Département de Chimie
Université de Fribourg (Suisse)

New polycondensed aromatic compounds for applications in the hydrogen cycle

Thèse

présentée à la Faculté des Sciences de l'Université
de Fribourg (Suisse) pour l'obtention du grade de
Doctor rerum naturalium

Nicolas Fragnière
de Sâles (FR)

Thèse N° 1724

UniPrint

2011

Acceptée par la Faculté des Sciences de l'Université de Fribourg (Suisse) sur la proposition du jury composé de:

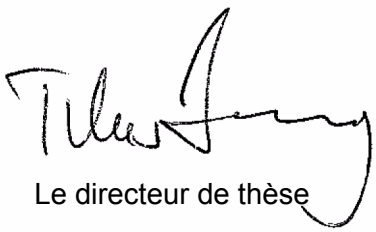
Prof. Dr. Katharina M. Fromm, Université de Fribourg, présidente du jury,

Prof. Dr. Titus A. Jenny, Université de Fribourg, directeur de thèse, rapporteur,

Prof. Dr. Andreas Kilbinger, Université de Fribourg, corapporteur,

Prof. Dr. Yves Rubin, University of California, Los Angeles, corapporteur.

Fribourg, le 19 septembre 2011



Le directeur de thèse
Prof. Dr. Titus A. Jenny

Le doyen
Prof. Dr. Rolf Ingold

A mes parents, Madeleine et André,

A mes soeurs, Florence et Anne-Laure,

A Valérie et Charline

«Le génie commence les beaux ouvrages,
mais le travail seul les achève.»

Joseph Joubert

Acknowledgments

This work has been realized under the guidance of Prof. Dr. Titus A. Jenny in the period of October 2007 until September 2011 at the Department of Chemistry, University of Fribourg (Switzerland).

I would like to express my deep gratitude to Prof. Dr. Titus A. Jenny for accepting me in his research group and for the possibility to realize this work. His enthusiasm and the numerous councils he has given me has been really helpful.

I would also like to express my gratefulness to Prof. Dr. Yves Rubin and Prof. Dr. Andreas Kilbinger for their kind acceptance as experts.

My gratitude goes to Katharina Fromm, the president of the Jury.

I also want to thank Prof. Dr. Norbert Engel and Prof. Dr. Titus A. Jenny to give me the opportunity to guide the students during their practical works.

Many thanks goes to the analytical service of the University of Fribourg: Freddy Nyddegger (mass analysis), Felix Fehr (NMR analysis) and Inge Müller (general support) for their help.

A special thank to Nicolas Monney, Julien Ducry and Ramona Staehli, who have participated to this project.

I also want to thank Xavier Hanselmann, Lucienne Rouiller, Bernadette Khun-Piccand, Noelle Chassot and Nicolas Hoyler of the central service.

Many thanks to Maja Ivanovic, Emerith Brügger and Verena Schwalm for all the administrative work.

Michel Piccand is acknowledged for the poster impressions and the IT.

All my gratitude to Anne Schuwey and her team for all the syntheses they have made for me.

I thank all the members of the Jenny group for the work very pleasant environment, Olivier Ae-

bischer, Deborah Gusmeroli, Daniela Bossi, Patrick Tondo, Mauro Schindler and Sofia Martin Caba.

Many thanks to all my colleagues for all the great moments we had. More than colleagues there are now some friends.

For the nine years we passed together, I really thank my friends Ursi, Karin and Michael.

Finally a real special thank goes to my family, Papa, Maman, Florence, Anne-Laure, Valérie et Charline for all the love and joy they give me every day.

This project was supported by the Swiss National Science Foundation

Summary

This work presents the synthesis of a new perfluorinated sulfonic acid function HBC which carries a sulfonic acid at the end of one perfluorinated side-chain.The aim of the introduction of this sulfonic acid is its ability to form proton channels which could be used as electrolyte in proton exchange membranes for fuel cells. The channels would be created by the formation of stacks of three molecules clusters oriented by the hydrophobic effect of the perfluorinated chains and hydrophilic effect of the sulfonic acid. The π-π stacking would occur by the well-known properties of HBCs compounds building columns, and hence protons channels would be formed.

The synthesis of the compound was achieved by a convergent strategy, coupling a perfluoroalkyl tetraphenyl cyclopentadienone and a perfluoroalkyl dissymmetric tolane, thanks to a Diels-Alder reaction. If no real difficulties were met for the formation of the required cyclopentadienone synthon, the preparation of the dissymmetric tolane was more complicated because of the presence of the sulfonic acid function, which decreases the reactivity, because of solubility issues. Finally the desired compound was obtained as a brown solid by a cyclodehydrogenation oxidation of a perfluoroalkyl hexaphenyl benzene sulfonic acid and could be analysed by MALDI-MS, UV absorption and fluorescence spectroscopy, which all confirmed the presence of this new HBC. With the deposition of this new material on a water impermeable porous membrane, this HBC could facilitate the selective proton transfer across the membrane and act therefore as a proton channel membrane.

For comparison, the synthesis of an alkylated HBC sulfonic acid was also planned, using the same approach as for the perfluorinated HBC analogue. Even if the synthesis of this HBC was not totally achieved, much preliminary work was done on the attachment of the sulfonic acid. The best strategy seems to be a nucleophilic substitution of an alcohol function by bromine followed by the exchange with a sulfonate, using sodium sulfite. Because of solubility problems, to best stage at which this sulfonate formation should be performed has to be found.

Second, for an envisioned application in hydrogen gas storage, the synthesis of a new bowl-shaped polycondensed aromatic compound based on the oxidation of pentaphenyl cyclopentadiene precursor will be discussed. This newly envisioned material is based on a property of corannulene, which is known as a potential hydrogen absorber. With a larger surface area than corannulene, our target compound would allow the storage of a larger quantity of hydrogen. As

synthetic approaches for corannulene are not applicable for our target molecule, the formation of a pentaphenyl cyclopentadiene derivative which would then be oxidized under Scholl conditions was planned. Commonly used for the oxidation of flat polycondensed aromatic compounds such as hexabenzocoronenes, the Scholl oxidation is a real challenge in the case of bowl-shaped molecules, because the carbon atoms are further away from each other and the reaction would have to overcome considerable strain.

So far, the desired bowl-shaped polyaromatic compound has not been obtained. The numerous oxidation attempts either yielded starting material or some unidentified molecules. Since complexation by iron could stabilize the desired product, the pentaphenyl cyclopentadienyl derivative was successfully complexed with iron, forming ferrocene-like compounds. Unfortunately, this complexation did not improve the reactivity of the pentaphenyl cyclopentadiene moiety towards cyclodehydrogenation. Therefore, this idea remains unachieved.

Résumé

Dans ce travail, nous allons présenter la synthèse d'un nouvel HBC perfluoroalkylé muni d'un acide sulfonique à la fin de l'une des chaînes perfluoroalkylé. Le but de l'introduction de cet acide est sa capacité à former de canaux à protons utilisable comme membrane dans des piles à combustible. Les canaux seraient créés par la formation de «stacks» de clusters de trois HBCs orientés par l'effet hydrophobe des chaînes perfluorées et par l'effet hydrophile de l'acide sulfonique. Grâce aux π-π stacking bien connu pour les composés polyaromatiques condensés comme les HBCs, des colonnes seraient formées, créant ainsi les canaux à protons.

La synthèse de ce composé a été réalisé par une stratégie convergeante, en couplant, grâce à une réaction de Diels-Alder, un tetraphenyl cyclopentadienone perfluoroalkylé et un tolane dissymetrique perfluoroalkylé. Si aucune difficulté n'a été rencontrée pour la synthèse du dérivé de cyclopentadienone, la préparation du tolane dissymétrique a été plus compliqué, à cause de la présence de l'acide sulfonique qui diminue la réactivité, du à une mauvaise solubilité. Finalement, le composé désiré a été obtenu sous la forme d'un solide brun par une réaction de cyclodéhydrogénation d'un hexaphenyl benzène perfluoroalkylé portant un acide sulfonique. Les analyses MALDI-MS, d'absorption UV et de fluorescence ont clairement démontré la formation du nouvel HBC. Par une déposition de ce nouveau matériau sur une membrane poreuse imperméable à l'eau, notre nouveau produit pourrait faciliter le transfert de protons à travers cette membrane, et ainsi fonctionner comme membrane à canaux de protons.

Comme comparaison, la synthèse d'un HBC alkylé avec également un acide sulfonique a été testée, en utilisant la même approche que pour l'HBC perfluoroalkylé. Même si la synthèse de cet HBC n'a pas été réussie, beaucoup de tests différents ont été faits pour mettre l'acide sulfonique sur une chaine alkylé. Il semble que la meilleure méthode commence par une substitution nucléophile d'un alcool par un brome, qui peut ensuite être échangé par le sulfonate, en utilisant du sulfite de sodium. Les problèmes de solubilité rencontrés durant cette synthèse nous oblige à poursuivre les recherches pour trouver à quel moment la formation du sulfonate est la plus judicieuse.

La synthèse d'un nouveau composé incurvé basé sur l'oxydation d'un cyclopentadiène substitué avec cinq phenyls sera également discutée dans ce travail. Ce nouveau matériau est basé sur une propriété connue du corannulène, qui peut fonctionner comme "réservoir" à hydrogè-

ne. Avec une surface plus large que celle du corannulène, une plus grande quantité d'hydrogène devrait pouvoir être stockée par notre produit cible. Comme les voies de synthèse pour former le corannulène ne peuvent pas s'appliquer dans notre cas, nous avons choisi de passer par la formation d'un dérivé de pentaphenyl cyclopentadienone qui pourrait ensuite être oxydé par une réaction de Scholl. Généralement utilisée sur des composés aromatiques polycondensés plats, la reaction de Scholl est un réel challenge dans le cas d'une molécule incurvée, car les carbones sont loins les uns des autres, et la réaction devrait surmonter des contraintes considérables.

Jusqu'à maintenant, ce composé polyaromatique incurvé n'a pas été obtenu. Les nombreux essais effectués ont toujours donné le matériel de départ ou des produits indéfinis. Comme la complexation par un atome de fer peut stabiliser le produit désiré, un dérivé de pentaphenyl cyclopentadienone a été complexé sur un atome de fer, formant un composé similaire au ferrocène. Malheureusement, ce complexe n'a pas permis d'améliorer la réactivité du pentaphenyl cyclopentadiene pour la cyclodéhydrogénation. Cette idée n'est donc, pour le moment, pas concluante.

Table of contents

III. Results and discussion 51

IV. Conclusion and outlooks 107

List of abbreviations

Ac:	Acetyl
ACN:	Acetonitrile
AIBN:	2,2'-Azobisisobutyronitrile
AFC:	Alkaline fuel cell
BDC:	1,4-benzenedicarboxylate
BSF:	Bio fuel system
BTAC:	Benzyltrimethylammonium chloride
BTF:	Benzotrifluorid
BTT.	1,3,5-benzenetristetrazolate
C-c:	Cross-coupling
CNF:	Carbon nanofiber
CNT:	Carbon nanotubes
CSA:	Camphorsulfonic acid
DCC:	N,N'-Dicyclohexylcarbodiimide
DCM:	Dichloromethane
DCTB:	trans-2-[3-(4-tert-buthylphenyl)-2-methyl-2-propenylidene]malononitrile
DDQ:	Dichlorodicyano-*p*-benzoquinone
DEA:	Dimethylamine
DEFC:	Direct ethanol fuel cell
DMAP:	4-Dimethylaminopyridine
DMF:	Dimethyl formamide
DMFC:	Direct methanol fuel cell
DMSO:	Dimethylsulfoxide
DOE:	Department of Energy
Eq:	Equivalent
ESR:	Electron Spin Resonance Spectroscopy
Et_2O:	Diethyl ether
EtOAc:	Ethyl acetate
FC:	Fuel cell
F-C:	Friedel-Crafts
FTIR:	Fourier transform infrared spectroscopy
FVP:	Flash vacuum pyrolysis
GDC:	Gadolinium doped ceria

GE: General Electric
HBC: Hexabenzocoronene
HFB: Hexafluorobenzene
HPB: Hexaphenylbenzene
ICP: Inductive coupled plasma
IEC: Ion exchange capacity
ILD: Interlayer distance
IR: Infra-red
MALDI: Matrix-assisted laser desorption/ionization
MCFC: Molten carbonate fuel cell
Me: Methyl
MEA: Membrane electrode assembly
MeCN: Acetonitrile
MOF: Metal-oragnic framework
MTBE: Metyhl tert-buthyl ether
MTOe: Million tonnes of oil equiovalent
MW: Microwave
NASA: National Aeronautics and Space Administration
NMR: Nuclear magnetic resonance
PAFC: Phosphoric acid fuel cell
PAN: Polyacrilonitryle
PBI: Polybenzimidazole
Ph: Phenyl
PEM: Proton exchange membrane
PEMFC: Proton exchange membrane fule cell
PFSA: Perfluorosulfonic acid
PFSI: Perfluorosulfonated ionomer
PTFE: Polytetrafluoroethylene
PTSA: *Para*-toluene sulfonic acid
Red-Al: Sodium bis(2-methoxyethoxy)aluminum hydride
Rf: Perfluorinated
RH: Relative humidity
Rt: Room temperature
SANS: Small-angle neutron scattering
SAXS: Small-angle X-ray scattering
SHE: Standard hydrogen electrode

SOFC: Solid oxide fuel cells

sPEEK: Sulfonated poly (ether ether ketone)

SPI: Sulfonic acid polyimide

$S_{RN}1$: Unimolecular radical nucleophililc substitution

SWNT: Single wall carbon nanotube

TCNQ: 7,7,8,8-tetracyanoquinodimethane

TEMPO: (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl

TFE: Tetrafluoroethane

TGA: Thermogravimetric analysis

THF: Tetrahydrofurane

TLC: Thin layer chromatography

TMP: 2,2,6,6-tetramethylpiperidinates

TMS: Tetramethylsilane

TMSA: Trimethylsilylacetylene

TPD: Temperature program desorption

W-K: Willgerodt- Kindler reaction

Wt: Weight

YSZ: Yttria-stabilized zirconia

9ScSZ: Scandia stabilized with 9 mol% zirconia

I. Theoretical background

1. Introduction

Regarding the actual energy consumption which is continuously growing (see Figure 1), it is

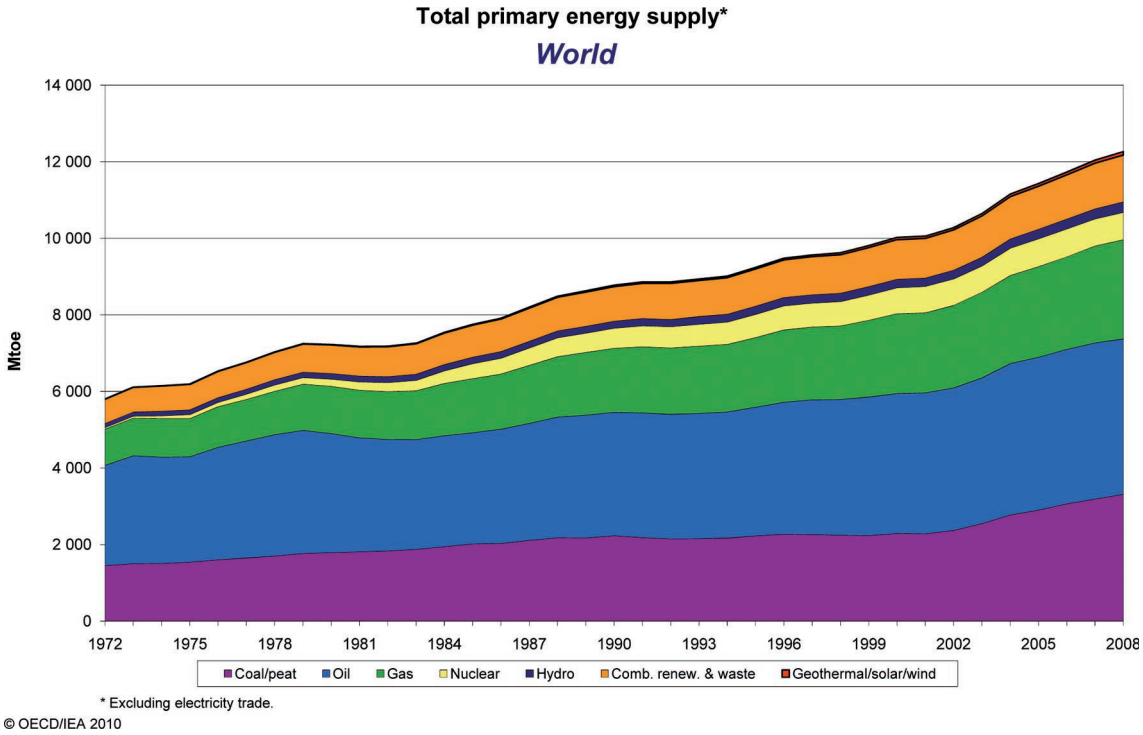


Figure 1: Energy consumption evolution since 1972 in the world [2]

evident that the fossil fuel resources will no longer be available in sufficient quantities. According to the previsions, the peak oil [1] is or will be reached during these years. This large energy

consumption which is covered principally by fossil energies (see Figure 2) is responsible in

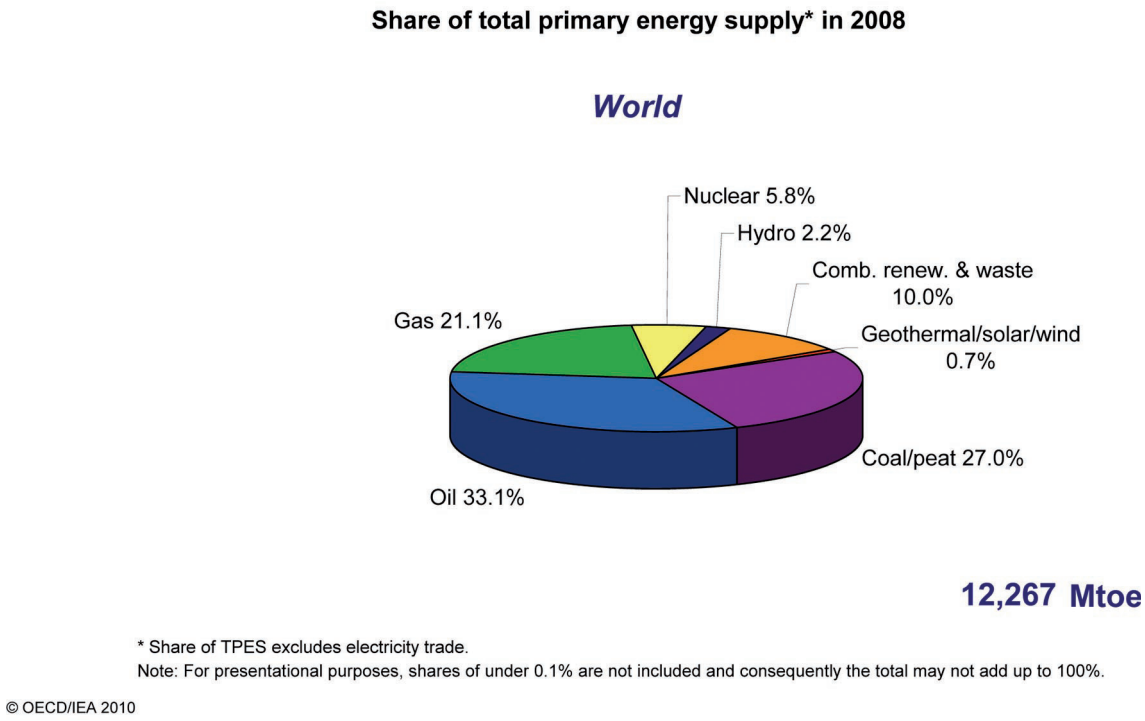


Figure 2: Share of total energy supply in 2008 [3]

majority for the greenhouse gases emission. To limit these emissions and to substitute the fossil fuels, a lot of research activities are focused on renewable energy sources such as sunlight, wind, rain, tide or geothermal. With a gravimetric energy density of 33 kWh/kg and a calorific value three times higher (around 143 MJ/kg) [4] as compared to petroleum, hydrogen has also been proposed as an ideal energy source in the future and is therefore widely studied for various applications such as power generation and automotion. The use of hydrogen as a cyclic energy source represents three major challenges: its production, storage and consumption which produces water as by-product. As water is involved in hydrogen production, we can speak about an “hydrogen cycle” (see Figure 3).

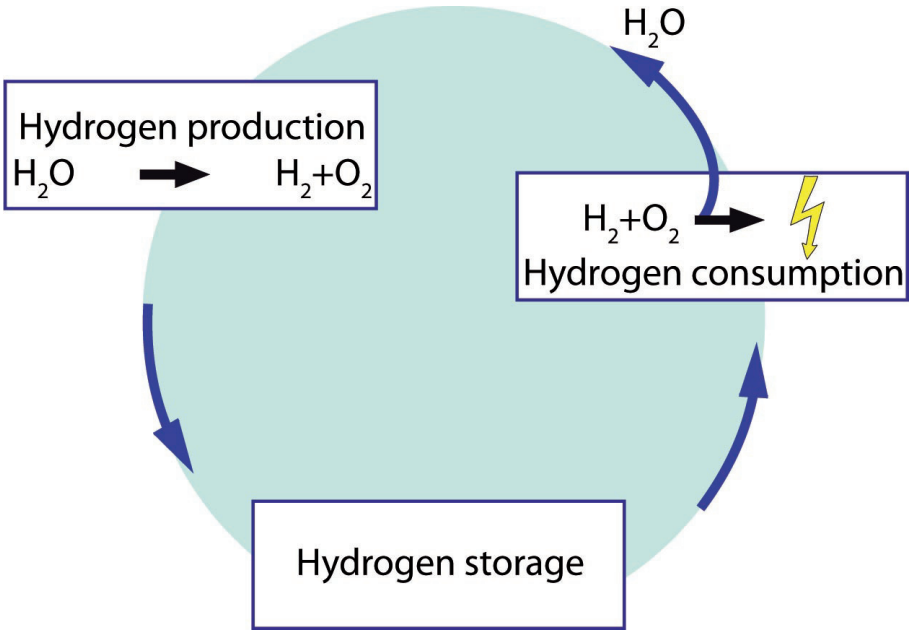


Figure 3: Hydrogen cycle

On earth, hydrogen gas is only present in small amounts [5]. Therefore, to be employed in large scale, this hydrogen has to be extracted from natural resources, such as fossil fuels, or produced from water, the most abundant hydrogen source on earth. Today the most important part is produced as a side-product in reforming reactions in the oil refining process. Of course this method is limited by the fossil fuel resources. Moreover, the concomitant formation of carbon monoxide and carbon dioxide is also a drawback because they add to greenhouse gas emission. A promising alternative to this reforming reaction is the decomposition of water into hydrogen and oxygen by electrolysis or thermolysis. Both have as main advantages a high gas purity and the co-production of oxygen. But because the large amount of energy required for such splitting, both processes become interesting only if energies from renewable sources are used. This is made for water thermolysis by concentrating the solar light to produce the heat of 800 °C to 1200 °C necessary for water thermolysis [6] or by using photoelectrolysis where the sunlight is used either to produce electrical current necessary for water electrolysis or by a photocatalytic water splitting reaction [7], [8]. Naturally other problems like the development of really efficient and durable proton exchange membranes in acidic electrolysis or the improvement of the catalyst in water thermolysis must be solved.

Nowadays, almost all locomotion means require fossil fuels. On the long run, this polluting energy must be replaced by another energy source such as light, with similar or better energy

density capacity (around 46 MJ/kg for Diesel) at a competing prize. The use of batteries has the advantage to be quickly charged, but the weight/energy ratio as well as their prize (because rare elements are often used) are not favorable. The production of artificial fuel from the biomass like bioethanol or methane is also envisioned. These fuels would be ideal for mobile devices because the energy density is similar to traditional fossil fuels. As major drawbacks, their production consumes a lot of energy and water, occupies large surfaces and forms carbon dioxide during their combustion. But according to the work of Bio fuel system (BSF), this carbon dioxide, as well as all other carbon dioxide sources can be converted to artificial petrol using microalgae and light. This revolutionary process already works and could be envisioned as an important energy source in the future [9].

Beside these possibilities, the most promising fuel replacement is hydrogen. But to be widely employed, hydrogen has to be stored safely and in a low-cost manner. The known methods have several disadvantages. The compression shows high storage volume efficiencies, but the operating costs are high and the storage volume is too large for mobile applications [10]. An example of compression storage is given by a 34 MPa pressurized hydrogen tank with a volume of 186 L and a weight of 32.5 kg which is sufficient to move a car for about 500 Km. But this thank, almost as big as a 200 L drum is too bulky for an individual car [11]. Moreover, high hydrogen pressure causes safety problems. The storage in liquid form resolves this high pressure problem but is too greedy in energy to reach and maintain the low temperature needed (around - 253 °C). In addition, the losses estimated to up to 1% a day by boiling, and up to 30% during the filling require efficient insulation [12] and are only fit for large scale applications.

Metal hydride complexes are also largely explored for hydrogen storage. The challenge is to find a complex with a high storage capacity and a low desorption temperature. One of the most interesting alloys is sodium borohydride. Mixed with water at 30 wt%, a volume storage efficiency around of 63 g H_2/L is reached, which is almost as high as the 71 g H_2/L for liquid hydrogen and higher than the 39 g H_2/L in a tank of hydrogen at 700 bar. This alloy is used in a Hydrogen on Demand^{TM} system (c.f. Figure 4) developed by Millennium Cell Inc. which is already used in a fuel cell vehicle [13]. But even if this method seems perfect producing pure humidified hydrogen directly applicable in fuel cells, the cost of its production must decrease and a low cost regeneration system of the sodium metaborate must be developed before such a system could compete.

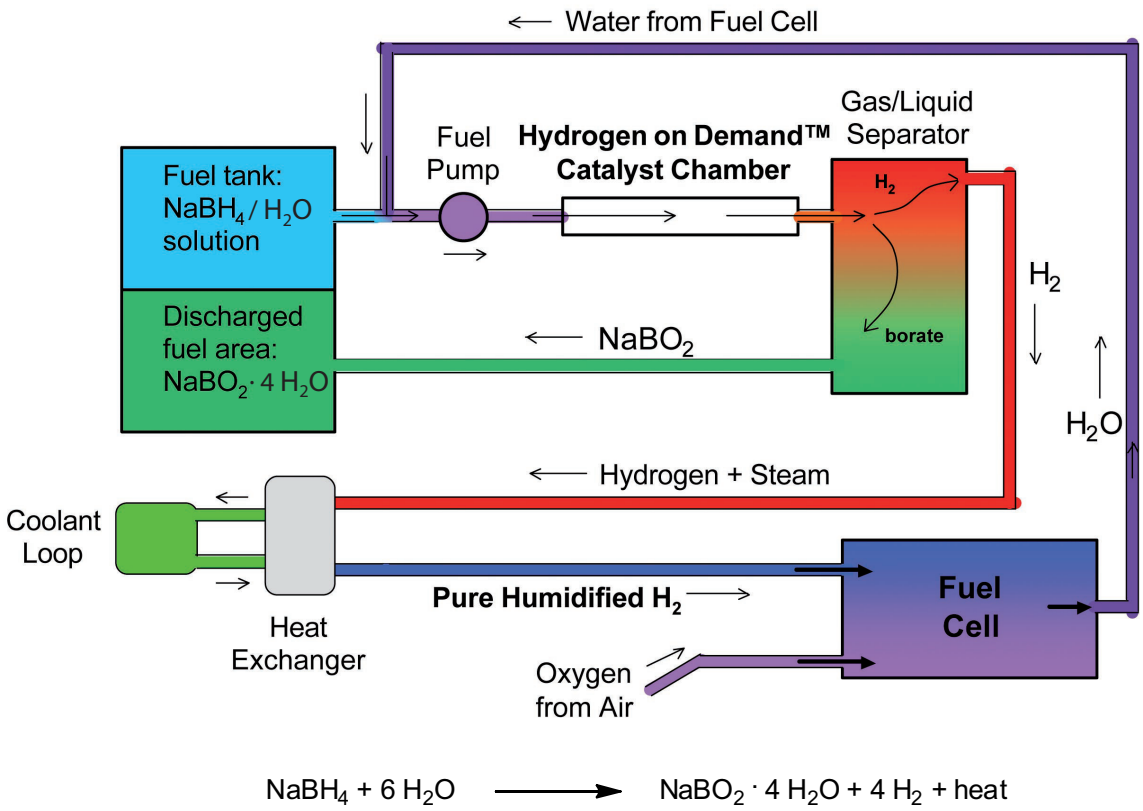


Figure 4: Hydrogen on Demand™ system scheme [13]

With exceptional high specific surface areas and chemically-tunable structures, the metal organic frameworks (MOF) have attracted a lot of attention for hydrogen storage [14]. Under specific conditions, interesting performances could be obtained. For example with the $Zn_4O(BDC)_3$ MOF at 77 K and with a pressure up to 100 bar, a rapid and fully-reversible hydrogen uptake of 10 wt% and 66 g H_2/L was obtained [15]. But for mobile applications, such conditions are not accessible. At ambient temperature and pressures below 100 bar envisioned for safe mobile systems, lower efficiencies of 1.49 wt% and 12.1 g H_2/L at 298 K and 90 bar are for instance obtained for frameworks with open metal coordination sites like $Mn_3[(Mn_4Cl)_3(BTT)_8]_2$ [16]. Moreover, improvements in gravimetric and volumetric capacity are still necessary.

Until now, all the materials for hydrogen adsorption have a relatively low gravimetric capacity and are therefore not very attractive for mobile applications. But it was observed that carbon materials also have interesting gravimetric capacities for hydrogen storage. Especially curved graphene compounds like carbon nanotubes and fullerenes have shown promising wt% ratios between 5 wt% and 10 wt% [17]. Recently a paper of Scanlon [18] discussed the ability of corannulene to store hydrogen. His encouraging results prompted us to deeply explore our own

ideas.

Contrary to water electrolysis or thermolysis where water is split in hydrogen and oxygen, the recombination of these two gases will allow to directly liberate heat and electrical current. This is a major advantage comparing to fossil fuels which require a generator to convert their chemical energy in electricity. The consumption of hydrogen can occur by two different mechanisms. Either it is burnt in presence of oxygen and heat (like fossil fuels) produces mechanical energy for vehicle motion (around 25% conversion, a bit better than fossil fuel combustion), or hydrogen can electrochemically react on a catalyst, decomposing it into protons and electrons. This reaction is used for the direct production of electricity in proton membrane exchange fuel cells, with an efficiency around 50% to 60% [19]. This high conversion efficiency as well as the consumption of “clean” fuels and the by-production of only heat and water have prompted researchers to work on fuel cells development.

2. Fuel Cells overview

2.1 General considerations

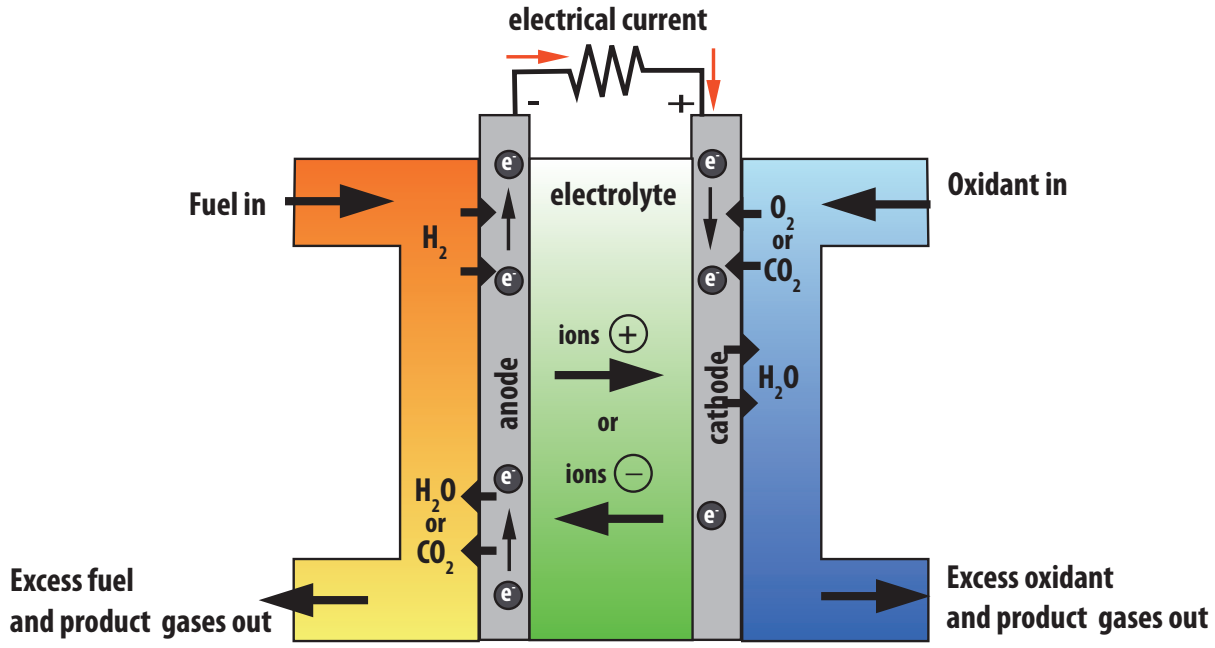


Figure 5: General scheme of a fuel cell

A fuel cell can be compared to a classical battery. Indeed, in both cases an electrical current is produced by chemical reactions. The main difference between batteries and fuel cells resides in the provisioning in fuel. Meanwhile in batteries no fuel can be reintroduced in the system, whereas fuel cells are clearly manufactured for refilling. This induces a second difference between the two systems. In batteries, the energy is directly stored in the system, what is not the case for fuel cells, which need an external tank for fuel storage.

Since the first successful application of an alkaline fuel cell in the 1960s for the production of electricity and drinkable water during the Apollo mission, a huge interest was focused on fuel cells, and a rapid development of new technologies allowed a variety of possible applications, such as combined heat and power generation, replacement of batteries for vehicles propulsion [20]. Due to their high efficiencies, modular design, low noise and low environmental impact, fuel cells are really promising for the future. However, important challenges to improve their durability and their efficiency with low production costs are still present.

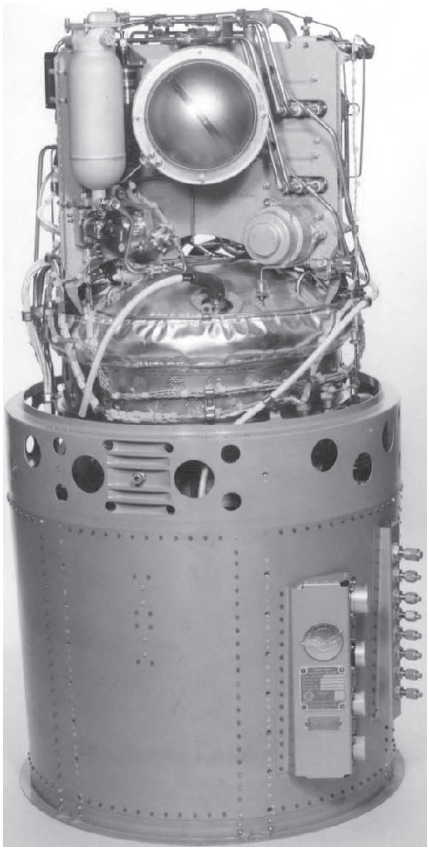


Image 1: 1.5 kW alkaline fuel cell used during the Apollo spacecraft [21]

A fuel cell is an electrochemical device which converts chemical energy of a fuel into electrical current and heat without fuel combustion. Depending on the type of fuel cells, different fuels could be used as hydrogen source: naturally hydrogen, which could cause some storage complications, alcohols like methanol or ethanol, hydrocarbons or biogas. The general mechanism for the electrical current generation consists in a separation of electrons and ions produced by a chemical oxidation. The electricity is generated thanks to the transport of the electrons through a conductive circuit to the cathode (see Figure 5). The nature of the ions depends on the type of fuel cells. The most common ions are protons, hydroxides, carbonates or oxides [22]. For a maximum efficiency, the choice of the electrolyte and the electrodes, as well as the temperature, pressure and fuel has to be optimized.

The different fuel cells could be first divided into two categories: (1) low temperature fuel cells which work typically with temperatures between 0 °C and 200 °C and (2) high temperature fuel cells with operating temperatures between 600 °C and 1000 °C. A more precise definition of the fuel cells is usually given by the electrolyte. Six different types of fuel cells will be discussed

in this work: (1) the direct methanol fuel cells (DMFC), (2) the alkaline fuel cells (AFC), (3) the phosphoric acid fuel cells (PAFC), (4) the molten carbonate fuel cells (MCFC), (5) the solid oxide fuel cells (SOFC), and (6) the proton exchange membrane fuel cells (PEMFC). The principal characteristics of each fuel cells are summarized in table 1 [22], [23], [24].

Table 1:Principal properties of the main fuel cells types

	PEMFC	DMFC	AFC	PAFC	MCFC	SOFC
Fuel	H_2	MeOH	H_2	H_2	H_2, CH_4, CO	H_2, CH_4, CO
Operating temperature [°C]	50 - 200	0 - 130	50 - 200	150 - 200	600 - 700	600 - 1000
Electrolyte/ membrane	Polymer solid acid	Polymer	KOH	H_3PO_4 in SiC	K_2CO_3/ Li_2CO_3	ZrO_2/Y_2O_3
Charge carrier	H^+	H^+	OH^-	H^+	CO_3^{2-}	O^{2-}
Power	< 100 kW	< 100 W	500 W to 10 kW	10 kW to 1 MW	100 kW to > 10 MW	1 kW to > 10 MW
Efficiency [%]	45 - 60	40	40 - 70	55	60 - 65	50 - 60

2.2 Fuel cells fuels

The choice of fuel is not very different between the different cells. It depends principally on the charge carrier wanted. All fuel cells can consume hydrogen except the direct methanol fuel cells which are designed to work with a methanol/water mixture (see (Eq. 1)). Allowing a easy storage as compared to hydrogen gas, methanol encounters two principal drawbacks, the toxicity of methanol and the formation of carbon dioxide as a side-product as shown in (Eq. 1). The

$$MeOH + H_2O \longrightarrow CO_2 + 6\,H^+ + 6\,e^- \quad \text{(Eq. 1)}$$

$$3/2\,O_2 + 6\,H^+ + 6\,e^- \longrightarrow 3\,H_2O \quad \text{(Eq. 2)}$$

development of direct ethanol fuel cells (DEFC) [25] is now under investigation to solve the toxicity problem. But the efficiency is usually half of the DMFC. Besides hydrogen and MeOH, other fuels like methane or other hydrocarbons and carbon monoxide are also used in molten carbonate or solid oxide fuel cells, working at high temperatures. The hydrocarbons could lib-

erate hydrogen gas by reforming reaction within the cells due to the high temperatures and carbon monoxide could react instead of hydrogen at the anode with carbonates or oxides used as charge carrier in SOFC ((Eq. 3)) and in MCFC ((Eq. 4)) forming carbon dioxide. But despite methane can be produced by fermentation its production as well as the carbon monoxide formation come essentially from fossil fuels, what makes these fuels uninteresting compared to hydrogen. It should be mentioned that in MCFCs, the carbon dioxide formed as by-product is collected and re-introduced in the system to be consumed at the cathode (see Figure 6) [26]. Indeed, the formation of the carbonates used as charge carrier requires a mixture of oxygen and carbon dioxide (see (Eq. 5)).

$$2\ CO + 2\ O^{2-} \longrightarrow 2\ CO_2 + 4\ e^- \qquad \text{(Eq. 3)}$$

$$CO\ (g) + CO_3^{2-} \longrightarrow 2\ CO_2 + 2\ e^- \qquad \text{(Eq. 4)}$$

$$O_2 + 2\ CO_2 + 4\ e^- \longrightarrow 2\ CO_3^{2-} \qquad \text{(Eq. 5)}$$

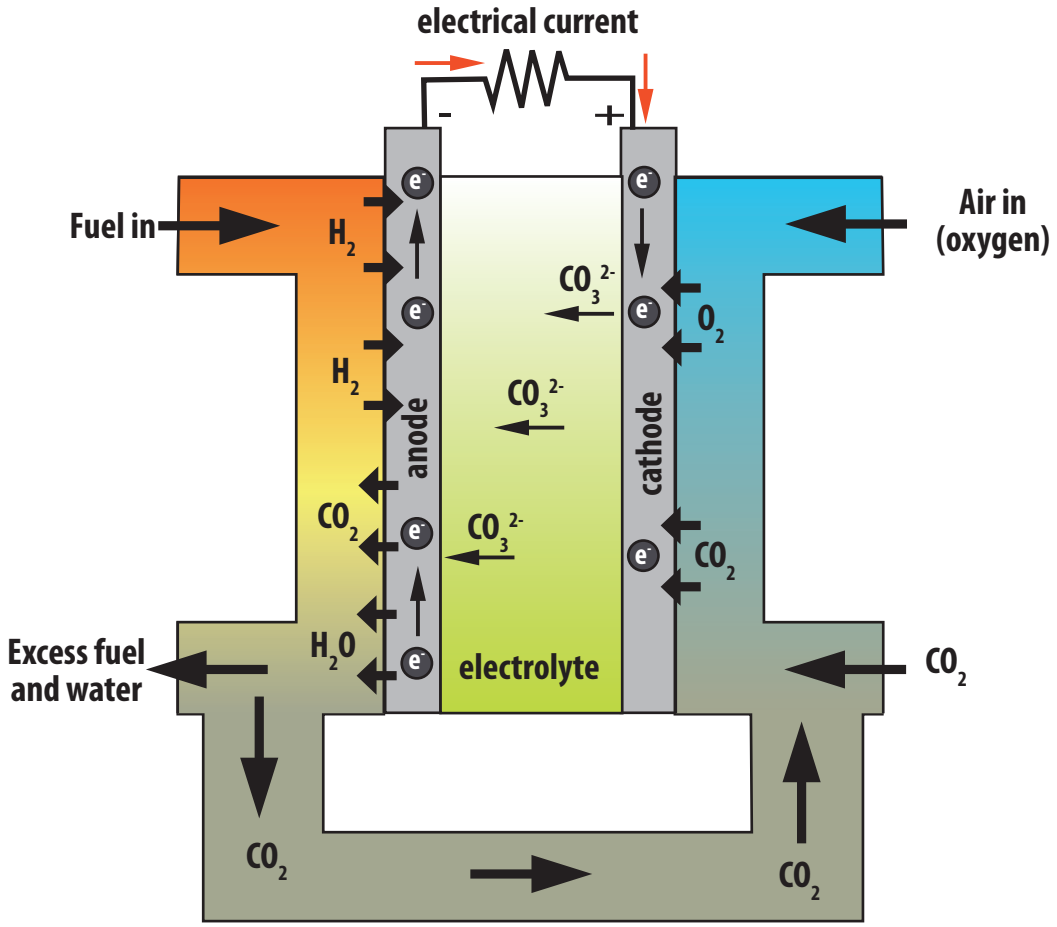


Figure 6: General scheme for a MCFC with recycling of carbon dioxide

The quality of the fuel is also essential in fuel cell applications. In low temperature fuel cells, the presence of carbon monoxide or dioxide in the hydrogen could kill the cell by poisoning. If a small tolerance is observed in PEMFC and in PAFC, real pure hydrogen must be employed in AFC to avoid the formation of carbonates by reaction of carbon dioxide with hydroxide anions. This side-reaction decreases the concentration of the electrolyte and the formed carbonates fill the electrode porosities, both altering the cell operation. To keep the starting concentration of hydroxides, the electrolyte can be continuously pumped, allowing “fresh” electrolyte to be injected in the cell. Although this method also helps to the cell cooling, this device is not really useful for mobile applications. The solution could come from electrolysis or thermolysis which produce very high hydrogen and oxygen quality. Coupled to a CO_2 scrubber, a very low carbon dioxide amount could be introduced in the alkaline fuel cell [21].

2.3 Electrodes

The electrode choice depends especially on the operation temperature. For low temperature fuel cells like PEMFC, DMFC and PAFC, the electrodes are generally composed of a noble metal such as platinum dispersed on porous carbon material which serves as support and gas diffusion layer [27]. Largely responsible of the high prize of fuel cells, the quantity of Pt needed is now around 0.4 to 0.8 mg/cm^2 instead of 25 mg/cm^2 with early platinum black catalysts, thanks to a better dispersion [28]. The efficiency of the platinum alone can be improved by the use of alloys. Pt-Ru alloy shows for example a better tolerance to carbon monoxide, certainly because it weakens the Pt-CO bonds [29] which become more reversible. The other low temperature fuel cells, the alkaline fuel cells, can work with nickel or silver as catalyst, in order to reduce the production cost. But because of the strong corrosion of the electrolyte, the durability is affected [30].

When higher temperatures are used, no noble metals are necessary because the temperature helps to the catalytic fuel decomposition. In SOFC, the anode is usually composed by a cermet (an intimate mixture of ceramic and metal), classically zirconia mixed with nickel, chosen for its high electronic conductivity and stability in reducing conditions. The composition of the cathode is still a challenge, but the most common material is a strontium-doped lanthanum manganite [31]. Nickel is also used in MCFC electrodes. The anode is prepared by porous nickel and around 10% of chromium, while at the cathode the nickel is recovered by nickel oxide. It is clear that the electrodes for high temperature fuel cells are less expensive, but the energy costs to reach these high temperatures kills this advantage.

2.4 Electrolytes and charge carriers

The electrolyte is the principal part which differentiates the fuel cells. It serves for charge carrier mobility and fuel gas separation and must therefore be adapted depending on the ions which have to migrate through it. Three types of electrolytes allow the transfer of anions. At low temperature, low cost KOH solutions with suitable membranes transfer hydroxides. The major drawbacks are the strong corrosion of the hydroxides as well as a sensitivity to carbon dioxide which reacts with the hydroxides to form carbonates, as already explained. The poisoning with carbonates is resolved in MCFC which employ these carbonates as charge carrier. Only recently developed, the molten carbonate fuel cells require high temperatures between 600 °C and 1000 °C to obtain a molten mixture of alkali metal carbonates (mixture of Li and K or Na carbonates) necessary for the ionic conduction. The carbonate mixture is retained in a ceramic

matrix of $LiAlO_2$ with a thickness of ~0.5 mm. But these high temperatures induce breakdown and corrosion of the fuel cell components. Moreover, a long start up time and a low power density hamper this FC type. The last anion charge carrier system is the solid oxide fuel cells. SOFC are complete solid-state devices working at really elevated temperatures between 600 °C and 1000 °C, using an oxide ion conducting ceramic material as electrolyte. The most popular electrolyte are zirconia stabilized with 8% to 10% of yttria (YSZ), but other oxides such as zirconia stabilized with 9 mol% scandia (9ScSZ) and gadolinium doped ceria (GDC) are also applied. However, besides the solved corrosion problem, the same long start up times are encountered.

Relative high temperatures around 200 °C and a corrosive electrolyte are also employed in the phosphoric acid fuel cells where 100% phosphoric acid contained in a silicon carbide particles matrix held by a small amount of polytetrafluoroethylene [26] serves as electrolyte. Even if these conditions seem harsh, the components are not affected, regarding their good durability in excess of 40 000 h. The last category to be discussed is the proton exchange membrane which comprises naturally the PEMFC and the DMFC. As for alkaline fuel cells, no high temperatures are employed, because most of the electrolyte membrane need water for a good conduction, what limits the maximal working temperature. But applications at 200 °C (PEMFC based on H_3PO_4-doped PBI) can be found [33]. The first and the most used membrane is the Nafion®, which was discovered by DuPont in the 1960s [32]. Even if good chemical and thermal resistivity as well as good proton conductivity is noted for this material, the durability of the membrane is problematic (c.f. paragraph 3).

The thickness of the electrolyte membrane also plays an important roll. To allow a good and quick ion transfer, the membranes have to be relatively thin. But naturally, the thinner the membrane, the lesser is its mechanical resistivity. Generally, the thickness of the membrane is comprised between a few mm to less than 0.1 mm for SOFC. The thickness also depends on the processability available for its preparation.

2.5 Lifetime and efficiency

The lifetime necessary for useful applications varies according to the envisioned aim. For instance, an operation durability of 5 000 hours could be sufficient for a private car, but 20 000 hours are needed for a public bus. Several parameters could deteriorate the efficiency and therefore the lifetime. Problems can come from for instance low reactant gas flows, too high and too low humidification levels, high and low temperatures. Physical degradations such as

loss of active catalyst surface, poisoning, loss of proton conductivity in the membrane, deterioration of mass transport properties in the porous layers, 'hotspots' and holes in the membrane, sealing degradation, corrosion on plates, can also negatively influence the fuel cell operation [34].

To produce sufficient electrical current for applications, fuel cells must be connected in series, known as a "stack" [35]. The simplest method is to connect each cathode to the anode of the next cell all along the stack. But this connection method causes a reduction in the voltage (voltage drop) already quite small in one fuel cell (around 0.7 V). A real better solution is to connect each fuel cell by a bipolar plate (see Figure 7) manufactured in good conductor materials such as graphite or stainless steel. The advantages are a connection of all the electrode surface and the possibility to supply the necessary fuel and oxygen to the system. Therefore the bipolar plates own channels on each side of the plate.

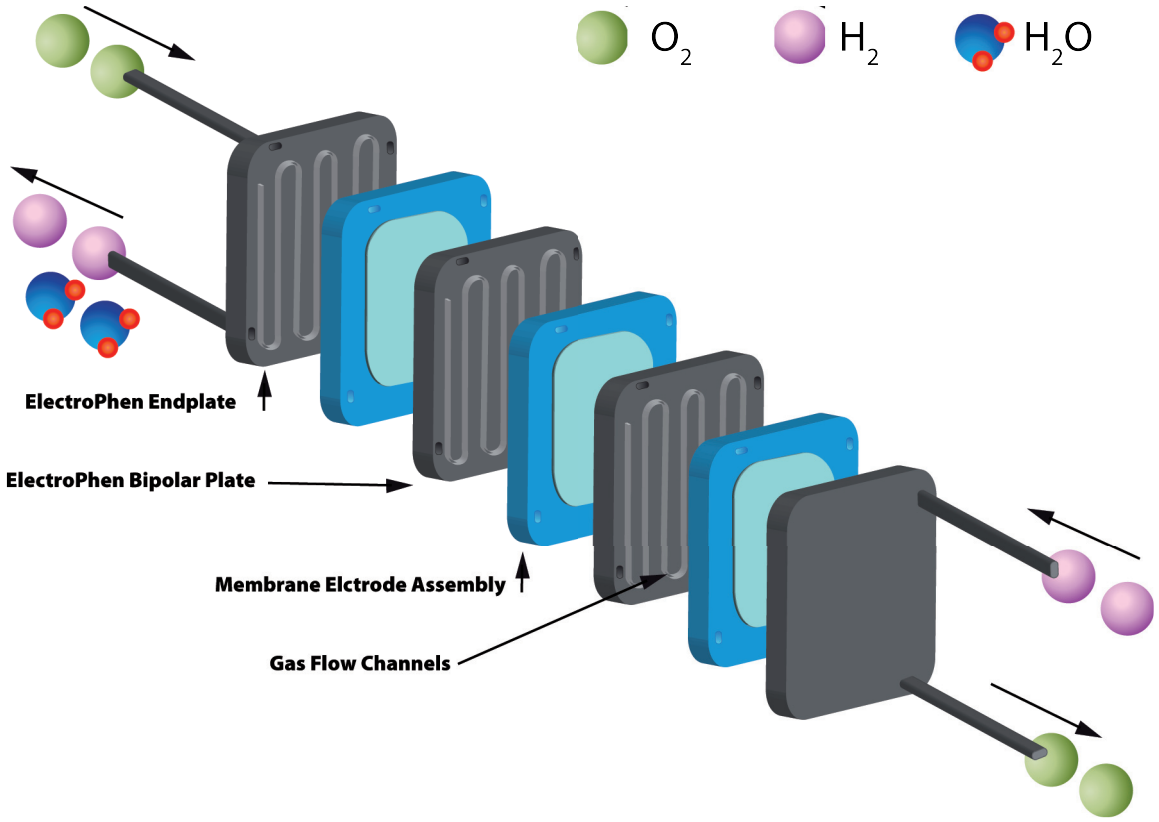


Figure 7: Fuel cells stack

It is clear according to this short discussion that each fuel cell type has its own advantages. If the high temperature fuel cells seem to be greedy in energy to obtain these high temperatures, their lower sensitivity to fuel pollutants like carbon monoxide and dioxide is a positive point.

Then, time and energy are consumed to reach the working temperature in MCFC or SOFC while low temperature systems can start almost immediately. The ratio weight/power is another major parameter, especially for mobile applications. The best ratio are obtained by PEMFC. As example Honda has installed on a car a 43 kW FC Stack PEMFC with a weight/power ratio of 1000 W/kg [36] which is really better than other fuel cell ratio, turning below 100 W/kg. Finally, regarding the capacity of the biggest fuel cells which can produce several MW compared to the 1000 MW of a nuclear reactor [37], it is easy to understand that improvements are still to be operated in a way to replace powerful classical electric production systems.

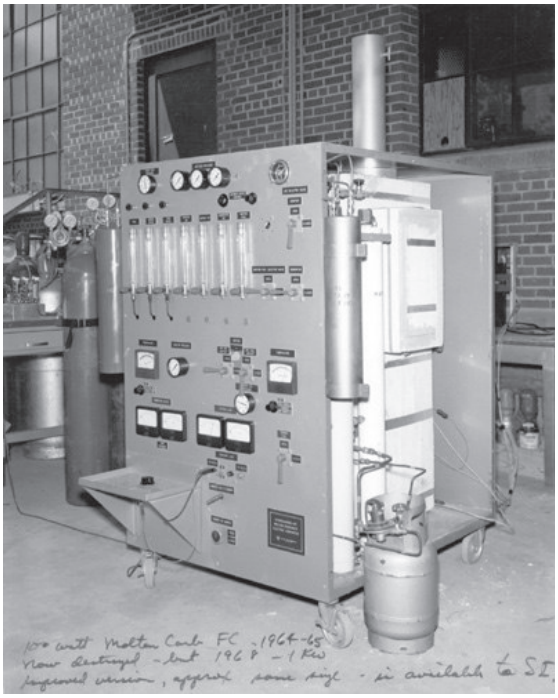


Image 2: A MCFC of 100 W module built by Texas Instrument (1964) [31]

Image 3: 1 MW CLEARgenTM Multi-MW Systems from Ballard [38]

3. Proton exchange membrane fuel cells (PEMFC) [21], [27], [39]

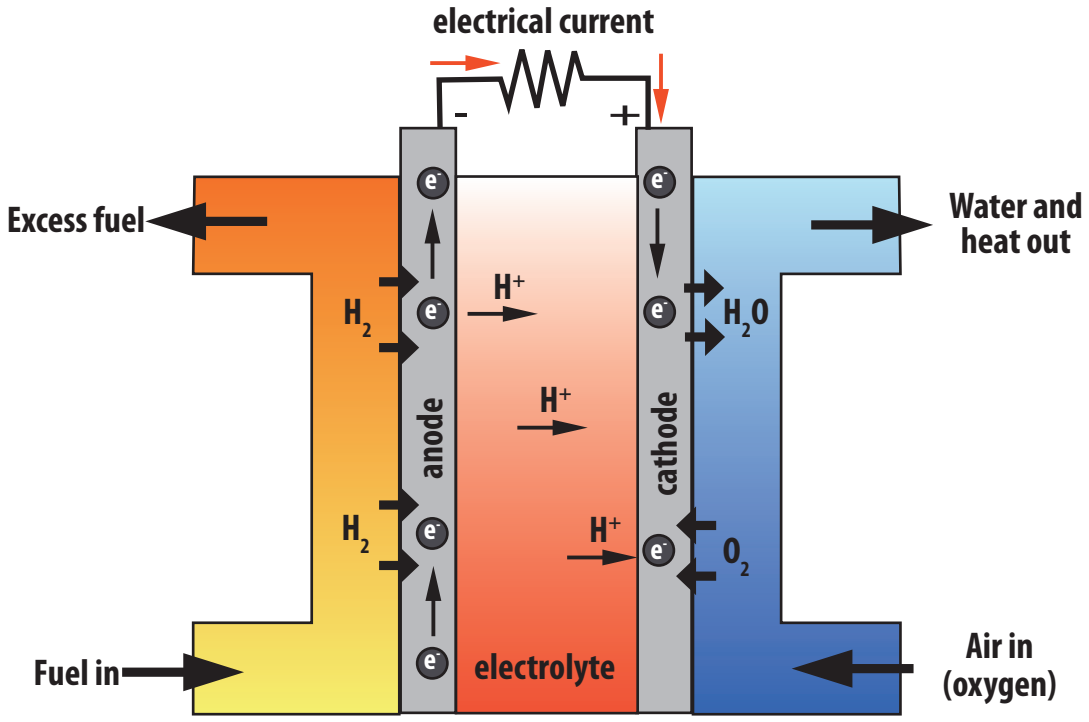


Figure 8: General scheme of a PEMFC

The first development in PEMFC was realized in the 1960s by the General Electric company. The cell was compact and portable, but expensive to produce, due to an important quantity of platinum (28 mg/cm^2). These fuel cells were used in the Gemini space program of the NASA, but were replaced by AFC for the Apollo mission. Then in the 1970s and 1980s, the US- and british NAVY began to install PEMFC. In 1990 Ballard developed its Mark 5 Fuel cell stack, which was able to produce 5 kW total power at a density of 0.2 kW/L of stack volume. Today only 0.2 mg/cm^2 of platinum are necessary, which reduces considerably the price. Their attractiveness is increased by a good efficiency around 60%, a quick start-up due to the low temperatures, a favorable power-to-weight ratio and a low sensitivity to orientation [20]. Applications are possible in mobile or stationary power generators. The main disadvantages come from the expensive catalyst, the intolerance to carbon monoxide and also the degradation of the electrolyte.

