Univerzita Karlova
Přírodovědecká fakulta

Studijní program: Chemie
Studijní obor: Chemie

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Syntéza extendovaných helicenů

The synthesis of extended helical aromatics

Bakalářská práce

Vedoucí závěrečné práce: RNDr. Ivo Starý, CSc.

Praha, 2018

Prohlášení:

Prohlašuji, že jsem závěrečnou práci zpracovala samostatně a že jsem uvedla všechny použité informační zdroje a literaturu. Tato práce ani její podstatná část nebyla předložena k získání jiného nebo stejného akademického titulu.

V Praze, *24. 5. 2018*

Podpis

Abstrakt

Heliceny jsou polycyklické aromatické sloučeniny vyznačující se inherentní chiralitou. Je-li helikální struktura na vnějším okraji rozšířena o jedno či více aromatických jader, mluvíme o laterálně rozšířených helicenech. Pro svoji strukturu mají heliceny unikátní optické a elektronové vlastnosti, díky nimž mohou nalézt uplatnění například v asymetrické katalýze či molekulární elektronice.

Obtížnost syntézy helicenů vzrůstá s mírou rozšíření jejich vnějších okrajů o další aromatická jádra. To je způsobeno zejména problematickou rozpustností. Často je nutná komplexní optimalizace reakčních podmínek.

Tato bakalářská práce se zabývá syntézou laterálně rozšířeného helicenu obsahujícího dvě hexabenzokoronenové jednotky. Jeden z klíčových meziproduktů, bromjódderivát hexafenylbenzenu, byl připraven pomocí Diels-Alderovy reakce. Optimalizace podmínek této reakce umožnila syntézu klíčových meziproduktů v nezbytných pro další kroky syntézy cílového helicenu.

Klíčová slova: *helicen*, *hexabenzokoronen*, *hexafenylbenzen*, *Diels-Alderova reakce, polyaromatické sloučeniny*

Abstract

Helicenes are inherently chiral polycyclic aromatic molecules. Laterally extended helicenes have their outer rim extended by one or more aromatic rings, which gives them unique optical and electron properties and makes them hot candidates for applications in asymmetric catalysis or molecular electronics, for instance.

However, the larger the outer rim is, the more difficult the synthesis of wide helicenes becomes. Frequently bad solubility of laterally extended helicenes, as well as their intermediates, requires comprehensive optimisation of the reaction conditions, which are commonly used in helicene synthesis.

In my Bachelor Thesis, I focus on synthesis of a laterally extended helicene with two hexabenzocoronene moieties incorporated in its structure. One of the essential intermediates, bromoiodohexaphenylbenzene derivative, was prepared by Diels-Alder reaction. Optimised conditions of this reaction enabled the synthesis of crucial intermediates necessary for further steps in the target helicene synthesis.

Key words: *helicene*, *hexabenzocoronene*, *hexaphenylbenzene*, *Diels-Alder, polyaromatics*

Table of Contents

Abbreviations and Signs

Ac	acetyl
APCI	atmospheric pressure chemical ionization
Ar	aryl
BTMA-ICl_2	benzyltrimethylammonium dichloroiodate
Cy	cyclohexyl
d	doublet
dba	dibenzylideneacetone
DCM	dichloromethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DIPA	diisopropylamine
ee	enantiomeric excess
EI	electron impact
equiv.	equivalent
Et	ethyl
FT-IR	Fourier transform infrared
GC	gas chromatography
HBC	hexabenzocoronene
HPB	hexaphenylbenzene
HR	high resolution
i-Pr	*iso*-propyl
IR	infrared
IUPAC	International Union of Pure and Applied Chemistry
LA	Lewis acid
m	multiplet (NMR) *or* medium (IR)
MALDI	matrix-assisted laser desorption/ionization

Me	methyl
Mp	melting point
MS	mass spectrometry
n-Bu or Bu	*normal* butyl
Nf	nonafluorobutanesulfonyl
$[Ni(cod)_2]$	bis(1,5-cyclooctadiene)nickel(0)
NMR	nuclear magnetic resonance
OLED	organic light-emitting diode
PAH	polycyclic aromatic hydrocarbon
Ph	phenyl
rac	racemic
RT	room temperature
s	singlet (NMR) *or* strong (IR)
Sphos	2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl
TBAF	n-tetrabutylammonium fluoride
t-Bu	*tert*-butyl
Tf	trifluoromethanesulfonyl
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin-layer chromatography
TMS	trimethylsilyl
TMSA	trimethylsilylacetylene
TOF	time-of-flight
Tol	*p*-tolyl
UV	ultraviolet
vs	very strong (IR)

vw	very weak (IR)
w	weak (IR)

1. Introduction

Due to their unique properties, helicenes have been the subject of scientific interest for many years. These inherently chiral molecules are mostly chemically stable and, unlike other large π-conjugated systems, soluble in organic solvents. Their characteristic twisted shape results from the repulsive steric overlap of the terminal aromatic cores.

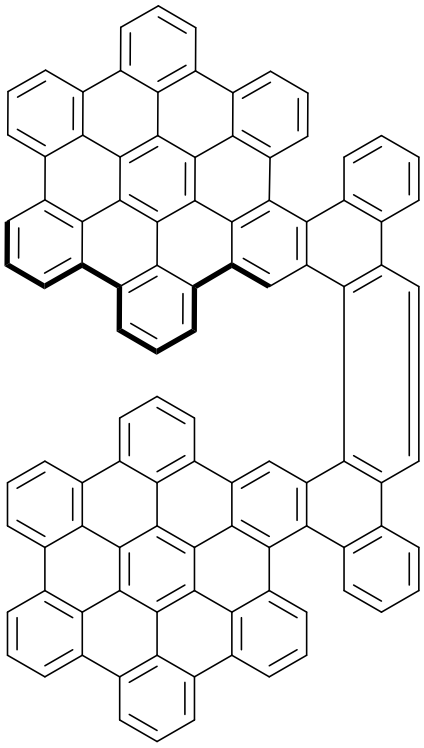
Wide or laterally π-extended helicenes are helicenes with one or more aromatic rings fused to their outer rim and are structurally similar to graphene fragments.

The unique properties of helicenes enable their possible application in asymmetric catalysis, as building blocks for helical polymers or as blue emitters in Organic Light Emitting Diodes (OLEDs).

2. Objectives

The ultimate goal of my Bachelor Thesis was to synthesise bromoiodo derivative of hexaphenylbenzene **2** as a key intermediate in the preparation of the laterally extended helicene **1** (Figure 1) and to explore the proposed synthetic approach to the extended helicene **1**.

The extended helicene **1** can be seen as a flake of helically twisted nanographene. It is interesting for its chiroptical and electron transport properties that might find application in nanotechnology.



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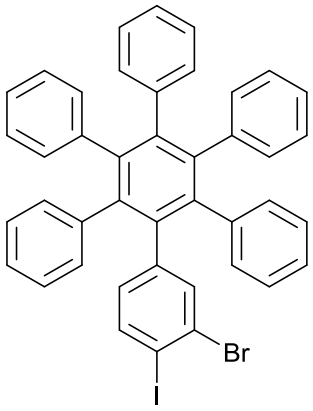


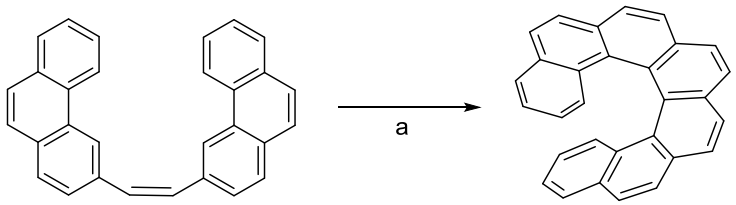
2

Figure 1: Structures of the target molecule 1 and intermediate 2

3. Theoretical background

3.1 Helicenes

Helicenes are nonplanar polycyclic aromatic compounds composed of *ortho*-fused aromatic or heteroaromatic rings[1,2]. Their molecules are inherently chiral thanks to their helical structure. The first helicene synthesis was conducted by Meisenheimer and Witte in 1903[3]. The year 1956, when Newman and co-workers[4] synthesised hexahelicene and resolved its enantiomers, marks an important milestone in helicene chemistry. In the late 1960s Martin's group[5] introduced the first general method for the preparation of helicenes utilising photocyclodehydrogenation of stilbene-type precursors, which rapidly initialised the preparation of higher helicenes (Scheme 1).



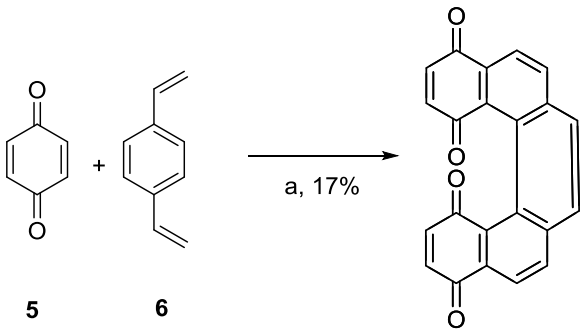
3 **4**

Scheme 1

Reagents and conditions:
a) hν, I_2, benzene, RT, 8 h.

Wynberg[6,7], Laarhoven[8] and Katz[9] used photocyclodehydrogenation reaction to synthesise carbohelicenes and heterohelicenes. They also studied their structural properties.

In 1990 Katz et al.[10] demonstrated a Diels-Alder synthetic approach, which enabled gram-scale preparation of helicenes (Scheme 2).



Scheme 2

Reagents and conditions:
a) CCl_3CO_2H, toluene, reflux, 33 h.

This groundbreaking preparative method was ensued by synthesis of a number of helicene derivatives[11–15] and by development of new synthetic strategies, for instance, employing organometallic catalysis[16–19].

To simplify the IUPAC nomenclature, the name "hexahelicene" was introduced for phenantro[3.4-*c*]phenantrene by Newman and Lednicer in 1956[4] (Figure 2). The number in brackets, [*n*], was adopted as an alternative to the Greek prefix before the helicene name, *e.g.* pentahelicene = [5]helicene[20].

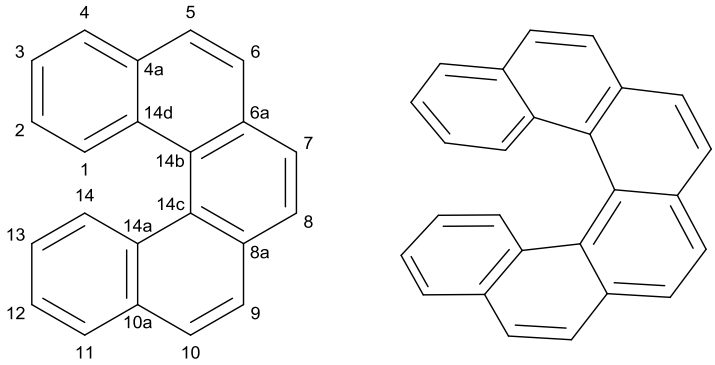


Figure 2: Numbering and nomenclature of helicenes

Helicenes composed solely of benzene rings are called carbohelicenes **4**[21], whereas heterohelicenes **10**[22] contain at least one heteroatom in their helical backbone. Laterally extended helicenes have their helical structures extended about one or more aromatic rings fused to their outer rim **11**[8].

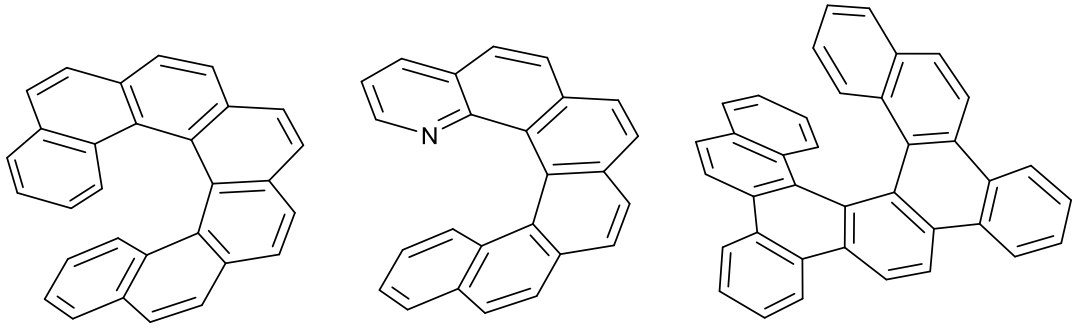


Figure 3: Examples of helical structures

3.2 General properties

Although helicene molecules lack any chiral centre, their helical shape causes their inherent chirality.[1,2] The basic helicene backbone has a C_2-symmetric axis perpendicular to the helical axis (Figure 4a). Absolute stereochemistry of helicene is denoted *M* ("minus") or *P* ("plus") depending on the handedness of its helical backbone.[23] An empirical rule based on chiroptical data states a relationship between the absolute configuration and chirality: (*P*)-carbohelicenes are dextrorotatory (+), (*M*)-carbohelicenes are levorotatory (-).[24, 25]

