Chemistry Department, University of Fribourg

Master Thesis

Synthesis of a new bowl-shaped polyarene aiming molecular hydrogen storage

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Abstract

Efficient hydrogen storage is one of the major hurdles towards a potential hydrogen economy. Curved molecules are very interesting for this purpose because of their permanent electrical dipole moment, which can induce a dipole moment on H_2 molecules increasing therefore the dipole-dipole interaction and so their adsorption.

This work presents the synthesis of a new bowl-shaped polyarene based on curved corannulene's motive. Since corannulene is known for its ability to adsorb hydrogen, the greater surface and curvature of our target molecule is assumed to increase the hydrogen adsorption.

The plan was to start from phenanthrene-9,10-dione and 1-phenylpropan-2-one to obtain a planar polycyclic aromatic hydrocarbon (PAH) containing a five-membered ring. Then, *via* a cross-coupling reaction and a classical Scholl reaction under Kovacic conditions, it would have been possible to obtain the bowl-shaped molecule.
Unfortunately, the synthesis of the first precursor presented obstacles and, from three proposed strategies, only one allowed the obtainment of the planar PAH in acceptable yield. Moreover, only one attempt for the coupling reaction was made and, because of the small amount and the impurity of the obtained product, no Scholl reaction was performed. Therefore, the desired bowl-shaped polyaromatic compound has not been obtained and the efficacy of the Scholl reaction for this synthesis has not been tested.

Acknowledgments

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AcOH	Acetic acid
Ar	Aromatic
BEH	Ethylene Bridged Hybrid
CRC	Cove-region closure process
DBU	1,8-Diazabicycloundec-7-ene
DCM	Dichloromethane
DCTB	2-[(2E)-3-(4-tert-Butylphenyl)-2-methylprop-2-enylidene]malononitrile
DEG	Diethylene glycol
DFT	Density functional theory
DMAP	4-Dimethylaminopyridine
DOE	U.S. Department of Energy
E_{ads}	Adsorption energy
EI	Electron ionization
ESI	Electrospray ionization
EtOAc	Ethyl acetate
FT/ICR	Fourier transform ion cyclotron resonance
FVP	Flash vacuum pyrolysis
GC	Gas chromatography
GGA	Generalized gradient approximation
ILD	Interlayer distance
LDA	Local density approximation
MALDI	Matrix-assisted laser desorption/ionization
MeCN	Acetonitrile
MOF	Metal organic framework
MS	Mass spectrometry
MWCNT	Multi-walled carbon nanotube
NMR	Nuclear magnetic resonance
PAH	Polycyclic aromatic hydrocarbon
PEMFC	Polymer electrolyte membrane fuel cell
PDA	Photodiode array
ppm	Part per million
PW91	Exchange component of Perdew and Wang’s 1991 functional

SPT	Standard pressure and temperature
SWCNT	Single-walled carbon nanotube
t-BuOK	Potassium *tert*-butoxide
t-BuLi	*tert*-Butyllithium
TEA	Triethylamine
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMS	Tetramethylsilane
TsCl	p-toluenesulfonyl chloride
TUV	Tunable UV
u	Unified atomic mass unit
UPLC	Ultra-high Pressure Liquid Chromatography
USCAR	U.S. Council for Automotive Research
UV	Ultraviolet
wt	Weight

1

INTRODUCTION

1.1 World energy needs

The doubling of the world's energy consumption over the next fifty years will require significant changes in the way to produce, distribute, store and use energy. [1] A crucial step in this process will be reducing the dependence on finite carbon-based fossil fuels. Because two-thirds of the oil used in the United States goes to meet the demands of the transportation industry, these alternative energy sources should also be able to satisfy these important industry's requirements.[2]

Batteries store electrical energy efficiently, but they are not economic for large scale storage; for transportation they are only practical in smaller vehicles with a limited driving range and certainly not in trucks, ships or airplanes.[3]

Since the development of the hydrogen fuel cell (*Figure 1*), hydrogen is considered as one of the best energy carriers in future energy systems.[4]

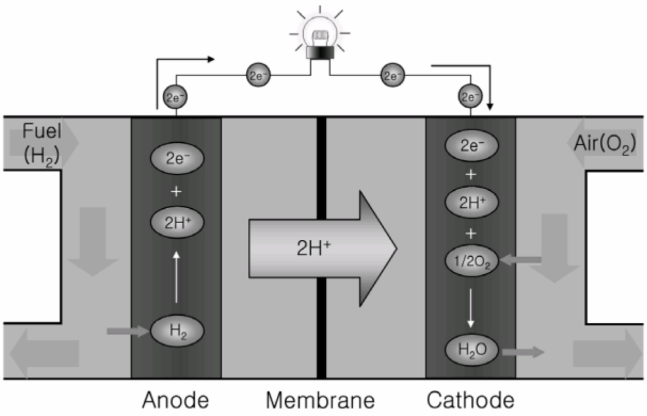


Figure 1. Schematic structure and operational principle of a polymer electrolyte membrane fuel cell (PEMFC). [5] When molecules of hydrogen are in contact with the negative anode catalyst layer, they splits into protons and electrons. The protons pass straight through the electrolyte, whilst the electrons produce electricity as they pass through the external circuit. The circuit returns the electrons to the positive cathode catalyst layer, where they bond and join with oxygen creating water and heat.

1.2 Hydrogen as ecologically clean fuel

Hydrogen is considered to be an ideal replacement for fossil fuels for many reasons. 1) It is not poisonous and the raw material for its production (water) is practically unlimited. 2) The chemical energy produced per mass of hydrogen is 142 MJ/kg, which is three times higher than in the case of chemical fuels such as liquid hydrocarbons, which provide 47 MJ/kg energy.[6] 3) It is easily combusted in an engine or converted back to electricity in a fuel cell (*Figure 2*).

Whether hydrogen can be considered as a clean form of energy on a global scale depends therefore on the primary energy that is used to split water.[7]

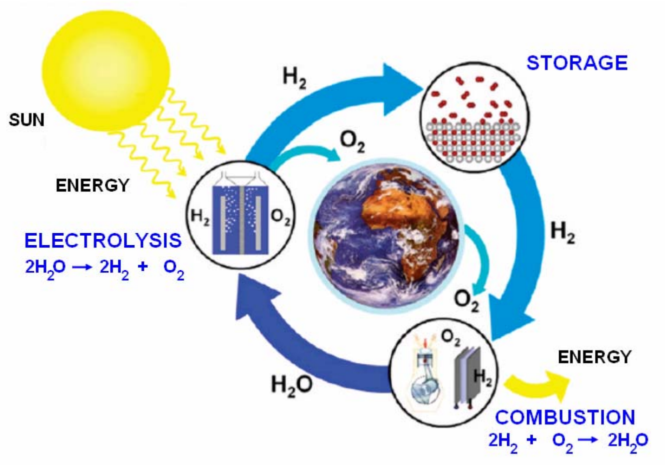


Figure 2. Hydrogen Cycle scheme.[2] Hydrogen can be extracted from water by electrical energy through electrolysis and later, when the energy is needed, hydrogen can recombine with oxygen from the air releasing mechanical energy through a combustion engine by means of an hydrogen fuel cell. The end product is water and the cycle is closed.

1.3 Hydrogen Storage

Hydrogen storage remains one of the more challenging technological barriers to the advancement of hydrogen fuel cell technologies for mobile applications.[8] Since hydrogen is a gas at standard pressure and temperature (SPT), it has a low volumetric density. Although one kilogram of H_2 can replace about 3 kg (3.79 L) of gasoline, on a volumetric scale more than 13000 L (≈ volume of a midsize car) of H_2 gas are necessary to replace just 3.79 L of gasoline at SPT.[1]

An ideal chemical hydrogen storage material will have a low molar weight (to decrease the reservoir/storage mass), be inexpensive, have rapid kinetics for absorbing and desorbing H_2 in the -40/85 °C temperature range, and store large quantities of hydrogen reversibly. The U.S. Department of Energy (DOE), in consultation with the U.S. Council for Automotive Research (USCAR), has established an evolving set of stringent technical targets for the onboard hydrogen storage systems shown in *Table 1*.[9, 10]

Storage parameter	**Units**	**New targets**	
		2017	**Ultimate**
Gravimetric capacity	kWh/kg	1.8	2.5
	wt% H_2	5.5	7.5
Volumetric capacity	kWh/L	1.3	2.3
	gH_2/L	40	70
Delivery temperature	°C (min/max)	-40/85	-40/85
Operational cycle life (1/4 tank to full)	Cycles	1500	1500
Pressure	bar (min/max)	5/12	3/12
Kinetics	$(gH_2/s)/kW$	0.02	0.02
System fill time (5 kg)	min	3.3	2.5
Cost	$/kW net	To be determined	

Table 1. The hydrogen commercialization target as set out by DOE.

No existing systems meet these conditions, therefore that much basic research needs to be done to better understand the interaction of hydrogen with matter.[2]

The current status of hydrogen storage is summarized in *Figure 3*. While hydrogen density increase from high-pressure tanks to storage in liquid form and in various solids, its accessibility continually decreases.

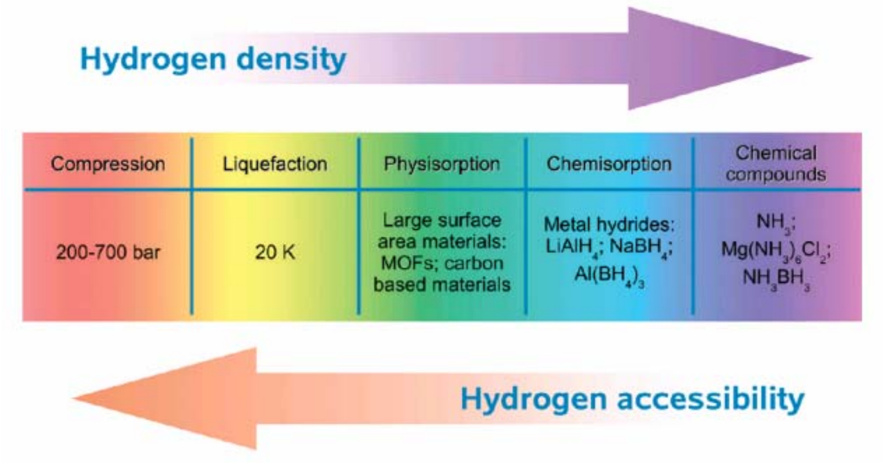


Figure 3. Hydrogen density and accessibility of different storage systems.[2]

The storage challenge is given by the need to fight the kinetic energy of the volatile hydrogen molecules. Basically there are three ways to go. (1) The gas can be confined at high pressure by external physical forces. (2) The energy of the molecules can be withdrawn by cooling and, ultimately, the gas condenses into a liquid. (3) The molecules can be bound to a surface or inside a solid material. This way hydrogen is more or less immobilized and, like in the case of liquid hydrogen, most of its kinetic energy is removed.[3]

1.3.1 High-pressure hydrogen storage

Despite many attempts to develop advanced techniques, pressurization is still dominating the field of H_2 storage. Compressed hydrogen is kept in a dense state by external physical forces only, like it happens in a pressure vessel. The gravimetric storage capacity ranges from 1-2 wt.% for 200 bar steel tanks to 5-10 wt.% for high pressure fibre composite tanks (more expensive).[3]

Volumetric capacity, high pressure, weight, conformability and cost, essentially dictated by the cost of the carbon fiber used for light-weight structural reinforcement, are thus key challenges for this storage method.[11]

1.3.2 Liquid Hydrogen storage

The energy density can be improved by storing hydrogen in a liquid state, in which hydrogen is kept together by weak chemical forces (van der Waals) at very low temperature (20 K) but at ambient pressure.[3] However, 30% of the heating value of hydrogen is required for the refrigeration process. Moreover, hydrogen boil-off (~1%/day) must be minimized or eliminated; insulation is therefore required, reducing system's gravimetric and volumetric capacity.

Liquid hydrogen tanks can store more hydrogen in a given volume (0.070 kg/L) than compressed gas tanks (0.030 kg/L for 690 bar gas tanks). If you include the mass of the tank, the gravimetric storage capacity is about 10%.[12]

A new hybrid tank concept combining both high-pressure gaseous and cryogenic storage is being studied. This method does not require temperatures as low as for liquid hydrogen, decreasing the energy penalty for liquefaction and the evaporative losses.[11]

1.3.3 Solid-state storage methods

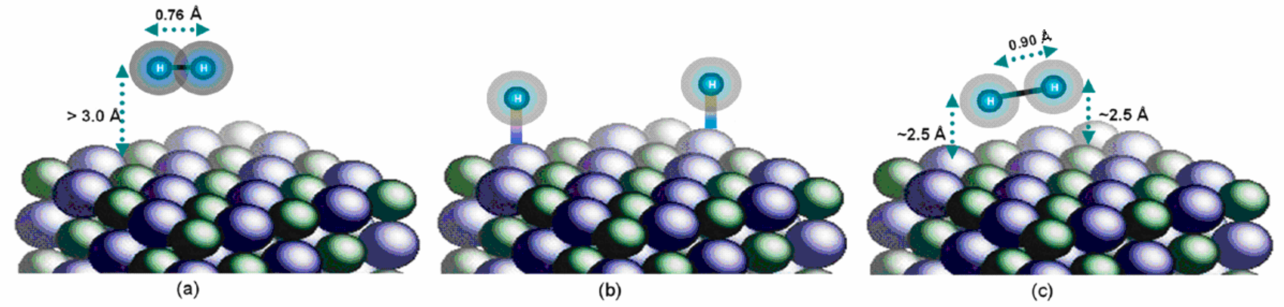


Figure 4. Adsorption of hydrogen on substrate.[2] (a) Physisorption, (b) chemisorption and (c) quasi-molecular bonding.