The electrodes are composed generally of carbon material (carbon cloth or carbon paper) which serves as support and as gas diffusion layer with dispersed platinum particles on it. The dispersion should be as regular as possible for a maximum efficiency. The oxidation and re-

duction equations are similar as those for phosphoric acid fuel cells. At the anode, hydrogen is decomposed in electrons and protons (see (Eq. 6)) which both migrate by a different way to the cathode where they react with oxygen forming water (see (Eq. 7)). To help the water elimination, PTFE can be added to the carbon material. Its hydrophobicity pushes the water on the electrode surface where it can be easier evaporated.

$$2\ H_2 \longrightarrow 4\ H^+ + 4\ e^- \qquad \text{(Eq. 6)}$$

$$O_2 + 4\ H^+ + 4\ e^- \longrightarrow 2\ H_2O \qquad \text{(Eq. 7)}$$

For a good efficiency, the proton exchange membrane with a usual thickness between 0.05 mm and 0.1 mm must own several qualities such as good proton conductivity, good mechanical properties, high thermal, electrochemical and chemical stability and low permeability to the reactants (hydrogen, oxygen or methanol) [24]. In the first studies on PEMFC made by GE for the US space program, polystyrene sulfonic acid polymer was used as electrolyte. But they rapidly saw that the membranes were unstable to the oxidizing environment of the fuel cell. The collaboration of GE with DuPont who was searching for applications for their new polymer, the Nafion®, allowed to proton exchange membrane to become a viable technology [32].

The transfer of the protons inside the polymeric membranes is governed by two principal modes [23], [40]. In proton hopping mechanism, the protons hop from one hydrolyzed site to another across the membrane (see Figure 9). The contribution of the hopping mechanism is only a small part of the proton transport in polymeric membranes. The second mechanism is a

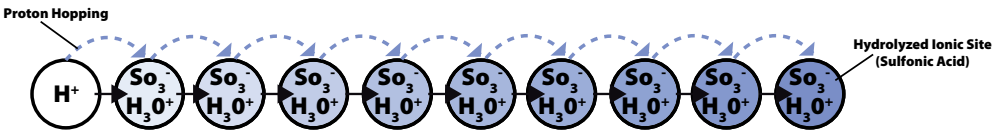


Figure 9: "Proton hopping" or "Grotthus mechanism"

diffusion mechanism. The hydrated protons (H_3O^+) diffuses through the aqueous medium in response to a electrochemical difference. In the membrane, the electroosmotic drag carries the molecules of water. The water connected protons are therefore transferred through the membrane with the water molecules. This vehicular mechanism is in majority due to the existence

of free volumes within the membrane. The water molecules have also two different transfer modes, first the electroosmotic drag and second the diffusion thanks to concentration gradients. The hydrophobic part of the membrane also helps to water transfer because the hydrophobic holes tend to repel the water molecules [41].

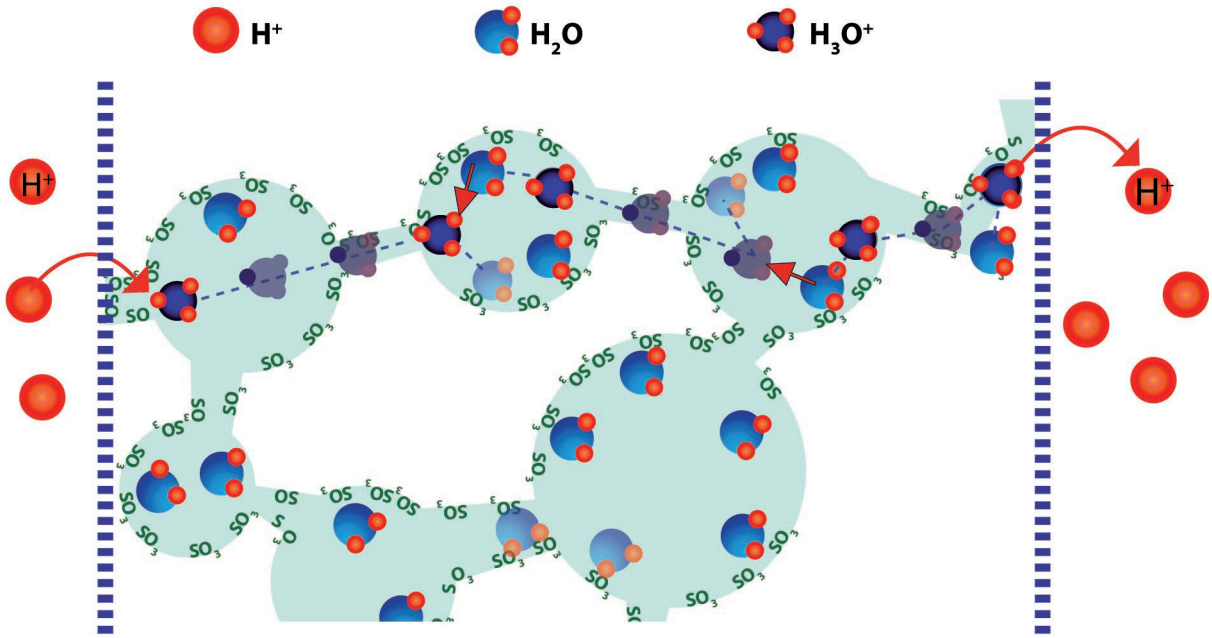
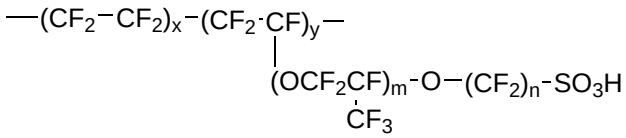


Figure 10: Vehicular mechanism transport of protons

3.1 Nafion® and other perfluoropolymer membranes

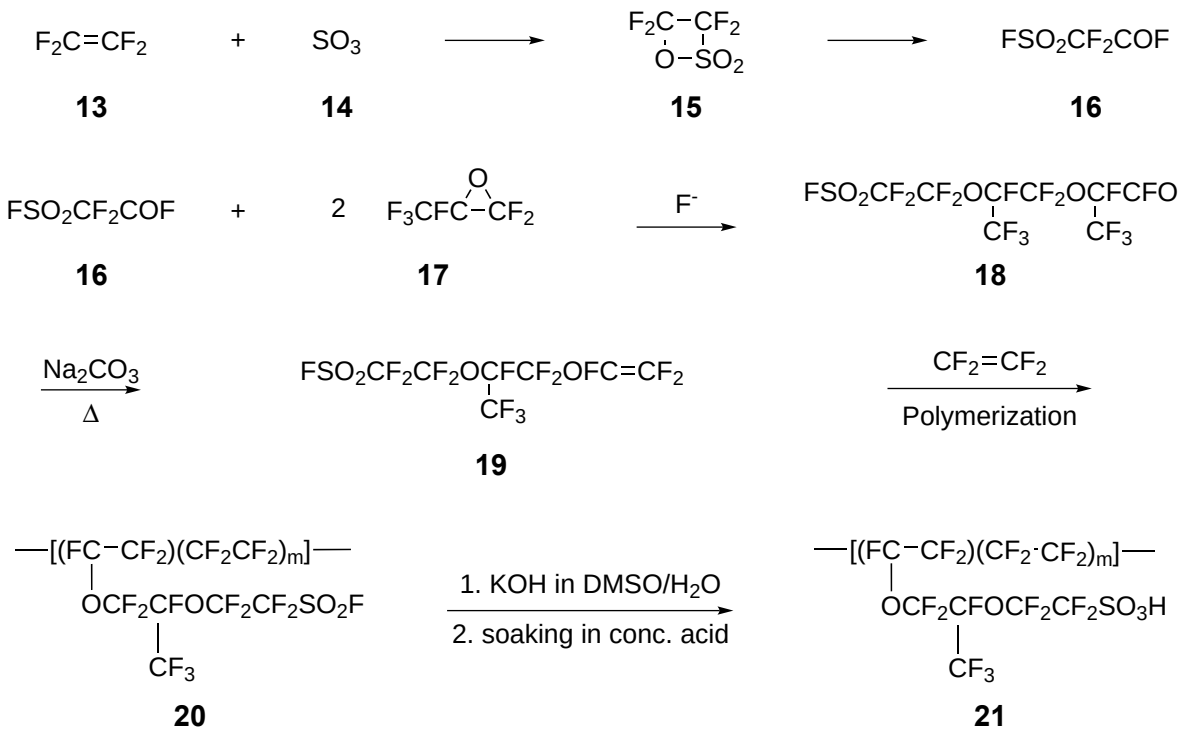
There are different perfluoropolymer membranes such as Flemion®, DowMembrane® or Aciplex®, each produced by different companies.



Flemion®: m = 0, 1; n = 1 - 5
Aciplex®: m = 1; n = 2; x = 6 - 8; y = 0, 1
DowMembrane®: m = 0; n = 2 - 5; x = 3 - 10; y = 1

Scheme 1: Different perfluoropolymer membranes

All these membranes have almost the same properties. Because Nafion® is the best known type, it will be discussed in more depth here. The Nafion® was discovered by DuPont in the early 1960s during a study on new monomers for copolymerization with tetrafuloroethylene (TFE). One of the fluoride acid which was formed starting from the TFE **13** and sulfur trioxide **14** led to the comonomer **19** needed for the Nafion® synthesis (see Scheme 2) [42]. The formation of Nafion® was then made by a copolymerization of the previously prepared monomer **19** with TFE, giving the thermoplastic -SO_2F precursor which can then be extruded into sheets of the desired thickness. This precursor has Teflon-like crystallinity which persists after the sulfonyl fluoride is converted to the sulfonic acid by first the formation of the potassium sulfonate by reaction with KOH in water and DMSO and second by soaking the film in a sufficiently concentrated aqueous solution of acid [22], [43]. Bonded to a perfluorinated chain, the sulfonic acid is extremely acidic. The stability of the sulfonate is enhanced by the strong electron-withdrawing effect of fluorinated moieties [44].



Scheme 2: Formation of the comonomer for Nafion® ionomer

Usually the perfluoropolymers are used for their unequalled dielectric properties, low coefficient of friction, antistatic properties and chemical barrier properties. The introduction of sulfonic acid groups on such polymer gave interesting new properties to the polymers, which was able to interact with the environment, conserving the inertness of the perfluorinated part. The Nafion® was not only applied in PEM fuel cell technology, but also acted as a separator membrane in

chloroalkali cells which is the largest market for Nafion®. In the 1990s, a new interest was focused on PEMFC thanks to the needs in new energy sources and the reduction of the quantity of platinum in the fuel cell electrodes.

The Nafion® structure is difficult to define because of its complexity. It depends on the chemical structure of the copolymer, the complexity of co-organized crystalline and ionic domains, the vast morphological variations with solvent swelling, the relatively low degree of crystallinity and the diffuse, heterogeneous nature of the morphology that lead to a wide range of domain dimensions [22]. However, since the early 1970s, several models describe the formation of aggregates due to the ionic groups, forming a network of clusters. Several analytical technics such as SAXS, SANS, NMR, ESR or IR spectroscopy [45], [46] were employed to understand the morphology. Especially the structural evolution of perfluorosulfonated ionomer (PFSI) membranes from dry materials to highly swollen membranes and solutions was investigated using mainly small-angle scattering techniques. Depending on the water content, several

changes were observed. In the dry membranes, ion clusters are isolated. The addition of water,

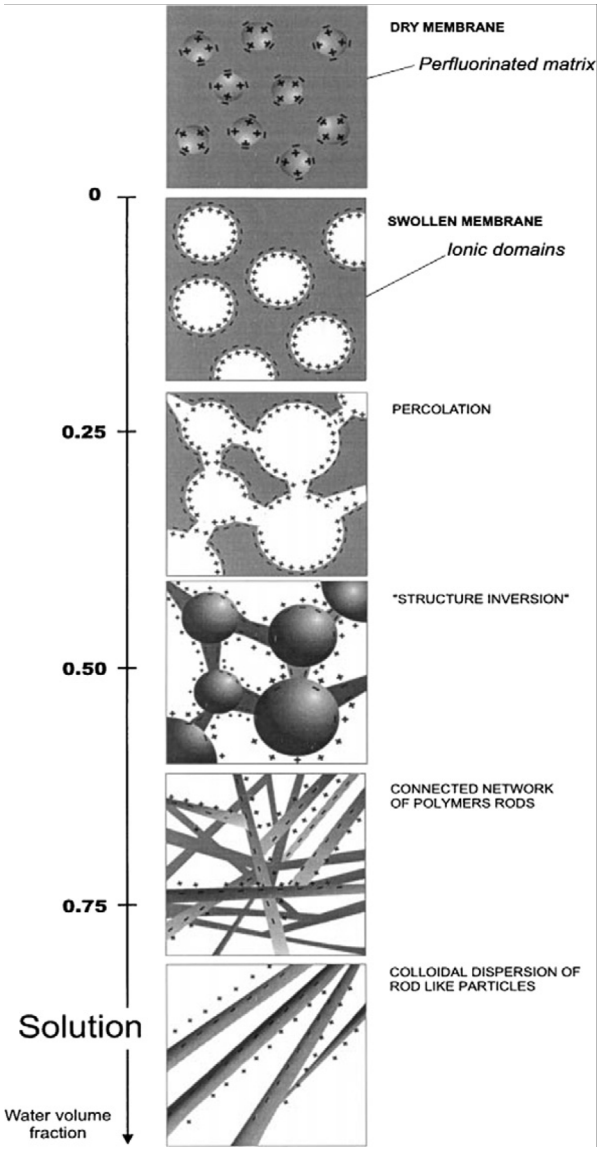


Figure 11: The different conformations of Nafion® [22]

which acts as a plasticizer, induces a modification of the cluster structures due to swelling which depends on the water volume fraction. Till 0.2 water volume fraction, the clusters swell but no percolation is observed. This begins with water volume fraction bigger than 0.2. Between 0.3 and 0.5 water volume fraction, the structure corresponds to a network of cylindrical ionic clusters bonded by cylinders of water. Around 0.5 water volume fraction, an inversion of the structures is observed and now a rod-like polymer aggregates network is formed. Finally between 0.5 and 0.9, the new polymer network swells [22].

In table 2, three types of Nafion membranes which are available on the market are presented. The solution-cast membranes have a thickness of 0.5 mil to 2 mil (0.01 mm to 0.05 mm) and are more uniform than extrusion-cast membranes [32].

Table 2:Curent Nafion® membranes offering [32]

	EW[a]	Thick-ness [mil]	Format	Preparation
NR 111 and NR 112	1100	1 - 2	Roll	Solution-cast
N 112, N 1135, N 115 and N 117	1100	2 - 7	Pieces or rolls	Extrusion-cast
N 1035 and N 105	1000	3.5 - 5	Pieces or rolls	Extrusion-cast

a. EW: equivalent weight which correspond to weight of Nafion® in grams per mole of sulfonic acid

Proton exchange membrane fuel cells working at temperatures above 100 °C could improve the efficiency of the cells by accelerating the electrode kinetics and increase the CO tolerance [47]. Nevertheless, several disadvantages are met with the Nafion® and the other PFSA membranes at these temperatures. The ionic conductivity is decreased because of membrane dehydration, the softening of the polymer backbone decreases the mechanical resistance of the membrane and the fuel crossover is increased. To counter the difficulties met with higher temperatures, two different ways can be envisioned: a polymeric blend membrane or a polymer/ inorganic composite membrane [23]. Nafion® can be modified with inorganic oxides such as TiO_2, SiO_2 to enhance the water uptake or inorganic solid acids such as ZrO_2/SO_4^{2-} to increase both water uptake and the acid sites concentration. Smectite clays like Laponite can have the same hygroscopic effect, as well as good thermal stability [48]. Pure Zeolite membranes have some defects like craks and gaps and have poor mechanical stability (brittleness and fragility) [49]. However. a mix of the Zeolite and of a perfluoropolymeric membrane can enhance the properties of both organic and inorganic parts giving real membrane improvements like higher thermal stability and lower fuel crossover for instance. A lot of other possibilities are described in the literature [23] such as polymer mixtures (Nafion®/polyaniline, Nafion®/sPEEK, Nafion®/ PAN) which decrease the fuel crossover and improve the conductivity and the thermal stability, but with a higher cost than Nafion® alone, what is a major disadvantage for industrialization. Modified Nafion® membranes with polymeric acid-base complexes like phosphoric acid-doped polybenzimidazole (H_3PO_4/PBI) showed excellent thermochemical stability, lower gas permeability and good conductivity after have been doped with H_3PO_4, even at 200 °C [33].

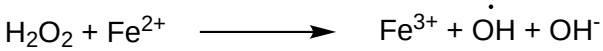
3.1.1 Nafion® degradation

It has been established that the degradation of a membrane electrode assembly (MEA) occurs principally under low humidity conditions and high temperature. Although thermal degradation and mechanical stress also induce physical and chemical changes in the membrane, it is thought that chemical attacks are the most important source of membrane degradation. Both chemical and physical modifications observed in the membrane are generated by the loss of small molecules like HF, H_2SO_4, CO_2, SO_2 and some fluorocarbons [50]. More exactly, the changes in the chemical structure by bond cleavage or by reformation of new moieties induce the physical property modifications of the membrane. Today, all the mechanisms responsible for the membrane deterioration are still not elucidated. It was described in a paper from Chen and co-workers [51] that S-O-S bonds as well as oxygen rich carbonyl and O-O groups were formed according to ex-situ Fenton tests. A study on the perfluorinated ionomer degradation made by Qiao et al. [52] has also shown by FTIR and thermogravimetric analysis (TGA) the presence of S-O-S bonds after hydrogen peroxide treatment of a membrane. According to the authors, this results in reduced proton conductivity due to a breakdown of hydrogen bonding in the water pockets and the destruction of ion clusters. But why testing resistivity of perfluorinated ionomers in the presence of hydrogen peroxide? In fact, in running fuel cells, the membrane is inserted between a chemically oxidizing environment on the cathode side, and a chemically reducing environment on the anode side. It is well-known that in fuel cells, the electrodes and the membrane are not totally impermeable to fuel, and therefore, oxygen and hydrogen cross-over can occur. When oxygen crosses the cathode without being reduced to oxide, the formation of a small amounts of hydrogen peroxide is detected, thanks to a reduction reaction (see (Eq. 8)) [53]. These hydrogen peroxide can react with iron(II) traces in a Fenton reaction [54]

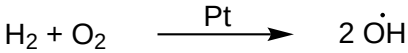
$$O_2 + 2\,H^+ + 2\,e^- \longrightarrow H_2O_2 \qquad \text{(Eq. 8)}$$

or with heat lead to the very reactive hydroxy radical (see (Eq. 9), (Eq. 10)). Another pathway for hydroxy radical formation is the reaction of oxygen and hydrogen on the platinum catalyst employed in fuel cells according to (Eq. 11). Moreover, other routes for the formation of radicals

$$H_2O_2 \xrightarrow{\text{heat}} 2\,\dot{O}H \qquad \text{(Eq. 9)}$$

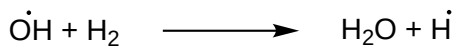


(Eq. 10)

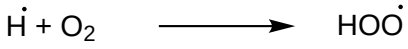


(Eq. 11)

are also envisioned for instance at the cathode when hydrogen is transported by the electroosmotic drag (see (Eq. 12) and (Eq. 13)). The presence of all these radicals in the membranes



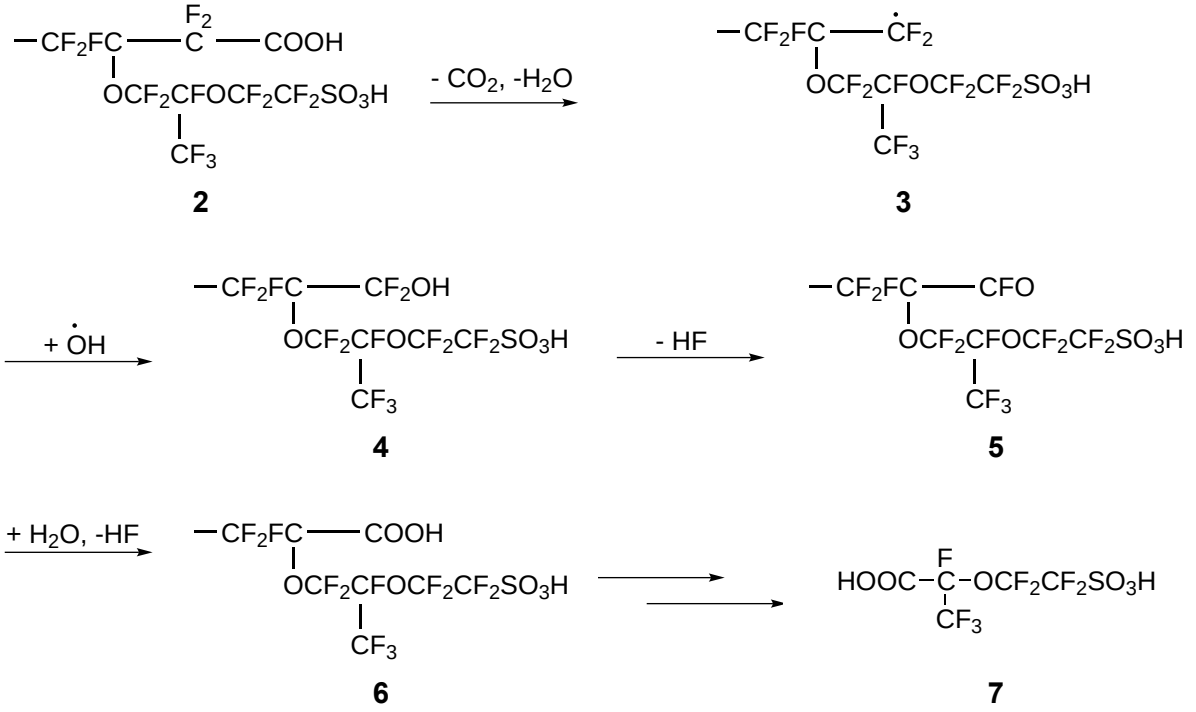
(Eq. 12)



(Eq. 13)

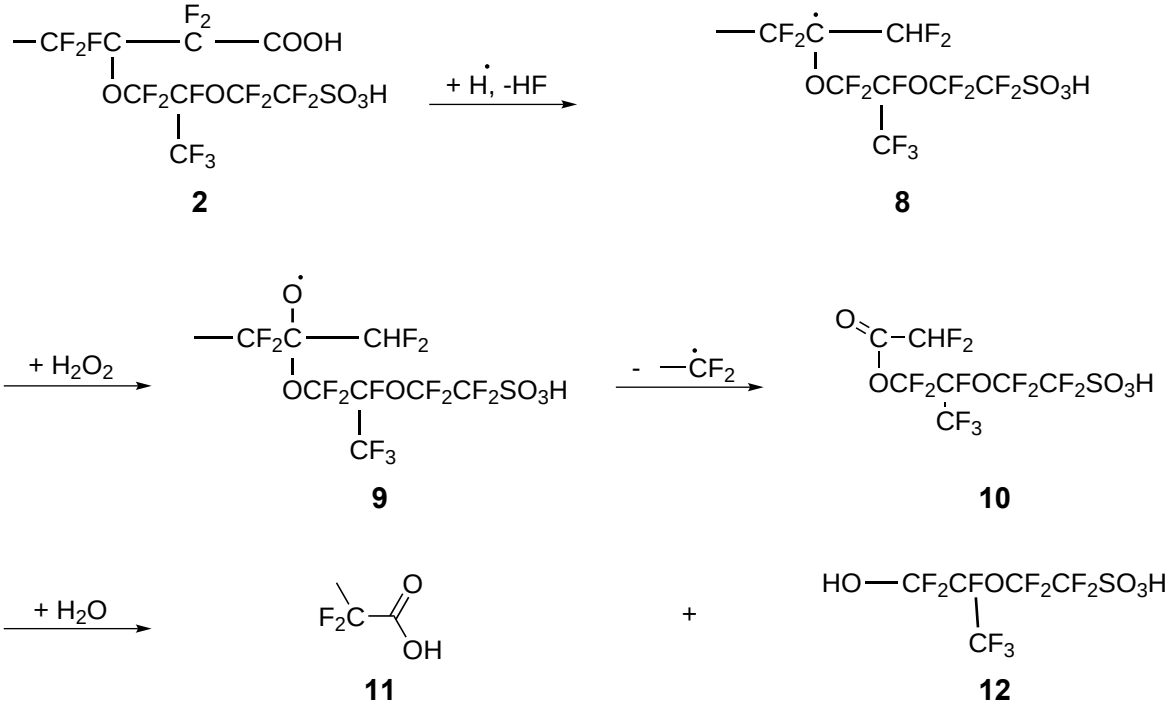
are considered to be largely responsible for the degradation [55].

Both backbone structure or side-chains can undergo radical degradations following different mechanisms.



Scheme 3: Degradation mechanism of the Nafion® backbone chain

Introduced during the manufacture of Nafion® membranes, carboxylic acid functions are the most sensitive groups within the backbone structure and therefore the degradation of the main chain begins by the radical attack on these acid groups, forming water, carbon dioxide and the perfluorinated radical **3**. Then after recombination with another hydroxy radical, an equivalent of HF is lost giving the acid fluoride **5** which is hydrolysed forming the compound **6** [56]. This mechanism can continue starting form the new produced carboxylic acid **6**, liberating some small perfluorinated compound like **7** [50]. The decomposition of the side-chains (Scheme 4) is also induced by hydroxy radicals, and according to the work of Müller et al., this is the predominant degradation in the membrane [55]. When the C-S bond, which is the weakest bond within the segment, is homolytically cleaved, the chain reaction give a carboxylic acid in a similar manner as explained in Scheme 3. The mechanism is a bit different when the attack occurs on one of the two tertiary carbons. The first radical reaction can be performed by a radical hydrogen. Then the formed radical **8** can react with a hydrogen peroxide molecule to give a radical oxide **9** and water. The abstraction of a radical CF_2 group produces an ester function which can finally be hydrolysed in the carboxylic acid **11** and the alcohol **12**.



Scheme 4: Degradation mechanism of the Nafion® side-chains

Naturally this radical deterioration of the membrane is not the alone responsible for defect formation. Certainly light and heat can induce similar or other degradations, as well as mechanic stress. This shows only that Nafion® is particularly sensitive to the conditions necessary for fuel

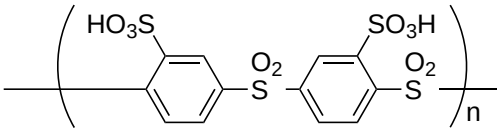
cells applications. Therefore, other membrane types have also to be studied and developed, with the final goal of creating an electrolyte with an exceptional resistance and durability.

3.2 Other membranes for PEMFC

Besides the perfluoropolymer membranes, other possibilities exist as electrolytes in PEMFC (or in DMFC).

It was already demonstrated that polyimides own the required qualities for proton membrane applications such as a good ionic conductivity and mechanical properties and an excellent water uptake behavior. The modification of polyimides by the introduction of aliphatic linkages in the structure of sulfonated copolyimides, synthesis of branched/crosslinked sulfonated polyimides, and semi and fully interpenetrating polymer networks of sulfonated polyimides enhance the already interesting polyimide properties for the Nafion® substitution [57]. For instance, the SPIs with a branched/crosslinked structure and derived from highly basic sulfonated diamines display reasonably high water stability of more than 200–300 h in water at 130 °C, suggesting high potential as PEMs operating at temperatures up to 100 °C [58].

The low conductivity of the perfluoropolymer membranes under low humidity conditions is a major defect, which avoids to prepare PEM fuel cells with working temperature greater than 100 °C. To overcome this obstacle and also their insufficient durability and their high fuel crossover, extensive research is made on the acid-functionalized aromatic hydrocarbon-based polymer and sulfonated aromatic polymers [59]. In this domain, it seems that the sulfonated/nonsulfonated multiblock copolymers which contain hydrophobic and hydrophilic oligomers are promising with ion exchange conductivity between 1.7 and 2.1 meq./g and a proton conductivity between 6 - 8 $*10^{-3}$ S/cm at 50% of relative humidity (RH) [60]. Other branched polymers with hydrophilic domains surrounded by outer hydrophobic domains or locally and densely sulfonated polymers with multiple sulfonic acid moieties along the principal chains were studied by Hay et al. and also show high proton conductivity 3.7 - 6.9 $*10^{-3}$ S/cm, but a very low IEC around 0.48 meq./g at 100% RH [61], [62], [63], [64] compared to the previously presented sulfonated/nonsulfonated multiblock copolymer. Then an easy way for the improvement of proton conductivity is to prepared IEC-polymer, with conducting values larger than 3 meq./g. As example, Schuster et al. have prepared 100% sulfonated poly(phenylene sulfone) with IEC values around 4.5 meq./g [65].



Scheme 5: Monomer of a high IEC by Schuster et al. ($sPSO_2$-220)

Another class of material for fuel cell membranes are the solid acids. They offer anhydrous proton transport, high-temperature stability (up to 250 °C) and really high proton conductivity around 10^{-1} S/cm [22]. One of the most studied solid acid is $CsHSO_4$ which was the first one to be used in a fuel cell [67].

Finally it should be mentioned that different methods such as sol-gel, post-sulfonation of high performance polymers, grafting polymerization, crosslinking can open the way for a lot of other electrolytes [23], [68]. Nevertheless, until now, even if good results can also be obtained with other membranes than Nafion®, no product has shown exceptional properties allowing fuel cells to become highly resistant.

4. Bowl-shaped molecules for hydrogen storage

It was already mentioned that one of the major difficulties to use hydrogen as a fuel in diverse cells, is to find means to stock effectively huge quantities of hydrogen. Compression is an already employed technology for hybrid cars. But because of the high pressures needed, security problems can not be eliminated. Liquid hydrogen was also tested, but too greedy in energy to keep the cold temperature needed. Then the research was oriented on compounds able to store hydrogen by physisorption or chemisorption. Metal and hydride-metal complexes gave the most promising results. But the weight/power ratio was often unfavorable. To improve this ratio, new compounds with a small mass/volume ratio able to fix hydrogen in higher quantity have to be elaborated. The aim to reach the target value of 6.5 wt% of extractable hydrogen has been fixed by the Department of Energy of the United States in a way to make hydrogen storage commercially possible. This opened one of the most hottest research area in science.

Nanostructures such as carbon nanotubes (CNTs), graphite carbon nanofibers (CNFs) or metal organic frameworks (MOFs) can adsorb physically or chemically substantial quantities of hydrogen. A huge interest was accorded to these materials because of low cost, good recycling accessibility or good chemical stability.

CNT is one of the most studied material for hydrogen adsorption since Dillon and co-workers showed the possibility to store 5 wt% - 10 wt% on carbon nanotubes at room temperature [17]. Then in 1999, Ye et al. have shown that adsorption bigger than 8 wt% was possible on crystalline ropes of carbon single-walled nanotubes [69]. However, these findings were later debated. Indeed, the presence of impurities like titanium in the used materials could explain these promising results. Another milestone on the study of the comportment of CNTs as hydrogen containers was published in 2002 by Shiraishi and co-workers [70]. They tested the adsorption of

hydrogen by SWNTs-bundles and by SWNTs-peapods. Based on the work of Fujiwara and his

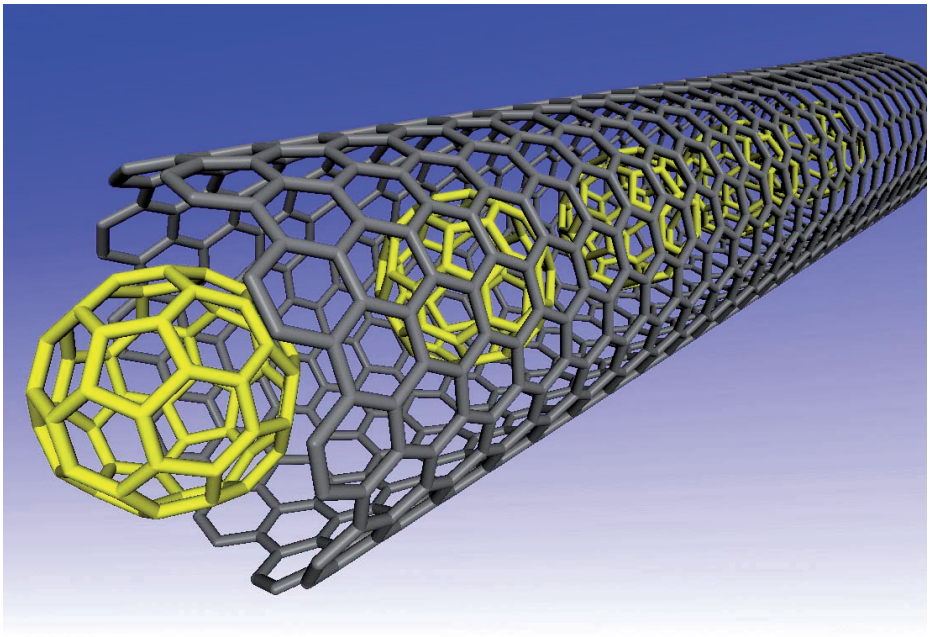


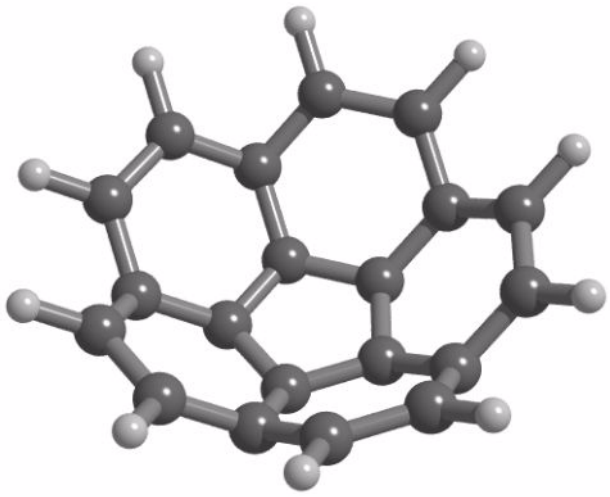
Figure 12: CNT peapod [71]

team who reported the storage of oxygen and nitrogen gases both inside and in inter-tube sites of as-grown and as-treated SWNT-bundles [72], Shiraishi also wanted to specify the sites which adsorbs the hydrogen. Therefore he prepared pure SWNTs previously synthesized by laser ablation using Ni/Co catalyst by refluxing the soot containing the SWNTs in H_2O_2 for 3 hours, then by overnight treatment with HCl and by ultrasonic treatment in NaOH. The obtained SWNTs-bundles and the prepared peapods were then “filled” under 6 MPa of hydrogen and the resulting material was studied by the temperature program desorption (TPD). The hydrogen desorption was observed around 350 K for both SWNTs-bundles and peapods. Moreover, regarding to the diameters of the particles and to the inter-tube size (estimation SWNT radius around 1.07 nm, inter-tubes space radius around 0.27 nm, size of hydrogen molecule around 0.24 nm) and of the similarities between the TPD diagrams for both bundles and peapods materials, it was postulated that the hydrogen was stored in inter-tubes sites by physisorption mechanism. More recently, Karatepe and Yuca have presented a paper where their pure CNTs were able to stock 0.6 wt% to 4.86 wt% of hydrogen at the liquid nitrogen temperature under a gas pressure of 100 bar. Nevertheless, this is still far away from the 6.5 wt% targeted for commercial applications by the DOE.

On the other side, physisorption can be reinforced by chemisorption when a metal is added to a carbon structure. Employing both mechanisms, the quantity of hydrogen which can be stored

is supposed to be higher. A review written by Yürüm, Taralp and Veziroglu allows to compare the efficiency of both mechanisms, but inconsistent results are demonstrated [10]. A common explanation is given by different activations due to impurites within the samples, which differ according to the method used for the carbon or doped-carbon material preparation.

The presence of impurities in most of the carbon material used for the experiments complicates the comprehension of the sorption mechanisms. Therefore, the choice of curve compounds with well defined syntheses and purifications would give an opportunity to understand the hydrogen sorption mechanisms in carbon material. Corannulene which is relatively easy to prepare is a simple curved sp^2-carbon compound which could give interesting comparison with fullerene or carbon nanotubes.

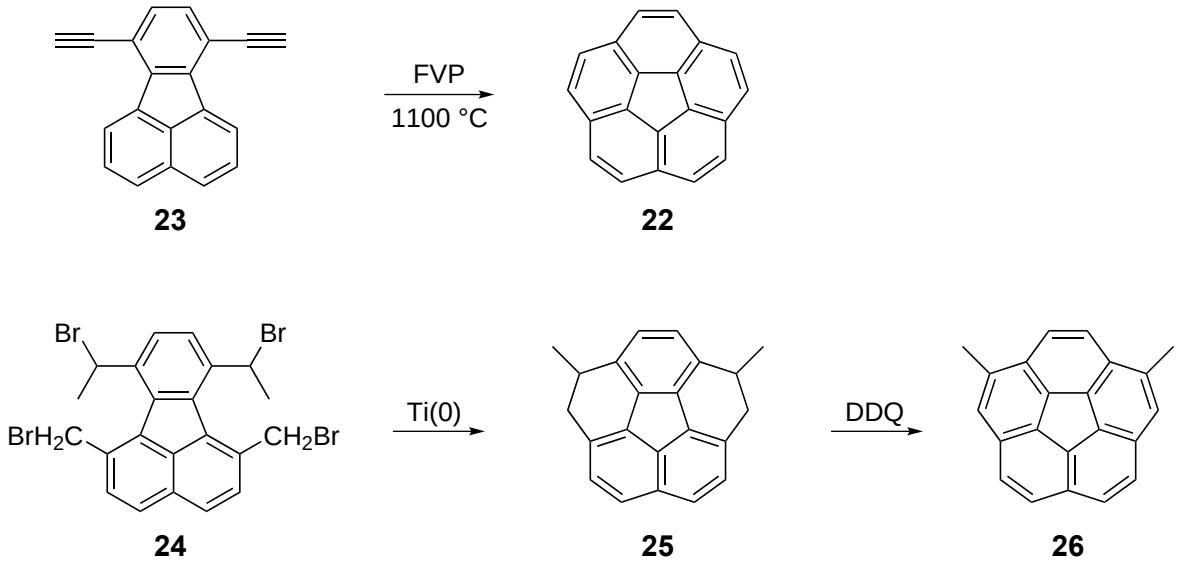


22

Scheme 6: Corannulene molecule

First discovered in 1966 by Barth and Lawton, the corannulene **22** was the first bowl-shaped molecule to be published [73], [74] with a depth of 0.85 Å between the planar planes defined by the center of the molecule and by the 10 rim CH carbon atoms. The first 17-steps synthesis proposed by Barth and Lawton with an overall yield of only 0.4% was too laborious to be reproduced on large scale. It was only at the beginning of the 1990s that a more convenient strategy was published by Scott at al. using flash vacuum pyrolysis (FVP) [75] and by Siegel and co-

workers [76] using chemistry in solution. Using the flash vacuum pyrolysis a number of curved



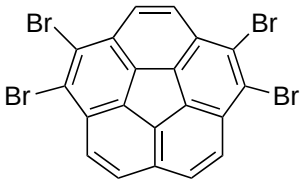
23 **22**

24 **25** **26**

Scheme 7: The two first convenient corannulene syntheses

PAHs were prepared and are presented in a review written by Scott and Tsefrikas [77]. Even the synthesis of the buckminsterfullerene C_{60} was achieved [78] by FVP. Then the evolution of the corannulene synthesis allowed to considerably improve the yield and decrease the number of steps [79], [80]. Finally after 30 years of chemical research, the synthesis of the corannulene is now efficient enough to produce multigram quantities and this was the starting point for elaboration of new compounds, based on corannulene core [81], [82].

Thanks to their curved form, corannulene derivatives have shown a significant dipole moment [83] and are able to form complexes with fullerenes [84], different metals [85] and molecular hydrogen [86]. Without any substituents, corannulene does not form columnar assemblies in the crystal phase [87]. But the decoration of the corannulene with substituents like bromine changes considerably the crystalline structure [88] and columnar structures are observed.



27

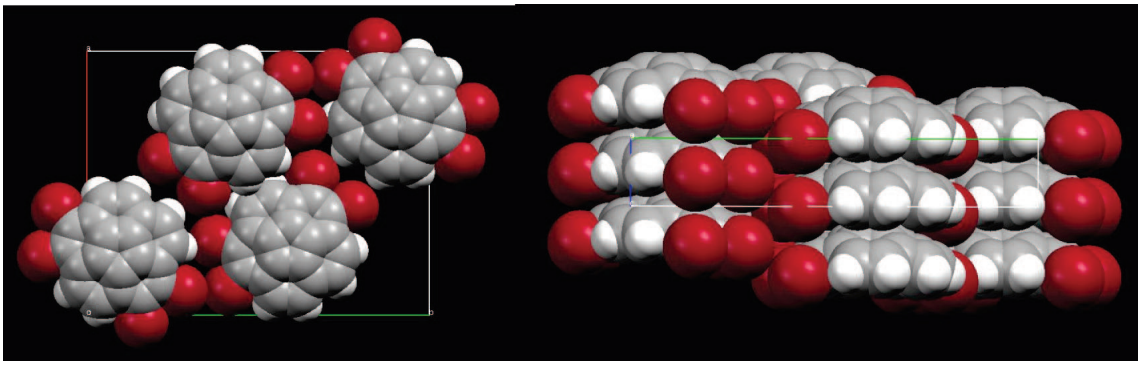


Figure 13: Columnar packing in the crystal structure of 27 [88].

The concave and convex faces of the corannulene are both exposed for reaction with hydrogen what can be employed to study the curvature influence on adsorption. In a first paper in 2006, Scanlon and co-workers [18] have investigated by computational chemistry and experimentations the physisorption of hydrogen uptake on corannulene. As results, 0.8 wt% of hydrogen were adsorbed under a pressure of 72 bar and 298 K according to experimentation, what is in very good agreement with the calculations. They have also determined that the hydrogen storage is favorable between two corannulenes thanks to cooperative interactions. The binding energy per hydrogen molecule in a corannulene sandwich is almost two times bigger than when hydrogen interacts with only one corannulene. This increase in binding energy is important, because higher operating temperatures and low pressure for hydrogen storage could be employed. It was also demonstrated that 14 or 15 hydrogen molecules can be stored on one corannulene ring. This would correspond to 10 wt% and 10.7 wt% respectively, higher than the target value of 6.5 wt%. Finally, the quantity of adsorbed hydrogen increases with the interlayer distance (ILD). For instance at 139 bar and with an ILD of 8 Å, 3.89 wt% of hydrogen uptake were calculated while only 1.67 wt% were obtained at 231 bar and an ILD of 4.8 Å. Indeed hydrogen molecules can penetrate the space between two corannulenes only with a minimum ILD of 6 Å, what explains the higher hydrogen uptake values with bigger ILD. They also have postulated that because desorption is easier with high ILDs, the substitution of the rim hydrogens by bulky alkyl groups could make possible larger hydrogen amounts uptake and easy

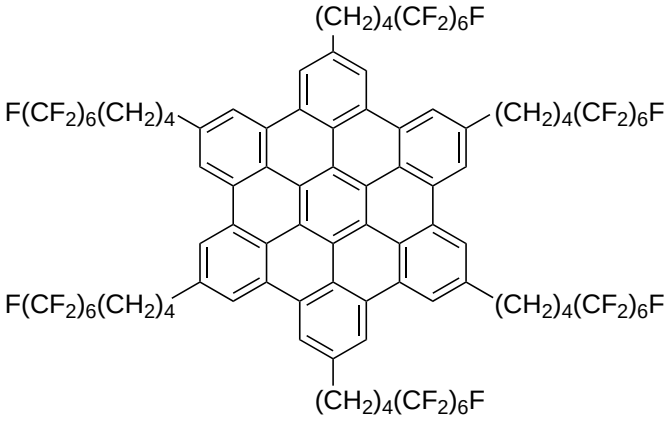
desorption. We could also imagine that preparing larger compounds than the corannulene, more hydrogen could be introduced between two adjacent molecules. The synthesis of such compounds will be discussed in this work.

In the same year, Balbuena et al. have proposed a computational investigation about the adsorption of molecular hydrogen on lithium-doped corannulene [89]. They concluded that the doping with lithium increases the adsorption capacity by enhancing the dipole moment, widening the space around the adsorbent molecules and strong interactions between hydrogen and the doping lithium. In 2011, Banerjee and Majumder have extended the computational research on other alkaline metals and earth metals, still with corannulene [90]. They found that the adsorption site of the metal ions depends on their ionic radii. The smaller radii show a higher binding energy on the convex plane, contrary to the bigger ions prefer be bound through the concave side. The adsorption of hydrogen is also improved in the alkali-corannulene complexes compared to “naked” corannulene. Regarding their results, it seems that the doping by sodium would give optimal performance for hydrogen uptake.

5. Aim of this work

As explained in the introduction, the membranes for proton exchange membrane fuel cells or for direct methanol fuel cells must own several qualities such as good proton conductivity, strong resistance in a chemical environment, gas permeability and low cost. One of the most used material as proton exchange membrane is the perfluoropolymers like Nafion®. The fluorinated skeleton gives the thermal and chemical stability while the sulfonic acid groups allow the proton transfer. But especially because of unwanted radical formation in the membrane, the stability for long term applications has to be improved.

Beside, the polyaromatic HBCs were already widely studied [91] and generally envisioned for charge carrier mobility [92], [93], [94] because they are able to form columnar stacks by π-π interactions [95]. Classically decorated by alkylated chains to improve the solubility and for allowing a better manipulation, the alkylated HBCs showed lateral aggregation due to van der Waals interactions between the stacks. The formation of very long conducting well-defined columns is therefore altered. A solution was proposed by Alameddine and Aebischer [96],[97] with the introduction of perfluorinated lateral chains. Indeed, thanks to a bigger van der Waals radi-



28

Scheme 8: Example of perfluorinated HBC

us (1.47 Å for fluorine and 1.20 Å for hydrogen) the perfluoroalkyl chains have a cross-section of 30 Å (compared to 20 Å for alkyl chain) and are therefore sterically more demanding and stiffer than the corresponding alkyl chains [98]. The alkyl chains adopt usually a «zigzag» conformation, while the perfluorinated structures are more helical and more rigid [99]. Moreover the addition of perfluorinated chains increases the thermal stability of the compound [97] and forms a Teflon®-like protection around the core. For synthetic reasons, it should be noticed that

exclusively perfluorinated chains were not used. An alkyl spacer was introduced between the perfluorinated part and the core [100]. By chance it had been shown that this spacer positively influences the effect of the perfluorinated part by giving to the chains more flexibility necessary for a better self-assembling.

With the aim to prepare a new type of proton exchange membranes owning very good thermal and chemical resistivity, a new type of substituted HBCs would be synthesized, in which the important part of the molecule is not the core anymore, but a functional group placed on one of the lateral side-chains, allowing the formation of clusters for proton channel formation. Being inspired by the Nafion® polymer, a sulfonic acid was chosen as functional group (see Figure 14) and the selected perfluorinated side-chain was the $(CH_2)_4(CF_2)_6F$. Indeed, the chemistry to attach this chain is well-known and good results were obtained for the preparation of monostranded stacks [101]. For comparison, a dodecyl-alkylated HBC carrying the same sulfonic acid will also be synthesized.

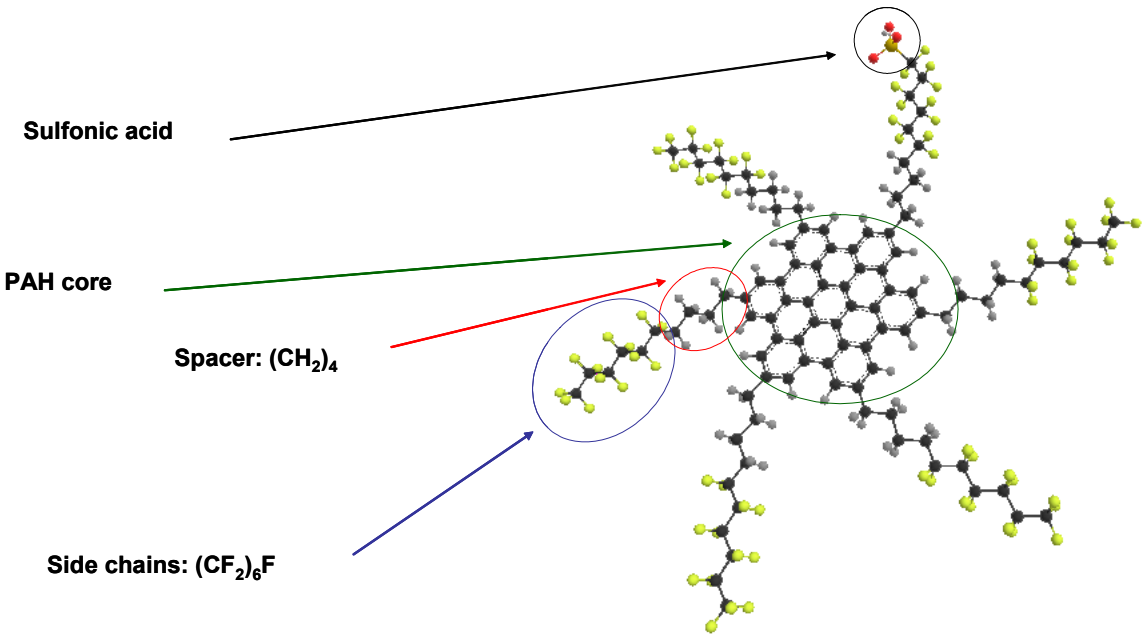


Figure 14: Envisioned perfluoro sulfonic acid HBC

The formation of the clusters (see Figure 15) should be induced by the sulfonate part which is hydrophilic and the perfluorinated chains highly hydrophobic.

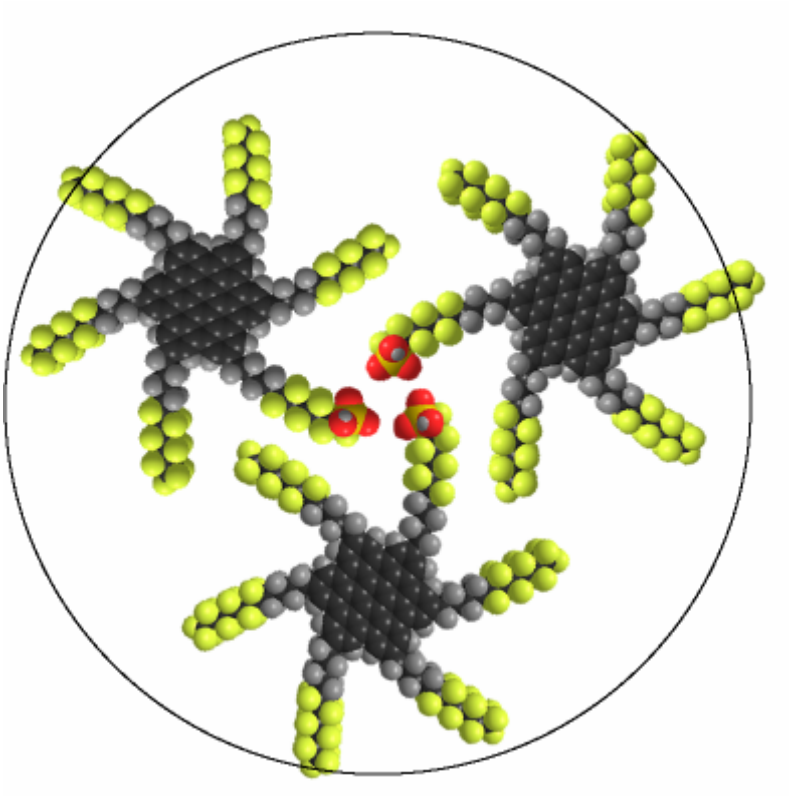


Figure 15: Supposed cluster formation

It was supposed that the clusters would be formed by three molecules, because of the size of the HBCs. Then thanks to the π-π staking, proton channels (see Figure 16) could be formed by the sulfonate groups. It was also proposed that the lateral chains as well as the triangle form of the clusters should arrange the proton channels in a hexagonal network (see Figure 17).

Succeeding these syntheses, the second part of this work was logically the exploration of the properties of the previously prepared products. A simple application was envisioned for these new HBCs. A deposition by slow evaporation on a porous hydrophobic membrane which is impermeable to water would give the desired proton channels, thanks to the organization of the HBCs stacks within the membrane pores. The efficiency of this membrane will then be tested by proton transfer from one side to the other, as controlled by pH evolution.

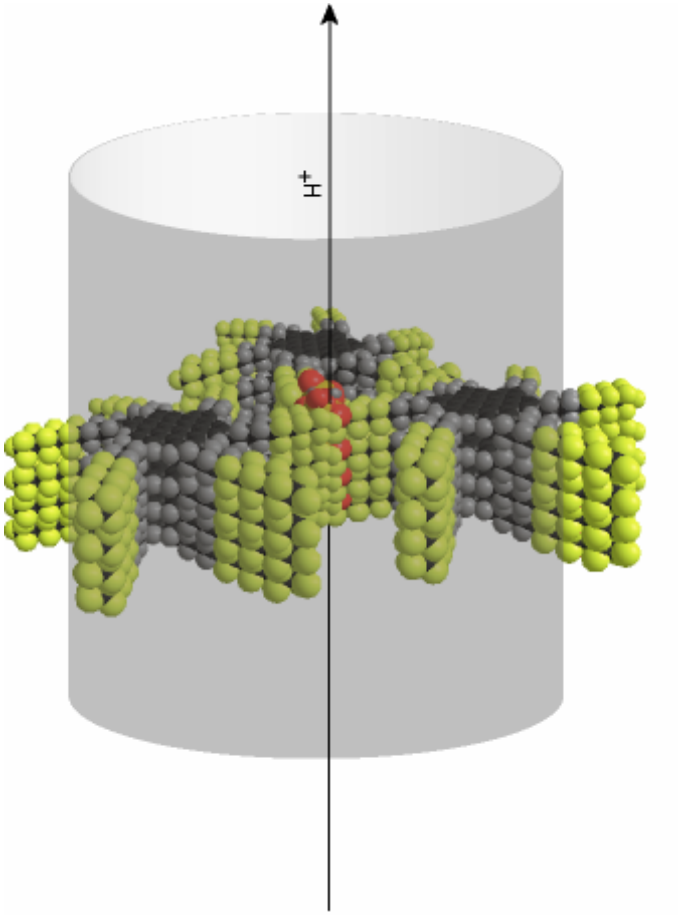


Figure 16: Supposed proton channel formation

As already presented in the introduction, computational chemistry and experiments have shown the interesting capacities of the corannulene molecule for hydrogen storage [18]. According to this publication, an interlayer distance between two corannulene molecules bigger than 6 Å allows hydrogen molecules to penetrate this space, increasing the storage capacity of corannulene. It is thought that similar bowl-shaped compounds with larger areas will allow to store more hydrogen. In this goal, the formation of new bowl-shaped molecules based on the cyclodehydrogenation of pentaphenyl cyclopentadiene precursors is envisioned. Never tested for the formation of bowl-shaped molecules, the Scholl reaction will be used for this oxidation. With this work, it should be established at which oxidative state the final compound would be formed. Then, the ability to form columns by π-π stacking will be investigated, as well as the hydrogen up-take.

