mono Br/Li exchange followed by a copper–catalyzed oxidative coupling. Then the two more acidic α-positions were protected with trimethylsilyl groups to give **20** which was then treated with LDA and the subsequent reaction with bis(phenylsulfonyl)sulfide provided intermediate **21**. The following mono Br/Li

exchange was not successful therefore one of the trimethylsilyl groups of **21** had to be cleaved selectively to give **22**.

The deprotection gave a mixture of **22** and **23**. The side–product **23** was separated and transformed back to **21**. After recycling the side–product **23**, **22** was obtained in a combined 80 % yield. The mono Br/Li exchange followed by the copper–catalyzed coupling provided **24**. The subsequent annelation of **24** by means of lithiation and the reaction with bis(phenylsulfonyl) sulfide gave the final helicene **17**.

Scheme 2

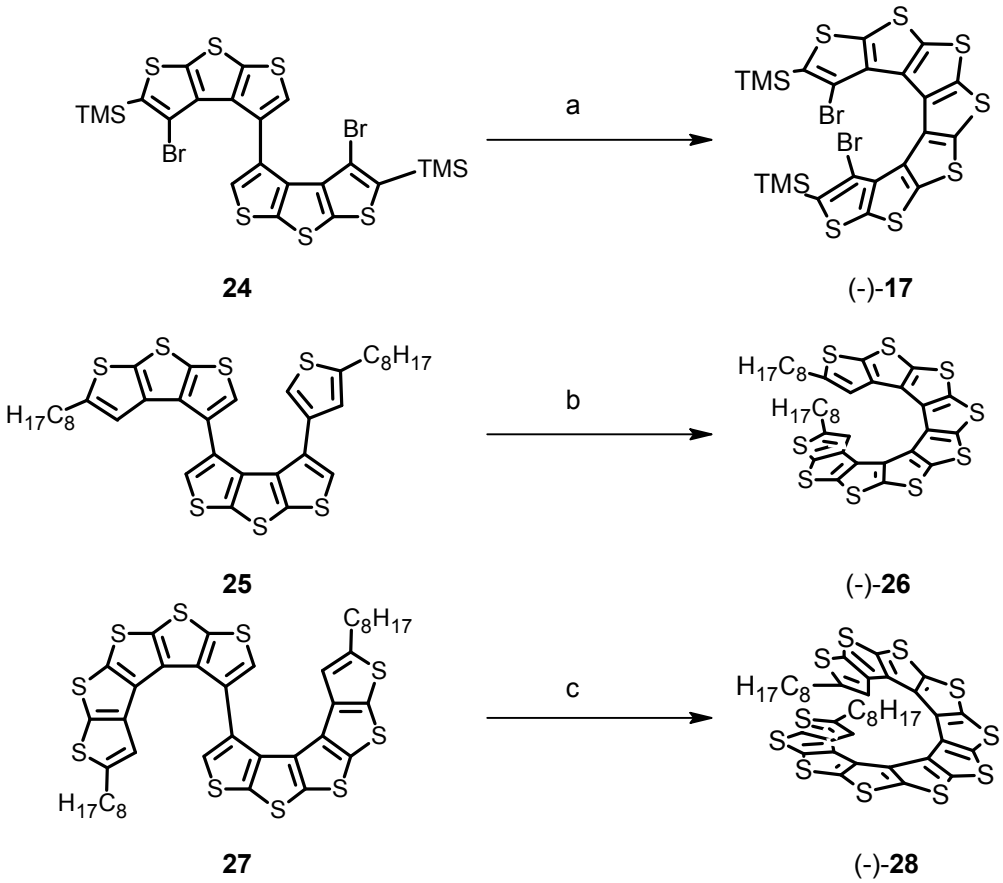


a) 1. *n*-BuLi (1.2 eq.), -70 °C, 2. $CuCl_2$ (1.4 eq.), -70 °C, 2 h, then rt, overnight, 40 %; b) 1. LDA (2.2 eq.), Et_2O, 0 °C, 3 h, 2. TMSCl (5.0 eq.) -78 °C, 3 h, then rt, overnight 46 %; c) 1. LDA (2.5 eq.), Et_2O, 0 °C, 2 h, 2. $(PhSO_2)_2S$ (1.0 eq.), -78 °C, 3 h, then rt, overnight, 65 %; d) TFA, $CHCl_3$, rt, 30 min, 58 % for **22** (80 % for **22** after recyclation of **23**); e) 1. LDA (2.2 eq.), Et_2O, 0 °C, 3 h, 2. TMSCl (5.0 eq.), -78 °C, 3 h, then rt, overnight; f) 1. *n*-BuLi (1.0 eq.), Et_2O, -78 °C, 3 h, 2. $CuCl_2$, -78 °C, 3 h, then rt, 2 d, 30 %; g) 1. LDA (2.3 eq.), Et_2O, 0 °C, 2 h, 2. $(PhSO_2)_2S$ (1.1 eq.), -78 °C, 40 %.

The analog of this helicene (**16**, Figure 3), having the center thiophene ring replaced with benzene one exhibits interesting properties in solid state.[15] Instead of crystallizing, it forms a rare chiral molecular glass that can be used in optics and optoelectronic requiring strictly isotropic glasses.

These helicenes can be also synthesized asymmetrically using (-)-sparteine mediated asymmetric induction to furnish nonracemic helicenes. [7]-, [9]- and [11] helicenes[16,17,18] (Scheme 3) were prepared using this procedure with *ee*'s up to 47 %.

Scheme 3

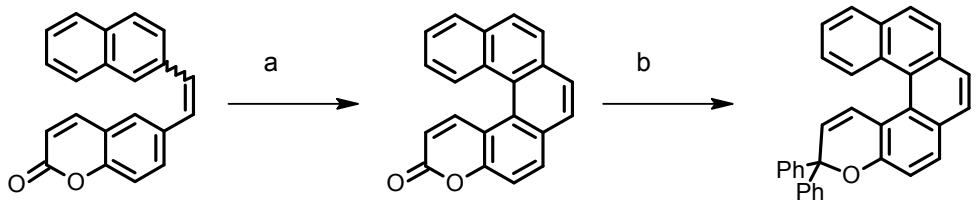


a) 1. LDA (2.3 eq.), (-)-sparteine (3.5 eq.), Et_2O, 0 °C, 2 h, 2. $(PhSO_2)_2S$ (1.0 eq.), -78 °C, 3 h, then rt, 12 h, 20 %, (47 % *ee*); b) 1. LDA (8.0 eq.), (-)-sparteine, Et_2O, 0 °C, 2 h, then rt, 4.5 h, 2. $(PhSO_2)_2S$ (6.0 eq.), -30 °C, then rt, 12 h, 15 %, (14 % *ee*); c) 1. LDA (2.4 eq.), (-)-sparteine (5.8 eq.), Et_2O, rt, 20 min; 2. $(PhSO_2)_2S$, -78 °C, 3 h, then rt, 12 h, 59 %, (19 % *ee*).

1.3 Oxahelicenes

Another type of heterohelicenes containing one or more oxygen atoms are called oxahelicenes. A convenient method for preparing oxahelicenes is photocyclization. For example, pyranone–annulated helicene **30** was prepared by this reaction (Scheme 4).[4] The disubstituted ethylene **29** was prepared by Wittig reaction of a phosphonium salt of 6-bromomethylcoumarine with napthaldehyde. The subsequent photocyclization of aryl coumaryl ethylene **29** followed by oxidation afforded helicene **30**. The product of cyclization was then treated with Gringard's reagent to give chromene **3**. This pyranone–annulated helicene exhibits interesting properties. It was shown that the helical structure has higher fluorescent efficiency compared to its nonhelical regioisomer which can also be formed in the photocyclization step.

Scheme 4



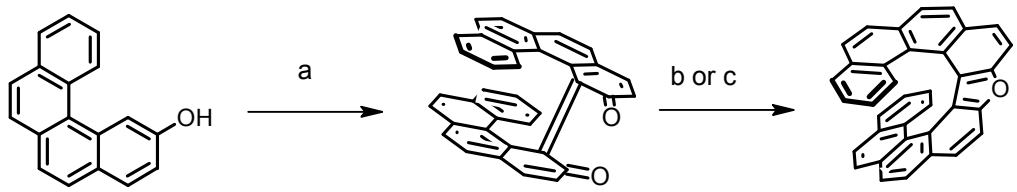
29 **30** **3**

a) I_2 (0.5 eq.)/O_2, hv, 24 h, 44 %; b) 1. PhMgBr (4.0 eq.), THF, rt, 3 h, 2. H^+, 50 °C, 3 h, 85 %.

Another efficient way to prepare oxahelicenes is through the construction of a furan ring. This could be done by cyclization of helical quinones,[19] prepared from 2-hydroxybenzo[*c*]phenantrene **31**[20] (Scheme 5).

The intermediate **32** was prepared by an oxidative coupling reaction which provides diquinone as a sole product. The cyclization could be accomplished by treating diquinone **32** with two reagents usually used for thionation – either Lawesson's reagent or phosphorus pentasulfide.

Scheme 5

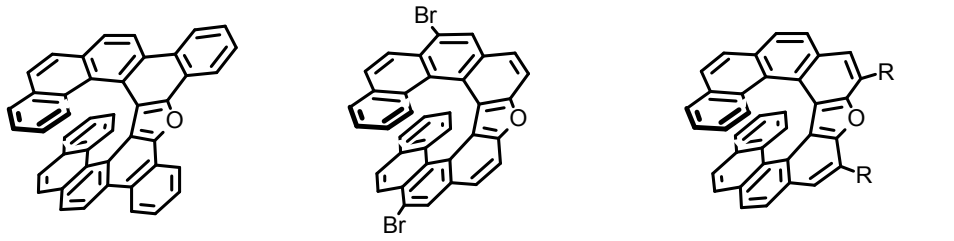


31 **32** **33**

a) CuCl(OH)-TMEDA, air, $CHCl_3$, 82 %; b) Lawesson's reagent (2.0 eq.), toluene, reflux, 15–20 h, 87 %; c) P_4S_{10} (2.0 eq.), toluene, reflux, 2–5 h, 72 %.

This is rather a general procedure and can be used to prepare differently substituted derivatives of oxahelicene **33** (Figure 4).

Figure 4

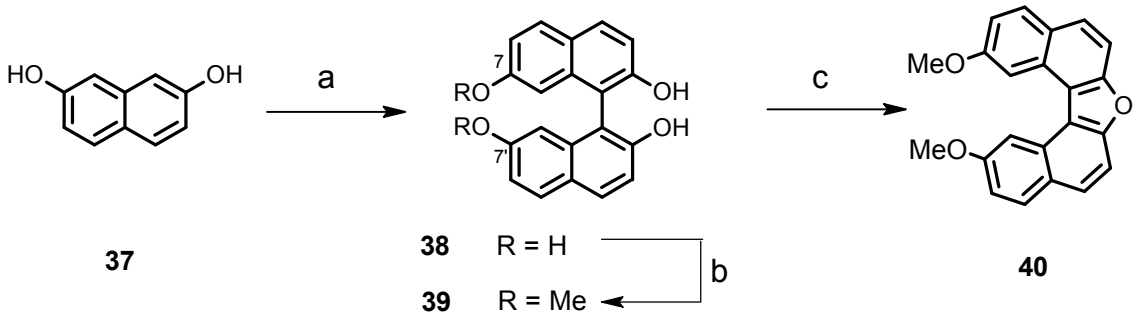


34 **35** **36** R = Me, Et, *t*-Bu

Another method for the construction of a furan ring is an acid catalyzed cyclization of binaphthol (Scheme 6).[21] First, 2,7-dihydroxynaphthalene **37** was transformed into the binaphthyl derivative **38** by an oxidative coupling in the presence of $FeCl_3$. Then 7- and 7'-dihydroxy groups were converted into methoxy functionalities.

The reaction of the hydroxyl group probably proceeds via its keto tautomer. Despite the fact that both hydroxyl groups at positions 2 and 7 can tautomerize, the reaction was observed only at the positions 7 and 7'. This was probably due the steric effect. In the next step, the binaphthol derivative **39** was cyclized to give oxa[5]helicene **40**. The advantage of this approach is that it is straightforward and scalable with all the starting materials available at low cost.

Scheme 6

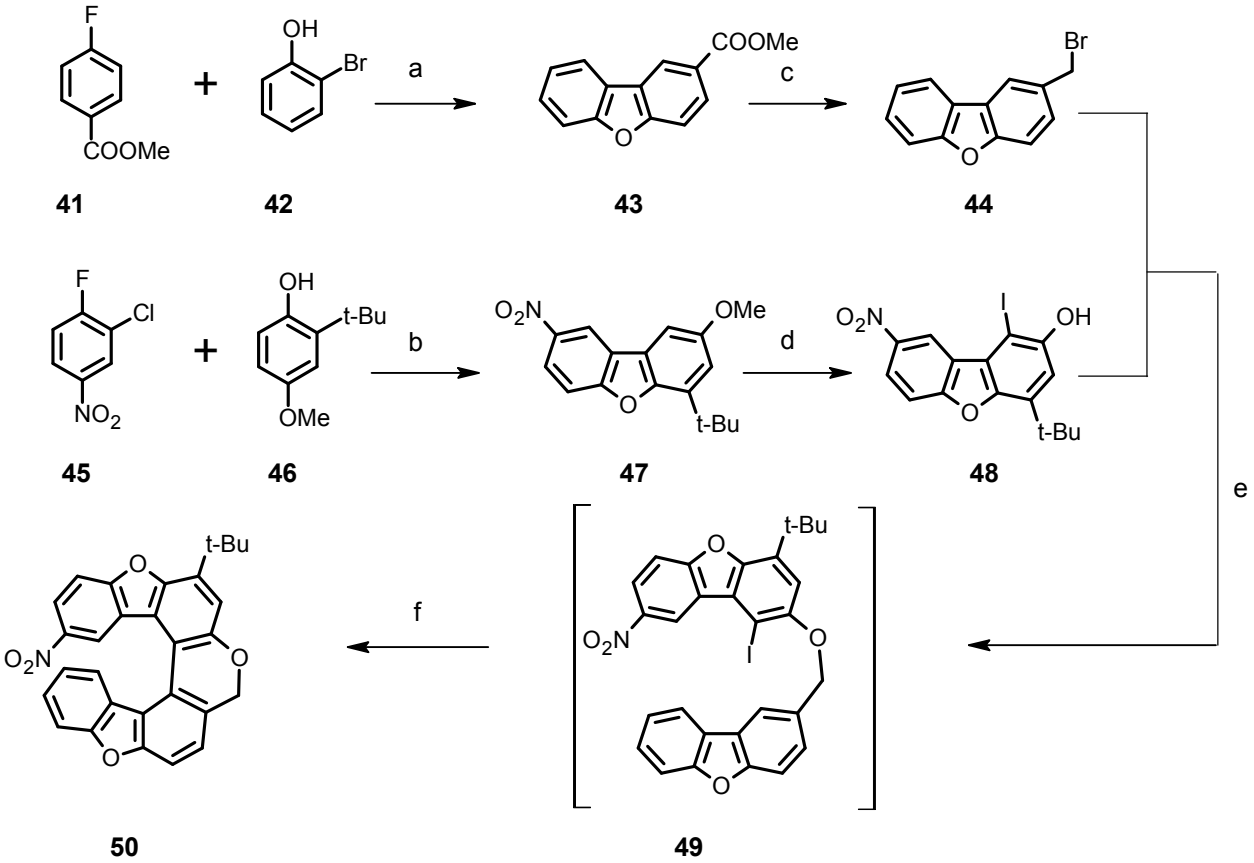


a) $FeCl_3$, H_2O, reflux, 4 h, 96 %; b) MeOH (excess), H_2SO_4 (1.0 eq.), rt, 3 d, 68 %; c) *p*-TSOH (1.0 eq.), toluene, reflux, overnight, 70 %.

It has been recently shown that the palladium mediated C–H activation is another suitable method for a furan ring construction to get oxahelicenes.[22]

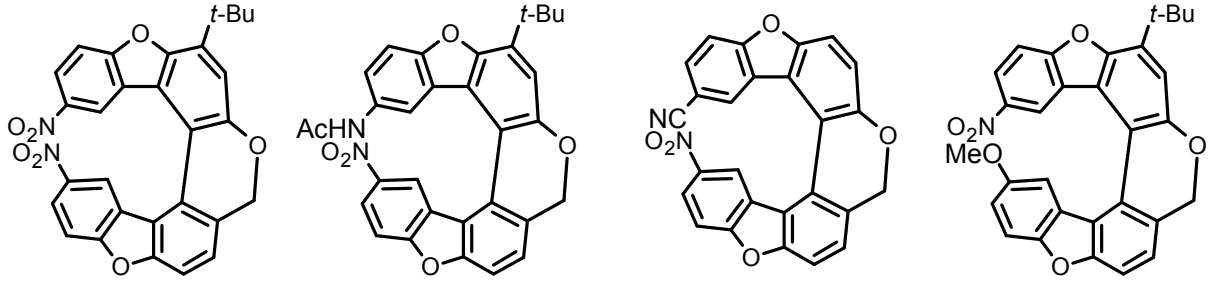
Scheme 7 shows the approach. First, the substituted dibenzofuran building blocks **41** and **42** were prepared. A nucleophilic aromatic substitution followed by a C–H arylation catalyzed by $Pd(OAc)_2$ and in the presence of PPh_3 gave the intermediate **43**. Then it was treated with DIBAL to afford a hydroxyl derivative which was brominated with PBr_3 to obtain **44**. Using the similar procedure, the intermediate **47** was prepared and then transformed into **48** by demethylation followed by iodination. The reaction of the building blocks **44** and **48** under the basic conditions gave the dimeric product **49** which was difficult to isolate due to its very low solubility. The following regioselective C–H arylation catalyzed by a palladium catalyst with triphenylphosphine gave rise to the desired product **50**. These two steps were carried out as a one–pot process. After optimization, the authors were able to prepare oxahelicenes bearing various functional both electron–withdrawing and electron–donating groups (Figure 5).

Scheme 7



a) 1. K_2CO_3, DMA, 150 °C, 43 h, 2. $Pd(OAc)_2$ (4 mol%), PPh_3 (8 mol%), K_2CO_3 (1.3 eq.), DMA, 26 %; b) 1. K_2CO_3 (1.2 eq.), DMA, reflux, 4 h, 2. $Pd(OAc)_2$ (4 mol%), $PCy_3.HBF_4$ (8 mol%), K_2CO_3 (1.25 eq.), DMA, 140 °C, 23 h, 78 %; c) 1. DIBAL (2.0 eq.), toluene, -78 °C, then rt, 2. PBr_3 (2.6 eq.), DCM, -78 °C, then rt overnight, 77 %; d) 1. BBr_3 (1.5 eq.), DCM, 0 °C, then rt, 4 h, 2. I_2 (1.1 eq), morpholine (3.0 eq.), rt, overnight, 84 %; e) K_2CO_3 (1.2 eq.), DMA, 100 °C, 1 h; f) $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), K_2CO_3 (1.2 eq.), DMA, 140 °C, 2 h, 79 %.

Figure 5

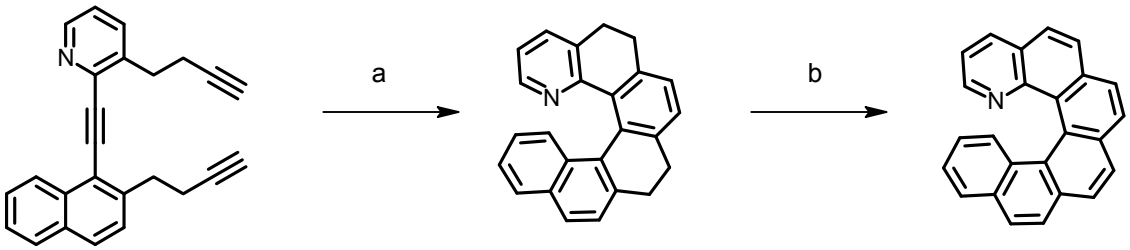


51 **52** **53** **54**

1.4 Azahelicenes

Helicenes with nitrogen atoms embedded in the helical backbone are called azahelicenes. These compounds can be effectively prepared, for example, by [2 + 2 + 2] cyclotrimerization (Scheme 8).[3] Azahelicenes will not be discussed further in my Thesis as a colleague of mine will cover this topic in his Thesis.

Scheme 8



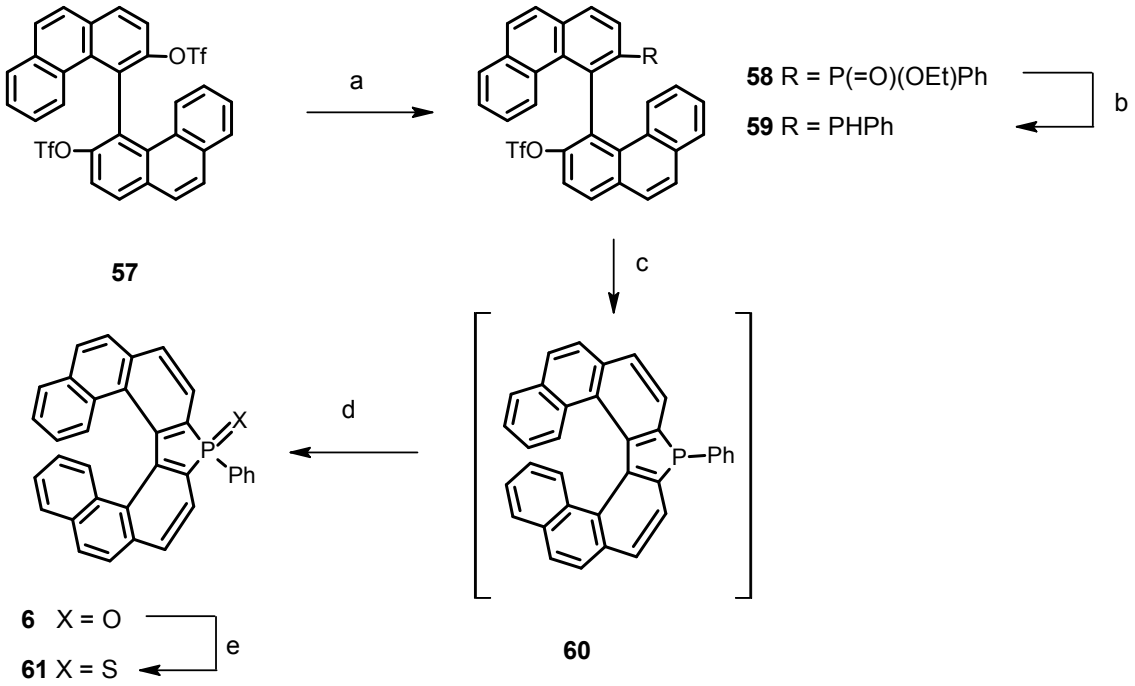
55 **56** **2**

a) $CpCo(CO)_2$ (20 mol%), PPh_3 (40 mol%), decane, halogen lamp, 140 °C, 1 h, 82 %; b) MnO_2 (30 eq.), toluene, microwave oven, 150 °C, 1.3 h, 65 %.

1.5 Phosphahelicenes

In the 90's, the first helicenes containing phosphorus were synthesized. A recent example is the synthesis of phospha[7]helicenes containing phosphole oxide or phosphole sulfide moieties (Scheme 9).[8] The starting material for this synthesis was racemic 4,4'-biphenanthryl-3,3'-diyl bis(trifluoromethanesulfonate) **57**. A cross–coupling reaction of this compound with ethyl phenylphosphinate gave the intermediate **58**. Phosphahelicene **60** was obtained after reduction of **58** with $LiAlH_4$ and a subsequent palladium–catalyzed *P*-arylation. Helicene **60** was without purification oxidized to give product **6** in 16 % overall yield. Finally, it was transformed into thiaderivative **61** by Lawesson's reagent.

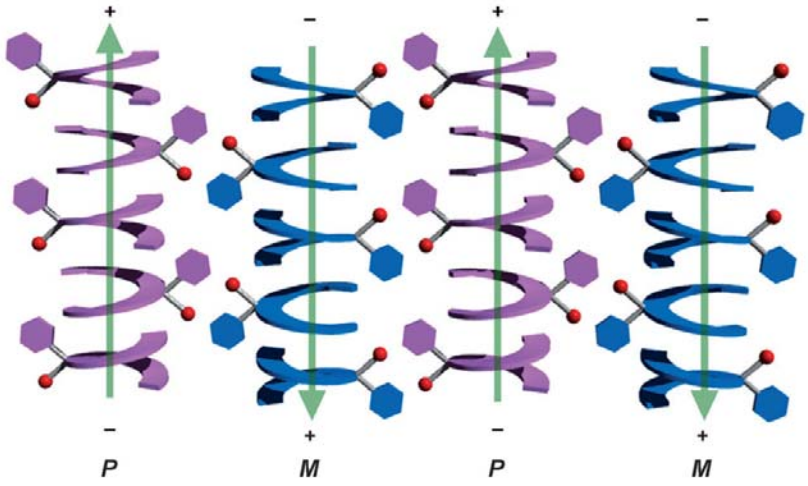
Scheme 9



a) HP(=O)(Et)Ph (6.0 eq.), $Pd(OAc)_2$ (20 mol%), DPPB (20 mol%), *i*-Pr_2NEt (10.0 eq.), HCOONa (60 mol%), DMSO, 110 °C, 5 d, 46 %; b) $LiAlH_4$ (5.0 eq.), TMSCl (5.0 eq.), THF, -78 °C to rt, 20 h; 98 % c) $Pd(OAc)_2$ (10 mol%), DPPB (10 mol%), *i*-Pr_2NEt (3.5 eq.), DMSO, 110 °C, 22 h; d) H_2O_2, DCM, rt, 7 h; 35 % e) Lawesson's reagent (2.0 eq), toluene, reflux, 3 h, 97 %.