There are mainly three different ways that hydrogen can be adsorbed on a material (*Figure 4*): the *physisorption* (a), in which hydrogen remains molecular and binds weakly on the surface with a binding energy ranging from about 0.01 to 0.10 eV (1 to 10 kJ/mol, van der Waals interactions) and desorbing at very low temperatures; the *chemisorption* (b), in which the H_2 molecule dissociates into individual atoms, migrates into the material, and binds chemically with a binding energy lying in the 2-4 eV (200-400 kJ/mol) range, desorbing therefore at higher temperatures; and finally an intermediate situation between physisorption and chemisorption (c), with a binding energy in the 0.1-0.8 eV (10-80 kJ/mol) range, where the bond between H atoms in a H_2 molecule is weakened but not broken, ideal for hydrogen storage under ambient conditions.[2, 6]

1.3.3.1 Complex hydrides

Metal hydrides

Interstitial metal hydrides, in which hydrogen is bound into interstitial positions in a host metal alloy in a more or less metallic way, are the most studied reversible metal hydride systems for hydrogen storage. They are considered very safe and easy to operate but, despite the desorption capacity under ambient conditions, their main drawback is the price and their poor reversibility. Examples are plentiful such as $LaNi_5H_6$, $TiFeH_{\sim 2}$, and $LaNi_5$-based alloys for nickel metal hydride batteries, which demonstrates reversible hydrogen capacities of 1-2 wt% at STP.[3]

Other reversible metal hydrides that obey the same thermodynamic laws but with different pressure-temperature characteristics are for example Mg_2NiH_4 (3.6 wt% of hydrogen reversibly released at 255 °C and 1 bar)[3], $NaAlH_4$ (5.5 wt% at 250 °C and 1 bar, or ~4 wt% at 160 °C if doped with Ti-based catalysts)[3, 9] and MgH_2 (7.6 wt% at 300 °C and 1 bar).[3] In these compounds hydrogen is strongly bonded to central atoms; as a consequence, the hydrogen release reactions typically require a significant energy input and also elevated temperatures to overcome the activation energy,[2] going therefore beyond the maximum delivery temperature established by the DOE (85 °C).[3,10]

Chemical hydrides

Chemical hydrides are not directly reversible under moderate hydrogenation conditions and typically require “off-board” chemical regeneration. Since the barrier to hydrogenation can be thermodynamic, kinetic, or both, these materials can have strong decomposition enthalpies.[1]

Solid sodium borohydride ($NaBH_4$), for example, begins to release most of its hydrogen at approximately 240 °C by thermal decomposition, but optimal gas production is only achieved over 450 °C.[13]

Through a low temperature hydrolysis reaction, on the contrary, H_2 is generated at rapid rates by the reaction with water over a catalyst (*Equation 1*):

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 + \text{Heat} \qquad \textit{Equation 1}$$

The introduction of water contributes favourably by increasing the effective storage capacity of the system. In fact, $NaBH_4$ can be stored as solid and then either liquid water or vapour water is provided when hydrogen is needed. The highest effective capacity ever measured is 9.0 wt% with liquid water.[14]

The main drawbacks of such a system are the limited solubility of sodium borohydride, the formation of borate by-products and the energy costs of reducing borate back to borohydride in solution.[13]

Moreover, there is a class of weakly bound chemical hydrides that can release hydrogen at rapid rates through a low temperature thermolysis reaction. One of the more popular examples is ammonia borane (NH_3BH_3), for which Bluhm *et al.* reported that 3.9 wt% of hydrogen can be recovered at 85 °C.[15] The main drawback of ammonia borane is the purity of generated H_2.[16]

1.3.3.2 Sorbent Materials

Carbon-based materials such as single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), graphene and fullerenes are the mostly used materials in this field because of the high volumetric and gravimetric densities. These structures are however too inert to attract hydrogen molecules. In fact the hydrogen molecule is in physical adsorption on these materials and the physisorption energies are too low (<0.1 eV or <10 kJ/mol H_2)[2, 6] for the practical usage under ambient conditions.[17]

Carbon variant	**H_2 Capacity [wt%]**	**Temp. [K]**	**Pressure [bar]**
SWCNTs	1.7	77	1
MWCNTs	1.12	77	101
Fullurenes	3.9	77	121
Graphenes	0.4	77	1

Table 2. Hydrogen storage capacity of few carbon nanostructured materials. [9]

Although carbon nanotubes exhibit promising hydrogen storage capacities at 77 K (*Table 2*), only less than 1 wt % of hydrogen can be stored at 298 K and 101 bar of pressure.[2]

Transition metal atoms adsorbed on nanostructures could develop the well known Dewar–Kubas interaction with hydrogen molecule adhered to it. The adsorbed hydrogen molecule transfers its σ electrons to the *d*-orbitals of transition metal atom, while the metal back-donates electrons to the hydrogen σ^*-orbitals inducing an elongation in the H-H bond length.[18] Shin *et al.* have shown that Ni-dispersed fullerenes are capable to store 6.8 wt% H_2.[19] There are however many disadvantages associated with the transition-metal-doped fullerenes. One of the serious drawbacks is that the transition-metal atoms tend to aggregate and form a cluster around the fullerene due to their high cohesive energy.[7]

Light metal atoms like Li are another species often used in modifying the properties of carbon nanostructures; they would gain net charge due to the charge transfer from the carbon nanostructures, generating an electric field that can polarize the hydrogen molecule. The rearranged asymmetrical electron distribution in the H-H bond could increase the binding strength for hydrogen molecule.[17]

Bowl-shaped polyarenes

A way to overcome the problem of the require of very low temperature is to find a surface where the isosteric heat of adsorption is significantly greater than for the normal physisorption case (about 40 meV/atom or 4 kJ/mol).[12]

Bowl-shaped polyarenes, also known in the chemical literature as open geodesic polyarenes, fullerene fragments or buckybowls, constitute a rapidly growing family of curved polycyclic aromatic hydrocarbons (PAHs); the present work is concentrated on this class as potential hydrogen storing material.

The factor responsible of the bowl shaped structures of geodesic polyarenes is the presence of one or more fully unsaturated five-membered rings.[20] This geometries results from the fact that the rim is too snug to accommodate the interior rings and bonds in a two-dimensional plane without compressing them severely in curved π systems composed of pyramidalized carbon atoms (*Figure 5*).

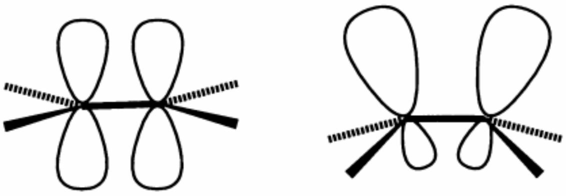


Figure 5. Planar π system (left) and curved π system (right).[20]

This is true for corannulene **1**, the first bowl-shaped molecule that has been thoroughly studied, as well as for all the larger bowl-shaped polyarenes as pentaindencorannulene **2** or carbon nanohorn **3** (*Figure 6*).[21]

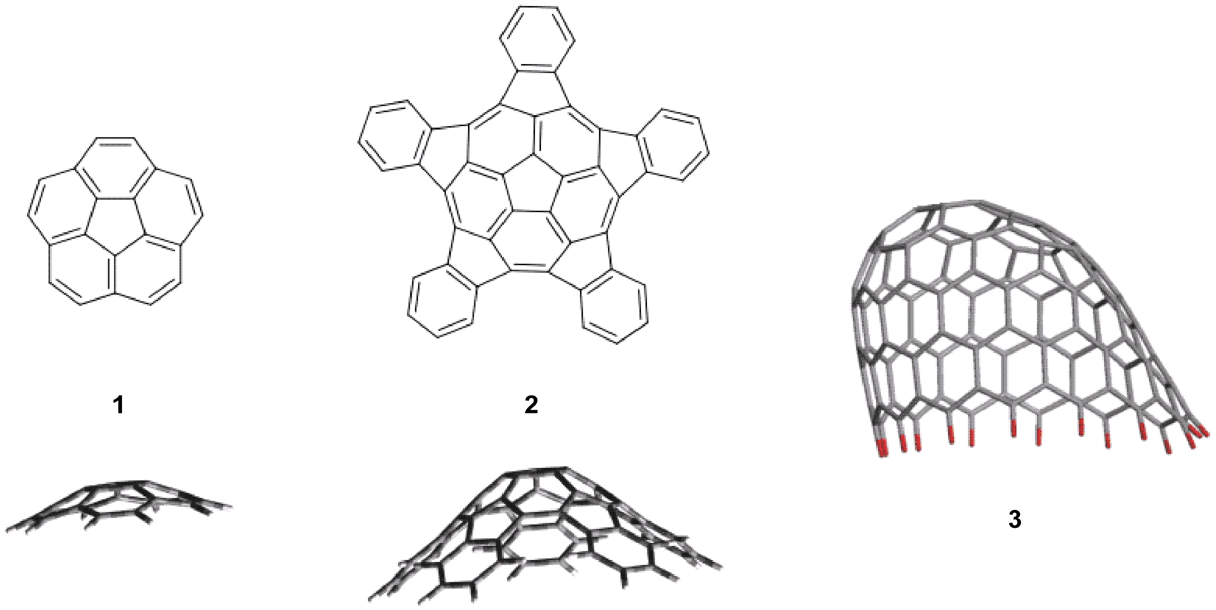


Figure 6*:* Corannulene **1** ($C_{20}H_{10}$), pentaindencorannulene **2** ($C_{50}H_{20}$), carbon nanohorn **3** ($C_{107}H_{15}$).

These molecules are very interesting because they have a relatively high permanent electrical dipole moment, which can induce a dipole moment on H_2 molecules increasing the dipole-dipole interaction.[22] This might also give rise to an increase of the H–H distance reducing the zero point energy for the H_2 vibration frequency, which could cause a significant increase of the adsorption energy (E_{ads}).[10] Greater is the dipole moment of the buckybowl, greater is his trapping energy (*Table 3*).[17, 23]

	1	**2**	**3**
Electric dipole moment [Debye]	2.0	4.0	Not specified
E_{ads} [eV]	0.104	0.130	0.179
[kJ/mol]	10.0	12.5	17.3

Table 3. Electric dipole moment and adsorption energy of corannulene **1**, pentaindencorannulene **2** and carbon nanohorn **3**.

Moreover, as predicted by Scanlon *et al.*,[22] by increasing the interlayer distance (ILD) between stacks of these molecules through the augmentation of their diameter, so consequently increasing the curvature and the volume available inside the cavity, it may be possible to store more and more H_2 molecules inside.[23]

Using the density functional theory (DFT) with local density approximation (LDA) and generalized gradient approximation (GGA) parameterized by Perdew and Wang (PW91), Chen *et al.*[17] have performed a detailed theoretical study on the hydrogen storage ability of **3**. They founded that the area adjacent to the closed top end inside a pure carbon nanohorn could bind hydrogen molecule much more strongly as compared to a graphene sheet, while the binding energy of a hydrogen molecule adsorbed on the area far away from the closed end and on the outer sidewall of the nanohorn is comparable to that for the graphene sheet. However, due to the limited space inside, the adsorption of hydrogen could not contribute a high percentage for hydrogen storage. Following the method by adding hydrogen molecules inside the nanohorn one by one (*Figure 7*), they optimized the configurations and obtained a hydrogen storage ability of 1.8 wt.% at a binding energy from 179 meV/H_2 (17.3 kJ/mol, first molecule adsorbed) to 145 meV/H_2 (14.0 kJ/mol, twelfth and last molecule adsorbed).[17]

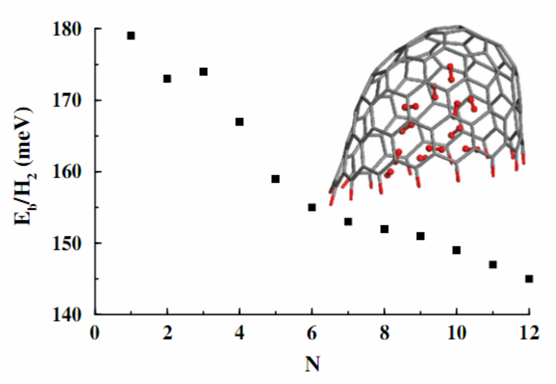


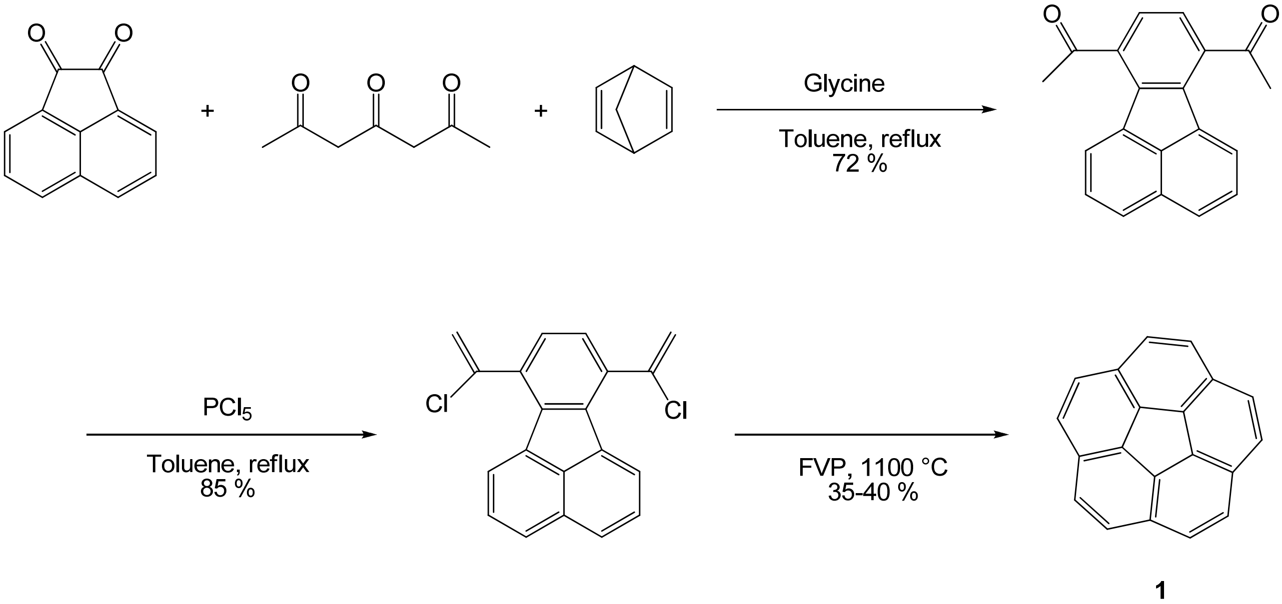
Figure 7. The evolution of the binding energy per H_2 molecule adsorbed inside the carbon nanohorn **3** as the hydrogen content increases.[17] The maximum number of adsorbed hydrogen molecules (shown in red) is 12.

In order to increase the gravimetric capacity, they carried out an extensive search on carbon nanohorn with Li atoms adsorbed on them. The total storage capacity they have found was 5.8 wt.% with 8 and 36 H_2 respectively adsorbed on the inner and the outer sidewalls ($E_{ads} > 200$ meV/H_2 or > 20 kJ/mol per H_2), surrounding the Li atoms. By adsorbing 24 more H_2 with binding energy of ~160 meV/H_2 (~16 kJ/mol per H_2) on the outer sidewall at the large hollow space circled by neighboring Li atoms and their attracted hydrogen molecules, they obtained a theoretical capacity of 8.6 wt.% [17], a very good result considering the US DOE target.

1.4 Brief literature summary of bowl-shaped molecules synthesis

In this section, synthetic methods for the preparation of some bowl-shaped molecules are quickly resumed.