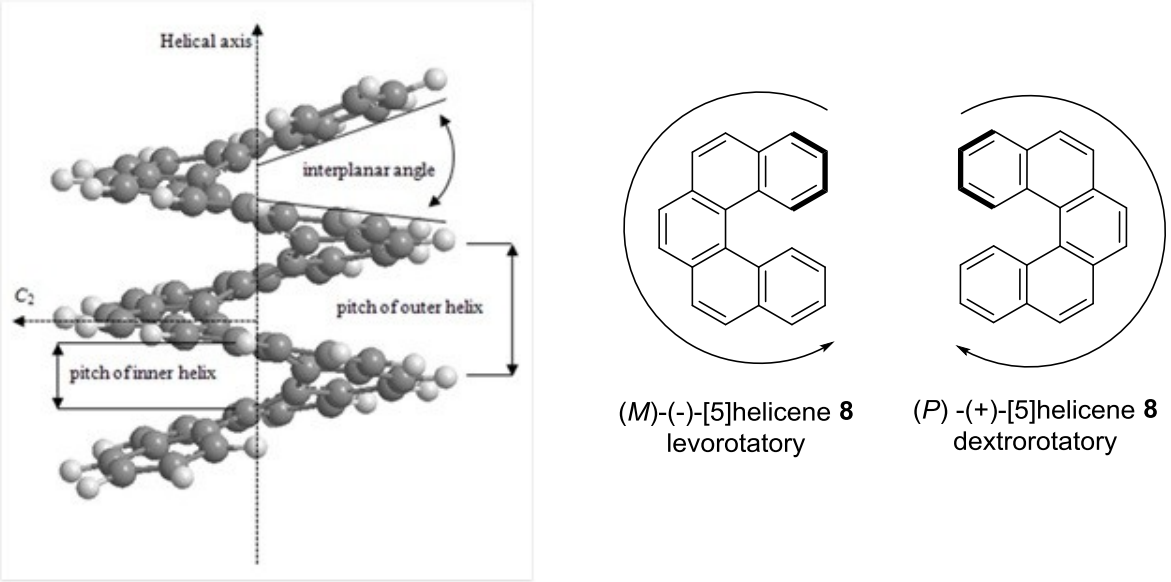


Figure 4: a) A model of [25]helicene, b) schematic representation of helicity

Compared to the corresponding planar aromatic systems, helicenes are significantly more soluble. The cause of this phenomenon presumably lies in their deflection from planarity, which prevents efficient π-π stacking. Moreover, the solubility can be improved by substitution of helicenes by alkoxyl or alkyl groups.[12, 15]

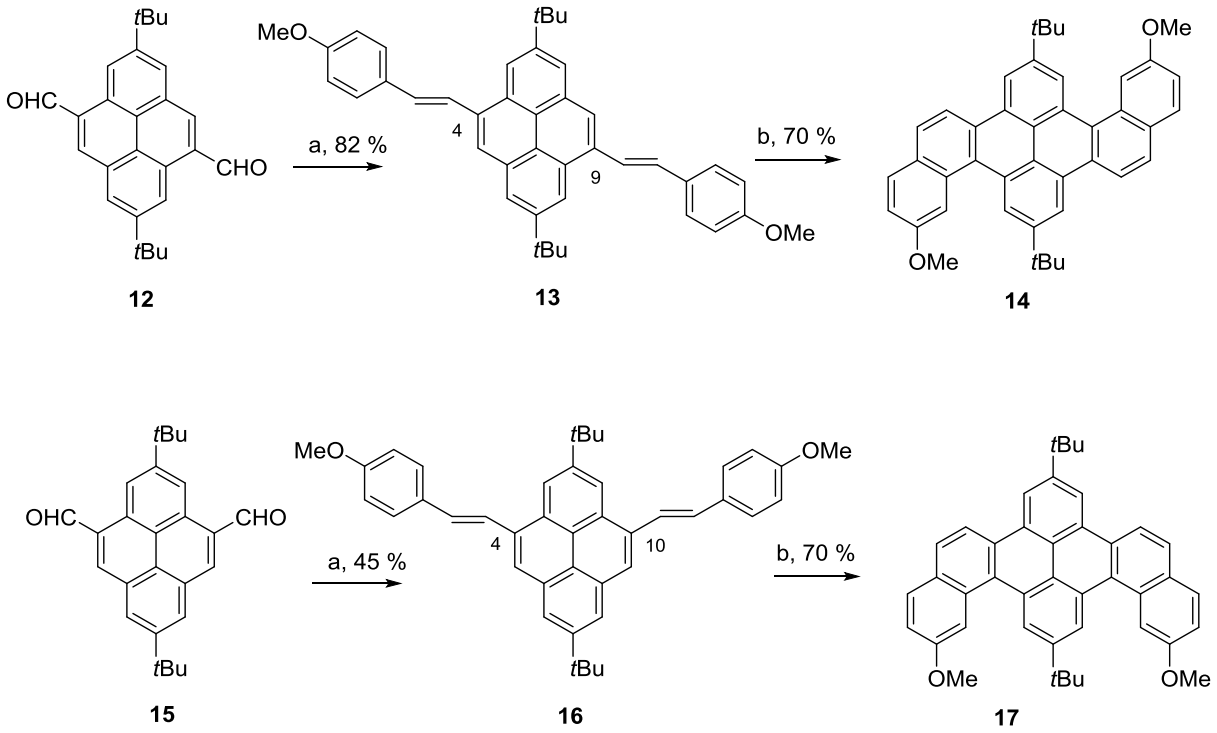
Racemisation barriers of helicenes increase with the increasing length of the helical backbone. Furthermore, bulky substituents attached to the terminal helicene rings in position 1 and 1' help to substantially increase their racemisation barrier.

The unique properties of helicenes open new possibilities for their applications, for instance, as chiral liquid crystalline materials,[26,27] building blocks for helical conjugated polymers,[28,29] sensors or dyes in molecular recognition,[30,31] catalysts in asymmetric synthesis[32, 33] or blue emitters in Organic Light-Emitting Diodes (OLEDs)[34].

3.3 Extended helicenes

Wide or π-extended helicenes – helicenes with one or more aromatic rings fused to their outer rim – have been studied owing to their structural similarity to graphene.

Wide helicene family members, pyrene-cored [4]helicenes, were prepared using the photocyclodehydrogenation reaction. Two formyl groups in the positions 4, 9 and 4, 10, respectively, were introduced to pyrene *t*-butylated in the positions 2 and 7 (Scheme 3). The Wittig reaction of bisformylated pyrenes **12** and **15** with various aryl methyl phosphonium ylides was carried out to give **13** and **16**. These compounds were then subjected to intramolecular photocyclization, which gave the extended [4]helicenes **14** and **17**. Both compounds were soluble in common organic solvents and showed bright fluorescent emissions in the whole blue light range giving them potential for applications in the field of organic electronic and optoelectronic devices such as blue emitters in OLEDs.[35, 36]

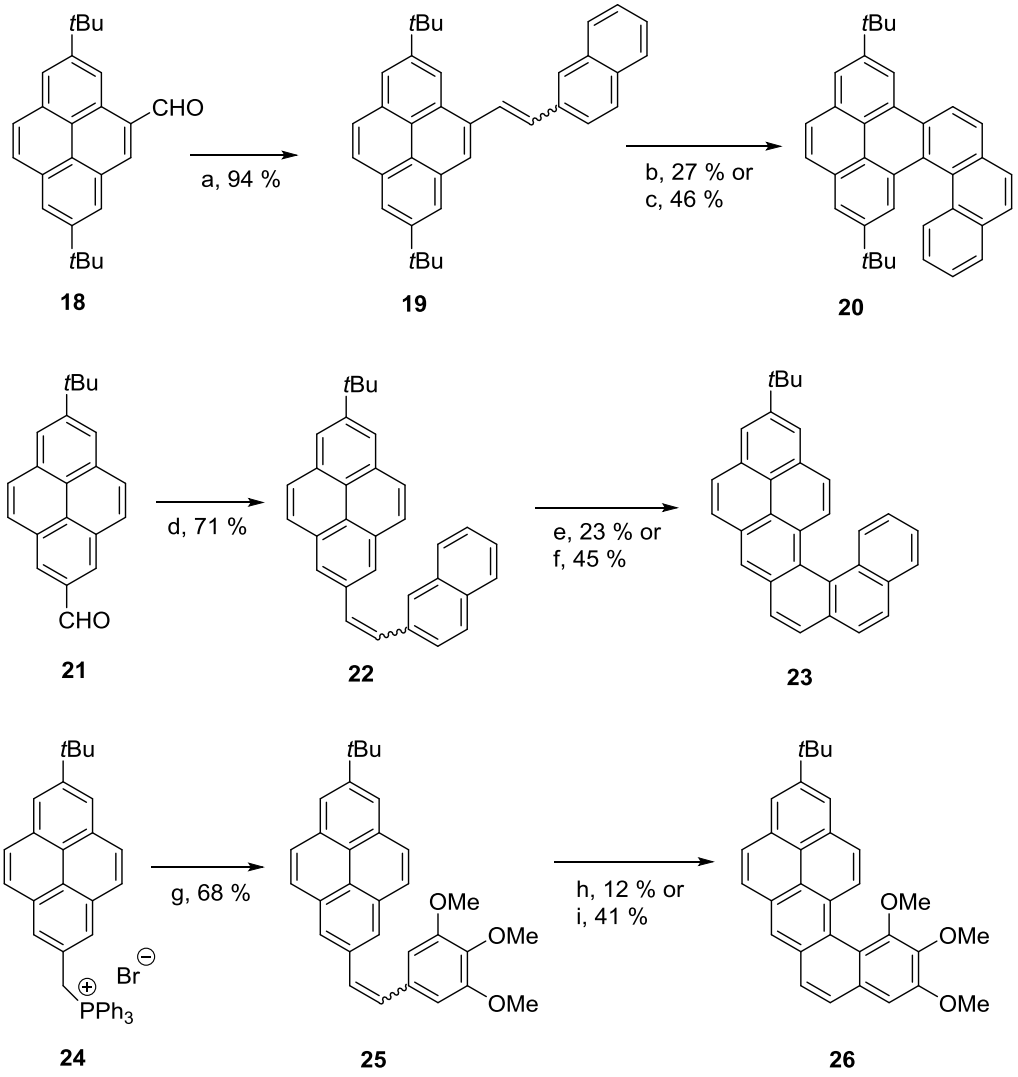


Scheme 3

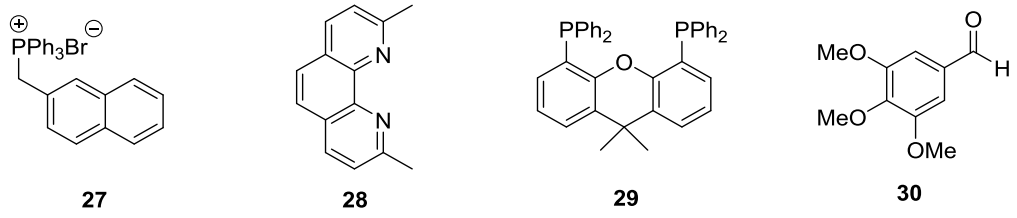
Reagents and conditions:
a) (4-methoxybenzyl)triphenylphosphonium bromide, *n*-BuLi, THF, RT, 6 h;
b) hν, I_2, propylene oxide, benzene, RT, 12 h.

A very similar approach was used for the synthesis of helicene-pyrene hybrids **20** and **23** (Scheme 4). The Wittig reaction of **27** with **18** and **21**, respectively, gave the derivatives **19** and **22**. Consequently, photocyclodehydrogenation conditions were employed, leading to **20** and **23**. The utilisation of flow reactor resulted in a considerable yield improvement.

The Wittig reaction of the aldehyde **30** with **24** provided the styrenyl derivative **25**, which was again subjected to photocyclodehydrogenation conditions and demonstrated similar trend in the yield improvement when using the flow reactor[37].



Building blocks and ligands:

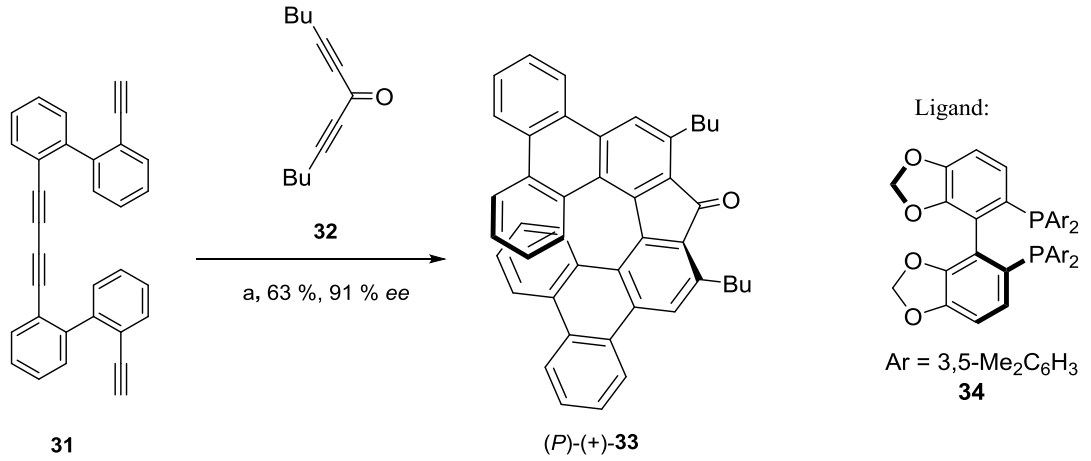


Scheme 4

Reagents and conditions:

a) **27**, *n*-BuLi, THF, -78 °C to RT, 15 h;
b) **28**, $Cu(MeCN)_4BF_4$, **29**, hν, I_2, propylene oxide, THF, RT, 5 d;
c) **28**, $Cu(MeCN)_4BF_4$, **29**, hν, I_2, propylene oxide, RT, flow reactor, 18 h;
d) **27**, *n*-BuLi, THF, RT, 18 h;
e) **28**, $Cu(MeCN)_4BF_4$, **29**, hν, I_2, propylene oxide, THF, RT, 5 d;
f) **28**, $Cu(MeCN)_4BF_4$, **29**, hν, I_2, propylene oxide, RT, flow reactor 18 h;
g) **30**, *n*-BuLi, THF, -78 °C to RT, 18 h;
h) **28**, $Cu(MeCN)_4BF_4$, **29**, hν, I_2, propylene oxide, THF, RT, 5 d;
i) **28**, $Cu(MeCN)_4BF_4$, **29**, hν, I_2, propylene oxide, RT, flow reactor, 18 h.