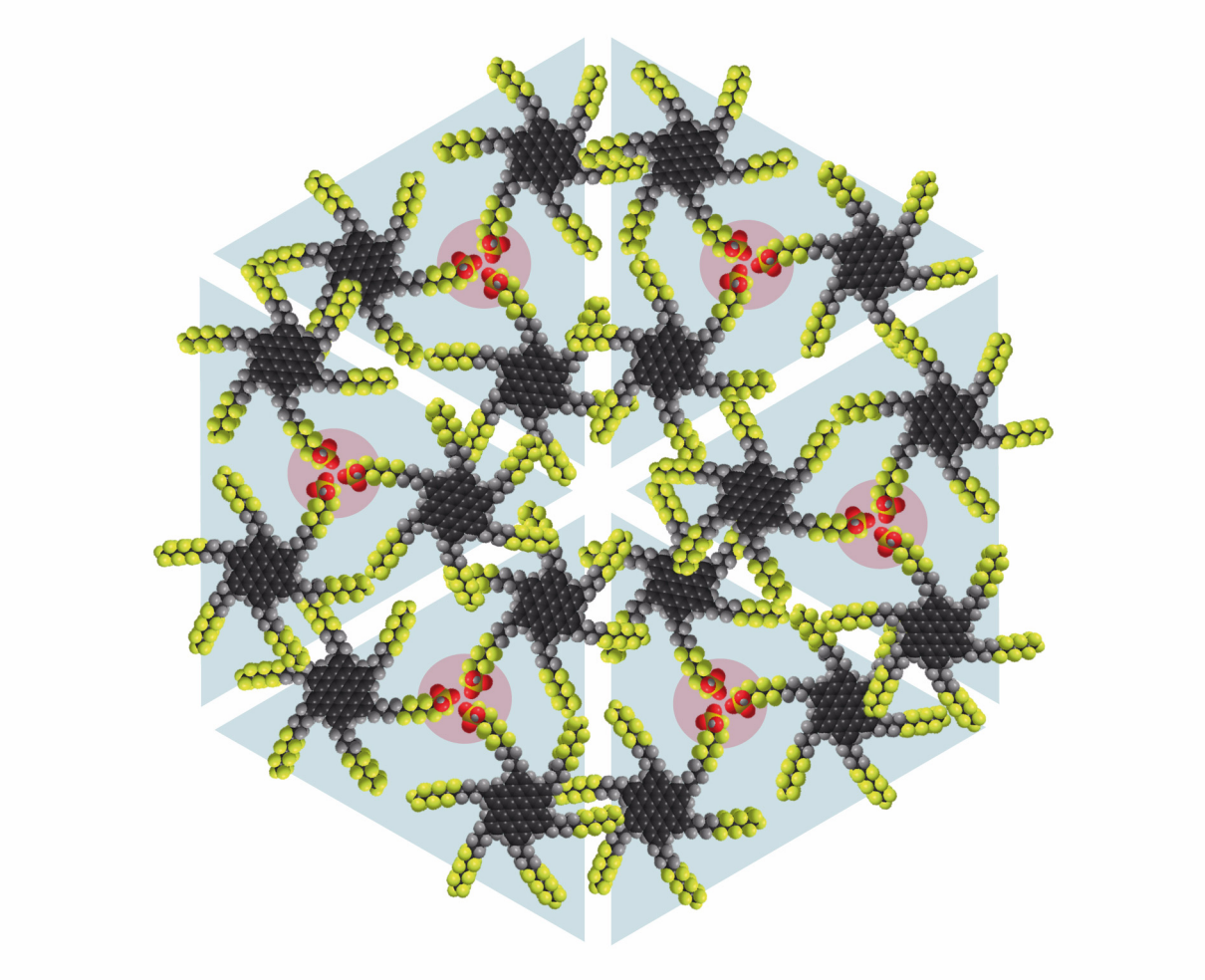
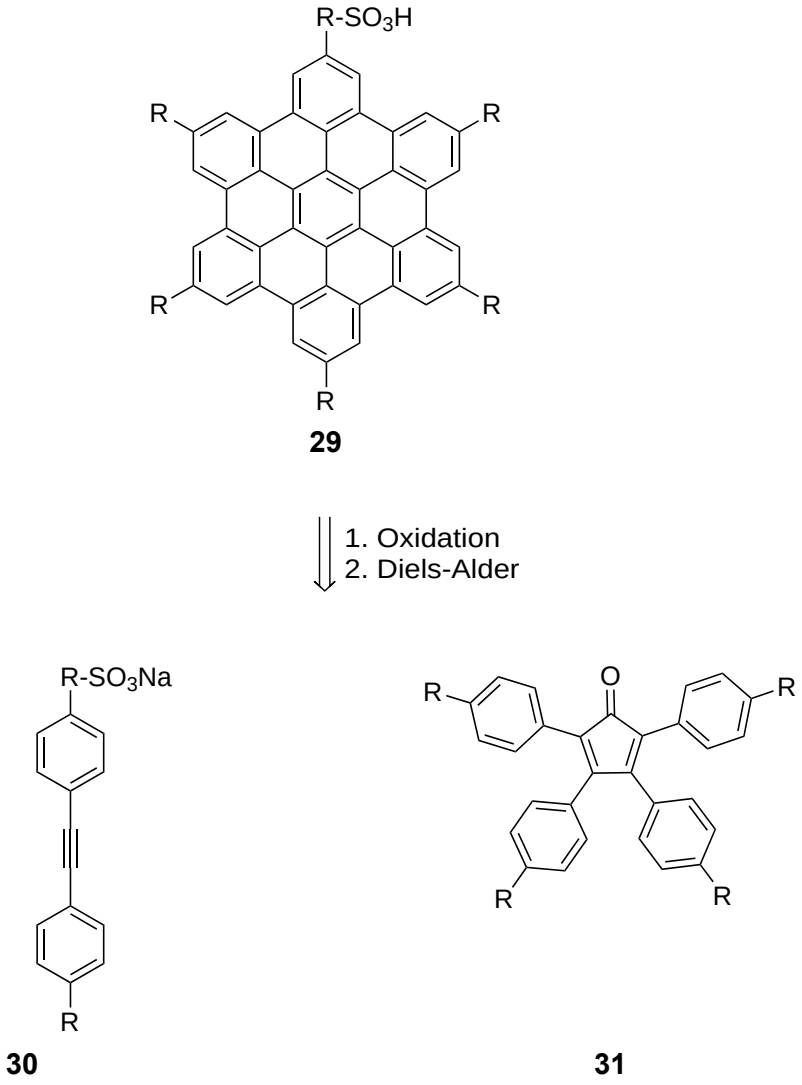


Figure 17: Supposed hexagonal arrangement of the clusters

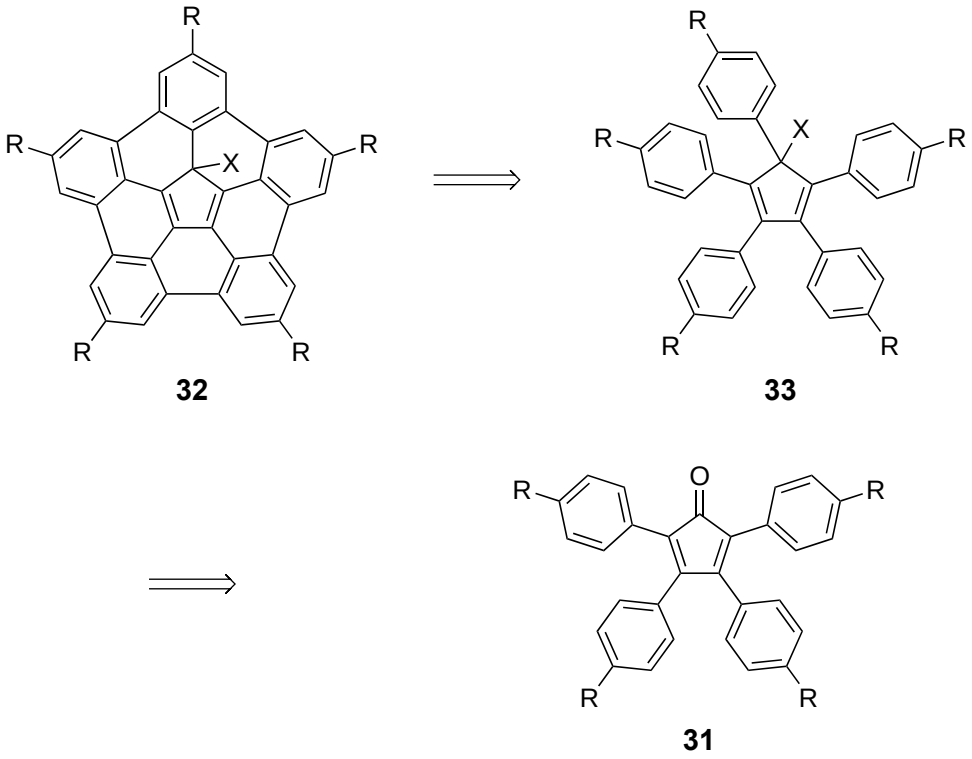
II. Retrosynthesis

1. Retrosynthetic approach

The synthetic approach to the two different types of polyaromatic hydrocarbon target molecules owns similarities. In the two cases, two different synthons have to be prepared and coupled together in a different way. Then, the formation of the substituted tetraphenyl cyclopentadienone **31** is necessary in both strategies. Finally, a cyclodehydrogenation concludes the synthetic pathway in both product preparations.



Scheme 9: General synthesis of HBC retrosynthesis

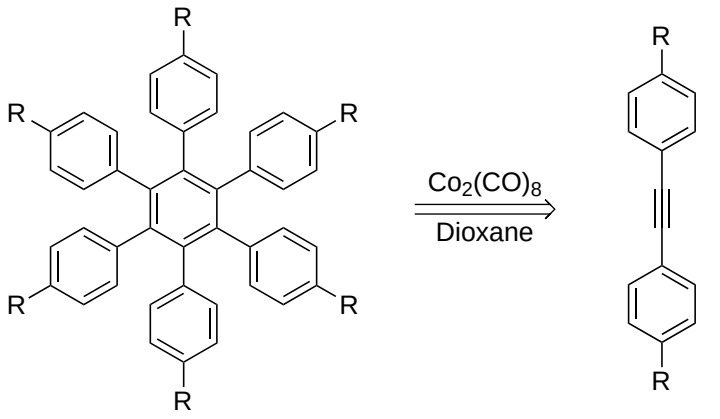


Scheme 10: General retrosynthetic approach of compound 32

Present in both pathways as the last step, the cyclodehydrogenation was already deeply explored [102]. We will first apply the “classical” conditions proposed by Aebischer [101] using iron trichloride as oxidant. Then we will test the oxidation using DDQ as the oxidant [103]. This could be an attractive alternative, because no metal would be introduced in the product.

1.1 HBC formation [101]

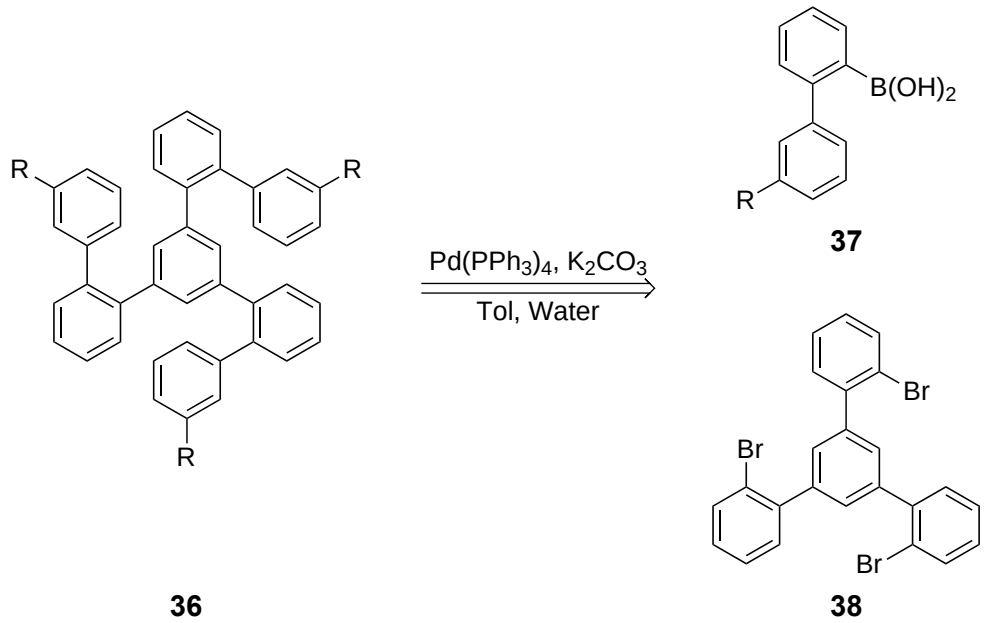
Before performing the oxidation step, the substituted hexaphenylbenzene (HPB) should be prepared. Depending on the symmetry of this HPB, the synthesis will be different from previous work. With totally symmetric derivatives (D_{6h}), the cyclotrimerization of substituted tolanes **35** gives really good results.



34 **35**

Scheme 11: Cyclotrimerization giving D_{6h} HPB

A second class of HBC with only three identical side-chains (D_{3h}) requires a different strategy, where a 1,3,5 tribromobenzene and a 3(R)phenylboronic acid are cross-coupled forming the desired HPB **36**.

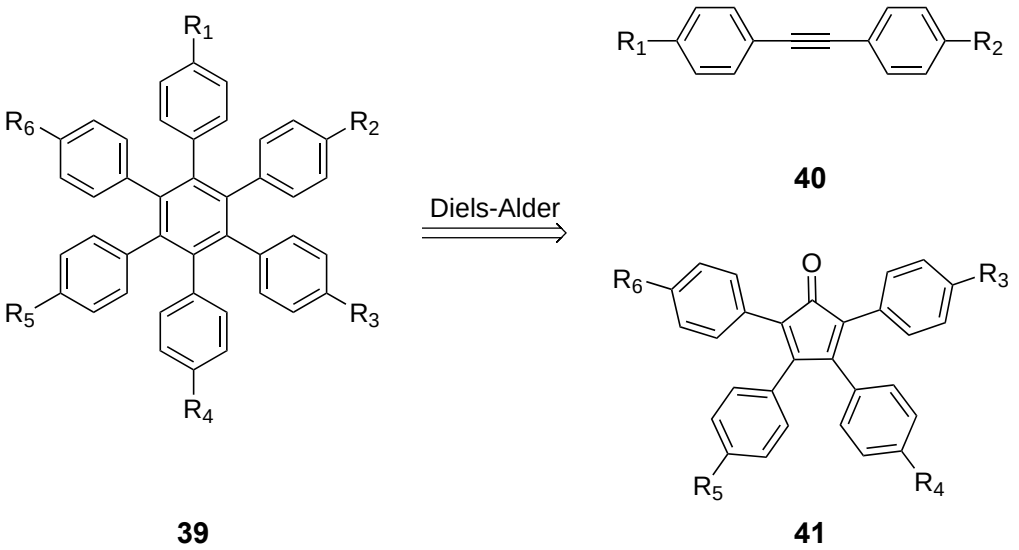


36 **37** **38**

Scheme 12: Preparation of D_{3h} HPB

Finally the last approach is used for the formation of HBC bearing one to six different lateral side-chains (D_{3h}, C_{2v}). In this case the two building blocks **40** and **41** have to be synthesized before being coupled in a Diels-Alder reaction with a decarbonylation reaction. In our project,

five side-chains will be similar. The sixth chain will carry the sulfonic acid group. Therefore, the

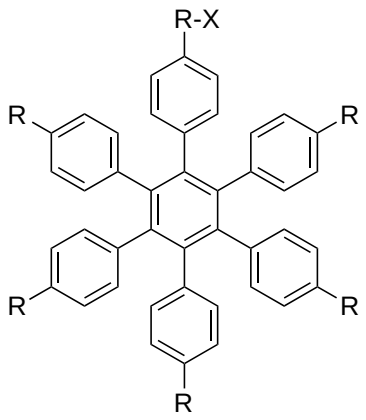


39 **40** **41**

Scheme 13: Preparation of D_{3h} HPB

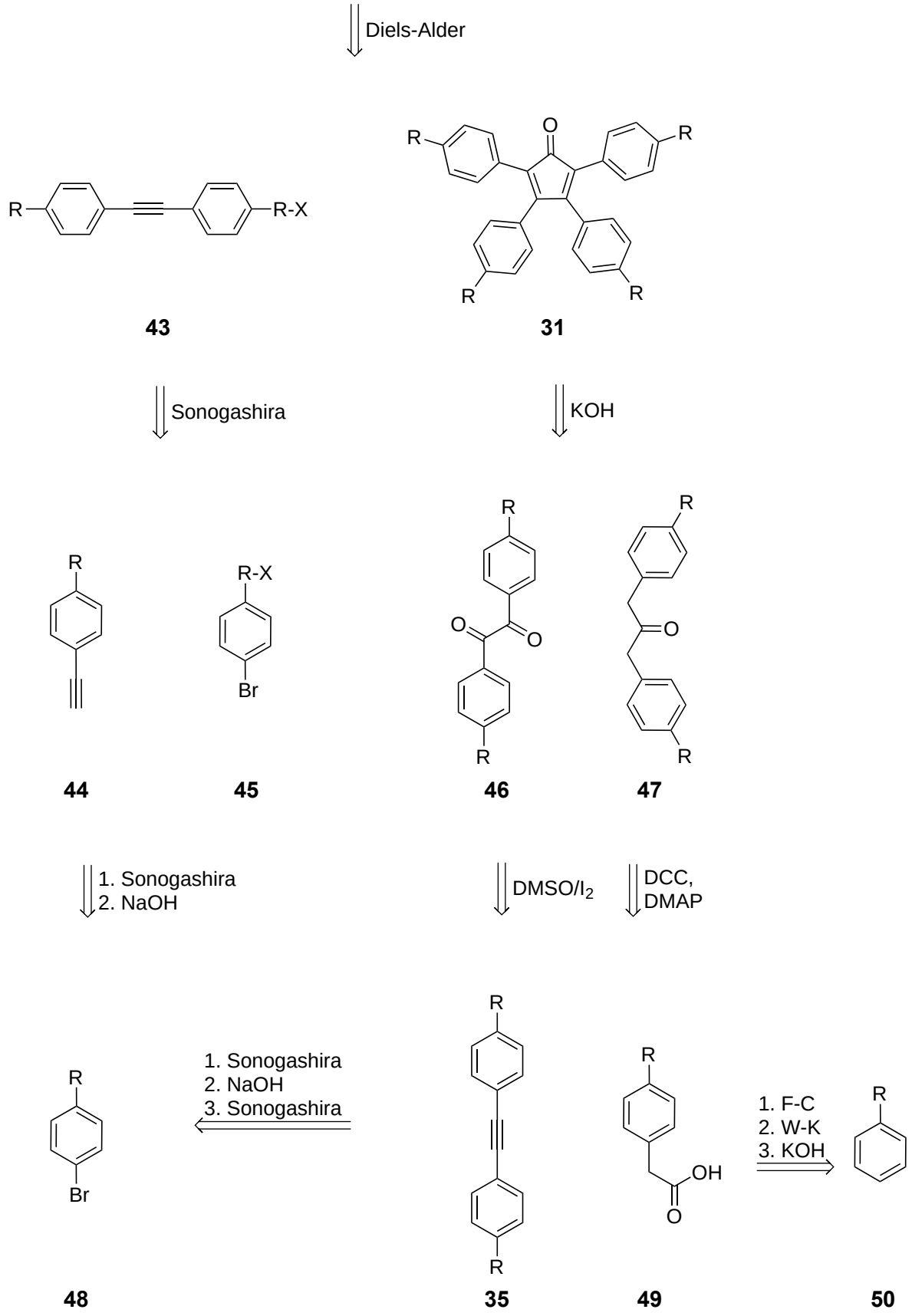
third strategy will be adopted. Indeed neither the first nor the second strategy could give a compound with different lateral chains. To produce a compound with five similar chains and only one different, a dissymmetric tolane with two different R groups should be prepared, meanwhile the cyclopentadienone moiety should carry four identical R groups.

The preparation of this two groups is picked up in Scheme 14. It is interesting to note that the formation of the three different building blocks **45**, **48**, **50** is sufficient to perform all the steps needed for the preparation of **42**.



42

Scheme 14: Retrosynthesis of HBC compound



Scheme 14: Retrosynthesis of HBC compound

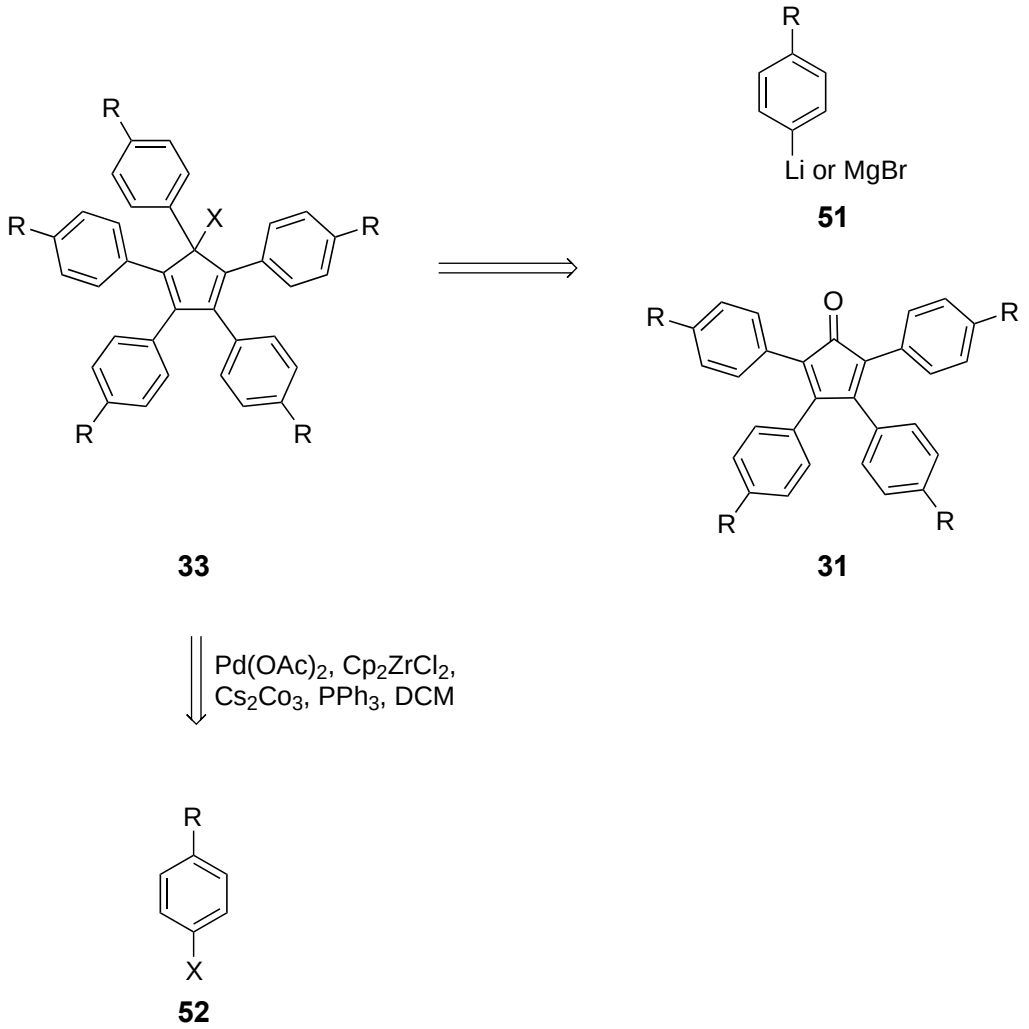
Starting from the building blocks **45** and **48**, the synthesis of the dissymmetric tolane **43** requires only Sonogashira cross-coupling reactions and an acetylene deprotection. Either with the alkylated or perfluorinated chains, the insertion of the sulfonate group will certainly be the most challenging part, because we will have to make organic chemistry in presence of a sulfonate salt, what could induce synthetic problems. It has to be found at which stage it is best to introduce the sulfonate group. The introduction as late as possible seems to be the best solution because the addition of an ionic part on an organic compound could give synthetic or solubility problems. On the other side, it could be easier to attach the sulfonate group when the perfluorinated or the alkyl part will be smaller because the bigger the compound, the less will be the solubility in polar solvents used for the sulfonate preparation.

The substituted tetraphenyl cyclopentadienone moiety demands a different chemistry. The first diketone compound will be made starting from the compound **48**, forming a symmetric tolane by the same way as for the formation of the dissymmetric tolane. This symmetric tolane could also be obtained by a one pot double Sonogashira reaction [101]. Then the oxidation of the acetylene group by iodine in DMSO [104] will yield the benzil derivative. The second group needed for the double Knoevenagel reaction is a substituted dibenzil ketone which will be produced by a Friedel-Crafts acylation [105] followed by a Willgerodt-Kindler reaction and hydrolysis [106]. The obtained phenyl acetic compound will be then condensed using DCC and DMAP [107]. It was also planned to keep halogen as “R” group as long as possible to introduce the chains as late as possible by Kumada reactions. This is the best solution to have the possibility to obtain quickly different compounds by the introduction of different side-chains. But according to our experience, problems will certainly be encountered for the formation of the Grignard reagents. And as the chemistry to insert the perfluorinated side-chains in the beginning of the synthetic sequence is well-known, this will certainly be the best solution.

Another challenge will be the preparation of the three building blocks **45**, **48**, **50**. When perfluorinated chains will be inserted at the beginning, the starting material will carry an allyl function on which the perfluorinated chain will be added by a radical reaction with Rf_6I [108]. The removal of the iodine will give the desired chain. The alkyl chain will be most of the time already present on the phenyl ring, except for the formation of the symmetric tolane, where dodecanoyl chloride will be added on a bromobenzene by a Friedel-Crafts reaction [105]. The carbonyl function will then be reduced by a Wolff-Kishner reaction [109], liberating the para-alkylated bromobenzene, a starting point for the Sonogashira reaction.

1.2 CP project

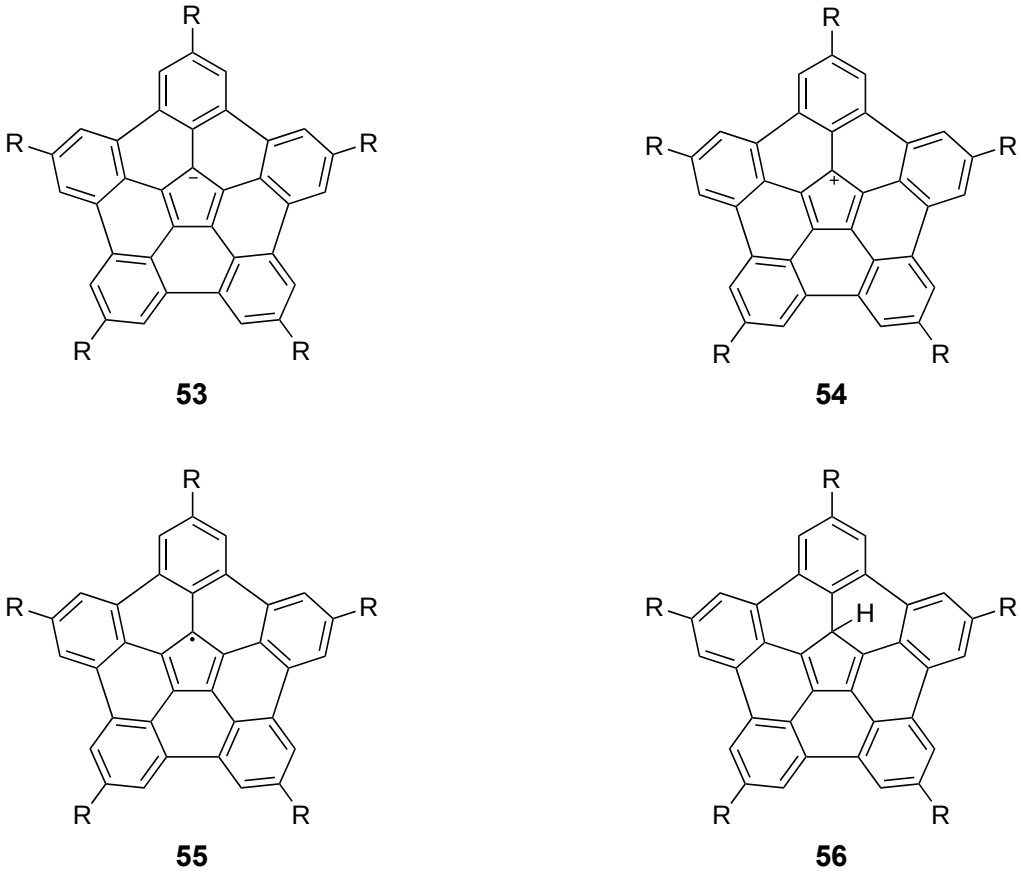
Even if we planned to synthesize a similar compound as corannulene, the synthetic strategy of the corannulene formation can not be employed in our case. We rather planned to prepare a pentaphenyl cyclopentadiene derivative which will be oxidized with a series of a Scholl reactions. The formation of the pentaphenyl cyclopentadiene compound **33** (X = OH, Br, H; R = H) was made classically by the nucleophilic addition of a substituted phenyllithium or magnesium bromide on the ketone function of **31** [101]. After the addition, the "X" group will of course be an alcohol function which could be replaced by a hydrogen or a bromine, depending on what will be necessary for the rest of the synthesis.



Scheme 15: Retrosynthesis of the pentaphenyl cyclopentadiene

The pentaphenyl cyclopentadiene could also be prepared by a direct penta-coupling reaction of a halogenophenyl moiety on a cyclopentadiene [110]. This would be a real shortcut in our synthetic pathway. Even if no real synthetic problems are envisioned for the preparation of the

pentaphenyl cyclopentadiene derivative, more complications will certainly be encountered for the oxidation. Indeed, thanks to the bowl-shaped conformation, the bond length will differ from the usual planar polyaromatic compound, what could render the oxidation harder. Moreover, the final form of the product is not known. It will certainly not be formed as an anion, since electron rich and hence easily oxidized. Therefore, a cation or the presence of a hydride on the cyclopentadienyl part would be expected. The formation of a radical which should be non-aromatic could also be envisioned. Therefore, the behaviour of this compound will be explored under Scholl reaction conditions.



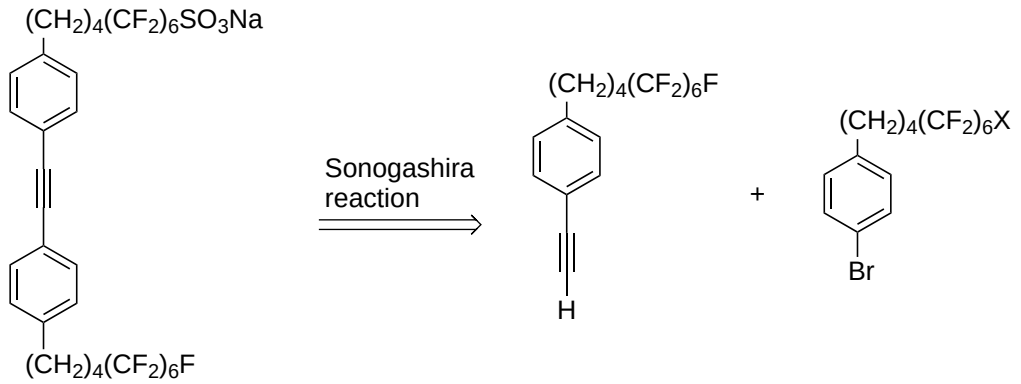
Scheme 16: Different envisioned forms of the final compound

III. Results and discussion

1. Perfluoro sulfonic acid HBC

The preparation of the dissymmetric tolane (c.f. paragraph 1.1) required the coupling of the two benzene moieties **58** and **59** or **60** carrying different lateral chains.

1.1 Formation of the perfluorinated acetylene

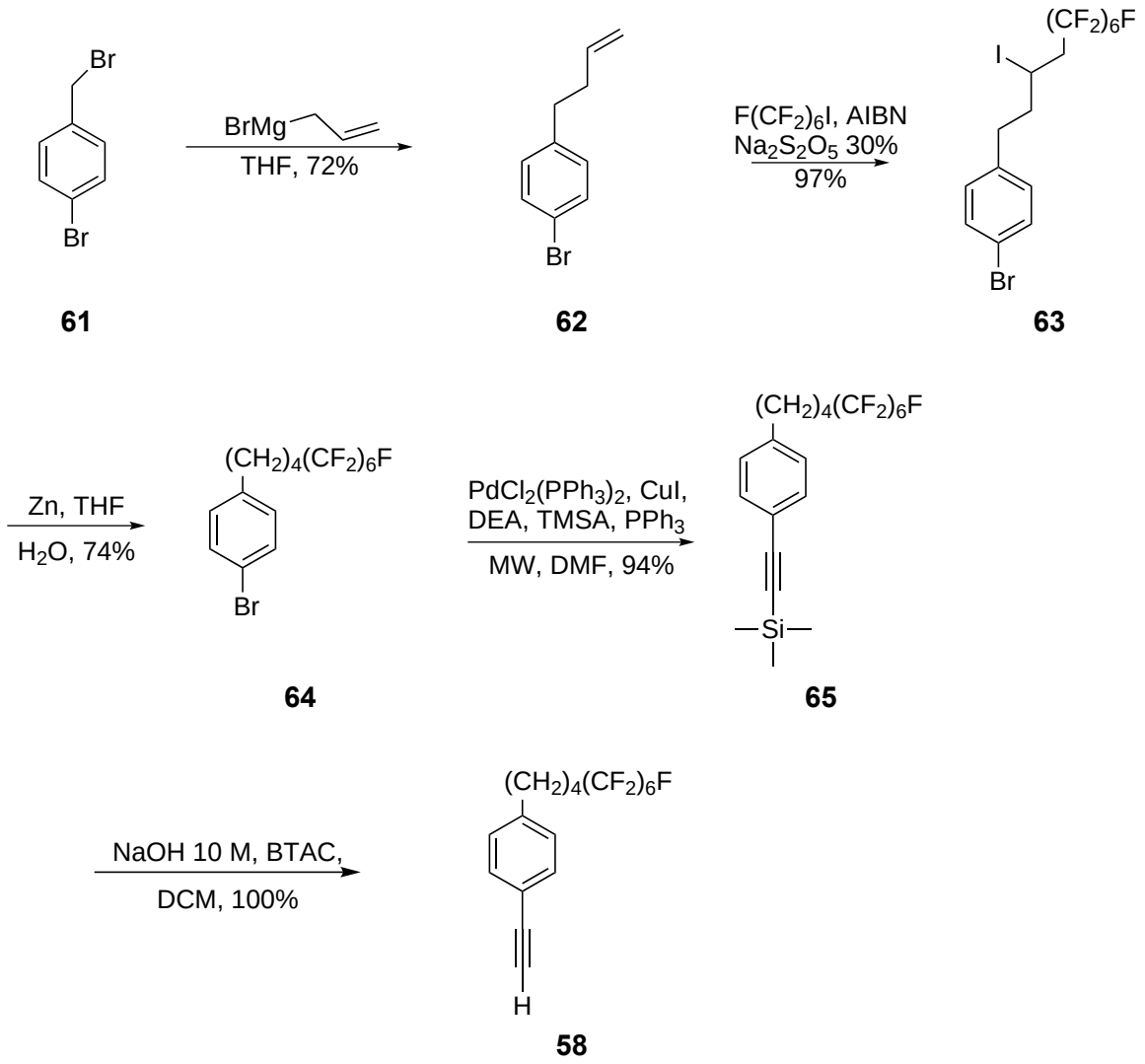


57 **58** **59 X = SO_3Na**
60 X = Cl

Scheme 17: Retrosynthesis of the dissymmetric tolane 57

The synthesis of the acetylene part **58** starts from the commercially available 4-bromobenzyl bromide **61** on which the allyl group is attached via a Wurtz reaction [111]. For this, a solution of the allylmagnesium bromide (1M in ether) is dropwise added to a solution of the dibromo compound **61** in THF. After overnight stirring at room temperature and a classic work up, the crude product is distilled under vacuum giving the pure allyl molecule in 72% yield. The perfluorinated chain is then added via a radical mechanism, using AIBN as initiator [108]. The starting material and the RfI chain are mixed together with an aqueous solution of sodium metabisulfite 30%, which suppresses side-reactions that slow the RfI addition, according to [108]. The initiator (half-life of 1.5 hours at 80 °C) is added every two hours till the reaction is complete. The desired compound is obtained as a pure product after extraction and drying of the organic phase under vacuum in an almost quantitative yield. The presence of the bromine atom on the benzene ring has forced us to take some precautions to remove the iodine. Indeed, the first tests made with $LiAlH_4$ according to the thesis of Aebischer [101] also showed the partial reduction of the C-Br bond. A doser look to this reaction was made on a similar compound (see paragraph 1.2.2). At the end, a better solution found was a metallation with Zn powder in THF followed by the hydrolysis with water. A good yield of 74% is obtained in this case. Finally the two last steps allow the formation of the acetylene compound. First a MW-assisted So-

nogashira cross-coupling reaction [112] gave in a very good yield of 94% the protected acetylene. Thanks to microwave irradiation, the reaction time of the Sonogashira cross-coupling can be reduced to only 20 minutes. Finally the deprotection of the acetylene with an aqueous 10 M NaOH solution in DCM with BTAC as phase transfer catalyst yields quantitatively **58** [113].

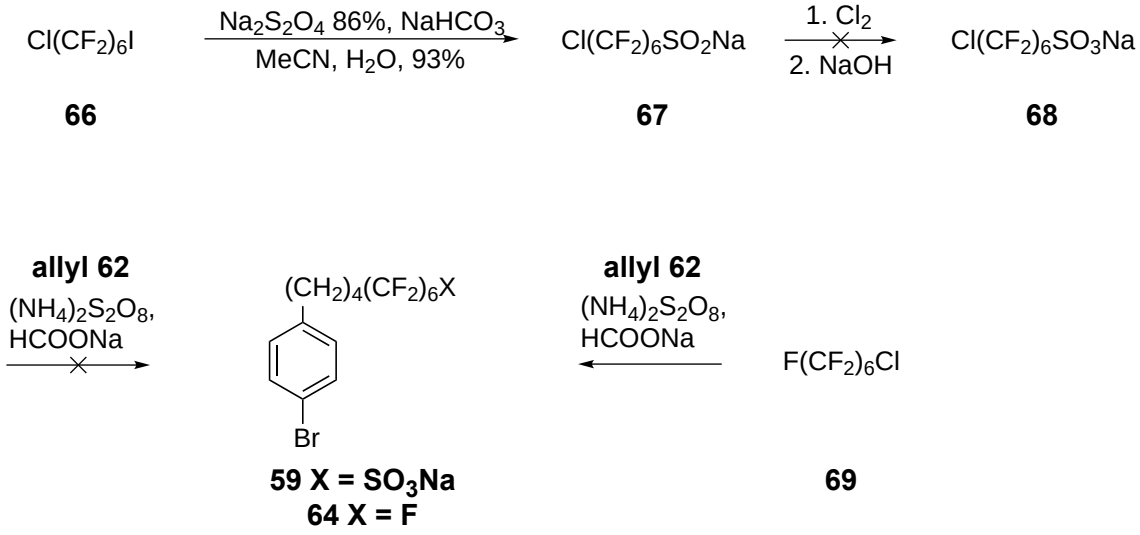


Scheme 18: Synthesis of the acetylene 58

This acetylene derivative **58** is the starting material for every dissymmetric tolane we wanted to obtain. The second part has to be coupled via a second Sonogashira reaction, using exactly the same conditions as those used for the formation of **65**.

1.2 Sulfonate part and tolane formation

1.2.1 Passing by a chloro-perfluorinated sulfonic acid



Scheme 19: Sulfonate compound 59 formation

Hu and Qing have shown in a 1991 paper [114] that the redox pair $(NH_4)_2S_2O_8/HCO_2Na$ was able to initiate the addition of a polyfluoroalkyl chloride on different kinds of olefins. The mechanism (see Scheme 20) passes through the spontaneous decomposition of the ammonium persulfate in a sulfate radical which, when mixed with sodium formate, transfers an electron to the formate giving a radical which is then able to attack the polyfluoroalkyl chloride compound, giving chloride, carbon dioxide and a polyfluoroalkyl radical. This new radical goes on the olefin and the reaction is completed by the transfer of a proton, certainly from the solvent. Therefore

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-}$$
$$SO_4^{\bullet-} + HCO_2^- \rightarrow HSO_4^- + CO_2^{\bullet-}$$
$$R_fCl + CO_2^{\bullet-} \rightarrow R_f^{\bullet} + CO_2 + Cl^-$$
$$R_f^{\bullet} + CH_2{=}CHR \rightarrow R_fCH_2\dot{C}HR \xrightarrow{H} R_fCH_2CH_2R$$

Scheme 20: Proposed mechanism for the addition of a polyfluoroalkyl chloride compound on an olefin

still according to their work, the preparation of the chain **68** was repeated, starting from the iodo-chloro-perfluorinated chain **66**. The functionalization began with a sulfination with sodium dithionite and $NaHCO_3$ in a mixture of water and acetonitrile. Different dithionite salts were tested. Even if the quality of the different salts was almost the same, good results were only obtained with the material from Riedel-de Haën (minimum purity of 86%).

Table 3:Sulfination of 66

Entry	66 [mmol]	$Na_2S_2O_4$ [eq]	$NaHCO_3$ [eq]	Conditions	T[°C]	67 [%]
1	2.16	1.5	1	4 hours	70	-
2	2.16	1.33	1.33	overnight	rt	92
3	2.16	2.1	3.7	4 hours	70	92
4	2.16	2.1	3.7	15 hours, inert atm.	40	81
5	2.16	1.33	1.33	4 hours, inert atm.	70	-
6	2.16	1.5	1	4 hours, inert atm.	70	75
7	2.16	1.33	1.33	15 hours, inert atm.	40	-
8	6.49	2.1	3.7	4 hours	70	93

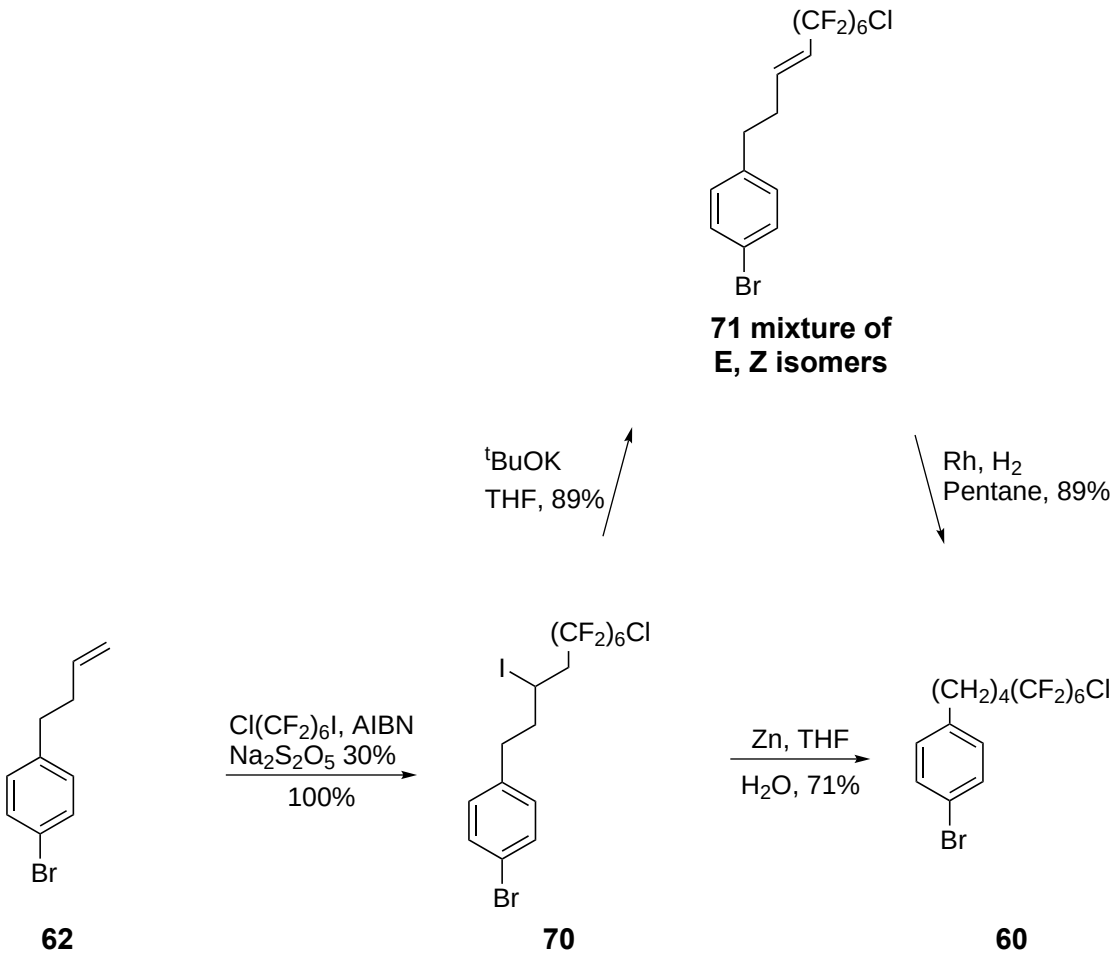
The crucial parameters for this reaction seem to be the ratio between starting material and sodium dithionite and the quantity of sodium carbonate. Indeed a large excess of $Na_2S_2O_4$ and $NaHCO_3$ seem to push the reaction to the end (entries 3, 4, 8, table 3), except for the second test (entry 2, table 3), where only 1.33 eq $Na_2S_2O_4$ of and 1.33 of $NaHCO_3$ gave a very good yield of 92%. Other parameters like reaction time or temperature did not really influence the reaction. Finally, the pure sulfinate was collected as a white solid which was analysed by ESI-MS, FT-IR and ^{19}F-NMR.

In a second step, an aqueous solution of the sulfinate compound was treated with chlorine gas produced by the reaction of concentrated HCl on $KMnO_4$ to form a sulfonyl chloride. The sulfonate product should be obtained by reaction of the sulfonyl chloride with NaOH. Nevertheless, the sulfonate compound was never collected as a pure product. Its presence was confirmed by ESI-MS in several attempts, but starting material was always present too, as seen by ^{19}F-NMR. It is evident that a purification method would be required to obtain the pure perfluorinated sulfonate salt, but chromatography is impeded by detection problems.

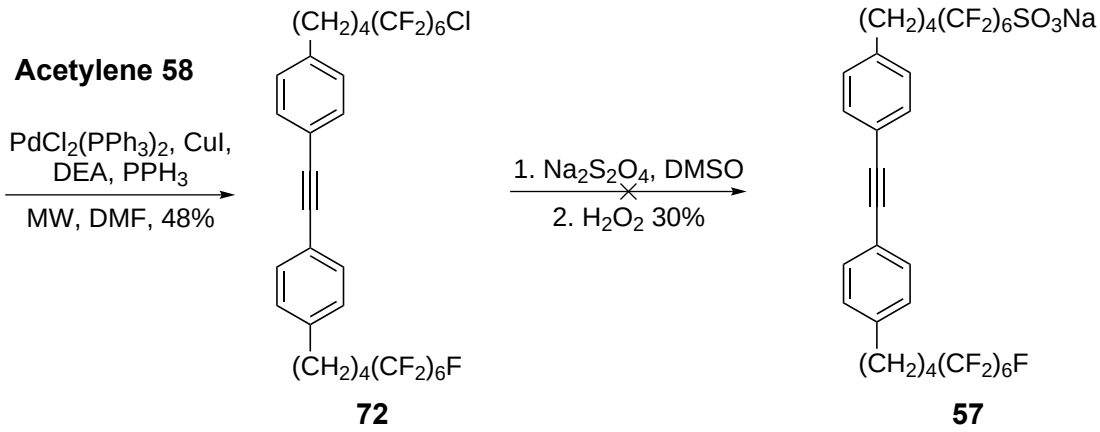
Still following the paper of Hu and Qing, the radical reaction allowing to introduce the perfluorinated chain on the allyl compound **62** was performed mixing ammonium peroxodisulfate (1 eq) and sodium formate (1 eq) with the perfluorinated chain and the starting material **62** in DMF at

60 °C during 4 hours and overnight at room temperature. The previously prepared starting sulfonate chain **68** used in this step was not pure, still containing starting material and unknown impurities, according to its preparation. After the work up, the starting material was recovered in majority. No traces of the desired product were detected by ESI-MS. Thinking that the problem came from the impurities contained in the chain **68**, which have perhaps interfered with the radicals, new attempts were made with the similar commercially available molecule **69**. But again the starting material was always found in majority after the work up. The addition of several equivalents of ammonium peroxodisulfate and formic acid sodium salt did not change anything, as well as a longer reaction times. As no idea was found to explain that the desired compound was not formed, a first step could have been to control the presence of the polyfluoroalkyl radicals by the addition of tert-butyl nitroxide in the reaction mixture allowing to trap the polyfluoroalkyl radicals, making them persistent to be analysed by ESR. This could have given a first indication.

1.2.2 Passing by the chlorinated tolane



Scheme 21: Synthesis of the chlorinated tolane 72

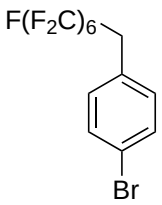


72 **57**

Scheme 21: Synthesis of the chlorinated tolane 72

The chloro-perfluorinated chain was placed on the double bond of the compound **62** by the already presented method (see paragraph 1.1) in quantitative yield. The reduction of the C-I bond was explored more deeply in this case, because of the presence of the four different halogen functions, which complicated the selectivity of the reaction[1].

A two step method gave first nice results. The iodine was eliminated with potassium tert-butoxide giving the olefins E, Z mixture **71** in 89% yield in the better case. The impurity **73** was observed in each batch, sometimes as major product, with a mass 40 m/z smaller than the desired compound. If no real explanation could be given, we can suppose that the presence of the bromomethyl bromobenzene **61** or the allyl compound **62** could induce the formation of this impurity.



73

Scheme 22: Formation of the by-product 73

The double bond was then reduced by hydrogenation in pentane with rhodium as catalyst giving again 89% yield. Even if the final yield for this hydrogenation is very good, it should be mentioned that not all batches gave so nice results. It was remarked that sometimes no reaction occurred or that a special long reaction time (around 140 hours) was necessary to convert all

1.The compound **63** as well as the iodinated precursor of **93** were also used for the tests.

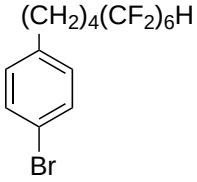
the starting material. No real explanation could be found. The presence of oxygen which killed the catalyst was proposed as a reason, but bubbling with argon did not influence the reaction. A second hypothesis was that nickel which was present in the autoclave wall helped to catalyse the reaction. In some attempts, the use of a glass tube in the autoclave to facilitate the preparation could therefore avoid the nickel effect. But again this hypothesis was refuted by repeating the reaction without the glass tube, without any improvements. Moreover, other attempts revealed that not only the iodine was removed, but also a fluorine, the bromine or both. Even if small amounts were observed, it was never possible to eliminate these impurities by chromatography. The reproducibility difficulties encountered with this method forced us to elaborate another more efficient method.

Therefore, efforts were made to find a simpler one step solution. The classical method employed by Aebischer [101] during his thesis with $LiAlH_4$ was considered. But the bromine and the chlorine atoms had the tendency to be exchanged by hydride. Slow additions at 0 °C helped for a better reaction control to avoid the reaction with the bromine on the aryl cycle, but did not change anything for the chlorine atom. Red-Al, successfully used for the formation of the 10-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorodecane chain (see paragraph 1.3.1.2) gave in this case similar results as $LiAlH_4$. Another method was to remove the iodine radical with lauroyl peroxide in cyclohexane [115]. The iodinated compound was dissolved in cyclohexane and the oxygen was removed by the freezing/vacuum method. Then at 50 °C, lauroyl peroxide was added and the mixture was stirred at 80 °C. Two further additions of lauroyl peroxide were performed after 3.5 and 6 hours and the stirring was continued for 20 hours. After evaporation of the volatiles, a silica gel column chromatography with pentane as eluent gave the desired compound in a moderate yield of 52%. This reaction was easy to control and therefore a better solution than those already presented methods. But the yield was still not satisfactory. Finally our attention was concentrated on finding a metal which could be inserted in the C-I bond selectively. Magnesium and zinc were chosen as first candidates. Where Mg gave back the starting material, Zn seemed to be the perfect metal. Indeed, even with the four halogens present on the compound **70**, good yields around 70% were obtained, what showed a very good selectivity for the C-I bond. The selective insertion was explained because the C-I bond was clearly the weakest one among all the carbon-halogen bonds present. According to these results, the metallation was chosen as the method of choice for this kind of reduction.

The synthesis of the compound **60** has allowed us to successfully continue with the second Sonogashira cross-coupling reaction again in a MW reactor [112] forming the dissymmetric tolane **72** in a moderate yield of 48%.

The difficulties met in the first presented pathway for the formation of the sulfonate function have oriented our research on a two-step idea. According to the paper of Cao and Chen [116], the chlorine atom of the starting material was first replaced by a sulfinate group which was then oxidized in sulfonate function employing a 30% hydrogen peroxide solution. So our tolane **72** was suspended in DMSO and sodium dithionite was added (4 eq). Then the mixture was heated by MW irradiation or by oil bath. According to ESI-MS in positive or negative mode, the sulfinate molecule was formed in most of the attempts. The starting material was not always totally consumed according to ^{19}F-NMR. This could be explained perhaps by a bad solubility of the starting material in DMSO or by the bad quality of the sodium dithionite salt. The presence of the reduced compound **74** was detected by ^{1}H-NMR, certainly due to the presence of water in the reaction mixture. But in no case the pure compound could be isolated, even after precipitation or chromatography purification. The temperature (100 °C or 150 °C) and the reaction time (from 3 to 6 hours) did not influence the sulfinate formation. Finally the crude product was directly suspended in a hydrogen peroxide solution and agitated overnight. Because of the insolubility of the sulfinate tolane, only starting material was recovered after extraction with EtOAc. The addition of acetic acid did not allow to improve the solubility.

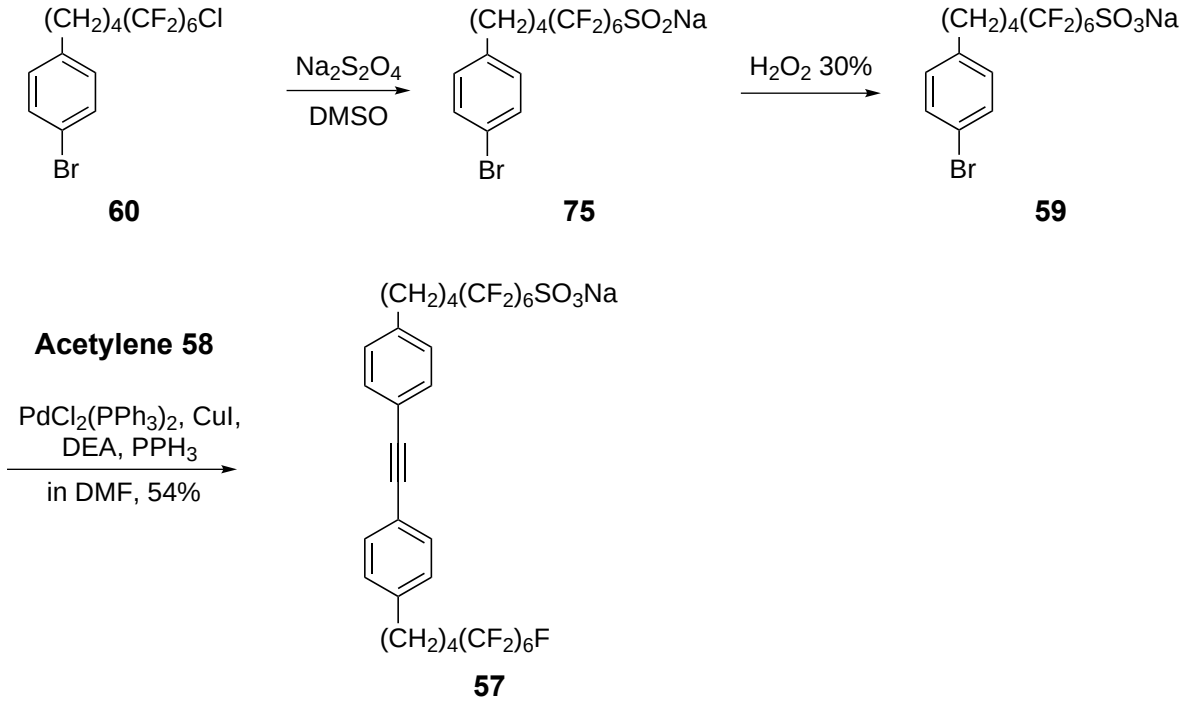
In both sulfinate formation and oxidation, the solubility of the staring material seemed to be problematic, certainly because of a big perfluoro-organic part with a low solubility in polar solvents. Therefore, the sulfonate formation was tested on the compound **60** which could be better soluble, because it was smaller and contained less fluorine atoms.



74

Scheme 23: Impurity observed in the sulfination step

1.2.3 Sulfonate formation before the second Sonogashira reaction



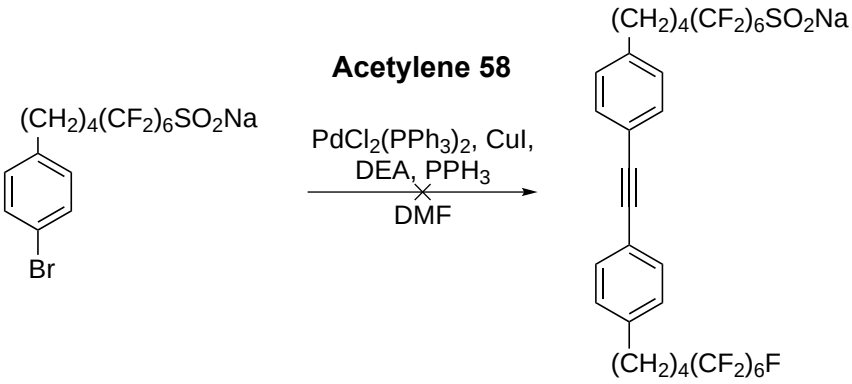
Scheme 24: Synthesis of the chlorinated tolane 72

Applied on this new molecule, the sulfinate formation **75** (DMSO, oil bath, 100°C, 3 hours) was achieved, according to the ESI-MS analyses. The ^{19}F-NMR showed no remaining starting material and ^{1}H-NMR confirmed the formation of one by-product, the reduced compound **74** in small amounts. The different conditions tested like different temperatures, heating by MW or oil bath, equivalents of dithionite or duration of the reaction did not improve the results. Moreover neither recrystallization nor chromatography were useful to purify our molecule. Therefore, after washing with water and concentration of the organic phase to remove the DMSO, the crude material was directly engaged for an oxidation with a 30% hydrogen peroxide solution without passing by the sulfonyl chloride. After overnight stirring in the hydrogen peroxide solution, the organic material was extracted with EtOAc, dried over sulfate salt and concentrated. Again ESI-MS was employed to confirm the presence of the desired sulfonate. This time chromatography on silica gel was successfully used with DCM/MeOH 87:13 as eluent giving the pure sulfonate compound as a white solid. Yields were really different from one batch to another without that any explanation could be found. Finally, overall yield over the two steps for the sulfonate formation were really low, at best 22%. Nevertheless, enough sulfonate material was produced to pursue the pathway and the tolane formation was succeeded with a Sonogashira reaction. Exactly the same conditions as used for the formation of the protected acetylene (see paragraph 1.1) were employed. The purification was again the most difficult part of this reac-

tion. Precipitation or recrystallization from different solvents mixtures were first explored without significant results. The pure product was finally isolated in the best case in 54% yield, thanks to a silica gel column chromatography, using DCM/MeOH 9:1 as eluent. In a few cases, several chromatographies were necessary to get the pure product.

According to these results, it seems that our hypothesis on the low solubility of the tolane part in polar solvents like DMSO and hydrogen peroxide was really the problem that prevented the formation of the sulfonate directly on the chlorinated tolane **72**.

1.2.4 Sonogashira with sulfinate compound



75 **76**

Scheme 25: Synthesis of the sulfinate tolane

The formation of the sulfinate tolane was also tested, starting with the acetylene **58** and the sulfinate **75**. But after MW irradiation (40 minutes at 120 °C), no trace of the sulfinate tolane was found after a silica gel column chromatography, using ether, EtOAc or acetone as eluents. As the desired sulfonated tolane was formed by another pathway, this strategy was given up.