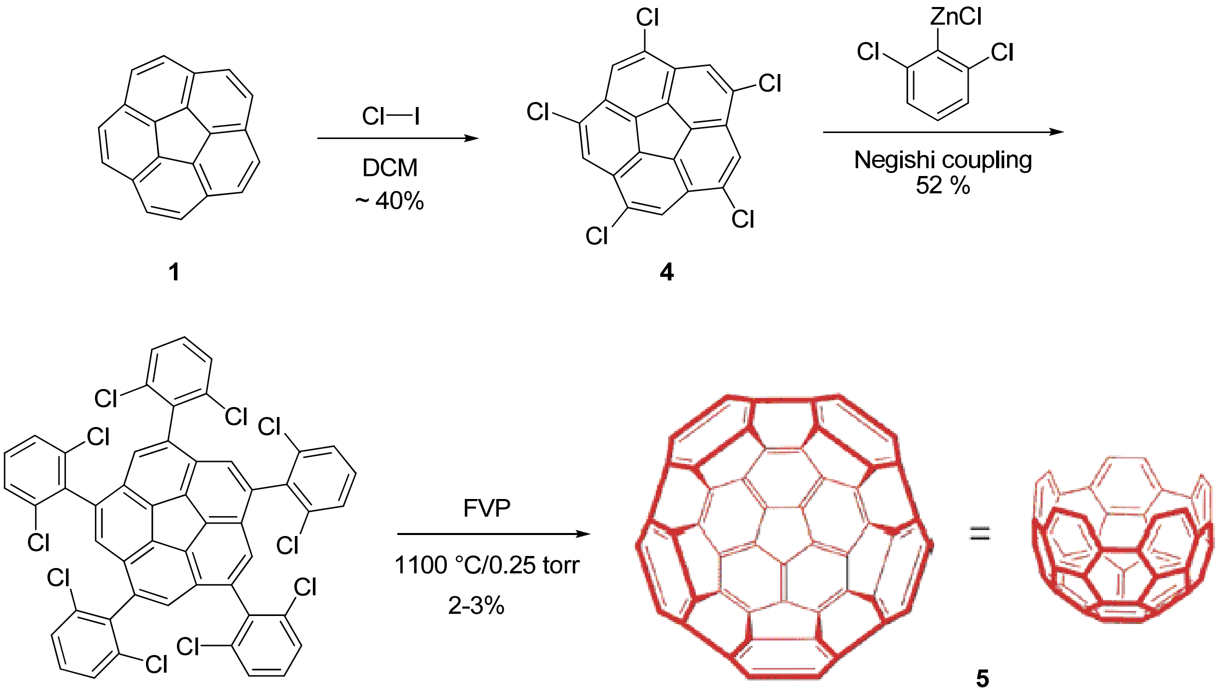
A convenient synthesis of corannulene **1** in three steps from commercially available starting materials was proposed by Scott *et al.*[24] in 1997 including an initial Knoevenagel/Diels-Alder reaction, followed by a conversion of the acetyl groups to 1-chlorovinyl side chains and finally a ring closing *via* flash vacuum pyrolysis (FVP) (*Scheme 1*).



Scheme 1. Scott *et al.* three step synthesis of corannulene **1**.

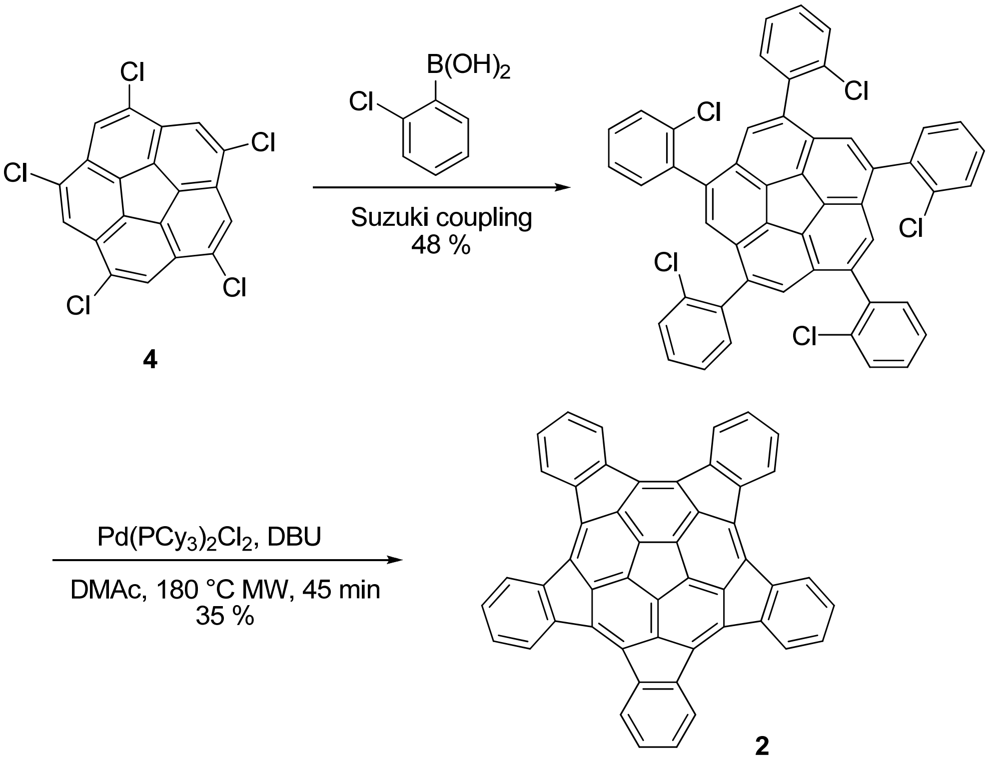
In 2012, Scott *et al.*[25] proposed a new strategy for the synthesis of a hemispherical geodesic polyarene **5** in a three steps including the already known chlorination of **1** proposed by Mizyed *et al.*[26] in 2001, followed by a 5-fold Negishi coupling and a ring closing *via* flash vacuum pyrolysis (FVP) (*Scheme 2).*

However, the conversion rates to the target molecules by FVP have remained disappointingly low. This approach has proven to be prolific for the synthesis of many small buckybowl structures, but has reached its limits in the case of large molecules.[27]



Scheme 2. Synthesis of **5** ($C_{50}H_{10}$) *via* the FVP.

An alternative method to FVP was proposed in 2006 by Jackson *et al.* After a five-fold Suzuki-Miyaura coupling of **4** with 2-chlorophenylboronic acid, they obtained compound **2** *via* a 5-fold palladium-catalyzed C-C coupling reaction using microwave heating (*Scheme 3).*[28]



Scheme 3. Synthesis of **2** *via* the palladium-catalyzed ring closing method.

In the search for a more effective method for ring closure applicable for highly insoluble fullerene precursors, Amsharov *et al.* have turned their attention to solid-state catalysis and fluorine functionality was found to be a good alternative for the initial precursor.[27, 29] In 2012, they present an efficient cove-region closure process (CRC), in which C-C bonds were formed by means of HF elimination using γ-Al_2O_3. Examination of the CRC approach for synthesis of buckybowl structures has demonstrated an unprecedentedly high selectivity and conversion level.[27]

Fluoroarene-based syntheses of bent polynuclear arenes benefit from the small steric requirement of F, generally good yields (98-99%),[27] and the relative inertness of the C-F bond in prevenient synthetic steps. Moreover, the reaction conditions are milder than those used in FVP. In fact, the general procedure requires an activation of γ-Al_2O_3 by annealing under vacuum (10^{-3} mbar) for 15 min at 600 °C, followed by the addition at room temperature of the respective fluoroarene. The condensation, by loss of HF, is run at 100−250 °C for several hours.[27, 29]

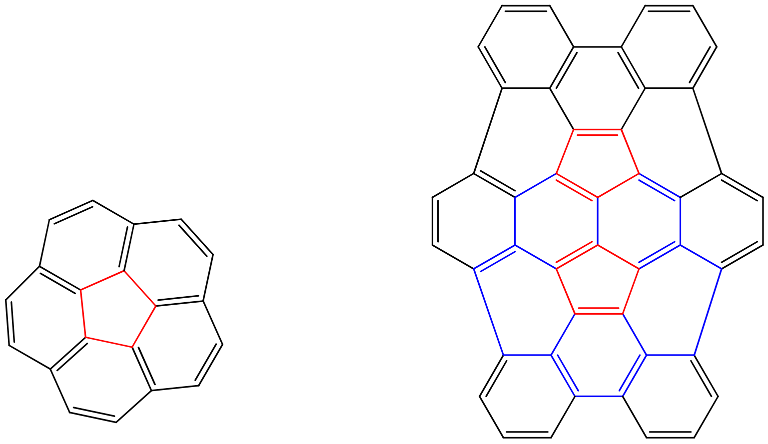
On the other hand, the potency of this method to prepare highly strained systems appears to be lower than that of FVP, but needs to be further explored.[30]

2

AIM OF THIS WORK

As explained in the introduction, several researchers [6, 17, 22] have shown that bowl-shaped molecules, thanks to their permanent electric dipole moment due to the asymmetric distribution of electrons, are promising candidates for molecular hydrogen storage. Based on such discoveries, scientific efforts focus on the development of procedures for the synthesis of a great variety of such compounds.

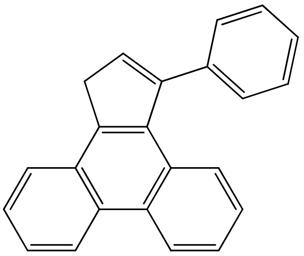
The aim of this Master Thesis project was, therefore, the synthesis of a new type of bowl-shaped polyarene **6**, which, compared to **1**, would have a larger diameter and a bigger surface in order to increase the interlayer distance (ILD) between stacks of molecules and consequently increasing the hydrogen storage potential (*Figure 8*).



1 **6**

Figure 8. Corannulene **1** and target bowl-shaped molecule **6**. In red are shown the fully unsaturated five-membered rings representing the key for the obtainment of the curved structure. In blue is possible to observe the corannulene's motif.

This work describes various attempts in the synthesis of compounds that may contribute to the obtaining of this novel bowl-shaped polyarene **6**. Efficient strategies have been evaluated for the preparation of planar polycyclic aromatic hydrocarbons (PAHs), which are required to contain five-membered rings to allow the formation of the target curved molecule; in fact, as predicted by Scott *et al.*,[20] the presence of these motifs were supposed to induce the curvature in the target molecule. The plan was to synthesize a planar PAH (*Figure 9)*, dimerize it *via* a cross-coupling reaction and perform a cyclodehydrogenation reaction to obtain the final bowl-shaped molecule.



7

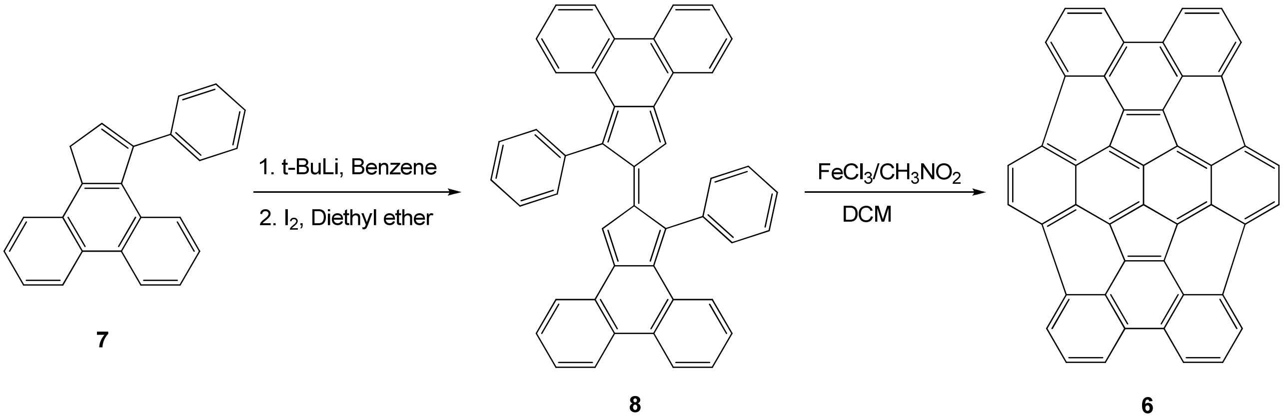
Figure 9. Planar PAH.

Actually, **7** was already synthesized by Dürr *et al.*[31] *via* photochemical excitation, however this work aims to search for an alternative pathway.

3

RESULTS AND DISCUSSION

As mentioned previously, the goal of this work was to obtain the bowl-shaped molecule **6**. Analyzing the structure it was decided that a possible pathway to get this molecule, as shown in *Scheme 4*, was to coupling two identical molecules of **7** following the procedure proposed by Pauson *et al.*[32] and then, under Kovacic conditions, proceed with the Scholl cyclodehydrogenation reaction using $FeCl_3$/nitromethane reagent,[33, 34] to obtain the desired target molecule.



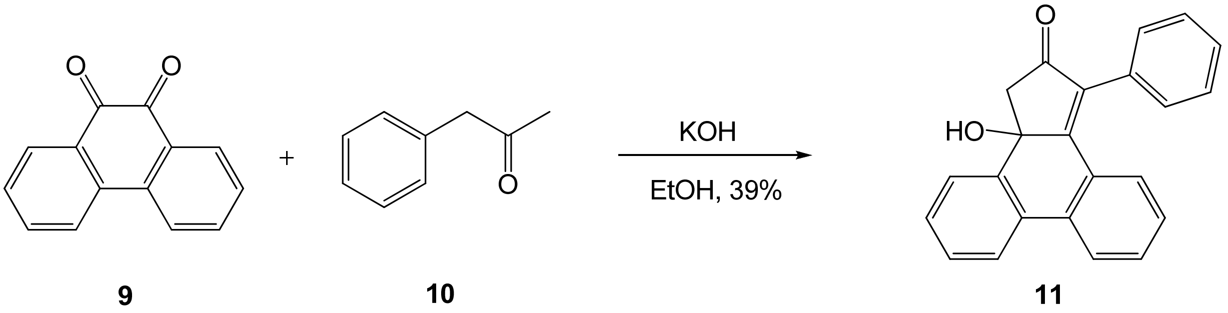
Scheme 4. Possible pathway to obtain the bowl-shaped molecule **6**.

The first synthetic pathway that was explored was therefore the synthesis of **7**.

3.1 Synthesis of 3-phenyl-1H-cyclopenta[l]phenanthrene

The first step of all investigated strategies to obtain **7** was the synthesis of **11** by a double Aldol condensation under basic conditions.

3.1.1 Double Aldol condensation



Scheme 5. Double Aldol condensation.

The condensation reaction necessary to obtain **11** was made according to the procedure described by Pauson and Williams.[32] In this reaction, **9** and a small excess of **10** were suspended in absolute alcoholic 0.5% potassium hydroxide and kept under nitrogen and protected against light at room temperature. UPLC analysis were made during the process to monitoring the progress of the reaction and stop it only when it was finished (after one hour). The solution was then filtered, washed with cold ethanol and evaporated to give a dark green dense oil, which was then purified by flash chromatography to obtain the product as a white-brown crystal powder in a yield of 39%.