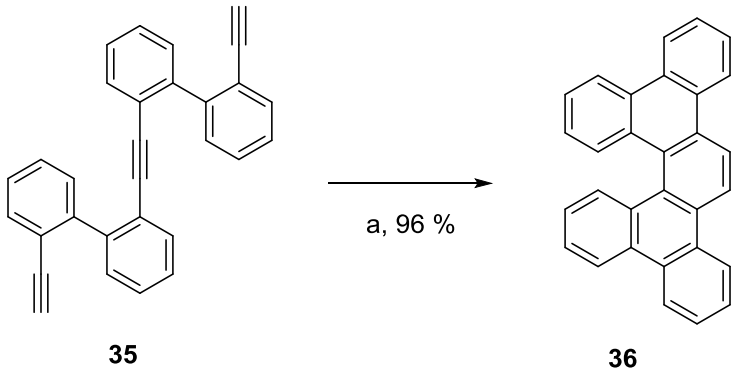
Enantiomerically enriched dibenzohelicene analogue (*P*)-(+)-**33** was synthesised via a highly enantioselective rhodium-catalysed double [2+2+2] cycloaddition of the biaryl-linked tetrayne **31** with 1,4-diyne **32** (Scheme 5). The use of axially chiral ligands (*e.g.* **34**) led to the dibenzohelicene analogue (*P*)-(+)-**33** with enantiomeric excess up to 91 %.[38]



Scheme 5

Reagents and conditions:
a) $[Rh(cod)_2]BF_4$, (S)-xyl-Segphos **34**, DCM, RT, 16 h.

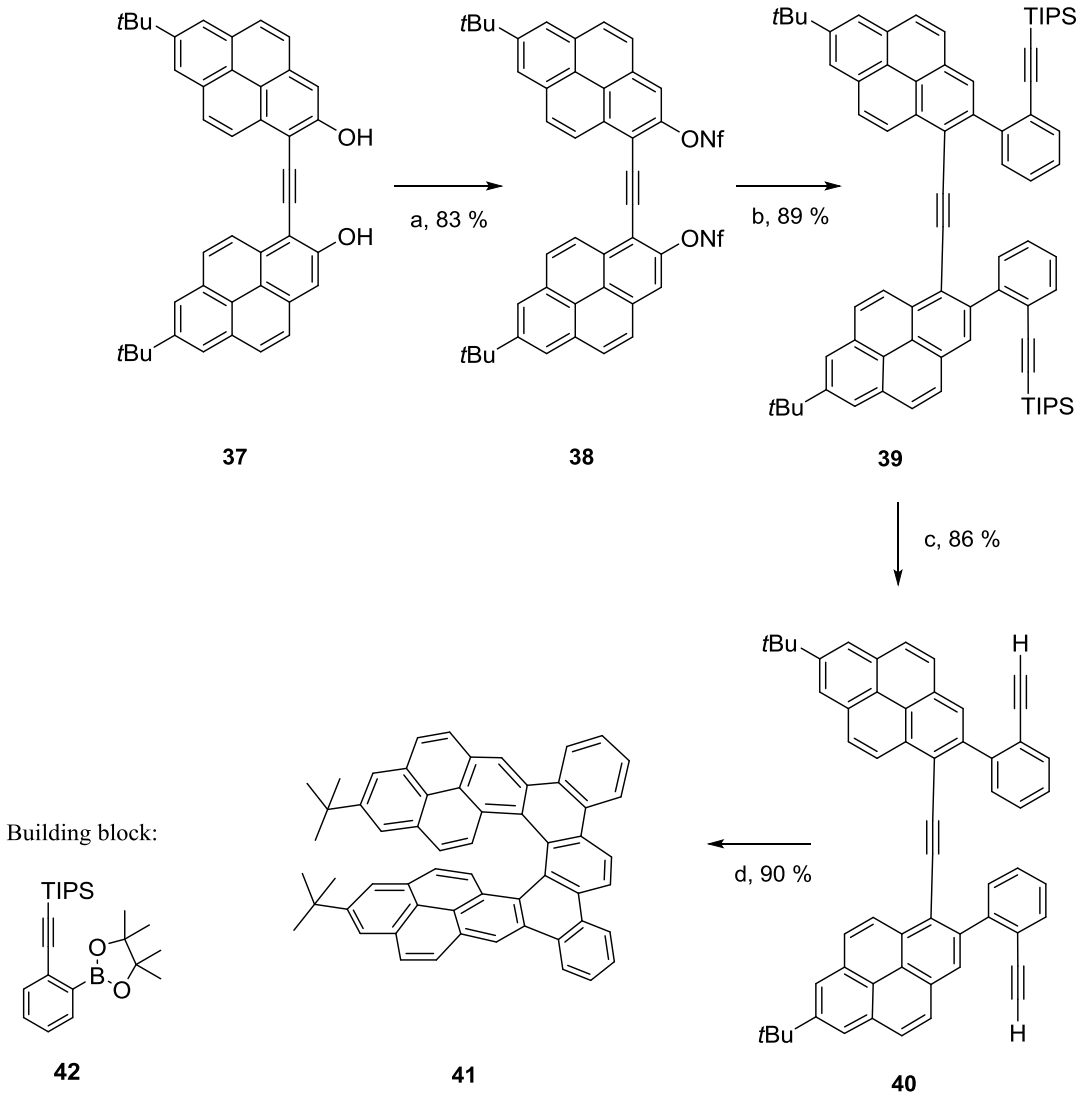
Starý and Stará[39] developed a simple and adjustable synthetis of dibenzohelicenes and their derivatives. The key step – formation of the helical backbone – is [2+2+2] cycloisomerisation of aromatic triynes. Dibenzo-[5]-, -[6]- and -[7]helicenes were prepared from the corresponding triynes. Introduction of the two extra benzene rings into the triyne structure improves the efficiency of the dibenzohelicene synthesis and enables the direct preparation of fully aromatic, inherently chiral systems. However, the extension of the aromatic system results in strengthening of the intermolecular π-π stacking effect, leading to a decrease in solubility. The precursor **35** was prepared by a Sonogashira/Suzuki reaction sequence and consequently subjected to the cyclotrimerisation conditions providing dibenzo[5]helicene **36** (Scheme 6).



Scheme 6

Reagents and conditions:
a) $Ni(cod)_2$, PPh_3, THF, RT, 10 min.

Proceeding with the same methodology, chimerical pyrene-based [7]helicenes were prepared employing Ni^0 or Co^I catalysed [2+2+2] cyclotrimerisation of dipyrenyl-acetylene-derived triynes.[40] Dipyrenyl acetylene diphenol **37** was transformed into dinonaflate **38**, which was then subjected to the Suzuki-Miyaura cross-coupling reaction conditions providing aromatic triyne **39** (Scheme 7). After triisopropylsilyl groups deprotection, Ni^0/PCy_3-catalysed [2+2+2] cycloisomerisation of **40** formed the target chimerical pyrene-based dibenzo[7]helicene **41**. Owing to the presence of two *tert*-butyl groups and the helical structure, the product exhibits good solubility in organic solvents such as chloroform and THF.

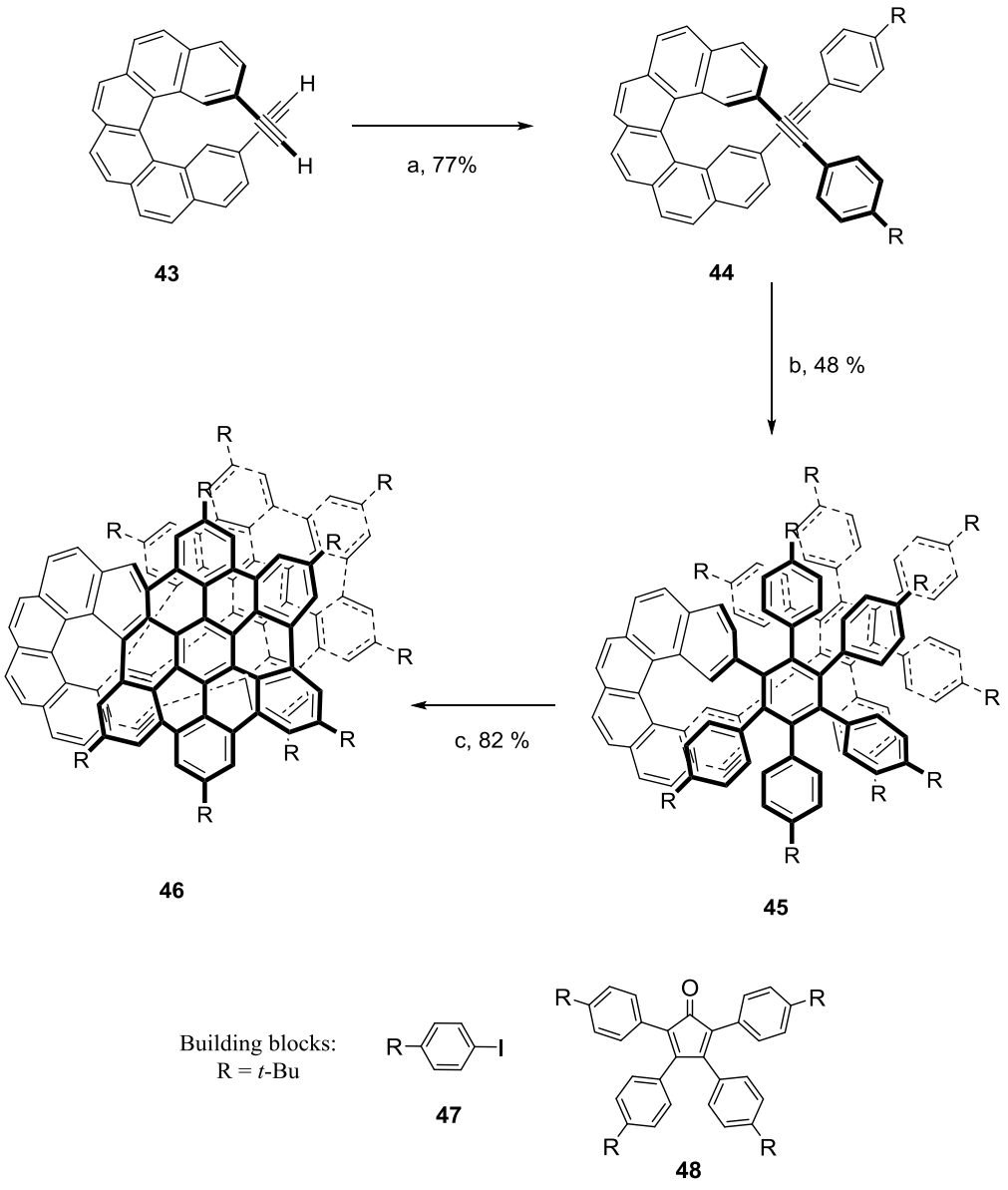


Scheme 7

Reagents and conditions:

a) $FSO_2(CF_2)_3CF_3$, K_2CO_3, THF, RT, 20 h;
b) **42**, $[Pd(PPh_3)_2Cl_2]$, K_2CO_3, toluene-ethanol-water (4:4:1), 100 °C, 12 h;
c) *n*-Bu_4NF, THF, RT, 20 min;
d) $[Ni(cod)_2]$, PCy_3, THF, RT, 10 min.

A bilayer nanographene structure **46** connected by a helical backbone was synthesised from the ethynyl [6]helicene **43** in three steps (Scheme 8). A double Sonogashira coupling of **43** with **47** gave the [6]helicene derivative **44**, which was then subjected to Diels-Alder cycloaddition conditions with **48** giving the bis-pentaphenylphenyl [6]helicene **45**. A Scholl cyclodehydrogenation of **45** provided the desired product **46**.[41] The *tert*-butyl groups have been introduced to improve the solubility of the product and the intermediates.



Scheme 8

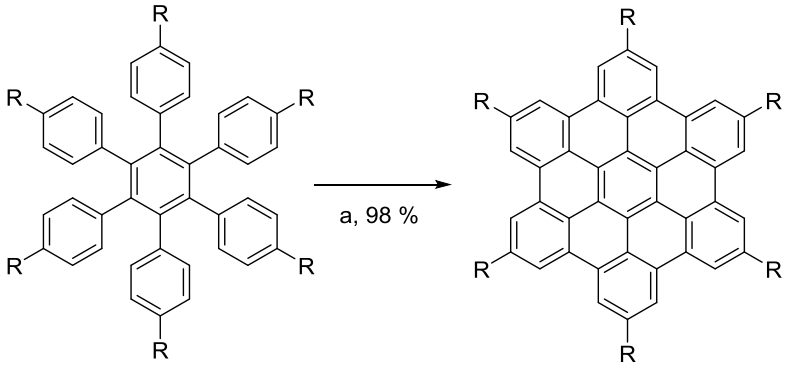
Reagents and conditions:

a) **47**, $PdCl_2(PPh_3)_2$, CuI, DIPA;
b) **48**, microwave oven, 280 °C;
c) DDQ, TfOH, DCM, 0 °C.

3.4 Hexa-*peri*-hexabenzocoronene

Hexa-*peri*-hexabenzocoronene derivatives (HBCs) have continuously been attracting interest due to their large planar π-conjugated aromatic systems and strong π-π-stacking, which may contribute to high charge carrier mobility[42]. HBCs serve as useful organic semiconductors in optoelectronic and electronic devices and show high thermal and chemical stability[43].

Müllen and co-workers demonstrated[44, 45, 46] that Scholl reaction of corresponding oligophenylenes represents an effective preparative method for the synthesis of HBCs. The hexaphenylbenzene derivative **49** was subjected to oxidative cyclodehydrogenation conditions, providing the HBC derivative **50** in nearly quantitative yield[45] (Scheme 9).



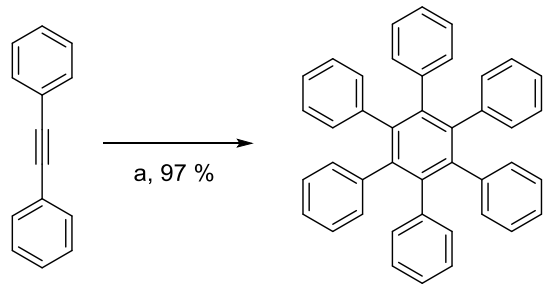
Scheme 9

Reagents and conditions:
a) $FeCl_3$, DCM, 18 h, R = *t*-Bu.