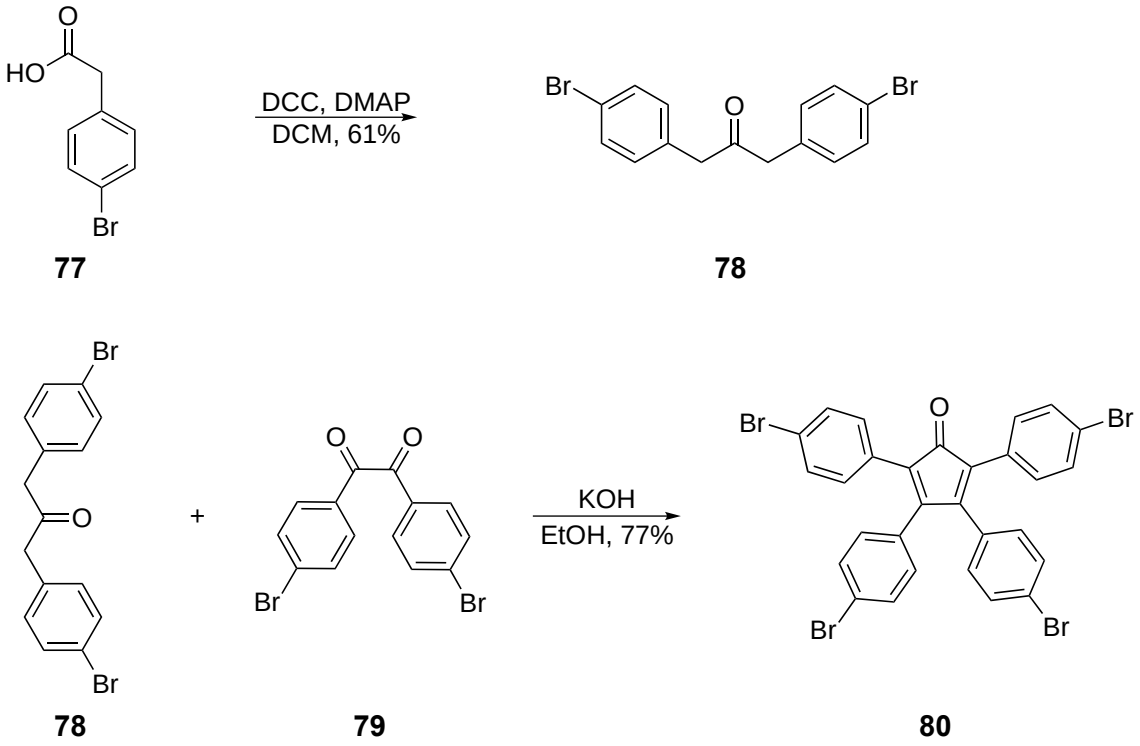
1.3 Synthesis of the substituted cyclopentadienone moiety

1.3.1 Pathway 1: by carbonyl group protection

One of the best ways to synthesize molecules with lateral chains consists to introduce the chains as late as possible. The principal reason is the bigger flexibility of the method, which allows to produce quickly a library of compounds by the introduction of various chains on a similar core. In this project, an ideal core would have been for instance the compound **80**. It was planned to protect the carbonyl group via acetalysation with ethylene glycol before forming a tetra-Grignard reagent to couple the lateral chains by four Kumada cross-coupling reactions.

Finally acid catalysed deprotection would have given the desired substituted cyclopentadienone **85**.

1.3.1.1Core synthesis

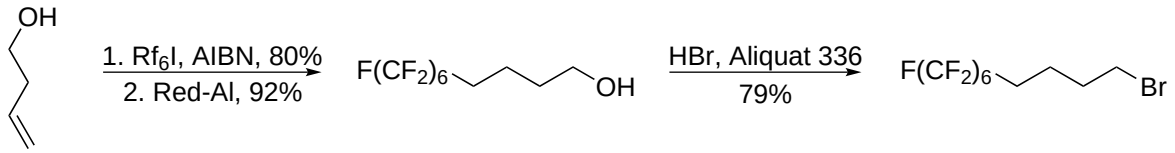


Scheme 26: Synthesis of the tetrabromophenylcyclopentadienone

The formation of the dibenzyl ketone moiety **78** was realized using a method described by Bhandari and Raya [107]. Usually used for the formation of peptides or esters (Steglich esterification), DCC and DMAP were used in this case to condense two arylacetic acid molecules, giving the desired compound in a moderate yield of 61% in the best case. The reproducibility of this reaction was really bad, and yields from ranging 30% to 61% were obtained.

Then a double Knoevenagel reaction [109] between **78** and **79** was performed in ethanol with potassium hydroxide. A direct deep purple coloration showed the formation of the desired cyclopentadienone. The pure product was then obtained by a silica gel chromatography in 77% yield as a deep purple solid.

1.3.1.2Perfluorinated chain formation

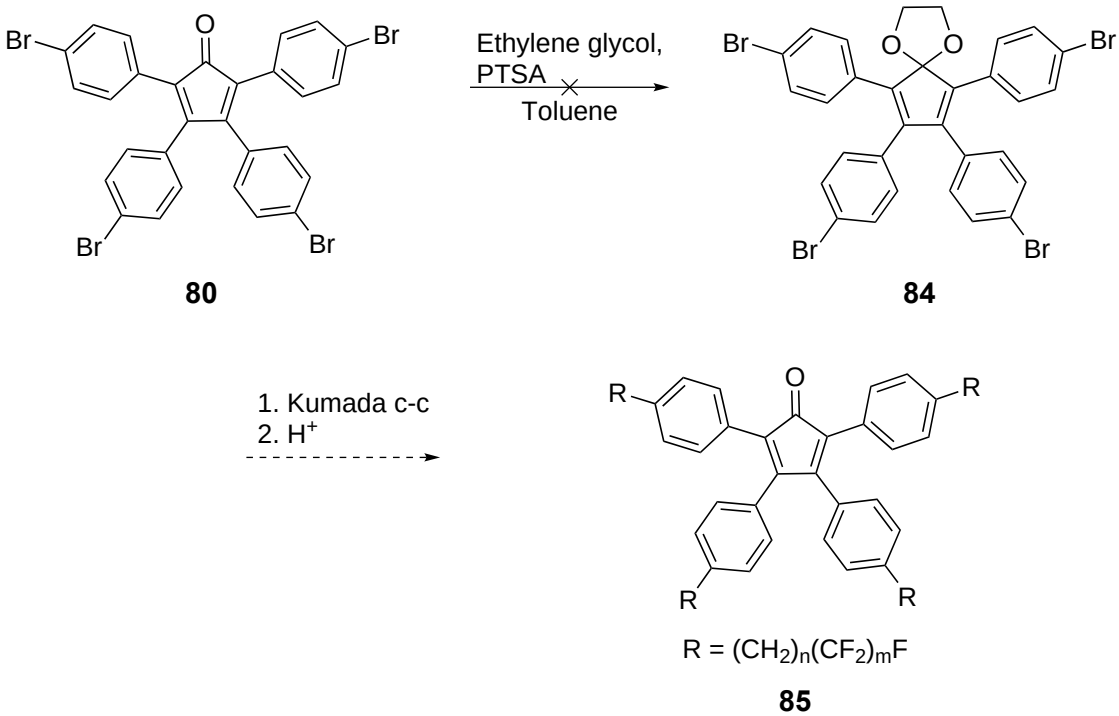


81 **82** **83**

Scheme 27: Perfluorinated chain formation

The perfluorinated chain which should be attached on the compound **80** had to be prepared from the butenol. First the perfluorinated chain was added on the double bond using the known method with AIBN as radical initiator [117]. The addition of a second AIBN portion (5 mol%) after 2 hours allowed to increase the yield from 60% to 80%. The reduction of the carbon-iodine bond with the reducing agent Red-Al gave a very good yield of 92% after classical work up and a silica gel column chromatography with ether/pentane 7:3 as eluent. It is evident that the previously developed method with zinc insertion as well as the reduction with $LiAlH_4$ could also have been applied in this reaction, because no other functional groups could have interacted with the reagents. Finally 79% of the desired brominated chain were obtained by bromation with HBr 48% and aliquat 336 as phase transfer catalyst [118].

1.3.2 Carbonyl group protection



80 **84** **85**

Scheme 28: Planned synthesis of the substituted tetraphenylcyclopentadienone

For the protection of the ketone function on compound **80**, the carbonyl compound, the ethylene glycol and the *p*-toluenesulfonic acid in toluene were heated at reflux in a round flask with a Dean-Stark apparatus [119]. In the first attempt (entry 1, table 4), not all the starting material was dissolved at the beginning. The reaction was in spite of that started because it was thought that the dissolution would be better at reflux, what was right. In the second case (entry 2, table 4), a bigger dilution was used to solubilize all the starting material. In both cases after overnight stirring, washings with a saturated solution of $NaHCO_3$ and brine followed by a drying over Na_2SO_4 and solvent evaporation only the starting material **80** was present.

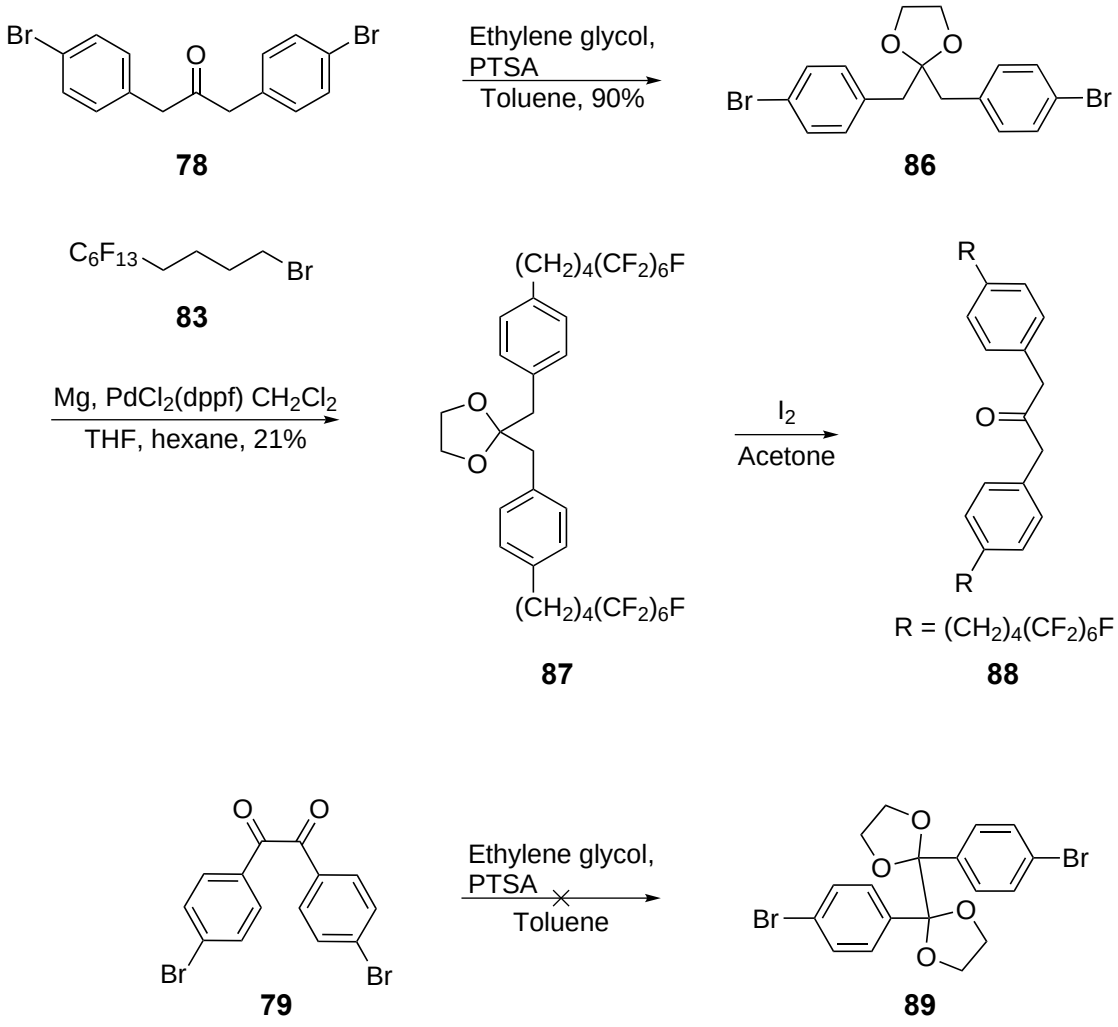
Table 4:Protection attempts of 80

Entry	80 [mmol]	Ethylene glycol [eq]	PTSA [eq]	Toluene [ml]	84 [%]
1	1.04	3	0.03	5	-
2	0.61	3	0.03	120	-

As no reaction was observed on the compound **80**, we directly tried to form the Grignard reagent of this compound, thinking that the conjugated ketone function would be unreactive.

In a Schlenk tube dried in an oven, activated magnesium (42 mg, 1.7 mmol) was agitated at 70 °C during 10 minutes. Then a solution of the cyclopentadienone compound (300 mg, 0.43 mmol) in dry THF (5 ml) was slowly injected and the stirring was continued at 70 °C for 6 hours and at 150 °C overnight. Because magnesium turnings were still present, the Schlenk tube was let in a ultrasonic bath during 6 hours after what the heat gun was used trying to activate the reaction, but again without success. The solution was collected (filtration of the Mg) and water was added without any reaction. Finally starting material **80** (200 mg) was recovered by extraction with dichloromethane. A possible explanation could be given by the quality of the magnesium turnings, which were certainly not activated enough. Even if the wanted Grignard reagent was not formed, this test has shown us that the conjugated ketone was inert enough to not be reduced by the magnesium turnings.

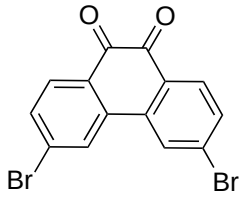
The difficulties met for the protection of the carbonyl group of **80** have forced us to adapt the pathway and it was decided to test the carbonyl protection and the coupling reactions on the two precursors **78** and **79**.



Scheme 29: Protection of 78 and 79

With the same conditions described for the protection of **80**, the acetalysation of the dibenzyl ketone worked perfectly giving a white solid in 90% yield. On the other side, the protection of the α-diketone **79** was more difficult. With the same method as before, only the starting material was recovered. Another method proposed in the work of Kevin F. Kelly and James M. Tour [120] employed CSA in THF in a Schlenk tube (150 °C, overnight) instead of PTSA in toluene. But at the end, no traces of the desired compound were found. Again the starting material with in this case unidentified by-products were collected. A possible explanation could be that our compound is free for rotation compared to the molecule **90** of Kelly and Tour, what could increase the steric hindrance and avoid any acetalization on compound **79**. A possible alternative for this diketone protection was given by Diederich and co-workers [121]. They succeeded to protect a cyclobutadienone derivative using bis(trimethylsilyloxy)ethane in the presence of tri-

methylsilyl triflate at 80 °C for 6 hours in 76% yield with the formation of only 5% of the monoketal by-product. The complete deprotection was achieved stirring the diketal product with concentrated H_2SO_4 for 30 minutes at room temperature. Applied on our dibenzil compound, this pathway could give nice results.



90

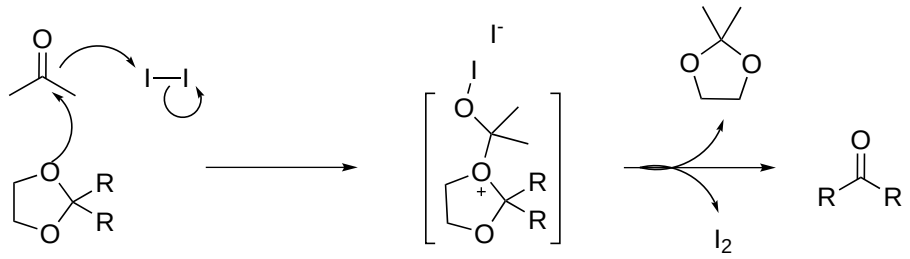
Scheme 30: Typical compound used in [120]

Even if the protection of the diketone moiety was problematic, tests to attach the lateral chains by Kumada cross-coupling on **86** as well as deprotection of the ketone function were begun. The coupling reaction was made following the conditions proposed by Aebischer in his thesis [101]. In an oven dried Schlenk tube under inert atmosphere, activated magnesium turnings (0.037 g, 1.534 mmol) were agitated during 1 hour and heated three times with a heat gun. At room temperature, hexane (1 ml) was added, as well as a solution of **83** (0.698 g, 1.534 mmol) in dry THF (1 ml). The mixture was heated at 75 °C for 2 hours. There was still some small magnesium turnings in the brown mixture, what showed that the Grignard reagent has not been totally formed. This mixture was diluted with dry THF (2 ml) and added to a suspension of **86** (0.158 g, 0.383 mmol) and (1,1'-Bis(diphenylphosphino)ferrocene)-dichloropalladium(II) CH_2Cl_2, (0.044 g, 0.061 mmol) in dry THF (1 ml) in an oven dried Schlenk tube. The mixture was then agitated at 75 °C during 67 hours. The red-brown mixture was cooled down to room temperature and quenched with methanol (5 ml). DCM was added to this solution, which was washed with a saturated NH_4Cl solution (20 ml), washed with water (20 ml), dried over Na_2SO_4 and finally evaporated to dryness to give a brown oily mixture. Two silica gel column chromatographies (eluent: pentane/ether 8:2, then 9:1) gave finally the desired product (80 mg, 0.08 mmol, 21%). One of the explanation of this low yield was clearly the formation of the Grignard reagent which was not complete, according to the magnesium turnings still present in the flask. The magnesium surface was perhaps not activated enough to start the oxidative addition, as already supposed for the formation of the tetra-Grignard reagent on the compound **80**.

Table 5:Deprotection tests on compound 87

Entry	87 [mmol]	Reagent	solvent ([ml])	t [°C]	Results
1	0.06	Acetic acid/water (0.25 ml/0.06ml)	Acetone (1)	rt	-
2	0.03	PTSA (0.02 eq)	Acetone (0.3)	rt	-
3	0.03	Iodine (0.5 eq)	Acetone (0.2)	rt	**88**

More difficulties were met during the deprotection and three different methods were tested. In the first attempt (entry 1, table 5), acetic acid was used as proton source [119]. Because our product was insoluble in the acetic acid/water mixture, acetone was added after 30 minutes of stirring at rt to dissolve the starting material, without success. After 4h30, the organics were extracted from the aqueous phase with ether. Then the organic phase was dried over Na_2SO_4 and evaporated to dryness. The starting material was totally recovered. For the second test (entry 2, table 5), *para*-toluenesulfonic acid was used catalytically in acetone. After classical work up, the starting material was recovered in majority, with another product, still not yet identified. Finally a method proposed by Sun et al. [122] (entry 3, table 5) was more effective. In a molecular iodine-catalysed substrate exchange mechanism as shown in Scheme 31, the ketal compound was dissolved in acetone and iodine was added. The almost pure desired compound was obtained after work up, according to ^{1}H-NMR and ^{13}C-NMR. No yield was calculated for this step because no purification was performed on this product.



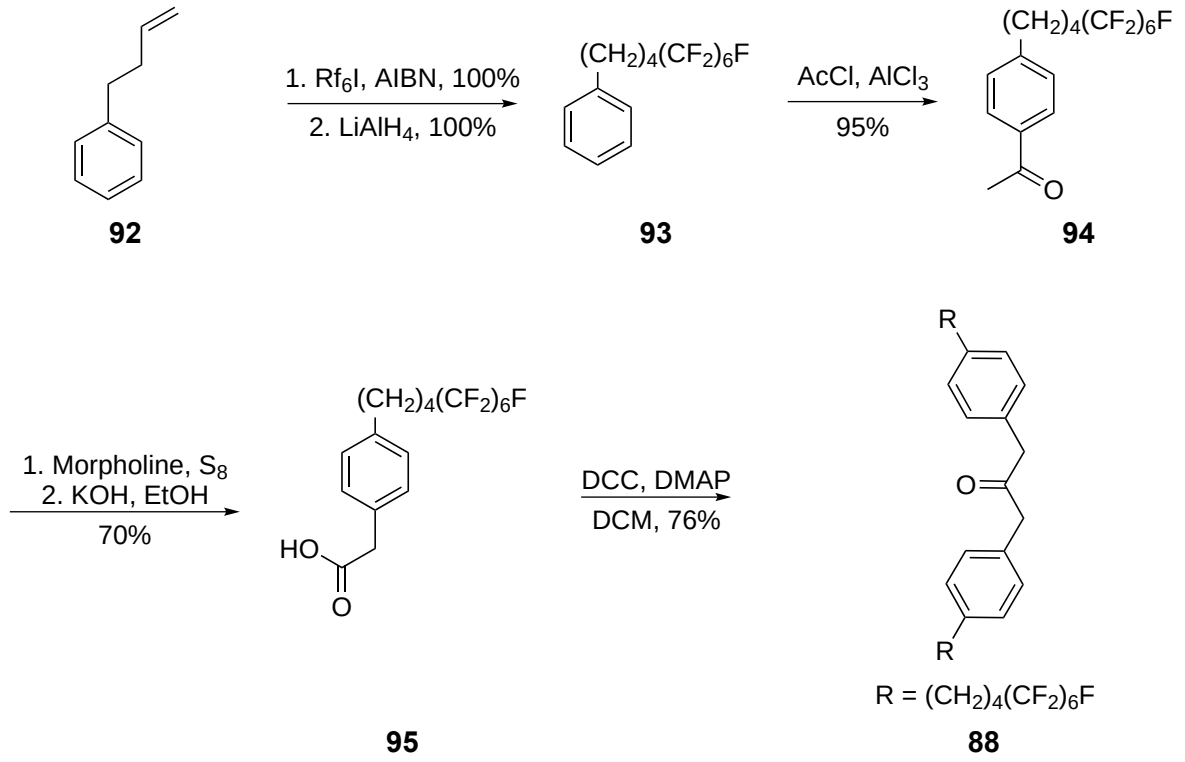
Scheme 31: ketone deprotection by substrate exchange mechanism

Finally the study of this deprotection as well as the protection of the diketone **79** were stopped at this point because another better synthetic pathway was developed simultaneously (see paragraph 1.3.3) for the formation of the perfluorinated cyclopentadienone.

1.3.3 Perfluorinated cyclopentadienone formation with side-chains since the beginning

Because it was difficult to protect the ketone group to attach the four lateral chains, another pathway was adopted.

1.3.3.1 Perfluoro-dibenzyl ketone synthesis

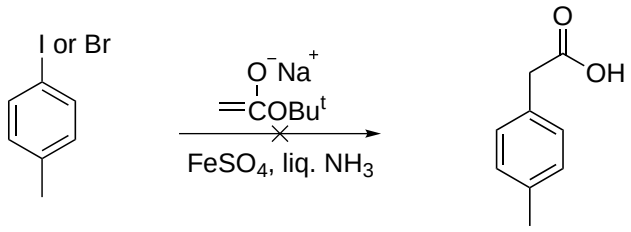


Scheme 32: Perfluoro-dibenzyl ketone synthesis

Already presented chemistry (see paragraph 1.1) was employed to form the compound **93** with an overall yield of 100% over the two steps.Then the substituted acetophenone **94** was prepared by a Friedel-Craft acylation performed from - 90 °C till room temperature over three hours with $AlCl_3$ as Lewis acid to activate the acyl chloride [105]. Even if the starting mixture was frozen at -90 °C, no influence on the reaction was detected, according to the very good yield of 95% obtained after classical work up and filtration over a plug of silica gel with pentane/ether 7:3 as eluent. The two next reactions gave the acetic acid **95**. First a Willgerodt-Kindler reaction with morpholine and sulfur (135 °C, 15 h) [106] has formed a thioamide which was in a second step hydrolysed with KOH in ethanol releasing the acetic acid with an overall yield of 70%. The thioamide compound was never obtained as a pure product, in spite of chromatography attempts, causing no problems for the hydrolysis. Finally the desired perfluoro-dibenzyl ketone **88** was produced by the method presented in paragraph 1.3.1.1. Again, as previously men-

tioned for the same reaction, varying yields were obtained, ranging from 28% to 76%.

Another approach proposed by Leeuwen and McKillop [123] for the synthesis of the acetic acid moiety **95** was tested, where a bromo or iodophenyl compound could be transformed by a unimolecular radical nucleophilic substitution ($S_{RN}1$) reaction in a phenylacetic acid.



96 **97**

Scheme 33: Formation of acetic acid compound by $S_{RN}1$ reaction

Some tests were performed on the simplest compounds **96** to find the good conditions according to the literature to form the phenylacetic acid molecule.

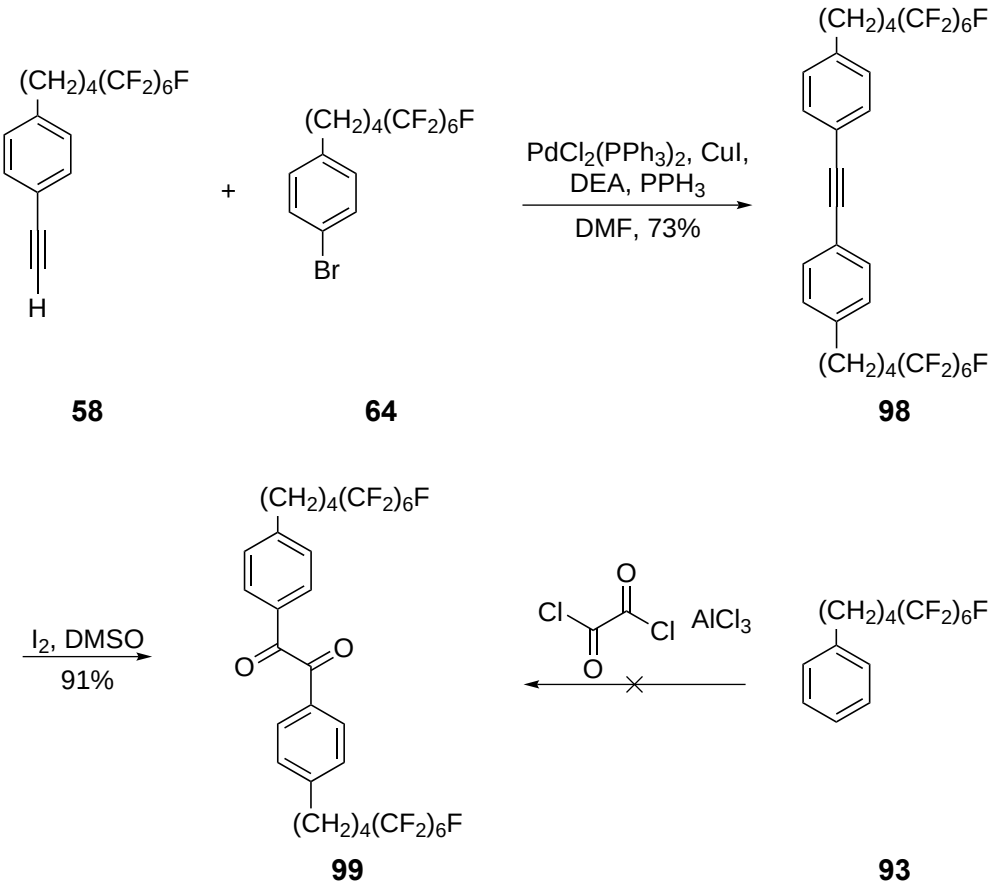
A heat gun dried three necked flask with an nitrogen inlet, a condenser cooled at - 70 °C and a bubble counter was placed in a acetone/nitrogen bath (- 70 °C) and filled with 50 ml of ammonia. Under inert conditions, the addition of sodium amide (6 eq) was followed by the slow addition of tert-Butyl acetate (6 eq). After 30 minutes of stirring at - 70 °C, the cooling bath was removed and iron(II) sulfate (1 eq) and 4-bromo or iodotoluene (1 eq) were quickly added. The stirring was continued for 3 hours (the colour became dark brown). The reaction was then quenched with portionwise additions of NH_4Cl and the ammonia was allowed to evaporate giving a brown mixture, which was suspended in water. The organic material was extracted with ether (3 x 70 ml) and the organic layer was washed with water (50 ml), 5% HCl (3 x 70 ml) and with brine (50 ml), dried over Na_2SO_4 and evaporated to dryness. In each attempt, only the pure starting material was recovered (see table 6). The reasons why in our case no reaction occurred are still unclear, especially because a yield of 63% was published [123] for the compound **96** with iodine.

Table 6:$S_{RN}1$ test on compound 96

Entry	96 [mmol]	Method to dry $FeSO_4$	Results
1	Br, 4.87	overnight vacuum	**96**
2	I, 4.59	overnight vacuum	**96**
3	I, 4.59	heat gun with vacuum	**96**
4[a]	I, 4.59	heat gun with vacuum	**96**

a. Performed in a Schlenk tube

1.3.3.2 Diketone part synthesis



Scheme 34: Formation of the diketone 99

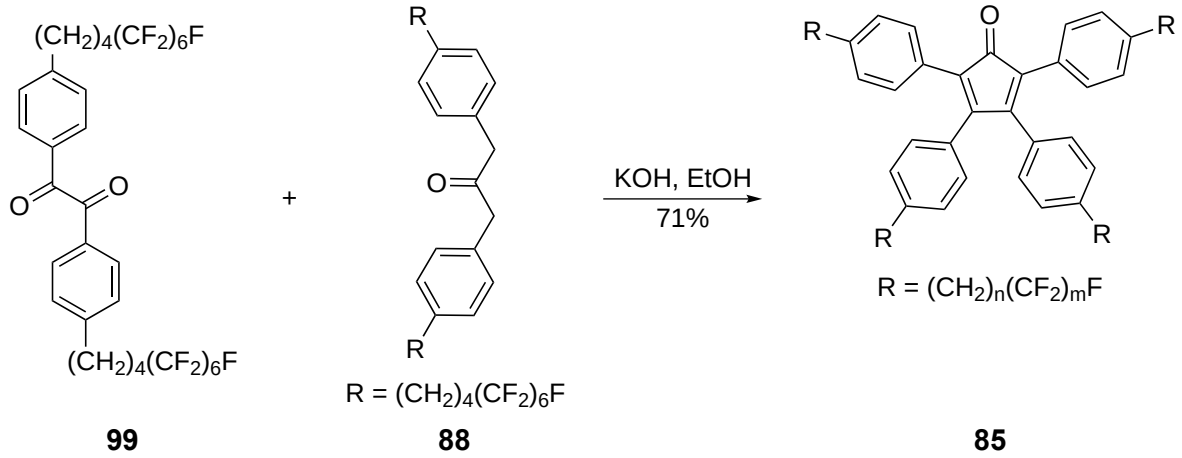
The diketone compound was easily obtained via a Sonogashira cross-coupling reaction between the two already synthesized molecules **58** and **64**. Exactly the same conditions as in paragraph 1.1 were used. The purification was achieved by a recrystallization followed by a silica gel column chromatography with pentane, then pentane/ether 97:3 as eluent, giving an ac-

ceptable yield of 73%. This yield would be certainly higher if the purification has been directly performed by chromatography. The oxidation of the triple bond succeeded in a good yield of 91% agitating the starting material with iodine in DMSO at 155 °C during 16 hours [104]. A simple filtration over a plug of silica gel with pentane/ether 9:1 as eluent was necessary to purify the crude material. Even if the method to produce the diketone **99** was efficient, a double Friedel-Craft reaction on oxalyl chloride was also tried with the molecule **93**.The three first attempts (entries 1 to 3, table 7) were performed in DCM with the slow addition of **93** at -80 °C [105]. The reaction mixture was then agitated at room temperature during 4 hours. After classical work up, even if all the starting material was consumed, the desired compound was observed by ^{1}H-NMR only in small amounts. The two last tests (entries 4 and 5, table 7) were tried in CS_2 instead of DCM, according to a paper of Wegner at al. [124]. This time the oxalyl chloride was added to the reaction mixture at -80 °C. But after 23 hours of reaction and the work up, we also obtained a mixture containing the desired product. In every case, no purification was done because of the low quantities of the desired product obtained.

Table 7:Double Friedel-Craft reactions on oxalyl chloride

Entry	93 [mmol]	oxalyl chloride [eq]	$AlCl_3$ [eq]	solvent [ml]	99
1	2.2	0.5	1.1	DCM 5.5	observed
2	1.1	0.5	5	DCM 2.7	observed
3	0.66	0.5	5	DCM 1.7	observed
4	0.66	0.6	1.36	CS_2 2	observed
5	0.66	0.6	5	CS_2 2	observed

1.3.3.3 Formation of the perfluorinated tetraphenyl cyclopentadiene



99 **88** **85**

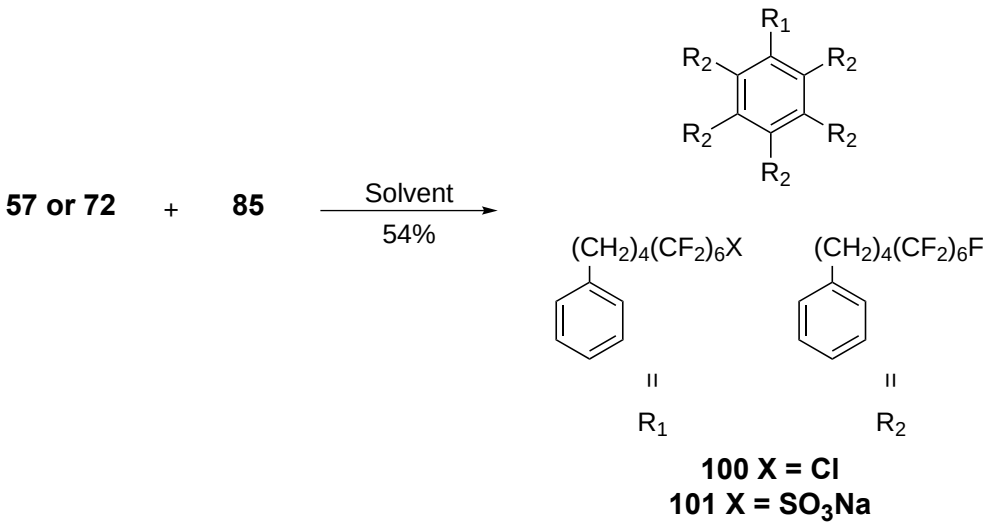
Scheme 35: Formation of the perfluorinated tetraphenyl cyclopentadiene

The double Knoevenagel reaction was again successfully applied for the formation of compound **85**. As in paragraph 1.3.1.1 for the formation of **80**, a deep purple solid was obtained after silica gel column chromatography in a relative good yield.

1.3.4 HBC formation

1.3.4.1 Hexaphenyl benzene formation

The previously prepared dissymmetric tolane **57** and perfluorinated tetraphenylcyclopentadienone compound **85** had now to be coupled together in a Diels-Alder reaction with a decarbonylation to liberate the substituted hexaphenyl benzene, which had then to be oxidized to give the desired HBC.



Scheme 36: Formation of the substituted HBC

The Diels-Alder reaction was already presented in the literature [125], [126]. Because a decarbonylation was necessary to regenerate the benzene ring, the temperature of the reaction had to be relatively high. Therefore solvents like diphenylether were used. Nowadays, with the possibility to heat easily under pressure by MW irradiations, solvents with lower boiling points could also be used. The preparation of the reaction was quite simple, suspending under inert atmosphere the two starting materials in the solvent in a concentration around 0.1 M. The purification was made by silica gel column chromatography. For the sulfonate compound, both reverse and normal phase were successfully employed. Normal phase was used with EtOAc or EtOAc/DCM 8:2 as eluent and reverse phase (C_{18} columns) was performed with MeOH/water mixture in gradient mode. Having a look at the different attempts realized for this reaction (see table 8), it was remarked that the yields were not really high, certainly because of a partial degradation of the starting materials due to high temperatures or light. If more tolane was used, the yield was increased only in one case (see entries 2, 3 and 5, table 8). Other by-products formations could explain the low yields. The only one which could be clearly identified (MALDI-MS) was the reduced compound from product **85** (only one double bond was reduced). Concerning the solvent choice, the best one was not the same for the two dissymmetric tolanes tested. With the chlorinated compound **72**, diphenylether gave the better yield, but for the sulfonate molecule **57**, DMF was the best. The reason was certainly a better solubility of the sulfonate product in DMF.

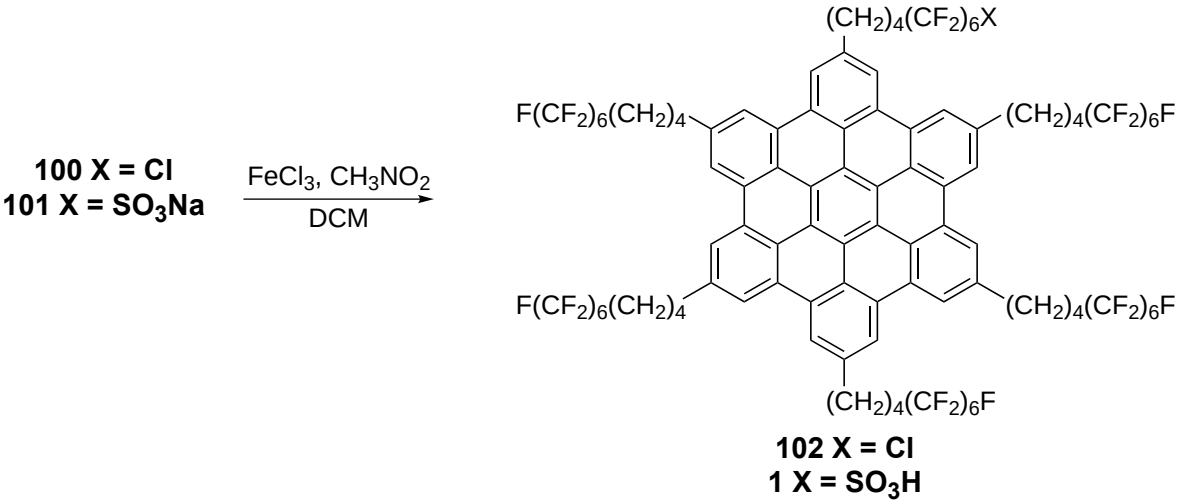
Table 8:Diels-Alder reaction

Entry	Diss. tolane	eq diss. tolane	solvents	Heating mean	[h]	[°C]	Results [%]
1	72	1	Ph_2O	oil bath	22	220	29
2	72	1.5	Toluene	MW oil bath	2 23	150 200	15[a]
3	72	1.5	DMF	MW	2	250	16
4	57	1	Ph_2O	oil bath	21	220	19
5	57	1.3	DMF	MW	11	250	54

a.NMR yield

Some tests to put the sulfinate instead of the chlorine atom on the hexaphenyl benzene **100** were performed using the same conditions as described in paragraph 1.2.2 for the formation of **57**. The starting material was heated with four eq of sodium dithionite in DMSO. But at 100 °C or 150 °C, the compound **100** was always totally recovered. This could certainly be explained by the low solubility of the hexaphenyl benzene in DMSO. The addition of DCM or BTF did not change the result.

1.3.4.2 Scholl reaction



Scheme 37: Formation of the perfluorinated sulfonic acid HBC

The oxidation reaction was performed under Scholl conditions, as proposed by Aebischer in his thesis [101], adding a solution of iron trichloride in nitromethane to a solution of the hexa-

phenyl benzene in DCM at 45 °C. After 6 hours of stirring at 45 °C under argon bubbling through a teflon capillary to remove the formed HCl, MeOH was added to quench the reaction and the precipitate was filtrated over millipore®. A black solid was obtained and washed with MeOH and DCM.

The two oxidations made with the chlorinated compound **100** gave the desired hexabenzocoronene product, according to MALDI-MS in positive mode, which also showed some undefined impurities. First produced to test a sulfination at this step, this HBC was finally not employed. Indeed, it was logically thought that all the problems met for the sulfination of the compound **100** certainly due to a bad solubility of the starting material in DMSO would be worse in this case.

As for the chlorinated HBC, the three reactions with the sulfonate compound gave the expected HBC in diverse purity, according to the MALDI-MS analyses in both positive and negative modes. On the two lasts attempts, a compound with a mass 18 m/z smaller than the HBC **1** was observed, even in a large quantity in one case. The only explanation we could give was the exchange of a fluorine by an hydrogen atom. But the reason for a such reaction was unclear. No traces of such impurity were observed in the previous steps, what allowed us to think that this side-reaction occurred during the oxidation. But this impurity was not detected in all three attempts and no similar by-products were identified in the thesis of Aebischer [101], who has made a huge work on this type of perfluorinated HBCs. Because this impurity seemed to be present only with the sulfonic acid HBC, it was thought that this exchange occurred on the perfluorosulfonic acid chain, certainly close to the acid group.

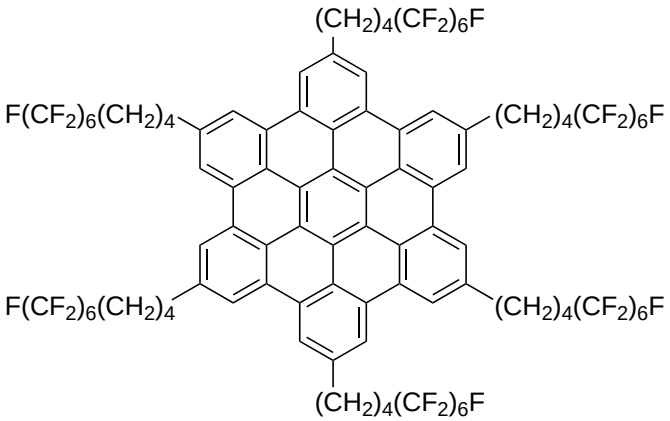
A lot of efforts were made for the purification of the compound **1** which had to be as pure as possible for the subsequent application tests. It was first tried to remove iron particles and organic impurities which could contaminate our sulfonic acid HBC by sonication and centrifugation in different solvents (MeOH, Et_2O, DCM, $NaHCO_3$ solution in MeOH, EtOAc). But MALDI-MS always showed the presence of the same impurities. Normally such HBC did not pass through a silica gel column, because of the aggregation of the molecules, due to the π-π stacking. In our case, the presence of the sulfonic acid seemed to have a big influence on the elution of our product on silica gel. Indeed, a mixture of MeOH/HFB 1:1 allowed to elute the desired HBC through silica gel column or on TLC. Because of the difficulties to obtain good analyses from these types of compounds, the purity was not really known. But several impurities could be removed by elution with EtOAc or remained stuck on the silica gel.

To avoid the presence of iron particles in our final product, another oxidation method was tested, according to the work of Rathore [103] where in presence of methanesulfonic acid they have succeeded to oxidize alkylated hexaphenylbenzene derivatives with DDQ.

In a two necked flask under inert atmosphere, the molecule **100** (0.087 g, 0.031 mmol) was dissolved in a mixture of DCM (3.8 ml) and methanesulfonic acid (0.422 ml) and cooled down to 0 °C. Then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.042 g, 0.187 mmol) was added and the mixture was agitated at 0 °C during 4 hours. Almost all the starting material was recovered, as confirmed by ^{1}H-NMR, after drying and concentration of the organic phase obtained by common work up. Small unknown impurities were also present.

1.3.5 Fluorescence analysis

To confirm the presence of the desired perfluorinated HBC, the fluorescence spectrum of our perfluorinated sulfonic acid HBC was compared with the fluorescence spectrum of the reference compound **28** prepared by Aebischer.



28

Scheme 38: HBC prepared by Aebischer

With the presence of the sulfonic acid on the HBC, the symmetry of the molecule is reduced, what introduces a small dipole moment and disorder in the stacks. The transition energies would be similar as in the compound **28**, except for the transition moment which could alter the relative intensities of individual bands. But generally, a similar spectrum as for **28** is expected. Although the measured spectrum shows a much lower resolution, the positions of the absorption bands perfectly match and confirm hence the formation of the HBC compound (see Figure 18).

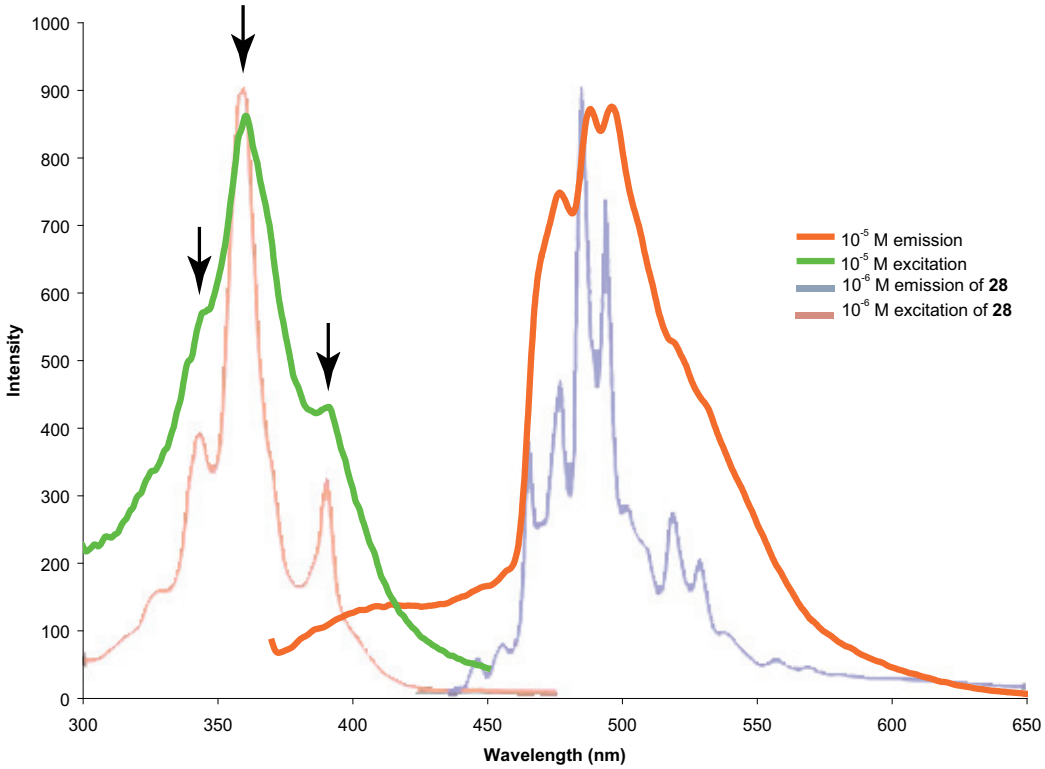


Figure 18: Comparison between emission and excitation spectra of our perfluorinated sulfonic HBC (10^{-5} M in HFB) and 28 (10^{-6} M in BTF, spectra with attenuated lines)

In the analyses of Aebischer, well resolved emission spectra were obtained in BTF, allowing to identify several transitions [101]. He also found that the well resolved fluorescence spectra were only obtained from the monomeric form of the HBCs, at high dilution. In our case hexafluorobenzene as solvent and a 10 fold higher concentration as compared to the work of Aebischer were chosen. Indeed when a 10^{-6} M solution was used in our case (see Figure 19), the quality of the spectrum severely degraded although a sharp band, typical for monomeric species, appears. The low resolution in our spectra could be explained by the presence of impurities in the product, or by the formation of strong clusters, which suppress the HBC monomeric form.

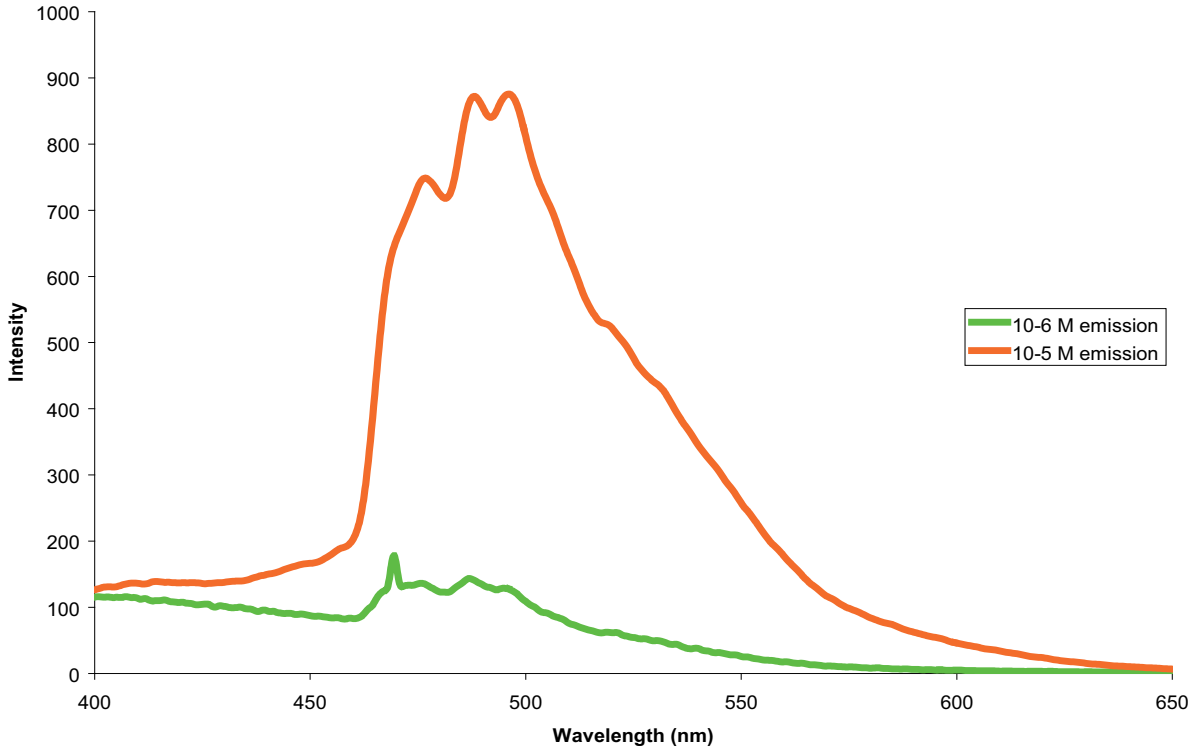
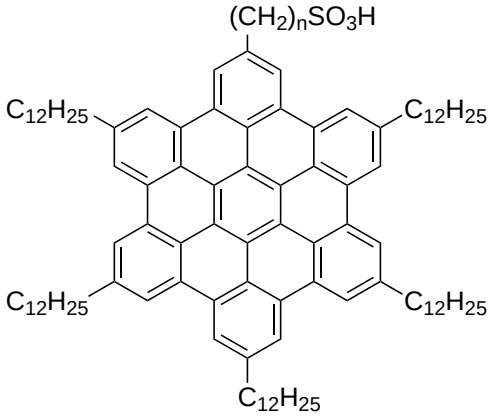


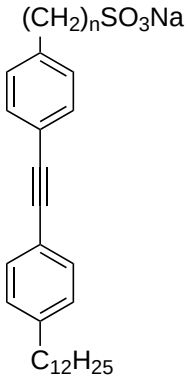
Figure 19: Comparison of fluorescence spectra of our perfluorinated sulfonic acid HBC at 10^{-6} M and 10^{-5} M in HFB

2. Alkylated sulfonic acid HBC

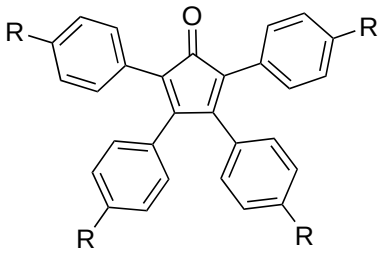


103

1. Oxidation
2. Diels-Alder



104



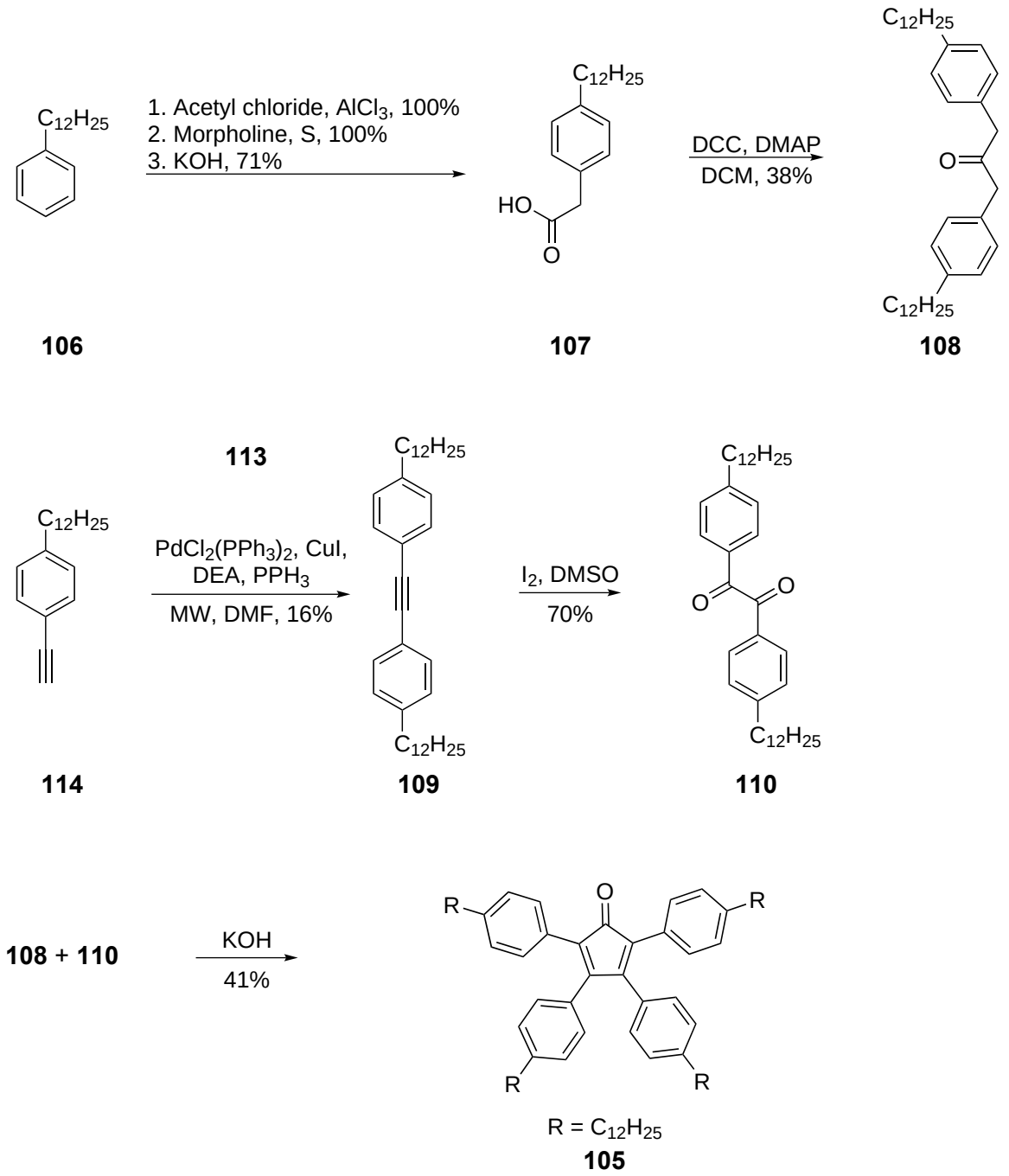
R = $C_{12}H_{25}$

105

Scheme 39: General synthesis for the desired alkylated HBC

The general strategy to synthesize the desired alkylated sulfonic acid HBC was similar to the method used for the perfluoro sulfonic acid HBC. A tetra-(4-alkylated-phenyl) cyclopentadienone and a dissymmetric tolane have to be prepared and coupled together by a Diels-Alder reaction, before being oxidized to the corresponding HBC. The best length of the chain carrying the sulfonic acid is until know not determined. In a first approach, it would depend on the method which would work. Moreover this length has only a small importance. As we have no idea on the behaviour of such a compound, we want to prepare relatively quickly a first compound and then to explore the influence of the chain length in a second time.

2.1 Alkylated tetraphenyl cyclopentadienone

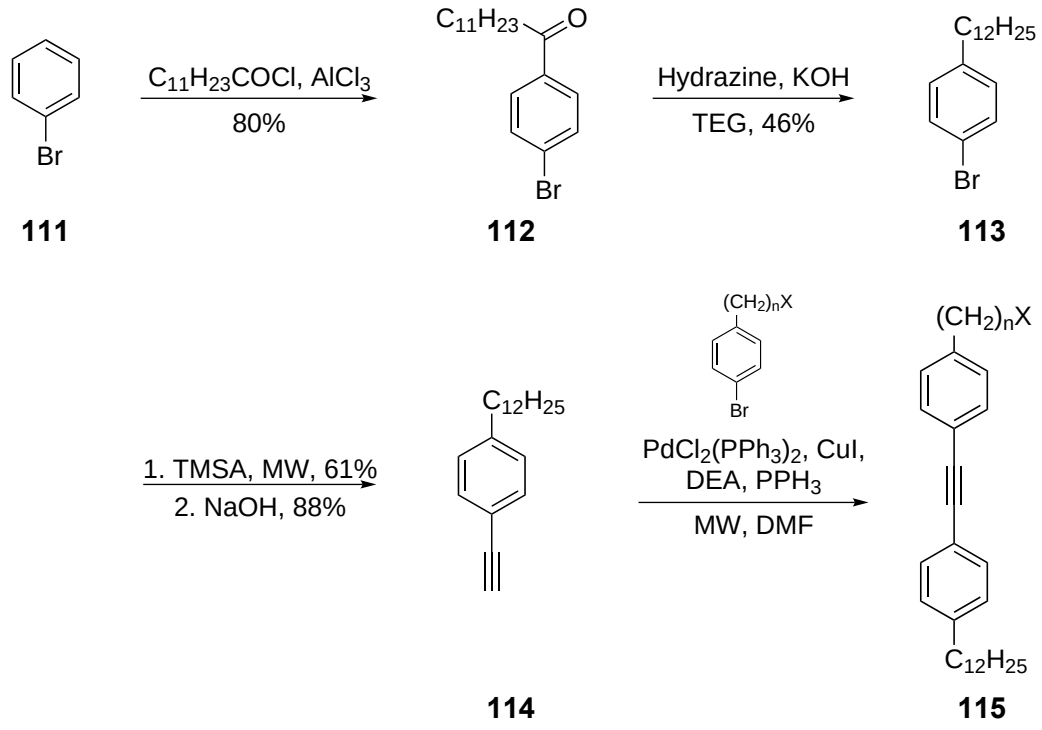


Scheme 40: Formation of the alkylated tetraphenyl cyclopentadienone

This synthesis was already presented for the perfluorinated tetraphenyl cyclopentadienone compound and exactly the same reactions were used in this case, with dodecanoyl chains instead of the perfluorinated chains. The formation of the dibenzil ketone moiety **108** began with a Friedel-Crafts acylation with acetyl chloride [105], followed by a Willgerodt-Kindler reaction and the hydrolysis of the formed thioamide [106]. The final condensation with DCC and DMAP [107] gave the desired compound in 38% yield. As for the synthesis of the similar perfluorinated

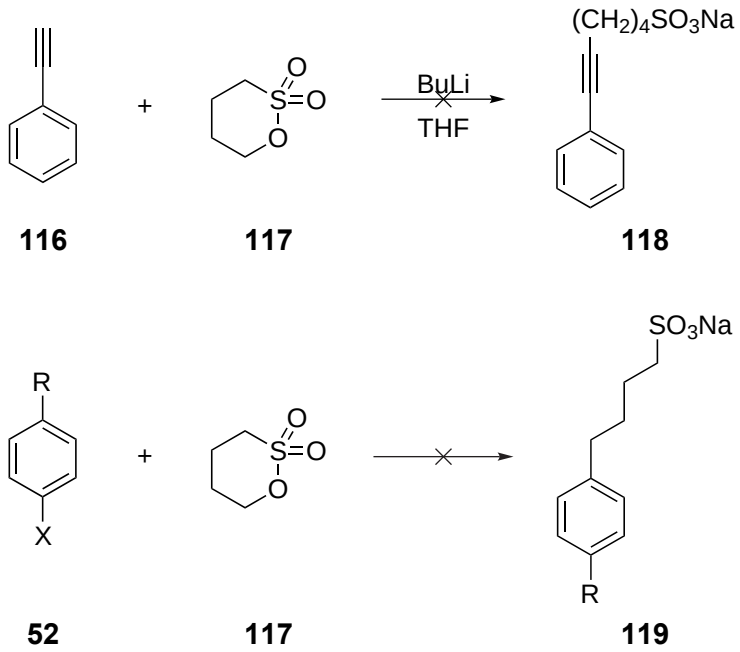
molecule, the yield of the last step was not really high. Then the substituted diketone **110**, which was formed by oxidation with iodine in DMSO [104] of the tolane **109**, was obtained in 70% yield. The tolane **115** was formed by a Sonogashira cross-coupling reaction on the compound **114** (c.f. next paragraph). Finally, the desired cyclopentadienone was synthesized by a double Knoevenagel reaction [109] in a moderate yield of 41%, as a deep purple solid.