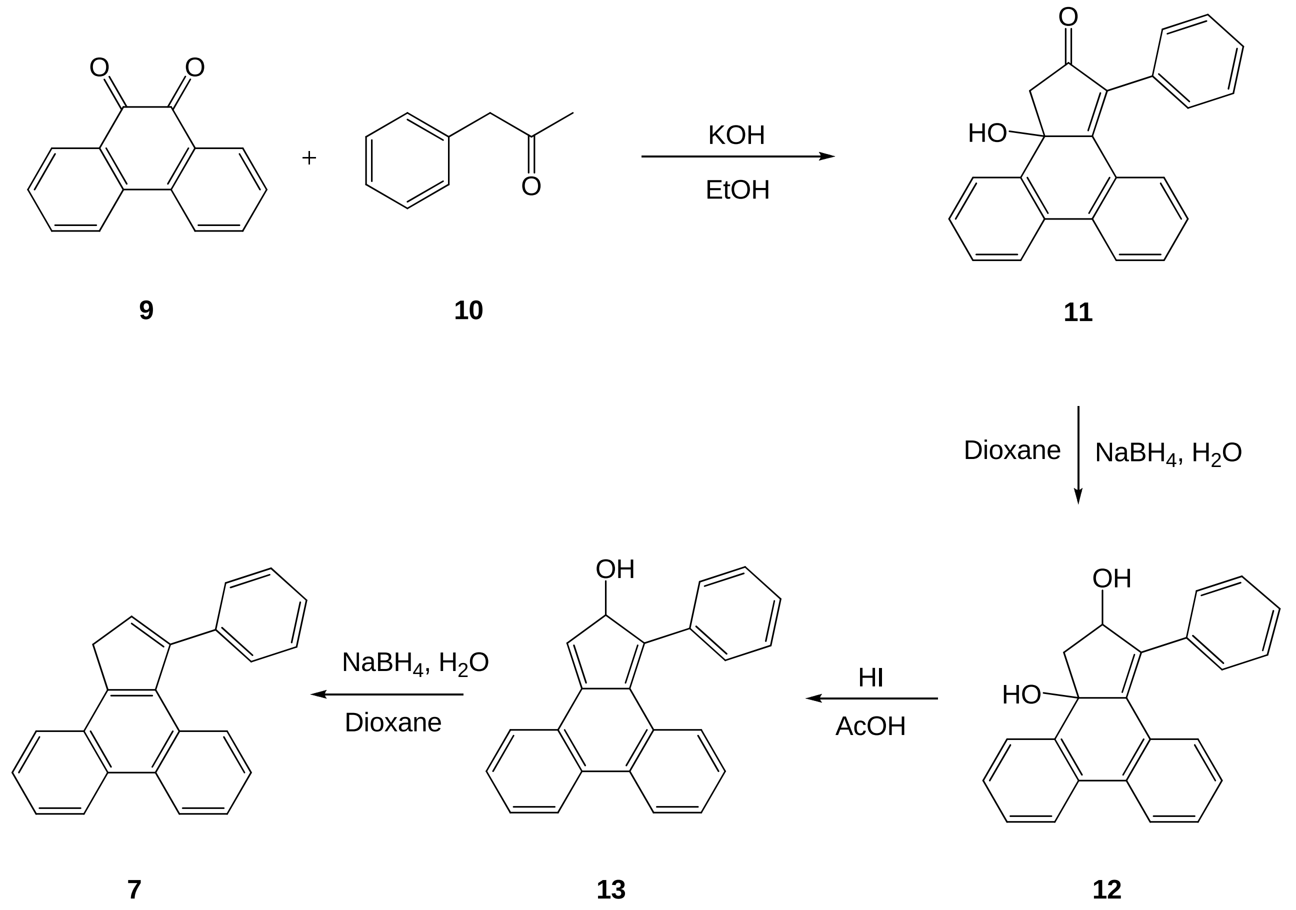
During this reaction the first condensation is completed by the dehydration, while the second closes the five-membered ring avoiding however the elimination of the alcoholic group to get the wanted molecule.

The structure of the product was confirmed thanks to mass spectrometry and NMR experiments, in which the signals of the aliphatic hydrogens in the five-membered ring, as well as the characteristic singulet of the alcohol group of the target molecule, could be easily observed.

Once obtained **11**, it was at this point necessary to explore possible pathways to synthesize **7**.

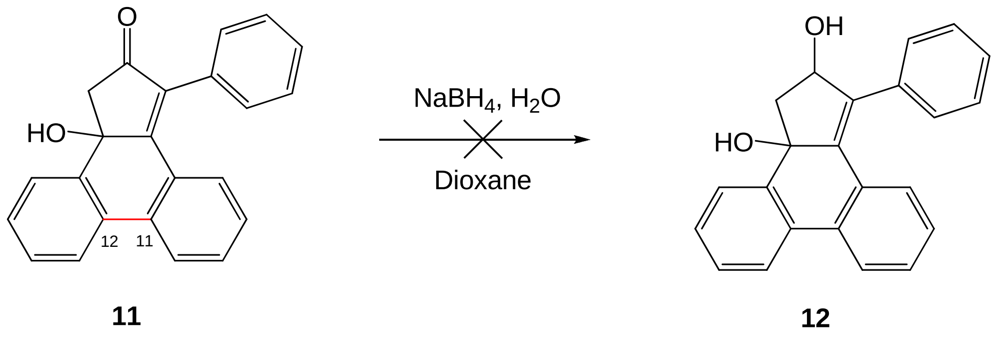
3.1.2 First strategy

The first strategy to obtain **7**, shown in *Scheme 6*, was a four step synthesis comprising the double Aldol condensation just explained, a carbonyl reduction with $NaBH_4$, a dehydration and a final reduction once more with $NaBH_4$.



Scheme 6. First strategy for the synthesis of **7**.

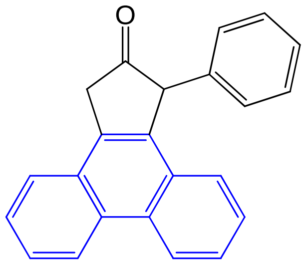
Once obtained **11**, the carbonyl group reduction was performed according to the procedure used by Pauson and Williams.[32]



Scheme 7. Reduction of the carbonyl group.

In such a reaction, an excess of sodium borohydride, dissolved in water, was added to **11** previously dissolved in dioxane and the mixture was left for two hours under nitrogen at room temperature. After the evaporation of the solvent under reduced pressure and the extraction with diethyl ether, the organic layer was dried over Na_2SO_4 and evaporated to give a yellow oil, which was purified by flash chromatography in normal phase using a gradient pentane/EtOAc from 80:20 to 0:100 as eluent. The obtained yellow solid was characterized by mass spectrometry and NMR analysis. The interpretation of the results suggested that the reaction had not happened as wanted and the obtained product was not the desired one. The absence of alcohol groups was furthermore verified by adding a small drop of D_2O in the NMR tube containing the product in deuterated chloroform. The disappearance of their characteristic peaks after addition of deuterium oxide would suggest the presence of alcoholic groups. This phenomenon was not observed, confirming the absence of alcoholic groups.

In reality, during this reaction the sodium borohydride doesn't reduce the ketone group but favors the elimination of the alcoholic group getting **14**.



14

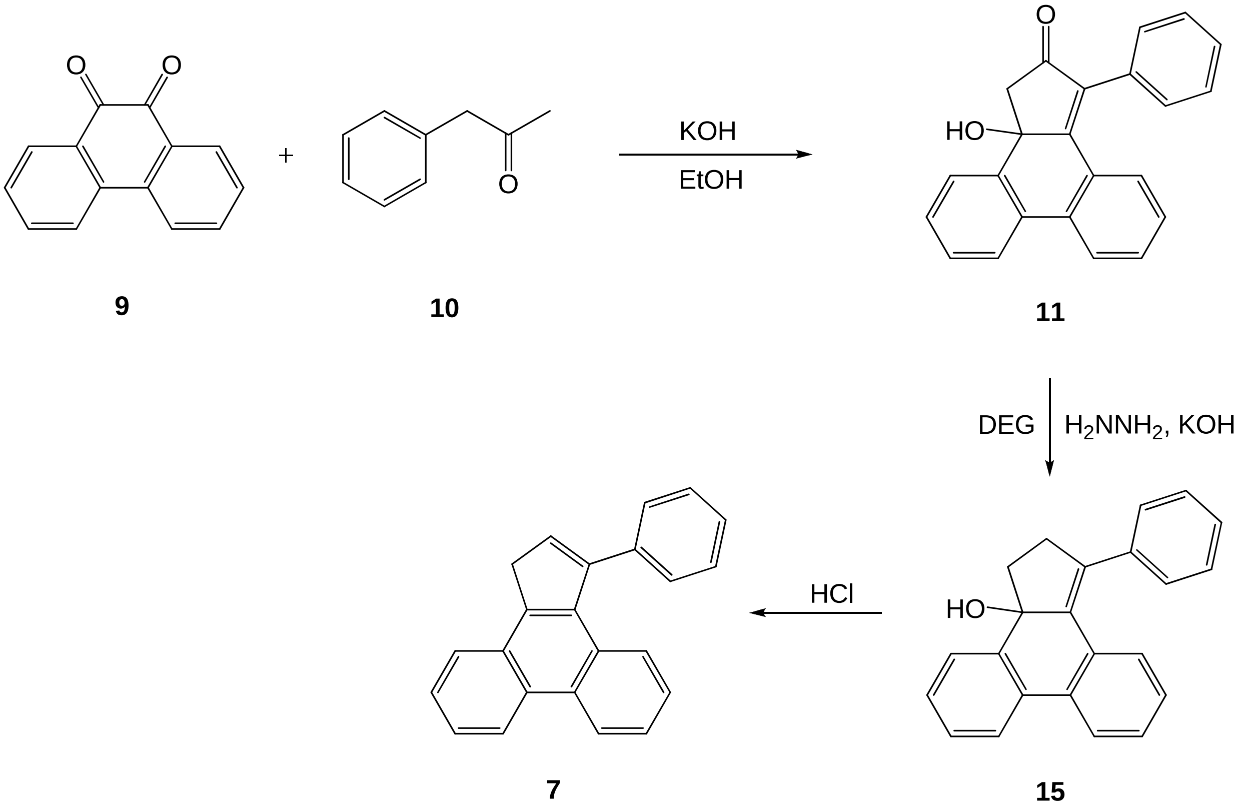
Figure 10. Product obtained from the reduction of **11**. Highlighted in blue is the phenanthrene motif.

This result is probably due to the presence of the bond between C11 and C12 (shown in red in *Scheme 7*) in the starting material that favors the formation of the stabilized phenanthrene motif (shown in blue in *Figure 9*).

A possible alternative way would be to begin with starting product deprived of that bond, so that the formation of the phenanthrene motif is avoided. Using benzil instead of **9** during the double Aldol condensation is possible to obtain a reagent that avoids the formation of the phenanthrene motif and probably allow the reduction of the ketone group without losing the alcohol group. Nevertheless, given the importance of that bond in the formation of the bowl-shaped final molecule, it was decided to maintain it and proceed with another pathway.

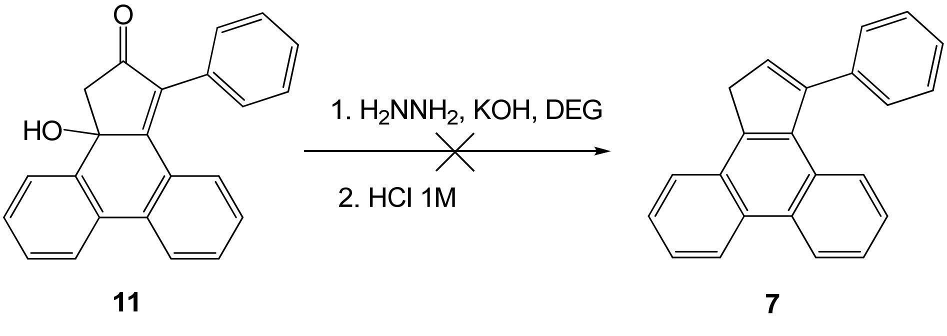
3.1.3 Second strategy

The second pathway to obtain **7**, shown in *Scheme 8*, was a three step synthesis comprising the double Aldol condensation previously explained, a Wolff-Kishner reduction and a final dehydration under acidic conditions.



Scheme 8. Second strategy for the synthesis of **7**.

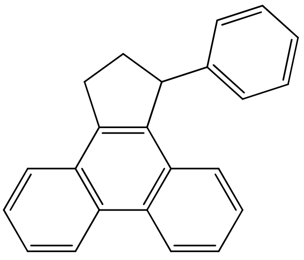
Once obtained **11**, the Wolff-Kishner reduction was performed according to the procedure used by Takaishi *et al.* [35]



Scheme 9. Wolff-Kishner reduction of the carbonyl group.

For this reaction, a mixture comprising diethylene glycol and an excess of potassium hydroxide was heated carefully under argon until the potassium hydroxide began to melt and go into solution. The mixture was then heated intermittently until the exothermic dissolution was completed. After the addition of **11** and an excess of a 65% hydrazine hydrate solution, the mixture was heated under reflux for three hours and then at 220 °C for two hours when the water formed and the excess of hydrazine were gradually distilled off. To the obtained solution was added diluted hydrochloric acid, then the mixture was extracted with diethyl ether. The organic extract was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave an oil, which was purified by flash chromatography on silica gel to obtain the final product as a white powder.

The mass spectrometry and NMR analysis suggest that the obtained product was not the desired one. The hydrazine, being a strong reducing agent, easily eliminates the alcohol group before completely reducing also the carbonyl as well; so that **16** is obtained. The presence of the three aliphatic groups in the five-membered ring was confirmed by the presence of their characteristic proton signals in the ^{1}H-NMR spectrum.