3.5 Hexaphenylbenzene

As important nanographene precursors, hexaphenylbenzene (HPB) and its derivatives have been studied for decades, therefore there are numerous documented synthetic methods for their preparation.

Butenschön et al. used cobalt-catalysed intermolecular alkyne cyclotrimerisation of **51** to provide hexaphenylbenzene **52** in nearly quantitative yield[47] (Scheme 10).

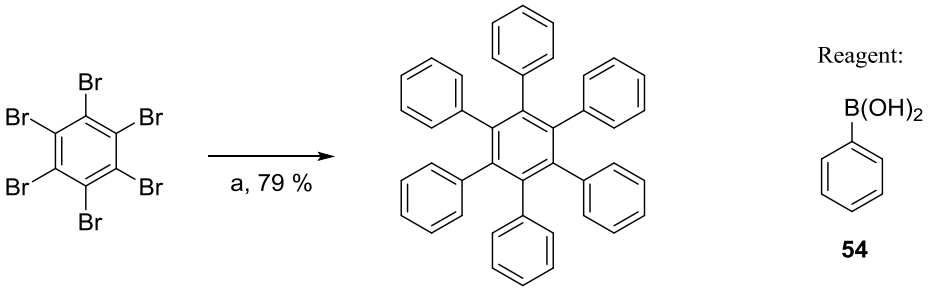


51 **52**

Scheme 10

Reagents and conditions:
a) $Co(PPh_3)_3Cl$, *o*-xylene, reflux, 16 h.

Reimann and co-workers have synthesised hexaphenylbenzene **52** utilising multiple Suzuki-Miyaura reaction of polybrominated benzene[48] (Scheme 11).

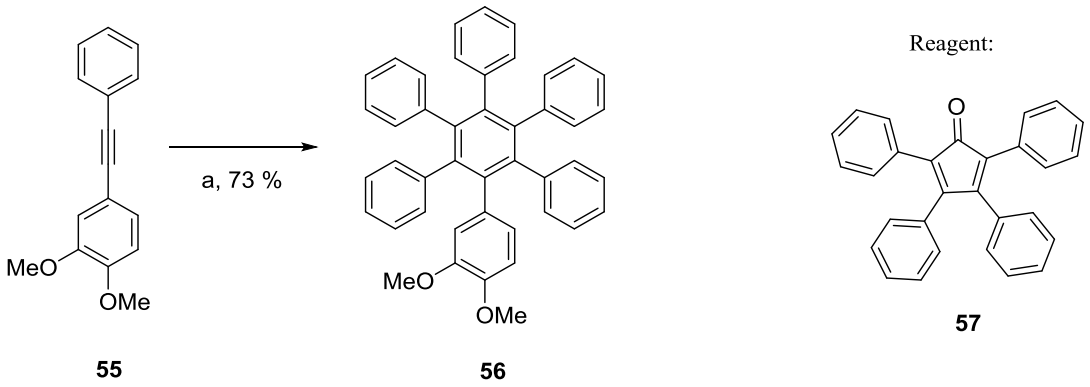


53 **52** **54**

Scheme 11

Reagents and conditions:
a) **54**, $PdCl_2(CH_3CN)_2$, SPhos, K_3PO_4, toluene, 110 °C, 6 days.

McKeown and co-workers[49] used Diels-Alder reaction of dimethoxy-substituted diphenylacetylene **55** with tetraphenylcyclopentadienone **57** to prepare HPB derivative **56** as a precursor for the synthesis of organic molecules of intrinsic microporosity (Scheme 12).



55 **56** **57**

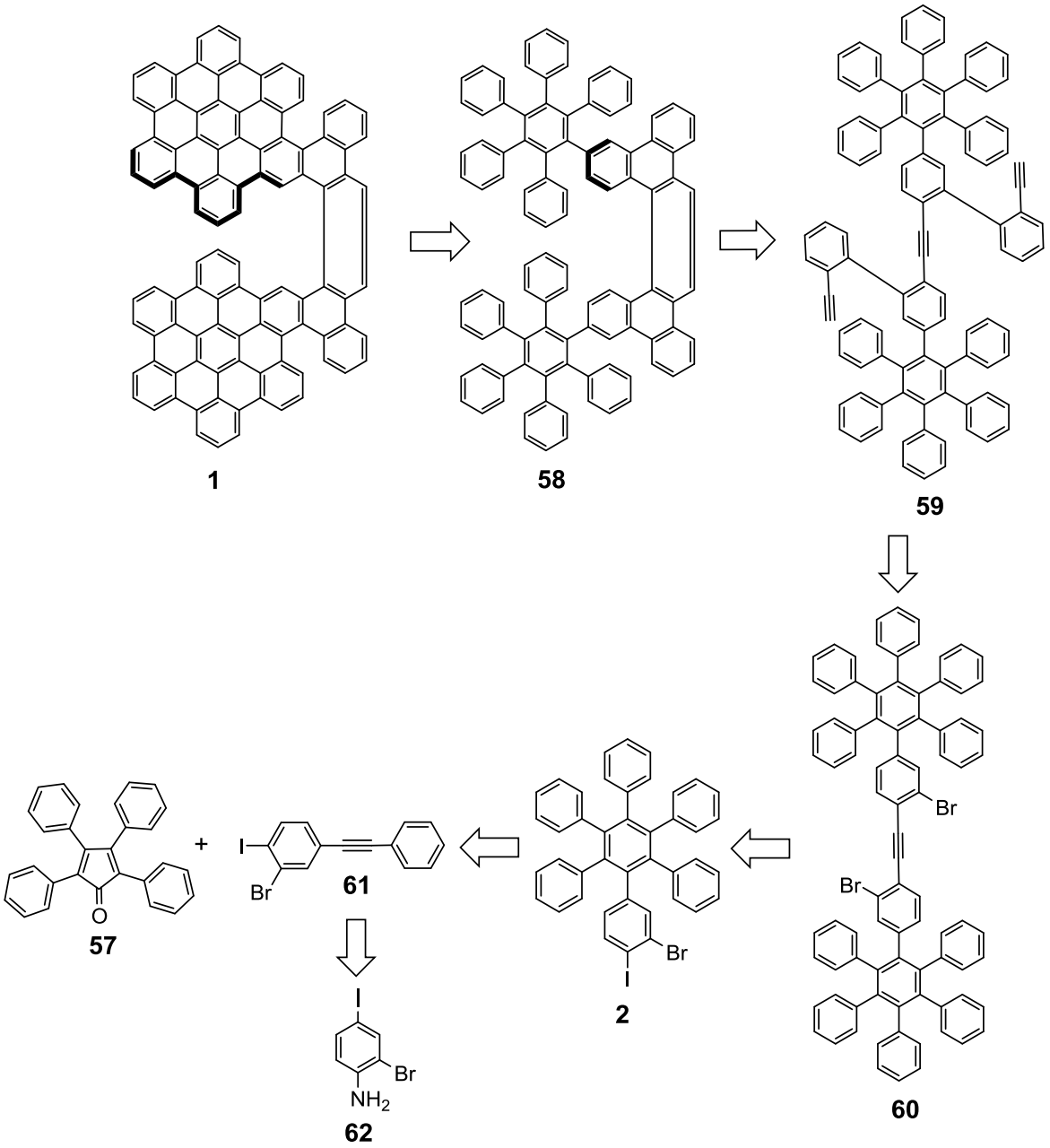
Scheme 12

Reagents and conditions:
a) **57**, Ph_2O, reflux, 15 h.

There has been an extensive research done in the area of π-extended helicenes, however, the focus of this Thesis was to study the synthetic route to dibenzo[5]helicenes extended by two hexabenzacoronene moieties and to optimise the reaction conditions of individual synthetic steps.

4. Results & Discussion

The objective of my Thesis was to explore the synthesis of the laterally extended helicene derivative **1**. A retrosynthetic analysis showed that the steps of the proposed synthesis would include Scholl oxidation of **58**, [2+2+2] cyclotrimerisation of triyne **59**, double Suzuki-Miyaura reaction of **60**, Sonogashira coupling of **2**, Diels-Alder reaction of **61** with **57** and Sonogashira coupling of **62** (Scheme 13).



Scheme 13

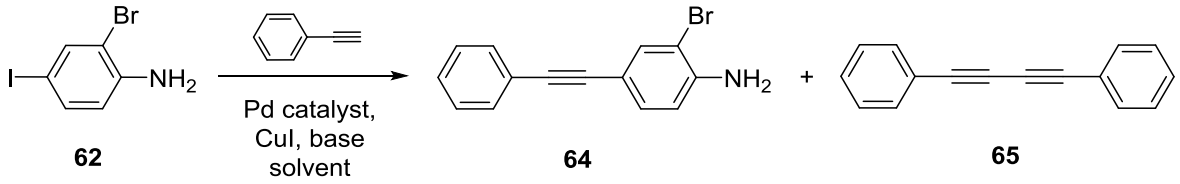
4.1 Synthesis of HPB derivative **2**

4.1.1 Synthesis of diphenylacetylene derivative **61**

First, I have synthesised diphenylacetylene derivative **61** using a sequence of iodination/Sonogashira coupling/diazotisation-halogenation reactions, which started from 2-bromoaniline **63**. Bromoiodoaniline **62** was prepared by iodination of **63** using BTMA-ICl_2 in alkaline environment of $CaCO_3$ (Scheme 14). The reaction provided the desired product **62** in 80% yield.

Subsequently, **62** was subjected to Sonogashira coupling conditions with phenylacetylene. The conditions of this reaction were optimised, supressing the phenylacetylene homocoupling by-product formation (Table 1).

Table 1: Optimisation of reaction conditions for synthesis of 64

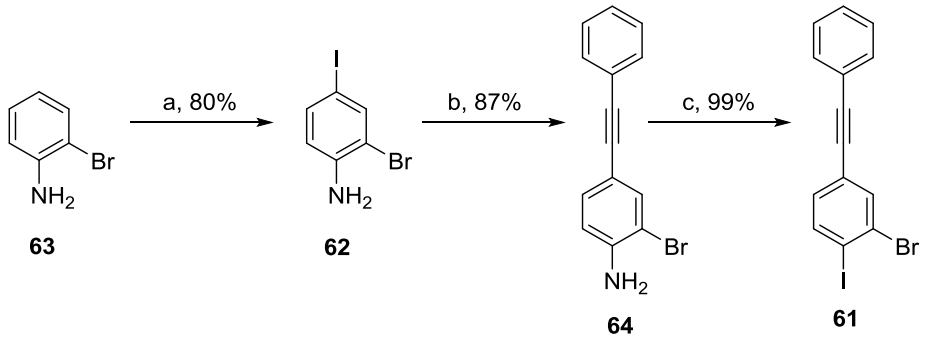


62 **64** **65**

Entry	Pd catalyst (2 mol %)	CuI (mol %)	Solvent	Base	Reaction period (h)	Temperature	**64**	**65**
1	$PdCl_2(PPh_3)_2$	4	THF	Et_3N	24	RT	**39%**	+
2	$Pd(PPh_3)_4$	3	THF	Et_3N	23	45 °C	mixture of products (yield not determined)	+
3	$Pd(PPh_3)_4$	3	Et_3N	Et_3N	23	RT	low conversion (yield not determined)	-
4	$Pd(PPh_3)_4$	3	DIPA	DIPA	2	60 °C	**87%**	-

The course of the reactions was monitored by GC-MS. At first, $PdCl_2(PPh_3)_2$ and CuI as catalysts, Et_3N as a base and THF as a solvent were used in Sonogashira coupling reaction at room temperature. However, these conditions led to moderate yield of the desired product **64** (39%) and to the formation of a significant amount of phenylacetylene homocoupling product **65**. Therefore, the conditions were altered, $Pd(PPh_3)_4$ was used instead of $PdCl_2(PPh_3)_2$ and the reaction mixture was heated to 45 °C. These conditions yielded the homocoupling product **65** as well as many other by-products and therefore the yield was not determined. When using Et_3N as a solvent instead of THF, the conversion was very low even after 23 hours. Eventually, replacing Et_3N with DIPA as a solvent and heating the reaction mixture to 60 °C for 2 hours provided the desired product in 87% yield.

Iodide **61** was prepared by subjecting amine **64** to diazotisation reaction with an excess of $BF_3{\cdot}OEt_2$ and *t*-BuONO and a subsequent addition of NaI dissolved in CH_3CN to the reaction mixture. This spot-to-spot reaction provided **61** in a quantitative yield with no need of further purification (Scheme 14).



Scheme 14

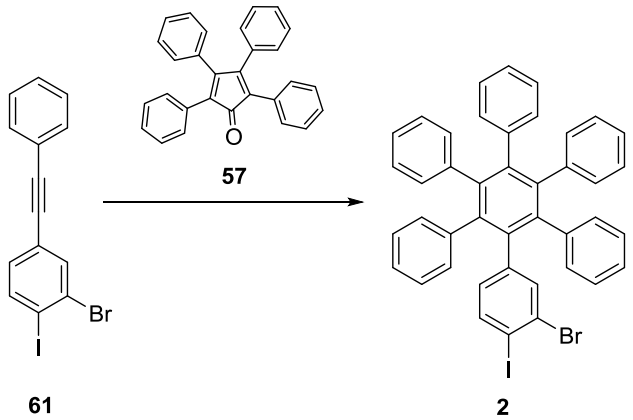
Reagents and conditions:

a) BTMA-ICl_2 (1.4 equiv.), $CaCO_3$ (1.85 equiv.), MeOH - DCM (1:2), RT, 19 h;
b) phenylacetylene (1.2 equiv.), $Pd(PPh_3)_4$ (2 mol %), CuI (3 mol %), DIPA, 60 °C, 2 h;
c) 1. $BF_3{\cdot}OEt_2$ (2.0 equiv.), *t*-BuONO (1.6 equiv.), DCM, 1 h, 0 °C; 2. NaI (2.0 equiv.), CH_3CN, RT, 20 h.