2.2 Dissymmetric tolane formation



Scheme 41: Dissymmetric alkylated tolane formation

The approach for the synthesis of the dissymmetric tolane **104** required the formation of an acetylene moiety starting from compound **111**. A Friedel-Crafts acylation followed by a Wolff-Kishner reduction [109] gave the dodecyl bromobenzene **113**, on which a Sonogashira cross-coupling reaction was performed according to the already presented method (see paragraph 1.1). After the deprotection, a second Sonogashira reaction with an aryl moiety carrying either the sulfonate chain or a function, which could be transformed in sulfonate group, would gave the desired dissymmetric tolane. The question is, with which X-group (OH, Br, SO_3Na) this second Sonogashira reaction should be performed to give the easiest and the cleanest reaction. Another challenge in this synthetic strategy is to find a clever route to form the alkyl sulfonate group. Two different ideas were tested.



Scheme 42: Attempt synthesis to form the alkyl sulfonate compound

First the most elegant method was explored, where the alkyl sulfonate chain would be directly placed on a phenylacetylene or on a benzene thanks to a nucleophilic attack on the sultone by the deprotonated sp carbon of the phenylacetylene or by an activated benzene. With the acetylenide, the resulting triple bond had then to be hydrogenated.

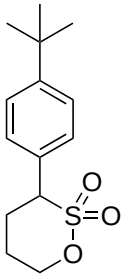
Table 9:Nucleophilic attacks on a sultone compound

Entry[a]	SM	Reagent	Solvents	Results [%]
1	Phenylacetylene	^{n}BuLi	THF	observed
2	^{t}Bu-bromobenzene	^{n}BuLi	THF	-
3	^{t}Bu-bromobenzene	^{t}BuLi	THF	-
4	PhLi	-	THF	-
5	PhMgBr	-	THF	-
6	Toluene	$AlCl_3$	-	-

a. These reactions were performed on test compounds

For our tolane synthesis, bromophenyl acetylene was necessary to allow the Sonogashira reaction. But the initial tests for this reaction were made on the simpler phenylacetylene. The deprotonation was always done by the addition of ^{n}BuLi before the addition of the sultone (entry

1, table 9). In spite of the different temperatures tested (-78 °C, 0 °C, rt), the desired compound was isolated in very small quantities in only two cases. The addition of a Lewis acid such as zinc chloride or aluminium chloride to activate the sultone did not improve the results. No success had the addition on a phenyl ring. Neither phenyllithium nor phenylmagnesium bromide allowed to open the sultone ring (entries 2 to 5, table 9). When ^{n}BuLi was employed for the transmetallation on the starting tert-butyl bromobenzene (entry 2, table 9), the 1-(tert-butyl)-4-butylbenzene was formed in 29% yield, what showed a higher reactivity of the in situ formed bromobutane than of the sultone. With ^{t}BuLi (entry 3, table 9), the other by-product **120** was formed, due to the deprotonation of the carbon in α-position of the sulfur atom of the sultone. Indeed, the deprotonated sultone could make a nucleophilic attack on the starting ^{t}Bu-bromobenzene and produced the compound **120**. According to these results, it seems that the reactivity of the sultone was not efficient enough to react with aryl-metal compounds or with acetylenides.



120

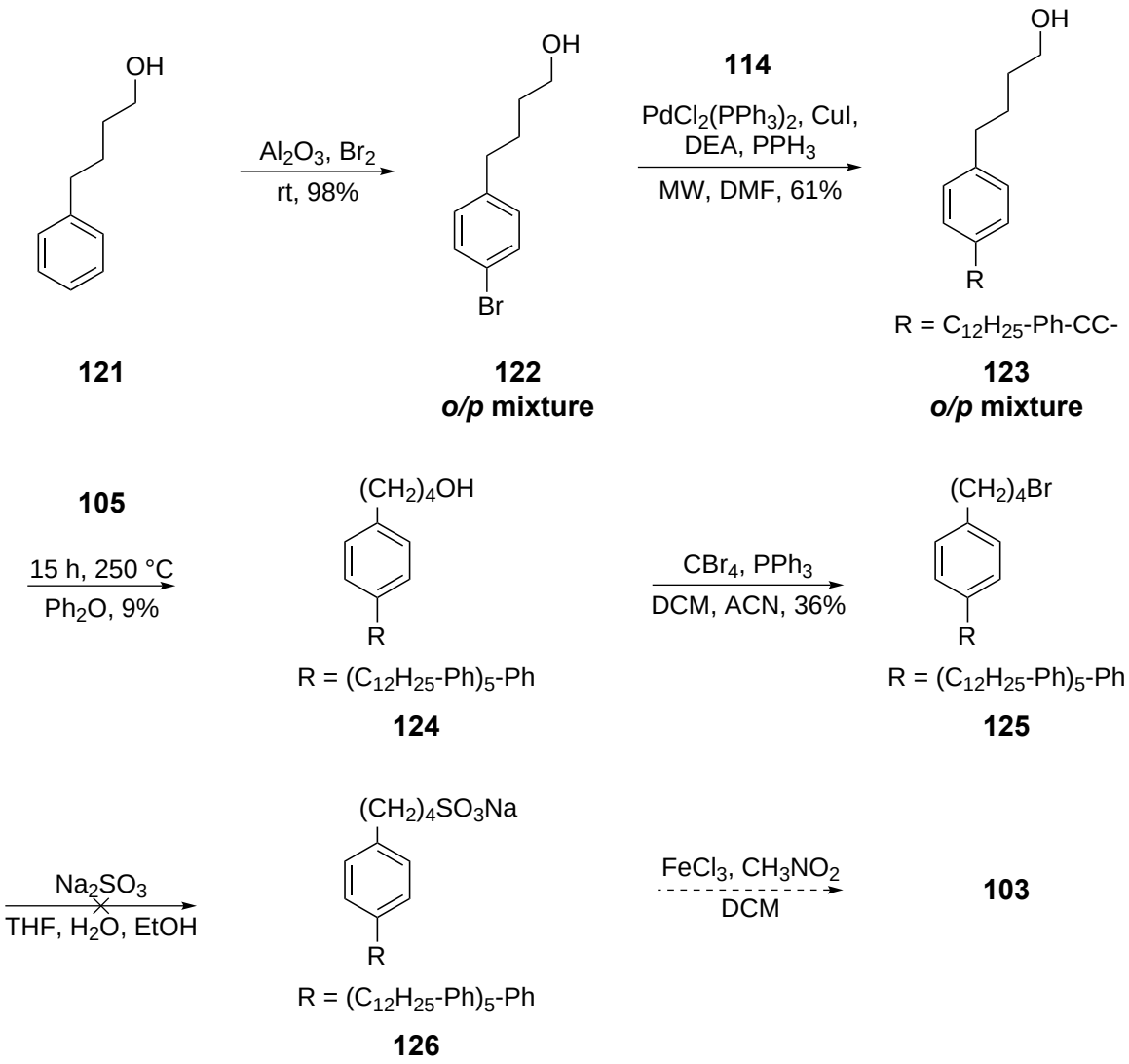
Scheme 43: Impurity observed with ^{t}BuLi

Finally, a Friedel-Crafts alkylation was also tested on toluene using $AlCl_3$ as Lewis acid (entry 6, table 9). According to ESI-MS and ^{1}H-NMR, the wanted compound seemed to be produced with this method as an ortho/para mixture. Even if the desired product was observed, this method was not further investigated because of the difficulties met during the work up and the isolation to obtain the pure para product.

The second strategy to form the alkylated dissymmetric tolane **104** used the formation of the sulfonate from a hydroxy compound via first an Appel reaction to produce a brominated product, and then a nucleophilic substitution with sodium sulfite. For an easy work, it was better to introduce the sulfonate group only after the tolane formation to reduce the problems due to the partial solubility of the sulfonate compound in water. For the tolane formation, the presence of a bromine atom on the phenyl ring in para position of the alkyl chain was necessary. But the cross-coupling reaction was only possible before the Appel reaction to avoid side-reactions due

to the presence of the bromine on the alkyl chain. Therefore the presented strategy (see Scheme 44) was tested. The bromination was done on the compound **121** using aluminum oxide and bromine at room temperature [127]. The desired compound was obtained in 98% yield as a mixture of ortho/para products in an approximative ratio of 1:2. Two different alox qualities were tested with different Brockmann grade without changing the ratio. All chromatography attempts employing different solvent mixtures were unsuccessful to separate the two isomers. Therefore the mixture was directly used for the next step. Indeed, it was thought that the separation could be possible later with larger molecules, for instance after the tolane formation, or even later. Moreover, if the separation was not possible before the oxidation, it is clear that the ortho compound could not accomplish a complete oxidation, due to the presence of the alkyl chain on a position needed for the oxidative dehydrogenation. The tolane formation was performed using the already presented conditions under microwave irradiations (see paragraph 1.1). After 40 minutes at 120 °C and classical work up, a silica gel column chromatography gave the crude dissymmetric tolane in 61% yield, still as a ortho/para mixture used as such for the continuation. The next step was the formation of the hexaphenyl benzene compound. It was not possible to exchange at this point the alcohol by a bromine because of the presence of the triple bond, which could also be brominated. The subsequent Diels-Alder reaction was therefore made with the dissymmetric compound **123** and the tetraphenyl cyclopentadienone **105** in diphenylether [125]. After decantation of the solvent with EtOH, the brown oily liquid obtained was chromatographied on silica gel with pentane/DCM 6:4 as eluent (solid deposition), giving at the end only 9% of the desired product. Even at this stage the separation of the ortho and the para compound was not achieved by chromatography. In fact, we could imagine that the molecule had become so big that the small functionalized chain has now only a very small influence compared to the rest of the molecule. The bromination at this stage with PPh_3 and CBr_4 in acetonitrile [128] required the addition of DCM to help for solubilizing the starting material. A yield of 36% was obtained after silica gel chromatography. The sulfonation was tried with the conditions proposed by Makriyannis and co-workers [129]. They used a mixture of three different solvents, ethanol, water and THF. In our case, the presence of all the alkylated chains forced us to adjust the solvents mixture (H_2O/EtOH/THF 1:3:9) allowing the dissolution of the apolar substrate and the sulfite salt. The reaction time as well as the temperature were also increased (12 hours at 180 °C), because no reaction were observed at 160 °C during 20 minutes. Finally a silica gel column chromatography with pentane/DCM 8:2, then 1:1 and with EtOAc did not allow to isolate the desired compound. An explanation could be given by the formation of aggregates due to the long alkyl chains in this particular solvent mixture which “close” the access to the bromine function. Therefore we could envision that a higher dilution could decrease these aggregates and facilitate this reaction. Of course, longer reaction

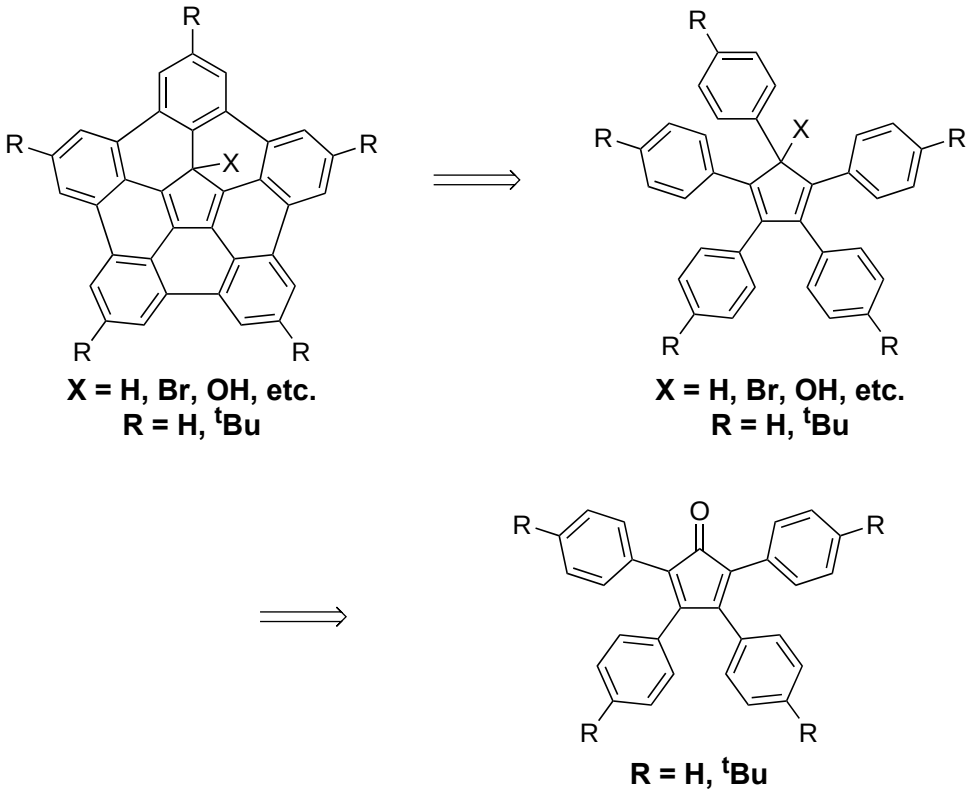
times would certainly be required.



Scheme 44: Attempted synthesis of the alkylated HBC

For these reasons, the desired compound is still elusive. With the chosen pathway, the problem was the substitution of the bromine by the sulfonate on the huge organic part (compound **125**). Because the accessibility of the bromine atom and certainly also the different solubility of the sulfite salt and the substrate, the formation of the sulfonate hexaphenyl benzene directly from the compound **125** seems difficult. Therefore, it would be better to work with the sulfonate function from the beginning. Indeed, even if the yields of each step would be lower, the attachment of the sulfonate group should be easier on the starting material **121**, before performing the bromation on the phenyl ring for the Sonogashira cross-coupling reaction.

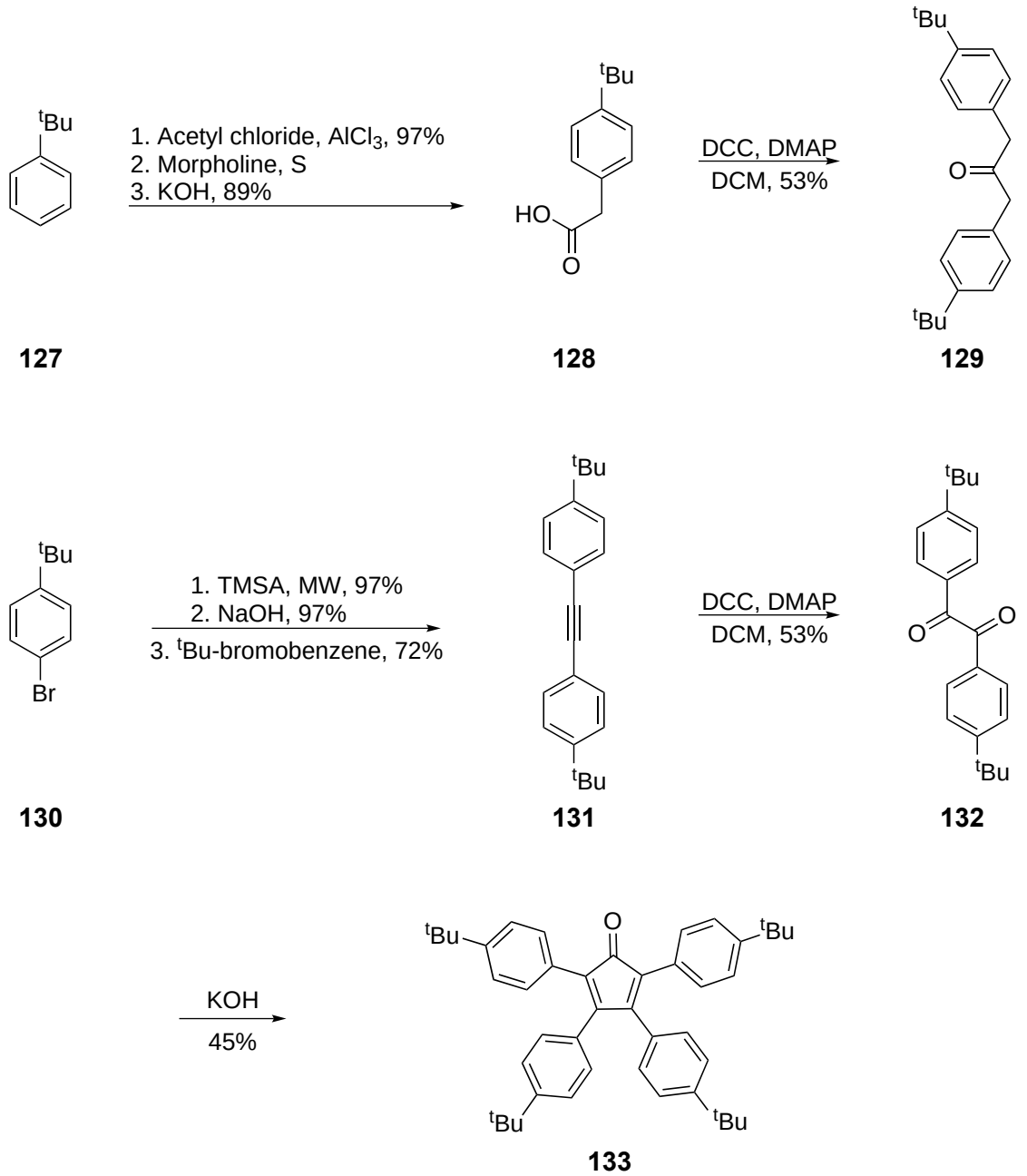
3. Pentaphenyl cyclopentadiene synthesis for oxidation attempts



Scheme 45: General retrosynthetic scheme

The oxidation of pentaphenyl cyclopentadiene derivatives is not known in the literature. The final molecule should adopt a bowl-shaped conformation. One of the great question would be, whether the cyclopentadiene will form a radical, a carbocation, an anion or keep a hydrogen on the cyclopentadienyl part. Two different pathways were studied. The first one passed by a nucleophilic attack by a phenyllithium compound on a tetraphenylcyclopentadienone forming the corresponding alcohol. The advantage of this method is the alcohol function which could then be reduced in hydrogen, or exchanged to bromine, depending on what would be necessary for the oxidation. The second pathway is a penta-coupling reaction of a halogenophenyl moiety on a cyclopentadiene complex [110], [130].

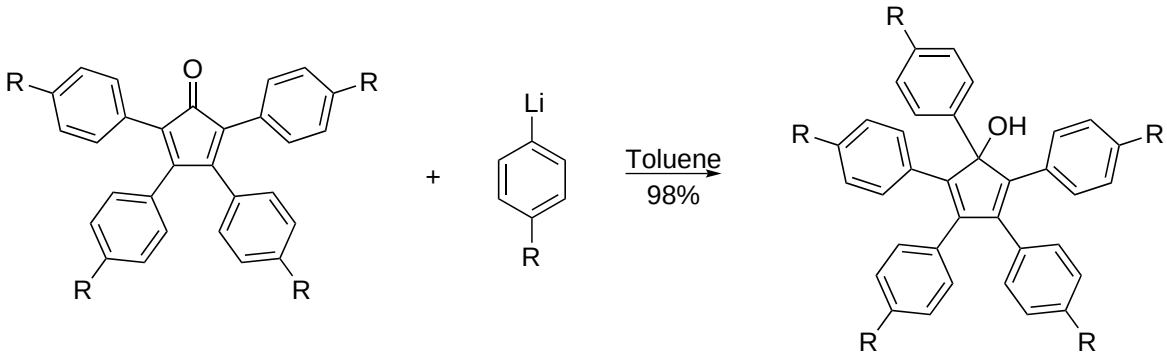
3.1 Tetraphenylcyclopentadienone formation



Scheme 46: Retrosynthesis of the dissymmetric tolane 57

Commercially not available, the compound **133** had to be prepared by the already presented method (see paragraph 2.1). No real difficulties were met during this synthesis. The yields were generally moderate to excellent, except for the second step of the preparation of the arylacetic moiety, where no yield could be given because of the presence of an impurity in the final product. In spite of that, the crude material was directly used for the condensation reaction.

3.2 Synthesis of the pentaphenyl cyclopentadienol



134 R = H
133 R = ^{t}Bu

135 R = H
136 R = ^{t}Bu

137 R = H
138 R = ^{t}Bu

Scheme 47: Nucleophilic attack on tetraphenyl cyclopentadienone molecules

For the parent compound **137**, the reaction was performed at room temperature [131]. In a two necked flask under inert atmosphere, phenyl lithium 1.9 M in buthylether (1 eq) was slowly added to a dark red suspension of the tetraphenyl cyclopentadienone in toluene. The yellow solution obtained was stirred during 1 hour and KOH 0.9 M in water (4.15 eq) was dropwise added. The biphasic system was agitated overnight. Water was then added and the organic compounds were extracted with ether. After drying with $MgSO_4$, the solvent was evaporated and the slightly yellow solid obtained was dried under vacuum, giving the desired compound as a slightly yellow-brown solid. In the first reaction (entry 1, table 10), no purification was necessary, what was different in the second and the third attempt (entries 2 and 3, table 10). A recrystallization in EtOH gave 86% yield in the second run, while in the third one (entry 3, table 10) the rest of the buthylether was first removed by suspension in pentane before the desired compound was recrystallized again from EtOH in 67%.

Table 10:Tetraphenyl cyclopentadienol formation

Entry	SM [mmol]	PhLi [eq]	Toluene [ml]	Results [%]
1	**134**, 1.3	1	30	**137**, 92
2	**134**, 13	1	250	**137**, 86
3	**134**, 13	1.2	250	**137**, 86
4	**133**, 0.82	1.1	10	**138**, 98

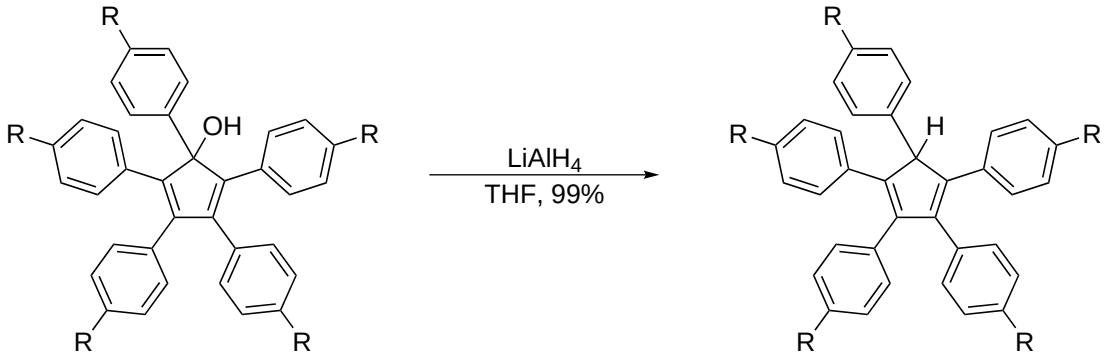
In the case of the tert-butyl compound **138**, the phenyllithium moiety had first to be prepared by a lithiation of the 1-bromo-4-(tert-butyl)benzene by ^{t}BuLi (2.2 eq) in a THF and pentane mixture at 0 °C. Normally done at lower temperature, typically -70 °C, This metallation was

achieved following Bailey and co-workers work [132] who succeeded this metallation at 0 °C, choosing the appropriate solvent mixture. In their work, ^{n}BuLi gave the best results in heptane/ THF 99:1. THF alone gave around 40% of 1-butyl-4-tert-butylbenzene, while almost all the starting material was recovered in heptane. With ^{t}BuLi the reaction seemed to be less sensitive to the solvent. Every heptane/ether (diethylether, THF or MTBE) mixture tested gave the desired phenyllithium moiety with more than 97% yield.

The previously prepared phenyllithium compound was then added dropwise to a mixture of **133** in toluene (entry 4, table 10). After two hours at room temperature, water was added and the organic phase was extracted with ether, dried with $MgSO_4$ and evaporated to dryness. Because a recrystallization in MeOH gave no crystals after two days, the purification was continued by column chromatography (silica gel) with pentane/DCM 2:1 as eluent. A yield of 98% was obtained.

3.3 Formation of the pentaphenyl cyclopentadiene compound

3.3.1 By reduction of the pentaphenyl cyclopentadienol



137 R = H
138 R = ^{t}Bu

139 R = H
140 R = ^{t}Bu

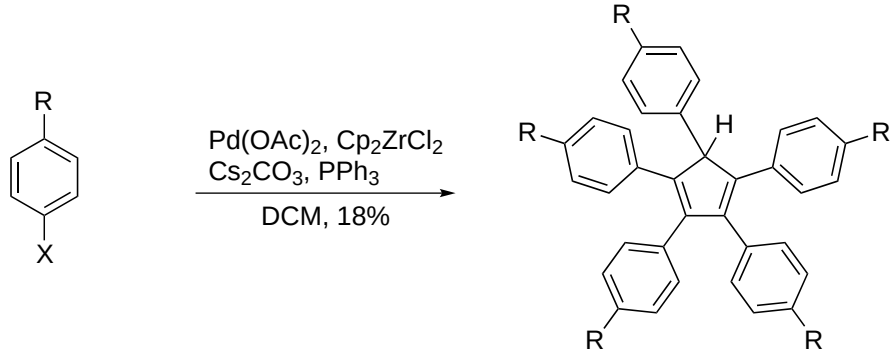
Scheme 48: Reduction of pentaphenyl cyclopentatienol compounds

This reduction was first attempted using the method proposed by McGlinchey et al. [133] where the reduction of an alkynol to the corresponding alkyne was achieved using the $Et_2O{\cdot}BF_3$ complex and triethylsilane. A possible mechanism was explained by the coordination of the alcohol function to the $Et_2O{\cdot}BF_3$ complex, a transfer of a fluorine from the boron to the silicon and finally the delivery of the hydride from the silicon to the carbon in a six-membered transition state. In our case, boron trifluoride diethyl etherate (0.7 ml, 2.57 mmol) was added to a solution of **137** (0.254 g, 0.549 mmol) in DCM (2.75 ml) at -10 °C in a two necked flask under inert atmosphere. A dark red coloration was observed. After 10 minutes, triethylsilane (1.312 ml, 8.24 mmol) was

added. After three hours at 0 °C, the reaction mixture was filtrated over a plug of silica gel with DCM to yield a yellow solution which was evaporated to dryness. At least four different fluorescent compounds were observed by TLC, among them our desired compound. Nevertheless, it was not possible to obtain it as a pure product after silica gel column chromatography.

It was found in literature [134] that $LiAlH_4$ could do the job alone. In this paper from Bäckvall, the obtained alcohol from a Grignard reagent addition on the compound **134** was in situ reduced by $LiAlH_4$. Applied in a large excess (2.5 eq) on our compounds **137** or **138** in dry THF, this hydride source led to the formation of the desired reduced compound in very good yield. Purification by silica gel column chromatography was nevertheless necessary. The presence of the aluminium which could act as a Lewis acid and complex the oxygen of the carbinol, thereby activating the compound towards a nucleophilic attack by a hydride was certainly responsible to make this reaction working.

3.3.2 By a one step reaction [130]



141 R = ^{t}Bu, X = Br
142 R = H, X = Br
143 R = Me, X = I

139 R = H
140 R = ^{t}Bu
144 R = Me

Scheme 49: Reduction of pentaphenyl cyclopentatienol compounds

Miura and Dyker [110] have explored in a paper of 1998 the direct formation of pentaphenyl cyclopentadienes by a reaction of aryl bromides on metallocenes like zirconocene dichloride in the presence of a palladium/phosphine catalyst and an appropriate base.

In a flask under inert atmosphere, the starting material, $Pd(OAc)_2$ (0.02 eq), Cs_2CO_3 (1 eq), PPh_3 (0.08 eq) and Cp_2ZrCl_2 (0.08 eq) were suspended in DMF and agitated at the appropriate temperature. Then, DCM and PTSA (2 eq) were added to quench the mixture. After 10 minutes of stirring, the dark-brown mixture was filtrated over a plug of silica gel with DCM as eluent. As shown in table 11, the formation of the desired compound was most of the time not observed

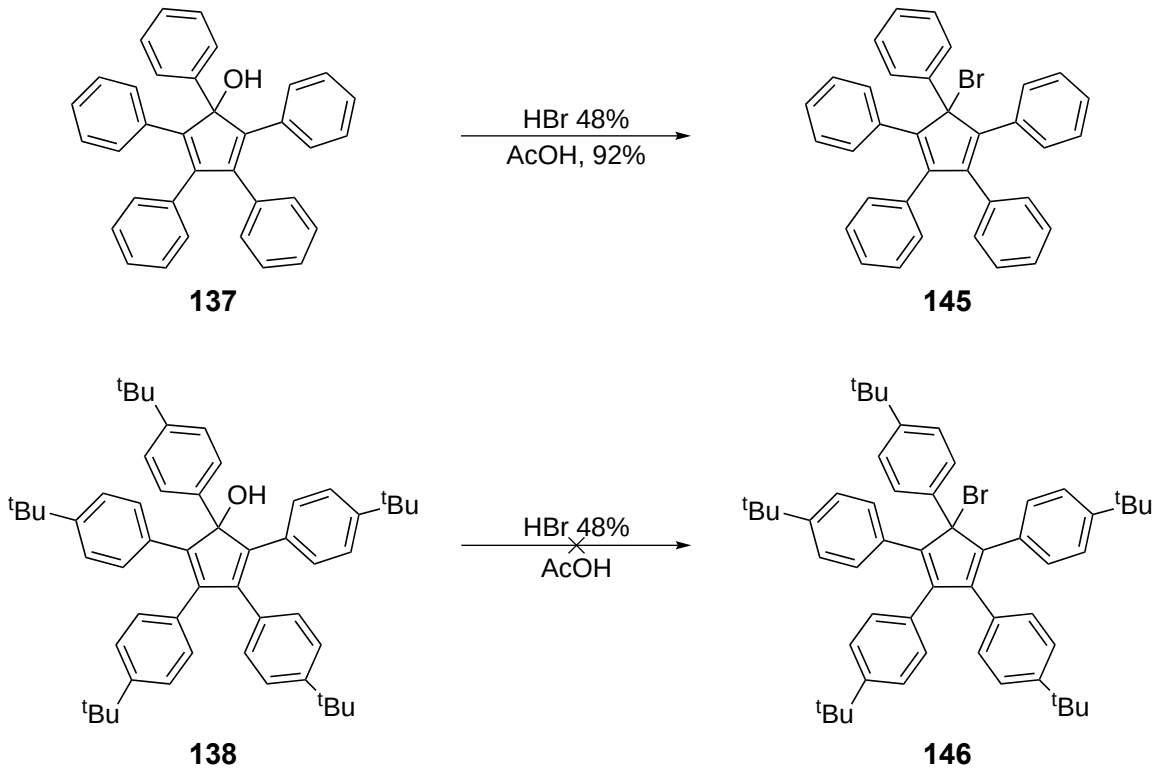
(entries 1 to 4 and 6, table 11). But in three attempts (entries 5, 7 and 8, table 11), the compound was formed (according to ^{1}H-NMR and EI-MS) and even isolated in one case (entry 7, table 11) in 18% yield by a silica gel column chromatography (pentane / DCM 8:2 as eluent). Classical heating mode by oil bath was better for this reaction than microwave. According to the publication [110], tri and tetra-aryl cyclopentadienes should also be formed. But their presence was not evidenced in the EI-MS and ^{1}H-NMR spectra and they were never isolated after purification. But the dimer of the starting material was regularly observed and isolated by silica gel column chromatography, as well as the starting material, both in small amounts.

It was demonstrated by Miura and Dyker that except for bromobenzene, the more basic and sterically hindered tri-tert-butyl-phosphine gave better results. Even if this could allow to our reaction to work better, no attempt was performed with this other ligand, because the first two step pathway proposed gave really good yields and therefore this pathway was not further investigated.

Table 11:One step formation of pentaphenyl cyclopentadienes

Entry	SM	heating method	t [hour]	T [°C]	DMF [ml]	Results [%]
1	141	microwave	0.5	170	1.6	-
2	141	classical	24	130	1.6	-
3	141	classical	6	130	4	-
4	141	microwave	1.5	170	4	-
5	141	classical	23	130	4	observed
6	142	microwave	0.75	160	3.2	-
7	142	classical	6	130	3.2	18
8	143	classical	23	130	3.8	observed

3.4 Bromination of tetraphenyl cyclopentadienol compounds



Scheme 50: Bromation of tetraphenyl cyclopentadienol compound

To achieve this substitution, the method applied by Vives and Rapenne [135] on similar compounds gave really nice results on the molecule **137**. The staring material was dissolved in acetic acid in a two necked flask under inert atmosphere. At 60 °C, a solution of HBr 48% in acetic acid was dropwise added (60 ml/h). The desired compound slowly precipitate as an orange solid during the reaction which was stopped after 2 hours. The reaction mixture was cooled down in an ice bath and cold water was added to improve the precipitation. The orange solid was filtrated off, rinsed with water and dried under vacuum. A silica gel column chromatography with pentane/dcm 2:1 as eluent gave the desired brominated compound in 92% yield as an orange solid. Two others attempts also gave some good yields of 76% and 86%. When exactly the same conditions were used for the bromation of the compound **138**, the starting material was recovered in majority. The formation of the desired molecule could not be confirmed by MALDI-MS and NMR, but NMR confirmed the presence of the compound **140**, formed as a by-product during the reaction.

3.5 Oxidation attempts

137, X = OH
139, X = H

32

Scheme 51: Oxidations tests

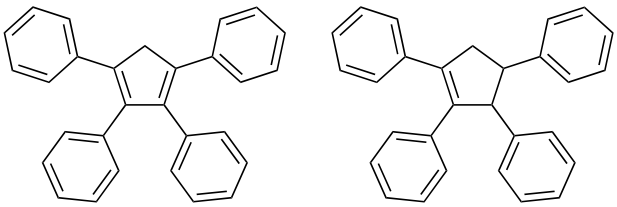
The oxidation of the pentaphenyl cyclopentadiene precursor was so far not thoroughly explored in the literature. But because of the similarity of this type of compound with hexaphenyl benzene, it was logically thought that similar conditions as those used for the oxidation of the hexaphenyl benzene could be applied in this case. Therefore some tests were made with iron chloride [101] or with DDQ/acid [103] as oxidant. Succeeding the total oxidation of a compound similar as **137** or **139**, the obtained product would adopt a bowl-shaped conformation. But the final oxidation state of the product is an open question, as explained in the introduction. But it could be envisioned that using methanesulfonic acid for activating the compound would lead after oxidation to a carbocation with methanesulfonate as non-nucleophilic counterion.

Although $FeCl_3$ was successfully used for the oxidation of the HBC **1**, more attention was placed on the DDQ/H^+ oxidation system because only one equivalent of DDQ per C-C bond would be necessary to complete the reaction instead of a large excess in case of the iron chloride and the work-up would be easier because the reduced DDQ-H_2 could be removed by extraction with water and regenerated by HNO_3. Moreover no additional iron would contaminate the crude product.

The conditions developed by Rathore [103] were first tested on the alcohol compound **137** (entry 1, table 12). A 0.09 M solution of the pentaphenyl cyclopentadienol **137** in a mixture of DCM/$MeSO_3H$ (10% v/v) was treated at 0 °C by DDQ (5 eq) under inert atmosphere during 2 hours. After the addition of the methane sulfonic acid, the reaction mixture turned directly to a deep red color, presumably due to the presence of a carbocation formed by the loss of the OH group. Then the treatment with DDQ gave a violet color which changed to green-brown after a while. The work up was done by the addition of a saturated solution of sodium bicarbonate and extraction with DCM. A discolouration to yellow was observed at the bicarbonate addition. Ac-

cording to the ^{1}H-NMR and ^{13}C-NMR spectra performed after the work up, all the starting material was consumed. The crowded aromatic region prevented any interpretation. When the same conditions were applied to compound **139** (entry 1, table 12), the same color changes took place in the reaction mixture, which was this time agitated during 18 hours. No more starting material was present as shown by TLC analysis. The NMR spectrum of the crude material was very similar to the one obtained for compound **137**.

The crude mixture of the oxidation test on compound **139**, was separated by silica gel column chromatography. A first fraction showed two compounds of mass 370.15 m/z and 372.17 m/z, by MALDI-MS analysis (DCTB used as matrix) tentatively assigned to compounds **147** and **148**. But even if the MALDI-MS gave the right masses, the methylene group and the alkyl part of the product **148** did not appear in the NMR spectrum. A second fraction showed by MALDI-MS a major peak at 671.16 m/z among other signals, which could correspond to a charge transfer complex formed by the ligand and DDQ (matching mass and molecular cluster intensities), but so far NMR did not confirm the presence of such a complex.



147 **148**

Scheme 52: By-product obtained during oxidation tests

Since the protonation of the hydroxyl function produces one molecule of water, the in situ formation of the methanesulfonic acid by hydrolysis of methanesulfonic anhydride was tried on the compound **137**, only the starting material was collected (entry 2, table 12). The formation of a radical which could react with both oxidant or reductant was also envisioned. As this supposed radical have to be conserved under inert atmosphere, the work up was made under inert atmosphere, and TEMPO was added to the reaction mixture to trap the supposed formed radical. But as already said, all these efforts gave nothing else than the starting material.

Following the method proposed by Li and Wang [136], another oxidation using DDQ and $Sc(OTf)_3$ instead of the methanesulfonic acid was tested on **139** (entry 2, table 12). Executed at 50 °C in the paper, the reaction was heated in our test to 110 °C after having seen that the starting compound was still present after 24 hours at 50 °C. Finally even after 40 hours of stirring at 110 °C, the desired compound was not observed. The ^{1}H-NMR analysis on the crude

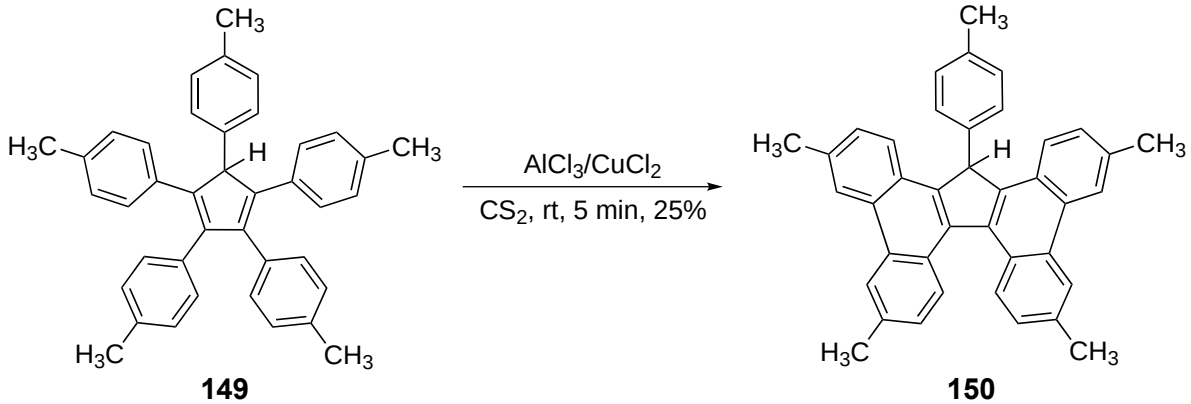
material confirmed that all the starting material was consumed, but chromatography attempts did not allow to obtain pure fractions to identify the side-products.

Finally two other methods were tested without obtaining interesting results. First the already used $FeCl_3$ (see paragraph 1.3.4.2) gave plenty of different compounds which could again not be separated and analysed. No more improvements were noted by applying UV light on a mixture of our compound, iodine and propylene oxide [137]. The propylene oxide was added to consume any HI formed during the reaction. Many compounds with similar retention times prevented any isolation of pure compounds.

Table 12: Oxidative C-C bond formation

Entry	SM	Oxidant	Additive	Solvent	Results
1	**137**, **139**	DDQ	$MeSO_3H$	DCM	dark green solid
2	**137**	DDQ	$(MeSO_2)_2O$	DCM	**137**
3	**139**	DDQ	$Sc(OTf)_3$	Toluene	black solid
4	**139**	$FeCl_3$	-	$DCM/MeNO_2$	dark green solid
5	**134**, **139**, **140**	I_2	Propylene oxide	Benzene	brown pasty solid

All these negative results suggested that either the compound could not be formed because the C-C bond formation was impossible, the carbons being too far from each other to be able to form a new C-C bond, or the formed carbocation being too stable to activate the oxidative dehydrogenation reaction.



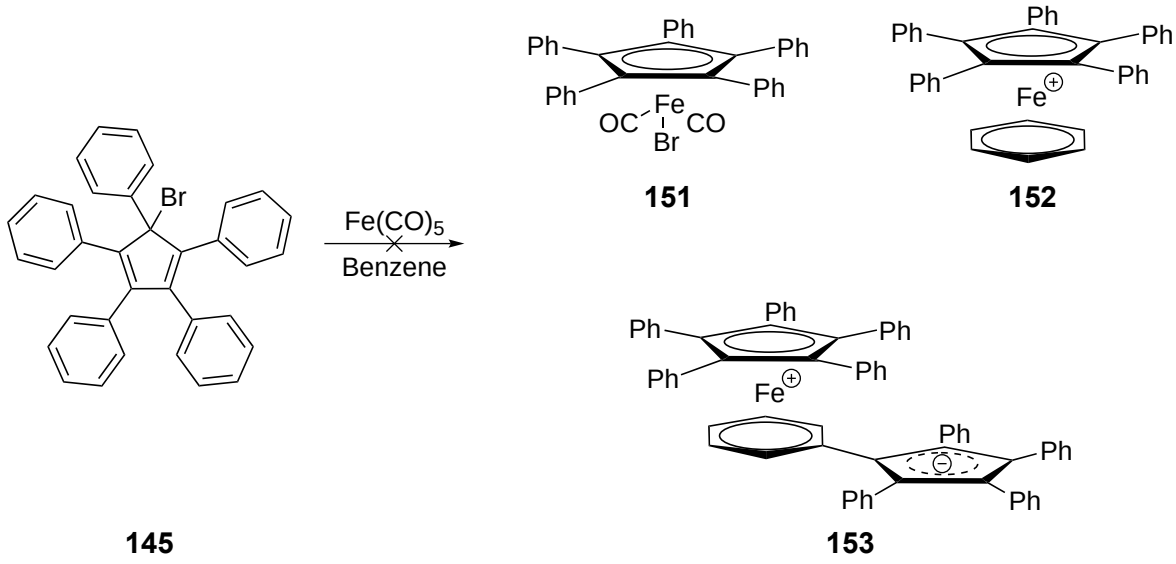
149 **150**

Scheme 53: Cyclodehydrogenation of the cyclopentadiene to the bis-phenanthrene [138]

A similar oxidation was attempted in a recent paper [138] published by Dyker and co-workers. They investigated the reactivity of pentaarylated cyclopentadienes and cyclopentenes in hydrogenation and dehydrogenation reactions. During their oxidation attempts on pentaphenyl cyclopentadienes to obtain the compound **32**, they showed that no clean photo-oxidation was possible. In contrast, non-photochemical conditions ($AlCl_3/CuCl_2$) allowed the formation and isolation in 25% yield of the partially oxidized bis-phenanthrene **150**, starting from compound **149** (see Scheme 53). We suppose that the reaction does not go further because an isomerization of the cyclopentadiene double bonds would be necessary for the cyclodehydrogenation to occur in the remaining places, what stopped the reaction at bis-phenanthrene stage, but this has still to be confirmed. According to these results, we could postulate that even in our oxidation tests, partial cyclodehydrogenation could have occurred, but in view of the complex mixture not isolated (see table 12). In the light of this paper, several oxidations have to be repeated, paying attention to the formation of phenanthroid compounds.

3.6 Complexation and oxidation tests

The direct oxidation of the pentaphenyl cyclopentadiene compounds seemed to be, according to the previously presented tests, difficult to realize. Each time, several side-compounds were observed without any chance to separate them. Therefore, a new approach was designed. Instead to directly oxidize the pentaphenyl cyclopentadienyl compounds, it was planned to first complex them on iron atoms forming ferrocene-like compounds and then to perform the oxidation on these complexes. This would give two advantages. First the complexes would certainly show a good stability after the oxidation, what could force the cyclodehydrogenation. The iron could then be remove by several means [139]. Second, after oxidation of the complex, the obtained Fe(III) could act as a catalyst, delocalizing its positive charge on the ligand, i.e. a pentaphenyl cyclopentadiene moiety and hence activated it. This could make our compound more receptive for the oxidative dehydrogenation.

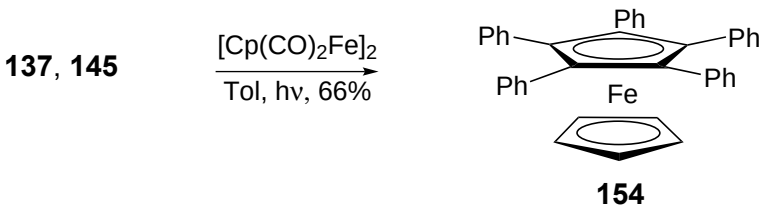


Scheme 54: Complexation of 145 on $Fe(CO)_5$

The complexation was tried with two different types of iron complexes. Starting the investigations with a solution of the bromo compound **145** in benzene under inert atmosphere, iron pentacarbonyl in a small excess was mixed at 80 °C for three hours [140] or at room temperature for 24 hours [141]. In both cases the solutions became immediately red. After filtration and distillation of the benzene, neither recrystallization nor chromatography allowed to obtained the desired compound **151**. The crude material was analysed by MADLI-MS and NMR. The ^{1}H-NMR was without any surprise not really interesting because all signals were concentrated in the aromatic region and difficult to interpret. But the mass analysis showed one major product which was the compound **137**, formed as a by-product. No traces of the desired complex could be detected. In 1990, a modification of this reaction was successfully employed by Masters et al. [142] where zinc dust (2 eq) was added to a mixture of iron pentacarbonyl (1 eq) and the molecule **145** (2 eq). This zinc was certainly present to be inserted in the C-Br bond of the ligand, creating an intermediate between the ligand under neutral form and the carbanion to facilitate the complexation. After 40 hours at room temperature and purification by chromatography, they got a mixture of the desired iron complex **151** in minority with complex **152**. The major product was the $[Fe(\eta^5\text{-}C_5Ph_5)\{(\eta^6\text{-}C_6H_5)C_5Ph_4\}]$ **153** obtained in 53% yield. It was not considered as an important thing that the wanted complex was formed in minority. Indeed, all the three complexes could undergo an oxidation on the iron and improve the reactivity of the ligand for the oxidation step. When these conditions were repeated by us, only the hydroxylated by-product **137** was isolated, as confirmed by MALDI-MS. The remaining material

could not be identified, purification attempts were unsuccessful.

Although the complex **151** was already published and characterized by single crystal X-ray diffraction [141], its synthesis was not as simple as published. Therefore our efforts were oriented on the complexation of our ligand **145** on cyclopentadienyl iron(II) dicarbonyl dimer in toluene or benzene under UV irradiations (mercury lamp). Because no difference was observed, the less toxic toluene was chosen. With the compound **137**, after 68 hours of irradiation under a mercury lamp, the crude material obtained by concentration of the reaction mixture was chromatographied on silica gel. Only ferrocene was collected in a small quantity. But when this reaction was repeated with the compound **145**, the desired complex **154** was obtained after silica gel column chromatography in a moderate yield of 66%, still containing the by-product **139**. By recrystallization in hexane/$CHCl_3$ 3:2, a better purity was achieved, but still containing a bit of the side-product. The presence of the reduced by-product **139** was not really important, because it would have no influence during the oxidation reaction. The complex was, certainly because of the temperature needed for the recrystallization, partially oxidized to the radical cation which could be easily reduced with $NaBH_4$ in DCM to reform the desired complex. This radical cation was characterized comparing the MALDI-MS of the wanted complex and of the supposed reduced complex which were identical. But the ^{1}H-NMR showed a 0.23 ppm left-shifted broad singlet for the cyclopentadienyl ligand (from 4.21 ppm to 4.44 ppm, Figure 20). The aromatic region was also a bit different and less resolved, as shown in Figure 20. The explanation could be given by a partial oxidation which had formed a radical cation normally invisible by NMR because of a to quick relaxation. But because not all the molecules were oxidized, this positive charge could be exchanged with the desired complex **154**, slowing down the relaxation, especially for the spins near to the iron. As result, the peaks were broader and shifted. On the ^{13}C-NMR, no signals were observed for the two cyclopentadienyl carbons. Moreover, the signals at 131.84 ppm appeared broader than the other and right-shifted of 0.48 ppm (from 132.32 to 131.84). This signal belongs to the ortho carbons of the phenyl substituents which were the nearer carbons to the iron in space and therefore the more influenced.



Scheme 55: Complexation of 145 on $[FeCp(CO)_2]_2$

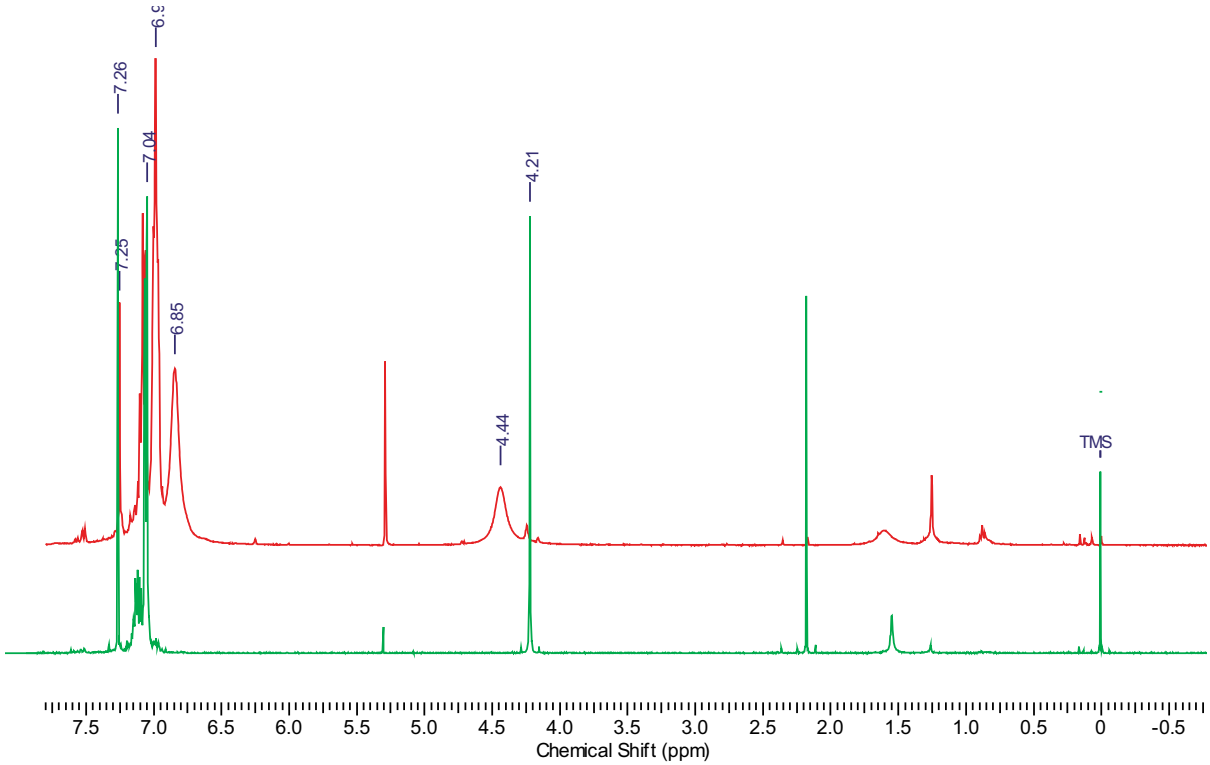


Figure 20: ^{1}H-NMR of the complex 154 in green, and the radical cation of this complex in red

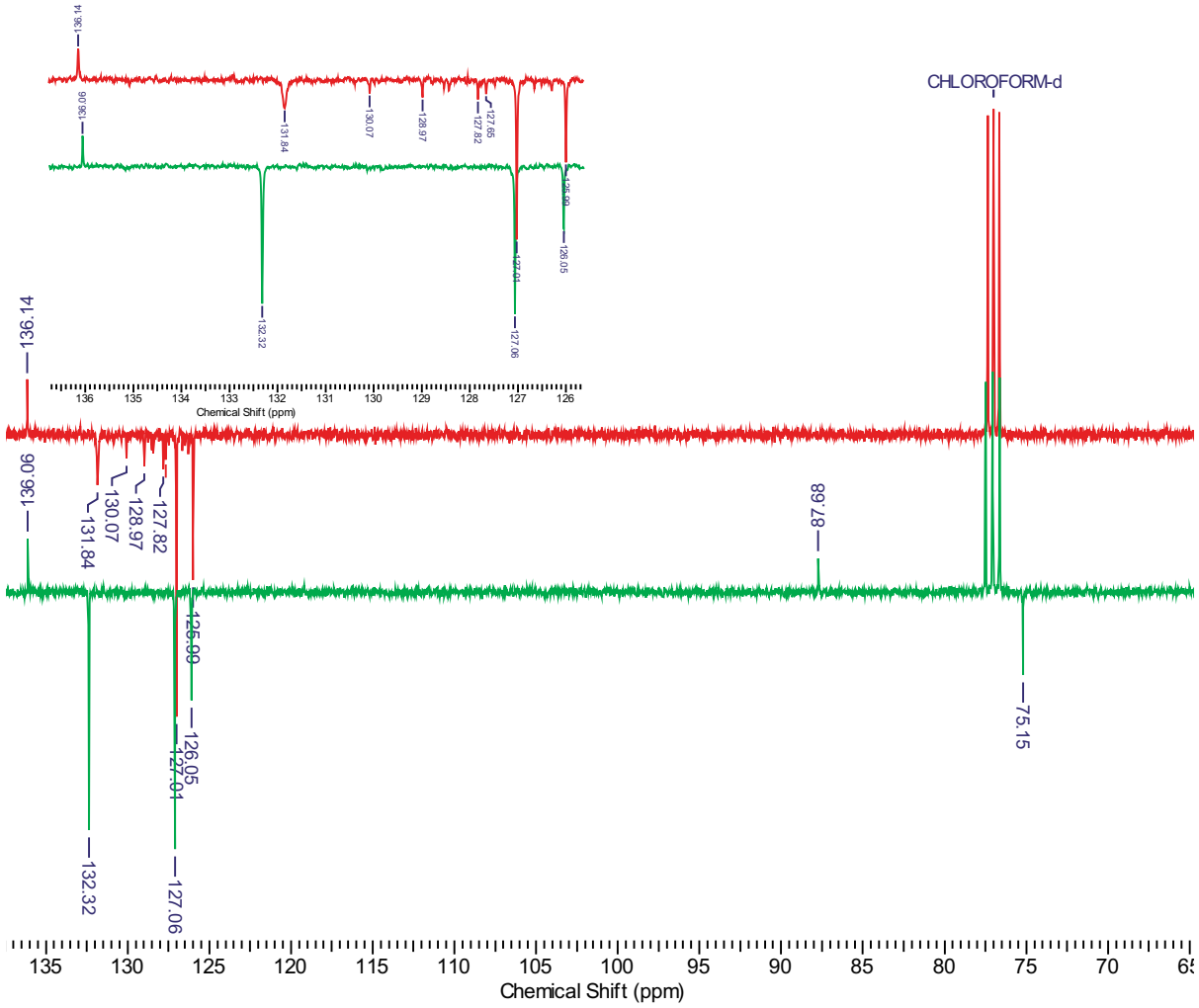
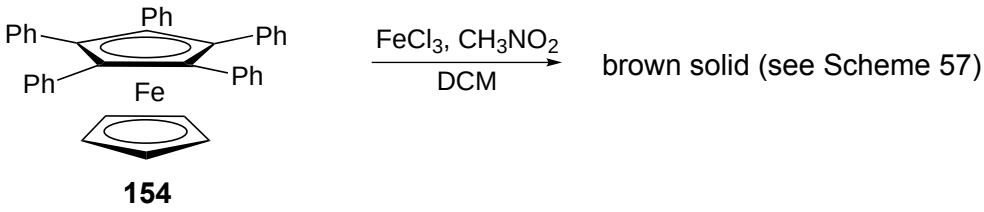


Figure 21: ^{13}C-NMR of the complex 154 in green, and the radical cation of this complex in red

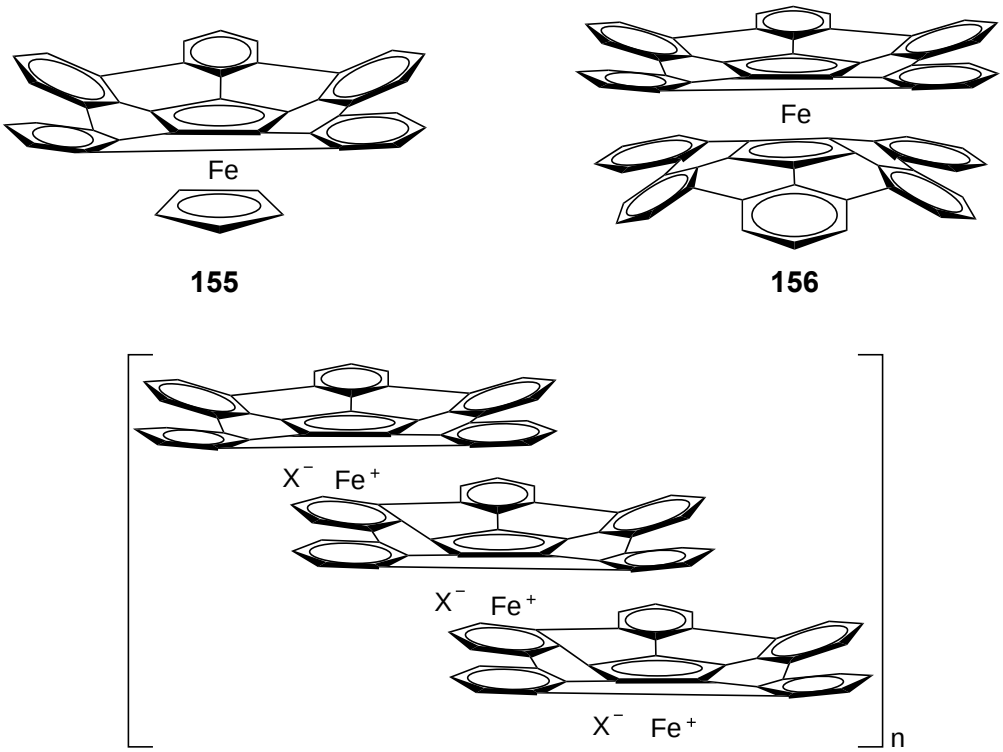


154

Scheme 56: Oxidation test on the complex 154

The oxidation tests on the obtained pentaphenyl ferrocene complex **154** were first performed with the proven Kovacic conditions, i.e. iron chloride in nitromethane and DCM, because only the oxidations with DDQ were until now unsuccessful. Therefore a solution of iron chloride in nitromethane was dropwise added to a solution of the complex **154** in DCM at 45 °C. After 6 hours, the classical work up gave a brown solid, insoluble in common solvents, which is not surprising. But no MALDI-MS could be obtained leaving it an open question what was produced. So far, only an ICP analysis was made, showing a large quantity of iron in this brown

solid. But because a filtration was necessary to eliminate the undissolved material during the sample preparation, the iron percentage could not be given. This iron could belong to the complex or come from the iron chloride used. If we suppose that this iron amount belong to a complex, we could envision the two structures **155** and **156** which contain around 10% Fe, 6% respectively. Moreover, the similar $[Fe(C_5Ph_5)_2]$ complex was described as totally insoluble by Schumann [143], what could match with our obtained insoluble material. Alternatively, the polymeric structure **157** could also be envisioned, in which one iron links two ligands. This could explain the total insolubility.