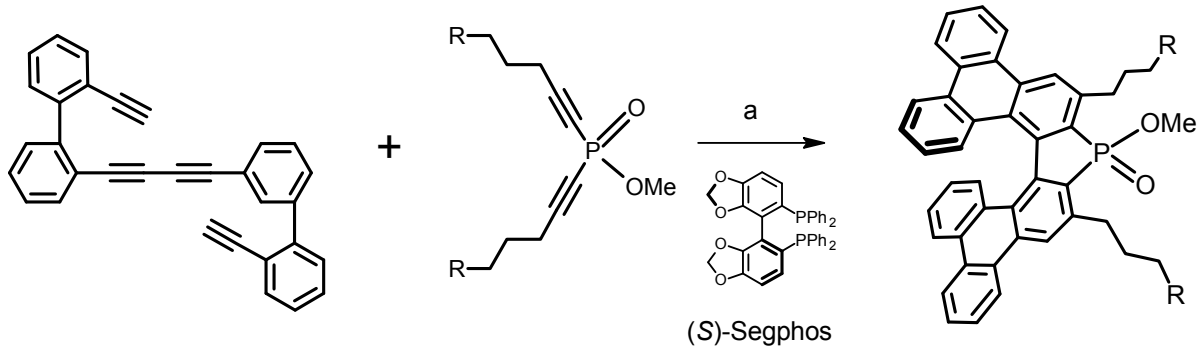
The phosphole oxide **6** and phosphole sulfide **61** moieties cause that these helicenes have a dipole–moment vector that is parallel to their helical axis, therefore they stack in columns. Interestingly, the racemate of phosphole sulfide **61** crystallizes with a unique packing motif; the columns with one dipole orientation consist always of a single enantiomer (Figure 6).

Figure 6[8]



Another way how to synthesize phosphahelicenes is [2 + 2 + 2] cyclotrimerization.[23] In this case, two nonracemic phosphahelicenes (+)-**65** and (+)-**66** were synthesized from tetrayne **62** and dialkynyl phosphine oxides **63** and **64** (Scheme 10), respectively. The reaction was catalyzed by the cationic rhodium(I)/axially chiral biaryl bisphosphine complex and gave the products with moderate yields and *ee* values up to 75 %.

Scheme 10



62

63 R = Me

64 R = Ph

(*S*)-Segphos

(+)-**65** R = Me

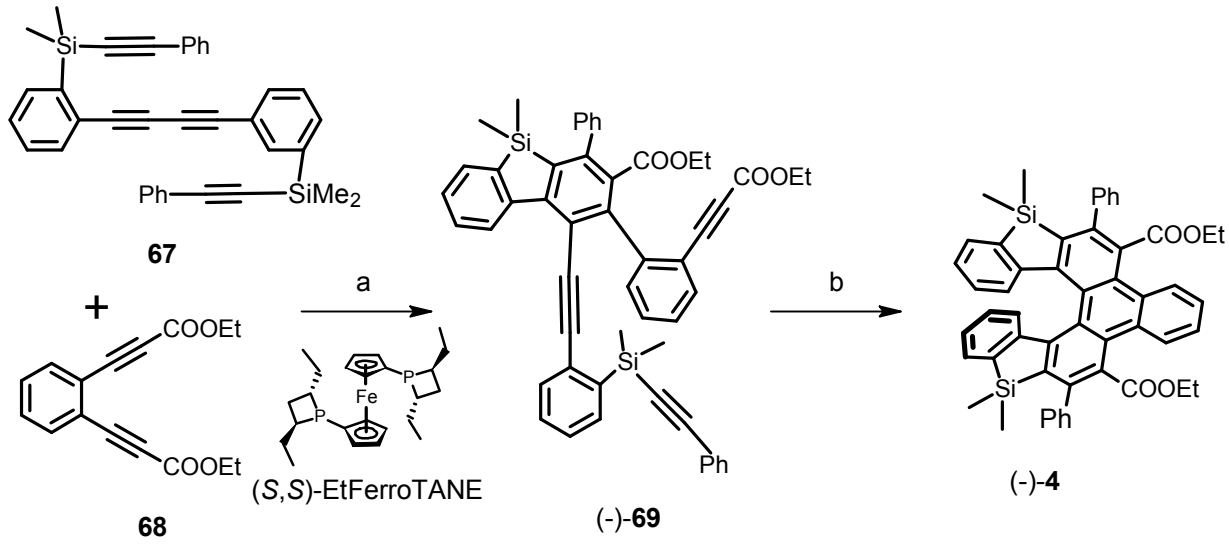
(+)-**66** R = Ph

a) **63** (1.2 eq.) or **64** (1.2 eq.), $[Rh(cod)_2]BF_4$/(*S*)-Segphos (20 mol%), DCM, rt, for (+)-**65**: 16 h, 46 % (68 % *ee*), (+)-**66**: 72 h, 43 % (75 % *ee*).

1.6 Other heterohelicenes

The enantioselective [2 + 2 + 2] cyclotrimerization can be also used to prepare helicenes containing silicon.[6] The synthesis is shown in Scheme 11. The first reaction step was an enantioselective intermolecular [2 + 2 + 2] cyclotrimerization catalyzed by chiral (*S*,*S*)-Ir-EtFerroTANE catalyst. The intermediate **69** underwent Ni-mediated intramolecular cyclotrimerization to give silahelicene (-)-**4**. The reaction proceeded with an almost perfect transfer of axial to helical chirality. This silahelicene exhibited high stability and could be used as emitting layer in OLEDs.

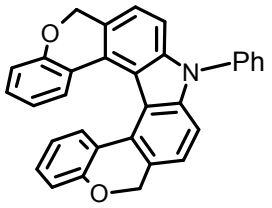
Scheme 11



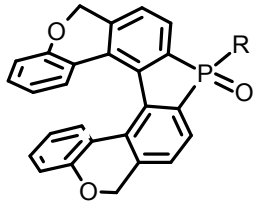
a) $[IrCl(cod)]_2$ (10 mol%), (*S*,*S*)-EtFerroTANE (20 mol%), xylene, 100 °C, 4 h. 74 % (94 % *ee*); b) $Ni(cod)_2$ (1.0 eq.), PPh_3 (2.0 eq.), THF, rt, 2h, 94 % (93 % *ee*).

The helicene skeleton can contain further different types of heteroatoms and some can be prepared by methods similar to the previously mentioned ones. For example, dioxa-aza[7]helicene[24] (**70**, Figure 7) or helicene containing oxygen and phosphorus atoms[25] (**71**, Figure 7).

Figure 7



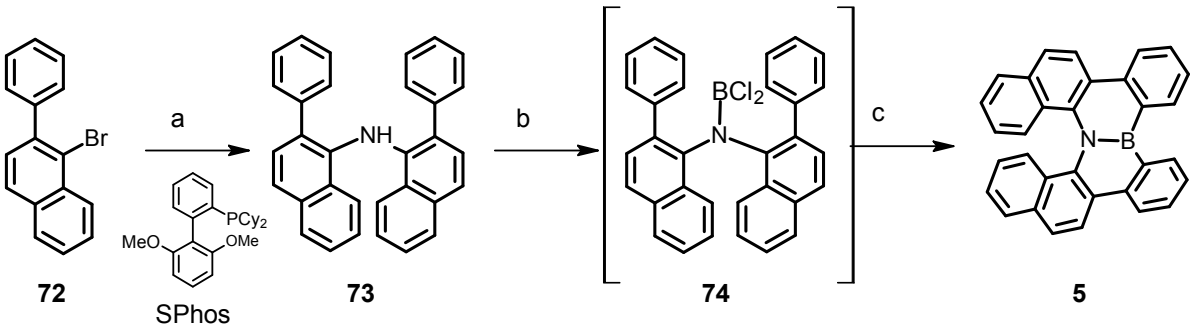
70



71

Another example of helicenes with two different heteroatoms is azaboradibenzo[6]helicene (Scheme 12). The starting material for its synthesis was 1-bromo-2-phenylnaphthalene **72** which was treated with lithium amide under Pd(0) catalysis in the presence of monodentate phosphine SPhos to give a product of the

Scheme 12



72 SPhos **73** **74** **5**

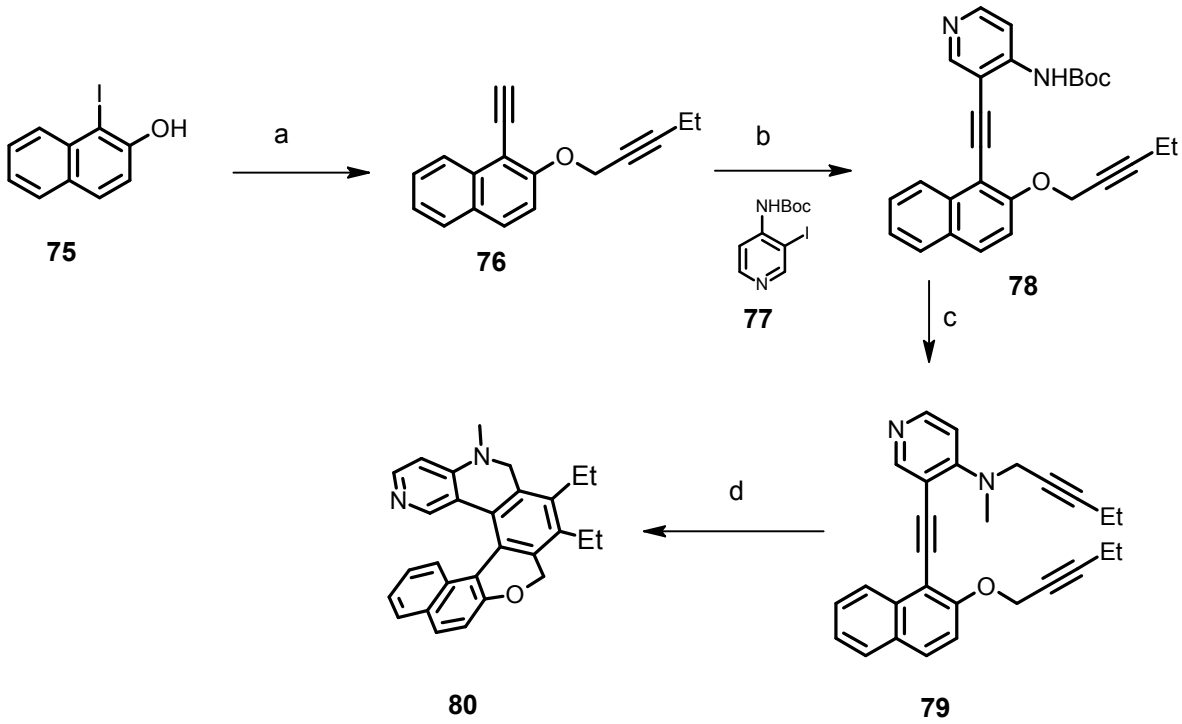
a) SPhos (2.4 mol%), $Pd_2(dba)_3$ (1 mol%), $LiNH_2$ (0.5 eq.), NaO*t*-Bu (2.0 eq.), dioxane, 100 °C, 3 h, 74 %; b) 1. *n*-BuLi (1.0 eq.) 2. BCl_3 (1.0 eq.), toluene, -78 °C to rt; c) 2,2,6,6-tetramethyl piperidine (4.0 eq.), $AlCl_3$ (8.0 eq.), 1,2-dichlorobenzene, 150 °C, 12 h, 68 %.

amination/arylation reactions **73**. A borylation by means of BuLi and BCl_3 followed by the tandem of a bora–Friedel−Crafts–type reaction with $AlCl_3$ and 2,2,6,6-tetramethylpiperidine afforded the desired product **5**. This compound shows interesting electronic properties. A charge mobility measurements based on the time–of–flight method suggested that the racemate and single enantiomer of **5** are p- and n-type semiconductors, respectively. Derivatives of this helicene could also form material for non–linear optics (NLO).[26]

Another example is a helical DMAP analog.[27] The synthesis of this compound is illustrated in Scheme 13. 1-Iodo-2-hydroxynaphthalene **75** was subjected to

Sonogashira reaction with trimethylsilylacetylene followed by an *O*-propargylation. The trimethylsilyl protective group was cleaved *in situ* providing the intermediate **76**. Another Sonogashira reaction between **76** and iodopyridine **77** gave the Boc-amide **78**. After *N*-propargylation of **78** followed by Boc deprotection and *N*-methylation, triyne **79** was obtained. Rh(I) catalyzed [2 + 2 + 2] cyclotrimerization of triyne **79** gave the product **80** in 41 % overall yield.

Scheme 13

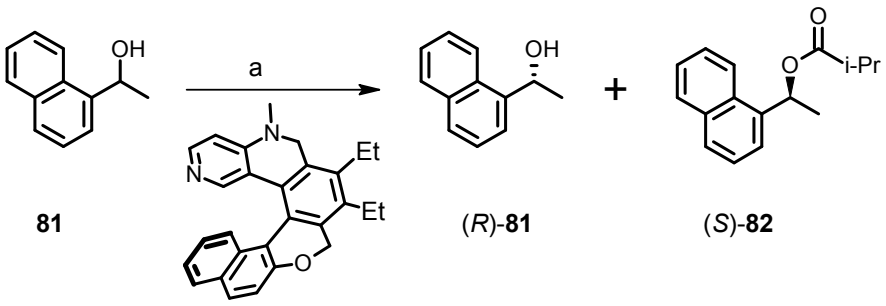


75 **76** **77** **78** **79** **80**

a) 1. TMS-C≡CH (3.0 eq.), $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (15 mol%), *i*-Pr_2NH, 1 h, 60 °C, 94 %, 2. 1-bromopent-2-yne (1.6 eq.), K_2CO_3 (1.6 eq.), DMF, rt, 1 h, then MeOH, 15 min, 99 %; b) **77** (1.2 eq.), $Pd(PPh_3)_4$ (5 mol%), CuI (15 mol%), *i*-Pr_2NH-toluene (2:3), 24 h, rt, 82 %; c) 1. 1-bromopent-2-yne (2.5 eq.), NaH (5.0 eq.), DMF, rt, 1 h, 90 %, 2. TMSOTf (2.0 eq.), Et_3N (1.5 eq.), DCM, rt, 1 h, then MeI (1.5 eq.), NaH (5.0 eq.), DMF, 23 °C, 1h, 80 %; d) $Rh(PPh_3)_3Cl$ (5 mol%), dioxane, 100 °C, 16 h, 74 %.

This helical DMAP analog (-)-(*M*)-**80** (after resolution by preparative-scale chiral HPLC) can be utilized for the kinetic resolution of secondary alkyl aryl alcohols.[27] Scheme 14 shows an example of this reaction.

Scheme 14



81 (*R*)-**81** (*S*)-**82**

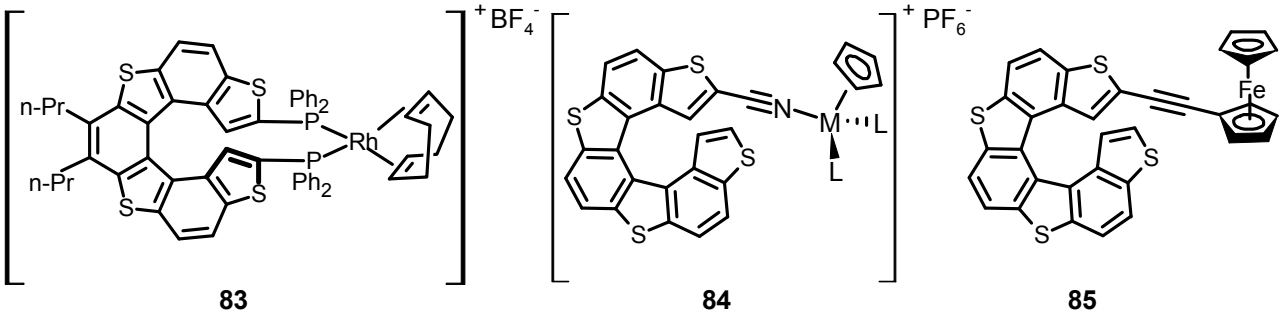
(-)-(M)-**80**

a) (-)-(*M*)-**80** (0.05 mol%), Et_3N (0.75 eq.), $(i\text{-PrCO})_2O$ (2.0 eq.), 48 h, 0 °C, 40 % for (*R*)-**81** (99.9 % *ee*), 60 % for (*S*)-**82** (65.6 % *ee*), S = 34.

1.7 Other uses of heterohelicenes

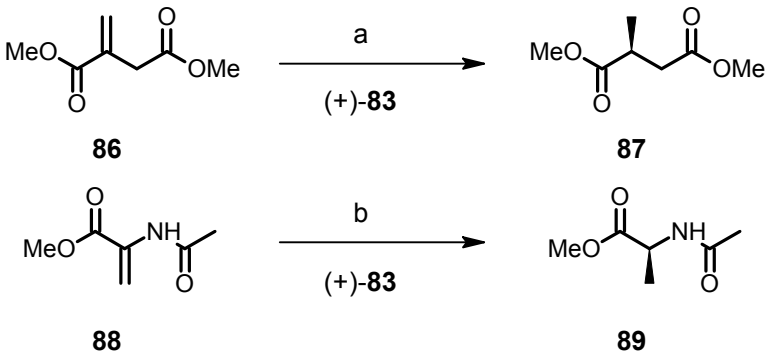
Like carbohelicenes, heterohelicenes can be used in catalysis.[28] For example, due to possibility of easy funcionalization of the terminal thiophene rings, thiahelicenes can be used as ligands to form transition metal complexes (Figure 8), such as Ru(II) or Fe(II) complexes **84**,[29] Rh(I) complex **83**[30] or ferrocene complex **85**.[31] Rh(I) complex **83** can be used as a hydrogenation catalyst (Scheme 15).

Figure 8



83 **84** **85**

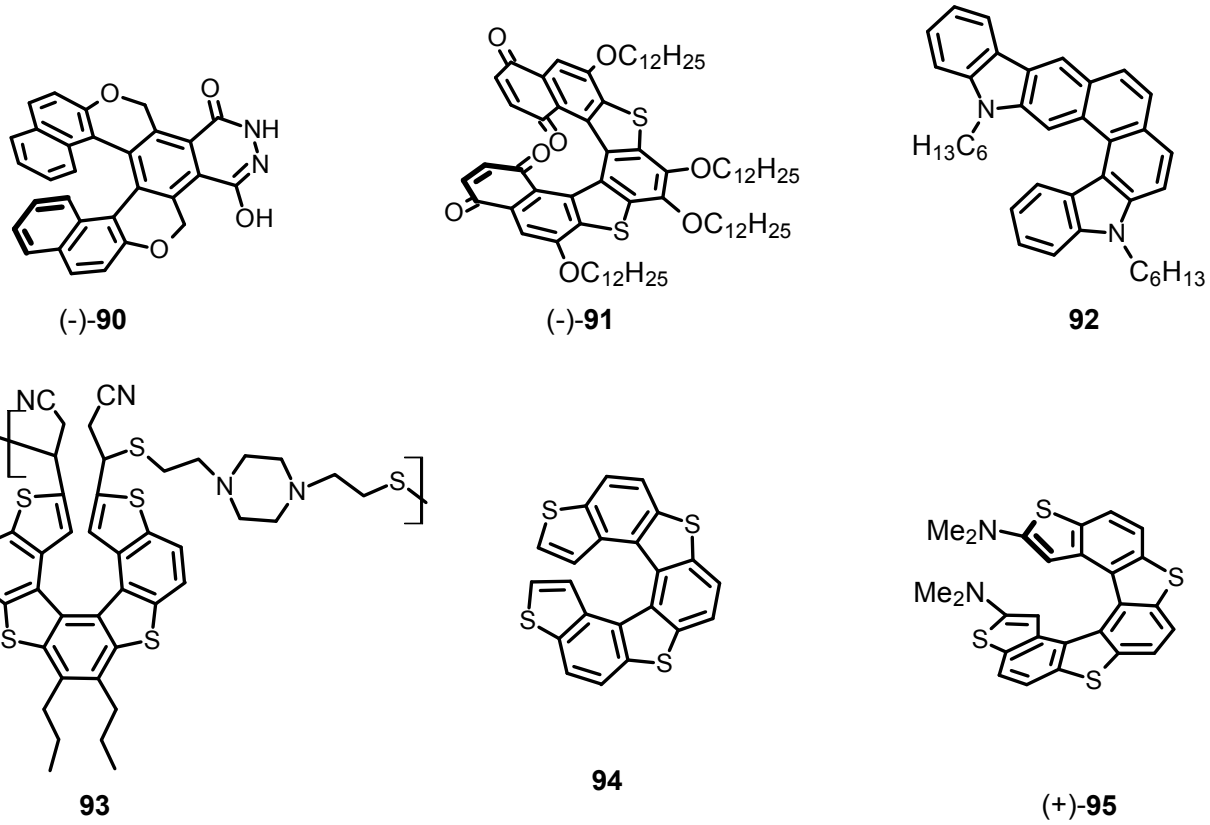
Scheme 15



a) (+)-**83** (0.2 mol%), H_2 (5 bar), DCM, rt, 24 h, 27 % (31 % *ee*); b) (+)-**83** (0.2 mol%), H_2 (5 bar), DCM, rt, 24 h, 99 % (40 % *ee*).

Heterohelicenes are promising materials in various fields of science. Figure 9 shows examples of some of these compounds. The phthalhydrazine–functionalized dioxa[7]helicene (-)-**90** exhibits the superior circularly polarized luminescence (CPL) properties,[32] dithia[7]helicene (-)-**91** forms chiral porous materials,[33] diaza[7]helicene **92** was used in OLED.[34] A polymer containing tetrathia[7]helicene **93** forms material for non–linear optics (NLO).[35] Tetrathia[7]helicene **94** could be used in organic thin–film transistors (OTFTs).[36] It has been shown that tetrathia[7]helicene (+)-**95** can selectively bind DNA,[37] thus can be used in molecular recognition.

Figure 9

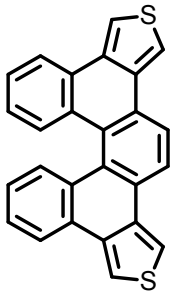


2. Objectives

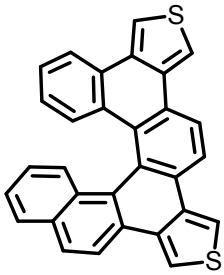
The objectives of this Thesis have been:

- To prepare dithiopheno[5]helicene **96**, dithiopheno[6]helicene **97** and trithiopheno[6]helicene **98** (Figure 10).
- To perform spectral characterization of dithiopheno[5]helicene **96** and dithiopheno[6]helicene **97** including UV/Vis, fluorescence and electrochemical characterization.
- To perform enantioselective [2 + 2 + 2] cyclotrimerization that leads to nonracemic dithiopheno[6]helicene **97**.
- To carry out separation of the racemic dithiopheno[6]helicene **97** into enantiomers and measure their CD spectra, optical rotation and determine the barrier of racemization.

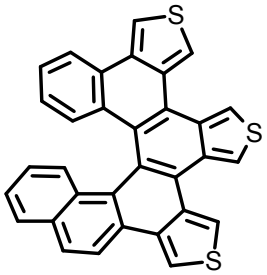
Figure 10



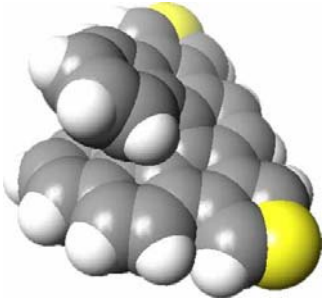
96

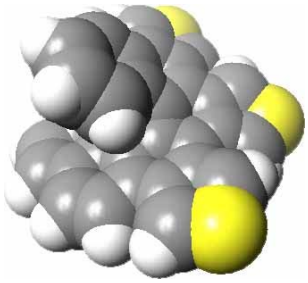


97



98



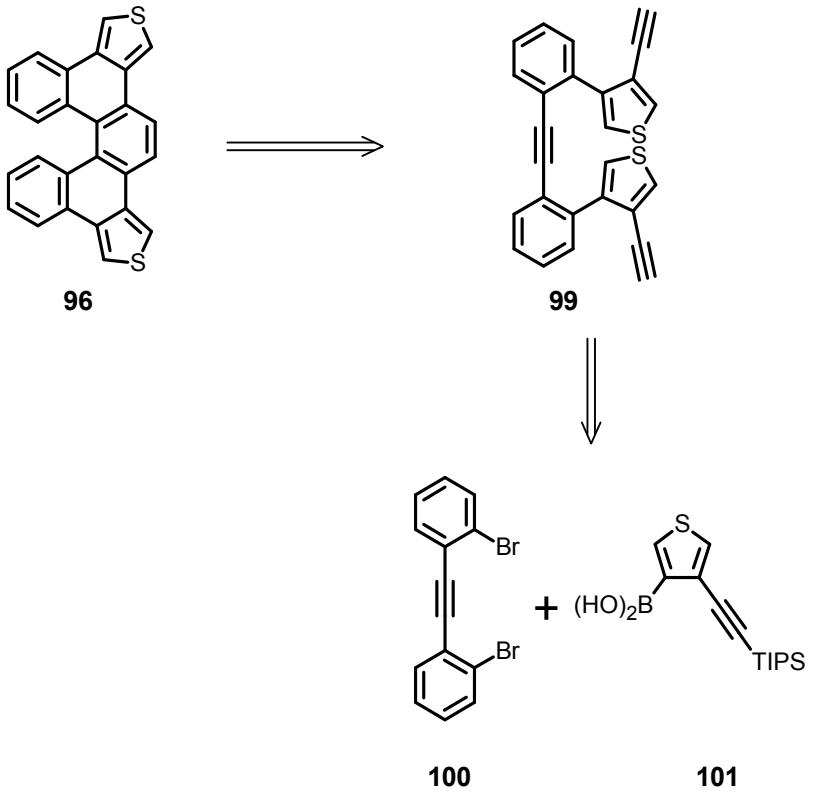


3. Results and discussion

3.1 Synthesis of dithiopheno[5]helicene

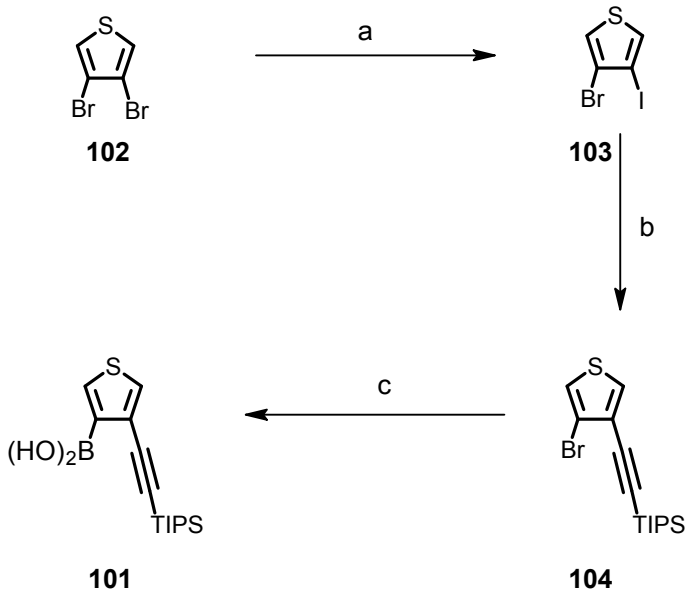
The first objective was to prepare dithiopheno[5]helicene **96**. A retrosynthetic analysis revealed that the crucial steps are: [2 + 2 + 2] cyclotrimerization of triyne (**99**→**96**) and Suzuki coupling of the two building blocks – boronic acid **101** and dibromide **100** (Scheme 16).