4.1.2 Synthesis of **2**

The next synthetic step, preparation of the HPB derivative **2** via Diels-Alder reaction of **61** and **57** required high temperature. A variety of reaction conditions was applied to optimise the synthetic procedure (Table 2).

Table 2: Reaction conditions for synthesis of 2



Entry	Solvent	Temperature (°C)	Reaction period	Reaction setup	Yield
1	toluene	200	22 h	pressure tube	no conversion
2	Ph_2O	210	20 h	sand as heating medium	no conversion
3	chlorobenzene	200	20 min	microwave oven	no conversion
4	Ph_2O	250	4 h	heating block	**67%**[a)]

[a)]isolated product

Anticipating difficulties with removal of Ph_2O from the product, different solvents were tested. Heating the educts dissolved in toluene in a pressure tube to 200 °C did not lead to any product. Subsequently, Ph_2O was used as a solvent and the mixture was heated to 210 °C with sand as a heating bath. Unfortunately, heat transfer was not sufficient and TLC analysis showed no conversion after 20 hours. Carrying out the reaction in a microwave oven at 200 °C for 20 minutes and using chlorobenzene as a solvent did not lead to any products either. Afterwards, a heating block was used to heat the mixture in a Schlenk flask with Ph_2O as a solvent at reflux (250 °C) for 4 hours. After the reaction, Ph_2O was removed from the reaction mixture by vacuum distillation using Kugelrohr apparatus and HPB derivative **2** was

isolated by column chromatography on silica gel. These reaction conditions provided the product **2** in 67% yield.

The HPB derivative **2** showed absorbance in the range between 235 and 335 nm with an absorption maximum at 252 nm (Figure 5). Broad fluorescence band of HPB derivative **2** was in the range between 300 and 500 nm with fluorescence maxima at 379 nm (Figure 6).

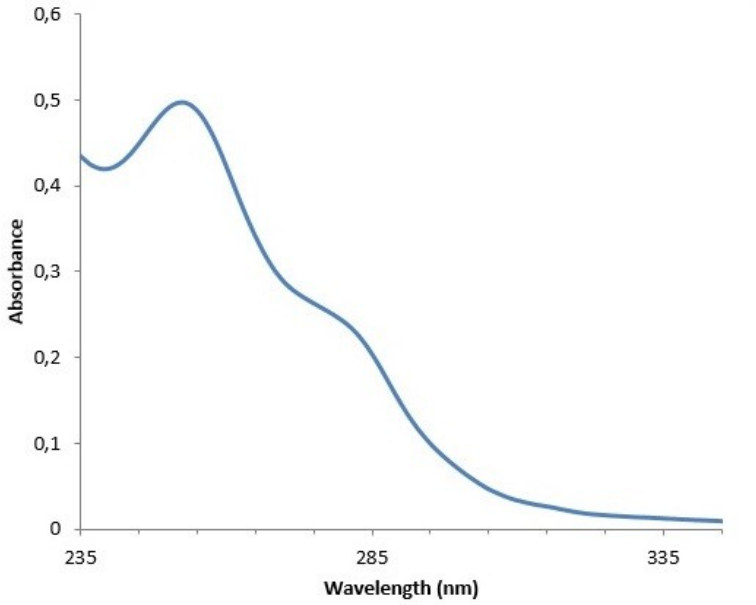


Figure 5: UV-Vis spectrum of 2 (10^{-4} mol/dm^3, $CHCl_3$)

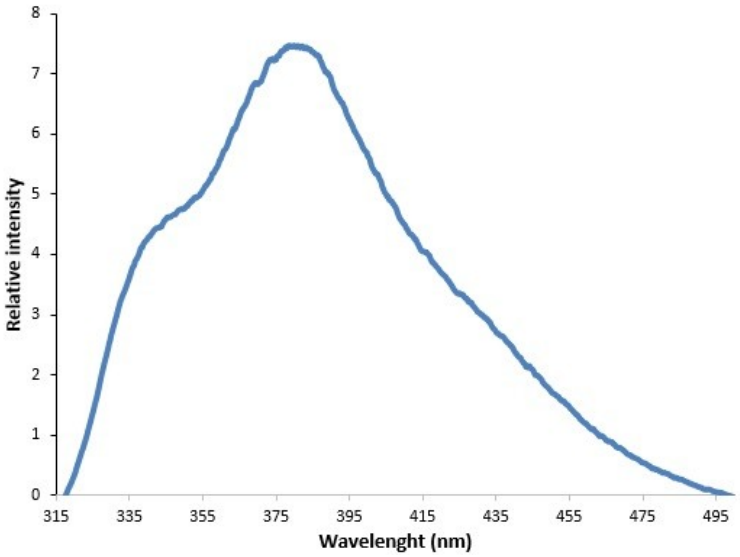
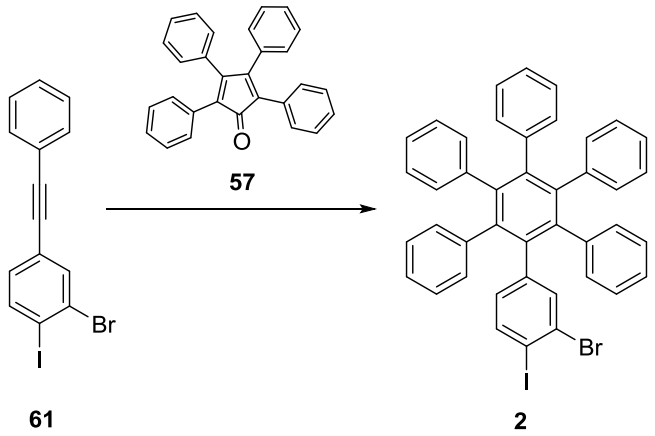


Figure 6: Fluorescence spectrum of 2 (10^{-4} mol/dm^3, $CHCl_3$, λ_{exc}= 285 nm)

4.1.3 Diels-Alder reaction catalysed by Lewis acid

Although there has been no Lewis acid catalysis of Diels-Alder reaction similar to **61**→**2** mentioned in the literature, I have decided to try it and the results of these attempts are summarised in Table 3. The course of the reactions (**61**+**57**→**2**) was monitored by TLC analysis while gradually increasing the reaction temperature. When $TiCl_4$ was used, formation of many by-products occurred even at room temperature. On contrary, no evidence of a catalytic effect was observed when $BF_3{\cdot}OEt_2$ and $Ti(O\mathit{i}Pr)_4$ were used, respectively. In both cases, the desired product was detected when the reaction mixture was heated to the same temperature as in the case of the non-catalysed reaction.

Table 3: Lewis acid catalysis of the Diels-Alder reaction



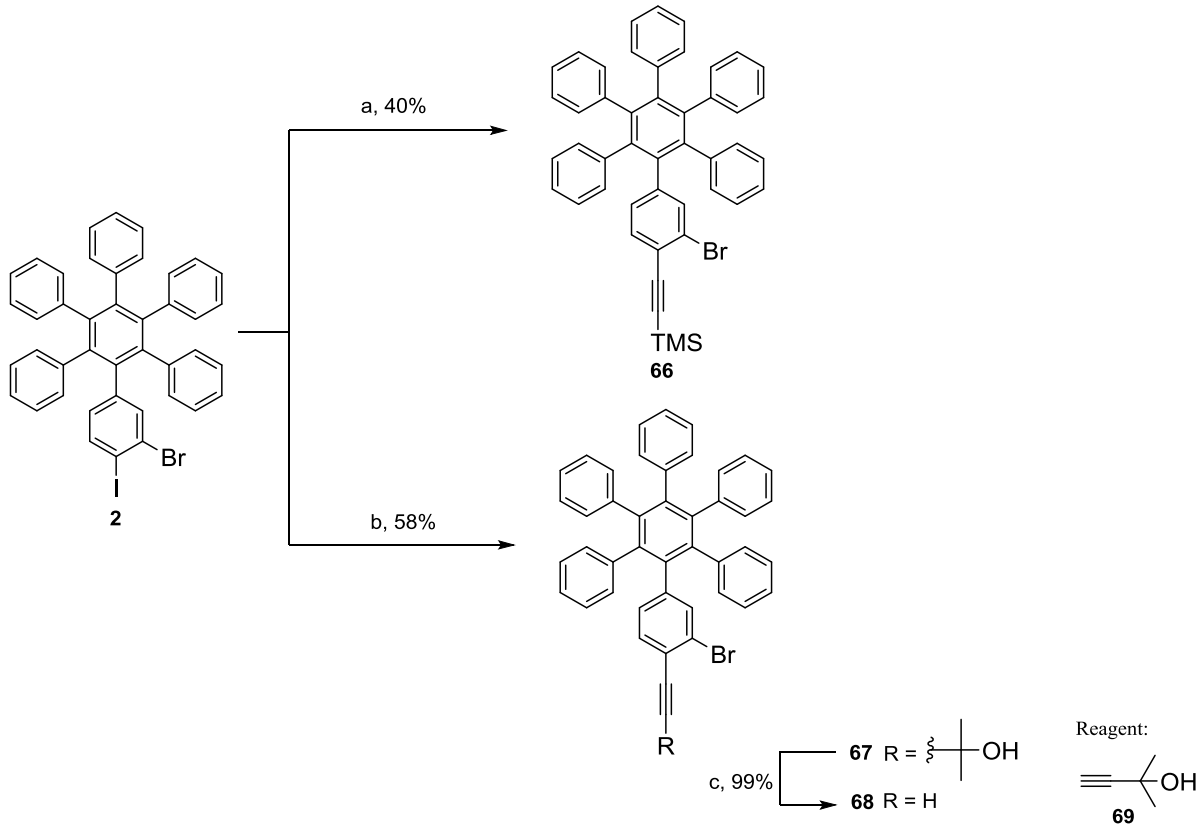
61 **2**

Entry	Lewis acid	temperature	result
1	$TiCl_4$	RT	many by-products
2	$BF_3{\cdot}OEt_2$	RT → 250 °C	no catalytic effect
3	$Ti(O\mathit{i}Pr)_4$	RT → 250 °C	no catalytic effect

All reactions were conducted in a Schlenk flask using a heating block with Ph_2O as a solvent.

4.2 Alkyne introduction

First, a triple bond was introduced by Sonogashira coupling of iodide **2** with trimethylsilylacetylene. However, the yield of the reaction was moderate and the retention factors of the product **66** and educt **2** are very similar in all tested mobile phases, which caused difficulty in isolation of the product **66** by column chromatography. Instead, the alkyne unit was introduced by Sonogashira coupling of **2** with 2-methyl-3-butyn-2-ol **69**, providing the desired product **67** in 58% yield. The following deprotection of the alkyne unit afforded **68** in quantitative yield (Scheme 15).



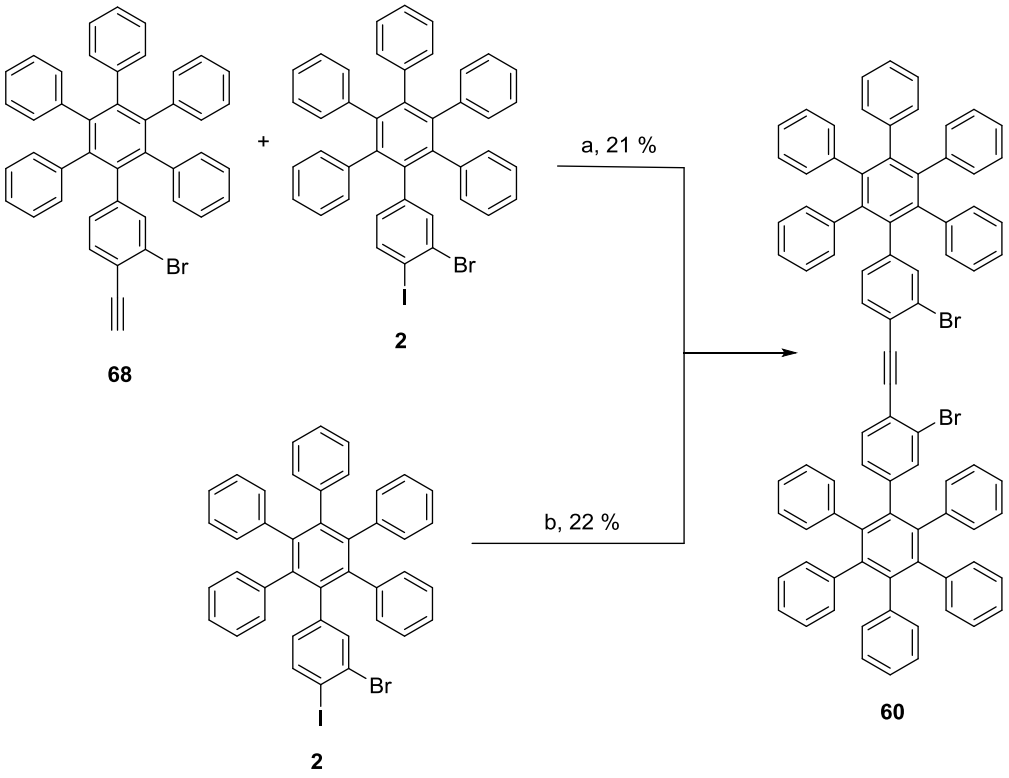
Scheme 15

Reagents and conditions:

a) TMSA (2.5 equiv.), $Pd(PPh_3)_4$ (2 mol %), CuI (4 mol %), DIPA, 60 °C, 6 h;
b) **69** (1.5 equiv.), $Pd(PPh_3)_4$ (2 mol %), CuI (4 mol %), DIPA, 60 °C, 7 h, then RT, 40 h;
c) NaOH (21 equiv.), toluene, 130 °C, 2.5 h.

4.3 Synthesis of bis(hexaphenylbenzene)acetylene derivative **60**

The symmetrical acetylene derivative **60** was prepared by two different approaches. Firstly, Sonogashira coupling of alkyne **68** with iodide **2** was carried out under conditions optimised for the Sonogashira coupling leading to amine **64**, which provided the desired product **60** in a moderate 21% yield. Secondly, **60** was prepared directly from iodide **2** using a sequence of Sonogashira coupling, *in situ* desilylation and another Sonogashira coupling, all in one reaction flask. This synthetic route provided product **60** in 22% yield. The overall yield of the step-by-step synthesis of **60** beginning from **2** (**2**→**67**→**68**→**60**) (Scheme 15 and Scheme 16) was only 12%. Therefore, the one-flask synthetic approach was used for the preparation of **60** on a larger scale (Scheme 16).