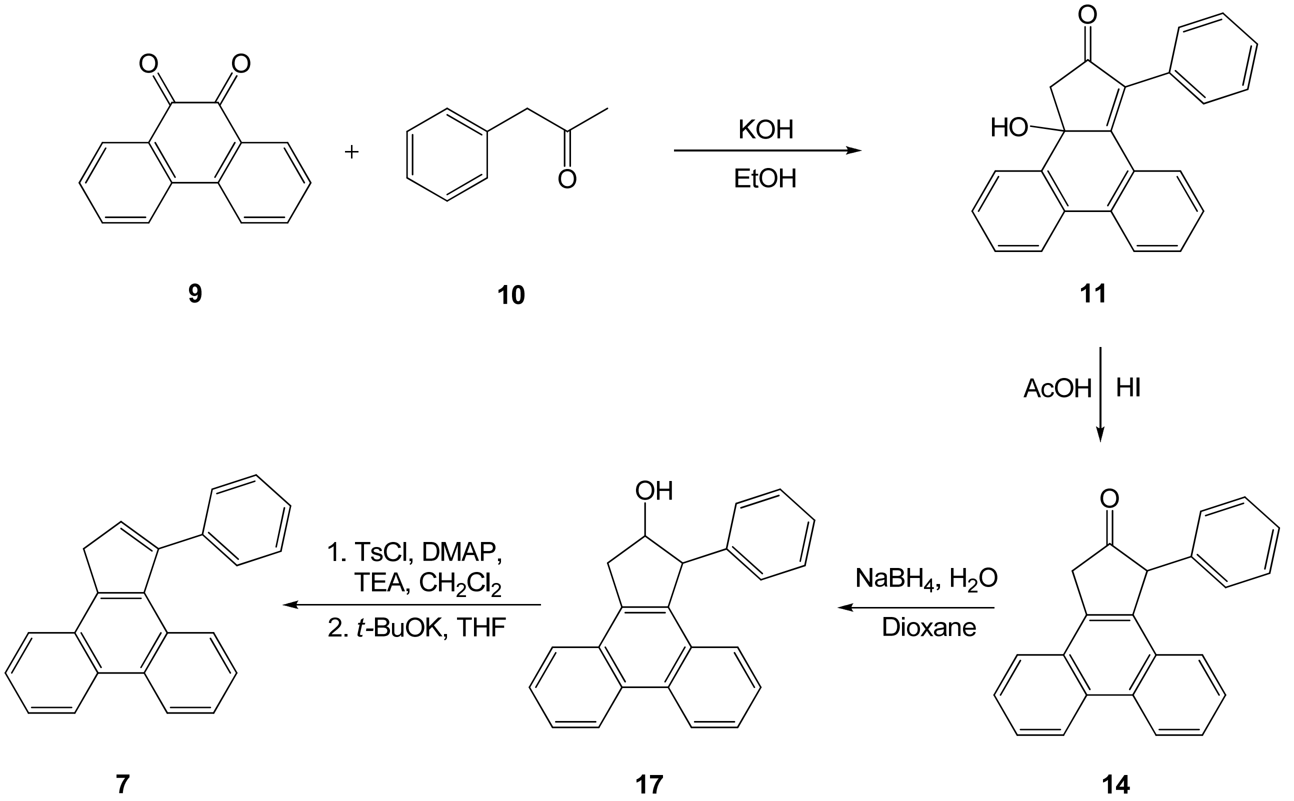
16

Figure 11. Product obtained from the Wolff-Kishner reduction of **11**.

A possible way to get **7** from **16** could be a bromination using bromine and then form the lacking double bond by a dehydrobromination under basic conditions as described by Meister *et al.* [36], but also in this case it was decided to explore a different way.

3.1.4 Third strategy

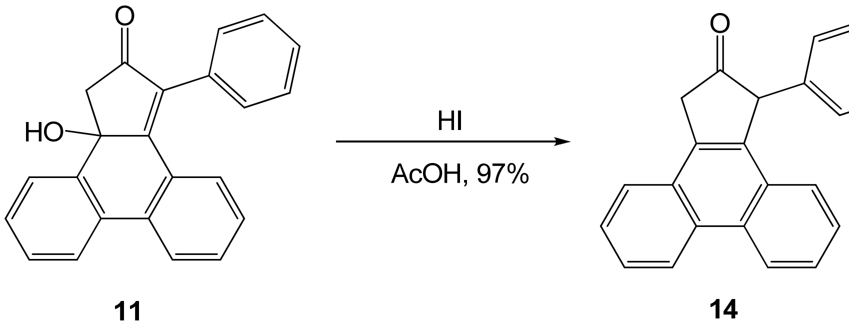
The third pathway to obtain **7**, shown in *Scheme 10*, was a four step synthesis comprising the double Aldol condensation previously explained, a reduction to replace the alcohol group with an H, a carbonyl reduction using $NaBH_4$ as reducing agent and finally a tosylation and elimination reaction under basic conditions to extract the alcohol group and form the lacking double bond.



Scheme 10. Third strategy for the synthesis of **7**.

3.1.4.1 Replacement of the OH-group by H

Once obtained **11**, always with the double Aldol condensation previously explained, the replacement of the OH-group by H was performed according to the procedure used by Koelsch and Geissman.[37]



11

14

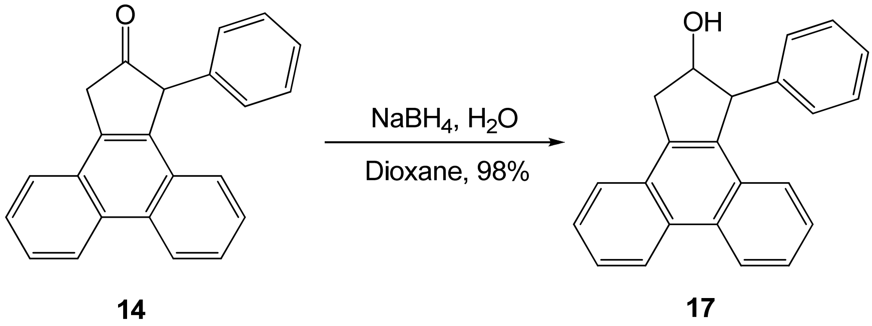
Scheme 11. Replacement of the OH-group by H.

For this reaction, to a solution of **11** in acetic acid was added in the cold a small excess of hydroiodic acid as a 67% solution; then the mixture was heated under reflux (around 120 °C) for five minutes. UPLC analysis were made after this time to verify the end of the reaction. After that, the violet solution was poured into aqueous sodium sulfite producing immediately a green-white precipitate. Then was filtrated, dissolved in CH_2Cl_2, dried over Na_2SO_4, filtrated again and evaporated to give the product as a green-white solid in a yield of 97%.

The mass spectrometry gave a mass of *308.16 u*, as expected, and the structure of this product was also confirmed by NMR experiments, in which the singulet of the CH-group and the signals of the CH_2-group could be easily observed.

A possible way to explain this reduction is given by Meyers *et al.*[38] through a single electron transfer from the hydroiodic acid to initially formed cation that provides free radical, which abstract an hydrogen atom from HI to form the desired product.

3.1.4.2 Carbonyl group reduction



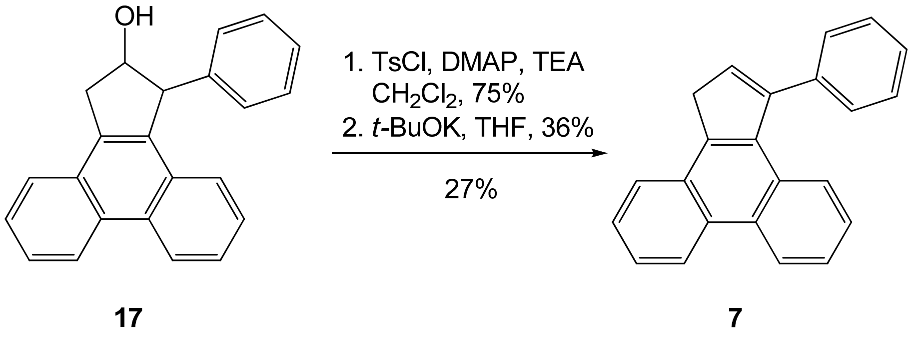
Scheme 12. Carbonyl group reduction.

The reduction was made following the conditions proposed by Koelsch and Geissman,[37] in which the carbonyl group was reduced by an hydride transfer reaction using $NaBH_4$ as reducing agent. An excess of sodium borohydride dissolved in water was added to **14** in dioxane and the mixture was left three days at room temperature under argon. The obtained light-yellow solution was then concentrated under reduced pressure, poured into water and extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4 and evaporated to give the product as a white solid in a yield of 98 %.

The structure of the product was confirmed thanks to mass spectrometry, in which an expected mass of *310.21 u* was measured, and NMR experiments, in which the signals of the aliphatic hydrogens in the five-membered ring as well as the characteristic doublet of the alcohol group could be easily observed.

3.1.4.3 Alcohol group elimination passing through a tosylation

The same procedure as the one described by Kim *et al.*[39] was applied to develop the tosylation reaction while the elimination of the tosyl group was achieved according to Simas *et al.*[40]



Scheme 13. Alcohol group elimination passing through a tosylation.

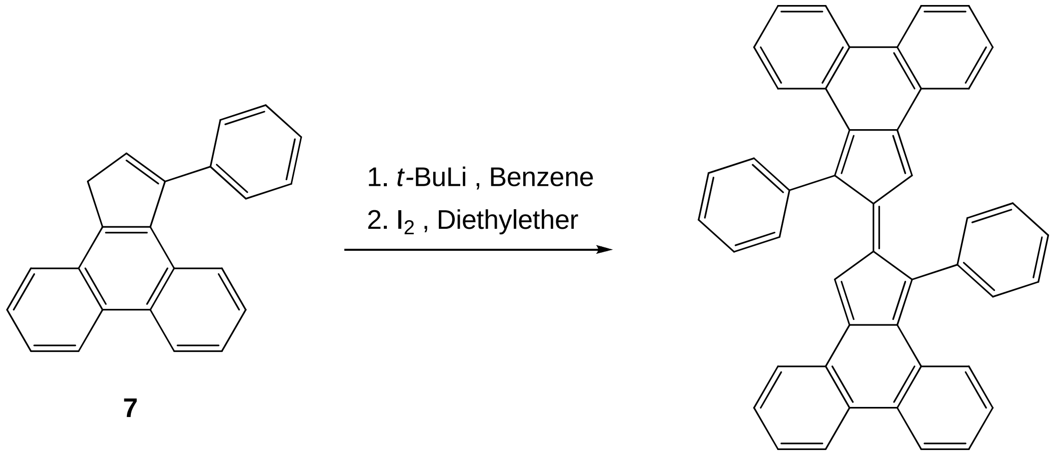
In such a reaction, an excess of TsCl, DMAP and TEA mixed with **17** in dry CH_2Cl_2 was set under argon at 70 °C for three hours in the microwave. The orange reaction mixture was diluted with 50% EtOAc in hexane and the resulting white precipitate was removed by filtration. The filtrate was concentrated under reduced pressure and the orange-yellow solid residue was purified by flash chromatography to give the tosylated intermediate as a light yellow solid. This was then dissolved in dry THF and potassium tert-butoxide was slowly added. Afterwards, the reaction was carried out under argon at 60 °C for four hours in the microwave. The obtained mixture was then concentrated under reduced pressure, adsorbed by silica and purified by flash chromatography to give the product as a white solid in a yield of 27 %.

Several attempts were necessary to find the correct procedure. In fact during the first attempt, in which only TEA was used as base to eliminate the tosyl group, the reaction didn't happen. It was concluded that TEA was not an enough strong base to allow the elimination. This way it was decided to increase the basicity of the reactant and it was followed the procedure described by Bonete and Nájera,[41] in which it was used an excess of DBU and the elimination was performed at room temperature. However the result was not satisfactory and it was decided to follow the procedure proposed by Tsai *et al.*,[42] in which, using again DBU as base, the mixture was heated at 60 °C for twenty hours. Unfortunately also with this method any reaction happened. At the end, inspired by Simas *et al.*[40], the sufficiently strong base to allow the elimination of the tosyl group was found. Using potassium tert-butoxide it was gotten a yield of 36% for the second step and a general yield of 27%.

The obtainment of **7** was confirmed by NMR experiments, in which was easily possible to identify the characteristic signals of the protons of the five-membered ring, and by MS analysis, which, as expected, revealed the molecular mass of *292.16 u*.

3.2 Cross-coupling reaction

The cross-coupling reaction was performed according to the procedure used by Pauson and Williams.[32]



7

8

Scheme 14. Cross-coupling reaction.

For this reaction **7** in benzene was added to *tert*-butyllithium stabilized in pentane and the mixture was refluxed (around 85 °C) under argon for two hours. After cooling, iodine solved in diethyl ether was added dropwise and the mixture, immediately shifted from an opaque orange colour to a brown-black one, was stirred overnight. Water was then added and the organic layer was separated, washed with sodium thiosulphate solution, and dried over Na_2SO_4. Evaporation yielded a dark coloured solid that was purified by flash chromatography to obtain the product not yet completely pure as a brown solid.

From the UPLC analysis (*Figure* 12) was possible to determine that the gotten product was not pure, in fact it was a mixture of different substances. Even if the NMR analyses clearly showed the presence of aromatic protons, the extreme complexity of the spectra, due to the presence of impurities, didn't allow to identify the main product. Furthermore, it was not possible to observe the characteristic singlet belonging to the C-H groups of the five-membered rings, which would have strongly suggested the presence of the correct product (*Figure 13*).

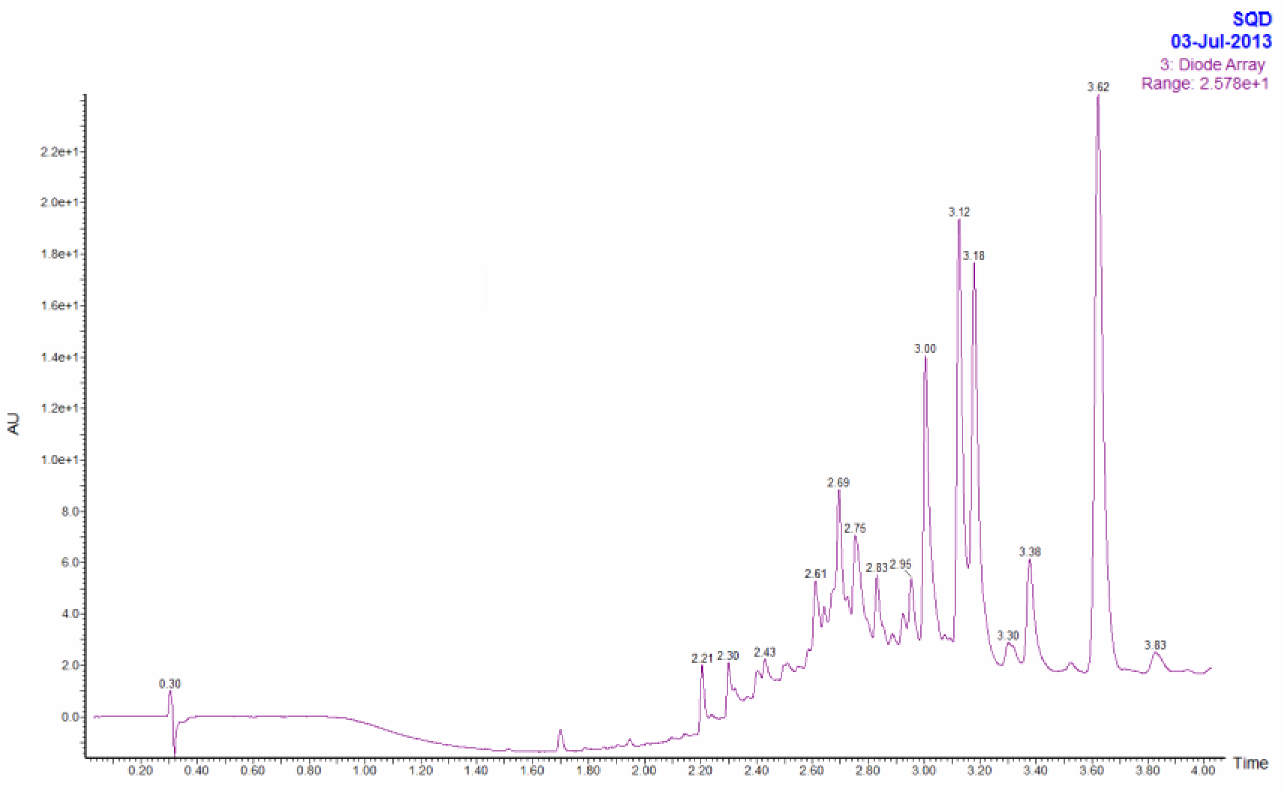


Figure 12. Spectrum of the UPLC analysis of the product obtained from the cross-coupling reaction (in MeCN).