155 **156**

157

Scheme 57: Possible iron complexes

To confirm that the iron did not comes from the iron chloride, DDQ was chosen as a second oxidant. When DDQ and $Sc(OTf)_3$ [136] were engaged, only the starting material was recovered. The second test was made in DCM with DDQ only, because according to our predictions, the oxidation should be activated thanks to the oxidation of the iron by the DDQ. A red coloration was observed directly after the DDQ addition, which showed certainly the oxidation of the iron. But after extraction and concentration, the ^{1}H-NMR showed the starting material partially oxidized (radical cation), as experienced before. This result prompted us to continue on this way, because the first part of the supposed mechanism was confirmed. Therefore, the same reaction was repeated in toluene to allow the heating of the reaction mixture, which should give

enough activation energy to cyclodehydrogenate the ligand. The reaction mixture was first heated during 5 hours with an oil bath till 110 °C, then with microwave technology till 180 °C during 1 hour. But even with this high temperature, no desired reaction was noted. According to these new failure, three hypotheses could be formulated. Either a crucial feature for the Scholl reaction was missing, or the reaction distance is too long, or the DDQ was not reactive enough (0.669 V vs. SHE) [144] for the oxidative dehydrogenation of such compounds. Indeed its oxidant power is a bit smaller than the Fe^{3+}/Fe^{2+} couple (0.771 V vs. SHE) [144]. According to [145] the ferrocene potential around 0.64 V vs. SHE decreases when electron donor groups are added on the cyclopentadienyls and increases when electron withdrawing groups are attached. Therefore, it is possible that DDQ is not strong enough in our case.

It was supposed that the insolubility problem of the brown material obtained after oxidation with $FeCl_3$ could be solved by the addition of tert-butyl groups in para-position on the phenyl rings. Tert-butyl groups are well-known to help to the solubilization of insoluble compounds like HBC [103] since they prevent π-π stacking. The oxidation and the attachment of the tert-butyl groups were first tested in a single reaction, according to the work of Rathore and Burns [146]. At the beginning only a few drops of a mixture of $FeCl_3$ in nitromethane were added on a mixture of pentaphenyl ferrocene and 2-chloro-2-methylpropane (14 eq) in DCM. It should be mentioned that more tert-butyl chloride equivalents were used because the cyclopentadienyl ligand could also be alkylated. After 3 hours, the rest of the iron chloride (19 eq) was added to the reaction mixture. After classical work up for oxidations with iron chloride, only the starting material was obtained. Therefore, the two reactions were attempted separately. The alkylation was performed with 1 eq of $AlCl_3$ instead of iron chloride and with 12 eq of the tert-butyl chloride. Several additions of $AlCl_3$ were necessary to consume all the starting material. After work up and silica gel column chromatography, the desired compound was obtained in a mixture of different products. Indeed, it was observed by MALDI-MS that besides the alkylation in para-position of the five phenyl rings, the partial alkylation of the cyclopentadienyl ligand is also possible, giving in addition to the desired compound, the wanted complex with mono, di and tri alkylated cyclopentadienyl ligand. A small quantity of a product with only four tert-butyl groups was observed by MALDI-MS, but it was impossible with only mass and NMR analyses of the mixture to determine the positions of these four tert-butyl groups. Only the separation of the different compounds by silica gel column chromatography would have allow to know the different tert-butyl positions. No yield was calculated for this reaction, because of the different alkylation levels obtained.

The iron chloride oxidant was then added as usual to the mixture. As for the reaction of the

complex without the tert-butyl substituents, a brown insoluble material was also formed without any improvement in solubility and no MALDI-MS could be recorded too.

Despite a clear proof for the formation of the desired compound, the insoluble brown material encourages us that we are on the right way. Indeed, the formation of the perfluorinated HBCs by the same Scholl reaction also gave insoluble polycondensed aromatic compounds. As we do not know the behavior of the target molecule we wanted to synthesize, it is completely possible that the new produced bowl-shaped compound is totally insoluble in common solvents or that aggregates of iron complexes avoid any mass analysis.

IV. Conclusion and outlooks

1. Conclusion and outlooks

In this work, a new functionalized HBC has successfully been synthesized. One of the biggest difficulties during this synthesis was to operate with the large perfluorinated apolar part in presence of a sulfonate group which creates molecules with different parts which are not soluble in the same solvents. Nevertheless, this polar function has allowed the chromatography of this new HBC derivative in a mixture of MeOH and HFB, what was not the case previously with the “classic” perfluorinated HBCs prepared by Aebischer [101].

On the other hand, the analysis of this compound was not really successful. No conclusive NMR spectra could be recorded because of the low solubility of the product, even in solvent mixtures. The structure of the compound was only confirmed by MALDI-MS and by the absorption and fluorescence spectra [101], although fluorescence spectrum is not well resolved, as compared to those recorded by Aebischer. Two reasons were envisioned. First, even if the product was purified by silica gel column chromatography, no real information about its purity could be obtained. It is possible that impurities remained “stuck” on the sulfonic acid, trapped between the HBCs discs or caged inside a bigger aggregate, what could explain the bad resolution obtained in fluorescence analysis. Second the pronounced formation of clusters could decrease the presence of «free» HBC monomers in the solution.

In addition, a selective method was developed to remove selectively an iodine from a non-activated C-I bond, in presence of an aromatic carbon - bromine bond and a chlorine atom attached to a perfluorinated chain in a good yield, using a metallation with zinc dust under microwave irradiation during 20 minutes at 120 °C, followed by hydrolysis. This facilitates a step which was done before with $LiAlH_4$ under a precise control to prevent the attack on the bromine on the phenyl ring, or with lauroyl peroxide in hexane giving low yields.

Even if the second target molecule, the alkyl sulfonic acid HBC derivative was not completely synthesized, a lot of preparation was done to find the best method to attach the sulfonate group on the alkyl chain. In the present state of the synthesis, it seems that the pathway starting by the exchange of an alcohol group by a bromine followed by a nucleophilic substitution with the sulfonate salt is the most promising solution. In the presented work, the attempt to introduce the sulfonate was made just before the final oxidation, directly on the hexaphenyl benzene derivative. But certainly due to an organic part which was too big, the bromine could have not been reached for the substitution. Therefore it must still be found at which stage of the synthe-

sis the sulfonate has to be introduced best, but certainly that the introduction before placing the bromine on the phenyl ring could give interesting results.

The oxidation of the pentaphenyl cyclopentadiene is still not under control. Even if an insoluble brown solid was obtained using iron chloride as oxidant, which was similar to the formation of the perfluorinated HBC compound, no characterization was possible, even by MALDI-MS analysis, which worked for the HBCs. As only two different types of oxidants were tested, the investigations must still be continued to find the good conditions needed for this oxidation.

More generally, the microwave technology was largely used for different types of reactions, such as cross-coupling Sonogashira reactions, metallations, Diels-Alder reactions or substitution reactions. The reaction time of all these reactions was clearly reduced. Moreover, the purity of the compounds was in general better due to these shorter reaction times. However, in the case of the Diels-Alder reaction, no real improvement was observed. Indeed, this reaction was already performed at high temperature under conventional heating mode. Moreover, the formation of carbon monoxide due to the decarbonylation could increase the pressure in the sealed microwave vial, what could slow down the reaction.

Besides the finalization of the syntheses of the alkylated sulfonic acid HBC and the oxidation of the pentaphenyl cyclopentadiene, a first membrane test has to be performed with the perfluorinated sulfonic HBC. A simple deposition on a polymeric hydrophobic membrane which would become permeable to protons was planned in a first time. If proton transfer would be observed by the addition of our compound, further investigations would have to be performed. Moreover, the synthesis of the same molecule with different lateral chains could also be envisioned. The number or the length of the lateral chains could influence the columns formation, improving the proton channels growth.

V. Experimental part

1 General considerations

All used chemicals were purchased from Sigma-Aldrich, Acros, Riedel-de-Haen, Fluorochem or Biotage and were used without further purification if not stated otherwise. The solvents (THF, ether, pentane, dichloromethane and toluene) were dried and deoxygenated by passing them over activated basic aluminium oxide [147]. Other solvents like DMF, DMSO or MeOH were used as received when employed in reaction mixtures.

The sensitive reactions were performed under inert atmosphere using dry nitrogen (45) or dry argon (48) purchased from Carbagas. The irradiations were performed with a high pressure mercury lamp HPK Philips 125 W). All the reactions made by microwave irradiation were performed in an Initiator or in an Advancer from Biotage.

The compounds **105** and **133** were prepared by our central laboratory. Therefore, the syntheses of these two molecules are not described here. Some parts of this work were performed by different students (work on the compound **121** was performed by Ramona Stähli and the opening attempts of the sultone **117** were made by Julien Ducry) and were therefore directly describe in their reports.

Thin layer chromatography (TLC) analyses were performed using aluminium sheets coated with silica gel 60 F_{254} or with silica gel 60 RP-18 F_{254S} and visualized under UV-light at 254 nm or 366 nm, or by a $KMnO_4$ solution. The column chromatography purifications were performed with Merck silica gel 60 (0.04-0.063 mm, 230-400 mesh) or in normal phase with KP-C18-HS Bulk Sorbent provided by Biotage.

NMR spectra were recorded on a Bruker Avance III 500 MHz (^{1}H: 500 MHz, ^{13}C: 125 MHz and ^{19}F: 470 MHz), 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, ^{19}F: 282 MHz) using $CDCl_3$ or MeOD as solvents. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) or to trifluoro toluene for ^{19}F-NMR. The coupling constants (J) are given in Hz. The NMR signals were assigned using APT, COSY, HETCOR and COLOC experiments.

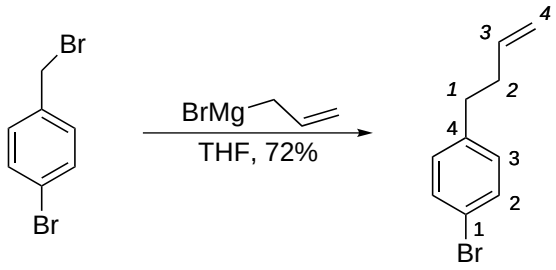
Mass spectra were recorded on a Bruker HCT Esquire ion trap spectrometer in the negative and positive modes (ESI ionization) or on a FT/ICR mass spectrometer Bruker 4.7 T BioApex II (MALDI-ICR ionization) with DCTB or TCNQ as matrices, in combination with a 337 nm ni-

trogen laser. The volatile compounds were measured on a GC/MS ThermoQuest TraceGC 2000/Voyager spectrometer equipped with a Zebron ZB-35 capillary column (30 m L x 0.25 mm ID x 0.25 μmdf, 35% phenyl-methyl polysiloxane) (EI ionization).

Fluorescence spectra were recorded on a Perkin Elmer Luminescence Spectrometer LS 50 B using hexafluorobenzene as solvent.

2 Synthesis of the perfluoro sulfonic acid HBC

2.1 Synthesis of the 1-bromo-4-but-3-enylbenzene



61 **62**

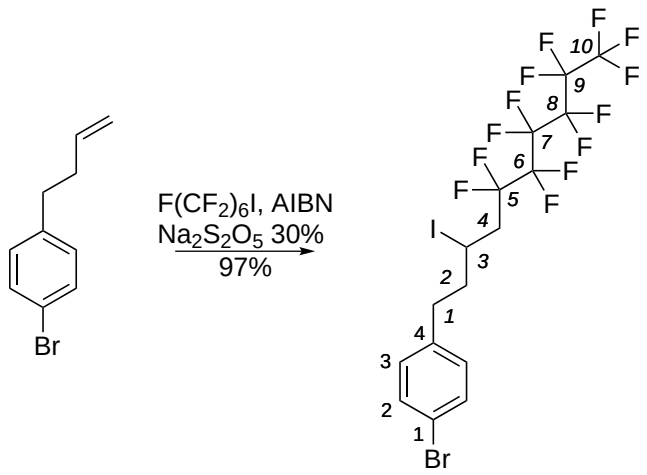
In a three necked flask under inert atmosphere with a condenser and a dropping funnel, 4-bromobenzyl bromide (7.5 g, 30 mmol) was dissolved in dry THF (45 ml). Under stirring, allylmagnesium bromide (37.5 ml, 37.5 mmol, 1 M in ether) was added dropwise at room temperature. After one night at reflux, the mixture was hydrolysed, extracted with pentane, dried over Na_2SO_4 and finally evaporated to dryness. The crude product was purified by distillation under vacuum (~40 mbar, ~107 °C) to give the desired product (4.53 g, 21.46 mmol, 72%).

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.39 (d, ^3J = 8.2 Hz, 2 H, CH(2)), 7.06 (d, ^3J = 8.2 Hz, 2 H, CH(3)), 5.74 - 5.90 (m, 1 H, CH(*3*)), 4.93 - 5.09 (m, 2 H, CH(*4*)), 2.66 (t, ^3J=7.7 Hz, 2 H, CH(*1*)), 2.28 - 2.40 (m, 2 H, CH(*2*)).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 140.74 (s, 1 C, C(4)), 137.58 (s, 1 C, C(*3*)), 131.31 (s, 2 C, C(2)), 130.21 (s, 2 C, C(3)), 119.52 (s, 1 C, C(1)), 115.29 (s, 1 C, C(*4*)), 35.28 (s, 1 C, C(*2*)), 34.72 (s, 1 C, C(*1*)).

EI-MS: m/z (%) 211.6 ($M^{\cdot+}$, 50%), 170.6 ($[M\text{-}C_3H_5]^+$, 80%), 130.7 ($[M\text{-}Br]^+$, 50%), 89.2 ($[M\text{-}(Br+C_3H_5)]^{\cdot+}$, 100%).

2.2 Synthesis of the rac-1-bromo-4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-3-iodododecyl)benzene



62 **63**

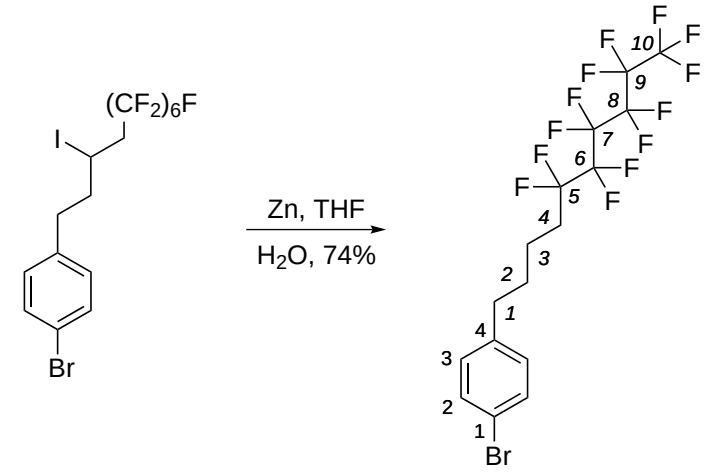
To the starting material **62** (5.025 g, 23.80 mmol) heated at 50 °C, a 30% aqueous solution of $Na_2S_2O_5$ (2.5 ml), 1-iodotridecafluorohexane (8.79 ml, 40.5 mmol) and AIBN (9 mg, 0.06 mmol) were added under inert atmosphere. The reaction mixture was then agitated at 80 °C. Every 2 hours, AIBN (9 mg, 0.06 mmol) was added until the reaction was complete (the reaction was followed by GC-MS). Water was added to the mixture and the aqueous phase was extracted with ether. The organic layer was dried over Na_2SO_4 and evaporated to dryness giving the desired compound **63** (15.16 g, 23.07 mmol, 97%) as a white solid.

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.41 (d, ^3J = 7.7 Hz, 2 H, CH(2)), 7.07 (d, ^3J = 8.2 Hz, 2 H, CH(3)), 4.16 - 4.30 (m, 1 H, CH(*3*)), 2.58 - 3.09 (m, 4 H, CH(*Alk*)), 1.97 - 2.18 (m, 2 H, CH(*Alk*)).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 138.82 (s, 1 C, C(4)), 131.72 (s, 2 C, C(2)), 130.24 (s, 2 C, C(3)), 120.25 (s, 1 C, C(1)), 41.72 (t, $^2J_{CF}$ = 21.1 Hz, 1 C, C(*4*)), 41.43 (m, 1 C, C(*2*)), 35.17 (s, 1 C, (*1*)), 19.69 (s, 1 C, C(*3*)).

EI-MS: m/z (%) 658.1 ($M^{\cdot+}$, 10%), 531.1 ($[M-I]^+$, 22%), 449.2 ($[M-(Br + I)]^{\cdot+}$, 8%), 171 ($[M-F(CF_2)_6CH_2CHICH_2]^+$, 100%).

2.3 Synthesis of the 1-bromo-4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)benzene



63 **64**

In a dried microwave oven tube, **63** (5.267 g, 8.02 mmol), zinc (0.577 g, 8.82 mmol) and THF (40 ml) were irradiated at 180 °C during 20 minutes. The reaction mixture was filtrated, hydrolysed with water and HCl 1M was added to dissolve the salts. After extraction with pentane, the organic phase was washed with a 10% solution of sodium thiosulfate, dried over Na_2SO_4, evaporated to dryness and filtrated over a plug of silica gel with pentane as eluent to give the desired compound **64** as a white solid (3.14 g, 5.91 mmol, 73.7%).

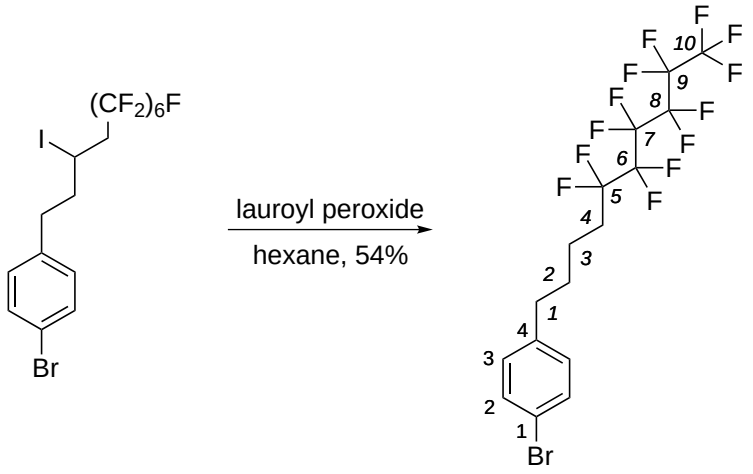
^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.41 (d, ^3J = 8.2 Hz, 2 H, CH(2)), 7.05 (d, ^3J = 8.2 Hz, 2 H, CH(3)), 2.61 (t, ^3J = 7.3 Hz, 2 H, CH(*1*)), 1.98 - 2.17 (m, 2 H, CH(*4*)), 1.60 - 1.75 (m, 4 H, CH(*2, 3*)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 140.69 (s, 1 C, C(4)), 131.55 (s, 2 C, C(2)), 130.10 (s, 2 C, C(3)), 119.79 (s, 1 C, C(1)), 34.98 (s, 1 C, C(*1*)), 30.35 - 31.16 (m, 2 C, C(*2, 4*)), 19.70 - 20.00 (m, 1 C, C(*3*)).

^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) -82.01 - -81.87 (m, 3 F, CF(*10*)), -115.67 - -115.36 (m, 2 F, CF(*5*)), -123.30 - -122.88 (m, 2 F), -124.24 - -123.83 (m, 2 F), -124.89 - -124.55 (m, 2 F).

EI-MS: m/z (%) 530.1 ($M^{\cdot+}$, 46%), 168.8 ($[M\text{-}F(CF_2)_6(CH_2)_3]^+$, 92%).

2.4 Synthesis of the 1-bromo-4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)benzene



63 **64**

In a two necked flask under inert atmosphere, **63** (0.314 g, 0.478 mmol) was dissolved in cyclohexane (5 ml) and the oxygen was removed by the freezing/vacuum method. At 50 °C, lauroyl peroxide (0.032 g, 0.081 mmol) was added in one portion. The mixture was then agitated at 80 °C during 11 hours. Seven additions of lauroyl peroxide (0.032 g, 0.081 mmol) were performed during the reaction regularly. Then the volatiles were evaporated to give an oil. The pure product **64** (0.136 g, 0.256 mmol, 53.6%) was obtained by a silica gel column chromatography with pentane as eluent.

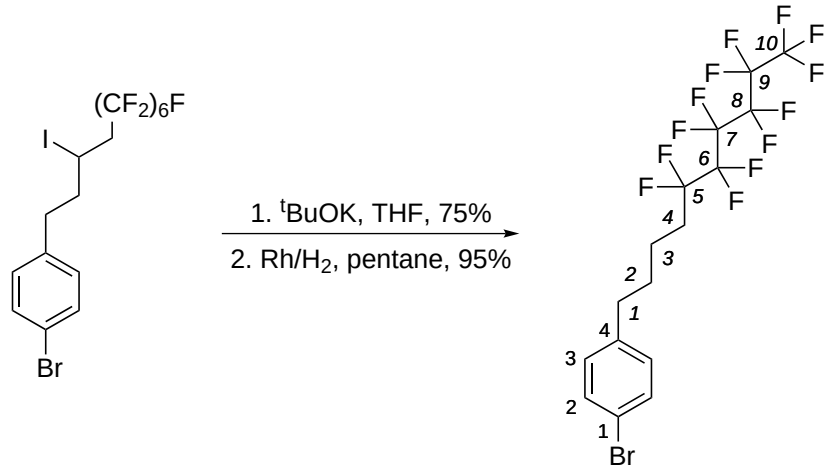
^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.41 (d, ^{3}J = 8.2 Hz, 2 H, CH(2)), 7.05 (d, ^{3}J = 8.2 Hz, 2 H, CH(3)), 2.61 (t, ^{3}J = 7.3 Hz, 2 H, CH(*1*)), 1.98 - 2.17 (m, 2 H, CH(*4*)), 1.60 - 1.75 (m, 4 H, CH(*2, 3*)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 140.69 (s, 1 C, C(4)), 131.55 (s, 2 C, C(2)), 130.10 (s, 2 C, C(3)), 119.79 (s, 1 C, C(1)), 34.98 (s, 1 C, C(*1*)), 30.35 - 31.16 (m, 2 C, C(*2, 4*)), 19.70 - 20.00 (m, 1 C, C(*3*)).

^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) -82.01 - -81.87 (m, 3 F, CF(*10*)), -115.67 - -115.36 (m, 2 F, CF(*5*)), -123.30 - -122.88 (m, 2 F), -124.24 - -123.83 (m, 2 F), -124.89 - -124.55 (m, 2 F).

EI-MS: m/z (%) 530.1 ($M^{\cdot+}$, 46%), 168.8 ($[M\text{-}F(CF_2)_6(CH_2)_3]^+$, 92%).

2.5 Synthesis of the 1-bromo-4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)benzene



63 **64**

In a two necked flask, the compound **63** (8.09 g, 12.31 mmol) was dissolved in THF (176 ml) under inert atmosphere. After addition of potassium t-butoxide (4.14 g, 36.9 mmol), the mixture was agitated at 67 °C during 14 hours and then cooled down to room temperature. The inorganic material was dissolved by water addition, then the aqueous phase was extracted with pentane. The organic layer was dried over Na_2SO_4 and evaporated to dryness to give 6.2 g of a orange-brown liquid. The desired product (4.84 g, 9.15 mmol, 74.3%) was obtained by a silica gel column chromatography with pentane as eluent as a mixture of olefins.

A part of the previously prepared olefins mixture (1.23 g, 2.325 mmol) was dissolved in pentane (77 ml) and Rh/C 5% (0.096 g, 0.046 mmol) was added. The mixture was agitated during 15 hours at room temperature under 50 bar of H_2. The mixture was then filtrated over a plug of celite with pentane and the solvent was removed to obtain the compound **64** (1.17 g, 2.2 mmol, 95%).

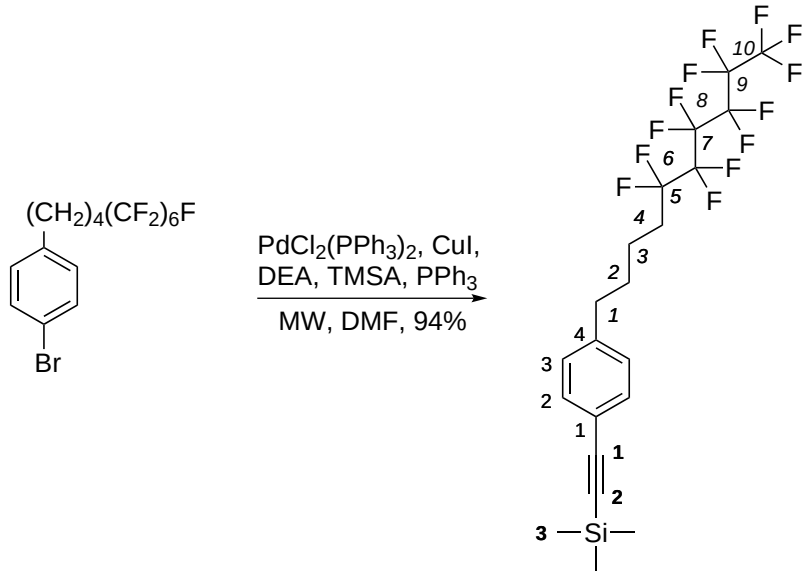
^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.41 (d, ^3J = 8.2 Hz, 2 H, CH(2)), 7.05 (d, ^3J = 8.2 Hz, 2 H, CH(3)), 2.61 (t, ^3J = 7.3 Hz, 2 H, CH(*1*)), 1.98 - 2.17 (m, 2 H, CH(*4*)), 1.60 - 1.75 (m, 4 H, CH(*2, 3*)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 140.69 (s, 1 C, C(4)), 131.55 (s, 2 C, C(2)), 130.10 (s, 2 C, C(3)), 119.79 (s, 1 C, C(1)), 34.98 (s, 1 C, C(*1*)), 30.35 - 31.16 (m, 2 C, C(*2, 4*)), 19.70 - 20.00 (m, 1 C, C(*3*)).

^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) -82.01 - -81.87 (m, 3 F, CF(*10*)), -115.67 - -115.36 (m, 2 F, CF(*5*)), -123.30 - -122.88 (m, 2 F), -124.24 - -123.83 (m, 2 F), -124.89 - -124.55 (m, 2 F).

EI-MS: m/z (%) 530.1 ($M^{\cdot+}$, 46%), 168.8 ($[M\text{-}F(CF_2)_6(CH_2)_3]^+$, 92%).

2.6 Synthesis of the trimethyl{[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]ethynyl}silane



64 **65**

In a microwave tube under inert atmosphere, **64** (0.417 g, 0.785 mmol), $PdCl_2(PPh_3)_2$ (0.030 g, 0.043 mmol), copper iodide (6.58 mg, 0.035 mmol), triphenylphosphine (0.041 g, 0.157 mmol), TMSA (0.124 ml, 0.871 mmol) and diethylamine (1.239 ml, 11.86 mmol) were suspended in DMF (0.436 ml). The mixture was then stirred in a microwave oven at 120 °C during 30 minutes. After filtration of the white salt, a brown mixture was obtained. HCl 0.1 M was then added and the aqueous phase was extracted three times with ether. The organic phase was then washed with sat. $NaHCO_3$ and water, dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by a silica gel column chromatography with pentane as eluent, giving **65** (0.406 g, 0.740 mmol, 94%) as a yellowish solid.

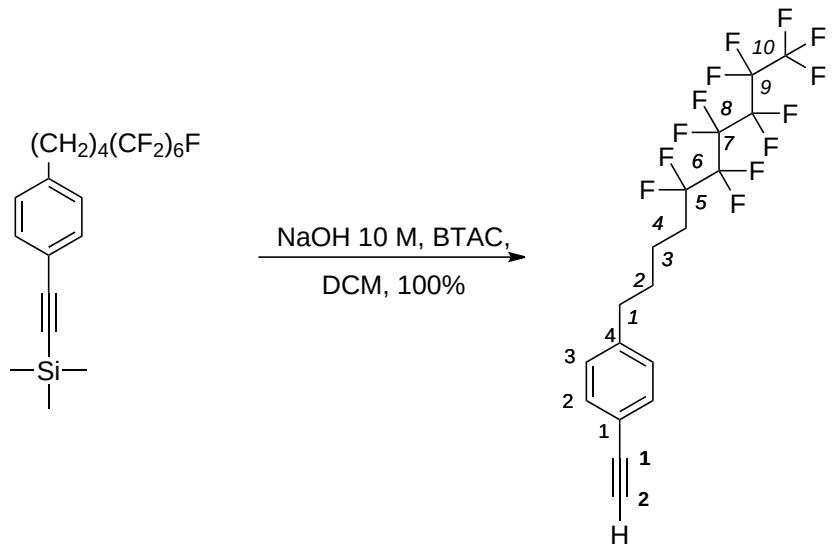
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.39 (d, ^3J = 8.3 Hz, 2 H, CH(2)), 7.10 (d, ^3J = 8.3 Hz, 2 H, CH(3)), 2.64 (t, ^3J = 7.2 Hz, 2 H, CH(*1*)), 1.96 - 2.19 (m, 2 H, CH(*4*)), 1.56 - 1.77 (m, 4 H, CH(*2, 3*)), 0.24 (s, 9 H, CH(**3**)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 142.22 (s, 1 C, C(4)), 132.06 (s, 2 C, C(2)), 128.22 (s, 2 C, C(3)), 120.73 (s, 1 C, C(1)), 105.10 (s, 1 C, C(**1**)), 93.61 (s, 1 C, C(**2**)), 35.42 (s, 1 C, C(*1*)), 30.56 (s, 1 C, C(*2*)), 30.67 (t, ^2J = 22.3 Hz, 1 C, C(*4*)), 19.74 (t, ^3J = 3.9 Hz, 1 C, C(*3*)), -0.02 (s, 3 C, C(1)).

EI-MS: m/z (%) 548.3 ($M^{\cdot+}$, 60%), 533.2 ($[M\text{-}CH_3]^+$, 10%), 191 (100%), 186.9 ([M-

$F(CF_2)_6(CH_2)_3]^{\cdot+}$, 36%), 128.5 (66%), 76.8 (60%).

2.7 Synthesis of the 1-ethynyl-4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)benzene



65 **58**

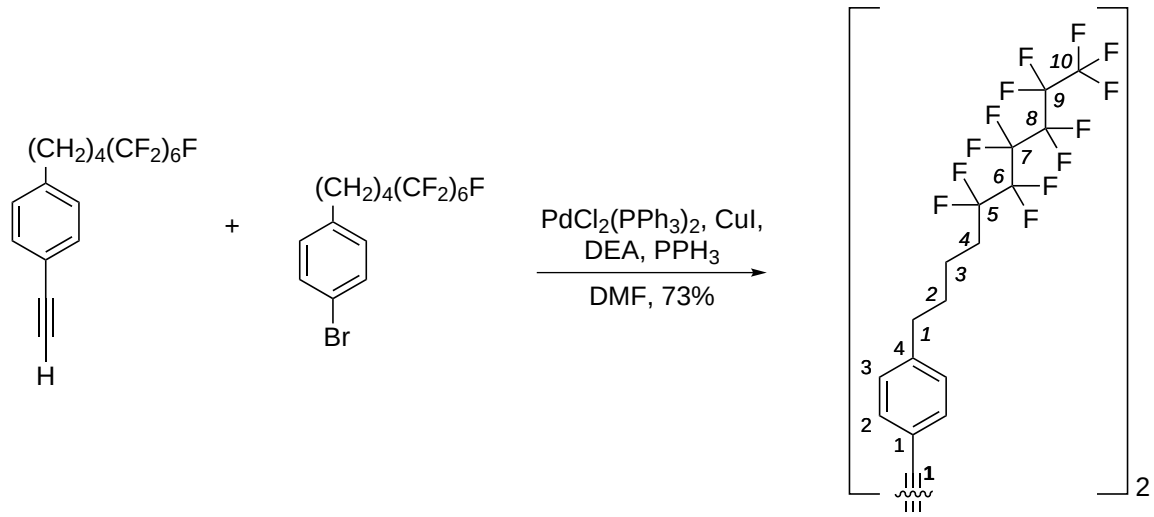
To a solution of **65** (3 g, 5.47 mmol) and benzyltrimethylammonium chloride (2.285 g, 12.31 mmol) in DCM (11 ml) was added a solution of NaOH 10 M in water (41.0 ml, 410 mmol). The biphasic mixture was agitated during 16 hours at room temperature. The organic material was extracted with ether. After drying of the organic phase with Na_2SO_4 and evaporation of the solvent, we got the crude product as a slightly yellow oil which was purified by a filtration over a plug of silica gel with pentane as eluent giving the desired acetylene (2.6 g, 5.46 mmol, 100%) as a yellow liquid which crystallized after a while.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.39 - 7.45 (m, 2 H CH(2)), 7.10 - 7.16 (m, 2 H CH(3)), 3.04 (s, 1 H CH(**2**)), 2.65 (t, ^3J = 7.3 Hz, 2 H CH(*1*)), 1.97 - 2.19 (m, 2 H CH(*4*)), 1.59 - 1.78 (m, 4 H CH(*2, 3*)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 142.59 (s, 1 C, C(4)), 132.23 (s, 2 C, C(3)), 128.35 (s, 2 C, C(2)), 119.74 (s, 1 C, C(1)), 83.65 (s, 1 C, C(**1**)), 76.70 (s, 1 C, C(**2**)), 35.44 (s, 1 C, C(*1*)), 30.59 (s, 1 C, C(*2*)), 30.72 (t, ^2J = 22.3 Hz, 1 C, C(*4*)), 19.80 (t, ^3J = 3.9 Hz, 1 C, C(*3*)).

EI-MS: m/z (%) 476.2 ($M^{\cdot+}$, 36%), 114.8 ($[M\text{-}F(CF_2)_6(CH_2)_3]^+$, 100%).

2.8 Synthesis of the 1-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)-4-{[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]ethynyl}benzene



58 **64** **98**

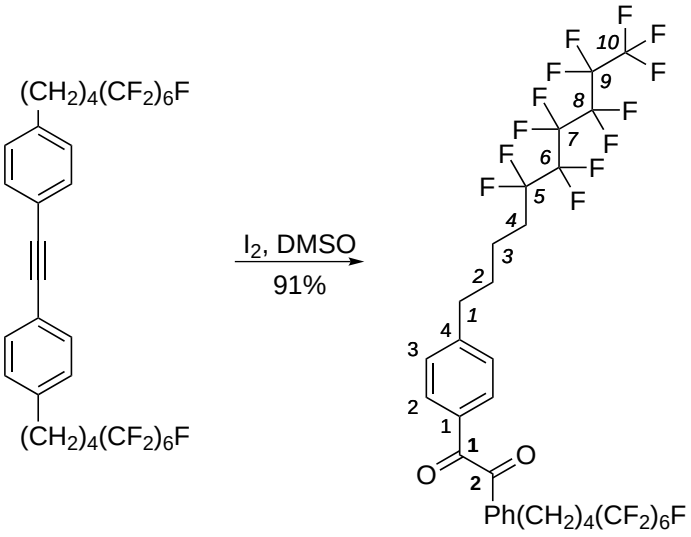
In a microwave vial under inert atmosphere, the acetylene **58** (0.922 g, 1.935 mmol), the bromophenyl compound **64** (1.028 g, 1.935 mmol), triphenylphosphine (0.102 g, 0.387 mmol), copper iodide (0.016 g, 0.085 mmol) and $PdCl_2(PPh_3)_2$ (0.075 g, 0.106 mmol) were suspended in diethylamine (3.06 ml, 29.2 mmol) and in DMF (1.1 ml). After microwave irradiation at 120 °C during 40 minutes, the reaction mixture was separated between ether and HCl 0.1 M. The organic phase was then washed with brine, dried over $MgSO_4$ and evaporated to dryness. The crude product, which was purified first by recrystallization in EtOH and by a silica gel column chromatography with pentane, then pentane/ether 97:3 as eluent gave the pure compound **98** as a yellow solid (1.3 g, 1.403 mmol, 73%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.41 - 7.49 (m, 4 H, CH(2)), 7.11 - 7.18 (m, 4 H, CH(3)), 2.67 (t, ^3J = 7.2 Hz, 4 H, CH(*1*)), 1.98 - 2.20 (m, 4 H, CH(*4*), 1.58 - 1.79 (m, 8 H, CH(*2, 3*)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 141.90 (s, 2 C, C(4)), 131.66 (s, 4 C, C(2)), 128.39 (s, 4 C, C(3)), 121.01 (s, 2 C, C(1)), 88.97 (s, 2 C, C(**1**)), 35.47 (s, 2 C, C(*1*)), 30.64 (s, 2 C, C(*2*)), 30.74 (t, ^2J = 22.6 Hz, 2 C, C(*4*)), 19.89 (m, 2 C, C(*3*)).

MALDI-ICR-MS (DCTB): m/z (%) 927.1 ($M^{\cdot+}$), 565.3 ($[M-(CH_2)_3(CF_2)_6F]^+$, 100%).

2.9 Synthesis of 1,2-bis[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]ethane-1,2-dione



98 **99**

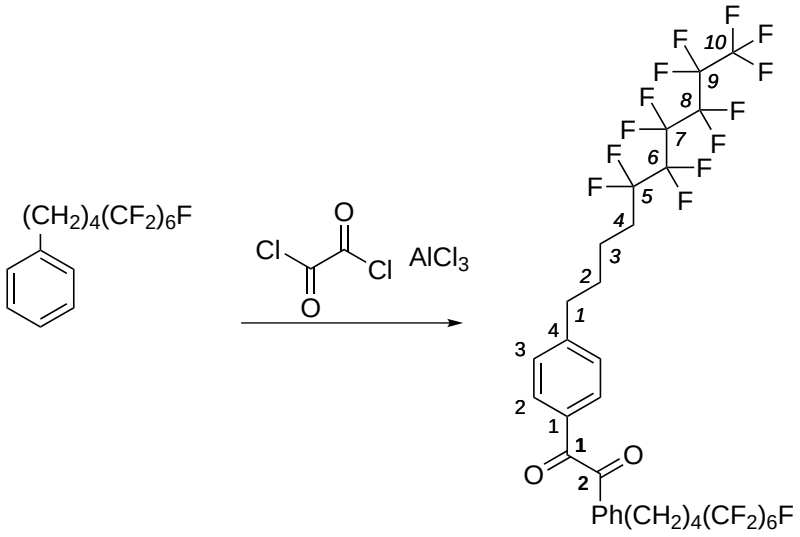
In a two necked flask under inert atmosphere, a mixture of the tolane **98** (0.616 g, 0.665 mmol) and iodine (0.101 g, 0.399 mmol) in DMSO (6 ml) was stirred at 155 °C for 16 hours. Then the mixture was separated between water and pentane. The organic phase was collected, washed with a 10% aqueous solution of sodium thiosulfate, dried over Na_2SO_4 and evaporated to dryness to give after a filtration over a plug of silica gel with pentane/ether 9:1 as eluent the dicetone compound (0.58 g, 0.605 mmol, 91%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.88 - 7.94 (m, 4 H, CH(2)), 7.28 - 7.35 (m, 4 H, CH(3)), 2.74 (t, ^3J = 7.3 Hz, 4 H, CH(*1*)), 1.98 - 2.19 (m, 4 H, CH(*4*)), 1.54 - 1.82 (m, 8 H, CH(*2, 3*)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 194.23 (s, 2 C, C(**1, 2**)), 149.53 (s, 2 C, C(4)), 131.18 (s, 2 C, C(1)), 130.25 (s, 4 C, C(2)), 129.02 (s, 4 C, C(3)), 35.78 (m, 2 C, C(*1*)), 30.23 - 31.08 (m, 4 C, C(*2, 4*)), 19.87 (t, ^3J = 3.6 Hz, 2 C, C(*3*)).

MALDI-ICR-MS (DCTB): m/z (%) 1231.26 ([M+DCTB+Na]$^+$, 10%), 981.13 ([M+Na]$^+$, 13%), 747.22 (56%), 705.13 (68%), 479 ([M-(CO-Ph-$(CH_2)_4(CF_2)_6F$]$^+$, 100%).

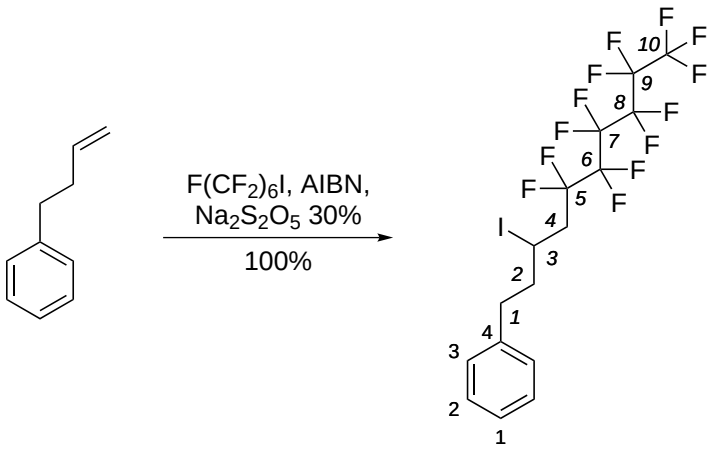
2.10 Synthesis of 1,2-bis[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]ethane-1,2-dione



93 **99**

In a two necked flask under inert atmosphere $AlCl_3$ (0.442 g, 3.32 mmol) was added to a magnetically stirred solution of oxalyl chloride (0.034 ml, 0.398 mmol) in DCM (2.010 ml) at - 80 °C. After 15 minutes, the compound **93** (0.3 g, 0.663 mmol) was added still at this temperature. The mixture was then allowed to warm up to room temperature and agitated during 23 hours. The mixture was then carefully poured into an ice/water mixture to quench de reaction. Then DCM was used to extract the organic material from the aqueous phase. Finally, the organic layer was washed with brine, dried over Na_2SO_4 and evaporated to dryness to give a brown solid. A purification was tried with pentane/DCM 9:1 as eluent. The desired compound was observed as by-product in a fraction containing one major unknown product (this fraction represents 2/3 of the starting material quantity). A second fraction with several unidentified compounds was also obtained.

2.11 Synthesis of (5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-3-iododecyl)benzene



92 **158**

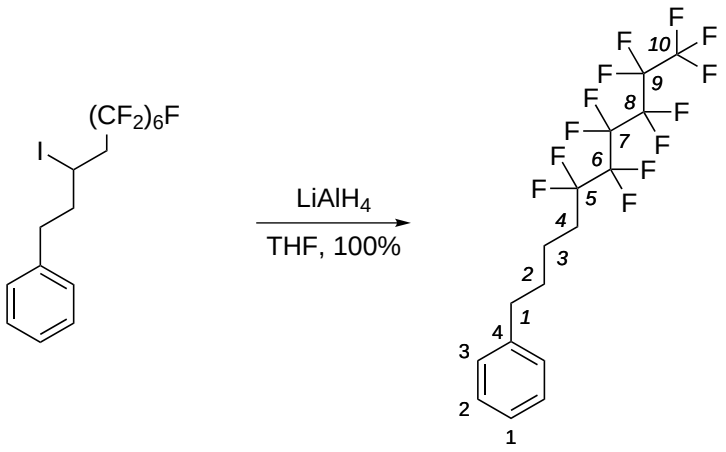
In a two necked flask under inert atmosphere, 4-phenyl-1-butene (7.9 ml, 52.6 mmol) was heated to 50 °C and a 30% aqueous solution of $Na_2S_2O_5$ (6.57 ml), Rf_6I (18.28 ml, 84 mmol) and AIBN (0.173 g, 1.052 mmol) were added. The mixture was heated at 80 °C. Every 2 hours, AIBN (0.173 g, 1.052 mmol) was added until the reaction was complete (16 h). Then water was added and the mixture was extracted with pentane. The organic phase was then dried over Na_2SO_4, evaporated to dryness to give the desired compound **158** (30.50 g, 52.8 mmol, 100%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.16 - 7.36 (m, 5 H, CH(1 to 3)), 4.20 - 4.33 (m, 1 H, CH(*3*)), 2.65 - 3.08 (m, 4 H, CH(*1, 4*)), 2.05 - 2.19 (m, 2 H, CH(*2*)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 139.86 (s, 1 C, C(4)), 128.60 (s, 1 C, C(Ar)), 128.48 (s, 1 C, C(Ar)), 126.39 (s, 1 C, C(Ar)), 41.35 - 42.06 (m, 2 C, C(*2, 4*)), 35.68 (s, 1 C, C(*1*)), 19.90 - 20.19 (m, 1 C, C(*3*)).

EI-MS: m/z (%) 578.1 ($M^{\cdot+}$, 10%), 451.1 ($[M-I]^+$, 32%), 91.1 ($C_7H_7^+$, 100%), 64.8 ($C_5H_5^+$, 44%).

2.12 Synthesis of (5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)benzene



158 **93**

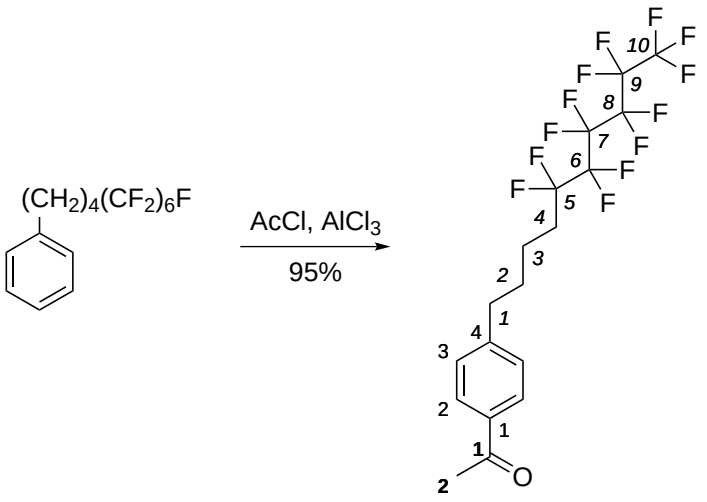
In a two necked flask under inert atmosphere, Lithium aluminium hydride (2.4 g, 63.2 mmol) was suspended in 70 ml of dry THF. A solution of **158** (29.273 g, 50.6 mmol) in 70 ml of dry THF was added dropwise at 0 °C. To complete the reaction, two other $LiAlH_4$ additions (300 mg, ~0.3 eq) were performed after 22 hours and 26 hours. After 28 hours, the reaction mixture was hydrolysed first with water, then with NaOH 2 M. Extraction with pentane, drying with Na_2SO_4 and evaporation of the solvent gave directly the pure compound **93** (22.03 g, 48.7 mmol, 96%).

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.12 - 7.35 (m, 5 H, CH(1 to 3)), 2.66 (t, ^3J= 7.0 Hz, 2 H, CH(*1*)), 1.99 - 2.19 (m, 2 H, CH(*4)*), 1.60 - 1.78 (m, 4 H, CH(*2, 3*)).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 141.62 (s, 1 C, C(4)), 128.41 (s, 1 C, C(Ar)), 128.32 (s, 1 C, C(Ar)), 125.95 (s, 1 C, C(Ar)), 35.52 (s, 1 C, C(*1*)), 30.63 - 31.04 (m, 2 C, C(*2, 4*)), 19.69 - 19.88 (m, 1 C, C(*3*)).

EI-MS: m/z (%) 452.1 ($M^{\cdot+}$, 46%), 91.1 ($C_7H_7^+$, 100%), 64.8 ($C_5H_5^+$, 36%).

2.13 Synthesis of 1-[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]ethanone



93 **94**

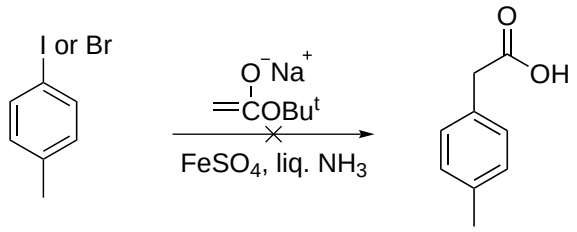
In a two necked flask under inert atmosphere, $AlCl_3$ (6.85 g, 51.4 mmol) was added to the magnetically stirred acetyl chloride (14.62 ml, 206 mmol) at - 90 °C. After 15 minutes, the starting material (9.3 g, 20.56 mmol) was added still at this temperature (The SM was freezed during the addition). The mixture was then allowed to warm up to room temperature and agitated during 3 hours. The mixture was then poured into 50 ml of an ice/water mixture to quench the reaction. After the ice melting, the aqueous phase was extracted with DCM and the organic phase was washed with a sat. $NaHCO_3$ solution and water, dried over Na_2SO_4 and evaporated to dryness to give 10.21 g of a brown liquid. The wanted product (9.7 g, 19.62 mmol, 95%) was obtained by a filtration over a plug of silica gel with pentane/ether 7:3 as eluent.

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.90 (d, ^3J = 7.3 Hz, 2 H, CH(2)), 7.27 (d, ^3J = 7.3 Hz, 2 H, CH(3)), 2.72 (t, ^3J = 7.3 Hz, 2 H, CH(*1*)), 2.59 (s, 3 H, CH(**2**)), 1.98 - 2.20 (m, 2 H, CH(*4*)), 1.58 - 1.81 (m, 4 H, CH(*2, 3*)).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 197.80 (s, 1 C, C(**1**)), 147.35 (s, 1 C, C(4)), 135.23 (s, 1 C, C(1)), 128.62 (s, 2 C, C(Ar)), 128.54 (s, 2 C, C(Ar)), 35.52 (s, 1 C, C(*1*)), 30.32 - 31.00 (m, 2 C, C(*2, 4*)), 26.55 (s, 1 C, C(**2**)), 19.81 (t, $^3J_{CF}$ = 3.6 Hz, 1 C, C(*3*)).

EI-MS: m/z (%) 494.1 ($M^{\cdot+}$, 6%), 479.1 ($[M\text{-}CH_3]^+$, 100%), 90.3 ($C_7H_6^+$, 56%).

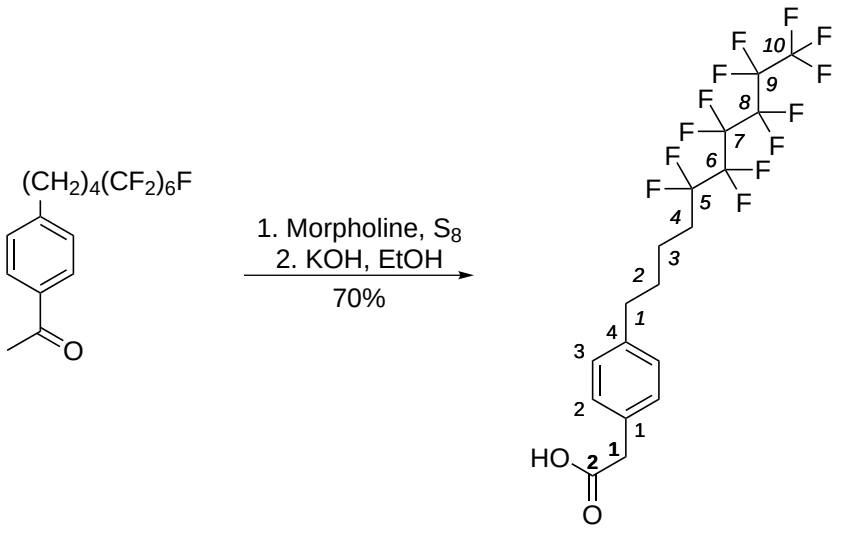
2.14 Synthesis of the (4-methylphenyl)acetic acid



96 **97**

A three necked flask with an nitrogen inlet, a condenser cooled at - 70 °C and a bubble counter was dried with a heat gun under vacuum, placed in a acetone/nitrogen bath (- 70 °C) and filled with 50 ml of ammonia. under inert conditions, the addition of sodium amide (1.140 g, 29.2 mmol) was followed by the slow addition of tert-butyl acetate (3.95 ml, 29.2 mmol). After 30 minutes of stirring at - 70 °C, the cooling bath was removed and iron(II) sulfate (0.74 g, 4.87 mmol) and 4-bromotoluene (0.833 g, 4.87 mmol) were quickly added. The stirring was continued for 3 hours (the colour became dark brown). The reaction was then quenched by portionwise additions of NH_4Cl (5 g) and the ammonia was allowed to evaporate giving a brown solid and a liquid (certainly t-buthyl acetate). The solid was dissolved in water and the organic material was extracted with ether. Then the organic layer was washed with water, 5% HCl and with brine, dried over Na_2SO_4 and evaporated to dryness to give a colourless liquid which was composed by the starting material and t-buthyl acetate.

2.15 Synthesis of [4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]acetic acid



94 **95**

In a round flask, the starting material (9.7 g, 19.62 mmol), morpholine (3.42 ml, 39.2 mmol) and sulphur (1.258 g, 39.2 mmol) were stirred at 135 °C for 15 hours. The mixture was then cooled down to room temperature and separated between water and ether. After the separation of the two phases, the organic one was washed with water, dried over Na_2SO_4 and evaporated to dryness to give the intermediate thioamide (12.08 g) still impure, which was directly used for the next step.

In a round flask, the previously obtained crude thioamide (0.140 g, ~0.235 mmol), KOH (0.185 g, 1.646 mmol) and ethanol (0.336 ml) were heated at reflux for 7 hours. The solvent was then evaporated and the yellow solid obtained was dissolved in water (a kind of gel was observed). Then the mixture was made acidic with conc. HCl and a yellow solid precipitated. ether was added to the aqueous phase to dissolved the solid and the phases were separated. The organic layer was dried over Na_2SO_4 and evaporated to dryness to give the desired carboxylic acid (84 mg, 0.17 mmol, 70%) as a yellow solid.

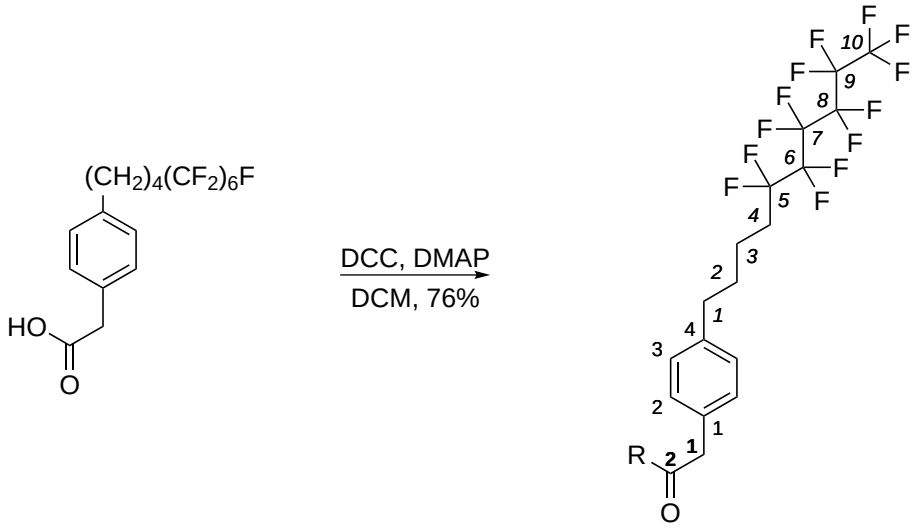
^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.21 (d, ^3J = 7.7 Hz, 2 H, CH(Ar)), 7.14 (d, ^3J = 7.7 Hz, 2 H CH(Ar)), 3.63 (s, 2 H CH(**1**)), 2.64 (t, ^3J = 7.0 Hz, 2 H CH(*1*)), 1.96 - 2.19 (m, 2 H CH(*4*)), 1.58 - 1.81 (m, 4 H CH(*2, 3*)).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 177.20 (s, 1 C, C(**2**)), 140.77 (s, 1 C, C(Ar)), 130.86 (s, 1 C, C(Ar)), 129.41 (s, 2 C, C(Ar)), 128.63 (s, 2 C, C(Ar)), 40.49 (s, 1 C, C(**1**)), 35.14 (s, 1 C,

C(*1*)), 30.77 (s, 1 C, C(*2*)), 30.71 (t, ^{2}J = 22.5 Hz, 1 C, C(*4*)), 19.70 - 19.95 (m, 1 C, C(*3*)).

EI-MS: m/z (%) 510.1 ($M^{\cdot+}$, 20%), 465.1 ($[M\text{-}CHO_2]^+$, 20%), 148.9 ($[M\text{-}(CH_2)_3(CF_2)_6F]^+$, 100%), 103.6 ($[M\text{-}(M\text{-}(CH_2)_3(CF_2)_6F + CHO_2)]^{\cdot+}$, 46%).