Scheme 16

Reagents and conditions:

a) $Pd(PPh_3)_4$ (20 mol %), CuI (30 mol%), DIPA, RT, 48 h;

b) 1. TMSA (1.5 equiv.), $Pd(PPh_3)_4$ (5 mol %), CuI (10 mol %), DIPA, RT, 21 h;
2. TBAF (1.5 equiv.), THF, RT, 2 h;
3. **2** (1 equiv.), $Pd(PPh_3)_4$ (5 mol %), CuI (10 mol %), DIPA, RT, 72 h.

4.4 Synthesis of triyne **59**

For the next synthetic step, a double Suzuki coupling of **60** with **70**, a variety of reaction conditions was tested. All reactions were performed on a 1mg-scale and the reaction mixtures were analysed by MALDI MS (Table 4). When using XPhos Pd G2 as a catalyst, K_3PO_4 as a base and THF as a solvent, the mass of the desired product **59** was not found in the mass spectrum. Using $Pd(PPh_3)_2Cl_2$ and K_2CO_3 in a mixture of toluene-H_2O (100:1) or $Pd_2(dba)_3$, SPhos and $LiOH \cdot H_2O$ in a mixture of THF-H_2O (100:1) led to the same result, no mass of **59** was detected. When the mixture of toluene-EtOH-H_2O (4:4:1) was used along with $Pd(PPh_3)_2Cl_2$ as a catalyst and K_2CO_3 as a base, the mass of the product was detected, as well as when $Pd(OAc)_2$ and Bu_3P were used as catalysts. However, the conversion was very low and owing to the small scale of the reaction, the amount of product, isolated by scratching out of TLC, was not sufficient for any analysis other than HR MALDI MS (Figure 7).

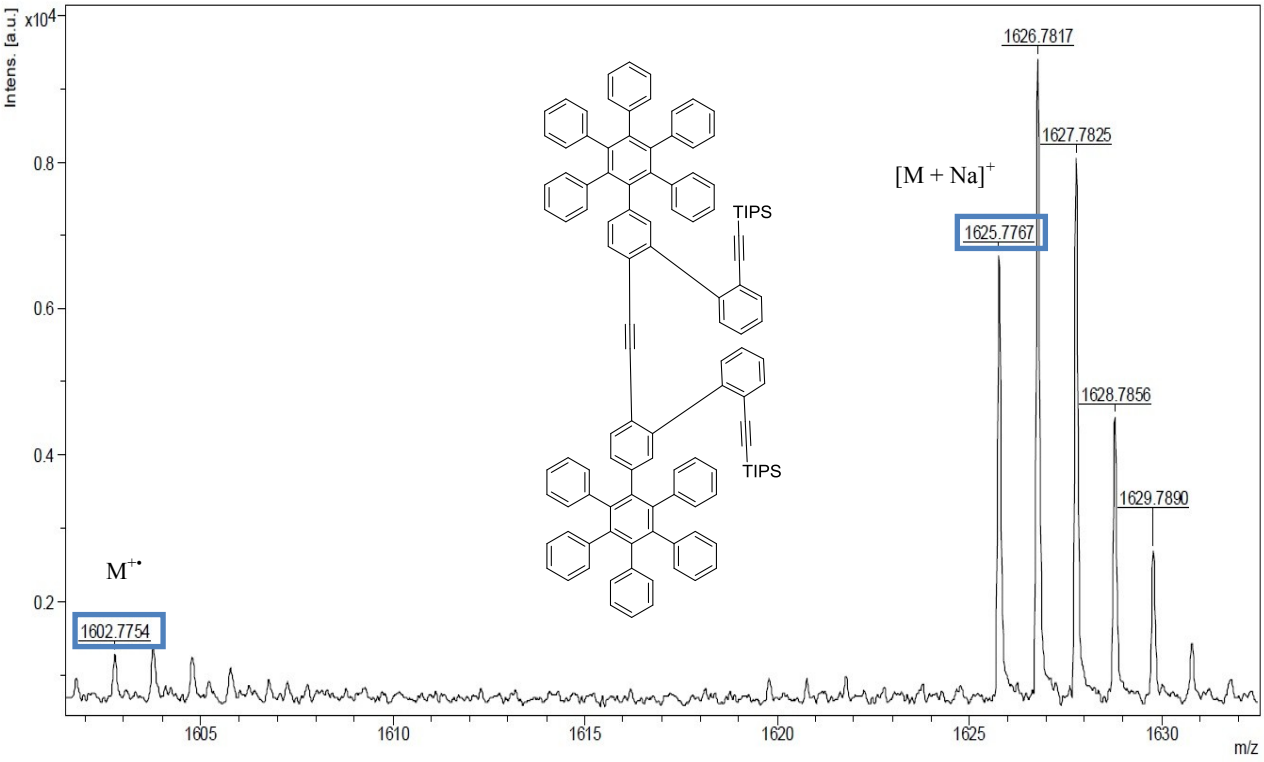
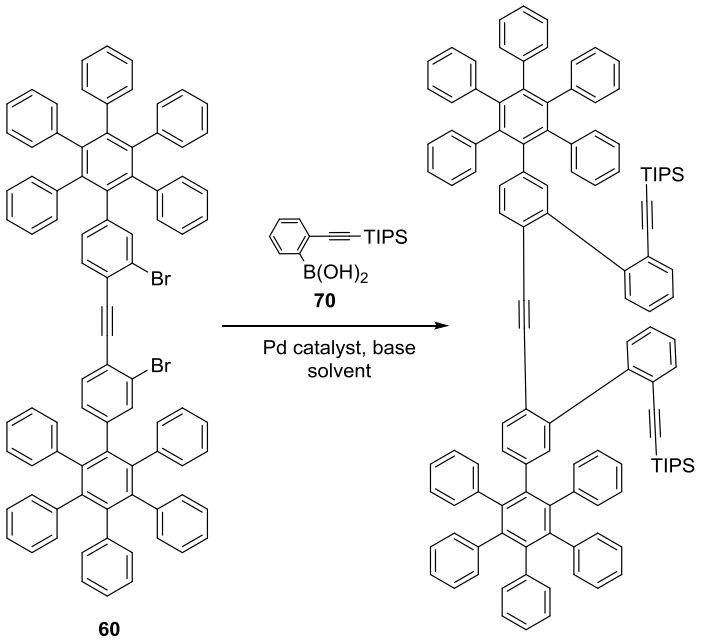


Figure 7: HR MALDI MS spectrum of triyne 59

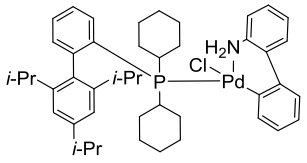
Table 4: Optimisation of reaction conditions for the synthesis of 59



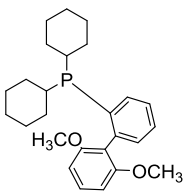
60 59

Entry	Pd catalyst	Base	Solvent	Temperature (°C)	Reaction period (h)	Product mass [1602.7828]
1	XPhos Pd G2	K_3PO_4 (0.5 M in H_2O)	THF	75	2	-
2	$Pd(PPh_3)_2Cl_2$	K_2CO_3	toluene-H_2O 100:1	90	4	-
3	$Pd_2(dba)_3$, SPhos	$LiOH{\cdot}H_2O$	THF-H_2O 100:1	50	4	-
4	$Pd(PPh_3)_2Cl_2$	K_2CO_3	toluene-EtOH-H_2O 4:4:1	90	3	+
5	$Pd(OAc)_2$, Bu_3P	K_2CO_3	toluene-EtOH-H_2O 4:4:1	90	3	+

Ligands:



XPhos Pd G2



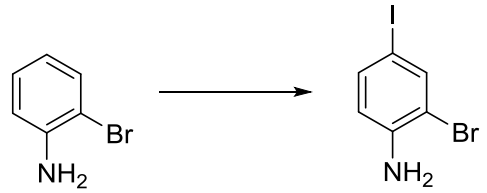
SPhos

5. Experimental section

5.1 General information

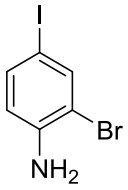
NMR spectra were acquired using Bruker Avance III HD 400 MHz and Bruker Avance III HD 600 MHz Cryo. The ^{1}H NMR spectra were measured at 400 and 600 MHz, the ^{13}C NMR spectra at 101 and 151 MHz in $CDCl_3$. The spectra were standardised using residual signals of the solvent (δ 7.26 for $CDCl_3$ in ^{1}H NMR spectra and δ 77.016 for $CDCl_3$ in ^{13}C NMR spectra). The chemical shifts are given in δ-scale, the coupling constants *J* are given in Hz. The IR spectra were measured in $CHCl_3$ using Nicolet 6700 spectrometer. The UV spectra were measured on Cary 5000 (Varian Inc.) spectrometer with pure solvent ($CHCl_3$) as a baseline. Melting points were determined on Mikro-Heiztisch Polytherm A (Hund, Wetzlar) apparatus and are uncorrected. 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 analyser which operated at 150 °C. The EI mass spectra were measured at an ionising voltage of 70 eV and were recorded in the positive ion mode. For exact mass measurement, the spectra were internally calibrated using perfluorotri-*n*-butylamine (Heptacosa). The APCI mass spectra were recorded using LTQ Orbitrap XL (Thermo Fisher Scientific) hybrid mass spectrometer equipped with an APCI ion source. The MALDI mass spectra were measured using UltrafleXtreme MALDI-TOF/TOF mass spectrometer (Bruker Daltonics). The commercially available catalysts and reagents were used as received. Diisopropylamine, triethylamine and dichloromethane were distilled from calcium hydride under nitrogen. Tetrahydrofuran and toluene were distilled from sodium/benzophenone under nitrogen. If mentioned, the solvents were degassed by three freeze-pump-thaw cycles. TLC was performed on silica gel 60 F_{254} – coated aluminium sheets (Merck). The substances were then detected using a UV lamp or a solution of $Ce(SO_4)_2 \cdot 4\ H_2O$ (1%) and $H_3P(Mo_3O_{10})_4$ (2%) in H_2SO_4 (10%). Silica gel 60 (40 – 60 μm, Fluka) or Silica gel 60 (40 – 63 μm, Sigma-Aldrich) were used for column chromatography.

5.2 Synthesis of bis(hexabenzocoronene)dibenzo[5]helicene **1**



63 **62**

5.2.1 2-Bromo-4-iodoaniline **62**[50]

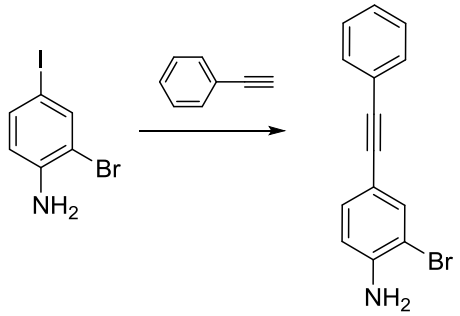


A dried three-neck round-bottom flask under inert atmosphere was charged with 2-bromoaniline **63** (10.0 g, 58.1 mmol), BTMA-ICl_2 (28.3 g, 81.4 mmol, 1.40 equiv.) and $CaCO_3$ (10.8 g, 108 mmol, 1.85 equiv.). The mixture was dissolved in dichloromethane (200 ml) and MeOH (100 ml). The flask was enwrapped in an aluminium foil and the reaction mixture was stirred at RT for 19 hours. The reaction was quenched by an addition of a saturated solution of $Na_2S_2O_3$ (550 ml). The mixture was then extracted by ethyl acetate (3×450 ml). The combined organic portions were dried over anhydrous $MgSO_4$ and the solvents were removed *in vacuo*. The residue was dissolved in a small portion of hot ethyl acetate (8 ml) and crystallised to provide the bromoaniline derivative **62** (13.9 g, 80%) in the form of a pinkish solid.

^{1}H NMR (400 MHz, $CDCl_3$): 3.81 (2 H, s), 6.53 (1 H, d, J = 8.4), 7.35 (1 H, dd, J = 2.0, 8.4), 7.68 (1 H, d, J = 2.0).

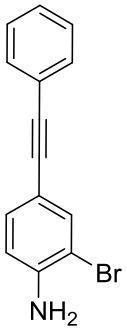
^{13}C NMR (101 MHz, $CDCl_3$): 78.45, 110.15, 117.44, 137.10, 140.12, 144.00.

All measured spectra (^{1}H NMR, ^{13}C NMR, MS, IR) corresponded with literature.[50]



62 **64**

5.2.2 2-Bromo-4-(phenylethynyl)aniline **64**



A Schlenk flask was charged with **62** (1.38 g, 4.62 mmol), $Pd(PPh_3)_4$ (107 mg, 0.09 mmol, 2 mol %) and CuI (26.0 mg, 0.14 mmol, 3 mol %). The mixture was dissolved in diisopropylamine (50 ml) and degassed using freeze-thaw-pump cycle three times. Afterwards, phenylacetylene (630 µl, 5.55 mmol, 1.20 equiv.) was added under nitrogen. The reaction mixture was stirred at 60 °C for 2 hours. A saturated solution of NH_4Cl (50 ml) was added to quench the reaction and the mixture was extracted by DCM (3×40 ml). The combined organic portions were dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica gel (hexane-ethyl acetate 8:1) to provide the diphenylethyne derivative **64** (1.09 g, 87%) as a crystalline yellow solid.

Mp: 103 - 107 °C (EtOAc).