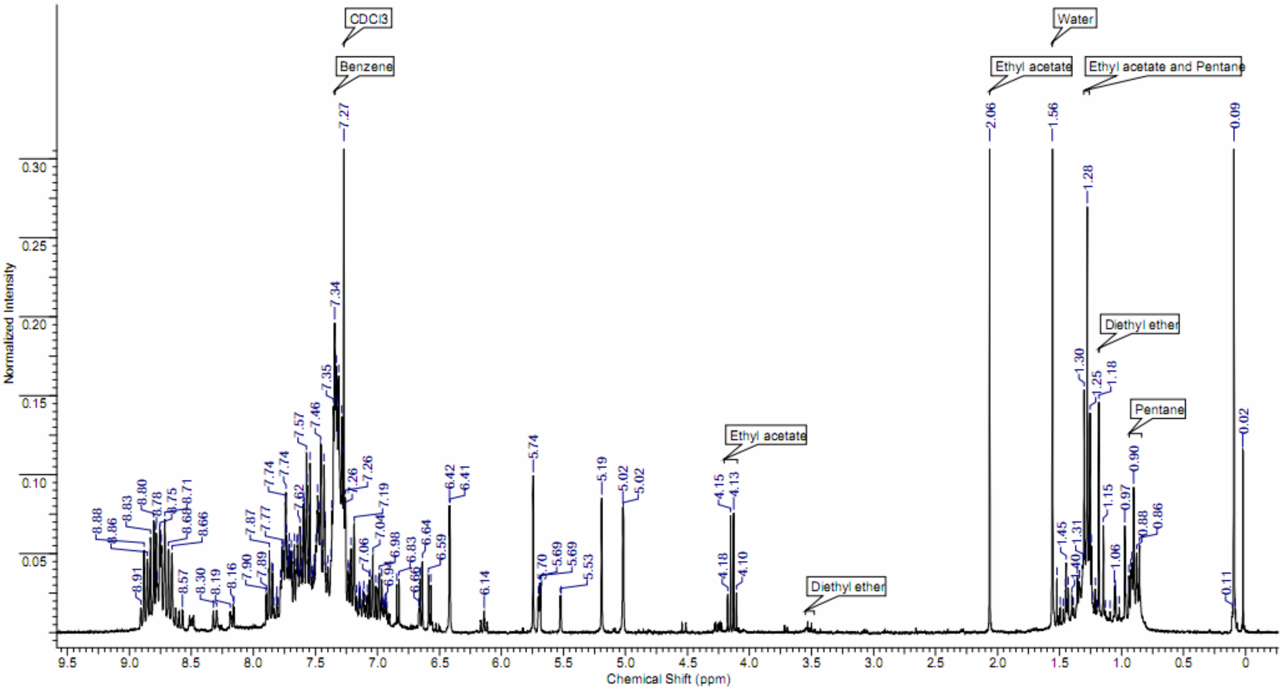
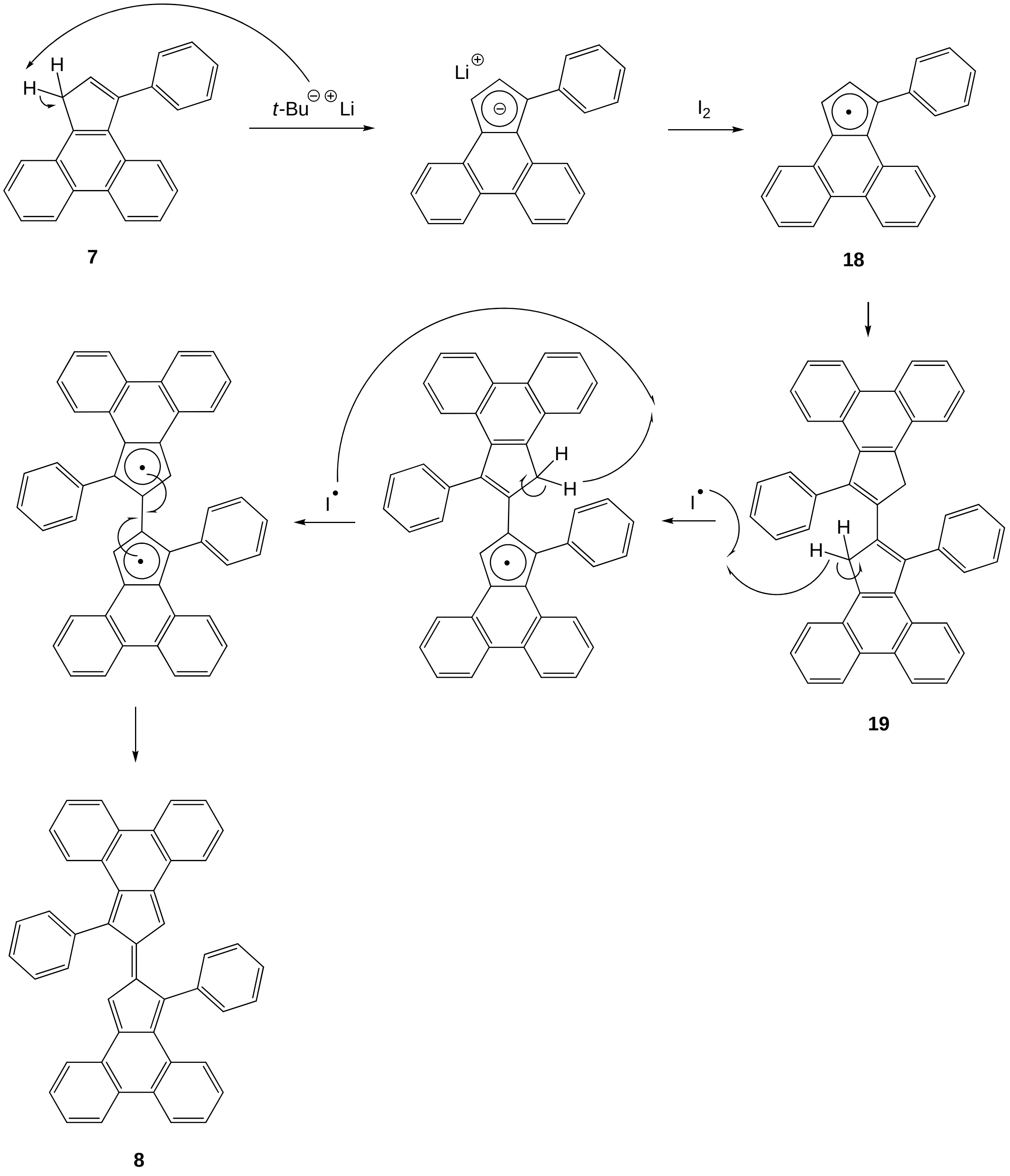


Figure 13. ^{1}H-NMR spectrum of the product obtained from the cross-coupling reaction (in $CDCl_3$).

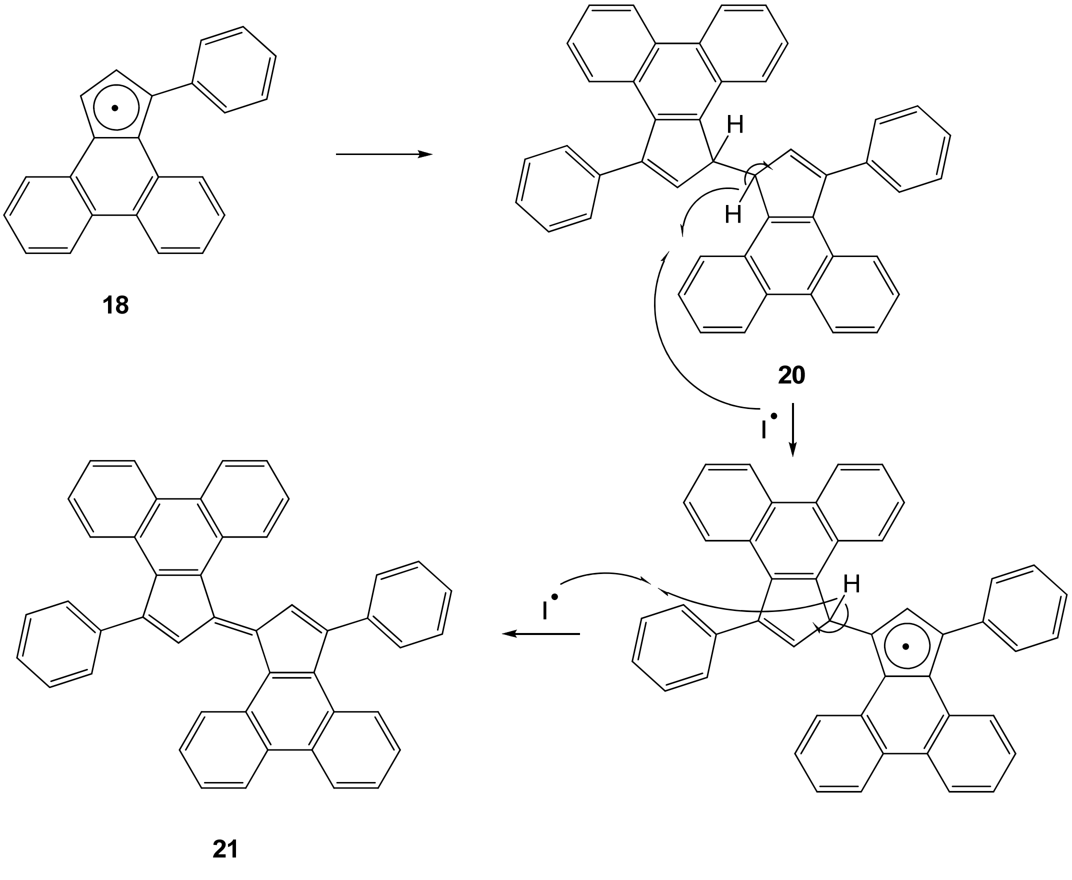
In order to better understand this cross-coupling reaction it was proposed a possible reaction mechanism (*Scheme 15*).



Scheme 15. Proposed mechanism for the formation of **8**.

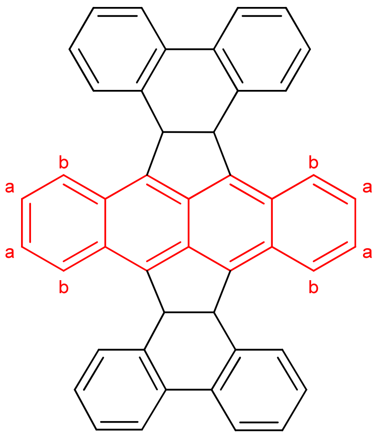
In the proposed mechanism (*Scheme 15*), the first step consists in the activation of **7** using *tert*-butyllithium as a sufficiently strong base in order to deprotonate the molecule and form the carbanion. The addition of iodine allow then the formation of the radical, stabilized over the whole five-membered cycle. The coupling between two **18** lead then to **19**. Iodine continue then the oxidation process *via* the formation of radicals which finally leads to the desired molecule **8**.

However, it should be noted that the coupling between two **18** could also occur in the other position of the five-membered ring. *Scheme 16* shows the molecule that may have been obtained by this reaction.



Scheme 16. Proposed mechanism for the coupling in different positions.

It is possible that the iodine not only allow the coupling of the two molecules **7**, but additionally led to other bonds, allowing the formation of the four aromatic rings shown in red in the *Figure 14*. This could explain the presence of a particular multiplet in the 1H-NMR spectrum between 8.5 and 9 ppm, which could be the overlap of the two multiplets belonging to the protons in positions *a* and *b*.



22

Figure 14. Possible molecule obtained from the cross-coupling reaction.

From MALDI-MS results (*Figure 15*), the heights of the isotopic peaks of the molecular ions were analyzed and, from their distribution, the presence of three species was hypothesized; *580.2 u* for the desired molecule **8** or for the variants **21** or **22** ($C_{46}H_{28}^{\cdot+}$), *581.2 u* for ($C_{46}H_{29}^{+}$), and *582.2 u* for molecules **19** or **20** ($C_{46}H_{30}^{\cdot+}$) shown in *Figure 16*.