Scheme 16



Boronic acid **101** was prepared from the commercially available 3,4-dibromothiophene **102** (Scheme 17). First, it was transformed into 3-bromo-4-iodothiophene **103** by means of *n*-BuLi and iodine at low temperature.[38] The product had the same R_F as the starting material, so the progress of the reaction was monitored by GC-MS. After work-up, the GC-MS and ^{1}H NMR showed that clean product was obtained. Then, the palladium catalyzed Sonogashira coupling of **103** and (triisopropylsilyl)acetylene gave intermediate **104**. Even after purification of the product by flash chromatography,

Scheme 17



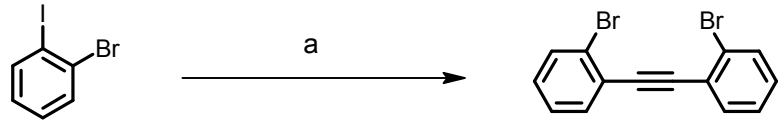
a) 1. *n*-BuLi (1.1 eq.), Et_2O, -78 °C, 1 h, 2. I_2 (1.0 eq.), Et_2O, -78 °C, 2 h, 95 %; b) TIPS-C≡CH (3.0 eq.), $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%), *i*-Pr_2NH-THF (1:1), rt, 1 h, 95 %; c) 1. *n*-BuLi (1.2 eq.), THF , -78 °C, 30 min, 2. (*i*-$PrO)_3B$ (3.0 eq.), THF, rt, 30 min, 52 %.

the GC-MS showed that the (triisopropylsilyl)acetylene is still present as it was used in excess, so the product was dried on an oil pump until there was no (triisopropylsilyl)acetylene left. Finally, the desired boronic acid **101** was prepared by lithiation-borylation of **104** with (triisopropyl)borate, followed by an acidic workup. Yields of this reaction were around 80 % when the reaction was done on a small scale. On the larger scale, however, the yields were lower. The GC-MS analysis of the reaction mixture showed that it contains a product of debromination and this was probably the reason of lower yields.

The second building block **100** was prepared by a double palladium catalyzed Sonogashira coupling of bromoiodobenzene **105** with gaseous acetylene (Scheme 18). This was done in the presence a stoichiometric amount of acetylene in order to avoid the formation of alkyne dimer because it is impossible to separate this dimer from the desired product. Acetylene was measured out in such a way that the calculated volume of the solvent was added into a flask of the known volume so that the empty volume corresponded with the theoretical amount of acetylene. The procedure was following: After freezing the mixture by liquid nitrogen, the flask was

evacuated, acetylene was added and the flask was closed. It was found out that this reaction is very air sensitive.

Scheme 18



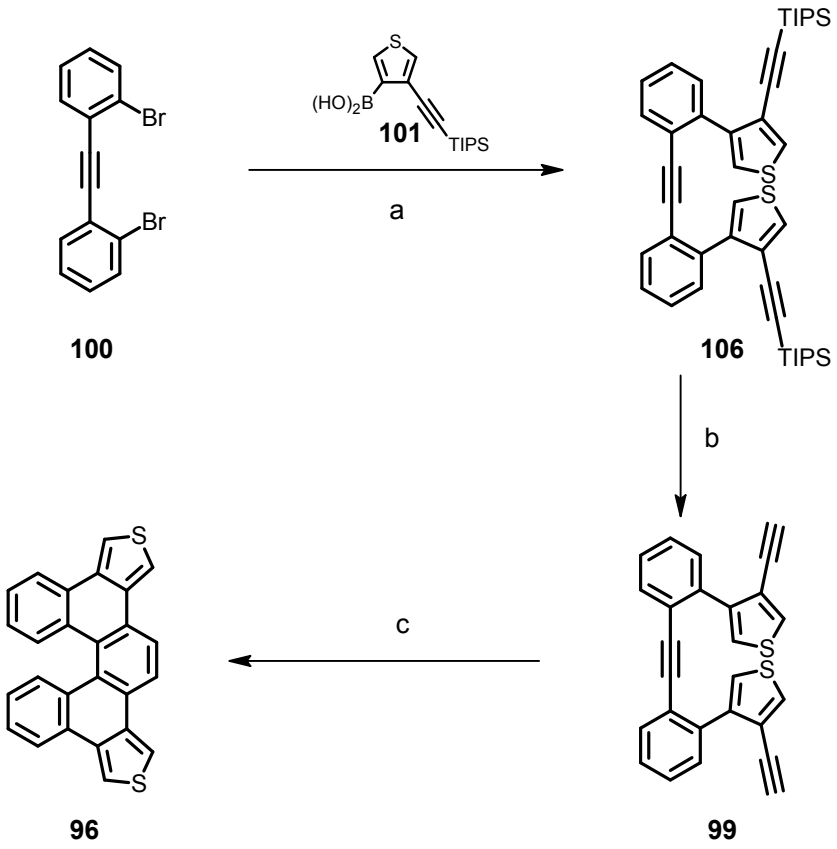
105 **100**

a) HC≡CH (0.5 eq.), $Pd(PPh_3)_4$ (9 mol%), CuI (18 mol%), *i*-Pr_2NH, 55 °C, 18 h, 31 %.

In principle, there is also another, longer way how to prepare the dibromide **100**: Sonogashira coupling of iodobromobenzene with (trimethylsilyl)acetylene, cleavage of the trimethylsilyl group and again Sonogashira coupling with iodobromobenzene. Although this three-reaction sequence is more versatile, sometimes it gives rather low yields and it is more time consuming than the direct method using gaseous acetylene.

Having these two building blocks in hand, it was possible to prepare the key intermediate – triyne **106**. As Scheme 19 shows, this was done by a double Pd-catalyzed Suzuki reaction of boronic acid **101** and dibromide **100** in the presence of potassium carbonate. The reaction was carried out in a mixture of toluene, ethanol and water at 90 °C. These conditions were chosen based on the previous experience in our group.[39] Prior to [2 + 2 + 2] cyclotrimerization, the (triisopropyl)silyl protecting groups at triyne **106** had to be cleaved because otherwise the reaction would not proceed.[40] The reaction was done by 3 equivalents of tetra-*n*-butylammonium fluoride trihydrate in tetrahydrofuran and proceeded with 66 % yield.

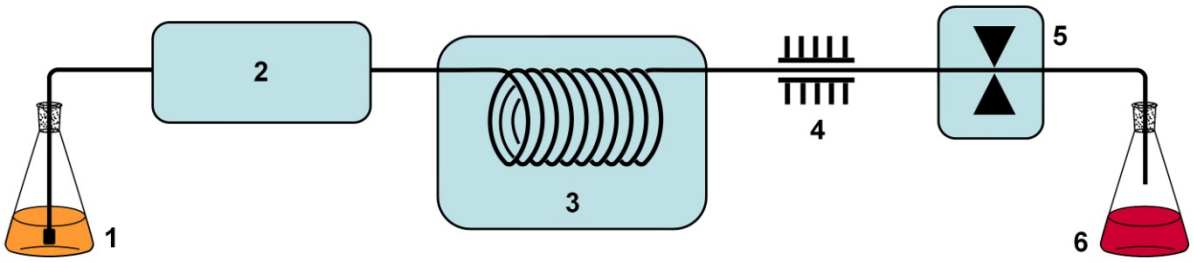
Scheme 19



a) **101** (2.4 eq.), $Pd(PPh_3)_2Cl_2$ (7 mol%), K_2CO_3 (2.0 eq.), toluene-*n*-PrOH-H_2O (16:16:4.3), 90 °C, 1.5 h. 93 %; b) TBAF (3.0 eq.), THF, rt, 2 h, 66 %; c) $CpCo(CO)_2$ (0.5 eq.), THF, flow reactor, 250 °C, 80 atm, 16 min, 60 %.

The deprotected triyne **99** was then subjected to [2 + 2 + 2] cyclotrimerization. Based on my previous experience,[41] the reaction was carried out in a flow reactor (Figure 11). The flow reactor uses a HPLC pump which pumps the reaction mixture through a section where the capillary is heated to the required temperature while a back pressure valve controls the pressure. After leaving the heated capillary, the reaction mixture is quickly cooled by the heat exchanger and, consequently, it is heated for the exactly defined time. The internal diameter of the capillary is 1 mm and its length is 10 m, which corresponds to the total volume of 8 ml. It is possible to set the pressure, temperature and flow rate with this instrument. The conditions chosen were previously applied in the synthesis of the similar carbohelicenes and thiahelicenes. Accordingly, [2 + 2 + 2] cyclotrimerization was carried out in tetrahydrofuran with 0.5 equivalent of $CpCo(CO)_2$ at 250 °C and 80 atm for 16 minutes. By this procedure the product **96** was obtained in 60 % yield.

Figure 11

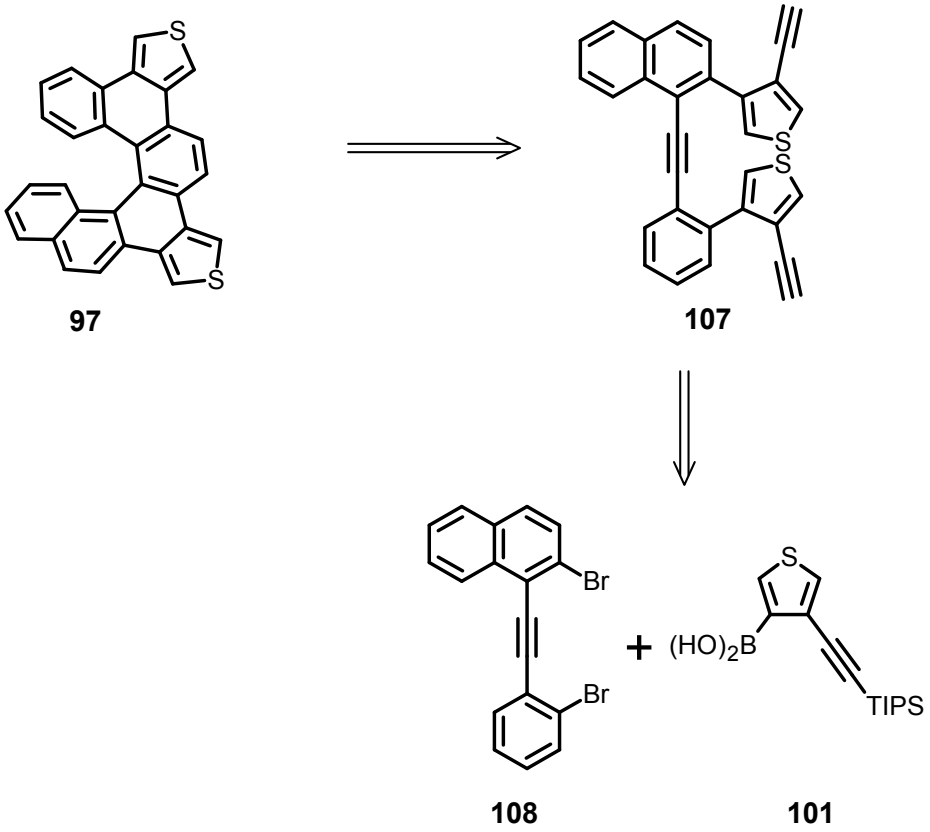


1. Reaction feed; **2**. HPLC pump; **3.** Heated block; **4.** Heat exchanger; **5.** Backpressure valve; **6.** Product.

3.2 Synthesis of dithiopheno[6]helicene

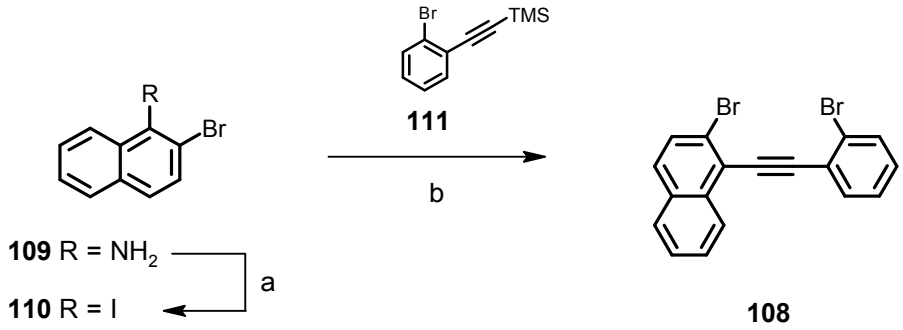
The strategy to synthesize dithiopheno[6]helicene **97** was very similar to that of dithiopheno[5]helicene **96** except for one of the starting compounds for the Suzuki reaction, this time it was an unsymmetrical dibromide **108** (Scheme 20).

Scheme 20



Dibromide **108** was prepared from the commercially available 1-amino-2-bromonaphthalene **109** (Scheme 21). First, the starting material **109** was transformed into 1-bromo-2-iodonaphthalene **110** by the diazotation/iodination reactions under treatment with hydrochloric acid, sodium nitrite and potassium iodide. Then, the desired intermediate **108** had to be prepared. It was not possible to prepare it by Sonogashira reaction of 1-bromo-2-iodonaphthalene **105**, removal of the trimethylsilyl group and another Sonogashira reaction with iodobromobenzene. The reason was that (trimethylsilyl)acetylene reacts first with the iodine and subsequently also with the bromine substituent. Therefore a different strategy was chosen. Dibromide **108** was prepared by Sonogashira coupling of 1-bromo-2-iodonaphthalene **110** and (trimethyl)silyl protected alkyne **111** while the (trimethyl)silyl protecting group was cleaved *in situ* by adding 1,8-diazabicycloundec-7-ene and a substoichiometric amount of water to the reaction mixture.[42] The 1,8-diazabicycloundec-7-ene deprotonates water and the formed OH^- cleaves the (trimethyl)silyl group. (Trimethyl)silyl hydroxide that is formed can also cleave the (trimethyl)silyl group in the presence of 1,8-diazabicycloundec-7-ene. This enabled to do the deprotection of alkyne **111** and Sonogashira coupling as an effective one pot process providing the dibromide **108** in 95 % yield.

Scheme 21

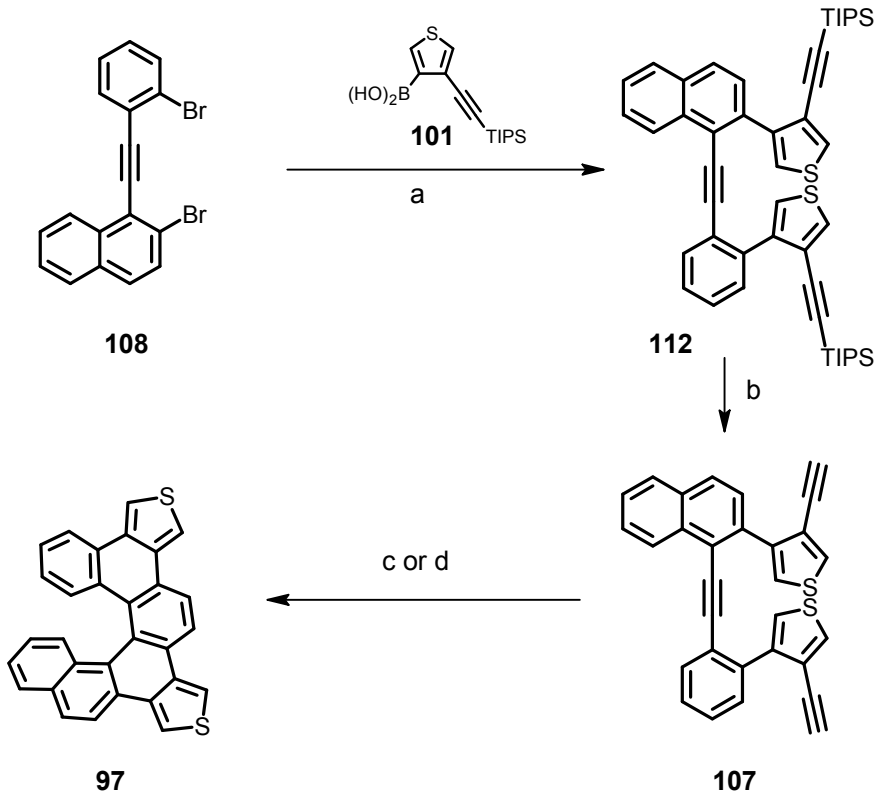


a) $NaNO_2$ (1.15 eq.), KI (4.0 eq.), HCl, 0 °C, 15 min, then rt, 1 h, then 60 °C, 45 min, 59 %; b) **110** (1.07 eq.), $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%), H_2O (40 mol%), Et_3N (6.0 eq.), DBU (12.0 eq.), benzene, 43 °C, 18 h, 95 %.

Similarly to the preparation of dithiopheno[5]helicene **96**, the next step in the synthesis of dithiopheno[6]helicene **97** was a double Suzuki coupling of dibromide **108** and boronic acid **101** (Scheme 22). The same conditions were utilized but the

reaction was not as efficient as the previous one and the yield was lower (20 %). Therefore *n*-propanol was used instead of ethanol in order to reach the higher temperature. This modification resulted in higher yields ranging from 50 to 89 %.

Scheme 22



a) **101** (2.4 eq.), $Pd(PPh_3)_2Cl_2$ (7 mol%), K_2CO_3 (2.0 eq.), toluene-*n*-PrOH-H_2O (16:16:4.3), 90 °C, 2 h. 89 %; b) TBAF (3.0 eq.), methanol (25.0 eq.), THF, rt, 45 min, 92 %; c) $CpCo(CO)_2$ (0.5 eq.), THF, flow reactor, 250 °C, 80 atm, 16 min, 65 %; d) $Ni(cod)_2$ (20 mol%), PPh_3 (40 mol%), THF, rt, 30 min, 67 %.

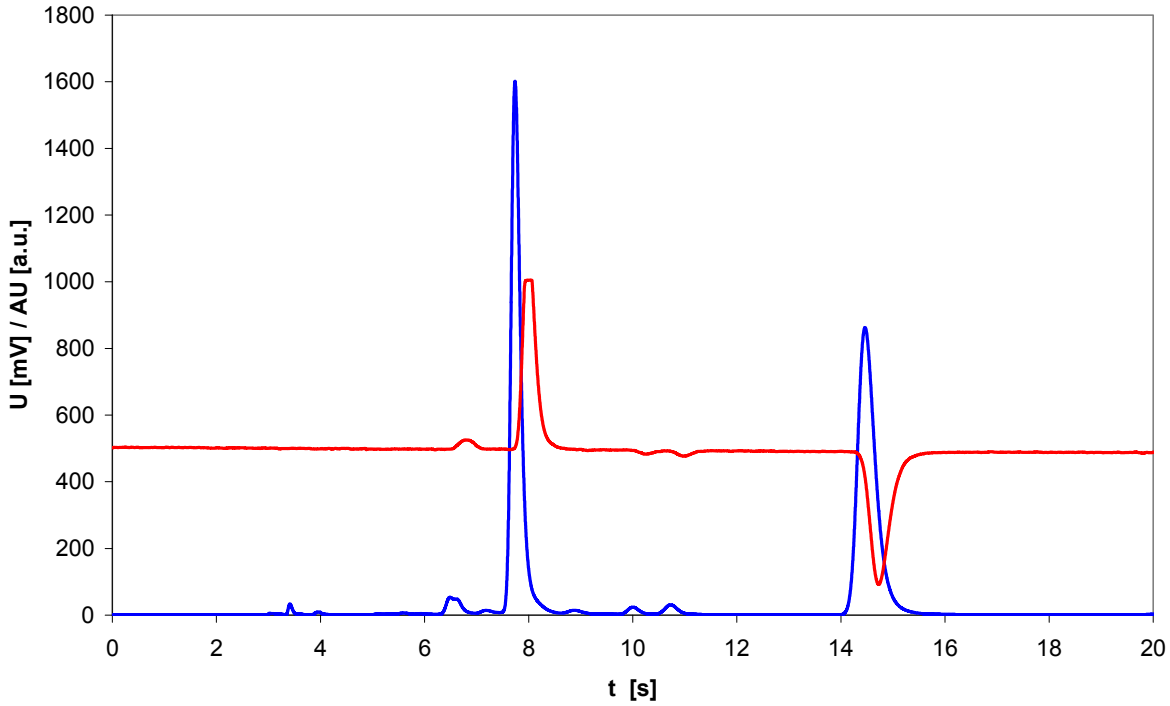
Although the cleavage of the (triisopropyl)silyl groups by means of tetra-*n*-butylammonium fluoride trihydrate gave satisfactory results, it was found out in our group that it can give better results by adding a small amount of methanol into the reaction mixture[43] because methanol can lower the basicity of tetra-*n*-butylammonium fluoride. Accordingly, the addition of the small amount of methanol proved to give better yield of the desilylated triyne **107** (92 % yield) compared to the reaction without methanol (that gave only 60 % yield).

The final step of the dithiopheno[6]helicene **97** synthesis was [2 + 2 + 2] cyclotrimerization. Based on the previous experience, the reaction was carried out in the flow reactor at 250 °C and 80 atm with $CpCo(CO)_2$ for 16 minutes and gave the desired product in 65 % yield.

Dithiopheno[6]helicene **97** was also prepared using $Ni(cod)_2$ catalyst giving the desired product in 67 % yield. Although the yield of this reaction was slightly higher, the flow reactor was preferred. The reason was that $CpCo(CO)_2$ complex is less air sensitive than $Ni(cod)_2$ which has to be handled in a glovebox.

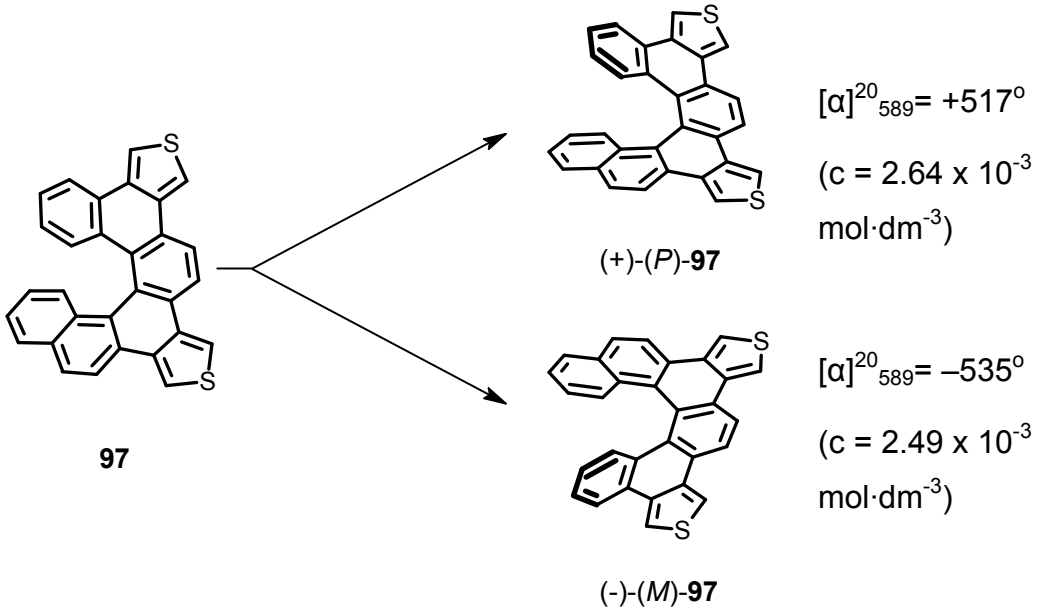
Another objective was to resolve the racemic dithiopheno[6]helicene **97** into enantiomers by chromatography on a chiral stationary phase. HPLC analysis on the analytical Chirapack IA column (immobilized CSP – amylose 3,5-dimethylphenylcarbamate, 250 x 4.6 mm, 5 µm) was performed with a mixture of heptane-*i*-PrOH (90:10) as eluent at 1 ml/min flow rate at 50 atm. The retention times were 7.7 and 14.5 minutes for (+)- and (-)-enantiomer, respectively (Figure 12, blue line – UV detector, red line – Chiralyser).

Figure 12



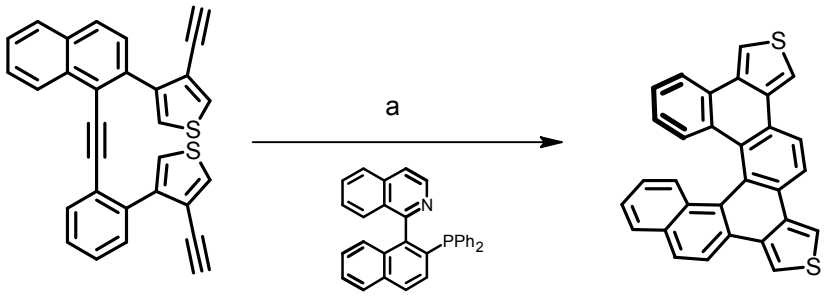
The preparative amount of (+)-**97** and (-)-**97** was obtained by a repeated separation (10 x 0.6 mg/20 µl of $CHCl_3$) on the same analytical column using the same conditions. The overall yield of the separation was 96 % and optical purity better than 98.4 % *ee*. Optical rotation of single enantiomers was measured in tetrahydrofuran at 589 nm being +517° for the first eluted enantiomer and –535° for the second eluted enantiomer (Figure 13).