2.16 Synthesis of 1,3-bis[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]acetone



95 **88**

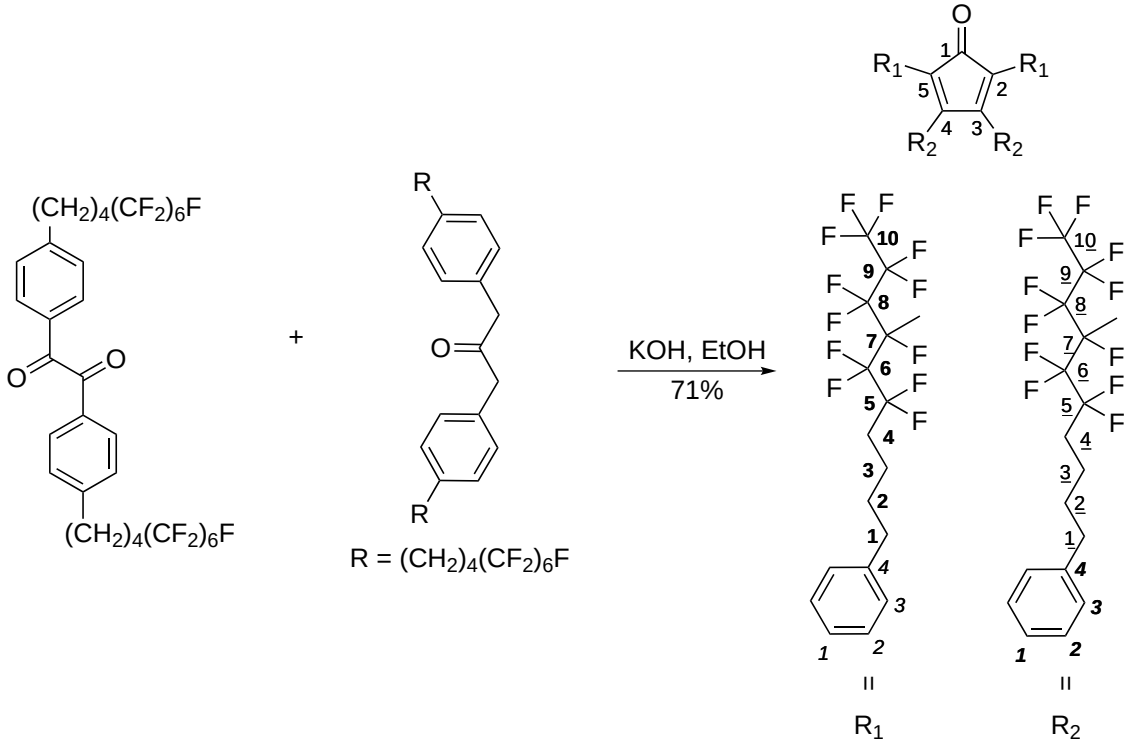
In a two necked flask under inert atmosphere, a solution of **95** (0.324 g, 0.635 mmol) in 1.7 ml of dry DCM was dropwise added to a solution of DCC (0.131 g, 0.635 mmol) and DMAP (0.155 g, 1.270 mmol) in 2 ml of DCM. The mixture was then agitated at room temperature during 24 hours. The reaction mixture was directly deposited on a silica gel plug and eluted with pentane/ether 8:2, giving the pure compound **88** (0.23 g, 0.240 mmol, 76%).

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.12 (d, ^{3}J = 7.8 Hz, 4 H, CH(Ar)), 7.06 (d, ^{3}J = 7.8 Hz, 4 H, CH(Ar)), 3.69 (s, 4 H, CH(**1**)), 2.64 (t, ^{3}J = 7.0 Hz, 4 H, CH(*1*)), 1.98 - 2.19 (m, 4 H, CH(*4*)), 1.54 - 1.78 (m, 8 H, CH(*2, 3*)).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 140.40 (s, 2 C, C(Ar)), 131.58 (s, 2 C, C(Ar)), 129.54 (s, 4 C, C(Ar)), 128.67 (s, 4 C, C(Ar)), 48.66 (s, 2 C, C(**1**)), 35.12 (s, 2 C, C(*1*)), 30.78 (s, 2 C, C(*2*)), 30.69 (t, ^{2}J = 22.5 Hz, 2 C, C(*4*)), 19.69 - 19.87 (m, 2 C, C(*3*)).

EI-MS: m/z (%) 959.2 ($M^{\cdot+}$, 4%), 170.6 ($[M\text{-}C_3H_5]^+$, 80%), 597.3 ($[M\text{-}(F(CF_2)_6(CH_2)_3)]^+$, 50%), 492.2 ($[M\text{-}(F(CF_2)_6(CH_2)_4\text{-}Ph\text{-}(CH_2))]^+$, 100%).

2.17 Synthesis of 2,3,4,5-tetrakis[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]cyclopenta-2,4-dien-1-one



99 **88** **85**

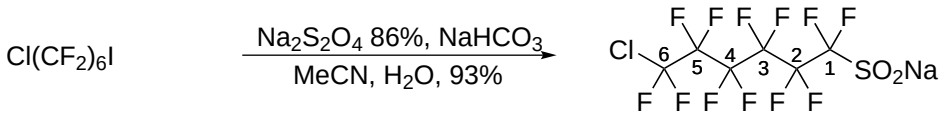
A solution of KOH (1.050 ml, 2.100 mmol, 1.96 M in EtOH) was added to a refluxing mixture of **99** (2.013 g, 2.100 mmol) and **88** (1.83 g, 1.909 mmol). A purple coloration was immediately observed. After 15 minutes, the mixture was let cool down to rt and a black product precipitated. After dissolution of the dark solid in DCM, the organic phase was washed with water, dried over $MgSO_4$ and evaporated to dryness. The pure desired compound **85** (2.533 g, 1.347 mmol, 70.5%) was obtained by a silica gel column chromatography with pentane/DCM 2:1 as eluent.

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.16 (d, ^3J = 8.3 Hz, 4 H, CH(*2*)), 7.03 (d, ^3J = 8.3 Hz, 4 H, CH(*3*)), 6.96 (d, ^3J = 8.3 Hz, 4 H, CH(***2***)), 6.83 (d, ^3J = 8.3 Hz, 4 H, CH(***3***)), 2.56 - 2.66 (m, 8 H, CH(**1**, 1)), 1.95 - 2.18 (m, 8 H, CH(**4**, 4)), 1.50 - 1.78 (m, 16 H, CH(**2**, 2, **3**, 3)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 200.79 (s, 1 C, C(1)), 154.02 (s, 2 C, C(3, 4)), 141.89 (s, 2 C, C(***1***)), 140.80 (s, 2 C, C(*1*)), 130.94 (s, 2 C, C(***4***)), 130.09 (s, 4 C, C(*2*)), 129.49 (s, 4 C, C(***2***)), 128.61 (s, 2 C, C(*4*)), 128.00 (s, 4 C, C(*3*)), 127.87 (s, 4 C, C(***3***)), 124.76 (s, 2 C, C(2, 5)), 35.20 - 35.35 (m, 2 C, C(**1**)), 35.01 - 35.19 (m, 2 C, C(1)), 30.08 - 31.15 (m, 8 C, C(**2**, **4**, 2, 4)), 19.64 - 19.23 (2 m, 4 C, C(**3**, 3)).

MALDI-ICR-MS (TCNQ): m/z (%) 1897.2([M + OH]$^+$, 100%), 1881.24 ([M + H]$^{\cdot+}$, 31%), 1852.38 ([M-CO]$^+$, 25%).

2.18 Synthesis of sodium 6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexane-1-sulfinate



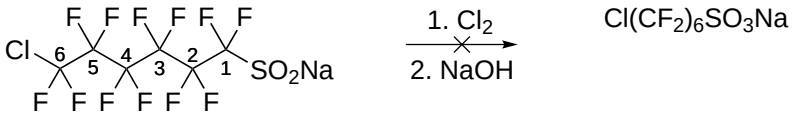
66 **67**

A mixture of the starting material **66** (1g, 2.16 mmol), the dithionite salt (791 mg, 4.54 mmol, Riedel-de Haën) and sodium bicarbonate (672 mg, 8 mmol) suspended in MeCN (1.2 ml) and in water (2 ml) was agitated at 70 °C during 4 hours. The mixture was then dissolved in brine and ethyl acetate. The two phases were separated, the aqueous phase washed with ethyl acetate. The combined organic phases were washed with brine, dried over Na_2SO_4 and evaporated to dryness to give the desired sulfinate (848 mg, 2 mmol, 93%) as a white solid.

^{19}F NMR (471 MHz, MeOD): δ (ppm) -69.18 (t, ^{3}J = 13.7 Hz, 2 F, CH(1)), -120.87 to -120.65 (m, 2 F), -121.89 to -121.65 (m, 2 F), -122.66 to -122.41 (m, 2 F), -123.08 to -122.89 (m, 2 F), -131.39 to -131.19 (m, 2 F).

ESI-MS: m/z (%) 445 ([M+Na]$^+$, 100%), 866.7 ([2M+Na]$^+$, 16%).

2.19 Synthesis of sodium 6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexane-1-sulfonate

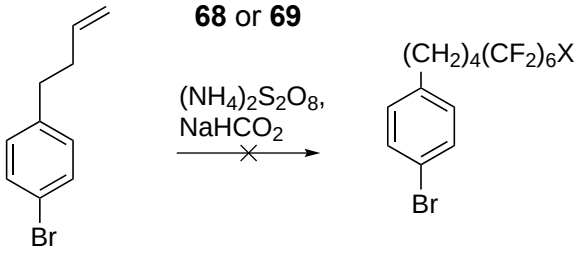


67 **68**

The starting material (830 mg, 1.964 mmol) was dissolved in 6 ml of water and Cl_2 was bubbled through the solution for 1 hour at room temperature. The two phases formed were separated, 6 ml of NaOH 0.8 M were added to the organic layer and the mixture was stirred at room temperature during 4 hours. The mixture was then poured into a mixture of EtOAc and brine. After separation of the two phases formed, the organic one was washed with brine, dried over Na_2SO_4 and the solvent was finally evaporated to obtain 442 mg of a white solid, which was in majority the starting material. But the desired compound was also present, as confirmed by ESI-MS.

ESI-MS: m/z (%) 415 ($[M-Na]^-$, 100%).

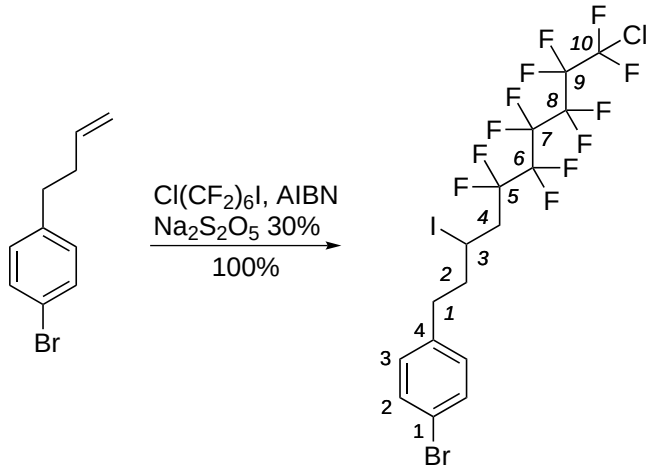
2.20 Synthesis of 1-bromo-4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)benzene and sodium 10-(4-bromophenyl)-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorodecane-1-sulfonate



62 **59 X = SO_3Na**
64 X = F

In a round flask, the allyl compound, ammonium peroxodisulfate, the perfluorinated chain and formic acid sodium salt in DMF were heated during 4.5 hours at 40 °C. Water was added to the mixture and the aqueous phase was extracted three times with pentane. The organic phase was then washed 3 times with a 1 M bicarbonate solution and 2 times with brine. After drying over Na_2SO_4 and solvent evaporation, a slightly yellow oil was obtained, composed by the starting allyl compound (almost all the starting quantity was recovered), the desired product and other unknown by-products.

2.21 Synthesis of the 1-bromo-4-(10-chloro-5,5,6,6,7,7,8,8,9,9,10,10-dodecafluoro-3-iododecyl)benzene



62 **70**

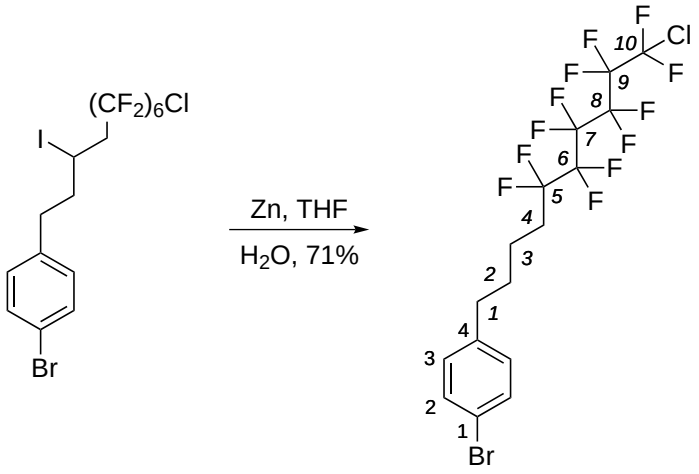
To the starting material **62** (6.33 g, 30 mmol) heated at 50 °C, a 30% aqueous solution of $Na_2S_2O_5$ (3.3 ml), 1-iodotridecafluorohexane (22.2 g, 48 mmol) and 2,2'-Azobisisobutyronitrile (148 mg, 0.9 mmol) were added under inert atmosphere. The reaction mixture was then agitated at 80 °C. Every 2 hours, AIBN (9 mg, 0.06 mmol) was added until the reaction was complete (the reaction was followed by GC-MS). Water was added to the mixture and the aqueous phase was extracted with ether. The organic layer was dried over Na_2SO_4 and evaporated to dryness giving the desired compound **70** (20.21 g, 30 mmol, 100%) as a white solid.

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.42 (d, ^3J = 8.2 Hz, 2 H, CH(2)), 7.09 (d, ^3J = 8.2 Hz, 2 H, CH(3)), 4.16 - 4.30 (m, 1 H, CH(*3*)), 2.61 - 3.06 (m, 4 H, CH(*Alk*)), 1.98 - 2.18 (m, 2 H, CH(*Alk*)).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 138.78 (s, 1 C, C(4)), 131.68 (s, 2 C, C(2)), 130.24 (s, 2 C, C(3)), 120.20 (s, 1 C, C(1)), 41.71 (t, ^2J = 20.8 Hz, 1 C, C(*4*)), 41.40 (m, 1 C, C(*2*)), 35.12 (s, 1 C, C(*1*)), 19.60 - 20.00 (m, 1 C, C(*3*)).

EI-MS: m/z (%) 672.1 ($M^{\cdot+}$, 50%), 544.9 ($[M-I]^+$, 84%), 168.8 ($[M-Cl(CF_2)_6CH_2CHICH_2]^+$, 60%), 89.4 ($[M-(Cl(CF_2)_6CH_2CHICH_2+Br)]^{\cdot\cdot+}$, 100%).

2.22 Synthesis of the 1-bromo-4-(10-chloro-5,5,6,6,7,7,8,8,9,9,10,10-dodecafluorodecyl)benzene



70 **60**

In a dried microwave oven tube, **70** (5.38 g, 7.99 mmol), zinc (0.575 g, 8.79 mmol) and THF (40 ml) were irradiated at 180 °C during 20 minutes. The reaction mixture was filtrated, hydrolysed with water and HCl 1M was added to dissolve the salts. After extraction with pentane, the organic phase was washed with a 10% solution of sodium thiosulfate, dried over Na_2SO_4, evaporated to dryness and filtrated over a plug of silica gel with pentane as eluent to give the desired compound **60** as a white solid (3.1 g, 5.66 mmol, 71%).

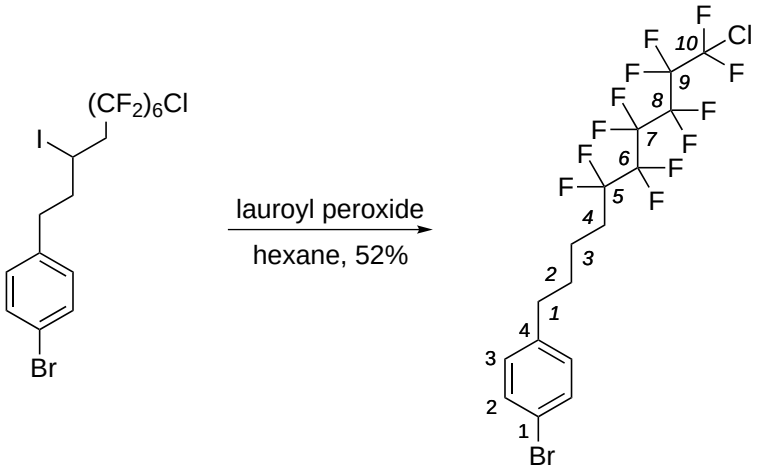
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.41 (m, 2 H, CH(2)), 7.04 (m, 2 H, CH(3)), 2.61 (t, ^3J = 7.2 Hz, 2 H, CH(*1*)), 1.97 - 2.19 (m, 2 H, CH(*4*)), 1.56 - 1.76 (m, 4 H, CH(*2, 3*)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 140.54 (s, 1 C, C(4)), 131.47 (s, 2 C, C(2)), 130.07 (s, 2 C, C(3)), 119.71 (s, 1 C, C(1)), 34.93 (s, 1 C, C(*1*)), 29.75 - 31.31 (m, 2 C, C(*2, 4*)), 19.76 (t, ^3J = 3.6 Hz, 1 C, C(*3*)).

^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) -69.22 - -69.03 (m, 2 F, CF(*10*)), -115.60 - -115.37 (m, 2 F, CF(*5*)), -121.42 - -121.15 (m, 2 F), -122.66 - -122.28 (m, 2 F), -123.10 - -122.77 (m, 2 F), -124.85 - -124.55 (m, 2 F).

EI-MS: m/z (%) 530.1 ($M^{\cdot+}$, 46%), 168.8 ($[M\text{-}F(CF_2)_6(CH_2)_3]^+$, 92%).

2.23 Synthesis of the 1-bromo-4-(10-chloro-5,5,6,6,7,7,8,8,9,9,10,10-dodecafluorodecyl)benzene



70 **60**

In a two necked flask under inert atmosphere, the compound **70** (0.35 g, 0.520 mmol) was dissolved in cyclohexane (6 ml) and the oxygen was removed by the freezing/vacuum method. At 50 °C, lauroyl peroxide (0.035 g, 0.088 mmol) was added in one portion. The mixture was then agitated at 80 °C. After 3h30, 6 hours lauroyl peroxide (0.035 g, 0.088 mmol) was again added and the reaction continued for 20 hours. Then the volatiles were evaporated and a yellow oil was obtained. The pure product (0.148 g, 0.270 mmol, 52.0%) was obtained by a silica gel column chromatography (eluent: pentane) as a white solid.

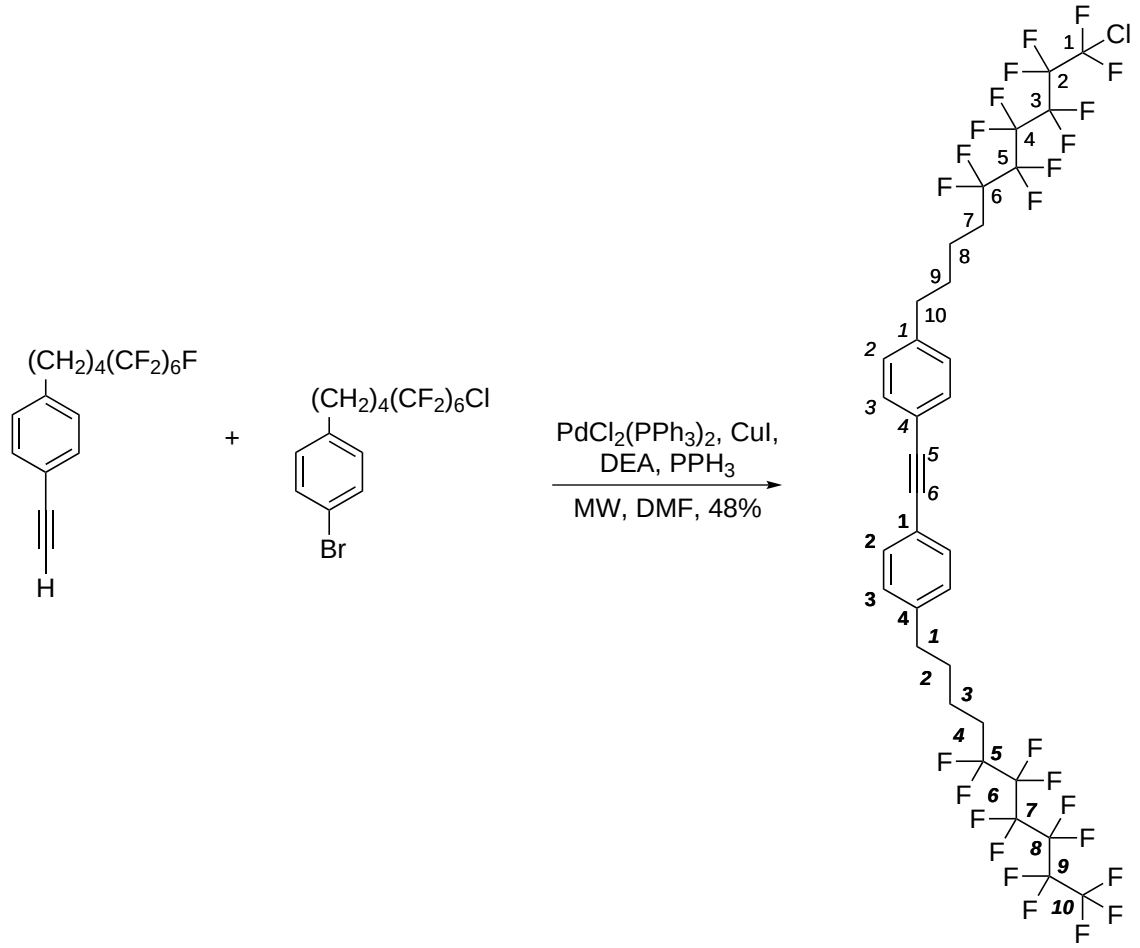
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.41 (ddd, ^{3}J = 8.8 Hz, ^{4}J = 2.4 Hz, ^{5}J = 2.2 Hz, 2 H, CH(2)), 7.04 (ddd, ^{3}J = 8.8 Hz, ^{4}J = 2.4 Hz, ^{5}J = 2.2 Hz, 2 H, CH(3)), 2.61 (t, ^{3}J = 7.2 Hz, 2 H, CH(*1*)), 1.97 - 2.19 (m, 2 H, CH(*4*)), 1.56 - 1.76 (m, 4 H, CH(*2, 3*)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 140.54 (s, 1 C, C(4)), 131.47 (s, 2 C, C(2)), 130.07 (s, 2 C, C(3)), 119.71 (s, 1 C, C(1)), 34.93 (s, 1 C, C(*1*)), 29.75 - 31.31 (m, 2 C, C(*2, 4*)), 19.76 (t, ^{3}J = 3.6 Hz, 1 C, C(*3*)).

^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) -69.22 - -69.03 (m, 2 F, CF(*10*)), -115.60 - -115.37 (m, 2 F, CF(*5*)), -121.42 - -121.15 (m, 2 F), -122.66 - -122.28 (m, 2 F), -123.10 - -122.77 (m, 2 F), -124.85 - -124.55 (m, 2 F).

EI-MS: m/z (%) 530.1 ($M^{\cdot+}$, 46%), 168.8 ($[M\text{-}F(CF_2)_6(CH_2)_3]^+$, 92%).

2.24 Synthesis of the 1-(10-chloro-5,5,6,6,7,7,8,8,9,9,10,10-dodecafluorodecyl)-4-{[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]ethynyl}benzene



58 **60** **72**

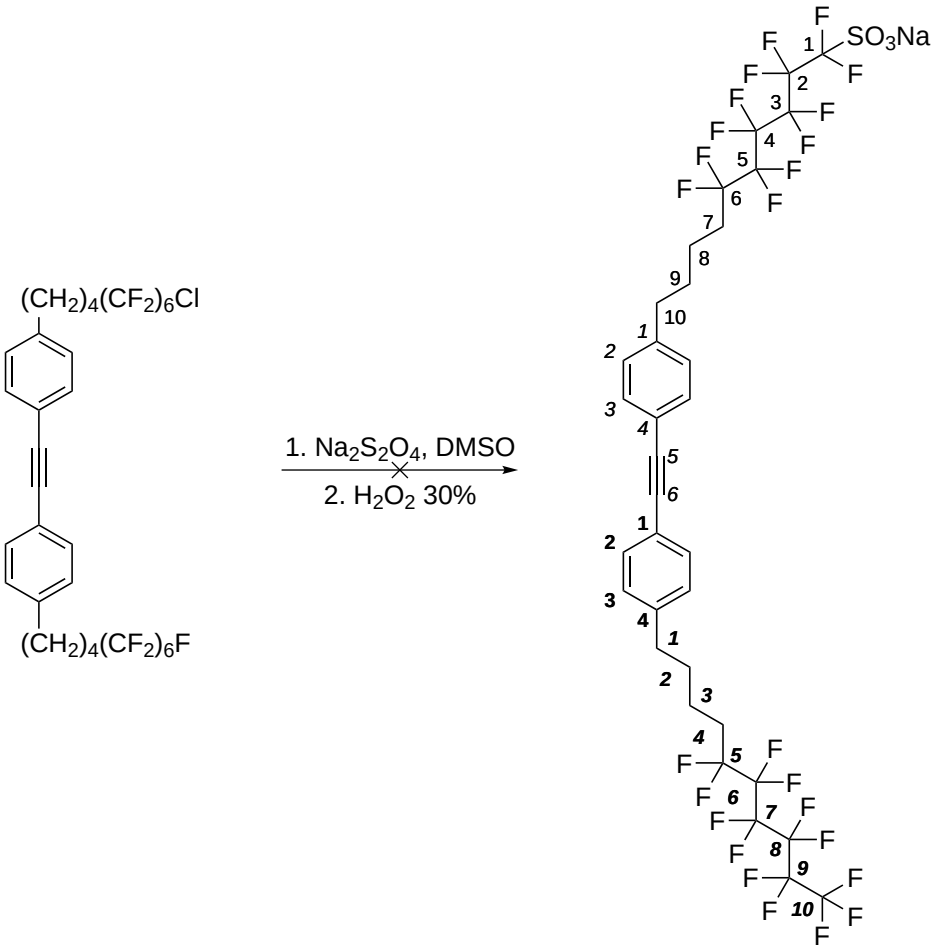
In a microwave vial under inert atmosphere, the acetylene **58** (1.129 g, 2.370 mmol), the bromophenyl compound **60** (1.298 g, 2.370 mmol), triphenylphosphine (0.124 g, 0.474 mmol), copper iodide (0.020 g, 0.104 mmol) and $PdCl_2(PPh_3)_2$ (0.092 g, 0.130 mmol) were suspended in diethylamine (3.74 ml, 35.8 mmol) and in DMF (1.317 ml). After microwave irradiation at 120 °C during 40 minutes, the reaction mixture was separated between ether and HCl 0.1 M. The organic phase was then washed with brine, dried over $MgSO_4$ and evaporated to dryness. The crude product, which was purified first by recrystallization in EtOH and by a silica gel column chromatography with pentane, then pentane/ether 97:3 as eluent was obtained as a yellow solid (1.07 g, 1.135 mmol, 48%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.42 - 7.48 (m, 4 H, CH(*3*, **2**)), 7.12 - 7.19 (m, 4 H, CH(*2*, **3**)), 2.67 (t, ^3J = 7.2 Hz, 4 H, CH(10, ***1***)), 1.98 - 2.20 (m, 4 H, CH(7, ***4***)), 1.59 - 1.80 (m, 8 H, CH(8, 9, ***2***, ***3***)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 141.89 (s, 2 C, C(*1*, **4**)), 131.64 (s, 4 C, C(*3*, **2**)), 128.38 (s, 4 C, C(*2*, **3**)), 121.01 (s, 2 C, C(*4*, **1**)), 88.96 (s, 2 C, C(*5, 6*)), 35.45 (s, 2 C, C(10, ***1***)), 30.64 (s, 2 C, C(9, ***2***)), 30.75 (t, ^2J = 22.6 Hz, 2 C, C(7, ***4***)), 19.80 (t, ^3J = 3.3 Hz, 2 C, C(8, ***3***)).

MALDI-ICR-MS (DCTB): m/z (%) 942.11 ($M^{\cdot+}$).

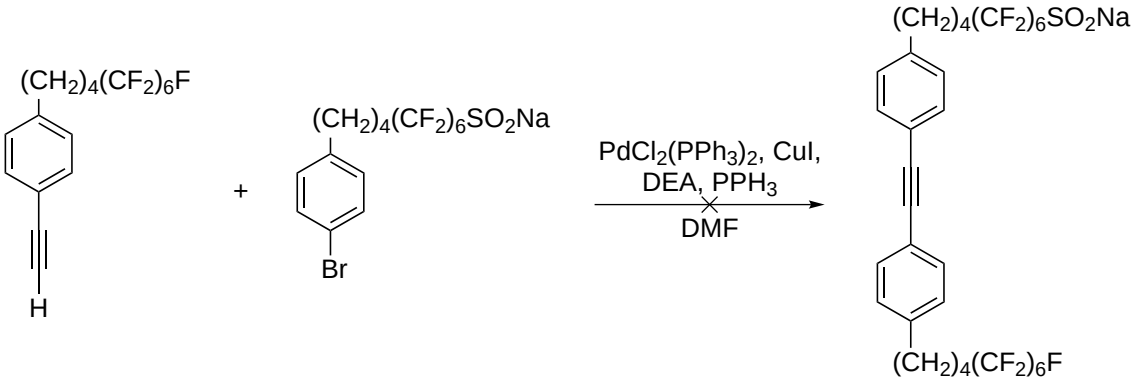
2.25 Synthesis of the 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-10-(4-{[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]ethynyl}phenyl)decane-1-sulfonate



72 **57**

In a microwave vial, **72** (0.041 g, 0.043 mmol) and sodium dithionite (0.030 g, 0.174 mmol) were suspended in DMSO (0.3 ml) and heated to 80 °C during 0.5 hour, then heated to 100 °C during 5.5 hours. The starting material was not immediately soluble (dissolved at 100 °C). Because ^{19}F-NMR did not show the CF_2Cl peak around -67 ppm, the reaction was stopped after 6 hours at 100 °C. The organic material was extracted with EtOAc, dried over Na_2SO_4 and evaporated to dryness giving the crude desired sulfinate compound which was directly suspended in a 30% hydrogen peroxide solution and agitated overnight. After extraction with EtOAc, no trace of the sulfonate compound was detected. The sulfinate compound was collected quantitatively.

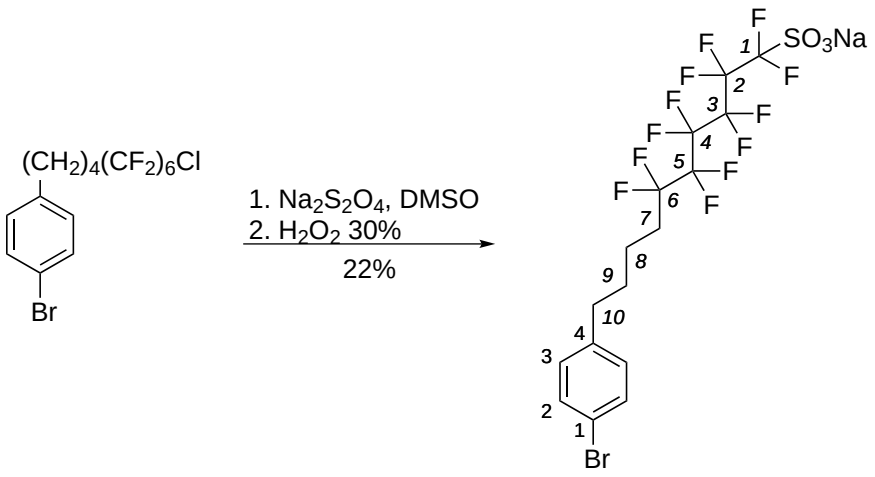
2.26 Synthesis of the 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-10-(4-{[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]ethynyl}phenyl)decane-1-sulfinate



58 **75** **76**

In a microwave vial under inert atmosphere, the sulfinate compound (0.1 g, 0.167 mmol), the acetylene moiety (0.079 g, 0.167 mmol), triphenylphosphine (8.75 mg, 0.033 mmol) and $PdCl_2(PPh_3)_2$ (6.44 mg, 9.18 µmol) were suspended in diethylamine (0.263 ml, 2.52 mmol) and in DMF (0.093 ml). After irradiation at 120 °C during 40 minutes, water was added and the organic material was extracted with ether. The organic phase was then dried over $MgSO_4$ and evaporated to dryness giving 162 mg of a brown oily-solid. Different silica gel column chromatographies did not allow to isolate the desired compound. Only the reduced compound (R-CF_2H) was isolated in 48% yield. The rest of the material was stuck on silica.

2.27 Synthesis of sodium 10-(4-bromophenyl)-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-decane-1-sulfonate



60 **59**

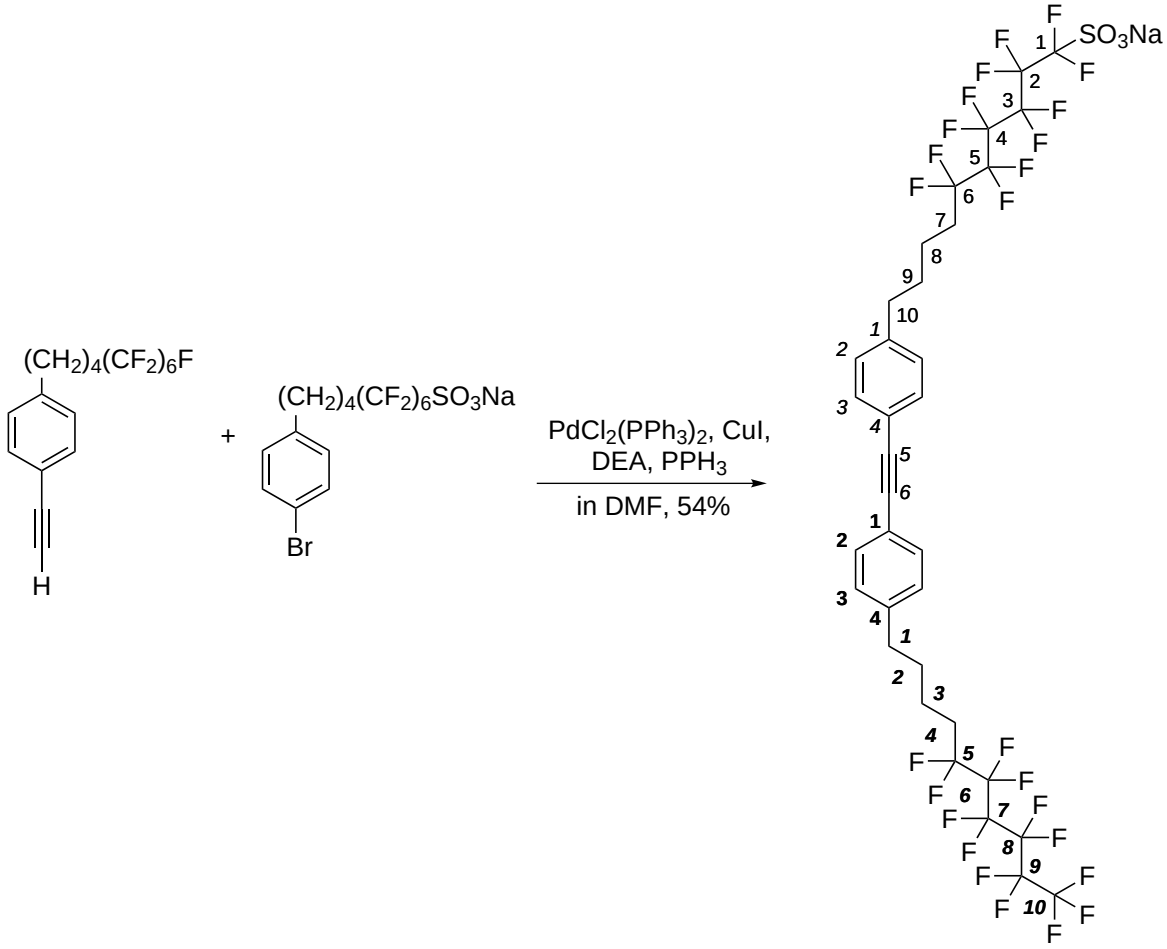
In a two necked flask under inert atmosphere, **60** (8.160 g, 14.90 mmol) and sodium dithionite (10.678 g, 52.7 mmol) were suspended in DMSO and agitated at 100 °C during 3 hours. The organic material was extracted with EtOAc. After washing with water and drying with $MgSO_4$, the solvent was evaporated to give a brown pasty solid (7.88 g) which is according to ^{1}H-NMR, ^{19}F-NMR and ESI-MS the crude desired compound. the reduce compound (CF_2H) was also observed in a small quantity. The crude sulfinate (7.88 g) was placed in 170 ml of concentrated hydrogen peroxide during 22 hours. After extraction with EtOAc, a silica gel column chromatography with DCM/MeOH 9:1 as eluent gave the desired compound (1.8 g, 2.93 mmol, 22.25% yield) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.41 (ddd, ^{3}J = 8.7 Hz, ^{4}J = 2.5 Hz, ^{5}J = 2.2 Hz, 2 H, CH(2)), 7.13 (ddd, ^{3}J = 8.7 Hz, ^{4}J = 2.5 Hz, ^{5}J = 2.2 Hz, 2 H, CH(3)), 2.63 (t, ^{3}J = 7.4 Hz, 2 H, CH(*1*)), 2.07 - 2.23 (m, 2 H, CH(*4*)), 1.59 - 1.75 (m, 4 H, CH(*2, 3*)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 142.61 (s, 1 C, C(4)), 132.58 (s, 2 C, C(2)), 131.57 (s, 2 C, C(3)), 120.66 (s, 1 C, C(1)), 35.95 (s, 1 C, C(*1*)), 31.92 (s, 1 C, (*2*)), 31.85 (t, ^{2}J = 22.0 Hz, 1 C, C(*4*)), 21.07 (t, ^{3}J = 3.9 Hz, 1 C, C(*3*)).

ESI-MS: m/z (%) 591 ($[M - Na]^-$).

2.28 Synthesis of the 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-10-(4-{[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]ethynyl}phenyl)decane-1-sulfonate



58 **59** **57**

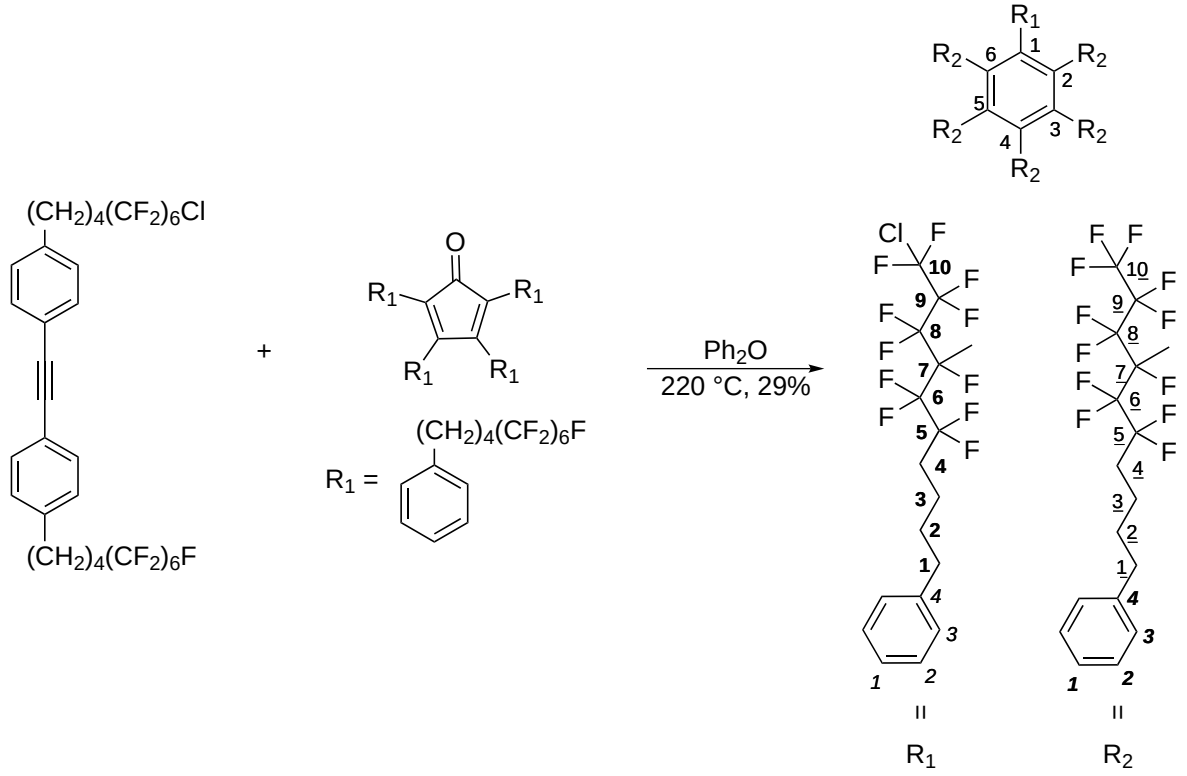
In a microwave vial under inert atmosphere, the acetylene **58** (1.018 g, 1.655 mmol), the sulfonate compound **59** (0.788 g, 1.655 mmol), triphenylphosphine (0.087 g, 0.331 mmol), copper iodide (0.014 g, 0.073 mmol) and $PdCl_2(PPh_3)_2$ (0.064 g, 0.091 mmol) were suspended in diethylamine (2.61 ml, 25.00 mmol) and in DMF (0.919 ml). After microwave irradiation at 120 °C during 45 minutes, water was added and the organic material was extracted with EtOAc. The organic phase was then dried over $MgSO_4$ and evaporated to dryness. Two silica gel column chromatographies with first DCM/MeOH 9:1 and second EtOAc as eluents allowed to obtain the desired tolane (1.5 g, 1.484 mmol, 53.7%) as a white powder.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38 - 7.45 (m, 4 H, CH(*3*, **2**)), 7.18 - 7.25 (m, 4 H, CH(*2*, **3**)), 2.69 (t, ^3J = 7.4 Hz, 4 H, CH(10, ***1***)), 2.07 - 2.29 (m, 4 H, CH(7, ***4***)), 1.57 - 1.81 (m, 8 H, CH(8, 9, ***2***, ***3***)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.83 (m, 2 C, C(*1*, **4**)), 132.68 (s, 4 C, C(*3*, **2**)), 129.78 (s, 4 C, C(*2*, **3**)), 122.44 (m, 2 C, C(*4*, **1**)), 89.90 (m, 2 C, C(*5, 6*)), 36.49 (m, 2 C, C(10, ***1***)), 31.90 (m, 4 C, C(7, 9, ***2***, ***4***)), 21.10 (m, 2 C, C(8, ***3***)).

ESI-MS: m/z (%) 987 ($[M - Na]^-$).

2.29 Synthesis of 1-[4-(10-chloro-5,5,6,6,7,7,8,8,9,9,10,10-dodecafluorodecyl)phenyl]-2,3,4,5,6-pentakis[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]benzene



72 **85** **100**

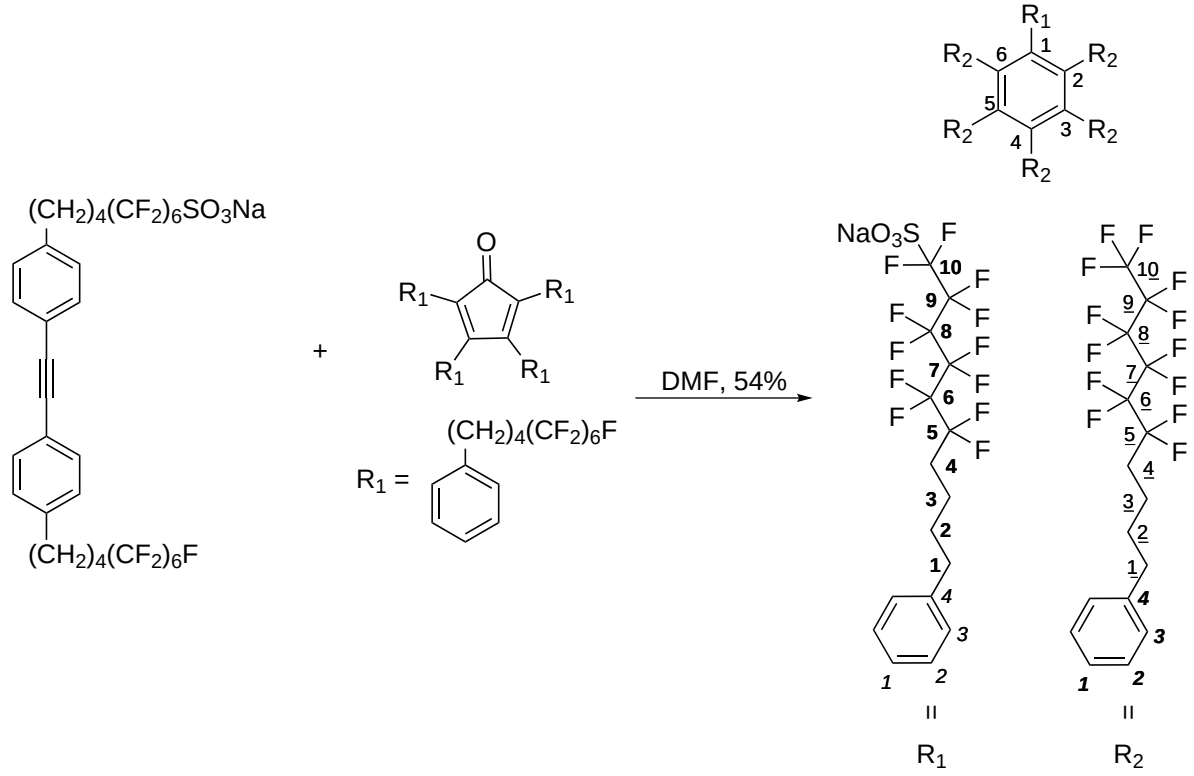
A mixture of the dissymmetric tolane **72** (0.05 g, 0.05 mmol) and **85** (0.1 g, 0.05 mmol) in Ph_2O (0.2 ml) was heated under inert atmosphere at 220 °C during 22 hours. The reaction mixture was then diluted with dcm, washed with water, dried over $MgSO_4$ and evaporated to dryness, giving around a brown pasty solid, which was chromatographied over silica gel with pentane/ dcm 9:1 as eluent. The pure desired compound was obtained as a slightly yellow solid (43 mg, 0.015 mmol, 29%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.68 (d, ^3J = 8.1 Hz, 12 H, CH(*2*, ***2***)), 6.62 (d, ^3J = 8.1 Hz, 12 H, CH(*3*, ***3***)), 2.39 (t, ^3J = 6.8 Hz, 12 H, CH(**1**, 1)), 1.85 - 2.09 (m, 12 H, CH(**4**, 4)), 1.32 - 1.58 (m, 24 H, CH(**2**, **3**, 2, 3)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 140.19 (s, 6 C, C(Ar)), 138.54 (s, 6 C, C(Ar)), 137.86 (s, 6 C, C(Ar)), 131.60 (s, 12 C, C(Ar)), 126.35 (s, 12 C, C(Ar)), 34.62 (m, 6 C, C(**1**, 1)), 30.37 (s, 6 C, C(**2**, 2)), 30.57 (t, ^3J = 22.0 Hz, 6 C, C(**4**, 4)), 18.87 - 19.10 (m, 6 C, C(**3**, 3)).

MALDI-ICR-MS (DCTB): m/z (%) 2794.41 ($M^{\cdot+}$, 100%).

2.30 Synthesis of 1-[4-(10-sulfonic acid-5,5,6,6,7,7,8,8,9,9,10,10-dodecafluorodecyl)phenyl]-2,3,4,5,6-pentakis[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]benzene



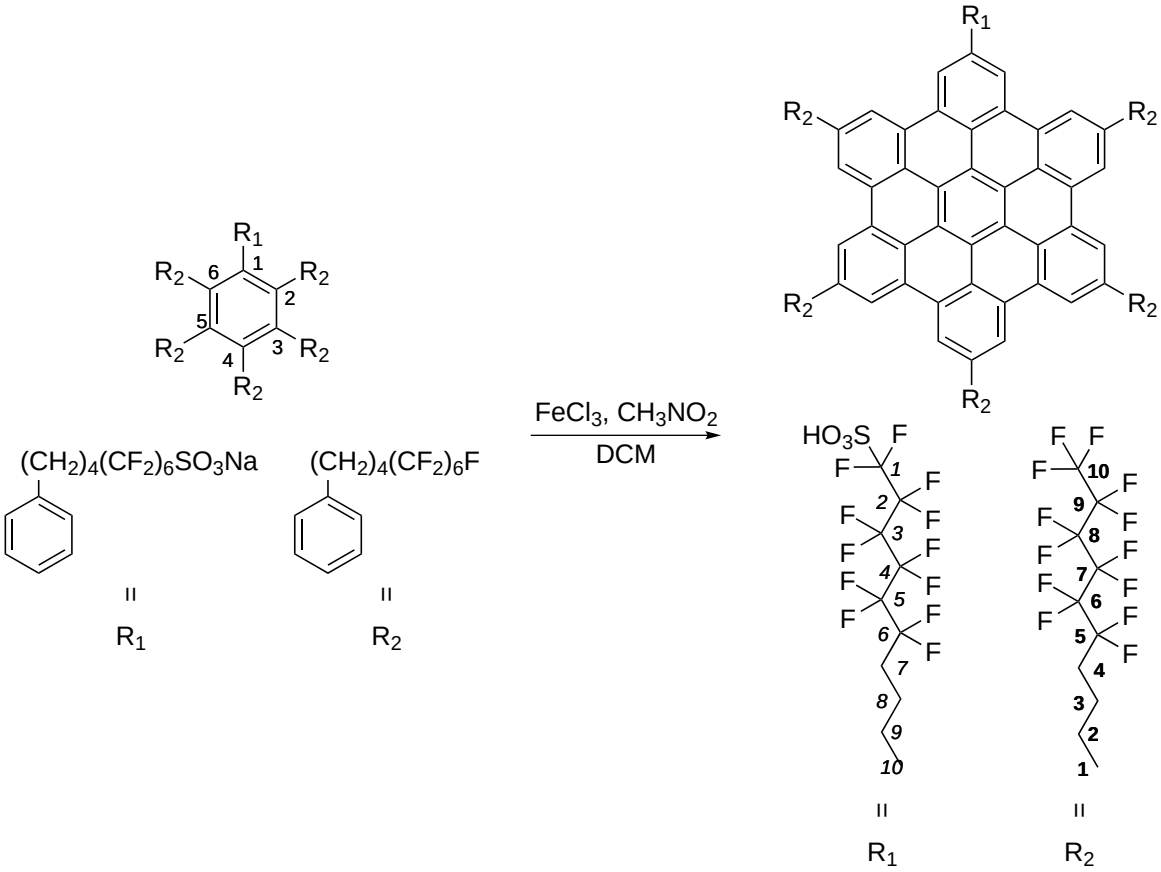
A mixture of the tolane **60** (0.105 g, 0.104 mmol) and **85** (0.150 g, 0.080 mmol) in DMF (0.5 ml) was irradiated in a microwave vial under inert atmophere at 250 °C during 11 hours. The reaction mixture was then transferred in a round flask with dcm and evaporated to dryness. The purification was performed with a silica gel column chromatography (EtOAc as eluent), which allow to give the desired compound **101** (0.124 g, 0.043 mmol, 54.3%) as a brown pasty solid.

^{1}H NMR (300 MHz, MeOD): δ (ppm) 6.72 (d, ^{3}J = 7.7 Hz, 12 H, CH(*2*, ***2***)), 6.63 (d, ^{3}J = 7.7 Hz, 12 H, CH(*3*, ***3***)), 2.36 - 2.46 (m, 12 H, CH(**1**, 1)), 1.90 - 2.15 (m, 12 H, CH(**4**, 4)), 1.32 - 1.61 (m, 24 H, CH(**2**, **3**, 2, 3)).

^{13}C NMR (75 MHz, MeOD): δ (ppm) 141.75 (s, 6 C, C(Ar)), 140.20 (s, 6 C, C(Ar)), 139.68 (s, 6 C, C(Ar)), 133.18 (s, 12 C, C(Ar)), 127.81 (s, 12 C, C(Ar)), 35.94 (m, 6 C, C(**1**, 1)), 31.44 - 32.46 (m, 12 C, C(**2**, **4**, 2, 4)), 20.08 - 20.73 (m, 6 C, C(**3**, 3)).

MALDI-ICR-MS (DCTB): m/z (%) 2839.40 ([M-Na]$^{-}$, 100%).

2.31 Synthesis of 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-10-[5,8,11,14,17-pentakis(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronen-2-yl]decane-1-sulfonic acid

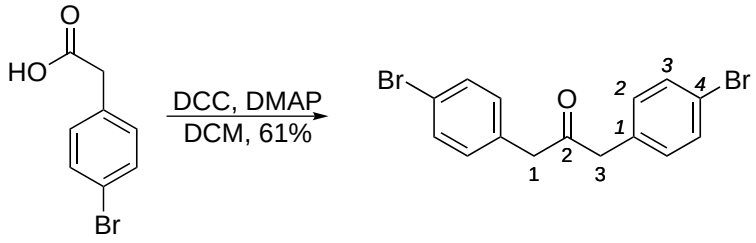


101 **1**

In a three necked flask under inert atmosphere, a solution of iron chloride (1.190 g, 7.33 mmol) in nitromethane was dropwise added to a solution of **101** (0.350 g, 0.122 mmol) in DCM (75 ml) preheated to 45 °C. Argon was bubbled through the reaction mixture by a teflon capillary during all the reaction to remove the formed HCl. After 6 hours, methanol was added and the dark-brown precipitate was filtrated over Millipore after overnight stand by. a silica gel column chromatography with first EtOAc, then MeOH and finally HFB/MeOH 1:1 was used to purify the compound. Because only MALDI-MS could be recorded, no information on the purity was available, and no yield is given.

MALDI-ICR-MS (DCTB): m/z (%) 2827.32 ($[M-H]^-$ 100%).

2.32 Synthesis of 1,3-bis(4-bromophenyl)acetone



77 **78**

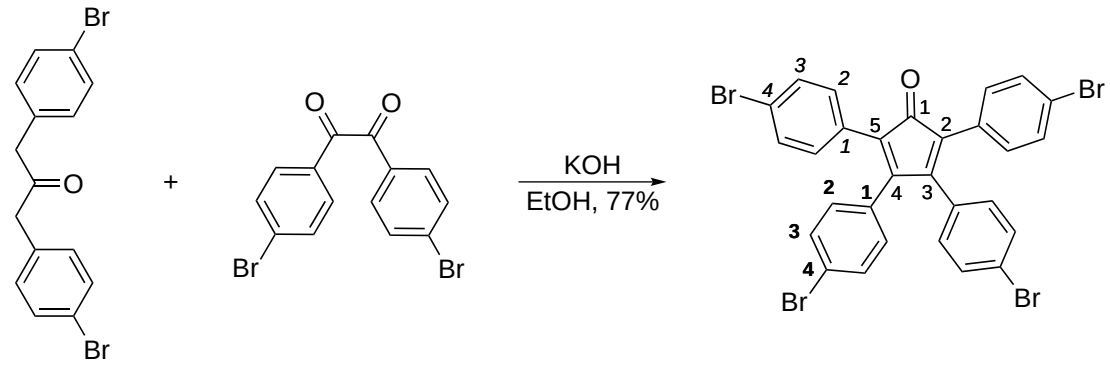
In a two necked flask under inert atmosphere, a solution of 4-bromophenylacetic acid (10 g, 46.5 mmol) in dry DCM (70 ml) was dropwise added (40 ml/min) to solution of DCC (9.59 g, 46.5 mmol) and DMAP (1.42 g, 11.63 mmol) in DCM (120 ml). After 22 hours, the white precipitate was filtrated off and the filtrate was evaporated to dryness. A filtration over a plug of silica gel (eluent: DCM/pentane 9:1) and a recristallisation in EtOH gave the desired product (5.25 g, 14.26 mmol, 61%).

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.45 (d, ^{3}J = 8.2 Hz, 4 H, CH(*3*)), 7.01 (d, ^{3}J = 8.2 Hz, 4 H, CH(*2*)), 3.68 (s, 4 H, CH(1, 3)).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 204.27 (s, 1 C, C(2)), 132.56 (s, 2 C, C(*1*)), 131.85 (s, 4 C, C(*Ar*)), 131.13 (s, 4 C, C(*Ar*)), 121.26 (s, 2 C, C(*4*)), 48.44 (s, 2 C, C(1, 3)).

EI-MS: m/z (%) 367.9 ($M^{\cdot+}$, 6%), 196.6 ($BrPhCH_2CO^+$, 16%), 168.8 ($BrPhCH_2^+$, 100%).

2.33 Synthesis of 2,3,4,5-tetrakis(4-bromophenyl)cyclopenta-2,4-dien-1-one



78 **79** **80**

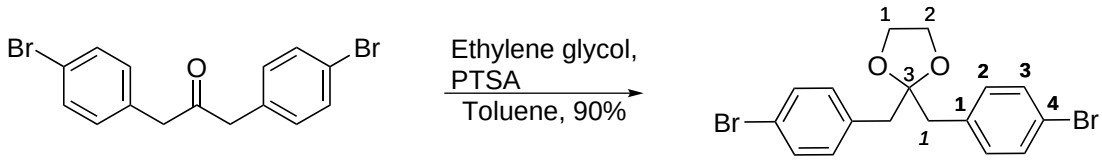
A solution of KOH (185 mg, 3.3 mmol) in EtOH (1.5 ml) was added to a refluxing mixture of 1,3-bis(4-bromophenyl)propane-2-one (1.1 g, 3 mmol) and of 4,4'-dibromobenzil (1.2 g, 3.3 mmol) in EtOH (5 ml). A purple coloration was immediately observed. After 5 minutes, the mixture was cooled down to 0 °C during 3 hours. The crude material was collected with DCM. After evaporation of the solvent, a filtration over a plug of silica gel with DCM/pentane 1:1 as eluent allowed to collect the pure product as a purple solid (1.2 g, 3.3 mmol, 77%).