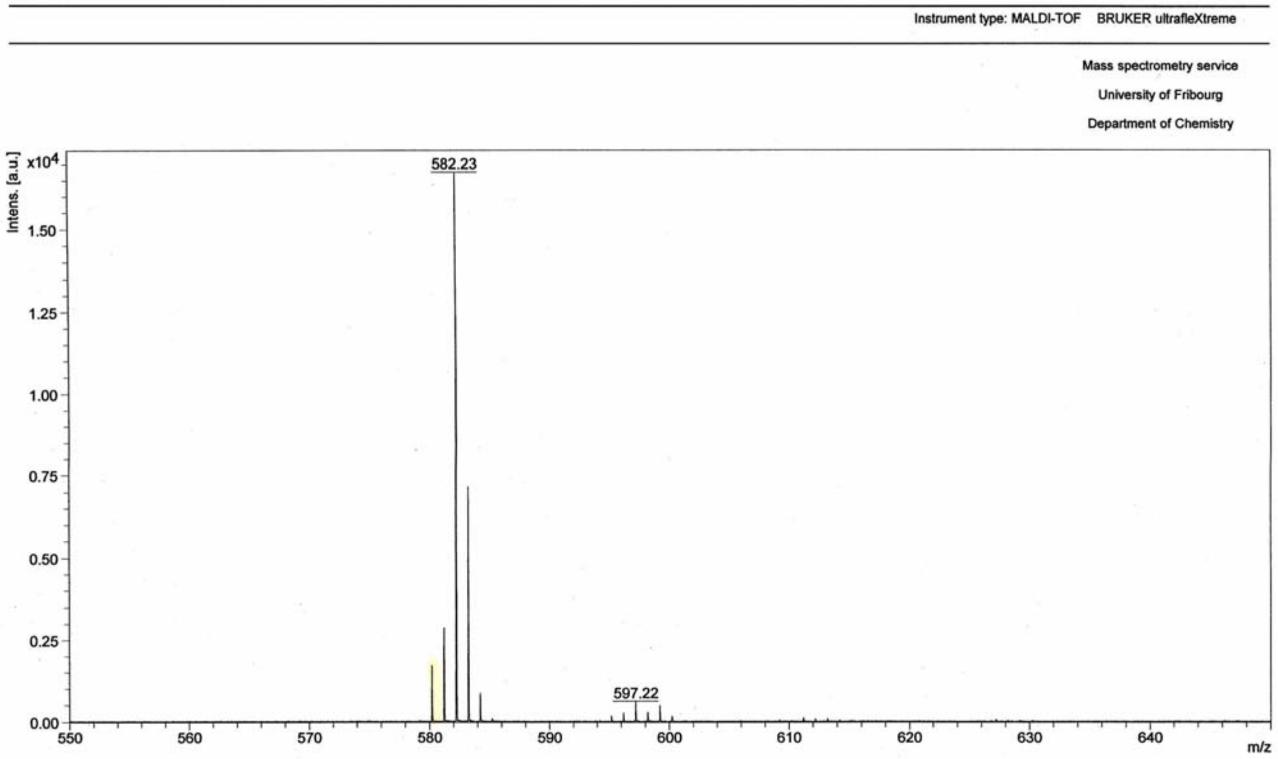
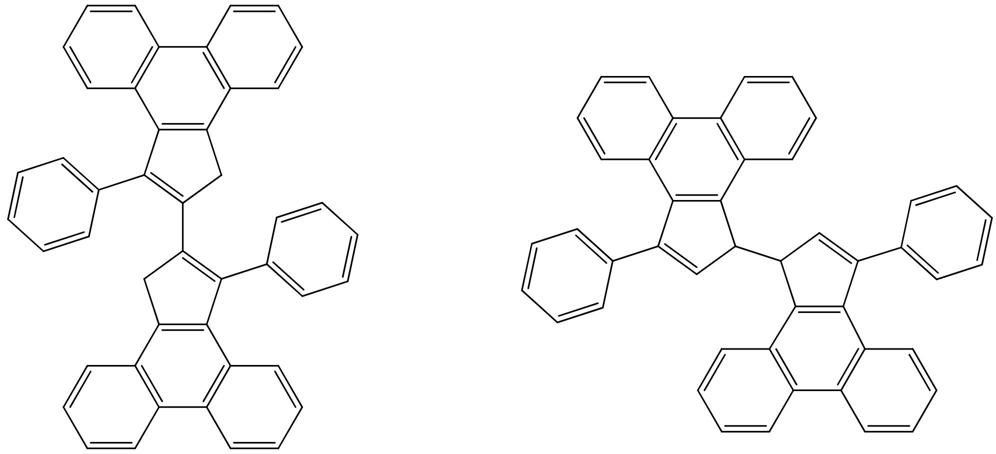


Figure 15. MALDI-MS spectrum of the product obtained from the cross-coupling reaction.



19 **20**

Figure 16. Possible not completely oxidized molecules obtained from the cross-coupling reaction.

It is also possible that the molecule reacts during the MALDI-MS analysis so that the results are different than expected.

Anyhow, even though these results don't exclude the presence of the desired molecule **8**, they are insufficient to incontestably prove their obtainment.

4

CONCLUSION AND OUTLOOK

The main goal of this Master Thesis was unfortunately not reached, as no cyclisation to obtain the expected buckybowl **6** was achieved. Furthermore, the results obtained for the cross-coupling reaction of **7** did not exclude the presence of the desired molecule **8** but were anyway not enough to incontestably prove their obtainment.

Nevertheless, this project demonstrated that it was possible to synthesize **7** by a four-step synthesis from **9** and **10**. Prior to this work, **7** was synthesized *via* photochemical excitation.[31]

Another good point to this work was the fully determination of the structures of **7**, **11**, **14** and **17**. On the other hand, the analysis of the compound **8** was not completely a success. No conclusive NMR spectra could be recorded because of the presence of a lot of other by-products. The ^{1}H-NMR spectrum showed the certain presence of aromatic protons and the MALDI-MS analysis showed promising results. Anyway, for greater certainty it might be preferable to repeat the entire synthesis trying to get purer product in order to facilitate the interpretation of the results. High resolution NMR analysis would be desirable to prove the presence of the characteristic singulet of the proton on the five-membered ring.

For the first strategy to obtain **7**, consisting in a carbonyl reduction with $NaBH_4$, a subsequent dehydration and a final reduction once more with $NaBH_4$, the direct reduction of ketone during the first step turned out to be impossible to realize because of the more favorable formation of the phenanthrene motif *via* elimination of the alcoholic group.

For the second pathway, including a Wolff-Kishner reduction and a final dehydration under acidic conditions, it was impossible to obtain the desired product because of the too strong reducing power of the hydrazine.

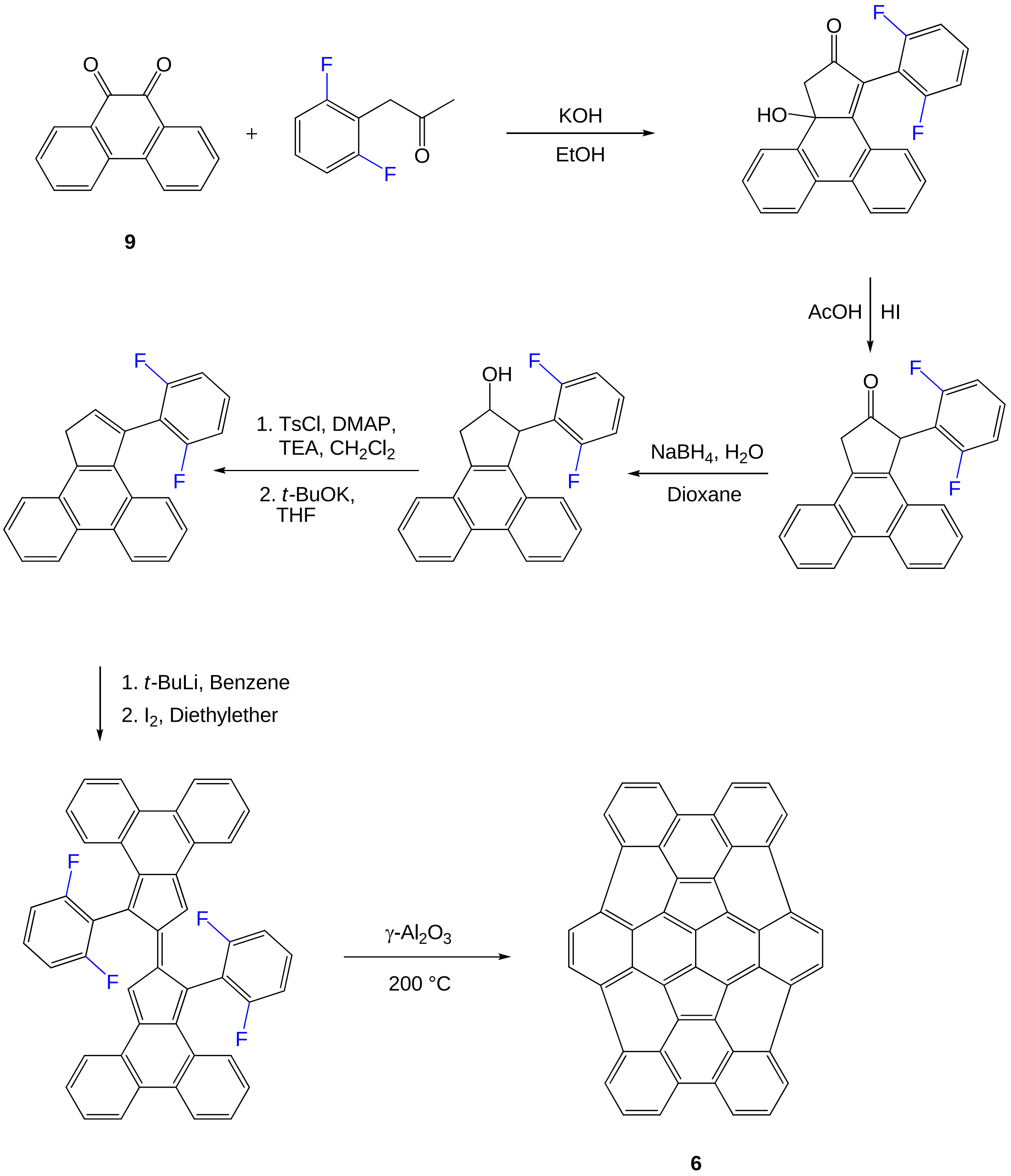
The third strategy, consisting in a replacement of the alcohol group by H, a carbonyl reduction using $NaBH_4$ and finally a tosylation and elimination reaction under basic conditions, was on the contrary successful. The main problem regarding this approach was the search for a sufficiently strong base to allow the elimination of the tosyl group during the last step. Despite this drawback, the desired product was obtained with an acceptable yield. Moreover, the microwave technology used in the last step suggests a possible improvement of yield and purity of the product investigating on the reaction time and the temperature adopted during this reaction. Lastly, as only three different types of bases were tested, the investigations must still be continued to find optimal conditions for this reaction.

Regarding the cross-coupling reaction, due to the low amount of starting product used and consequently also of the final product obtained, it was not possible to optimize the purification. The analysis were therefore not completely exhaustive.

As mentioned in the introduction, an interesting new strategy for effective intramolecular aryl−aryl coupling was porposed by Amsharov *et al.*[27, 29] This approach, showing generally good yields, suggests a possible alternative pathway for the synthesis of **6** (*Scheme 17*) by coupling fluoroarenes through γ-Al_2O_3-mediated HF elimination. It is important to note that, compared to the consulted references, the proposed pathway used the ring-closing process to form 6-membered rings and it is not known whether it would work as well for 5-membered rings.

Moreover, as explained by Thilgen, [30] the potency to prepare highly strained systems using this method appears to be lower than that of FVP, so the final step could be performed combining both methods in succession.

Further investigations could be done also in the field of computational calculations, as shown by several research groups for other bowl-shaped molecules.[17, 22] The gravimetric capacity of **6** can be evaluated following a computational method consisting in adding hydrogen molecules inside and outside the molecule one at the time. This theoretical investigation could also be done with Li atoms adsorbed on the surface of the molecule, increasing even more his permanent electrical dipole moment and therefore the binding strength towards hydrogen molecules.



Scheme 17. Proposed alternative pathway applying the Amsharov *et al.* new cyclisation method.

5

EXPERIMENTAL PART

5.1 General consideration

All chemicals used in the synthesis were purchased from Sigma-Aldrich, Fluka or Acros and were used without further purification. Technical solvents were distilled prior to use and dry solvents were obtained from a drying system if not indicated otherwise. Other solvents used in reaction mixtures were used as received.

The sensitive reactions were conducted under inert atmosphere, using dry nitrogen (45) or dry argon (48) purchased from Carbagas. A Biotage Initiator was used for the reactions ran under microwave irradiation.

Thin layer chromatography (TLC) analyses were performed using aluminium sheets coated with silica gel 60 F_{254} and visualized under UV-light at 254 nm or 366 nm. Column chromatography purifications were performed with Merck silica gel 60 (0.04-0.063 mm, 230-400 mesh) using a Biotage Isolera One system.

NMR spectra were recorded on a Bruker Avance III 500 MHz (^{1}H: 500 MHz and ^{13}C: 125 MHz) spectrometer, a Bruker Avance DPX 360 MHz (^{1}H: 360 MHz and ^{13}C: 90 MHz) spectrometer or on a Bruker Avance III 300 MHz (^{1}H: 300 MHz, ^{13}C: 75 MHz) spectrometer using $CDCl_3$ as solvents. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) or to the solvent residual peak. The coupling constants (*J*) are given in Hz and the splitting patterns are designated as s (singlet), d (doublet), t (triplet) and m (multiplet).

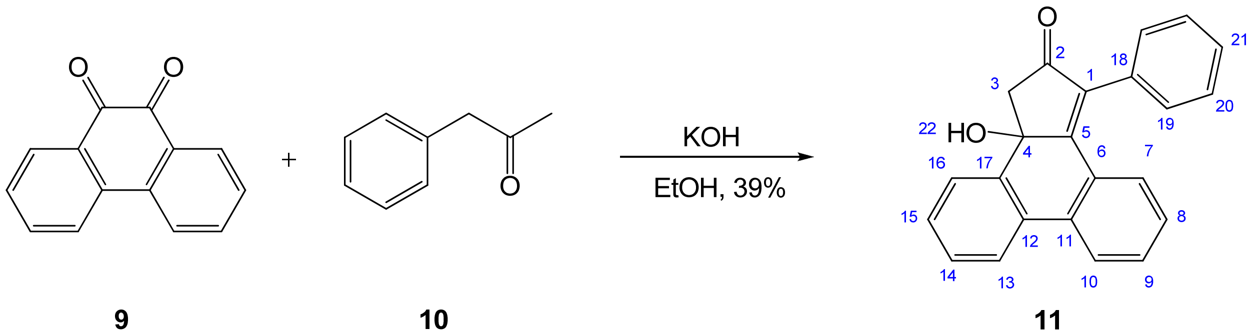
UPLC-MS routine analyses were conducted with an ACQUITY UPLC H-Class system from Waters equipped with a PDA detector, a TUV detector and an electrospray ionization (ESI) system.

As Column was used an ACQUITY UPLC BEH C18 Column (130 Å, 1.7 µm, 1 mm x 50 mm). All samples were dissolved in pure MeCN.

Mass spectra were recorded on a GC/MS ThermoScientific TraceGC-MS DSQII spectrometer equipped with a Zebron ZB-5MS capillary column (30 m L x 0.25 mm ID x 0.25 µm film thickness) (EI ionization) or on a FT/ICR mass spectrometer Bruker 4.7 T BioApex II (MALDI-ICR ionization) with DCTB as matrice, in combination with a 337 nm nitrogen laser.

5.2 Products

5.2.1 Synthesis of 11b-hydroxy-3-phenyl-1H-cyclopenta[l]phenanthren-2(11bH)-one



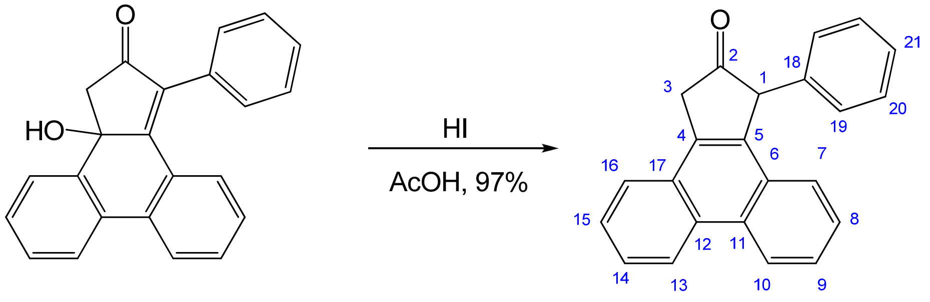
9 (800 mg, 3.840 mmol) and **10** (1.028 ml, 7.680 mmol) in absolute alcoholic 0.5% potassium hydroxide (10 ml) were kept under nitrogen and protected against light at room temperature for one hour. The solution was filtered and washed with cold ethanol obtaining a green solution that was evaporated to give a dark green dense oil. This oil was then purified by flash chromatography (using a gradient pentane/EtOAc 95:5 to 0:100 as eluent) to obtain the product (982 mg, 3.030 mmol, 39 % yield) as a white-brown crystal powder.