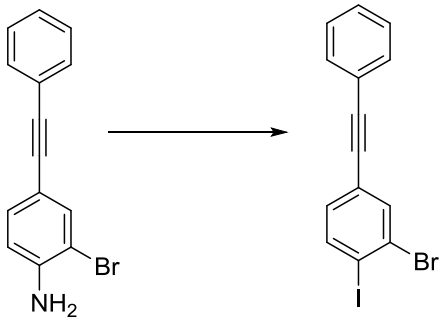
^{1}H NMR (400 MHz, $CDCl_3$): 6.71 (1 H, d, J = 8.3), 7.30 (4 H, m), 7.48 (2 H, m), 7.6 (1 H, d, J = 1.8).

^{13}C NMR (101 MHz, $CDCl_3$): 88.13, 108.41, 113.6, 115.09, 123.47, 127.95, 128.31, 131.40, 131.84, 134.21, 135.67, 144.27.

IR ($CHCl_3$): 3498 w, 3400 m, 3084 vw, 3064 w, 2222 w, 1618 s, 1599 m, 1572 vw, 1504 vs, 1485 w, 1443 w, 1405 w, 1319 w, 1289 w, 1253 w, 1177 w, 1160 w, 1153 w, 1144 w, 1070 w, 1059 w, 1025 vw, 914 w, 887 m, 861 vw, 818 m, 704 w, 691 m, 578 w, 523 w.

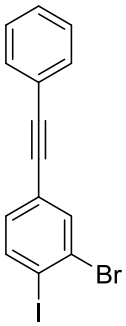
EI MS: 271 ($M^{+\bullet}$, 100), 191 (17), 165 (11), 136 (5).

HR EI MS: calcd for $C_{14}H_{10}N^{79}Br$ 270.9997, found 270.9993.



64 61

5.2.3 2-Bromo-1-iodo-4-(phenylethynyl)benzene **61**



A dried three-neck round-bottom flask under inert atmosphere was charged with **64** (3.46 g, 12.7 mmol). It was then dissolved in dichloromethane (100 ml) and the mixture was cooled to 0 °C in an ice bath. Consequently, $BF_3{\cdot}OEt_2$ (3.2 ml, 25.4 mmol, 2.0 equiv) was added through a septum, upon which the colour of the mixture changed from yellow to green. After 5 minutes *t*-BuONO (2.5 ml, 20.3 mmol, 1.6 equiv.) was added and the mixture turned red. After stirring at 0 °C for 1 hour, NaI (3.81 g, 25.4 mmol, 2.0 equiv.) in CH_3CN (25 ml) was added slowly during 25 minutes. The mixture was stirred at 0 °C for 20 additional minutes and then 20 hours after warming up to RT. Afterwards, a saturated solution of K_2CO_3 (400 ml) was poured into the mixture, the organic and water layers were separated in a separation funnel and the water layer was then extracted by DCM (4×200 ml). The combined organic portions were dried over anhydrous $MgSO_4$ and freed from the solvent *in vacuo* to give diphenylethyne derivative **61** (4.83 g, 99%) as an amorphous brown solid.

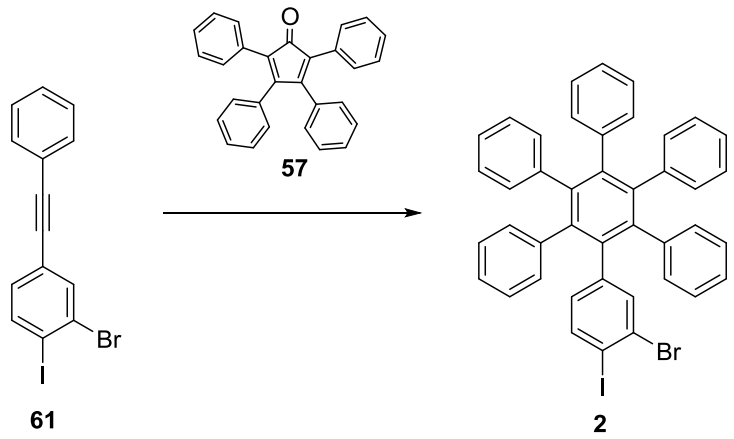
^{1}H NMR (400 MHz, $CDCl_3$): 7.15 (1 H, dd, J = 8.2, 1.9), 7.36 – 7.40 (3 H, m), 7.51 – 7.56 (2 H, m), 7.80 (1 H, d, J = 1.9), 7.85 (1 H, d, J = 8.2).

^{13}C NMR (101 MHz, $CDCl_3$): 91.80, 101.03, 105.29, 114.00, 124.94, 128.45, 128.82, 131.14, 131.67, 135.16, 140.05, 141.49.

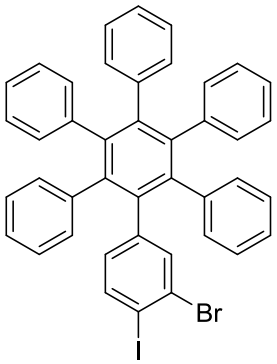
IR ($CHCl_3$): 3084 w, 3066 w, 2221 w, 1599 m, 1590 w, 1575 w, 1557 w, 1493 vs, 1460 w, 1443 m, 1364 m, 1311 w, 1178 vw, 1147 w, 1099 m, 1071 w, 1027 w, 1007 m, 916 w, 883 m, 871 m, 821 m, 690 vs, 681 w, 637 vw, 618 vw, 574 w.

EI MS: 382 ($M^{+\bullet}$, 100), 191 (10), 176 (13), 150 (12), 127 (28), 88 (9) .

HR EI MS: calcd for $C_{14}H_8{}^{79}BrI$ 381.8854, found 381.8855.



5.2.4 3-Bromo-4-iodo-3',4',5',6'-tetraphenyl-1,1':2',1''-terphenyl **2**



A Schlenk flask was charged with **61** (1.00 g, 2.61 mmol) and tetraphenylcyclopentadienone **57** (1.01 g, 2.61 mmol, 1.0 equiv). The mixture was suspended in diphenylether (2 ml) and refluxed in a heating block at 250 °C for 7 hours. Afterwards, diphenylether was removed from the reaction mixture by distillation *in vacuo*. The crude product was purified by flash chromatography on silica gel (hexane – DCM 7:3) to provide hexaphenylbenzene derivative **2** (1.30 g, 67%) as an amorphous light yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): 6.62 (1 H, dd, J = 8.2, 2.0), 6.79 – 6.94 (25 H, m), 7.21 (1 H, d, J = 2.0), 7.38 (1 H, d, J = 8.2).

^{13}C NMR (151 MHz, $CDCl_3$): 98.68, 120.92, 125.64, 125.66, 125.98, 126.77, 129.97, 127.38, 130.95, 131.00, 131.03, 131.82, 135.15, 137.68, 138.28, 139.75, 139.92, 139.94, 140.02, 140.35, 140.76, 142.21.

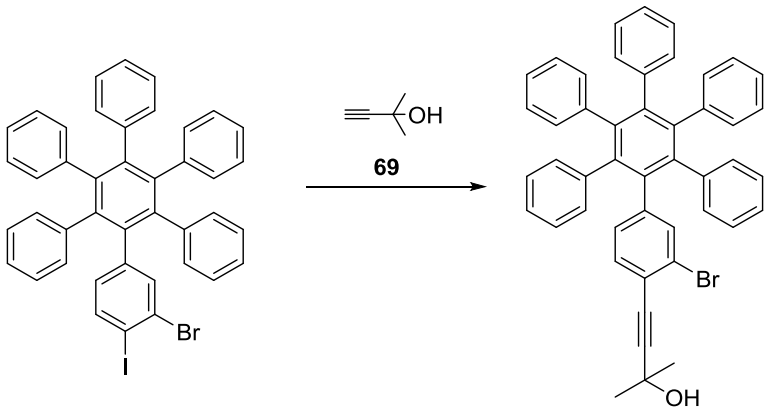
IR ($CHCl_3$): 3105 w, 3084 vw, 3061 m, 1601 w, 1578 w, 1560 w, 1496 w, 1475 w, 1442 w, 1388 w, 1362 w, 1178 w, 1147 w, 1100 w, 1075 w, 1028 w, 886 w, 875 w, 818 w, 700 s, 629 w.

APCI MS: 738 ($M^{+\bullet}$).

HR APCI MS: calcd for $C_{42}H_{28}{}^{79}BrI$ 738.0414, found 738.0416.

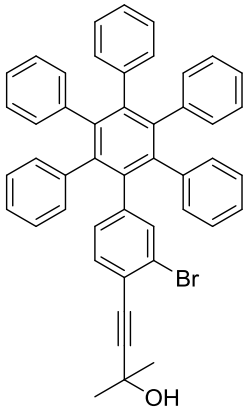
UV-Vis ($CHCl_3$, 10^{-4} mol/dm^3)**:** λ_{max} = 252.

Fluorescence ($CHCl_3$, 10^{-4} mol/dm^3, λ_{exc} = 285 nm): λ_{max} = 379 nm.



2 67

5.2.5 4-(3-Bromo-3',4',5',6'-tetraphenyl-[1,1':2',1''-terphenyl]-4-yl)-2-methylbut-3-yn-2-ol **67**



A pressure tube was charged with **2** (50 mg, 68 µmol), $Pd(PPh_3)_4$ (1.6 mg, 1.4 µmol, 2 mol %) and CuI (0.50 mg, 2.7 µmol, 4 mol %) in diisopropylamine (2 ml). The mixture was degassed using freeze-pump-thaw cycle three times. Upon warming up to RT, 2-methyl-3-butyn-2-ol **69** (10 µl, 103 µmol, 1.5 equiv.) was added to the mixture under inert atmosphere. Afterwards, the mixture was heated to 60 °C for 4 hours and then stirred at RT for 20 hours. The reaction was quenched by addition of a saturated solution of NH_4Cl (5 ml) and afterwards the mixture was extracted by DCM (3×5 ml). The combined organic fractions were extracted by water (2×10 ml), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica gel (DCM – hexane 8:2) to give **67** (27 mg, 58%) as an amorphous white solid.

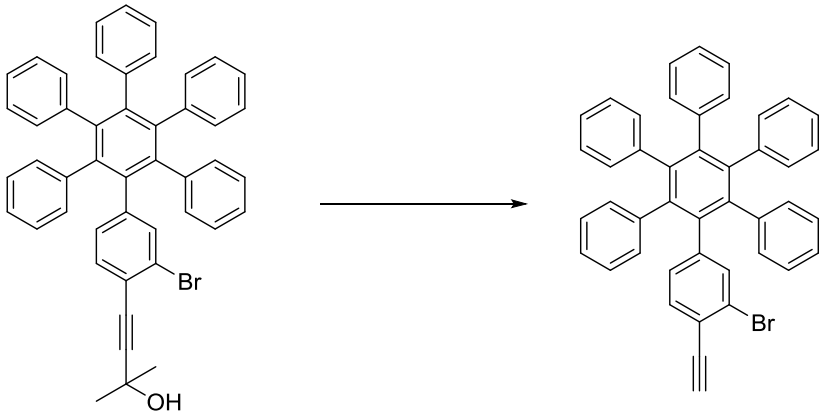
^{1}H NMR (400 MHz, $CDCl_3$): 1.54 (6 H, s), 6.71 (1 H, dd, J = 8.0, 1.7), 6.76 – 6.96 (25 H, m), 7.08 (1 H, d, J = 1.6), 7.22 (1 H d, J = 8.0).

^{13}C NMR (101 MHz, $CDCl_3$): 31.26, 81.11, 85.71, 97.58, 121.23, 123.95, 124.08, 125.34, 125.68, 126.63, 126.88, 127.00, 130.02, 131.09, 131.28, 131.40, 135.25, 139.92, 140.11, 140.21, 140.30, 140.55, 142.60.

IR ($CHCl_3$): 3597 w, 3084 w, 3061 w, 3034 vw, 2985 w, 2963 w, 2872 w, 1601 w, 1578 vw, 1544 vw, 1510 vw, 1496 m, 1462 vw, 1442 w, 1401 w, 1378 w, 1365 w, 1180 vw, 1161 w, 1113 vw, 1075 w, 1029 w, 1001 vw, 959 w, 910 w, 888 vw, 838 w, 818 w, 700 vs, 633 vw.

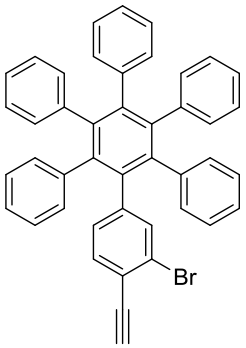
MALDI MS: 717 $(M+Na)^+$, 694 $(M^{+\bullet})$.

HR MALDI MS: calcd for $C_{47}H_{35}{}^{79}BrO$ 694.1866, found 694.1887.



67 68

5.2.6 3-Bromo-4-ethynyl-3',4',5',6'-tetraphenyl-1,1':2',1''-terphenyl **68**



A mixture of **67** (13 mg, 18.7 µmol) and mashed NaOH (20 mg, 402 µmol, 21 equiv.) in toluene was refluxed at 130 °C for 2.5 hours. The reaction mixture was filtered through a frit with a layer of silica gel, which was consequently washed with $CHCl_3$ and the filtrate was evaporated *in vacuo* to give hexaphenylbenzene derivative **68** (12 mg, 99%) as an amorphous white solid.

^{1}H NMR (401 MHz, $CDCl_3$): 3.22 (1 H, s), 6.73 (1 H, dd, J = 8.0, 1.6), 6.78 – 6.96 (25 H, m), 7.01 (1 H, d, J = 8.0), 7.09 (1H, d, J = 1.6).