Figure 13



The next objective was to examine whether the cyclotrimerization can be done under the enantiocontrol. Accordingly, the nickel catalyzed reaction in the presence of a chiral ligand was carried out. A wide variety of chiral ligands was investigated in our group.[44] The “priviledge ligands” for [2 + 2 + 2] cyclotrimerization[45] proved to be axially chiral monophosphines. Therefore, the commercially available phosphine (*R*)-QUINAP[39] **113** (Scheme 23) was tested. It gave the (+)-(*P*)-dithiopheno[6]helicene **97** in 92 % yield with 28.2 % *ee*, which was determined by an HPLC analysis on a

Scheme 23

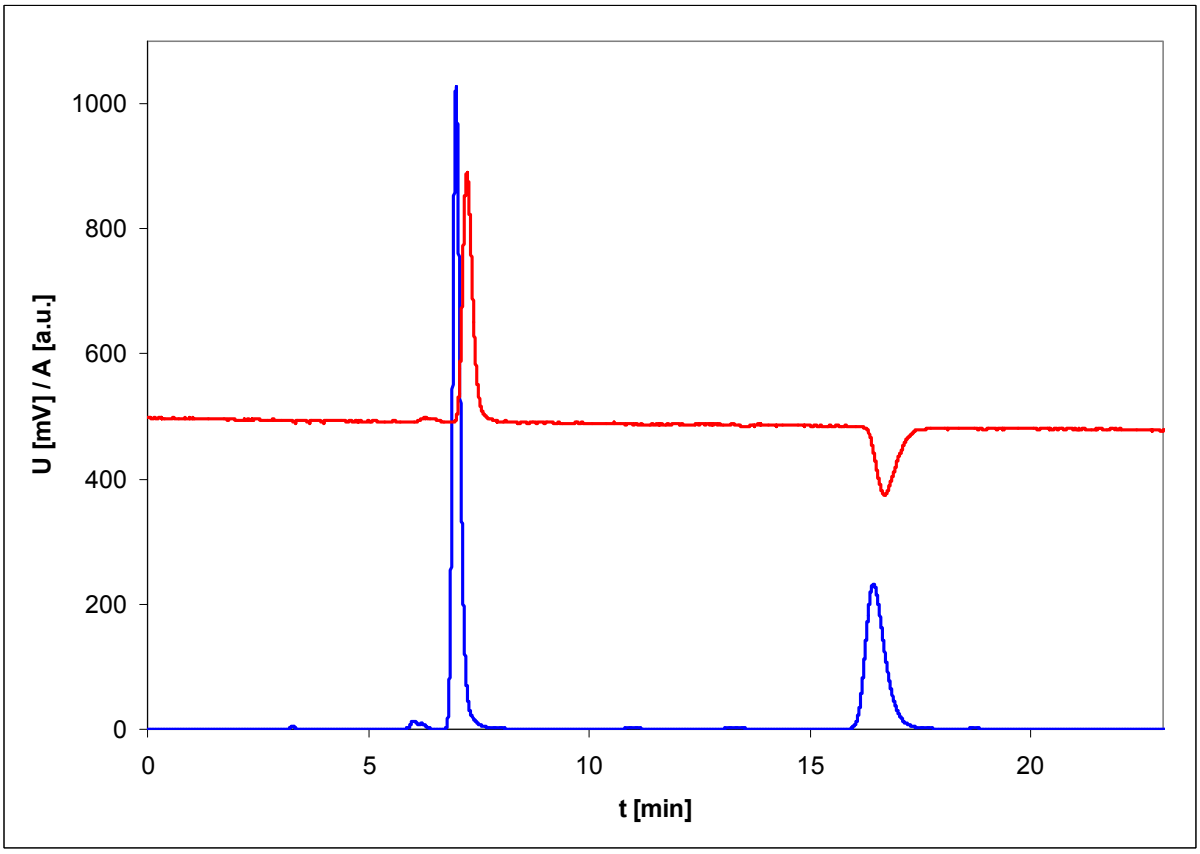


107 (*R*)-**113** (+)-(*P*)-**97**

a) $Ni(cod)_2$ (20 mol%), (*R*)-QUINAP **113** (45 mol%), THF, rt, 10 min, 92 % (28 % *ee*).

Chirapack IA column (heptane – chloroform 70:30), the retention times were 7.0 minutes for (+)-**97** and 16.4 minutes for (-)-**97** (Figure 14, blue line – UV detector, red line - Chiralyser).

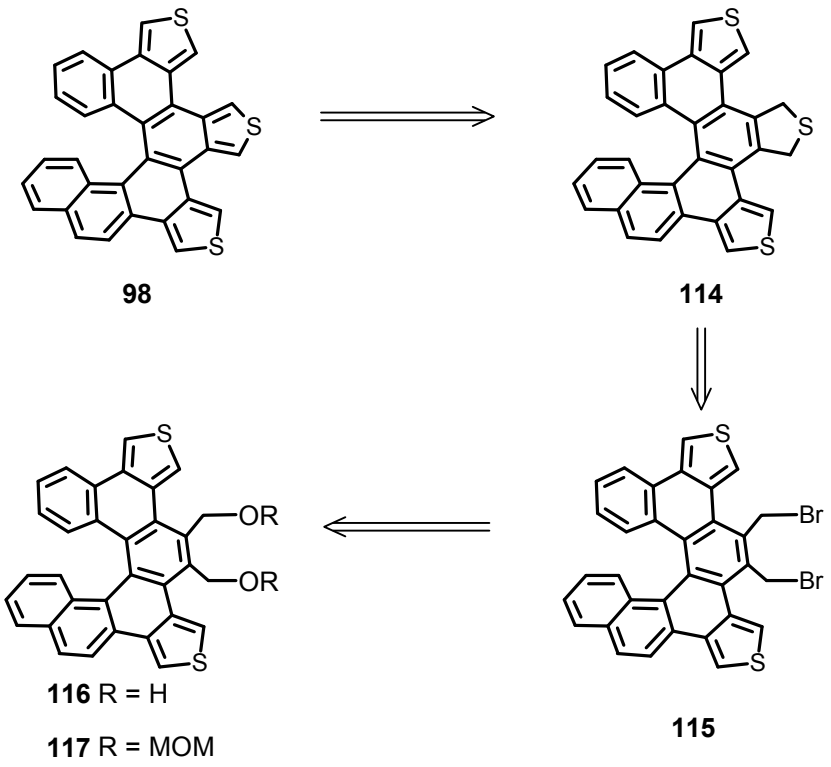
Figure 14



3.3 Synthesis of trithiopheno[6]helicene

In order to prepare trithiopheno[6]helicene **98** from the previously described dithiopheno[6]helicene **97**, the third thiophene ring had to be constructed on the helicene. A retrosynthetic analysis shows that the key steps to reach this task are: The aromatization of sulfide **114** which is formed from dibromide **115** and preparation of the corresponding alcohol **116** or protected alcohol **117** (Scheme 24).

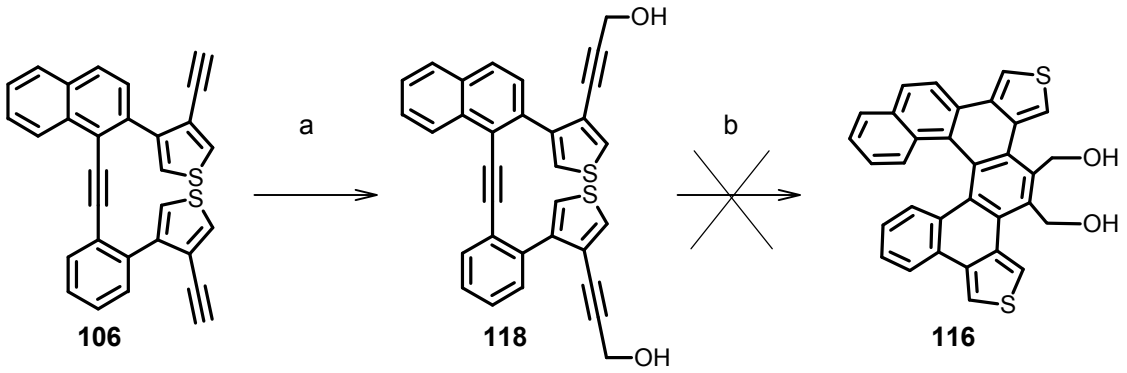
Scheme 24



As a starting material to prepare alcohol **116** was chosen the already synthesized triyne **107** (Scheme 25). The first step was lithiation of triyne **107** by means of *n*-BuLi at low temperature and the subsequent reaction with paraformaldehyde. Unfortunately, this reaction proceeded with very low yield. It was found out that the lithiation reaction proceeded quantitatively, which was proved by ^{1}H NMR spectra after quenching the reaction with D_2O when alkyne protons disappeared after deuteration. Thus, the problem was probably in the reaction with paraformaldehyde. Only few milligrams of the alcohol **118** were obtained, therefore **118** could be only characterized by ^{1}H NMR. The consequent [2 + 2 + 2]

cyclotrimerization of alcohol **118** in the flow reactor catalyzed by $CpCo(CO)_2$ did not provide any product.

Scheme 25



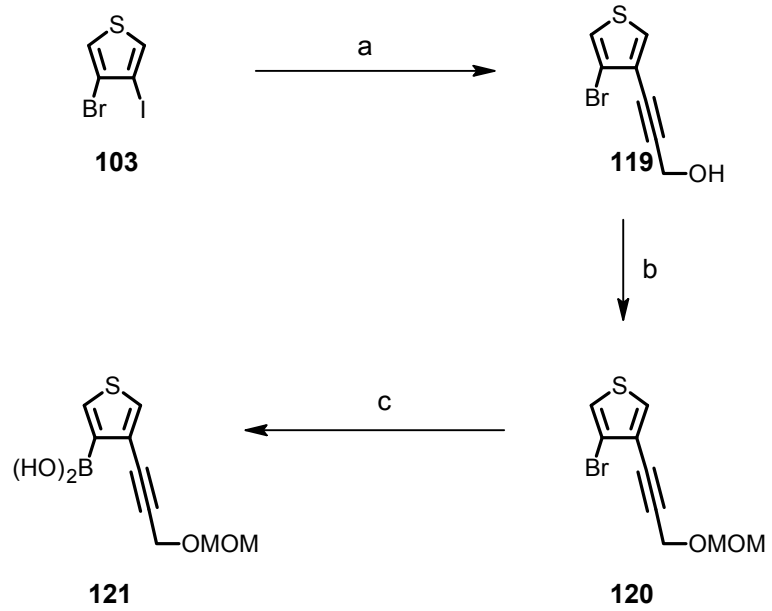
a) 1. *n*-BuLi (2.0 eq.), THF, -78 °C, 30 min, 2. paraformaldehyde (2.2 eq.), rt, 1 h, 29 %; b) $CpCo(CO)_2$ (0.5 eq.), THF, flow reactor, 250 °C, 80 atm, 16 min, decomposition.

Therefore another strategy that would be more efficient was investigated. The suggestion was to introduce the hydroxymethyl moiety into the molecule in an earlier stage of the synthesis. Accordingly, a different building block for the Suzuki coupling was needed to form the properly substituted triyne from which the helicene **98** would be prepared.

As the Scheme 26 shows, the starting material was 3-bromo-4-iodothiophene **103**, which was transformed into the propargylic derivative **119** by Pd-catalyzed Sonogashira coupling with propargyl alcohol. Then, the hydroxyl group was protected by a methoxymethyl group using 2.2 equivalents of chloromethyl methyl ether with 2.2 equivalents of diisopropylethylamine as a base. In order to transform **120** into boronic acid **121**, the same conditions as previously were used. Unfortunately, this time they did not work and only starting material and a product of protonation of the lithiated species were isolated. Therefore, we tried to let the reaction mixture stir with *n*-BuLi only for one minute at low temperature and then add (triisopropyl)borate. This procedure showed to be successful and the reaction gave the desired product **121**. Despite the reaction mixture was clean without any byproducts according to TLC, the yield was only about 40 %. The product probably decomposed on silica gel. Owing to

this instability, the crude reaction mixture was used further without any purification. Fortunately, this modification of the procedure did not affect the subsequent reaction.

Scheme 26

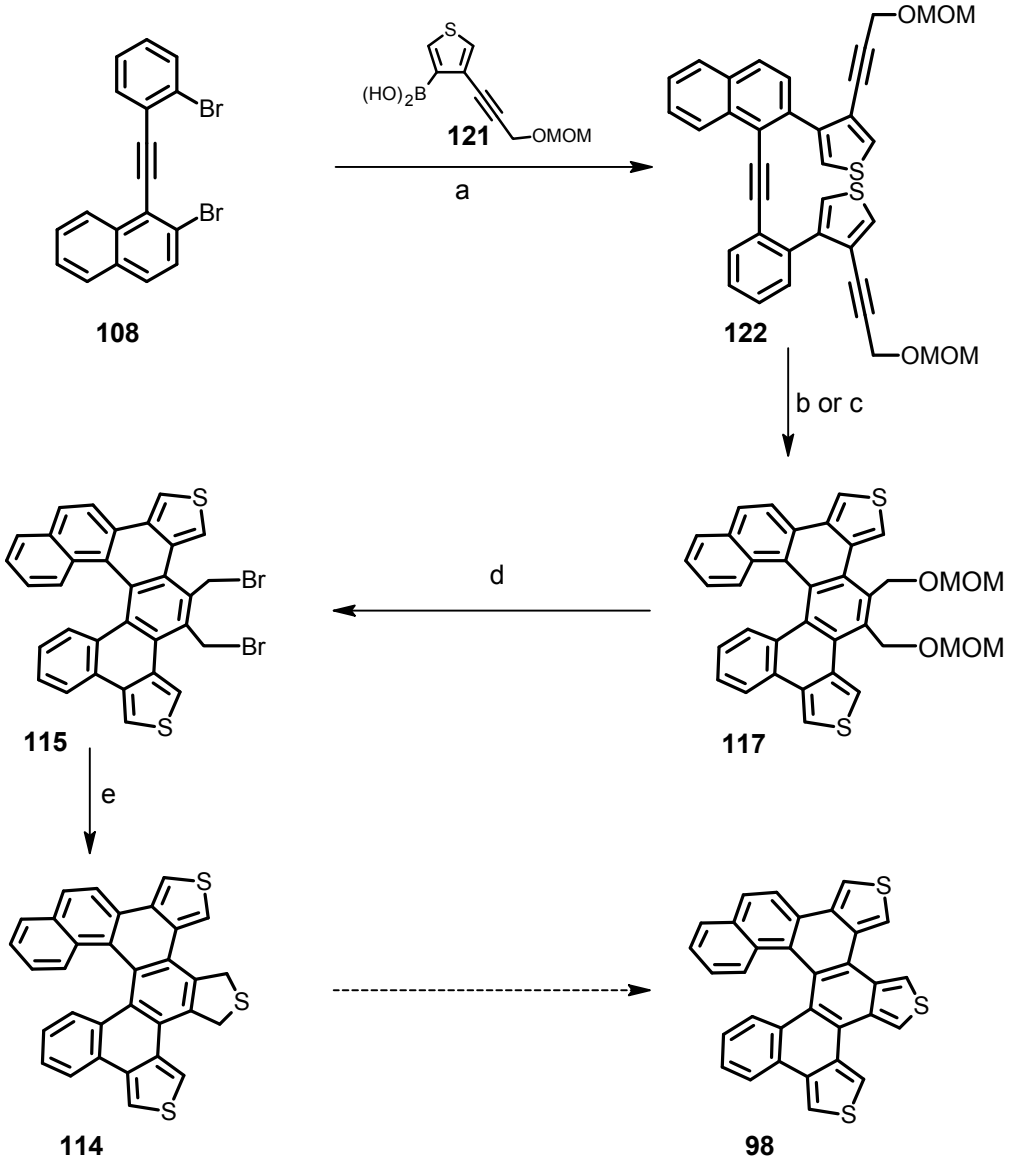


103 **119** **120** **121**

a) propargyl alcohol (3.0 eq.), $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%), *i*-Pr_2NH-THF (1:1), rt, 1 h, 86 %; b) chloromethyl methyl ether (2.2 eq.), *i*-Pr_2EtN (2.2 eq.), DCM, 0 °C, 24 h, 88 %; c) 1. *n*-BuLi (1.2 eq.), THF, -78 °C, 1 min, 2. $(i\text{-PrO})_3B$ (3.0 eq.), THF, rt, 45 min, 95 %.

The next step of the reaction sequence was Suzuki coupling of dibromide **108** and boronic acid **121** (Scheme 27). This was done under the same conditions as previously ($Pd(PPh_3)_2Cl_2$ and K_2CO_3 in toluene-*n*-PrOH-H_2O at 90 °C). The yields of this reaction also varied from 40 to 63 % as in the previous case.

Scheme 27

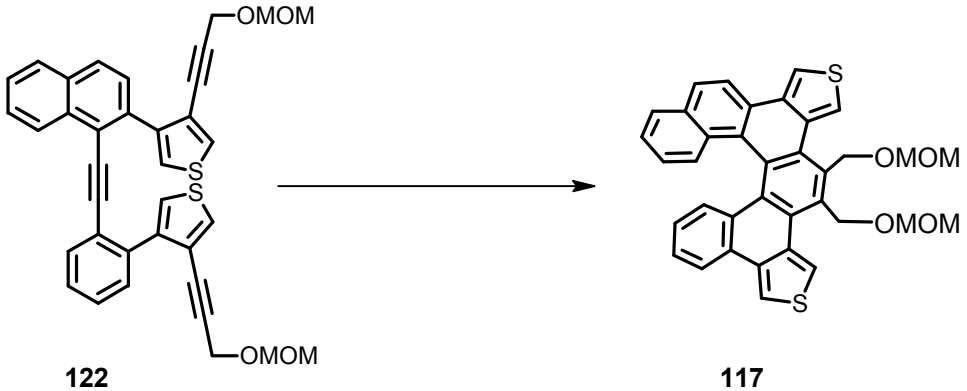


a) $Pd(PPh_3)_2Cl_2$ (10 mol%), K_2CO_3 (2.0 eq.), toluene-*n*-PrOH-H_2O (16:16:4.3), 90 °C, 2 h. 63 %; b) $CpCo(CO)_2$ (0.5 eq.), THF, flow reactor, 250 °C, 80 atm, 16 min, 22 %; c) $CpCo(CO)_2$ (1.0 eq.), PPh_3 (2.0 eq.), decane, 140 °C, 1.5 h, 36 %; d) HBr (7.0 eq.), acetic acid-DCM (780:1), 50 min, 48 %; e) Na_2S (20.0 eq.), $BnEt_3NCl$ (10 mol%), DCM-H_2O (1:1), 45 °C, 24 h, 44 %.

After that, triyne **122** was subjected to [2 + 2 + 2] cyclotrimerization applying several conditions (Table 1). First, the reaction was carried out in the flow reactor at 250 °C and 80 atm with $CpCo(CO)_2$ for 16 minutes. Unfortunately, the yield of this

reaction was only 22 % and majority of the reaction mixture was a complex mixture of products that could not be separated and identified.

Table 1



122 **117**

Catalyst	**Method**	**Temperature** [°C]	**Yield of 117**
$CpCo(CO)_2/PPh_3$	flow reactor	250	22 %
$Ni(cod)_2$	batch	rt	no reaction
$CpCo(CO)_2/PPh_3$	halogen lamp	140	36 %

Therefore a series of small-scale experiments (1-2 mg of the starting material) was carried out using different temperatures ranging from 160 °C to 200 °C and residence times from 4 to 16 minutes. The reaction was monitored by TLC (after 4, 8 and 16 minutes). At lower temperature (160 °C), the reaction did not proceed even after a prolonged reaction period. At higher temperature (till 180 °C), only a partial conversion took place. At 200 °C four minutes was sufficient to reach the full conversion. However, the products of decomposition formed the majority of the reaction mixture. Therefore other methods were investigated.

We tested a procedure that uses the same Co-catalyst but with irradiation by a halogen lamp, *i.e.* the classical Vollhardt's conditions for cyclotrimerizations. The reaction was carried out in decane using $CpCo(CO)_2$ catalyst with PPh_3 at 140 °C. The TLC analysis of the reaction mixture revealed that it was very similar to the reaction in the flow reactor. The reaction gave the desired helicene **117** in slightly higher isolated yield (up to 36 %) along with the products of decomposition. However, the reaction scope was limited. With the amount of starting triyne **122** larger than 100

mg, the yield dropped off. The nickel catalyzed cyclotrimerization was also performed but it did not provide the desired product.

The next step was deprotection of the methoxymethyl group. Since we wanted to prepare dibromide **115**, the deprotection had to be followed by substitution to form dibromide **115**. Therefore, the reaction was performed by treatment of **117** with a solution of hydrobromic acid in acetic acid and dichloromethane. The reaction was monitored by TLC. First, two equivalents of hydrobromic acid were added and after 20 minutes, the starting material was still present in the mixture. Therefore, additional 5 equivalents were added and in 30 minutes the starting material disappeared. This procedure provided dibromide **115** in 48 % yield. It was found out that if all 7 equivalents of hydrobromic acid are added at once, even after one hour the starting material is still present and an additional hydrobromic acid had to be added.

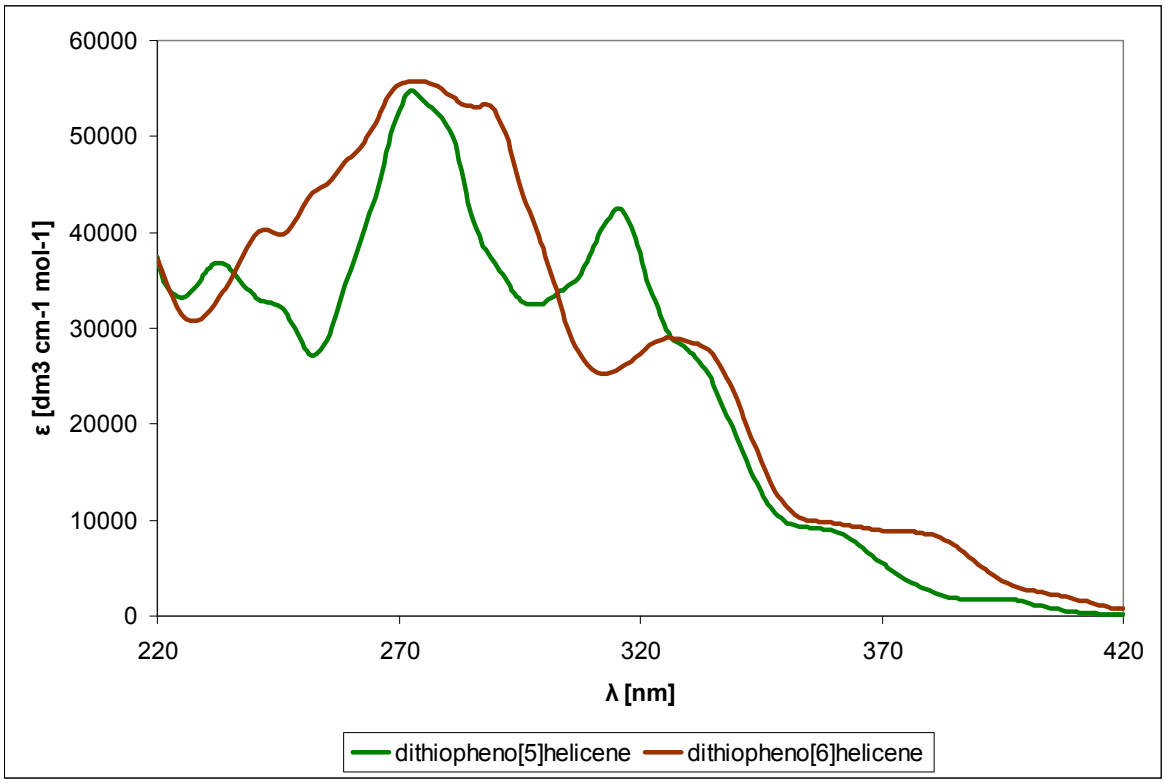
The next step was the construction of the five-membered ring containing sulfur. This was done in a two-phase system of dichloromethane and water (1:1) using sodium sulfide and benzyltriethylammonium chloride as a phase transfer catalyst. As proved by high resolution MS, (dihydro)trithiopheno[6]helicene **114** was formed but it was difficult to separate it due to its instability on silica gel. Despite that, a partial purification was achieved using reverse phase silica gel C18. The characterization as well as aromatization to the desired trithiopheno[6]helicene **98** are under way.

3.4 Physico-chemical properties of dithiopheno[5]helicene and dithiopheno[6]helicene

3.4.1 Spectral characterization

The spectral characterizations of dithiopheno[5]helicene **96** and dithiopheno[6]helicene **97** were performed using UV/Vis and fluorescence spectroscopy. The spectra were measured in tetrahydrofuran (in a 1 cm cell). The UV/Vis absorption spectrum of dithiopheno[5]helicene **96** shows the characteristic spectral bands at 316 nm and 273 nm (Figure 15, green line, c = 1.27 x 10^{-4} mol·dm^{-3}). The spectrum of dithiopheno[6]helicene **97** has the characteristic spectral bands at 326 nm and 272 nm (Figure 15, red line, c = 1.112 x 10^{-4} mol·dm^{-3}). Thus, the absorption maximum of dithiopheno[6]helicene **97** at 326 nm is red shifted compared to dithiopheno[5]helicene **96** at 316 nm.