^{1}H NMR (300 MHz, CHLOROFORM-d): δ ppm 2.37 (s, 1 H, COH(22)), 3.19 - 3.29 (m, 1 H, CH_2(3)), 3.37 - 3.46 (m, 1 H, CH_2(3)), 7.15 - 7.22 (m, 1 H, CH(Ar)), 7.28 - 7.32 (m, 1 H, CH(Ar)), 7.32 - 7.41 (m, 5 H, CH(Ar)), 7.44 - 7.54 (m, 3 H, CH(Ar)), 7.57 - 7.63 (m, 1 H, CH(Ar)), 7.92 - 8.01 (m, 2 H, CH(Ar)).

^{13}C NMR (91 MHz, CHLOROFORM-d): δ ppm 46.71 (s, 1 C, C(3)), 74.26 (s, 1 C, C(4)), 124.51 (s, 1 C, C(6)), 125.07 (s, 1 C, C(Ar)), 126.69 (s, 1 C, C(Ar)), 127.27 (s, 1 C, C(Ar)), 127.94 (s, 1 C, C(Ar)), 128.48 (s, 1 C, C(Ar)), 128.58 (s, 2 C, C(Ar)), 129.29 (s, 3 C, C(Ar)), 129.77 (s, 1 C, C(Ar)), 129.82 (s, 1 C, C(Ar)), 130.68 (s, 1 C, C(Ar)), 131.41 (s, 1 C, C(18)), 132.42 (s, 1 C, C(12)), 133.59 (s, 1 C, C(11)), 137.58 (s, 1 C, C(1)), 137.89 (s, 1 C, C(17)), 163.45 (s, 1 C, C(5)), 203.60 (s, 1 C, C(2)).

ESI-MS: m/z (%) 347.19 ([M+Na]$^+$, 60 %), 325.19 ([M+H]$^+$, 100 %), 247.17 ([M–C$_6$H$_5$]$^+$, 4 %).

5.2.2 Synthesis of 1-phenyl-1H-cyclopenta[l]phenanthren-2(3H)-one



11 **14**

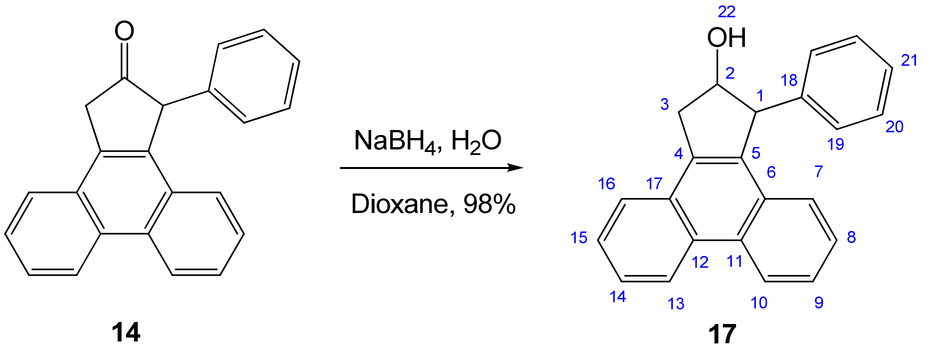
11 (500 mg, 1.541 mmol) was placed in 6 ml of acetic acid; 0.208 ml of 67% hydroiodic acid (353 mg, 1.850 mmol) were added in the cold and the mixture was then heated under reflux for five minutes. The solution was poured into aqueous sodium sulfite (Na_2SO_3) producing immediately a green-white precipitate and was filtrated, dissolved in CH_2Cl_2, dried over Na_2SO_4, filtrated again and evaporated to give the product (463 mg, 1.501 mmol, 97% yield) as a green-white solid.

^{1}H NMR (300 MHz, CHLOROFORM-d): δ ppm 3.91 - 3.99 (m, 1 H, CH$_2$(3)), 4.03 - 4.12 (m, 1 H, CH$_2$(3)), 5.12 (s, 1 H, CH(1)), 7.16 - 7.21 (m, 2 H, CH(Ar)), 7.25 - 7.34 (m, 3 H, CH(Ar)), 7.43 - 7.55 (m, 2 H, CH(Ar)), 7.64 (ddd, *J*=8.3, 6.7, 1.6 Hz, 1 H, CH(Ar)), 7.75 (ddd, *J*=7.4, 5.1, 1.8 Hz, 2 H, CH(Ar)), 7.83 - 7.90 (m, 1 H, CH(Ar)), 8.74 - 8.85 (m, 2 H, CH(Ar)).

^{13}C NMR (91 MHz, CDCl$_3$): δ ppm 41.88 (s, 1 C, C(3)), 59.84 (s, 1 C, C(1)), 123.34 (s, 1 C, C(Ar)), 123.40 (s, 1 C, C(Ar)), 125.38 (s, 1 C, C(Ar)), 125.46 (s, 1 C, C(Ar)), 125.89 (s, 1 C, C(Ar)), 126.51 (s, 1 C, C(Ar)), 127.06 (s, 1 C, C(Ar)), 127.26 (s, 1 C, C(Ar)), 127.43 (s, 1 C, C(Ar)), 127.82 (s, 2 C, C(Ar)), 128.53 (s, 1 C, C(Ar)), 128.59 (s, 1 C, C(Ar)), 128.97 (s, 2 C, C(Ar)), 130.62 (s, 1 C, C(Ar)), 130.74 (s, 1 C, C(Ar)), 133.41 (s, 1 C, C(Ar)), 134.79 (s, 1 C, C(Ar)), 137.38 (s, 1 C, C(Ar)), 212.38 (s, 1 C, C(2)).

EI-MS: m/z (%) 308.16 (M$^{\cdot+}$, 100 %).

5.2.3 Synthesis of 1-phenyl-2,3-dihydro-1H-cyclopenta[l]phenanthren-2-ol



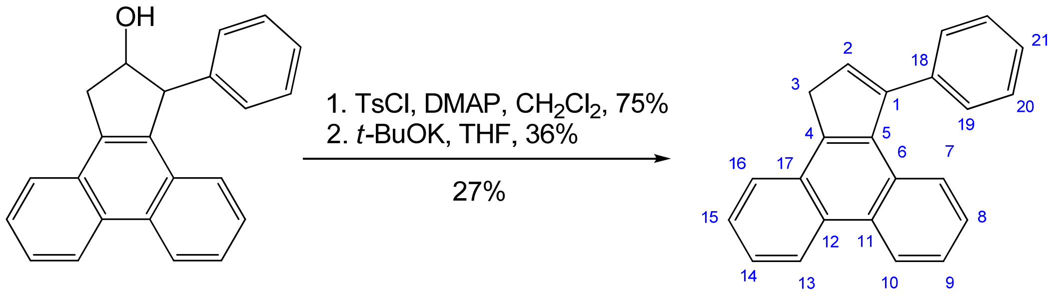
Sodium borohydride (407 mg, 10.770 mmol) in water (4 ml) was added to **14** (400 mg, 1.297 mmol) in dioxane (12 ml) and the mixture was left three days at room temperature under argon. It was then concentrated under reduced pressure, poured into water and extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4 and evaporated to give the product (393 mg, 1.266 mmol, 98 % yield) as a white solid.

^{1}H NMR (300 MHz, CHLOROFORM-d): δ ppm 1.38 (d, *J*=8.5 Hz, 1 H, COH(22)), 3.17 - 3.28 (m, 1 H, CH_2(3)), 3.71 - 3.82 (m, 1 H, CH_2(3)), 5.03 - 5.16 (m, 2 H, CH(1, 2)), 7.11 - 7.17 (m, 2 H, CH(Ar)), 7.28 - 7.35 (m, 3 H, CH(Ar)), 7.40 - 7.49 (m, 1 H, CH(Ar)), 7.54 - 7.62 (m, 2 H, CH(Ar)), 7.66 - 7.74 (m, 2 H, CH(Ar)), 7.92 - 7.98 (m, 1 H, CH(Ar)), 8.69 - 8.80 (m, 2 H, CH(Ar)).

^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 39.25 (s, 1 C, C(3)), 54.97 (s, 1 C, C(1)), 74.34 (s, 1 C, C(2)), 123.13 (s, 1 C, C(Ar)), 123.20 (s, 1 C, C(Ar)), 125.18 (s, 1 C, C(Ar)), 125.22 (s, 1 C, C(Ar)), 125.85 (s, 1 C, C(Ar)), 126.38 (s, 1 C, C(Ar)), 126.73 (s, 1 C, C(Ar)), 126.84 (s, 1 C, C(Ar)), 127.49 (s, 1 C, C(Ar)), 128.90 (s, 2 C, C(Ar)), 129.15 (s, 1 C, C(Ar)), 129.29 (s, 1 C, C(Ar)), 129.40 (s, 2 C, C(Ar)), 130.66 (s, 1 C, C(Ar)), 130.69 (s, 1 C, C(Ar)), 135.51 (s, 1 C, C(Ar)), 136.52 (s, 1 C, C(Ar)), 137.03 (s, 1 C, C(2)).

EI-MS: m/z (%) 310.21 ($M^{\cdot+}$, 100%).

5.2.4 Synthesis of 3-phenyl-1H-cyclopenta[l]phenanthrene



17 **7**

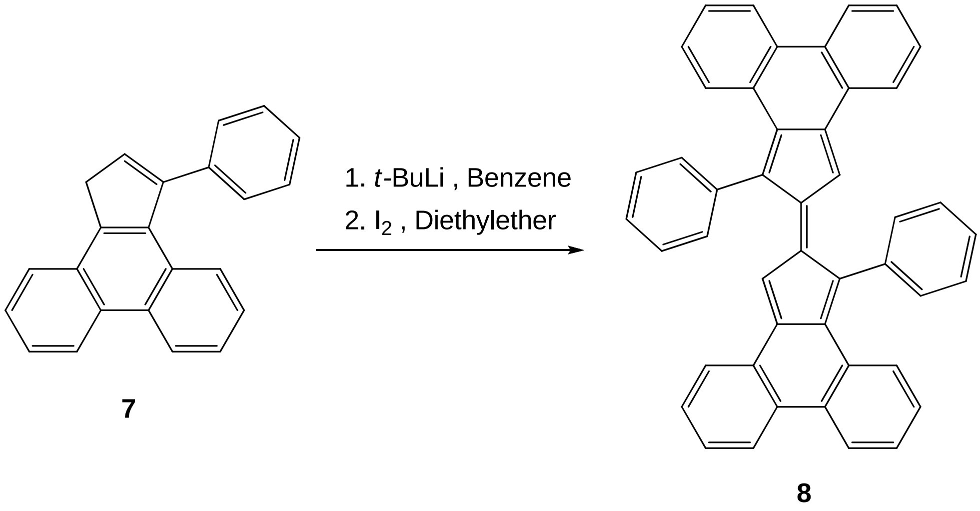
A mixture containing **17** (300 mg, 0.967 mmol), p-toluenesulfonyl chloride (553 mg, 2.900 mmol), DMAP (354 mg, 2.900 mmol) and dry triethylamine (1.105 ml, 7.926 mmol) in around 3 ml of dry CH_2Cl_2 was set under argon at 70 °C for three hours in the microwave. The reaction mixture was diluted with 50% EtOAc in hexane (about 50 ml) and the resulting white precipitate was removed by filtration. The filtrate was concentrated under reduced pressure and the orange-yellow solid residue was purified by flash chromatography (using a gradient pentane/DCM 70:30 to 0:100 as eluent) to give the tosylated intermediate as a light yellow solid (337 mg, 0.725 mmol, 75% yield). This solid was then dissolved in dry THF (5 ml) and potassium tert-butoxide (430 mg, 5.800 mmol) was slowly added. The reaction was carried out under argon at 60 °C for four hours in the microwave. The obtained mixture was then concentrated under reduced pressure, adsorbed by silica and purified by flash chromatography (using a gradient pentane/DCM 100:0 to 0:100 as eluent) to give the product (75 mg, 0.257 mmol, 27 % yield) as a white solid.

^{1}H NMR (360 MHz, CHLOROFORM-*d*): δ ppm 3.92 (s, 2 H, CH_2(3)), 6.58 (s, 1 H, CH(2)), 7.34 (t, *J*=7.6 Hz, 1 H, CH(Ar)), 7.45 - 7.59 (m, 6 H, CH(Ar)), 7.61 - 7.68 (m, 2 H, CH(Ar)), 7.83 (d, *J*=8.4 Hz, 1 H, CH(Ar)), 8.03 - 8.19 (m, 1 H, CH(Ar)), 8.71 - 8.80 (m, 2 H, CH(Ar)).

^{13}C NMR (91 MHz, $CDCl_3$): δ ppm 37.77 (s, 1 C, C(3)), 123.28 (s, 1 C, C(Ar)), 123.32 (s, 1 C, C(Ar)), 124.00 (s, 1 C, C(Ar)), 124.98 (s, 1 C, C(Ar)), 125.35 (s, 1 C, C(Ar)), 125.54 (s, 1 C, C(Ar)), 125.74 (s, 1 C, C(Ar)), 126.80 (s, 1 C, C(2)), 127.40 (s, 1 C, C(Ar)), 127.94 (s, 1 C, C(Ar)), 128.29 (s, 2 C, C(Ar)), 128.86 (s, 2 C, C(Ar)), 129.05 (s, 1 C, C(6)), 129.49 (s, 1 C, C(17)), 130.63 (s, 1 C, C(11)), 132.85 (s, 1 C, C(12)), 137.60 (s, 1 C, C(4)), 139.24 (s, 1 C, C(18)), 140.36 (s, 1 C, C(5)), 147.70 (s, 1 C, C(1)).

EI-MS: m/z (%) 292.16 ($M^{\cdot+}$, 100%), 215.06 ($[M–C_6H_5]^+$, 12 %).

5.2.5 Synthesis of (E)-1,1'-diphenyl-2,2'-bi(cyclopenta[l]phenanthrenylidene



7 (50 mg, 0.171 mmol) in benzene (2 ml) was added to 0.214 ml of butyllithium stabilized in pentane (22 mg, 0.342 mmol), and the mixture was refluxed under argon for two hours. After cooling, iodine (43 mg , 0.171 mmol) in diethyl ether was added dropwise and the mixture stirred overnight. Water was added and the organic layer was separated, washed with sodium thiosulphate solution and dried over Na_2SO_4. Evaporation yielded a dark coloured solid that was purified by flash chromatography to obtain the product not yet completely pure as a brown solid.

MALDI-ICR-MS (DCTB): m/z (%) 580.2 ($M^{\cdot+}$, 10 %), 581.2 ($[M+H]^+$, 17 %), 582.2 ($[M+2H]^+$, 100 %).

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