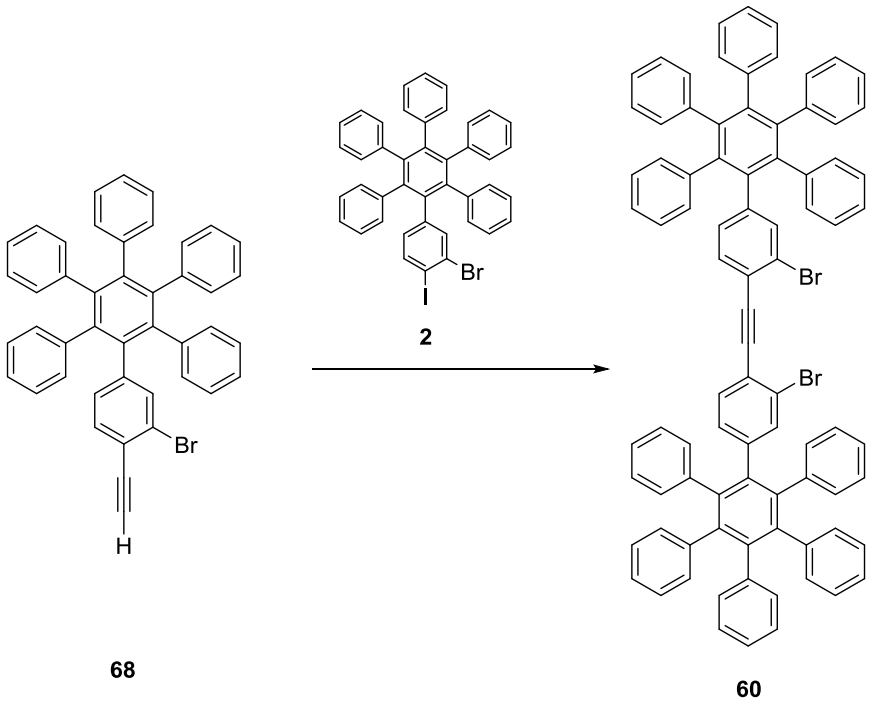
^{13}C NMR (101 MHz, $CDCl_3$): 98.23, 107.16, 122.61, 123.74, 125.33, 125.37, 125.40, 126.65, 126.70, 126.89, 126.94, 127.03, 128.00, 129.20, 131.04, 131.08, 131.28, 131.34, 135.14, 137.43, 139.86, 140.17, 140.56, 157.24.

IR ($CHCl_3$): 3301 w, 1603 w, 1589 w, 1496 w, 1466 w, 1443 w, 1397 w, 1305 w, 1187 w, 1081 w, 1028 w, 839 w, 699 m.

APCI MS: 637 ($M^{+\bullet}$).

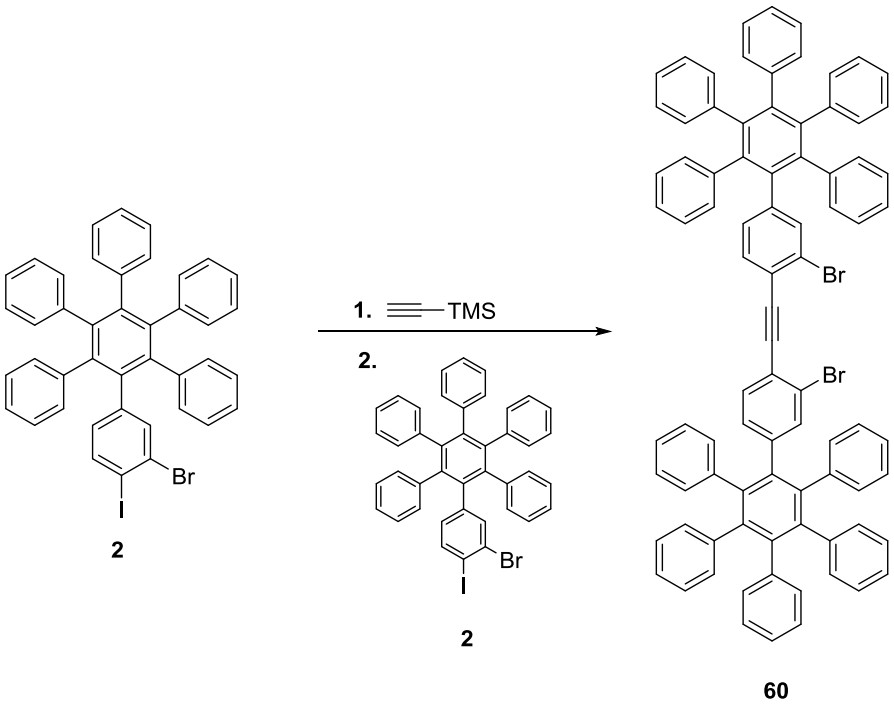
HR MALDI MS: calcd for $C_{44}H_{30}{}^{79}Br$ 637.1525, found 637.1519.

5.2.7 1,2-Bis(3-bromo-3',4',5',6'-tetraphenyl-[1,1':2',1''-terphenyl]-4-yl)ethyne **60**



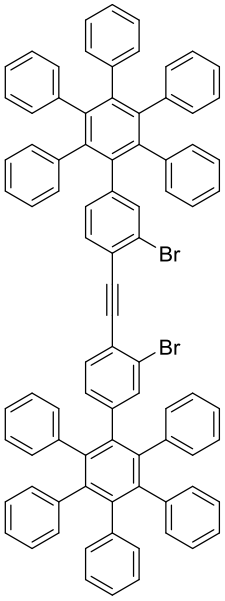
5.2.7.1 Synthesis from **68**

A Schlenk flask was filled with **2** (12.7 mg, 17.2 µmol, 0.9 equiv.), $Pd(PPh_3)_4$ (4.00 mg, 3.77 µmol, 20 mol %) and CuI (1.00 mg, 5.67 µmol, 30 mol %) and the mixture was dissolved in diisopropylamine (0.5 ml). In a second Schlenk flask, **68** (12.0 mg, 18.9 µmol) was dissolved in diisopropylamine (1.5 ml). Both solutions were degassed using freeze-pump-thaw cycle three times. After warming up to room temperature, the solution of **68** in diisopropylamine was added to the reaction mixture through a septum. The mixture was stirred at RT for 48 hours and then the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica gel (DCM – hexane 3:7) to give **60** (5 mg, 21%) as a light yellow crystalline solid.



5.2.7.2 One flask procedure from **2**

A Schlenk flask was charged with **2** (70 mg, 95 µmol), $Pd(PPh_3)_4$ (5.5 mg, 4.7 µmol, 5 mol %) and CuI (1.8 mg, 9.5 µmol, 10 mol %), the mixture was dissolved in diisopropylamine (5 ml) and degassed three times using the freeze-pump-thaw cycle. After warming of the mixture to RT, trimethylsilylacetylene (20 µl, 140 µmol, 1.5 equiv.) was added through a septum and reaction mixture was stirred at RT for 20 hours. Consequently, a degassed solution of tetra-n-butylammonium fluoride (300 µl, 142 µmol, 1.5 equiv.) in THF was added through a septum (142 µmol, 1.5 equiv.). The mixture was left stirring at RT for 2 hours. A second Schlenk flask was filled with **2** (70 mg, 95 µmol, 1.0 equiv.), $Pd(PPh_3)_4$ (5.5 mg, 4.7 µmol, 5 mol %) and CuI (1.8 mg, 9.5 µmol, 10 mol %). The mixture was dissolved in diisopropylamine (4 ml) and degassed using the freeze-pump-thaw cycle three times. After warming up to RT, the content of the second Schlenk flask was added to the reaction mixture by a syringe through a septum. The mixture was stirred at room temperature for 72 hours. The reaction was quenched by adding a saturated NH_4Cl solution (20 ml). The mixture was extracted by DCM (3×20 ml) and the joined organic portions were then extracted by water (3×50 ml), collected and dried over anhydrous $MgSO_4$. The organic solution was then evaporated *in vacuo* and the crude product was purified by flash chromatography on silica gel (DCM – hexane 3:7) to give the product **60** (26 mg, 22%) in the form of a crystalline yellow solid.



Mp: over 398 °C (DCM – hexane 3:7)

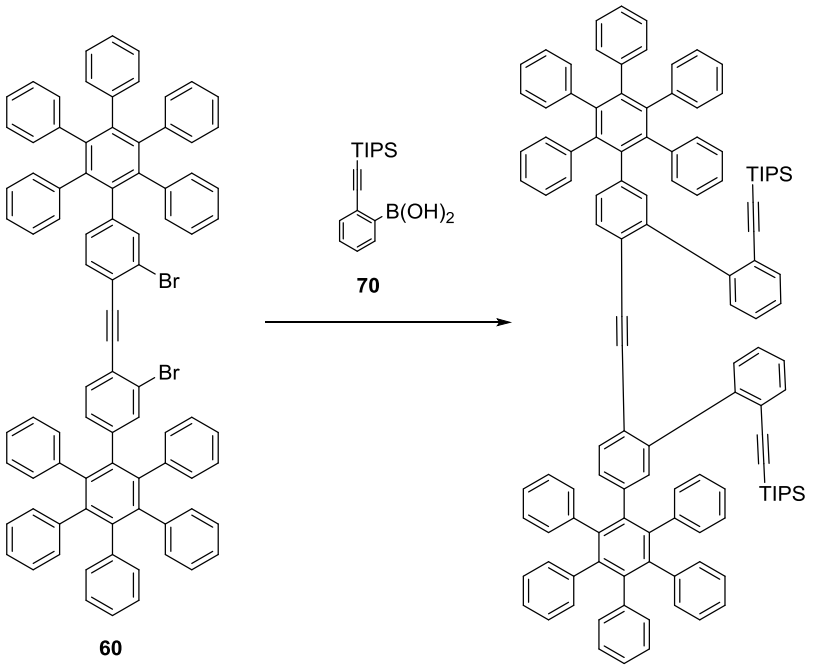
^{1}H NMR (400 MHz, $CDCl_3$): 6.70 (2 H, dd, *J* = 8.0, 1.6), 6.79 – 6.94 (50 H, m), 6.99 (2 H, d, *J* = 7.9), 7.07 (2 H, d, *J* = 1.5).

^{13}C NMR (101 MHz, $CDCl_3$): 81.22, 125.37, 125.79, 126.65, 126.93, 127.04, 131.05, 131.28, 132.54, 133.49, 135.45, 135.78, 137.99, 138.71, 139.78, 140.05, 140.13, 140.25, 140.56, 143.64, 159.54.

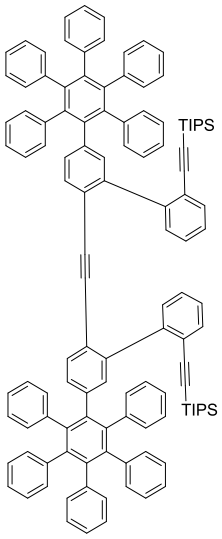
IR ($CHCl_3$): 3084 w, 3058 w, 2199 vvw, 1600 w, 1593 vw, 1578 vw, 1526 vw, 1496 w, 1442 w, 1401 w, 1179 w, 1157 vw, 1073 w, 1028 w, 1001 vw, 918 w, 910 vw, 889 vw, 812 w, 699 vs.

MALDI MS: 1246 ($M^{+\bullet}$).

HR MALDI MS: calcd for $C_{86}H_{56}{}^{79}Br_2$ 1246.2743, found 1246.2758.



5.2.8 1,2-Bis(3',4',5',6'-tetraphenyl-2'''-((triisopropylsilyl)ethynyl)-[1,1':2',1'':3'', 1'''-quaterphenyl]-4''-yl)ethyne **59**



A pressure tube was charged with **60** (1 mg, 0.8 µmol), $Pd(PPh_3)_2Cl_2$ (0.1 mg, 0.14 µmol, 18 mol %), K_2CO_3 (0.5 mg, 3.6 µmol, 4.5 equiv) and **70** (1 mg, 3.3 µmol, 4.1 equiv.). The mixture was dissolved in a mixture of toluene-EtOH-H_2O (4:4:1, 300 µl) and bubbled by nitrogen for 15 min. Consequently, the reaction mixture was heated to 90 °C for 3 hours under nitrogen atmosphere. After cooling to room temperature and addition of water (3 ml), the mixture was extracted by DCM (3×5 ml). The combined organic portions were then extracted by water (1×15 ml), dried over anhydrous $MgSO_4$ and the solvents were removed *in vacuo*. The mixture was then dissolved in a small amount of $CHCl_3$ (1 ml) and separated on a TLC plate (DCM – hexane 4:6). The part of the TLC with the corresponding spot was scratched out and extracted by $CHCl_3$, the solvent was then removed *in vacuo* and the product was analysed by MALDI MS.

MALDI MS: 1626.8 ($[M + Na]^+$).

HR MALDI MS: calcd for $C_{120}H_{106}NaSi_2$ 1625.7725, found 1625.7767;

calcd for $C_{120}H_{106}Si_2$ 1602.7828, found 1602.7754.

6. Conclusion

A synthesis of hexaphenylbenzene derivative **2** has been successfully developed with a special focus on tuning the reaction conditions of Diels-Alder reaction, which was one of the crucial steps of the synthesis of laterally extended helicene **1**. The developed synthetic route allowed the synthesis of the hexaphenylbenzene derivative **2** in high purity and in reasonable yield and is scalable. Therefore, the newly synthesised compounds could be fully characterised and used in further steps of the synthetic route towards the desired helicene **1**.

Many obstacles had to be overcome during the development of further steps in helicene **1** synthesis, most likely due to the low solubility of the intermediates containing one or even two hexaphenylbenzene moieties (*e.g.* **60**, **67** and **68**).

However, despite the troubles, I have successfully synthesised tryine **59**. Optimisation of the reaction conditions of this synthetic step (**60**→**59**) in order to obtain the product in reasonable yield is now the priority of the future research regarding this project. Afterwards, just a few steps remain in the synthetic route towards the desired laterally extended helicene **1**.

7. 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. My thanks belong to all the members of our research group for their advice and for creating a pleasant working enviroment. Particularly, I would like to thank Ing. Jan Holec for his help, counsel and immense patience throughout the whole project.

I would like to thank RNDr. Miloš Buděšínský, CSc. for measuring NMR spectra, Ing. Beáta Seidlerová and Ing. Pavel Fiedler for measuring IR spectra, RNDr. Lucie Bednárová, CSc. for measuring the fluorescence spectrum and the analytical department at IOCB for mesuring mass spectra.

Last but not least, my thanks belong to all my friends, without whom my studies would not be the same and especially to my parents, for their understanding and their support in all my decisions.

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