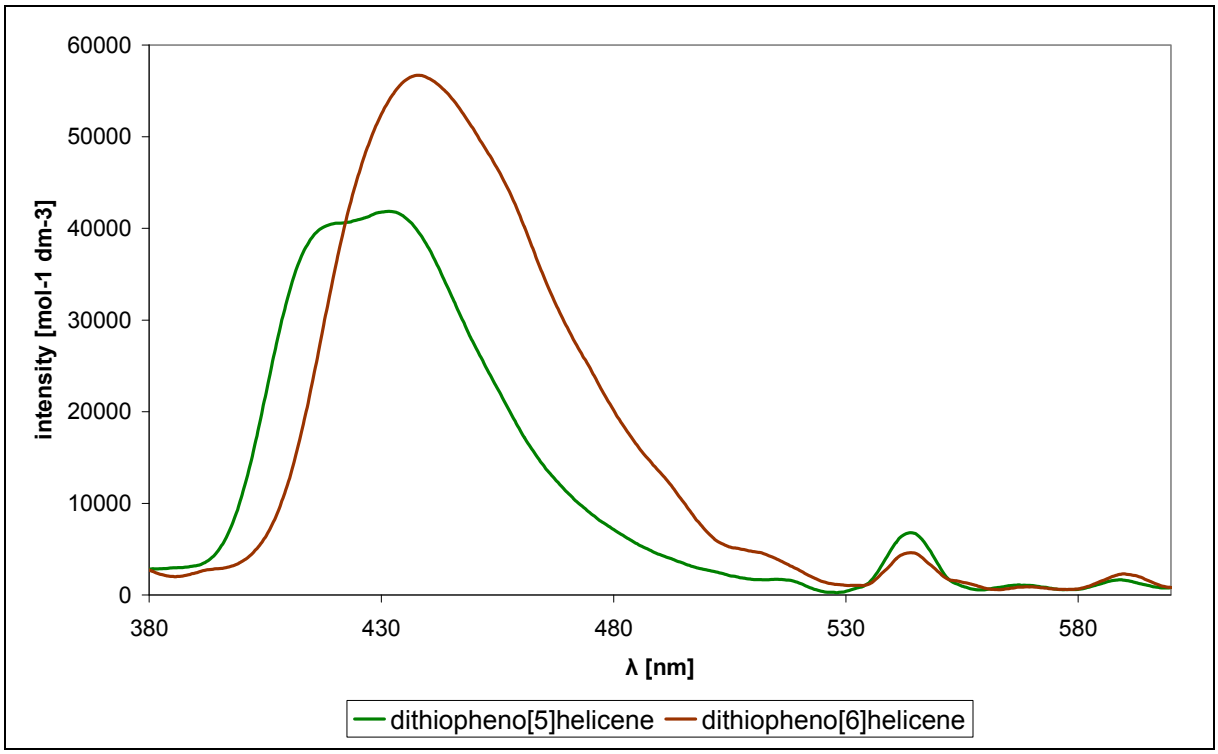
Figure 15



The fluorescence emission spectra of **96** and **97** are presented in Figure 16. The solution of dithiopheno[5]helicene **96** was irradiated by light at wavelength of the absorption maximum of 273 nm, the fluorescence maximum is at 432 nm (Figure 16,

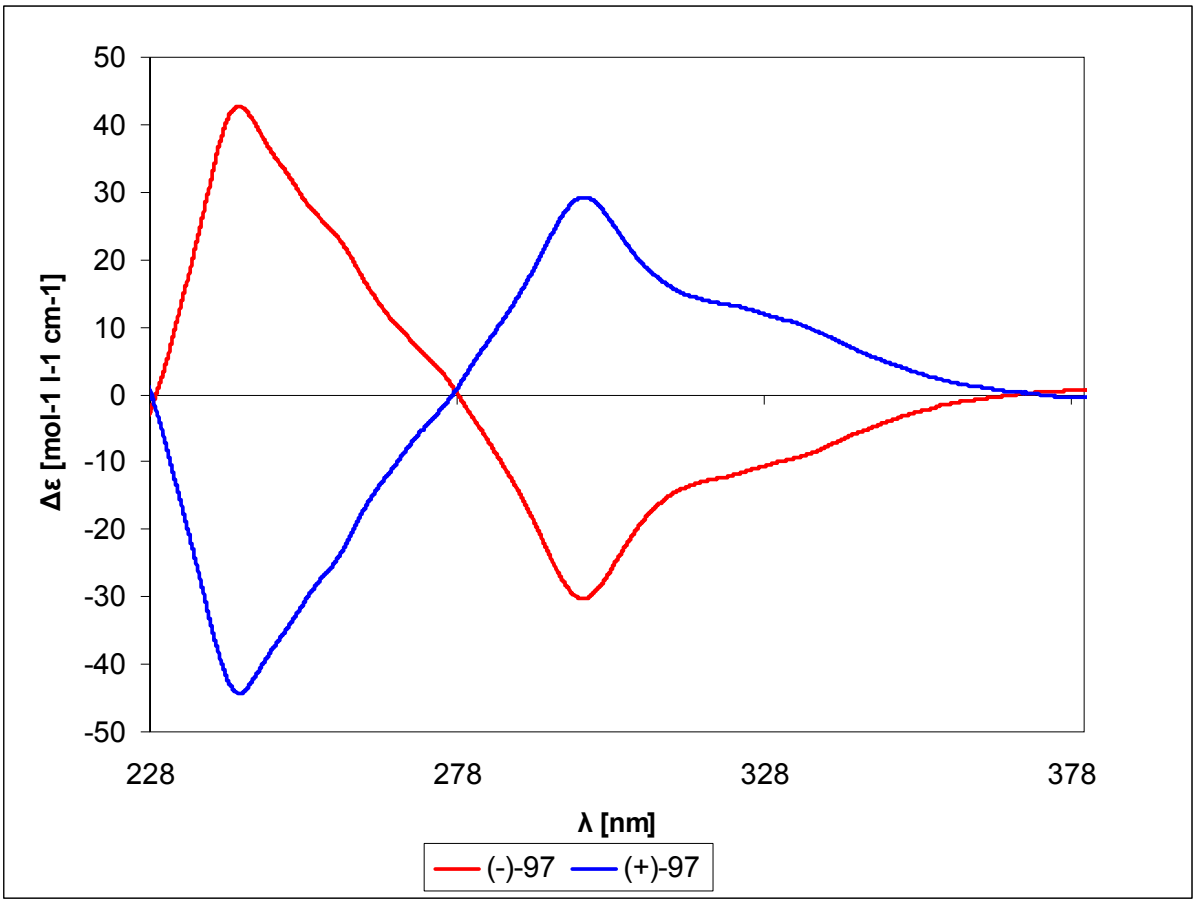
green line, c = 1.02 x 10^{-5} mol·dm^{-3}). Dithiopheno[6]helicene **97** was measured under similar conditions, its solution being irradiated by light at wavelength of the absorption maximum of 272 nm (Figure 16, red line, c = 9.2 x 10^{-6} mol·dm^{-3}). In this case, the fluorescence maximum at 440 nm is red shifted compared to the maximum of dithiopheno[5]helicene **96**. The red shifts in the UV/Vis and fluorescence spectra are in accordance with the fact that dithiopheno[6]helicene **97** posses a larger conjugated system compared with dithiopheno[5]helicene **96**.

Figure 16



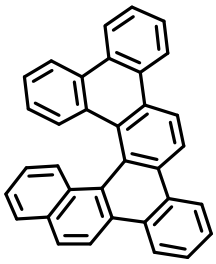
The CD spectra for each enantiomer of dithiopheno[6]helicene **97** (Figure 17) were recorded in tetrahydrofuran ((+)-**97**: blue line, c = 6.25 x 10^{-4} mol·dm^{-3}, (-)-**97**: red line, c = 5.96 x 10^{-4} mol·dm^{-3}, in a 0.1 cm cell). The CD spectra show maxima at 297 nm and 241 nm.

Figure 17

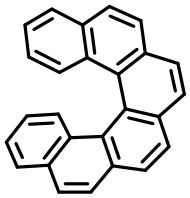


To assign helicity to the individual enantiomers, their CD spectra were compared to those of (+)-(*P*)-[6]helicene **124** (Figure 18, red line, c = 1.645 x 10^{-5} in methanol)[46] and (+)-(*P*)-dibenzo[6]helicene **123** (Figure 18, blue line, c = 1.20 x 10^{-4} M in tetrahydrofuran).[39] We can conclude that for dithiopheno[6]helicene **97** (Figure 18, green line) the (+)-enantiomer is of (*P*)-helicity and the (-)-enantiomer is of (*M*)-helicity. A hypsochromic shift was observed for (+)-(*P*)-dithiopheno[6]helicene **97** compared to (+)-(*P*)-[6]helicene **124** (maxima at 326 nm and 245 nm) and batochromic shift when comparing it with (+)-(*P*)-dibenzo[6]helicene **123** (maxima at 279 nm and 239 nm).

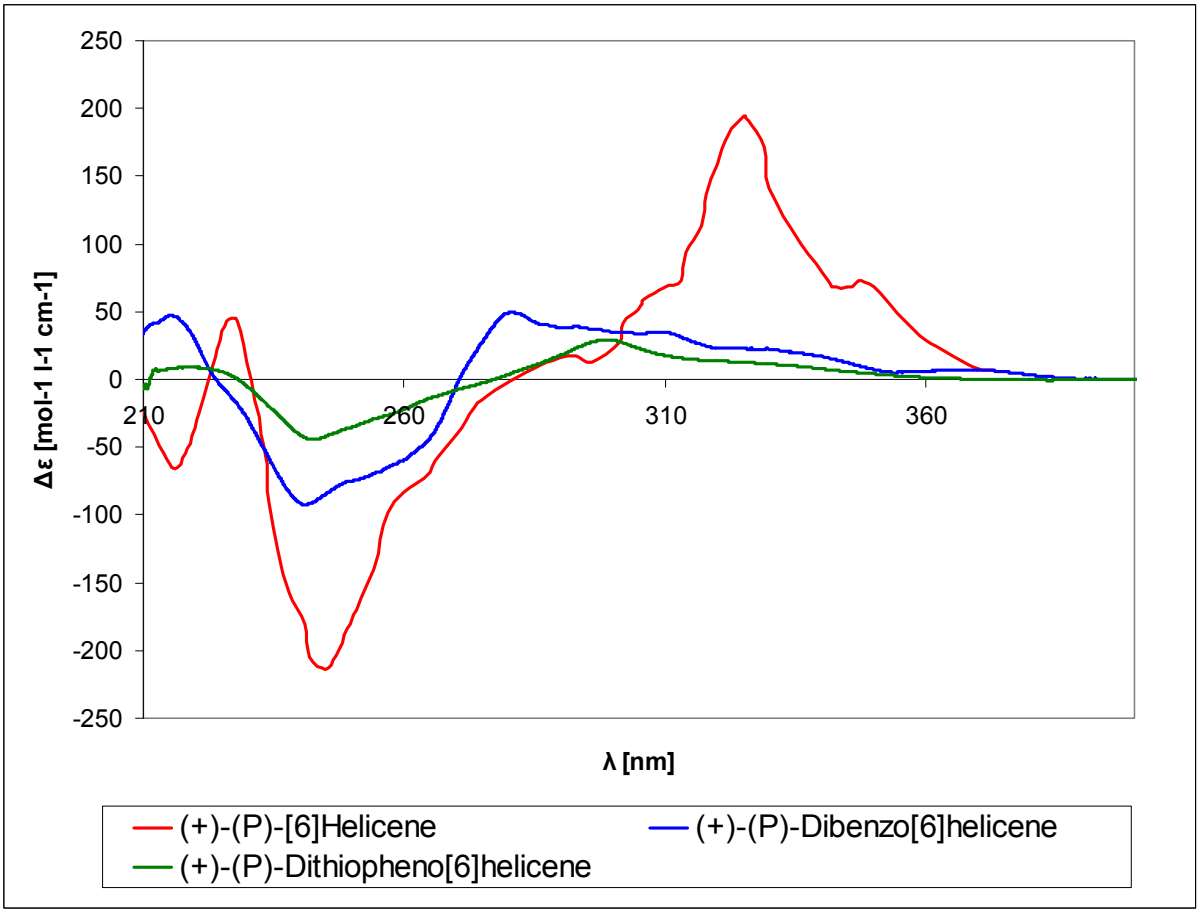
Figure 18



123



124

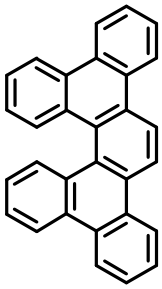


3.4.2 Electrochemical characterization

The electrochemical properties of dithiopheno[5]helicene **96** were studied. The cyclic voltammetry, DC polarography and AC polarography were measured and compared to that of dibenzo[5]helicene **125** (Figure 19). The cyclic voltammetry was measured in an acetonitrile solution (0.73 mM solution of **96**, in 0.1 M tetra-*n*-butylammonium hexafluorophosphate, the scan rate of 0.5 V/s) with mercury dropping electrode. The current-voltage curve (Figure 20) shows a reversible redox process at –1.95 V, irreversible redox process at –2.34 V and small maximum at –2.57 V.

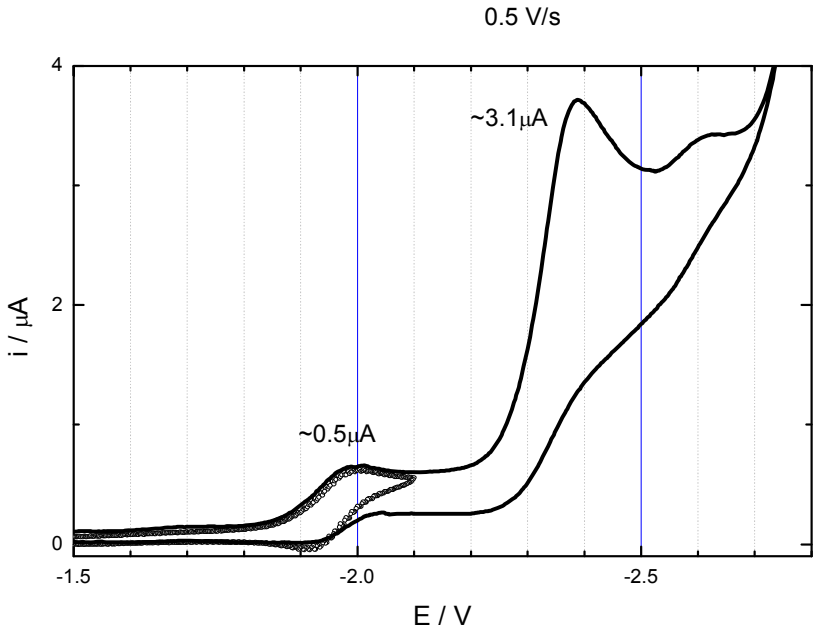
.

Figure 19



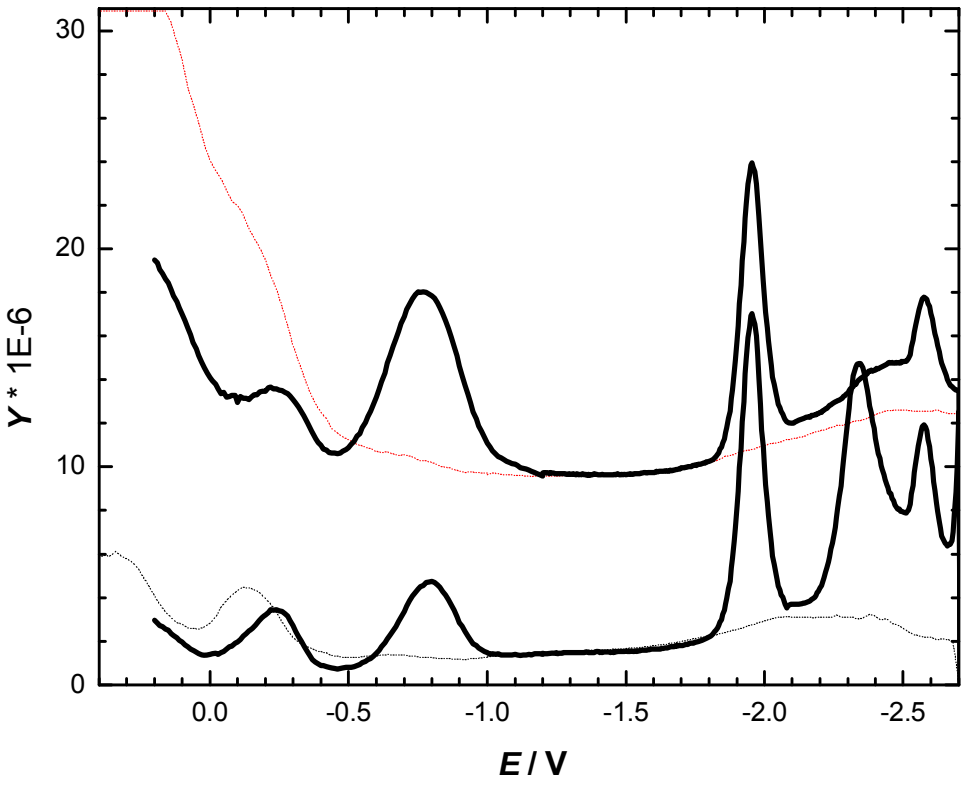
125

Figure 20



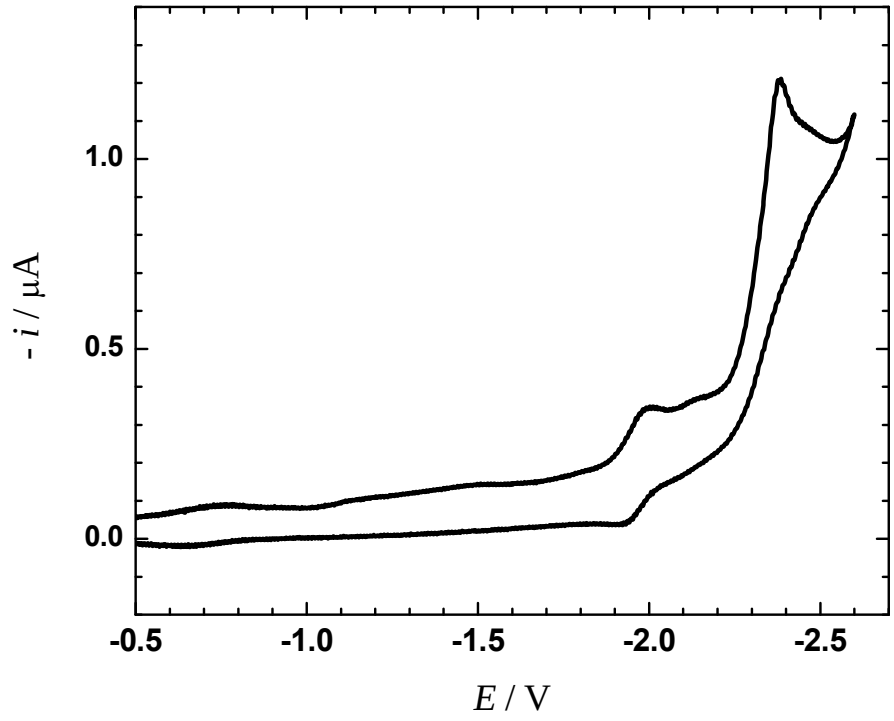
The DC polarography provides an insufficient resolution of the redox processes for this system. However, the AC polarography at 160 Hz gives very good resolution of these processes. The redox potentials are determined by three maxima with values: –1.955 V (reversible), –2.340 V (irreversible) and –2.575 V (reversible). There is also an adsorption maximum at –0.8 V (Figure 21). The strong adsorption of dithiopheno[5]helicene **96** on the mercury electrode was observed.

Figure 21



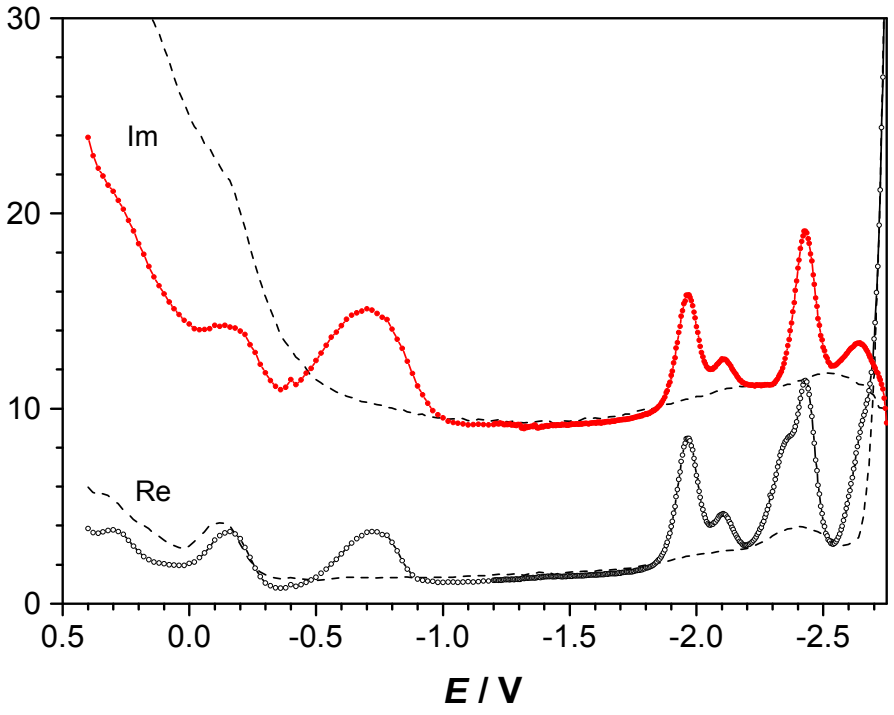
The same experiments were performed with dibenzo[5]helicene **125**. Figure 22 shows a current-voltage curve of dibenzo[5]helicene **125** measured under the same conditions (0.471 mM solution of **125** in 0.1 M tetra-*n*-butylammonium hexafluorophosphate, the scan rate of 0.5 V/s).

Figure 22



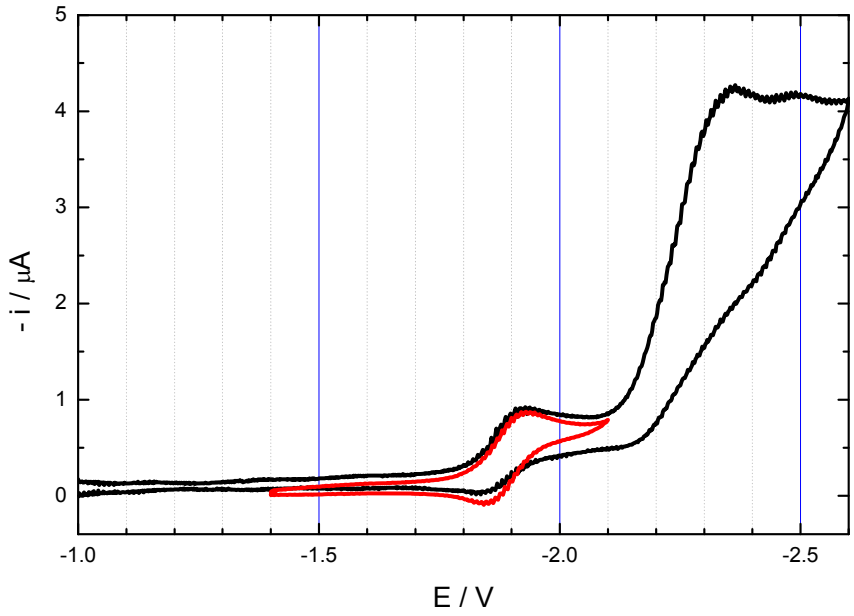
The AC polarography (Figure 23) shows an adsorption maximum at –0.7 V and doubled reduction maxima at –1.965 V, –2.105 V and –2.360 V, –2.430 V and another maximum at –2.643 V.

Figure 23



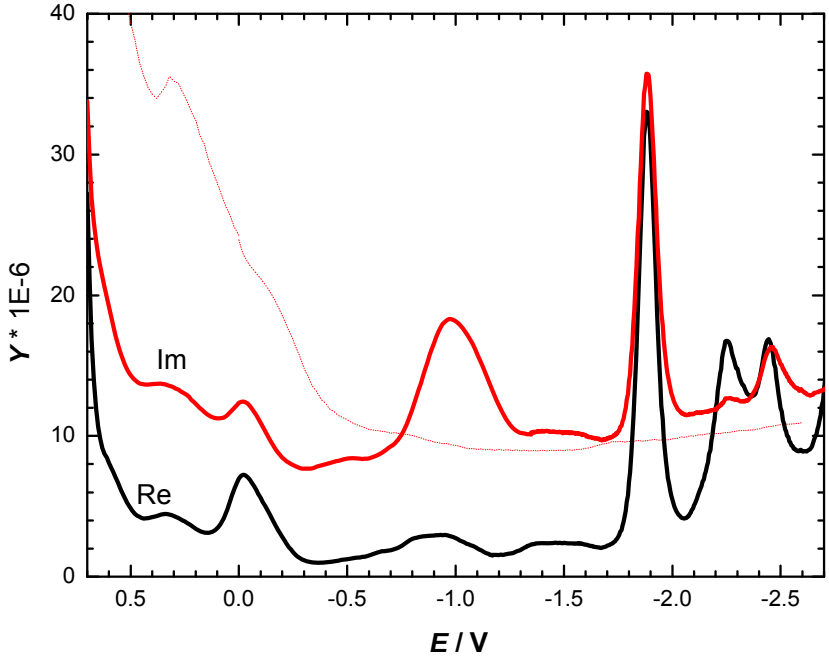
As a next objective the electrochemical properties of dithiopheno[6]helicene **97** were studied. Therefore, the cyclic voltammetry, DC polarography and AC polarography were measured and compared to that of dibenzo[6]helicene **123**. The cyclic voltammetry was measured in an acetonitrile solution (0.368 mM solution of **97**, in 0.1 M tetra-*n*-butylammonium hexafluorophosphate, the scan rate of 0.5 V/s) with a mercury dropping electrode and it is similar to that of dithiopheno[5]helicene **97**. The current-voltage curve (Figure 24) shows a reversible redox process at –1.885 V, irreversible redox process at –2.250 V and small maximum at –2.445 V.

Figure 24



Similarly to dithiopheno[5]helicene **96**, the DC polarography of dithiopheno[6]helicene **97** had an insufficient resolution for this system, whereas the AC polarography shows a very good resolution of the three redox processes (Figure 25) at –1.885, –2.255 and –2.445 V. (*cf.* –1.955 V, –2.340 V and –2,575 V for **96**). The first maximum corresponds to the reversible electron transfer in accordance with the cyclic voltammetry. The differential capacity *C* of the indifferent electrolyte is showed by the dotted line. The extensive change of *C* between –0.7 V and +0.7 V in the presence of **97** indicates a strong adsorption on the electrode. The maximum at –0.95 V corresponds to the desorption process.

Figure 25



The same experiments were performed with dibenzo[6]helicene **123**. Figure 26 shows a current-voltage curve of dibenzo[6]helicene **123** measured under the same conditions (0.471 mM solution of **123**, in 0.1 M tetra-*n*-butylammonium hexafluorophosphate, the scan rate of 0.5 V/s). The AC polarography (Figure 27) shows the reduction maxima at –1.896 V, –2.081 V and –2.281 V.

Figure 26

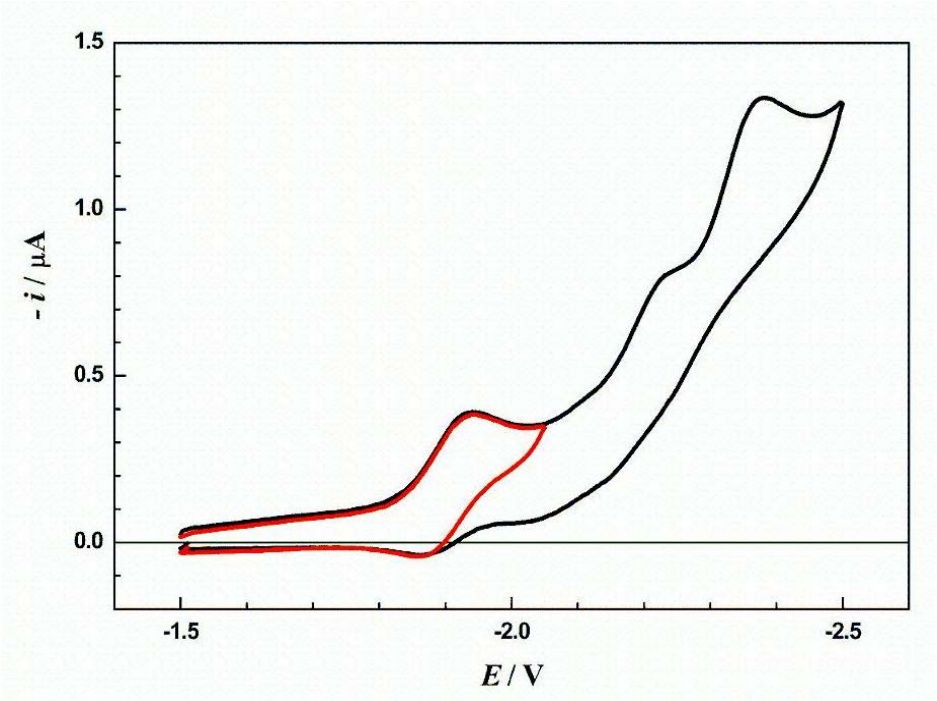


Figure 27

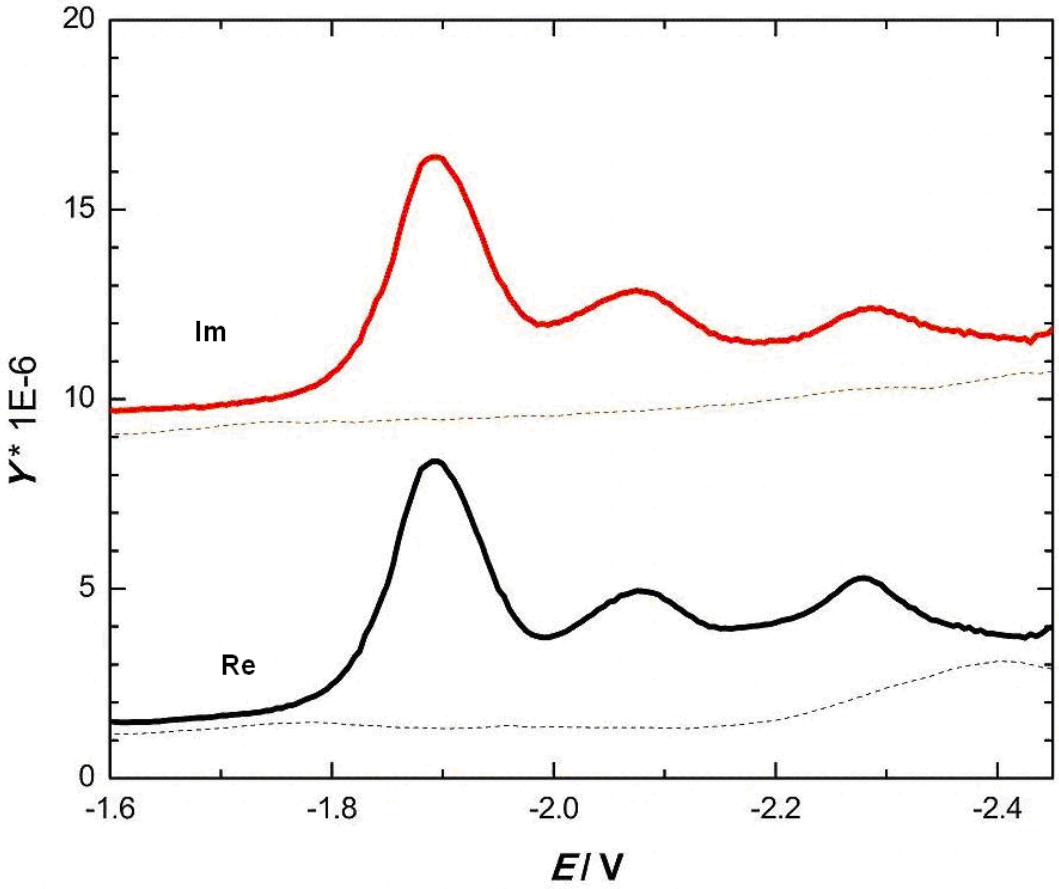


Table 2 summerizes values of the redox processes for all the compounds (related to the potential of ferrocene/ferricenium redox couple Fc/Fc^{+}).

Table 2

compound	E_1 [V]	E_2 [V]	E_3 [V]
96	–2.426	–2.811	–3.046
97	–2.364	–2.734	–2.959
125	–2.447, –2.587	–2.842, –2.912	–3.122
123	–2.375	–2.560	–2.760

3.4.3 Racemization barrier of dithiopheno[6]helicene

Racemization barrier was determined for both enantiomers of **97**. This was done by heating a hexadecane solution (1.5 mg in 1.1 ml) of the each enantiomer rapidly from room temperature to 200 °C. Small samples (50 µl) were taken by a syringe every 10 minutes at the begining till 70 minutes and then after 15 minutes and, at the end, after a 30 minute period. The ratio of enantiomers was determined in each sample by a HPLC analysis. Table 2 shows the gradually decreasing amount of the major enantiomer in the samples.

Table 2

time [min]	**amount of** (+)-**97** [%]	**amount of** (-)-**97** [%]
0	100	100
10	98.6	96.9
20	98.1	97.8
30	97.5	97.0
40	96.3	96.5
50	94.6	95.2
60	93.7	93.6
70	93.0	92.3
85	89.1	90.4
115	84.4	86.5

The time dependence of the enantiomers ratio is defined by an equation:

$\ln([c]_0 - [c]_e/([c]_t - [c]_e) = 2kt$

where $[c]_0$ is the concentration of one enantiomer at the begining, $[c]_e$ is the concentration of one enantiomer in the equilibrium, $[c]_t$ is the concentration of one enantiomer in time and k is the rate constant.

Figure 28 shows the dependence for (+)-enantiomer, Figure 29 for for (-)- enantiomer. The data were fitted with a linear regression from which the rate constant was determined for each enantiomer. Then, the barrier of racemization was calculated from the Eyiring's equation:

$k = k_B T / h \cdot \exp(-\Delta G^{\ddagger}/RT)$

where k_B is Boltzmann constant, T is the absolute temperature, h is Planck's constant, $\Delta G^{\ddagger}$ is Gibbs energy of activation and R is the gas constant. The arithmetic mean of the values determined for each enantiomer is 38.2 kcal/mol. This value differs from that of hexahelicene **124** (determined in naphthalene at 188 °C)[47] and dibenzo[6]helicene **123** (determined in hexadecane at 200 °C),[39] (Table 3).

Figure 28

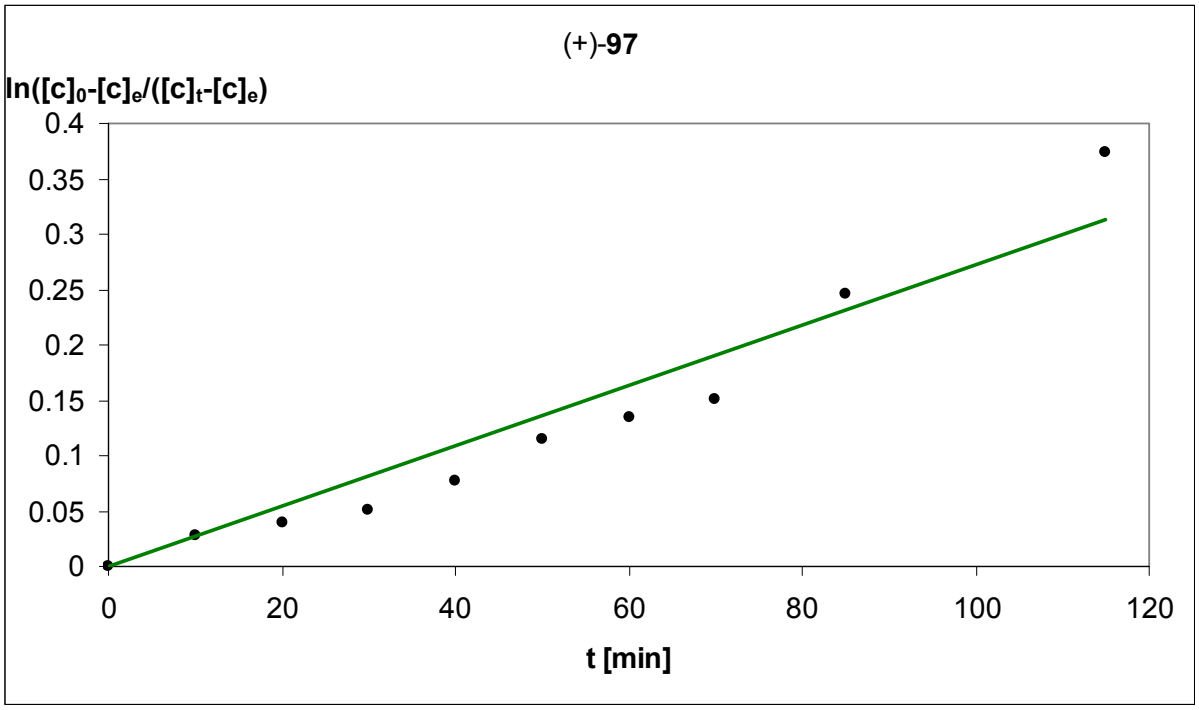


Figure 29

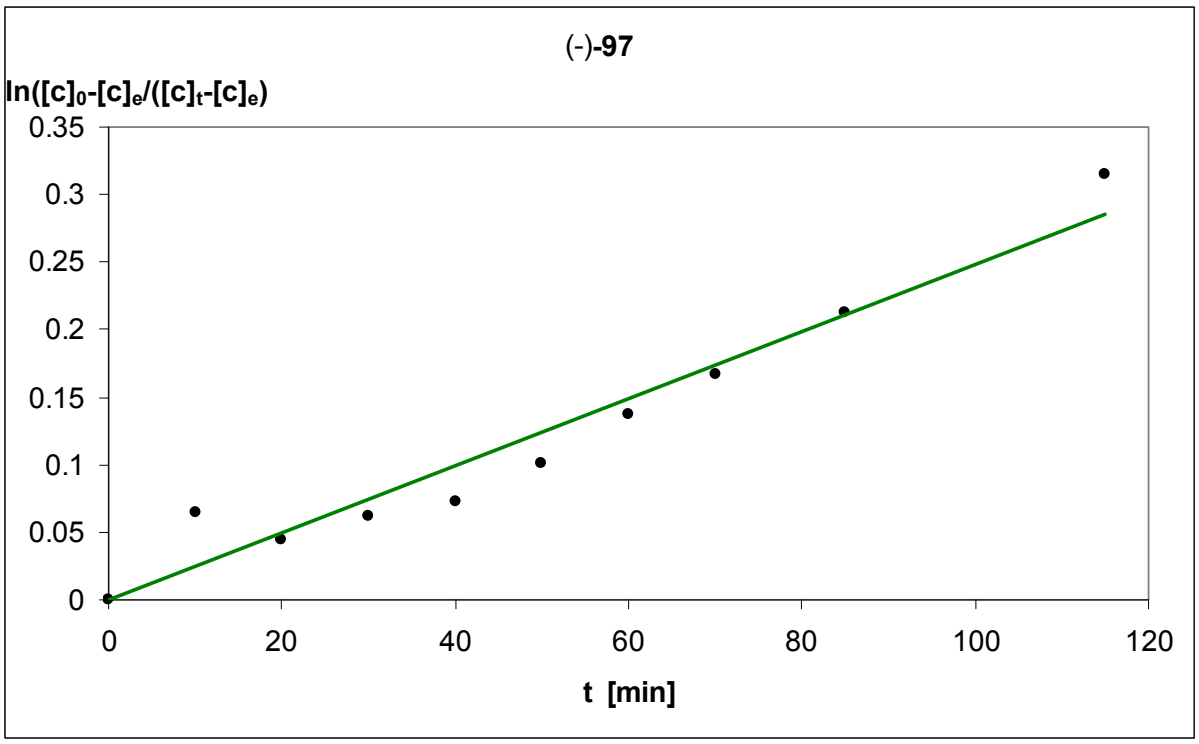


Table 3 shows also the comparison of the optical rotations of dithiopheno[6]helicene **97** with hexahelicene **124**[48] and dibenzo[6]helicene **123**[39] Interestingly, an introduction of two thiophene rings at dithiopheno[6]helicene **97** significantly diminishes the specific optical rotatory power but increases the racemization barrier (dithiopheno[6]helicene **97** vs. hexahelicene **124** or dibenzo[6]helicene **123**).

Table 3

	$[\alpha]_D^{25}$ [°]	$\Delta G^{\ddagger}$ [kcal/mol]
dithiopheno[6]helicene **97**	+517°	38.2
hexahelicene **124**	+3750°	36.2
dibenzo[6]helicene **123**	+1470°	35.8

4. Conclusion

Dithiopheno[5]helicene **96** and dithiopheno[6]helicene **97** were synthesized from the corresponding aromatic triynes by intramolecular [2+2+2] cyclotrimerization. The synthesis of trithiopheno[6]helicene **98** is still in progress. The enantioenriched dithiopheno[6]helicene **97** was prepared by enantioselective catalysis using $Ni(cod)_2$/(*R*)-QUINAP catalytical system.

The spectral characterization was performed and it was found out that the UV/Vis spectrum as well as the fluorescence spectrum of dithiopheno[6]helicene **97** showed the red shift of the maxima compared to dithiopheno[5]helicene **96**.

The electrochemical measurements were performed and compared to the corresponding dibenzohelicenes. The cyclic voltammograms and AC polarograms of dithiopheno[5]helicene **96** and dithiopheno[6]helicene **97** were similar to those of dibenzo[5]helicene **125** and dibenzo[6]helicene **123**, respectively. However, both thiopheno derivatives showed the strong adsorption on the mercury electrode.

Enantiomers of dithiopheno[6]helicene **97** were separated on a HPLC column with the chiral stationary phase. The CD spectra were measured and compared to that of (+)-(*P*)-[6]helicene and (+)-(*P*)-dibenzo[6]helicene to assign the absolute configuration: (+)-enantiomer is of (*P*)-helicity and (-)-enantiomer is of (*M*)-helicity. The barrier to racemization dithiopheno[6]helicene **97** was determined to be 38.2 kcal/mol.

5. Experimental

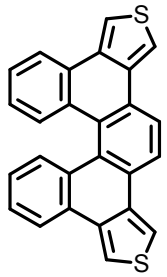
General: Melting points were determined on Mikro-Heiztisch Polytherm A (Hund, Wetzlar) apparatus and are uncorrected. The ^{1}H NMR spectra were measured at 400.13 MHz, 499.88 MHz and 600.13 MHz, the ^{13}C NMR spectra at 100.61 MHz, 125.71 MHz and 150.90 MHz in $CDCl_3$, CD_2Cl_2, d_6-acetone or d_8-tetrahydrofuran as indicated in 5 mm PFG probe. For standardization of ^{1}H NMR spectra the internal signal of TMS (δ 0.0, CDCl3) or residual signals of solvents (δ 2.26 for d_6-acetone and 3.58 for d_8-tetrahydrofuran) were used. In the case of ^{13}C spectra the residual signals of solvents (δ 77.00 for $CDCl_3$, δ 25.37 and 67.57 for d_8-tetrahydrofuran) were used. 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 chloroform or KBr on FT-IR spectrometer Bruker Equinox 55. The EI mass spectra were determined at an ionizing voltage of 70 eV, the *m/z* values are given along with their relative intenities (%). The standard 70 eV spectra were recorded in the positive ion mode. 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. Alternatively, the low resolution ESI mass spectra were recorded using a quadrupole orthogonal acceleration time-of-flight tandem mass spectrometer (Q-Tof micro, Waters) and high resolution ESI mass spectra using a hybrid FT mass spectrometer combining a linear ion trap MS and the Orbitrap mass analyzer (LTQ Orbitrap XL, Thermo Fisher Scientific). The conditions were optimized for suitable ionization in the ESI Orbitrap source (sheat gas flow rate 35 a.u., aux gas flow rate 10 a.u. of nitrogen, source voltage 4.3 kV, capillary voltage 40 V, capillary temperature 275 °C, tube lens voltage 155 V). The samples were dissolved in methanol and applied by direct injection. As a mobile phase was used 80% methanol (flow rate 100 µl/min). The low and high resolution CI mass spectra were measured using an orthogonal acceleration time-of-flight (OA-TOF) mass spectrometer (GCT premier, Waters) at an ionizing voltage of 70 eV, the m/z values are given with their relative intenzities (%). The spectra were recorded in positive mode and the source

temperature was 150 °C. Methane was present as a reagent gas in the CI source. For exact measurement the spectra were internally calibrated using Heptacosa or 2,4,6-tris(trifluoromethyl)-1,3,5-triazine (Metri). 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 recorded on Cary 50 (Varian Inc.) with pure solvent (distilled tetrahydrofuran) as a baseline, the fluorescence spectra on JASCO FP-6600 Spectrofluorometer. The *ee* values of helicenes were determined by integration of UV traces (254 nm) of HPLC chromatograms. The analyses were performed on Chiralpak IA column (250 × 4.6 mm, 5 μm) using *n*-heptane-*i*-PrOH (90:10) or *n*-heptane-chloroform (50:50) as mobile phase at a flow rate of 1.0 ml/min. The samples were injected as solutions in chloroform (4 μl of 1 mg/ml solution). The peaks corresponding to (+)- and (-)-helicenes were assigned by comparison of the UV trace with a trace from a downstream polarimetric detector. The optical rotations were measured in tetrahydrofuran using an Autopol IV instrument (Rudolph Research Analytical). The samples for electrochemical measurements were prepared in acetonitrile using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) as the indifferent electrolyte. The acetonitrile was dried over activated molecular sieves and TBAPF6 was recrystallized and dried in vacuum. The electrochemical measurements were done using a system for DC polarography, cyclic voltammetry and phase-sensitive AC polarography. It consisted of a fast rise-time potentiostat, a lock-in amplifier (Stanford Research, model SRS830) and a frequency response analyzer (Stanford Research, model SRS760). The instruments were 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 for both A/D and D/A conversion. A three-electrode electrochemical cell was used. The reference electrode, Ag|AgCl|1 M LiCl, was separated from the test solution by a salt bridge. The working electrode was a valve-operated static mercury electrode (SMDE2, Laboratorní Přístroje, Prague) with an area of 2.73×10^{-3} cm^2 and a computer controlled drop time of 1.5 s. The auxiliary electrode was a platinum wire. Oxygen was removed from the solution by passing a

stream of argon saturated with vapors of the solvent. All measurements were obtained at room temperature.

All reactions were carried out under the atmosphere of argon. The commercially available HPLC grade methanol, catalysts and reagent grade materials were used as received. The diisopropylamine, diisopropylethylamine and triethylamine were distilled from calcium hydride under argon. The tetrahydrofuran, benzene and toluene were freshly distilled from sodium/benzophenone under argon. If mentioned, the solvents were degassed by three freeze-pump-thaw cycles before use. TLC was performed on Silica gel 60 F_{254}-coated or 60 RP-18 $F_{254}S$-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%). The flash chromatography was performed on Silica gel 60 (0.040-0.063 mm, Fluka) or on Biotage® KP-C18-HS or KP-Sil® SNAP cartridges using the Isolera One HPFC system (Biotage, Inc.).

Pentaheliceno[10,9-*c*:5,6-*c'*]bisthiophene 96



The heated part of a flow reactor was heated up to 250 °C and the tetrahydrofuran flow was set to 0.5 ml/min, pressure to 80 atm. Triyne **107** (36.2 mg, 0.093 mmol) was dissolved in tetrahydrofuran (8 ml) and $CpCo(CO)_2$ (6.2 µl, 0.046 mmol, 0.5 eq.) was added. The reaction mixture was then injected into the flow reactor. The residence time in the heated capillary was 16 min. The effluent on the output was collected and the solvent was removed *in vacuo*. Then the residue was dissolved in a small amount of dichloromethane, filtered through a short pad of silica gel and eluted with dichloromethane (20 ml). The solvent was removed *in vacuo*. The residue was dissolved in dichloromethane (1 ml) and pentane (10 ml) was added. The formed precipitate was filtered and dried on a pump to give the product **96** (21.8 mg, 60 %) as a light-brown powder.

M.p.: 276 – 278 °C (pentane).

^{1}H NMR (600 MHz, $CDCl_3$): 6.82 (2 H, ddd, *J* = 8.3, 7.0, 1.4), 7.14 (2 H, ddd, *J* = 2.1, 7.0, 1.3), 7.56 (2 H, d, *J* = 3.0), 7.59 (2 H, d, *J* = 3.0), , 7.85 (2 H, ddd, *J* = 8.1, 1.4, 0.3), 7.87 (2H, s), 8.19 (2 H, ddt, *J* = 8.3, 1.3, 0.6, 0.6).

^{13}C NMR (150 MHz, $CDCl_3$): 117.33 (d), 117.73 (d), 123.57 (d), 125.04 (d), 125.52 (d), 127.86 (d), 129.38 (s), 129.48 (s), 129.89 (s), 131.96 (s), 132.51 (d), 136.37 (s), 136.49 (s).

IR (KBr): 3099 w, 3050 vw, 3028 vw, 1627 w, 1467 w, 1234 vw, 1218 vw, 770 m, 760 vs cm^{-1}.

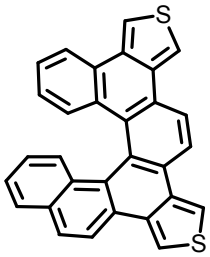
UV/Vis (tetrahydrofuran): λ_{max} (log ε): 273 (4.69), 316 (4.6).

Fluorescence (tetrahydrofuran, λ_{exc} = 273 nm): λ_{max} = 432 nm.

APCI MS: 391 ($[M+H]^+$).

HR MS: calcd for $C_{26}H_{15}S_2$ 391.061, found 391.0606.

Hexaheliceno[10,9-*c*:5,6-*c'*]bisthiophene 97



Method A (Co catalyst, flow reactor): The heated part of the flow reactor was heated up to 250 °C and the tetrahydrofuran flow was set to 0.5 ml/min and pressure to 80 atm. Triyne **99** (43.0 mg, 0.098 mmol) was dissolved in tetrahydrofuran (4 ml) and $CpCo(CO)_2$ (6.6 µl, 0.049 mmol, 0.5 eq.) was added. The reaction mixture was then injected into the flow reactor. The residence time in the heated capillary was 16 min. The effluent on an output was collected and the solvent was removed *in vacuo*. Then the residue was dissolved with small amount of dichloromethane, filtered through a short pad of silica gel and eluted with dichloromethane (20 ml). The solvent was removed *in vacuo*. The product was purified by flash chromatography on reverse phase silica gel C18 (acetonitrile) to give **97** (28.0 mg, 65 %) as a light-brown powder.

Method B (Ni catalyst): A Schlenk flask was charged with $Ni(cod)_2$ (2.5 mg, 0.0091 mmol, 20 mol%) and triphenylphosphine (4.75 mg, 0.018 mmol, 40 mol%). Tetrahydrofuran (1 ml) was added and the mixture was stirred at room temperature for 10 min. Then a solution of triyne **107** (20.0 mg, 0.045 mmol) in tetrahydrofuran (1 ml) was added. The reaction mixture was stirred at room temperature for 30 min. Then it was filtered through a short pad of silica gel and eluted with dichloromethane (20 ml). The solvent was removed *in vacuo*. The product was purified by flash chromatography on a reverse phase silica gel C18 (acetonitrile) to give **97** (13.4 mg, 67 %) as a light-brown powder.

M.p.:160 – 163 °C (pentane)

^{1}H NMR (600 MHz, $CDCl_3$): 6.46 (1 H, ddd, *J* = 8.2, 7.0, 1.4), 6.78 (1 H, ddd, *J* = 8.6, 6.8, 1.4), 7.08 (1 H, ddd, *J* = 8.0, 7.0, 1.3), 7.11 (1 H, ddd, *J* = 8.2, 1.3, 0.5), 7.15 (1 H, ddd, *J* = 8.0, 6.8, 1.1), 7.62 (1 H, dq, *J* = 8.6, 0.9, 0.9, 0.9), 7.72 (1 H, ddt, *J* = 8.0, 1.4, 0.8, 0.8), 7.93 (1 H, dt, *J* = 8.5, 0.6, 0.6), 8.02 (1 H, ddd, *J* = 8.0, 1.4, 0.5), 8.08 (1 H, d, *J* = 3.0), 8.14 (1 H, d, *J* = 3.0), 8.14 (1 H, d, *J* = 3.0), 8.17 (1 H, d, *J* = 3.0), 8.28 (1 H, d, *J* = 8.5), 8.34 (1 H, d, *J* = 8.1), 8.37 (1 H, d, *J* = 8.1).

^{13}C NMR (150 MHz, $CDCl_3$): 116.75 (d), 116.91 (d), 117.13 (d), 117.21 (d), 122.04 (d), 122.45 (d), 122.81 (d), 123.64 (d), 124.65 (d), 124.99 (d), 125.18 (d), 125.75 (s), 126.62 (d), 126.67 (s), 127.37 (d), 127.48 (s), 127.53 (s), 127.72 (s), 127.99 (d), 128.68 (d), 129.42 (s), 129.59 (d), 130.30 (s), 130.53 (s), 130.73 (s), 132.28 (s), 135.58 (s), 135.72 (s), 135.76 (s), 136.09 (s).

IR (KBr): 3100 w, 3051 w, 1352 vw, 1171 w, 869 m, 746 vs cm^{-1}.

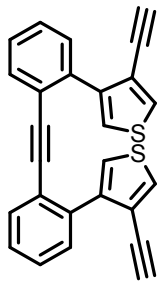
APCI MS: 441 ($[M+H]^+$).

APCI HR MS: calcd for $C_{30}H_{17}S_2$ 441.0766, found 441.0765.

UV/Vis (tetrahydrofuran): λ_{max} (log ε): 272 (4.74), 326 (4.46).

Fluorescence (tetrahydrofuran, λ_{exc} = 272 nm): λ_{max} = 440 nm.

3,3'-(Ethyne-1,2-diyldibenzene-2,1-diyl)bis(4-ethynylthiophene) 99



To a solution of silylated triyne **106** (232.5 mg, 0.33 mmol) in tetrahydrofuran (20 ml) under argon a solution of tetra-*n*-butylammonium fluoride trihydrate (312.4 mg, 0.99 mmol, 3.0 eq.) in tetrahydrofuran (2 ml) was added. The reaction mixture was stirred at room temperature for 2 h. Then it was filtered through a small pad of silica gel and eluted with tetrahydrofuran (30 ml). The solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (hexane–tetrahydrofuran 100:0 to 50:50, dry–loaded on alumina) to afford the deprotected triyne **99** (84.7 mg, 66 %) as a white amorphous solid.

^{1}H NMR (600 MHz, $CDCl_3$): 2.69 (2 H, s), 7.04 (2 H, dt, *J* = 7.6, 7.6, 1.4), 7.13 (2 H, dt, *J* = 7.6, 7.6, 1.4), 7.16 (2 H, d, *J* = 3.3), 7.28 (2 H, d, *J* = 3.3), 7.57 (2 H, ddd, *J* = 7.7, 1.4, 0.6), 7.63 (2 H, ddd, *J* = 7.8, 1.4, 0.6).

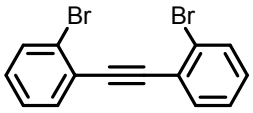
^{13}C NMR (150 MHz, $CDCl_3$): 79.24 (s), 79.94 (d), 92.89 (s), 122.89 (s), 123.66 (s), 125.56 (d), 128.02 (d), 128.48 (d), 130.71 (d), 131.21 (d), 133.52 (d), 137.80 (s), 142.60 (s).

IR ($CHCl_3$): 3307 vs, 3112 w, 3112 w, 3065 w, 2216 vw, 2118 vw, 2105 w, 1598 w, 1565 vw, 1528 w, 1492 m, 1454 w, 1424 vw, 1340 w, 1314 vw, 1104 w, 1043 w, 1015 vw, 972 w, 951 w, 872 m, 658 s, 609 m, 554 vw, 526 vw, 465 vw cm^{-1}.

TOF ESI MS: 753 ($[M+H]^+$), 775 ($[M+Na]^+$), 791 ($[M+K]^+$).

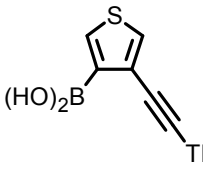
HR MS: calcd for $C_{26}H_{15}S_2$ 391.0610, found 391.0608.

1,1'-Ethyne-1,2-diylbis(2-bromobenzene) 100



A Schlenk flask was charged with bromoiodobenzene (1.103 g, 3.90 mmol), $Pd(PPh_3)_4$ (405.4 mg, 0.35 mmol, 9 mol%), CuI (133.6 mg, 0.70 mmol, 18 mol%) and then diisopropylamine (17.5 ml) was added. The reaction mixture was degassed and acetylene (47 ml, 1.95 mmol, 0.5 eq.) was added. The reaction mixture was stirred at 55 °C for 18 h. Then it was filtered through a small pad of silica gel, eluted with hexane (150 ml) and the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (heptane) to give **100** (406 mg, 31 %) as a white solid. ^{1}H NMR and ^{13}C NMR were in agreement with the published data.[49]

(4-{[Tris(1-methylethyl)silyl]ethynyl}thiophen-3-yl)boronic acid 101



To a solution of silane **104** (2.92 g, 8.5 mmol), in tetrahydrofuran (90 ml) at –78 °C *n*-BuLi (1.6 m in hexanes, 5.9 ml, 9.36 mmol, 1.1 eq.) was added. The reaction mixture was stirred at −78 °C for 30 min then (triisopropyl)borate (5.85 ml, 25.5 mmol, 3.0 eq.) was added. After warming up to room temperature, the mixture was stirred for 30 min and hydrochloric acid (1 M, 25 ml) was added. After stirring for 45 min at room temperature, diethyl ether (50 ml) was added. The organic layer was washed with water (3 x 50 ml). The aqueous layer was extracted with diethyl ether (3 x 50 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–diethyl ether 100:0 to 80:20) to give boronic acid **101** (1.36 g, 52 %) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.09 – 1.21 (21 H, m), 5.68 (2 H, s), 7.55 (1 H, d, *J* = 3.0), 7.92 (1 H, d, *J* = 3.0).

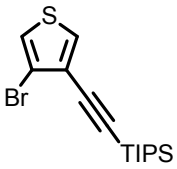
^{13}C NMR (150 MHz, $CDCl_3$): 11.25 (d), 18.57 (q), 93.89 (s), 102.99 (s), 125.40 (s), 130.88 (d), 136.64 (d). Carbon next to borone was not visible in the spectrum.

IR ($CHCl_3$): 3622 m, 3537 m, 3110 w, 2960 s, 2946 vs, 2893 m, 2867 vs, 2141 m, 1504 s, 1463 s, 1437 s, 1386 vs, 1333 s, 1306 vs, 1170 w, 1156 w, 1073 m, 1018 m, 996 m, 988 m, 883 s, 873 m, 679 s, 662 m, 466 w cm^{-1}.

TOF ESI MS: 307 ($[M-H]^-$).

HR ESI MS: calcd for $C_{15}H_{24}O_2BSSi$ 307.1365, found 307.1364.

[(4-Bromothiophen-3-yl)ethynyl][tris(1-methylethyl)]silane 104



To a solution of 3-bromo-4-iodothiophene **103** (5.9 g, 20.4 mmol), $Pd(PPh_3)_2Cl_2$ (714.3 mg, 1.02 mmol, 5 mol%) and CuI (387.7 mg, 2.04 mmol, 10 mol%) in a mixture of diisopropylamine and tetrahydrofuran (150 ml, 1:1, degassed) (triisopropylsilyl)acetylene (13.7 ml, 61.06 mmol, 3.0 eq.) was added. The reaction mixture was stirred at room temperature for 1 h. Then it was filtered through a small pad of silica gel, eluted with hexane (200 ml) and the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane) to give silane **104** (6.65 g, 95 %) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.12 – 1.18 (21 H, m), 7.22 (1 H, d, *J* = 3.4), 7.46 (1 H, d, *J* = 3.4).

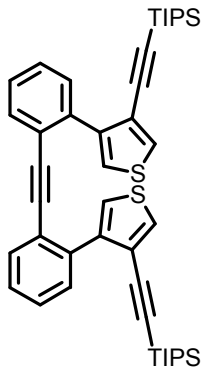
^{13}C NMR (150 MHz, $CDCl_3$): 11.26 (d), 18.64 (q), 94.27 (s), 99.38 (s), 114.18 (s), 122.68 (d), 125.04 (s), 129.38 (d)

IR ($CHCl_3$): 3119 w, 2960 s, 2945 vs, 2926 s, 2893 m, 2866 vs, 2177 w, 2150 m,1501 w, 1464 m, 1420 w, 1385 w, 1365 w, 1335 m, 1174 w, 1159 w, 1073 w, 1017 w, 999 s, 883 s, 873 m, 679 s, 661 m, 464 w cm^{-1}.

TOF EI MS: 342 ($M^{+\bullet}$, with ^{79}Br, 4), 299 (with ^{79}Br, 100), 271 (31), 257 (26), 243 (42), 229 (with ^{79}Br, 57), 217 (6), 215 (12), 213 (7), 151 (5), 149 (7), 135 (11), 122 (9), 107 (7).

HR TOF EI MS: calcd for $C_{15}H_{23}{}^{79}BrSSi$ 342.0473, found 342.0471.

[Ethyne-1,2-diylbis(benzene-2,1-diylthiene-4,3-diylethyne-2,1-diyl)]bis[tris(1-methylethyl)silane 106



A Schlenk flask was charged with dibromide **100** (137.8 mg, 0.41 mmol), boronic acid **101** (303.7 mg, 0.985 mmol, 2.4 eq.), $Pd(PPh_3)_2Cl_2$ (20.2 mg, 0.0287 mmol, 7 mol%) and K_2CO_3 (113.6 mg, 0.821 mmol, 2.0 eq.). A mixture of toluene-*n*-PrOH-H_2O (15 ml, 16:16:4.3) was added. The mixture was bubbled with argon for 30 min. Then it was stirred at 90 °C for 1.5 h. The aqueous layer was extracted with chloroform (3 x 20 ml). The combined organic portions were dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo*. The product was purified by flash chromatography on reverse phase silica gel C18 (acetonitrile–ethyl acetate 100:0 to 0:100) to give triyne **106** (270 mg, 93 %) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): 1.01 – 1.07 (42 H, m), 7.38 (2 H, dt, *J* = 7.5, 7.5, 1.5), 7.42 (2 H, dt, *J* = 7.5, 7.5, 1.5), 7.51 (2 H, ddd, *J* = 7.5, 1.5, 0.6), 7.54 (2 H, d, *J* = 3.2), 7.62 (2 H, ddd, *J* = 7.7, 1.5, 0.6), 7.85 (2 H, d, *J* = 3.2).

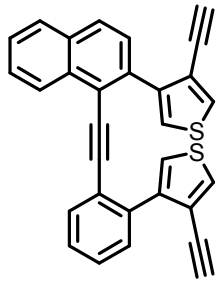
^{13}C NMR (150 MHz, $CDCl_3$): 11.98 (d), 18.91 (q), 92.53 (s), 92.84 (s), 102.64 (s), 123.54 (s), 124.17 (s), 125.64 (d), 128.24 (d), 128.83 (d), 130.90 (d), 131.28 (d), 133.58 (d), 137.89 (s), 142.65 (s).

IR ($CHCl_3$): 3307 vs, 3112 w, 3112 w, 3065 w, 2217 vw, 2118 vw, 2105 w, 1598 w, 1565 vw, 1528 w, 1492 m, 1454 w, 1424 vw, 1340 w, 1314 vw, 1104 w, 1043 w, 1015 vw, 972 w, 951 w, 872 m, 658 s, 609 m, 554 vw, 526 vw, 465 vw cm^{-1}.

TOF EI MS: 702 ($M^{+\bullet}$, 14), 659 (88), 617 (14), 575 (4), 545 (8), 503 (10), 356 (4), 277 (4), 252 (5), 245 (6, 238 (5), 157 (35), 131 (21).

HR TOF EI MS: calcd for $C_{44}H_{54}S_2Si_2$ 702.3206, found 702.3218.

3-Ethynyl-4-(2-{[2-(4-ethynylthiophen-3-yl)naphthalen-1-yl]ethynyl}phenyl)-thiophene 107



To a solution of silylated triyne **112** (348.0 mg, 0.46 mmol) in tetrahydrofuran (40 ml) under argon methanol (480 µl, 11.55 mmol, 25 eq.) and tetra-*n*-butylammonium fluoride trihydrate (1.357 g, 4.30 mmol, 3.0 eq.) in tetrahydrofuran (5 ml) were added. The reaction mixture was stirred at room temperature for 45 min. Then methanol (10 ml) and triethylamine (5 ml) were added and the reaction mixture was filtered through a small pad of silica gel (chloroform–triethylamine 100 ml 100:1). The solvents were removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (hexane–tetrahydrofuran 100:0 to 50:50, dry–loaded on alumina) to obtain **107** (187.3 mg, 92 %) as a white powder.

M.p.: 198 -201 °C (hexane – tetrahydrofuran).

^{1}H NMR (600 MHz, d_8-THF): 3.37 (1 H, s), 3.38 (1 H, s), 7.32 (1 H, dt, *J* = 7.5, 7.5, 1.4), 7.37 (1 H, dt, *J* = 7.5, 7.5, 1.5), 7.46 (1 H, ddd, *J* = 8.2, 7.0, 15.), 7.48 (1 H, ddd, *J* = 7.7, 1.5, 0.6), 7.49 (1 H, dd, J = 8.0, 7.0, 1.6), 7.53 (1 H, ddd, *J* = 7.7, 1.4, 0.6), 7.54 (1 H, d, *J* = 3.2), 7.63 (1 H, d, *J* = 3.2), 7.65 (1 H, d, *J* = 8.6), 7.79 (1 H, d, *J* = 3.2), 7.80 (1 H, d, *J* = 3.2), 7.84 (1 H, ddt, *J* = 8.0, 1.5, 0.7, 0.7), 7.85 (1 H, dt, J = 8.6, 0.6, 0.6), 8.00 (1 H, ddt, *J* = 8.2, 1.6, 0.7, 0.7).

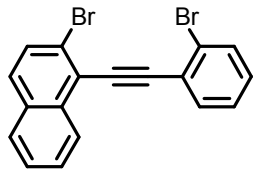
^{13}C NMR (150 MHz, d_8-THF): 79.41 (s), 79.48 (s), 80.73 (d), 80.86 (d), 91.13 (s), 98.23 (s), 120.77 (s), 123.48 (s), 123.61 (s), 124.28 (s), 126.09 (d), 126.65 (d), 127.28 (d), 127.81 (d), 128.02 (d), 128.41 (d), 128.58 (d), 128.64 (d), 128.81 (d), 128.87 (d), 131.08 (d), 131.62 (d), 131.79 (d), 133.65 (s), 133.80 (d), 134.70 (s), 137.21 (s), 138.36 (s), 143.35 (s), 143.43 (s).

IR (KBr): 3284 vs, 3129 w, 3107 w, 3057 w, 2101 vw, 1982 vw, 1619 w, 1592 w, 1561 vw, 1561 vw, 1527 w, 1499 w, 1489 w, 1443 vw, 1425 vw, 1336 w, 1269 vw, 1162 vw, 1144 w, 1104 vw, 1043 vw, 971 w, 948 vw, 876 w, 871 w, 865 w, 829 m, 661 m, 613 m, 532 vw, 492 w, 438 w cm^{-1}.

MS APCI: 441 ($[M+H]^+$).

HR EI MS: calcd for $C_{30}H_{17}S_2$ 441.07662, found 441.07657.

2-Bromo-1-[(2-bromophenyl)ethynyl]naphthalene 108



A Schlenk flask was charged with 2-bromo-1-iodonaphtalene (168.5 mg, 0.51 mmol), $Pd(PPh_3)_2Cl_2$ (17.9 mg, 0.025 mmol, 5 mol%), CuI (9.6 mg, 0.051 mmol, 10 mol%), water (4 µl, 0.2 mmol, 40 mol%), triethylamine (0.42 ml, 3.04 mmol, 6.0 eq.) and 1,8-diazabicycloundec-7-ene (0.9 ml, 6.07 mmol, 12.0 eq., distilled). Benzene (4 ml) was added and the mixture was bubbled with argon for 30 min. (2-Bromophenylethynyl)trimethylsilane **111** (115 µl, 0.54 mmol, 1.07 eq.) was added and the reaction mixture was stirred at 43 °C for 18 h. The solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane) to give dibromide **108** (186 mg, 95 %) as a white powder.

M.p.: 85.5–86.9 °C (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): 7.21–7.26 (1H, m), 7.35 (1H, td, *J* = 7.6, 7.6, 1.2), 7.54 (1H, ddd, *J* = 8.1, 6.9, 1.2), 7.60–7.70 (4H, m), 7.74 (1H, dd, *J* = 7.7, 1.7), 7.81–7.83 (1H, m), 8.58–8.60 (1H, m).

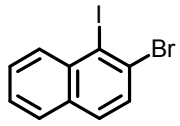
^{13}C NMR (101 MHz, $CDCl_3$): 91.06, 97.63, 122.29, 125.18, 125.54, 125.60, 126.76, 126.86, 127.28, 128.04, 128.37, 129.79, 129.91, 129.97, 131.89, 132.74, 134.01, 134.72.

IR ($CHCl_3$): 3070 w, 3060 w, 2214 vw, 1618 w, 1587 w, 1579 m, 1565 m, 1502 m, 1475 vs, 1465 w, 1434 m, 1426 w, 1319 w, 1308 vw, 1258 w, 1123 m, 1055 m, 1027 m, 961 vw, 947 w, 883 w, 868 w, 858 vw, 838 m, 812 vs, 690 w, 652 m, 577 w, 564 w, 447 w, 432 w cm^{-1}.

EI MS: 384 ($M^{+\bullet}$, with ^{79}Br, 52), 306 (4), 226 (78), 200 (5), 174 (3), 113 (12), 99 (3), 87(2).

HR EI MS: calcd for $C_{18}H_{10}{}^{79}Br_2$ 383.9149, found 383.9154.

2-Bromo-1-iodonaphthalene 110



Amine **109** (3.062 g, 13.78 mmol) was slowly added to conc. hydrochloric acid (13.5 ml) and the mixture was stirred at room temperature for 20 min. After this period, ice was added (37 g). Then a solution of sodium nitrite (1.09 g, 15.80 mmol, 1.15. eq.) in water (10 ml) was added very slowly at 0 °C to the stirred reaction mixture. Subsequently a

solution of potassium iodide (9.19 g, 55.3 mmol, 4.0 eq.) in water (20 ml) was slowly added and the reaction mixture was stirred at 0 °C for 15 min. The temperature was allowed to increase to room temperature while stirring continued for another 1 h and then it was heated to 60 °C while stirred for 45 min. The resulted dark mixture was cooled to room temperature and quenched by a saturated solution of $Na_2S_2O_5$ (100 ml). The formed dark precipitate was filtered off, dissolved in chloroform (200 ml), filtered through a small pad of silica gel and eluted with hexane (300 ml). The crude product was purified by flash chromatography on silica gel (hexane) to give the product **110** (2.7 g, 59 %) as a light brown solid.

M.p.: 55.5–56.2 °C (ethanol)

^{1}H NMR (400 MHz, $CDCl_3$): 7.49–7.53 (1H, m), 7.54–7.58 (1H, m), 7.66–7.71 (2H, m), 7.74–7.76 (1H, m), 8.22–8.24 (1H, m).

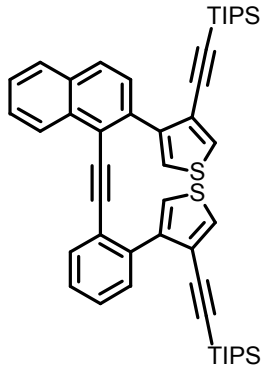
^{13}C NMR (101 MHz, $CDCl_3$): 106.60, 126.73, 128.41, 128.76, 129.60, 129.92, 129.94, 131.86, 133.88, 136.65.

IR ($CHCl_3$): 3100 vw, 3059 w, 1617 w, 1601 vw, 1582 w, 1550 w, 1497 s, 1421 w, 1341 m, 1303 m, 1250 m, 1168 w, 1135 w, 1106 m, 1029 vw, 961 w, 946 m, 863 w, 829 m, 809 vs, 653 w, 588 w, 522 m, 441 w, 408 w cm^{-1}.

EI MS: 331 ($M^{+\bullet}$, 93), 207 (23), 126 (59), 98 (4), 87 (3), 74 (7), 63 (3).

HR EI MS: calcd for $C_{10}H_6{}^{79}BrI$ 331.8698, found 331.8708.

Tris(1-methylethyl){[4-(2-{[2-(4-{[tris(1-methylethyl)silyl]ethynyl}thiophen-3-yl)naphthalen-1-yl]ethynyl}phenyl)thiophen-3-yl]ethynyl}silane 112



A Schlenk flask was charged with dibromide **108** (200.0 mg, 0.52 mmol), boronic acid **101** (383.4 mg, 1.24 mmol, 2.4 eq.), $Pd(PPh_3)_2Cl_2$ (25.5 mg, 0.036 mmol, 7 mol%) and K_2CO_3 (143.2 mg, 1.04 mmol, 2.0 eq.). A mixture of toluene-*n*-PrOH-H_2O (20 ml, 16:16:4.3) was added. The mixture was bubbled with argon for 30 min. Then it was stirred at 90 °C for 2 h. After cooling to room temperature, the reaction mixture was filtered through a small pad of silica gel and eluted with dichloromethane (50 ml). The solvents were removed *in vacuo*. The product was purified by flash chromatography

on reverse phase silica gel C18 (methanol–ethyl acetate 100:0 to 80:20) to furnish triyne **112** (348 mg, 89 %) as a light brown oil.

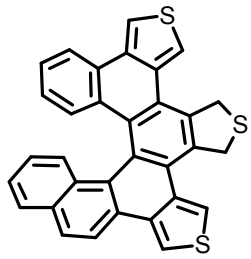
^{1}H NMR (400 MHz, $CDCl_3$): 0.90 – 0.92 (21 H, m), 0.93 – 0.96 (21 H, m), 7.28 – 7.32 (2 H, m), 7.41 (1 H, d, *J* = 3.2), 7.43 – 7.49 (3 H, m), 7.52 (1 H, d, *J* = 3.2), 7.55 – 7.59 (1 H, m), 7.61 (2 H, dd, *J* = 3.3, 1.3), 7.71 (1 H, d, *J* = 8.5), 7.75 (1 H, d, *J* = 8.5), 7.79 – 7.82 (1 H, m), 7.98 – 8.02 (1 H, m).

IR ($CHCl_3$): 3112 w, 3060 w, 2944 vs, 2926 vs, 2891 s, 2865 vs, 2200vw, 2150 s, 1619 vw, 1594 w, 1562 w, 1527 w, 1499 w, 1488 m, 1463 s, 1448 m, 1426 w, 1383 m, 1367 m, 1337 m, 1155 m, 1147 m, 1104 m, 1070 s, 1040 m, 997s, 979 s, 949 w, 883 vs, 872 s, 822 s, 678 vs, 660 s, 531 w, 437 m cm^{-1}.

TOF ESI MS: 775 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{48}H_{57}S_2Si_2$ 753.3435, found 753.3436.

17,19-Dihydrohexaheliceno[10,9-*c*:11,12-*c′*:7,8-*c″*]tristhiophene 114

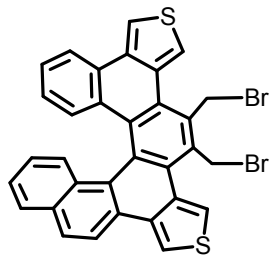


To a solution of dibromide **115** (20 mg, 0.032 mmol) and benzyltriethylammonium chloride (0.9 mg, 0.0032 mmol, 10 mol%) in dichloromethane (2.5 ml) anhydrous sodium sulfide (51.7 mg, 0.64 mmol, 20 eq.) in water (2.5 ml) was added. The reaction mixture was stirred at 45 °C for 24 h. The organic layer was separated and evaporated *in vacuo*. The product was purified by flash chromatography on reverse phase silica gel C18 (acetonitrile-ethyl acetate 50:50) to afford **114** (6 mg, 37 %) as a yellow amorphous solid.

APCI MS: 499 ($[M+H]^+$).

HR APCI MS: calcd for $C_{32}H_{19}S_3$ 499.0643, found 499.0646.

17,18-Bis(bromomethyl)hexaheliceno[10,9-*c*:5,6-*c′*]bisthiophene 115



To a solution of **117** (30.0 mg, 0.051 mmol) in dichloromethane (10 ml) a solution of hydrobromic acid in acetic acid (33 wt %, 17.6 µl, 0.102 mmol, 2.0 eq.) was added. The reaction mixture was stirred at room temperature for 20 min and an additional solution of hydrobromic acid in acetic acid (33 wt %, 44 µl,

0.255 mmol, 5.0 eq.) was added. Then water (10 ml) was added. The aqueous layer was extracted with dichloromethane (3 x 15 ml). The combined organic portions were dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo*. The product was purified by flash chromatography on reverse phase silica gel C18 (acetonitrile) to obtain product **115** (15.6 mg, 48 %) as a yellow powder.

M.p.: 192 °C decomp., (acetonitrile).

^{1}H NMR (600 MHz, $CDCl_3$): 5.59 (1 H, d, *J* = 11.6), 5.59 (1 H, d, *J* = 11.6), 5.70 (1 H, d, *J* = 11.6), 5.75 (1 H, d, *J* = 11.6), 6.51 (1 H, ddd, *J* = 8.4, 7.0, 1.4), 6.81 (1 H, ddd, *J* = 8.5, 6.8, 1.4), 7.00 (1 H, bd, *J* = 8.4), 7.05 (1 H, ddd, *J* = 8.0, 7.0, 1.2), 7.13 (1 H, ddd, *J* = 8.0, 6.8, 1.1), 7.41 (1 H, bd, *J* = 8.5), 7.66 (1 H, ddt, *J* = 8.0, 1.4, 0.7, 0.7), 7.92 (1 H, ddd, *J* = 8.0, 1.4, 0.5), 7.92 (1 H, dt, *J* = 8.6, 0.6, 0.6), 8.15 (1 H, d, *J* = 3.0), 8.25 (1 H, d, *J* = 8.6), 8.29 (1 H, d, *J* = 2.9), 8.80 (1 H, d, *J* = 2.9), 8.80 (1 H, d, *J* = 3.0).

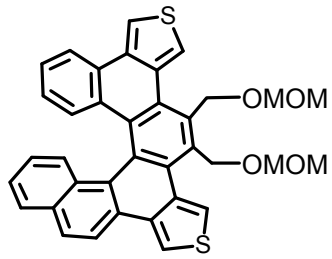
^{13}C NMR (150 MHz, $CDCl_3$): 32.98 (t), 33.19 (t), 116.83 (d), 117.32 (d), 121.66 (d), 123.22 (d), 123.32 (d), 123.36 (d), 125.23 (d), 125.46 (d), 126.06 (d), 126.51 (s), 127.21 (d), 127.32 (s), 127.59 (d), 127.70 (s), 127.75 (d), 128.38 (s), 128.79 (s), 129.64 (d), 129.64 (d), 129.86 (d), 130.15 (s), 130.18 (s), 130.88 (s), 131.13 (s), 131.74 (s), 131.81 (s), 132.14 (s), 132.75 (s), 134 32 (s), 137.19 (s), 137.55 (s).

IR ($CHCl_3$): 3112 w, 3054 w, 3038 vw, 2924 s, 2854 m, 1602 m, 1577 vw, 1565 vw, 1523 vw, 1511 w, 1466 m, 1454 m, 1429 m, 1223 s, 615 vw cm^{-1}.

APCI MS: 625 ($[M+H]^+$, with ^{79}Br).

HR APCI MS: calcd for $C_{32}H_{19}{}^{79}Br_2S_2$ 624.9289, found 624.9285.

17,18-Bis[(methoxymethoxy)methyl]hexaheliceno[10,9-*c*:5,6-*c*']bisthiophene 117



Method A (flow reactor): The heated part of a flow reactor was heated up to 250 °C and the tetrahydrofuran flow was set to 0.5 ml/min and pressure to 100 atm. Triyne **122** (11.6 mg, 0.02 mmol) was dissolved in tetrahydrofuran (2 ml) and $CpCo(CO)_2$ (1.32 µl, 0.01 mmol, 0.5 eq.) was added. The reaction mixture was then injected into the flow reactor. The residence time in the heated capillary was 16 min. The effluent on an output was collected and the solvent was removed *in vacuo*. The

product was purified by flash chromatography on reverse phase silica gel C18 (methanol) to furnish **117** (2.5 mg, 22 %) as a yellow powder.

Method B (halogen lamp): A Schlenk flask under argon was charged with triyne **122** (99 mg, 0.168 mmol) and triphenylphosphine (88.2 mg, 0.336 mmol, 2.0 eq.). Decane (20 ml, anhydrous, degased) was added. The solution was heated by a heat gun to 100 °C until both of the reactants were dissolved. Then a solution of $CpCo(CO)_2$ (22.5 µl, 0.168 mmol, 1.0 eq.) in decane (0.5 ml, anhydrous, degased) was added. The reaction mixture was irradiated with a halogen lamp at 140 °C for 1.5 h. The mixture was cooled down to room temperature, filtered through a short pad of silica gel and eluted with hexane (40 ml) to remove decane. The silica gel was then eluted with diethyl ether. The solvents were removed *in vacuo*. The product was purified by flash chromatography on reverse phase silica gel C18 (acetonitrile) to give **117** (36 mg, 36 %) as a yellow powder.

M.p.: 95 – 97 °C (chloroform – pentane).

^{1}H NMR (600 MHz, $CDCl_3$): 3.68 (3 H, s), 3.68 (3 H, s), 5.08 (1 H, d, *J* = 6.4), 5.08 (1 H, d, *J* = 6.5), 5.11 (1 H, d, *J* = 6.4), 5.11 (1 H, d, *J* = 6.5), 5.43 (1 H, d, *J* = 11.2), 5.51 (2 H, s), 5.57 (1 H, d, *J* = 11.2), 6.49 (1 H, ddd, *J* = 8.5, 7.0, 1.4), 6.77 (1 H, ddd, *J* = 8.7, 6.8, 1.3), 7.03 (1 H, dd, *J* = 8.5, 1.2), 7.04 (1 H, *J* = 8.2, 7.0, 1.2), 7.12 (1 H, ddd, *J* = 8.0, 6.8, 1.1), 7.47 (1 H, bd, *J* = 8.7), 7.66 (1 H, dd, *J* = 8.0, 1.3), 7.90 (1 H, bd, *J* = 8.5), 7.93 (1 H, dd, *J* = 8.2, 1.4), 8.10 (1 H, d, *J* = 3.0), 8.23 (1 H, d, *J* = 3.0), 8.25 (1 H, d, *J* = 8.5), 8.62 (1 H, d, *J* = 3.0), 8.65 (1 H, d, *J* = 3.0).

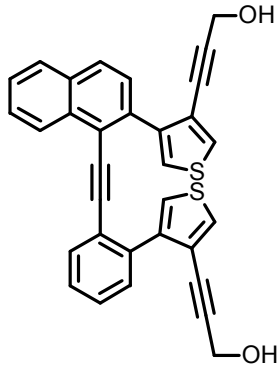
^{13}C NMR (150 MHz, $CDCl_3$): 56.81 (q), 56.93 (q), 65.72 (t), 66.30 (t), 97.08 (t), 97.27 (t), 116.08 (d), 116.60 (d), 121.79 (d), 122.15 (d), 122.41 (d), 123.30 (d), 125.05 (d), 125.16 (d), 125.73 (d), 126.28 (s), 127.01 (d), 127.36 (s), 127.53 (d), 127.55 (d), 127.71 (s), 127.97 (s), 128.06 (s), 129.24 (d), 129.75 (d), 130.39 (s), 130.64 (s), 131 76 (s), 131.81 (s), 132.22 (s), 132.66 (s), 132.97 (s), 132.99 (s), 133.49 (s), 137.39 (s), 137.64 (s).

IR ($CHCl_3$): 3121 w, 3091 vvw, 3060 w, 3040 vw, 2948 w, 2890 w, 2843 vw, 2827 w, 1618 vw, 1567 vvw, 1545 vw, 1513 w, 1473 w, 1467 w, 1452 vw, 1442 w, 1406 vw, 1381 w, 1356 w, 1321 vw, 1306 vw, 1181 vw, 1150 m, 1091 m, 1043 vs, 922 w cm^{-1}.

TOF EI MS: 588 ($M^{+\bullet}$, 16), 558 (6), 526 (23), 498 (13), 482 (100), 466 (51), 453 (79), 438 (34), 419 (52), 406 (40), 393 (23), 380 (11), 348 (10), 277 (8), 232 (8), 225 (12), 209 (12), 202 (6), 157 (69), 149 (5), 115 (26), 87 (12), 75 (14), 61 (4), 45 (15).

HR TOF EI MS: calcd for $C_{36}H_{28}O_4S_2$ 588.1429, found 588.1426.

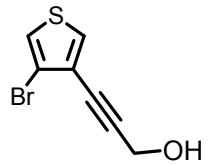
Hexaheliceno[10,9-*c*:5,6-*c*']bisthiene-17,18-diyldimethanol 118



To a solution of **106** (27 mg, 0.061 mmol) in tetrahydrofuran (1.5 ml) at -78 °C a solution of *n*-BuLi (81 µl, 1.6 m in hexanes, 0.013 mmol, 2.2 eq.) was added. The reaction mixture was stirred at -78 °C for 40 min and paraformaldehyde (4.05 mg, 0.013 mmol, 2.2 eq.) was added. After 30 min, the reaction mixture was warmed to room temperature and stirred for additional 24 h. The reaction mixture was diluted with ethyl acetate (5 ml) and washed with a saturated solution of NH_4Cl (5 ml). The aqueous layer was extracted with ethyl acetate (3 x 15 ml). The combined organic portions were dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo*. The product was purified by flash chromatography on silica gel (hexane-ethyl acetate 70:30 to 50:50) to afford product **118** (8.9 mg, 29 %) as a yellow oil.

^{1}H NMR (400 MHz, d_6-acetone): 4.12 – 4.17 (2 H, m), 4.24 (4 H, d, *J* = 6.2), 7.38 – 7.48 (2 H, m), 7.51 – 7.60 (4 H, m), 7.63 (1 H, d, *J* = 3.2), 7.69 (1 H, d, *J* = 8.5), 7.4 (1 H, d, *J* = 3.2), 7.79 – 7.82 (2 H, m), 7.93 – 7.97 (2 H, m), 7.98 – 8.03 (1 H, m).

3-(4-Bromothiophen-3-yl)prop-2-yn-1-ol 119



To a solution of 3-bromo-4-iodothiophene **103** (17.70 g, 0.051 mol), $Pd(PPh_3)_2Cl_2$ (1786.0 mg, 2.54 mmol, 5 mol%) and CuI (970.0 mg, 5.09 mmol, 10 mol%) In a mixture of diisopropylamine and tetrahydrofuran (300 ml, 1:1, degassed) propargyl alcohol (8.89 ml, 0.15 mol, 3.0 eq.) 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 tetrahydrofuran (300 ml) and the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexane–ethyl acetate, 100:0 to 70:30) to give **119** (9.547 g, 86 %) as a light-yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): 4.53 (2 H, s), 7.24 (1 H, d, *J* = 3.4), 7.46 (1 H, d, *J* = 3.4).

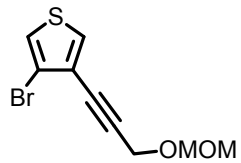
^{13}C NMR (150 MHz, $CDCl_3$): 51.58 (t), 79.04 (s), 90.18 (s), 113.47 (s), 122.99 (d), 123.79 (s), 129.66 (d).

IR ($CHCl_3$): 3608 w, 3453 w, 3120 m, 2924 w, 2871 w, 2256 w, 2226 w, 1505 w, 1451 w, 1425 m, 1381 w, 1338 m, 1160 w, 1047 vs, 1008 s, 858 m, 476 w cm^{-1}.

TOF CI MS: 217 ($[M+H]^+$, with ^{79}Br).

TOF CI HR MS: calcd for $C_7H_6{}^{79}BrOS$ 216.9323, found 216.9324.

3-Bromo-4-[3-(methoxymethoxy)prop-1-yn-1-yl]thiophene 120



Alcohol **119** (5.0 g, 0.023 mol) was dissolved in dichloromethane (150 ml, distilled from CaH_2). The solution was cooled down to 0 °C. Then chloromethyl methyl ether (3.85 ml, 0.51 mol, 2.2 eq.) and diisopropylethylamine (8.83 ml, 0.051 mol, 2.2 eq.) were added. The reaction mixture was stirred at room temperature for 24 hs. It was quenched with saturated $NaHCO_3$ (100 ml) and extracted with diethyl ether (3 x 100 ml). The combined organic portions were dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo*. The product was purified by flash chromatography (hexane) to give **120** (5.31 g, 88 %) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): 3.43 (3 H, s), 4.47 (2 H, s), 4.80 (2 h, s), 7.24 (1 H, d, *J* = 3.4), 7.46 (1 H, d, *J* = 3.4).

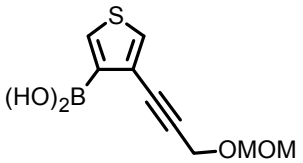
^{13}C NMR (150 MHz, $CDCl_3$): 54.65 (t), 55.68 (q), 79.41 (s), 87.67 (s), 94.77 (t), 113.63 (s), 122.92 (d), 123.89 (s), 129.63 (d).

IR ($CHCl_3$): 3120 w, 2953 w, 2934 w, 2934 w, 2890 w, 2861 w, 2846 w, 2827 w, 2252 vw, 2222 vw, 1505 w, 1472 w, 1465 w, 1445 w, 1424 w, 1401 vw, 1372 w, 1357 w, 1338 w, 1308 vw, 1173 w, 1150 s, 1102 s, 1043 vs, 989 m, 923 m, 860 w, 476 vw cm^{-1}.

TOF CI MS: 261 ($[M+H]^+$, with ^{79}Br).

HR TOF CI MS: calcd for $C_9H_{10}SO_2{}^{79}Br$ 260.9585, found 260.9581.

{4-[3-(Methoxymethoxy)prop-1-yn-1-yl]thiophen-3-yl}boronic acid 121



To a solution of **120** (3.3 g, 0.0126 mol) in tetrahydrofuran (90 ml) at -78 °C a solution of *n*-BuLi (1.6 m in hexanes, 9.5 ml, 0.0152 mol, 1.2 eq.) was added. After 1 min at −78 °C (triisopropyl)borate(8.75 ml, 0.038 mol, 3.0 eq.) was added while the reaction was

stirred. After warming up to room temperature the stirring continued for 45 min. After that the reaction was quenched with water (20 ml). The aqueous layer was extracted with diethyl ether (3 x 100 ml). The combined organic portions were dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo* to give the product **121** (2.7 g, 95 %) as an orange oil.

^{1}H NMR (600 MHz, $CDCl_3$): 3.43 (3 H, s), 4.48 (2 H, s), 4.78 (2 H, s), 5.06 (2 H, s), 7.53 (1 H, d, *J* = 3.0), 7.93 (1 H, d, *J* = 3.0).

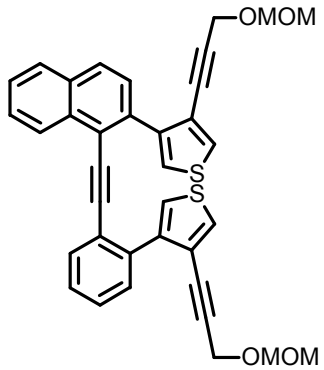
^{13}C NMR (150 MHz, $CDCl_3$): 55.07 (t), 55.70 (q), 82.09 (s), 87.47 (s), 95.39 (t), 124.24 (s), 129.88 (s), 130.78 (d), 136.92 (d).

IR ($CHCl_3$): 3625 w, 3110 w, 2953 m, 2933 m, 2848 w, 2827 w, 2224 w, 1504 m, 1475 w, 1441 s, 1419 m, 1379 s, 1334 s, 1307 s, 1150 s, 1102 s, 1045 vs, 990 m, 920 m, 868 m cm^{-1}.

ESI MS: 249 ($[M+Na]^+$).

HR ESI MS: calcd for $C_9H_{11}O_4BNaS$ 249.0363, found 249.0364.

3-[3-(Methoxymethoxy)prop-1-yn-1-yl]-4-{2-[(2-{4-[3-(methoxymethoxy)prop-1-yn-1-yl]thiophen-3-yl}naphthalen-1-yl)ethynyl]phenyl}thiophene 122



A Schlenk flask was charged with dibromide **108** (368.0 mg, 0.95 mmol), boronic acid **121** (539.0 mg, 2.38 mmol, 2.5 eq.), $Pd(PPh_3)_2Cl_2$ (66.8 mg, 0.095 mmol, 10 mol%) and K_2CO_3 (263.1 mg, 1.9 mmol, 2.0 eq.). A mixture of toluene-*n*-PrOH-H_2O (100 ml, 16:16:4.3) was added. The mixture was bubbled with argon for 45 min and stirred at 90 °C for 2 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel and eluted with dichloromethane (50 ml). The solvents were removed *in vacuo*. The product was purified by flash chromatography (hexane-tetrahydrofuran 100:0 to 80:20) to obtain triyne **122** (352.0 mg, 63 %) as a brown oil.

^{1}H NMR (600 MHz, $CDCl_3$): 3.26 (3 H, s), 3.29 (3 H, s), 4.27 (2 H, s), 4.28 (2 H, s), 4.56 (2 H, s), 4.57 (2 H, s), 7.32 (1 H, dt. *J* = 7.6, 7.6, 1.4), 7.37 (1 H, dt. *J* = 7.6, 7.6, 1.5), 7.42 (1 H, d, *J* = 3.2), 7.46 (1 H, ddd, *J* = 8.1, 7.1, 1.5), 7.47 (1 H, ddd, *J* = 7.7, 1.5, 0.6), 7.50 (1 H, ddd, *J* = 8.2, 7.1, 1.5), 7.51 (1 H, ddd, *J* = 7.7, 1.4, 0.6), 7.51

(1 H, d, *J* = 3.3), 7.59 (1 H, d, *J* = 3.3), 7.60 (1 H, d, *J* = 3.2), 7.64 (1 H, d, *J* = 8.3), 7.81 (1 H, bd, *J* = 8.3), 7.83 (1 H, ddt, *J* = 8.2, 1.5, 0.7, 0.7), 7.98 (1 H, ddt, *J* = 8.1, 1.5, 0.8, 0.8).

^{13}C NMR (150 MHz, $CDCl_3$): 54.66 (t), 54.66 (t), 55.46 (q), 55.49 (q), 81.01 (s), 81.08 (s), 86.28 (s), 86.42 (s), 90.17 (s), 94.44 (t), 94.52 (t), 97.10 (s), 119.64 (s), 122.37 (s), 122.45 (s), 123.04 (s), 124.74 (d), 125.36 (d), 126.35 (d), 126.88 (d), 126.96 (d), 127.45 (d), 127.52 (d), 127.66 (d), 127.86 (d), 127.90 (d), 129.68 (d), 129.75 (d), 129.96 (d), 132.29 (s), 132.83 (d), 133.54 (s), 135.88 (s), 136.96 (s), 141.99 (s), 142.03 (s).

IR ($CHCl_3$): 3112 w, 3060 w, 2952 w, 2934 w, 2845 vw, 2826 w, 2235 vw, 1619 vw, 1593 vw, 1563 vw, 1535 vw, 1500 w, 1490 w, 1472 vw, 1465 vw, 1447 w, 1427 vw, 1400 vw, 1340 vw, 1300 vw, 1150 s, 1101 s, 1044 vs, 1016 w, 989 m, 951 vw, 918 w, 898 w, 822 w, 534 vw, 438 w cm^{-1}.

ESI MS: 611 ($[M+Na]^+$), 627 ($[M+K]^+$).

HR ESI MS: calcd for $C_{36}H_{28}O_4NaS_2$ 611.1321, found 611.1319.

6. Abbreviations

AC	alternating current
APCI	atmospheric pressure chemical ionization
Boc	*tert*-butoxycarbonyl protecting group
CD	circular dichroism
CI	chemical ionization
COSY	correlation spectroscopy
CPL	circularly polarized luminescence
CSP	chiral stationary phase
CV	cyclic voltammetry
DBU	1,8-diazabicycloundec-7-ene
DC	direct current
DCM	dichloromethane
DIBAL	diisobutylaluminium hydride
DMA	dimethylamine
DMAP	4-(dimethylamino)pyridine
DMF	*N,N*-dimethylformamide
DPPB	1,4-bis(diphenylphosphino)butane
dd	doublet of doublets
ddd	doublet of doublets of doublets
dq	doublet of quartets
dt	doublet of triplets
ee	enantiomeric excess
EI	electron ionization
ESI	electrospray ionization
FT	Fourier transform
GC	gas chromatography
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
LDA	lithium diisopropylamide
m	multiplet, medium intensity
MOM	methoxymethyl
M.p.	melting point
MS	mass spectrometry
NLO	non–linear optics
NMR	nuclear magnetic resonance
OLED	organic light-emitting diode
OTFT	organic thin-film transistors
q	quartet
R_F	retention factor
rt	room temperature
s	singlet, strong intensity
TBAF	tetra-*n*-butylammonium fluoride
TBAPF6	tetrabutylammonium hexafluorophosphate
THF	tetrahydrofuran
TLC	thin layer chromatography
TMEDA	tetramethylethylenediamine
TMS	(trimethyl)silyl protecting group
TOF	time of flight analyser
UV/Vis	ultraviolet/visible spectroscopy
vs	very strong intensity
vw	very weak intensity
w	weak intensity

7. References

[1] Gingras, M. *Chem. Soc. Rev.,* **2013**, *42*, 968.

[2] Shen, Y.; Chen, C-F. *Chem. Rev.*, **2012**, *112*, 1463.

[3] Míšek, J.; Teplý, F.; Stará, I. G.; Tichý, M.; Šaman, D.; Císařová, I.; Vojtíšek, P.; Starý, I.; *Angew. Chem. Int. Ed.,* **2008**, *47*, 3188.

[4] Moorthy, J. N.; Venkatakrishnan, P.; Sengupta, S.; Baidya, M. *Org Lett.,* **2006**, *8*, 4891.

[5] Moussa, S.; Aloui, F.; Ben Hassine, B. *Synthetic Communications*, **2011**, *41*, 1006.

[6] Shibata, T.; Uchiyama, T.; Yoshinami, Y.; Takayasu, S.; Tsuchikama, K.; Endo, K. *Chem. Commun*., **2012**, *48*, 1311.

[7] Hatakeyama, T.; Hashimoto, S.; Oba, T.; Nakamura, M. *J. Am. Chem. Soc.,* **2012**, *134*, 19600.

[8] Nakano, K.; Oyama, H.; Nishimura, Y.; Nakasako, S.; Nozaki K. *Angew. Chem. Int. Ed.,* **2012**, *51*, 695.

[9] Yasuike, S.; Iida, T.; Okajima, S.; Yamaguchi, K.; Seku, H.; Kurita, J. *Tetrahedron*, **2001**, *57*, 10047.

[10] Murata, S.; Suzuki, T.; Yanagisawa, A.; Suga, S. *J. Heterocyclic Chem.,* **1991**, *28*, 433.

[11] Yasuike, S.; Iida, T.; Yamaguchi, K.; Seki, H.; Kurita, J. *Tetrahedron Lett.,* **2001**, *42*, 441.

[12] Waghray, D.; Nulens, W.; Dehaen, W. *Org. Lett.,* **2011**, *13*, 5516.

[13] Moussa, S.; Aloui, F.; Hassine, B. B. *Tetrahedron Lett*., **2012**, *53*, 5824.

[14] Rajca, A.; Wang, H.; Pink, M.; Rajca, S. *Angew. Chem. Int. Ed.,* **2000**, *39*, 4481.

[15] Myiasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *Chem. Eur. J.,* **2004**, *10*, 6531.

[16] Myiasaka, M.; Pink, M.; Wang, H.; Rajca, S. *J. Am. Chem. Soc.,* **2004**, *126*, 15211.

[17] Myiasaka, M.; Pink, M.; Olankitwanit, A.; Rajca, S.; Rajca, A. *Org. Lett.,* **2012**, *14*, 3076.

[18] Myiasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.,* **2005**, *127*, 13806.

[19] Salim, M.; Akutsu, A.; Kimura, T.; Minabe, M.; Karikomi, M. *Tetrahedron Lett.,* **2011**, *52*, 4518.

[20] Karikomi, M.; Yamada, M.; Ogawa, Y.; Houjou, H.; Seku, K.; Hiratani, K.; Haga, K.; Uyehara, T. *Tetrahedron Lett.,* **2005**, *46*, 5867.

[21] Areephong, J.; Ruangsupapichart, N.; Thongpanchang, T. *Tetrahedron Lett*., **2004**, *45*, 3067.

[22] Kelgtermans, H.; Dobrzańska, L.; Meervelt, L. V.; Dehaen, W. *Org. Lett.,* **2012**, *14*, 5200.

[23] Sawada, Y.; Furumi, S.; Takai, A.; Takeuchi, M.; Noguchi, K.; Tanaka, K. *J. Am. Chem. Soc.,* **2012**, *134*, 4080.

[24] Kelgtermans, H.; Dobrzańska, L.; Meervelt, L.V.; Dehaen, W. *Org. Lett.,* **2012**, *14*, 1500.

[25] Fukawa, N.; Osaka, T.; Noguchi, K.; Tanaka, K. *Org. Lett.,* **2010**, *12*, 1324.

[26] Si, Y.; Yang, G. *J. Mater. Chem. C.* , **2013**, *1*, 2354.

[27] Crittall, M. R.; Rzepa, H. S.; Carbery, D. R. *Org. Lett.,* **2011**, *13*, 1250.

[28] Krausová, Z.; Sehnal, P.; Bondzic, B. P.; Chercheja, S.; Eilbracht, P.; Stará, I. G.; Šaman, D.; Starý, I. *Eur. J. Org. Chem.*, **2011**, 3849.

[29] Garcia, M. H.; Florindo, P.; Piedade, M. de F. M.; Maiorana , S.; Licandro, E. *Polyhedron,* **2009**, *28*, 621.

[30] Monteforte, M.; Cauteruccio, S.; Maiorana, S.; Benincori, T.; Forni, A.; Raimondi, L.; Graiff, C.; Tiripicchio, A.; Stephenson, G. R.; Licandro, E. *Eur. J. Org. Chem.,* **2011**, 5649.

[31] Rose-Munch, F.; Li, M.; Rose, E.; Daran, J. C.; Bossi, A.; Licandro, E.; Mussini, P. R. *Organometallics*, **2012**, *31*, 92.

[32] Kaseyama, T.; Furumi, S.; Zhang, X.; Tanaka, K.; Takeuchi, M. *Angew. Chem. Int. Ed.*, **2011**, *50*, 3684.

[33] Shcherbina, M. A.; Zeng, X.; Tadjiev, T.; Ungar, G.; Eichhorn, S. H.; Phillips, K. E. S.; Katz, T. J. *Angew. Chem. Int. Ed.,* **2009**, *48*, 7837.

[34] Shi, L.; Liu, Z.; Dong, G.; Duan, L.; Qiu, Y.; Jia, J.; Guo, W.; Zhao, D.; Cui, D.; Tao, X. *Chem. Eur. J.,* **2012**, *18*, 8092.

[35] Fenili, F.; Rigamonti, C.; Bossi, A.; Ferruti, P.; Manfredi, A.; Maiorana, S.; Baldoli, C.; Cauteruccio, S.; Licandro, E.; Ranucci, E. *J. Polym. Sci. A Polym. Chem.,* **2010**, *48*, 4704.

[36] Kim, C.; Marks, T. J.; Facchetti, A.; Schiavo, M.; Bossi, A.; Maiorana, S.; Licandro, E.; Todescato, F.; Toffanin,M S.; Muccini, M.; Graiff, C.; Tiripicchio, A. *Org. Electron.,* **2009**, *10*, 1511.

[37] Xu, Y.; Zhang, Y. X.; Sugiyama, H.; Umano, T.; Osuga, H.; Tahala, K. *J. Am. Chem. Soc.*, **2004**, *126*, 6566.

[38] Spagnolo, P.; Zanirato, P.; Gronowitz, S. *J. Org. Chem.* **1982**, *47*, 3177.

[39] Jančařík, A.; Rybáček, J.; Cocq, K.; Vacek Chocholoušová, J.; Vacek, J., Pohl, R.; Bednárová, L.; Fiedler, P.; Císařová, I.; Stará, I. G.; Starý, I. Manuscript submitted.

[40] Stará, I. G.; Starý, I.; Kollárovič, A.; Teplý, F.; Šaman, D.; Fiedler, P. *Collect. Czech. Chem. Commun.* **2003**, *68*, 917.

[41] Palata, O. Bachleor's thesis, Charles university. **2011.**

[42] Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett*, **2002**, *4*, 3199.

[43] Krausová, Z. Ph.D. Thesis, Charles university, **2008**.

[44] Stará, I. G.; Andronova, A.; Kollárovič, A.; Vyskočil, Š.; Jugé, S.; Lloyd-Jones, G. C.; Guiry, P. G.; Starý, I. *Collect. Czech. Chem. Commun.* **2011**, *76*, 2005.

[45] Heller, B.; Hapke, M.; Fischer, C.; Andronova, A.; Starý, I.; Stará, I.G. *J. Organomet. Chem.* **2013**, *723,* 98.

[46] Newman, S.; Darlak, R. S.; Tsai, L. *J. Am. Chem. Soc*. **1967**, *89*, 6191.

[47] Martin, R. H.; Marchant, M. J. *Tetrahedron Lett.* **1972**, *13*, 3707; Wassenmann, H. H.; Keehn, P. M. *J. Am. Chem. Soc.* 1967, *89*, 2770.

[48] M. S. Newman, R. S. Darlak, L. Tsai, *J. Am. Chem. Soc*. **1967**, *89*, 6191–6193.

[49] Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett*. **2002**, *4*, 3199.