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.33 - 7.44 (m, 8 H, CH(Ar)), 7.06 (ddd, *J* = 8.8, 2.4, 2.2 Hz, 4 H, CH(Ar)), 6.77 (ddd, *J* = 8.8, 2.4, 2.2 Hz, 4 H, CH(Ar)).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 198.75 (s, 1 C, C(1)), 153.05 (s, 2 C, C(2, 3)), 131.75 (s, 4 C, C(Ar)), 131.54 (s, 8 C, C(Ar)), 131.13 (s, 2 C), 130.73 (s, 4 C, C(Ar)), 128.90 (s, 2 C), 124.93 (s, 2 C), 123.57 (s, 2 C), 122.43 (s, 2 C).

MALDI-MS (DCTB): m/z (%) 695.80 ($M^{\cdot -}$, 100%).

2.34 Synthesis of 2,2-bis(4-bromobenzyl)-1,3-dioxolane



78 **86**

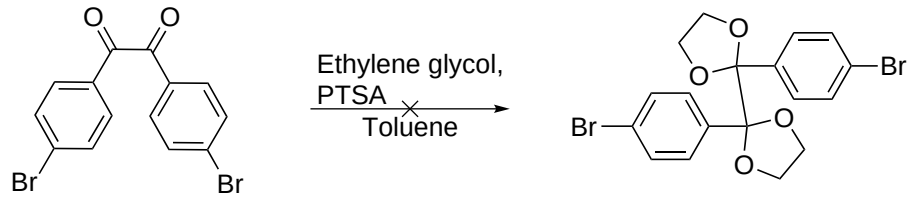
In a round flask with a Dean-Stark apparatus, the carbonyl compound (2 g, 5.43 mmol), ethylene glycol (0.9 ml, 16.3 mmol) and *p*-toluenesulfonic acid (31 mg, 0.16 mmol) in toluene (13 ml) were heated at reflux. After overnight stirring, the yellow mixture was washed three times with saturated $NaHCO_3$, three times with brine, dried over Na_2SO_4 and finally evaporated to dryness to give (2.01 g, 4.88 mmol, 90%) of a white compound.

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.39 (d, ^3J = 8.4 Hz, 4 H CH(**3**)), 7.13 (d, ^3J = 8.4 Hz, 4 H CH(**2**)), 3.45 (s, 4 H CH(1, 2)), 2.86 (s, 4 H CH(*1*)).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 135.31 (s, 2 C, C(**1**)), 132.45 (s, 4 C, C(**Ar**)), 130.96 (s, 4 C, C(**Ar**)), 120.51 (s, 2 C, C(**4**)), 110.24 (s, 2 C, C(3)), 65.43 (s, 2 C, C(1, 2)), 43.98 (s, 2 C, C(*1*)).

ESI-MS: m/z (%) 413.4 ($[M+H]^+$, 100%).

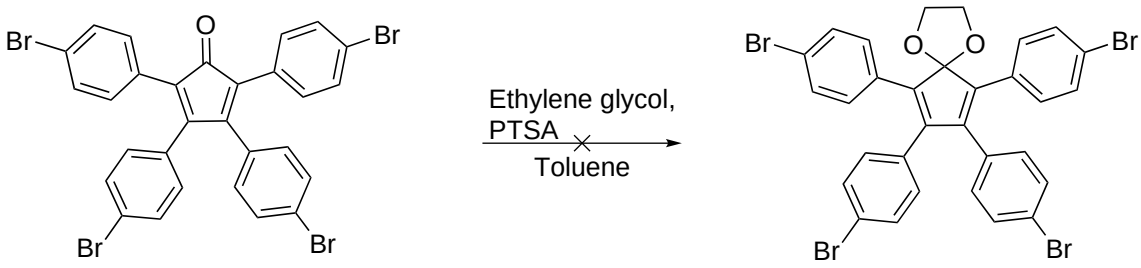
2.35 1,2-bis(4-bromophenyl)ethane-1,2-dione



79 **89**

In a round flask with a Dean-Stark apparatus, the dicarbonyl compound (1.1 g, 2.99 mmol), ethylene glycol (1 ml, 17.93 mmol) and p-toluenesulfonic acid (34 mg, 0.18 mmol) in toluene (8 ml) were heated at reflux during 19 hours. During the cooling until room temperature, a yellow solid precipitated. A recristallisation in toluene was tried as purification, what gave 922 mg of a yellow compound, which was the starting material with impurities.

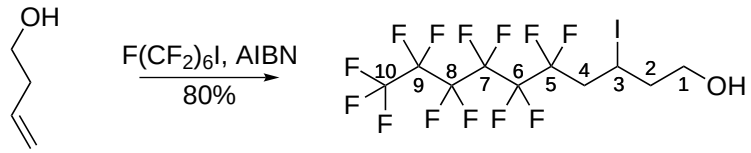
2.36 Synthesis of 6,7,8,9-tetrakis(4-bromophenyl)-1,4-dioxaspiro[4.4]nona-6,8-diene



80 **84**

In a round flask with a Dean-Stark apparatus, the starting material (424 mg, 0.61 mmol), ethylene glycol (101 ml, 1.82 mmol) and p-toluenesulfonic acid (3.46 mg, 0.02 mmol) dissolved in dry toluene (120 ml) were heated at reflux during 17 hours. Washing of the organic phase with a saturated bicarbonate solution and brine followed by drying over Na_2SO_4 and evaporation of the volatiles gave back the starting material quantitatively.

2.37 Synthesis of 5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-3-iododecan-1-ol



81 **91**

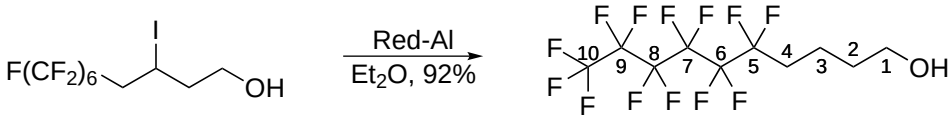
In a Schlenk tube under inert atmosphere the starting material (8.30 ml, 97 mmol), the perfluorohexyl iodide (17.57 ml, 81 mmol) and AIBN (0.664 g, 4.04 mmol) were degassed by the freezing/vacuum method. After 2 hours of stirring at 80 °C, the reaction mixture was cooled to room temperature and another portion of AIBN (0.664 g, 4.04 mmol) was added. Then the stirring was continued during 3 hours at 80 °C. The reaction mixture was poured into 180 ml of hot hexane and let cooled down first to room temperature, then to ~0 °C. The crystallized desired compound (33.48 g, 64.6 mmol, 80%) was isolated by filtration.

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 4.42 - 4.62 (m, 1 H, CH(3)), 3.69 - 3.96 (m, 2 H), 2.72 - 3.12 (m, 2 H), 1.94 - 2.14 (m, 2 H), 1.90 (s, 1 H, OH).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 62.49 (s, 1 C, C(1)), 42.31 (m, 1 C, C(2)), 41.92 (t, ^{2}J = 20.8 Hz, 1 C, C(4)), 16.67 (br. s., 1 C, C(3)).

EI-MS: m/z (%) 518 ($M^{\cdot+}$, <1%), 501 ($[M\text{-}OH]^{+}$, 4%), 391 ($[M\text{-}I]^{+}$, 100%), 373 ($[M\text{-}[I+H_2O]]$, 50%), 340.9 (64%).

2.38 Synthesis of 5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecan-1-ol



91 **82**

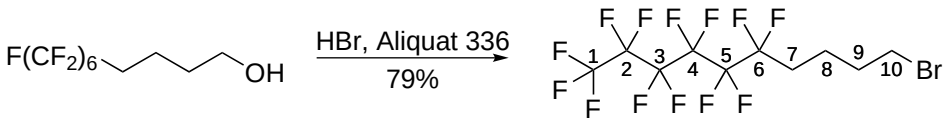
A solution of **91** (1.44 g, 2.78 mmol) in dry Et_2O (7 ml) was dropwise added to a magnetically stirred solution of RED-Al 70% in toluene(1.480 ml, 5.28 mmol) in dry Et_2O (23 ml). The mixture was agitated at room temperature during 4 hours. Then 20 ml of HCl 2 M were added and the two phases were separated. The aqueous phase was washed three times with diethyl ether and the combined organic phases were washed three times with brine, dried over Na_2SO_4 and finally evaporated to dryness to give a slightly yellow oil. A silica gel column chromatography with ether/pentane 7:3 as eluent allowed to obtain the desired product (1 g, 2.55 mmol, 92%).

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 3.70 (t, ^3J = 5.9 Hz, 2 H, CH(1)), 2.01 - 2.21 (m, 2 H, CH(4)), 1.52 - 1.79 (m, 4 H, CH(2, 3)).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 62.17 (s, 1 C, C(1)), 31.86 (s, 1 C, C(2)), 30.66 (t, ^2J = 22.5 Hz, 1 C, C(4)), 16.79 (t, ^3J = 4.0 Hz, 1 C, C(3)).

EI-MS: m/z (%) 391 ($[M-H]^+$, 4%), 375 ($[M-OH]^+$, 14%), 354.1 ($[M-OH-HF]^+$100%).

2.39 Synthesis of 10-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorodecane



82 **83**

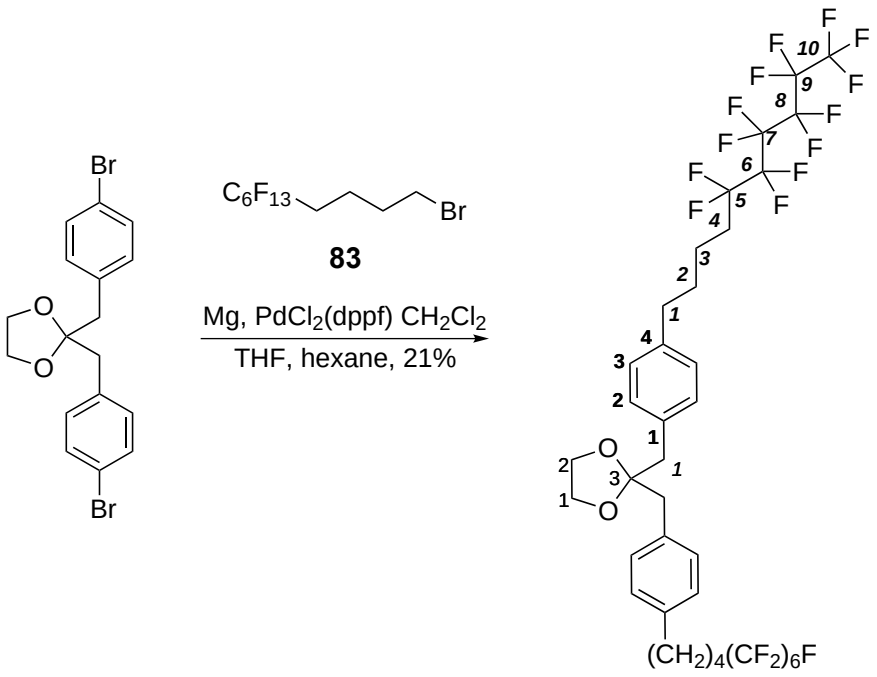
In a two necked flask with a condenser, the starting material (22.15 g, 56.5 mmol), Hydrobromic acid 48% (13.16 ml, 116 mmol) and Aliquat 336 (1.038 ml, 2.259 mmol) were agitated at 100 °C during 40 h. After extraction with Et_2O, the organic layer was washed with water, dried over Na_2SO_4 and evaporated to dryness to give a brown liquid. A filtration over a plug of silica gel with pentane/ether 9:1 followed by a silica gel column chromatography with pentane as eluent gave the brominated molecule (20.26 g, 44.5 mmol, 79%).

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 3.44 (t, ^3J = 6.4 Hz, 2 H, CH(10)), 2.02 - 2.21 (m, 2 H, CH(7)), 1.90 - 2.01 (m, 2 H), 1.73 - 1.86 (m, 2 H).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 32.47 (s, 1 C), 31.85 (s, 1 C), 30.04 (t, ^2J = 22.5 Hz, 1 C, C(7)), 19.05 (t, ^3J = 3.6 Hz, 1 C C(8)).

EI-MS: m/z (%) 375.1 ($[M-Br]^+$, 100%), 355.1 ($[M-[Br+HF]]^+$, 84%), 335.1 ($[M-[Br+2HF]]^+$, 24%).

2.40 Synthesis of 2,2-bis[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)benzyl]-1,3-dioxolane



86 **87**

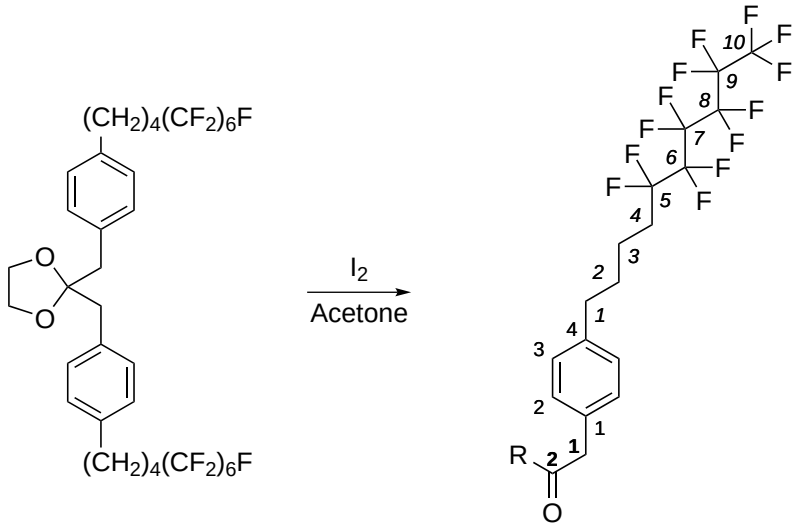
In a oven dried Schlenk tube under inert atmosphere, activated magnesium turnings (0.037 g, 1.534 mmol) were agitated during 1 hour and heated three times with a heat gun. At room temperature, hexane (1 ml) was added, as well as a solution of **83** (0.698 g, 1.534 mmol) in dry THF (1 ml). The mixture was heated at 75 °C for 2 hours (there was still some small magnesium turnings in the brown mixture, what showed that the Grignard reagent has not been totally formed). This mixture was diluted with dry THF (2 ml) and added to a suspension of **86** (0.158 g, 0.383 mmol) and (1,1'-Bis(diphenylphosphino)ferrocene)-dichloropalladium(II) CH_2Cl_2, (0.044 g, 0.061 mmol) in dry THF (1 ml) in a oven dried Schlenk tube. The mixture was then agitated at 75 °C during 67 hours. The red-brown mixture was cooled down to room temperature and quenched with methanol (5 ml). DCM was added to this solution, which was extracted with a saturated NH_4Cl solution (20 ml), washed with water (20 ml), dried over Na_2SO_4 and finally evaporated to dryness to give a brown oily mixture. Two silica gel column chromatographies (eluent: pentane/ether 8:2, then 9:1) gave finally the desired product (80 mg, 0.08 mmol, 21%).

^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.19 (d, ^3J = 7.5 Hz, 4 H, CH(**Ar**)), 7.07 (d, ^3J = 7.5 Hz, 4 H, CH(**Ar**)), 3.44 (s, 4 H, CH(*1*)), 2.86 - 2.97 (m, 4 H, CH(1, 2)), 2.63 (t, ^3J = 7.0 Hz, 4 H, CH(***1***)), 2.06 (d, *J*=5.5 Hz, 4 H, CH(***4***)), 1.58 - 1.77 (m, 8 H, CH(***2***, ***3***)).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 139.54 (s, 2 C, C(**4**), 134.20 (s, 2 C, C(**1**)), 130.80 (s, 4 C, C(**Ar**)), 127.84 (s, 4 C, C(**Ar**)), 110.88 (s, 1 C, C(3)), 65.38 (s, 2 C, C(1, 2)), 35.10 (s, 2 C, C(***1***)), 30.22 - 31.15 (m, 4 C, C(***4***, ***2***)), 19.47 - 19.97 (m, 2 C, C(***3***)).

EI-MS: m/z (%) 1002 ($M^{\cdot+}$, 1%), 537.5 ($[F(CF_2)_6(CH_2)_4PhCH_2CO_2C_2H_4]^+$, 100%), 465.6 ($[F(CF_2)_6(CH_2)_4PhCH_2]^+$, 100%).

2.41 Synthesis of 1,3-bis[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]acetone



R = $CH_2Ph(CH_2)_4(CF_2)_6F$

87 **88**

The starting material (0.031 g, 0.031 mmol) was dissolved in acetone (0.2 ml) and iodine (4 mg, 0.016 mmol) was added (a brown coloration was immediately observed). The mixture was agitated at room temperature during 3 hours. Acetone was then removed under vacuum. The residue was dissolved in DCM, washed with sodium thiosulfate 10% and brine, dried over $MgSO_4$ and concentrated. The crude desired compound was obtained quantitatively.

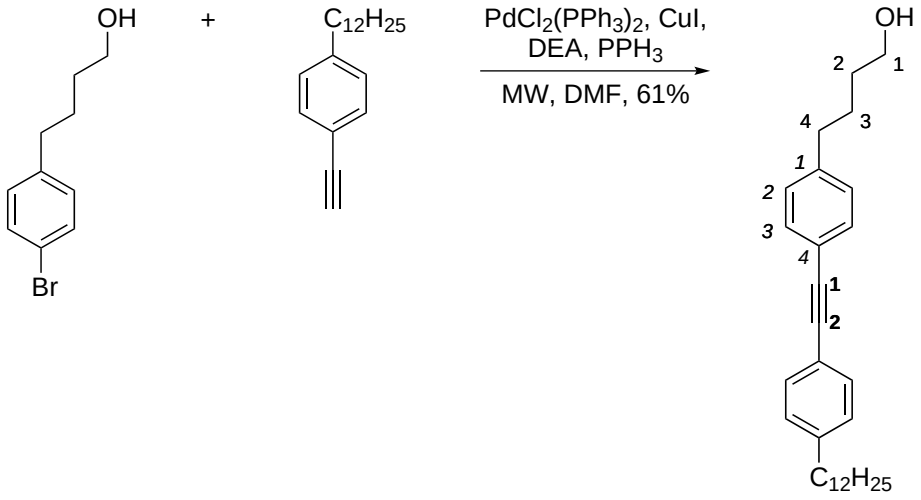
^{1}H NMR (360 MHz, $CDCl_3$): δ (ppm) 7.12 (d, ^3J = 7.8 Hz, 4 H, CH(Ar)), 7.06 (d, ^3J = 7.8 Hz, 4 H, CH(Ar)), 3.69 (s, 4 H, CH(**1**)), 2.64 (t, ^3J = 7.0 Hz, 4 H, CH(*1*)), 1.98 - 2.19 (m, 4 H, CH(*4*)), 1.54 - 1.78 (m, 8 H, CH(*2, 3*)).

^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 140.40 (s, 2 C, C(Ar)), 131.58 (s, 2 C, C(Ar)), 129.54 (s, 4 C, C(Ar)), 128.67 (s, 4 C, C(Ar)), 48.66 (s, 2 C, C(**1**)), 35.12 (s, 2 C, C(*1*)), 30.78 (s, 2 C, C(*2*)), 30.69 (t, ^2J = 22.5 Hz, 2 C, C(*4*)), 19.69 - 19.87 (m, 2 C, C(*3*)).

EI-MS: m/z (%) 959.2 ($M^{\cdot+}$, 4%), 170.6 ($[M\text{-}C_3H_5]^+$, 80%), 597.3 ($[M\text{-}(F(CF_2)_6(CH_2)_3)]^+$, 50%), 492.2 ($[M\text{-}(F(CF_2)_6(CH_2)_4\text{-}Ph\text{-}(CH_2))]^+$, 100%).

3 Synthesis of the alkylated sulfonic acid HBC

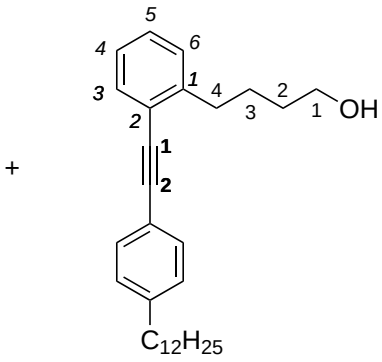
3.1 Synthesis of 4-{4-[(4-dodecylphenyl)ethynyl]phenyl}butan-1-ol



122
***o/p* mixture**

114

123



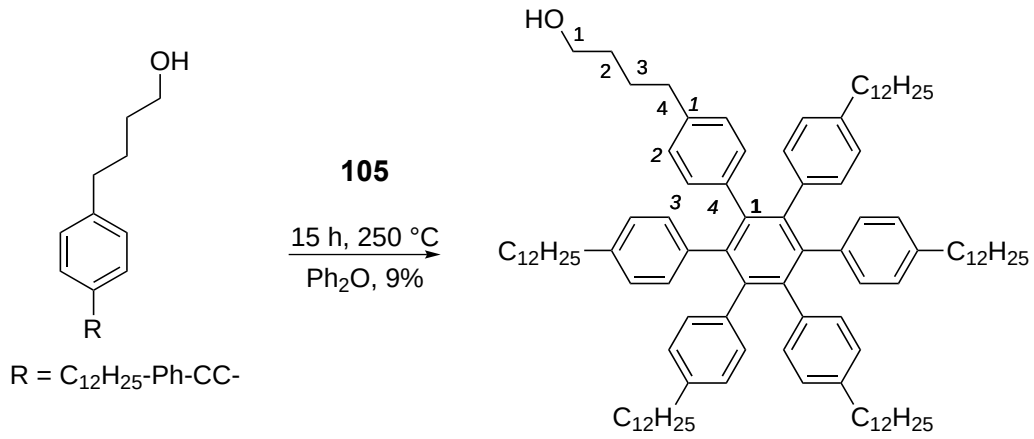
160

In an oven dried microwave tube under inert atmosphere 4-(4-bromophenyl)butan-1-ol (0.195 g, 0.851 mmol), 1-dodecyl-4-ethynylbenzene (0.230 g, 0.851 mmol), copper Iodide (7.13 mg, 0.037 mmol), triphenylphosphine (0.045 g, 0.170 mmol) and diethylamine (1.344 ml, 12.86 mmol) were suspended in DMF (0.473 ml). The mixture was then stirred in a microwave oven at 120 °C during 40 minutes. The mixture was separated between water and ether. Then the organic phase was washed with water, dried over $MgSO_4$ and evaporated to dryness, giving a brown liquid which was chromatographied over silica gel with pentane as eluent, then pentane/ether 8:2, and finally pentane/ether 2:1. The compound was collected with the third eluent mixture (0.22 g, 0.525 mmol, 61%), still containing some impurities.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.42 (d, ^3J = 8.2 Hz, 2 H, CH(Ar), **123**), 7.17 - 7.21 (m, 2 H, **160**), 7.13 (d, ^3J = 8.2 Hz, 2 H, CH(Ar), **123**), 6.98 - 7.05 (m, 2 H, **160**), 3.55 - 3.66 (m, 4 H, CH(1)), 2.70 - 2.76 (m, 2 H, CH(4), **160**), 2.52 - 2.66 (m, CH(4), **123**, **160**), 1.49 - 1.73 (m, CH(Alk)), 1.21 - 1.35 (m, CH(Alk)), 0.84 - 0.91 (m, CH(Alk)).

ESI-MS: m/z (%) 441.3 ($[M+Na]^+$).

3.2 Synthesis of 4-{4-[2,3,4,5,6(4-dodecylphenyl)phenyl]phenyl}butan-1-ol



123
***o/p* mixture**

124
***o/p* mixture**

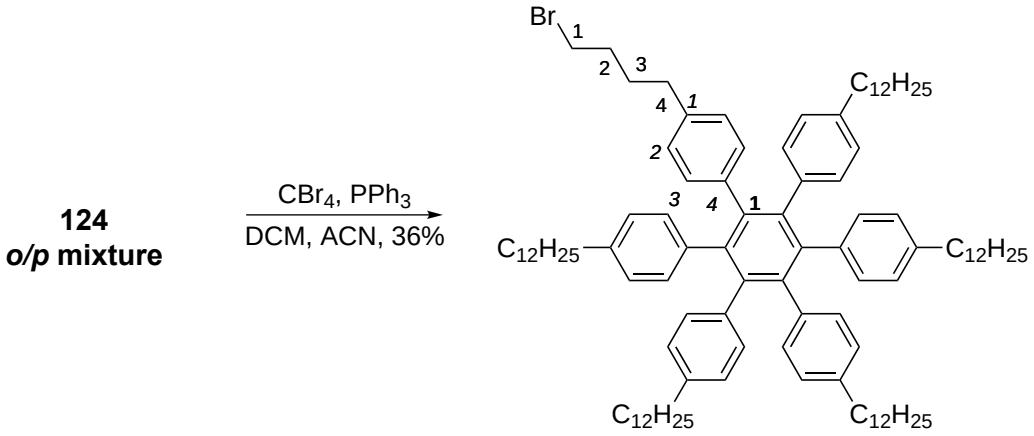
In a two necked flask under inert atmosphere a mixture of 2,3,4,5-tetrakis(4-dodecylphenyl)cyclopenta-2,4-dienone (1.337 g, 1.264 mmol) and 4-(4-((4-dodecylphenyl)ethynyl)phenyl)butan-1-ol (0.529 g, 1.264 mmol) in Ph_2O (2 ml) were heated at 250 °C during 20 hours. The solvent was removed by decantation with EtOH (2 times with ~60 ml). The brown oily liquid obtained was chromatographied on silica gel with pentane/DCM 6:4 as eluent (solid deposition), giving the desired compound (0.157 g, 0.108 mmol, 9%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.56 - 6.73 (m, 24 H, CH(Ar)), 3.52 (t, ^3J = 6.3 Hz, 2 H, CH(1)), 2.27 - 2.44 (m, 12 H, CH(4 + Alk)), 1.04 - 1.50 (m, CH(Alk)), 0.80 - 0.95 (m, 15 H, CH(Alk)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 139.88 - 140.60 (m, 6 H, C(Ar)), 139.04 (s, 6 C, C(**1**)), 137.96 - 138.46 (m, 6 C, C(Ar)), 131.38 (s, 24 C, C(Ar)), 125.95 - 126.82 (m, 24 C, C(Ar)), 62.71 (s, 1 C, C(1)), 13.73 - 35.76 (m, 63 C, C(Alk)).

MALDI-ICR-MS (DCTB): m/z (%) 1447.28 ($M^{\cdot+}$).

3.3 Synthesis of 4-{4-[2,3,4,5,6(4-dodecylphenyl)phenyl]phenyl}1-bromobutane

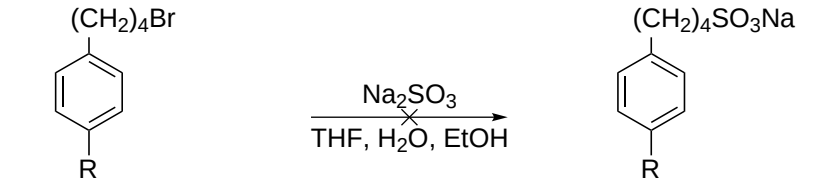


In a two necked flask under inert atmosphere, 4-(4''-dodecyl-3',4',5',6'-tetrakis(4-dodecylphenyl)-[1,1':2',1''-terphenyl]-4-yl)butan-1-ol (0.154 g, 0.106 mmol) was dissolved in DCM (1 ml) and perbromomethane (0.053 g, 0.159 mmol), triphenylphosphine (0.042 g, 0.159 mmol) and ACN (0.3 ml) were added. the reaction mixture was agitated at rt during 4 hours. Extraction with brine, drying of the organic phase (DCM) with $MgSO_4$ and concentration gave a brown solid. A silica gel column chromatography with pentane/dcm 8:2 gave the desired compound (0.058 g, 0.038 mmol, 36%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.45 - 6.82 (m, 24 H, CH(Ar)), 3.27 (t, ^3J = 6.5 Hz, 2 H, CH(1)), 2.25 - 2.46 (m, 12 H, CH(4 + Alk)), 0.79 - 1.48 (m, 119 H, CH(Alk)).

MALDI-ICR-MS (DCTB): m/z (%) 1509.15 ($M^{\cdot+}$).

3.4 Synthesis of sodium 1-[4-(butane-1-sulfonate)phenyl]-2,3,4,5,6-pentakis(dodecyl)benzene



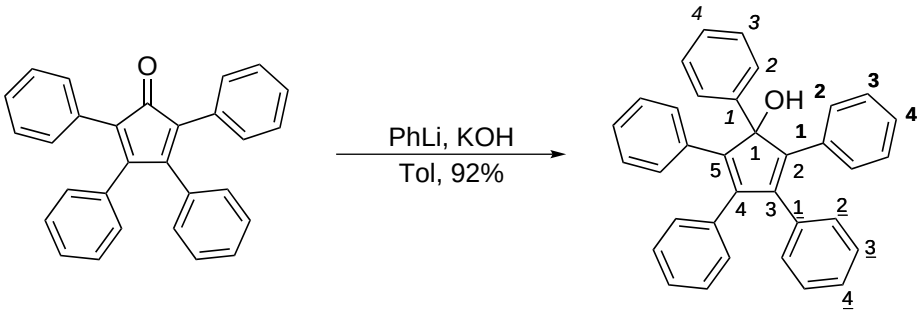
R = $(C_{12}H_{25}\text{-Ph})_5\text{-Ph}$ — **125** ***o/p* mixture**

R = $(C_{12}H_{25}\text{-Ph})_5\text{-Ph}$ — **126**

The starting material (67 mg, 0.044 mmol) and sodium sulfite (7 mg, 0.056 mmol) were dissolved in a mixture of H_2O (0.3 ml), THF (3 ml) and EtOH (9 ml) and irradiated at 180 °C during 12 hours. After classical work up, the starting material was recovered quantitatively.

4 Toward the oxidation of the pentaphenyl cyclopentadiene

4.1 Synthesis of 1,2,3,4,5-pentaphenylcyclopenta-2,4-dien-1-ol



134 **137**

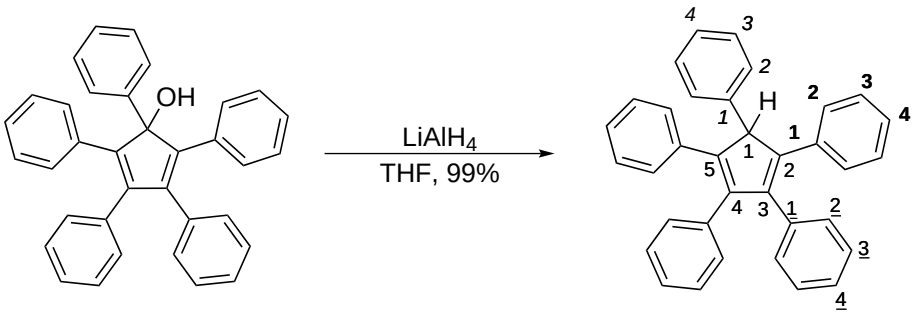
In a two necked flask under inert atmosphere, phenyllithium 1.9 M in buthylether (0.684 ml, 1.300 mmol) was slowly added to a dark red suspension of 2,3,4,5-tetraphenylcyclopenta-2,4-dienone (0.5 g, 1.300 mmol) in toluene (30 ml). The yellow solution was stirred during 1 hour and potassium hydroxide 0.9 M (6.00 ml, 5.40 mmol) was dropwise added. This emulsion was agitated during 72 hours. Water was then added and the organic compounds were extracted with ether. After drying with $MgSO_4$, the solvent was evaporated giving the desired compound **137** (0.552 g, 1.193 mmol, 92%) as a slightly brown solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.92 - 7.63 (m, 25 H, CH(Ar)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 147.94 (s, 2 C, C(3, 4)), 142.45, 140.17, 135.03, 133.82, 129.91 (s, 4 C, C(Ar)), 129.51 (s, 4 C, C(Ar)), 128.43 (s, 2 C, C(Ar)), 127.87 (s, 4 C, C(Ar)), 127.73 (s, 4 C, C(Ar)), 127.06 (s, 2 C, C(Ar)), 126.98 (s, 2 C, C(Ar)), 126.90 (s, 1 C, C(Ar)), 125.02 (s, 2 C, C(Ar)), 90.16 (s, 1 C, C(1)).

ESI-MS: m/z (%) 463.2 ($[M+H]^+$, 18%), 445.2 ($[M-OH]^+$, 100%).

4.2 Synthesis of 1,2,3,4,5-pentaphenylcyclopenta-2,4-diene



137 **139**

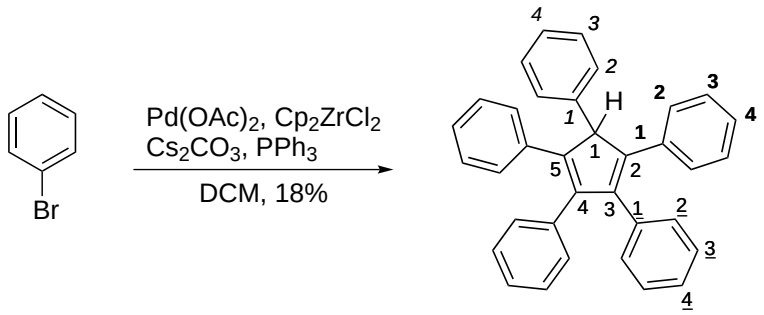
In a two necked flask under inert atmosphere, lithium aluminium hydride (0.057 g, 1.492 mmol) was added in one pot to a solution of **137** (0.276 g, 0.597 mmol) in THF (1.3 ml). After 2 hours, the reaction was quenched with water and the organic material was extracted with DCM. The organic phase was dried over $MgSO_4$ and evaporated to dryness giving **139** (0.264 g, 0.591 mmol, 99%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.93 - 7.24 (m, 25 H, CH(Ar)), 5.08 (s, 1 H, CH(1)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 146.51 (s, 2 C, C(3, 4)), 143.99, 138.06, 136.12, 135.78, 130.09 (s, 4 C, C(Ar)), 129.00 (s, 4 C, C(Ar)), 128.53 (s, 2 C, C(Ar)), 128.41 (s, 2 C, C(Ar)), 127.85 (s, 4 C, C(Ar)), 127.62 (s, 4 C, C(Ar)), 126.66 (s, 2 C, C(Ar)), 126.51 (s, 1 C, C(Ar)), 126.28 (s, 2 C, C(Ar)), 62.66 (s, 1 C, C(1)).

ESI-MS: m/z (%) 446.5 ($M^{\cdot+}$, 100%).

4.3 Synthesis of 1,2,3,4,5-pentaphenylcyclopenta-2,4-diene



111 **139**

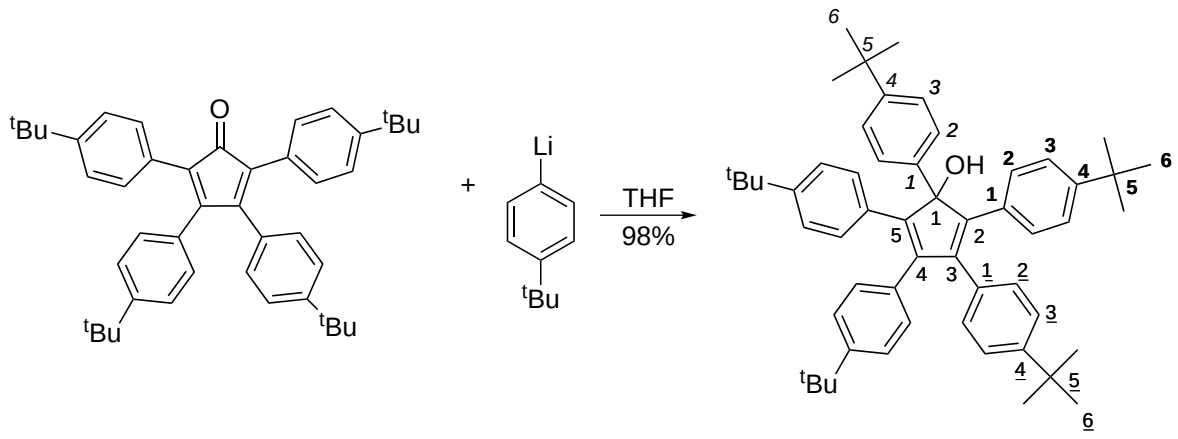
In a two necked flask under inert atmosphere, cesium carbonate (0.623 g, 1.911 mmol), diacetoxypalladium (9.01 mg, 0.040 mmol), triphenylphosphine (0.042 g, 0.159 mmol), di(cyclopenta-1,3-dien-1-yl)zirconium(IV) chloride (0.046 g, 0.159 mmol) and bromobenzene (0.201 ml, 1.911 mmol) were suspended in DMF (Volume: 3.18 ml). After 6 hours at 130 °C, a deep violet colour was observed. The violet mixture was let cooled down to rt and p-toluenesulfonic acid monohydrate (0.727 g, 3.82 mmol) and 10 ml DCM were added. The mixture turned to brown. After 10 minutes the mixture was filtrated through silica gel plug with DCM. Finally, a column chromatography (pentane/DCM 8:2) as eluent gave the desired compound **139** (0.025 g, 0.056 mmol, 18%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.93 - 7.24 (m, 25 H, CH(Ar)), 5.08 (s, 1 H, CH(1)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 146.51 (s, 2 C, C(3, 4)), 143.99, 138.06, 136.12, 135.78, 130.09 (s, 4 C, C(Ar)), 129.00 (s, 4 C, C(Ar)), 128.53 (s, 2 C, C(Ar)), 128.41 (s, 2 C, C(Ar)), 127.85 (s, 4 C, C(Ar)), 127.62 (s, 4 C, C(Ar)), 126.66 (s, 2 C, C(Ar)), 126.51 (s, 1 C, C(Ar)), 126.28 (s, 2 C, C(Ar)), 62.66 (s, 1 C, C(1)).

ESI-MS: m/z (%) 446.5 ($M^{\cdot+}$, 100%).

4.4 Synthesis of 1,2,3,4,5-pentakis(4-tert-butylphenyl)cyclopenta-2,4-dien-1-ol



133 **136** **138**

In a two necked flask under inert atmosphere, tert-butyllithium (0.127 g, 1.987 mmol, 1.6 M in pentane) was added at 0 °C to a solution of 1-bromo-4-(tert-butyl)benzene (0.157 ml, 0.903 mmol) in a THF (0.8 ml)/pentane (8.2 ml) mixture and let agitated at 0 °C during 15 minutes.

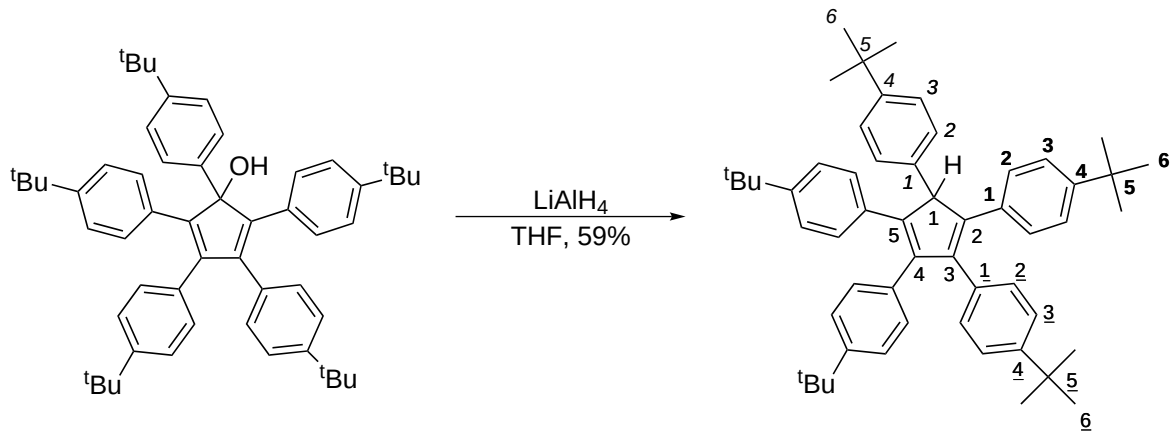
The previously prepared (4-(tert-butyl)phenyl)lithium (0.127 g, 0.903 mmol) solution was slowly added at rt to a solution of 2,3,4,5-tetrakis(4-(tert-butyl)phenyl)cyclopenta-2,4-dienone (0.5 g, 0.821 mmol) in toluene (10 ml). The yellow mixture was then agitated during 2 hours. Water was added as well as Et_2O to rinse the Schlenk tube. Then the two phases were separated and the organic one was washed with brine, dried over $MgSO_4$ and finally evaporated to dryness to give a yellow solid which was purified by a silica gel column chromatography with pentane/ DCM 2:1 as eluent giving the 1,2,3,4,5-pentakis(4-(tert-butyl)phenyl)cyclopenta-2,4-dienol (0.6 g, 0.807 mmol, 98%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.51 (m, 2 H, CH(Ar)), 7.24 - 7.28 (m, 2 H, CH(Ar)), 7.10 (m, 4 H, CH(Ar)), 6.98 - 7.03 (m, 8 H, CH(Ar)), 6.90 (m, 4 H, CH(Ar)), 1.28 (s, 9 H, CH(*6*)), 1.25 (s, 18 H, CH(^{t}Bu)), 1.19 (s, 18 H, CH(^{t}Bu)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 149.53, 149.26, 149.23, 146.73, 142.32, 137.77, 132.84, 131.01, 129.48 (s, 4 C, C(Ar)), 128.89 (s, 4 C, C(Ar)), 125.16 (s, 2 C, C(Ar)), 124.77 (s, 2 C, C(Ar)), 124.50 (s, 4 C, C(Ar)), 124.44 (s, 4 C, C(Ar)), 90.01 (s, 1 C, C(1)), 34.42 (s, 2 C, C(^{t}Bu)), 34.36 (s, 3 C, C(^{t}Bu)), 31.37 (s, 3 C, C(*6*)), 31.29 (s, 6 C, C(^{t}Bu)), 31.17 (s, 6 C, C(^{t}Bu)).

ESI-MS: m/z (%) 1508.99 ([2M + Na]$^+$, 11%)765.50 ([M + Na]$^+$, 100%).

4.5 Synthesis of 1,2,3,4,5-pentakis(4-tert-butylphenyl)cyclopenta-2,4-diene



138 **140**

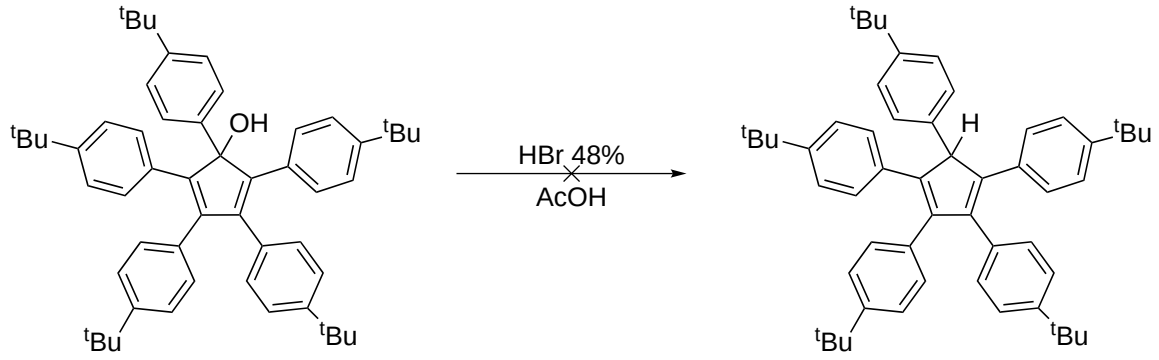
In a two necked flask under inert atmosphere, $LiAlH_4$ (0.060 g, 1.568 mmol) was added portionwise to a solution of **138** (0.466 g, 0.627 mmol) in THF (2.5 ml). The reaction mixture was agitated at rt during 3 hours, quenched with water and the organic material was extracted with DCM. After drying of the organic phase with $MgSO_4$ and evaporation of the solvent, the crude yellow solid was purified by a silica gel column chromatography (eluent pentane/DCM 9:1) giving the desired compound **140** (0.27 g, 0.371 mmol, 59.2%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.14 - 7.23 (m, 4 H, CH(Ar)), 7.11 (m, 4 H, CH(Ar)), 6.96 - 7.04 (m, 8 H, CH(Ar)), 6.91 (m, 4 H, CH(Ar)), 5.06 (s, 1 H, CH(1)), 1.25 (s, 18 H, CH(^{t}Bu)), 1.23 (s, 9 H, CH(*6*)), 1.19 (s, 18 H, CH(^{t}Bu)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 149.09, 148.70, 148.53, 145.07, 144.11, 135.95, 133.95, 133.03, 129.64 (s, 4 C, C(Ar)), 128.26 (s, 4 C, C(Ar)), 127.96 (s, 2 C, C(Ar)), 125.31 (s, 2 C, C(Ar)), 124.49 (s, 4 C, C(Ar)), 124.43 (s, 4 C, C(Ar)), 61.29 (s, 1 C, C(1)), 34.39 (s, 2 C, C(^{t}Bu)), 34.30 (s, 3 C, C(^{t}Bu)), 31.37 (s, 27 C, C(^{t}Bu)), 31.21 (s, 18 C, C(^{t}Bu)).

MALDI-ICR-MS: m/z (%) 726.52 ($M^{\cdot+}$, 100%), 711.49 ($[M\text{-}CH_3]^+$, 70%).

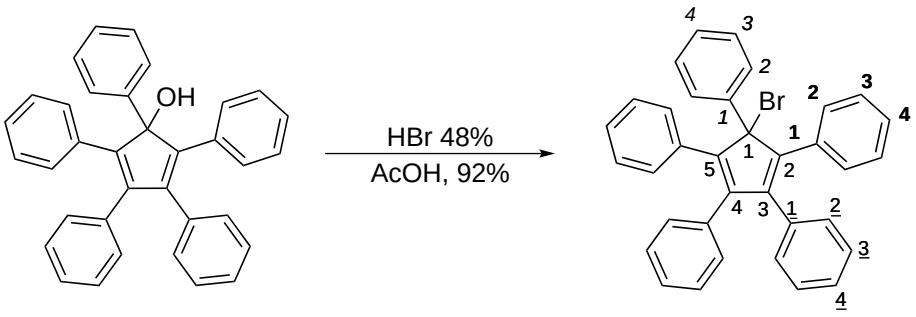
4.6 Synthesis of 1-bromo-[1,2,3,4,5-pentakis(4-tert-butylphenyl)cyclopenta-2,4-diene]



138 **146**

In a two necked flask under inert atmosphere, 1,2,3,4,5-pentakis(4-(tert-butyl)phenyl)cyclopenta-2,4-dienol (0.2 g, 0.269 mmol) was dissolved in acetic acid (8 ml). at 60 °C, only a small quantity of the starting material was dissolved. The dissolution was not improved at 100 °C. Therefore, Aliquat 336 (4.94 µl, 10.77 µmol, 1 drop) was added. Then a solution of HBr 48% (0.498 ml, 4.40 mmol) in acetic acid (1.880 ml) was dropwise added. After 5 hours, the reaction mixture was cooled down to room temperature. Then water was added and the yellow solid was filtrated off and dried under vacuum. Only the starting material (33%) and small impurities were collected back after a silica gel column chromatography with pentane/dcm 7:3 as eluent.

4.7 Synthesis of (1-bromo-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-yl)benzene



137 **145**

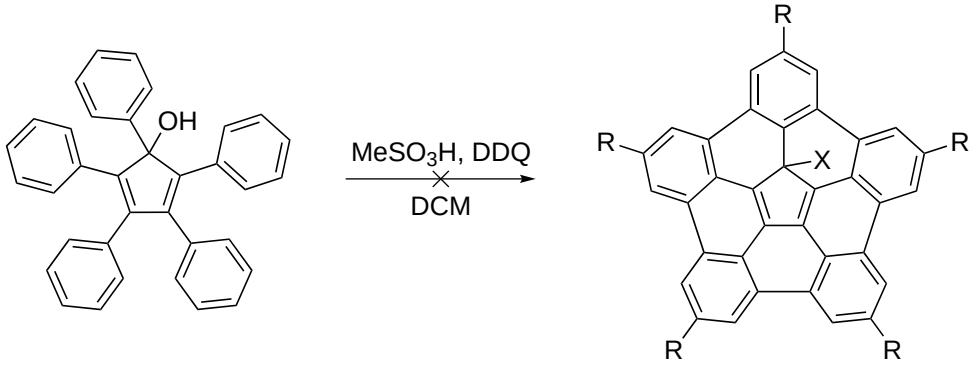
In a two necked flask under inert atmosphere, 1,2,3,4,5-pentaphenylcyclopenta-2,4-dienol (4 g, 8.65 mmol) was dissolved in acetic acid (160 ml). At 60 °C, a solution of HBr 48% (16.00 ml, 141 mmol) in acetic acid (60.0 ml) was dropwise added (60 ml/h). The stirring was continued at 100 °C during 2 hours (after 20 minutes, a precipitate was observed in the reaction flask). After cooling in an ice bath, water was added and the orange solid was filtrated off, rinsed with water and dried under vacuum. A silica gel column chromatography with pentane/dcm 2:1 as eluent gave the desired compound (4.170 g, 7.94 mmol, 92%) as an orange solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.88 - 7.53 (m, 25 H, CH(Ar)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 148.26 (s, 2 C, C(3, 4)), 141.78, 135.79, 134.63, 134.09, 130.40 (s, 4 C, C(Ar)), 130.00 (s, 4 C, C(Ar)), 128.34 (s, 2 C, C(Ar)), 127.81 (s, 1 C, C(Ar)), 127.71 (s, 4 C, C(Ar)), 127.44 (s, 2 C, C(Ar)), 127.37 (s, 4 C, C(Ar)), 127.17 (s, 2 C, C(Ar)), 127.05 (s, 2 C, C(Ar)), 76.56 (s, 1 C, C(1)).

MALDI-ICR-MS (DCTB): m/z (%) 445.19 ($[M-Br]^+$, 100%), 367.15 ($[M-Br-Ph]^{\cdot+}$, 83%).

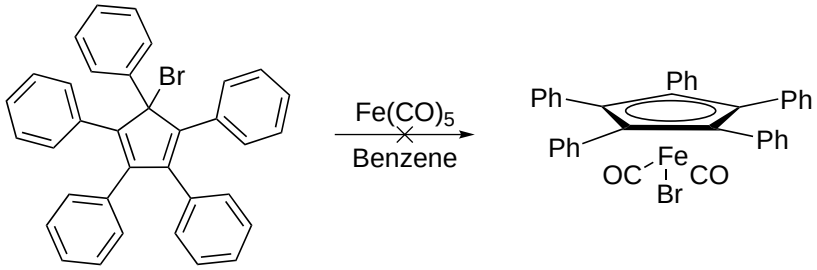
4.8 Synthesis of the 15fH-benzo[5,6]acenaphtho[4,3,2,1,8,7-pqrstuv]dibenzo[fg,ij]pentaphene derivative



137 **32**

In a two necked flasked under inert atmosphere, 1,2,3,4,5-pentaphenylcyclopenta-2,4-dienol (0.125 g, 0.270 mmol) was dissolved in DCM (3 ml) and methanesulfonic acid (0.3 ml, 4.62 mmol) (10 % vol/DCM) was added. A deep red color was observed. Then DDQ (0.307 g, 1.351 mmol) was added at 0 °C and agitated during 2 hours. A violet coloration was first observed turning in brown green after a while. The reaction mixture was quenched with a saturated solution of $NaHCO_3$. A decoloration in a yellow mixture was observed during the addition. The aqueous phase was extracted with DCM. Finally, the organic layer was washed with a sat $NaHCO_3$ solution, dried over $MgSO_4$ and evaporated to dryness giving a mixture of unidentified compounds after filtration over silica gel with DCM.

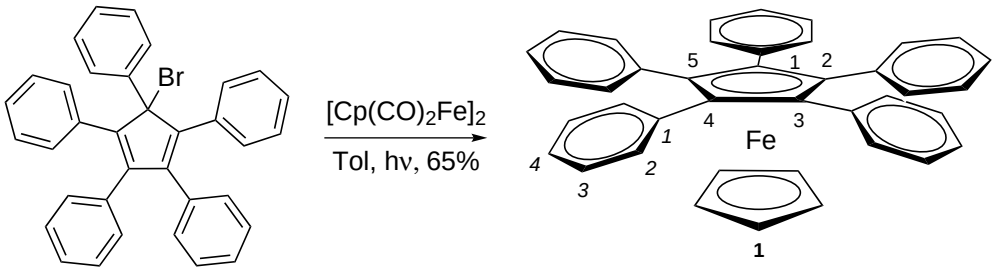
4.9 Complexation of the 1-bromo-[(1,2,3,4,5-pentapheny)-cyclopentadiene] on iron pentacarbonyl]



145 **151**

In a round flask under inert atmosphere, iron pentacarbonyl (0.080 ml, 0.589 mmol) was added to a solution of **145** (0.258 g, 0.491 mmol) in benzene (20 ml). The colour of the reaction mixture immediately turned to dark red. After 22 hours of stirring at room temperature, the reaction mixture was dried under vacuum (40 °C, 200 mbar). Neither recristallisation from DCM/hexane nor silica gel column chromatography gave the desired compound. Only the product from the exchange of the bromine by an alcohol function was observed by ESI-MS.

4.10 Synthesis of 1,2,3,4,5-pentaphenylferrocene



145 **154**

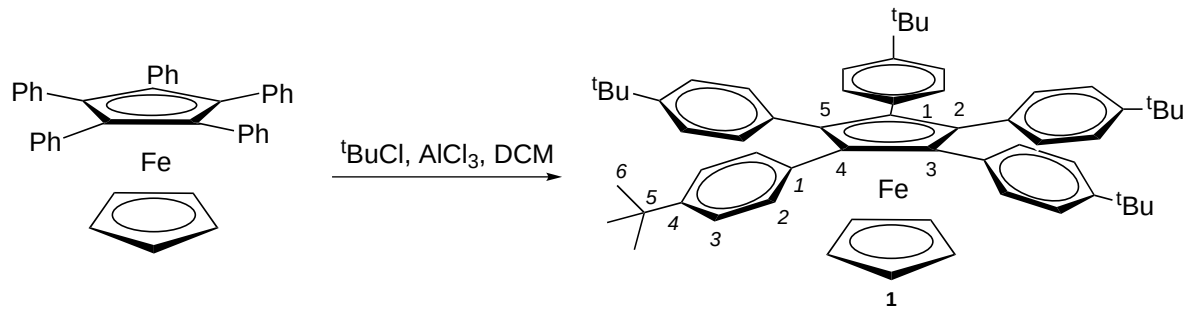
In a Schlenk tube under inert atmosphere equipped with a balloon, the starting material **145** (0.494 g, 0.94 mmol) and the cyclopentadienyl iron(II) dicarbonyl dimer (0.342 g, 0.966 mmol) were dissolved in toluene (190 ml). The Schlenk tube and a mercury lamp were partially immerged in water to regulate the temperature (~rt) during the reaction. After 70 hours, the reaction was stopped and the reaction mixture was concentrated under reduced pressure. The crude material was then suspended in pentane/dcm 7:3 and elute over a plug of silica gel. The desired compound was obtained as a pure orange solid (0.35 g, 0.618 mmol, 66%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.99 - 7.18 (m, 25 H, CH(Ar)), 4.21 (s, 5 H, CH(**1**)).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 136.06 (s, 5 C, C(*1*)), 132.32 (s, 10 C, C(Ar)), 127.06 (s, 10 C, C(Ar)), 126.05 (s, 5 C, C(Ar)), 87.68 (s, 5 C, C(1, 2, 3, 4, 5)), 75.15 (s, 5 C, C(**1**)).

MALDI-ICR-MS (DCTB): m/z (%) 566.17 ([$M^{\cdot+}$, 100%).

4.11 Synthesis of 1,2,3,4,5-(4-*tert*-butylpentaphenyl)ferrocene



154 **161**

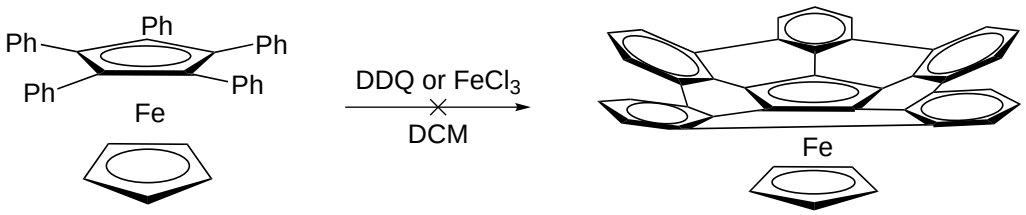
In a two necked flask under inert atmosphere, aluminium chloride (0.031 g, 0.229 mmol) was added to a solution of **154** (0.130 g, 0.229 mmol) and 2-chloro-2-methylpropane (0.303 ml, 2.75 mmol) in DCM (5 ml) at 0 °C. A direct dark brown coloration was observed. Several other $AlCl_3$ additions (1 eq) were necessary to complete the reaction. After overnight stirring at rt, the reaction mixture was poured on ice. The organic material was extracted with DCM and the combined organic phases were dried over $MgSO_4$ and evaporated to dryness. A silica gel column chromatography with first pentane, then pentane/ether 9:1 and finally ether gave the desired product in a mixture of similar compounds (different levels of alkylation). No yield could therefore be given.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.82 - 7.20 (m, CH(*2*, *3*)), 4.02 - 4.29 (m, CH(**1**)), 1.12 - 1.39 (m, CH(*6*)), 0.87 - 1.12 (m).

^{13}C NMR (75 MHz, $CDCl_3$): d (ppm) 147.88 - 149.02 (m, 5 C), 132.97 - 134.01 (m, 5 C), 131.46 - 132.46 (m, 10 C), 123.11 - 124.21 (m, 10 C), 87.16 - 87.71 (m, 5 C), 74.78 - 75.40 (m, 5 C), 34.30 - 34.51 (m, 5 C), 31.14 - 31.51 (m, 15 C).

MALDI-ICR-MS (DCTB): m/z (%) 1014.66 ([M + 3 ^{t}Bu]$^{\cdot+}$, 16%), 958.61 ([M + 2 ^{t}Bu]$^{\cdot+}$, 64%), 902.54 ([M+ ^{t}Bu]$^{\cdot+}$, 100%), 846.48 (M$^{\cdot+}$, 61%), 790.42 ([M - ^{t}Bu]$^{\cdot+}$, 17%).

4.12 Oxidation of the 1,2,3,4,5-(pentaphenyl)ferrocene

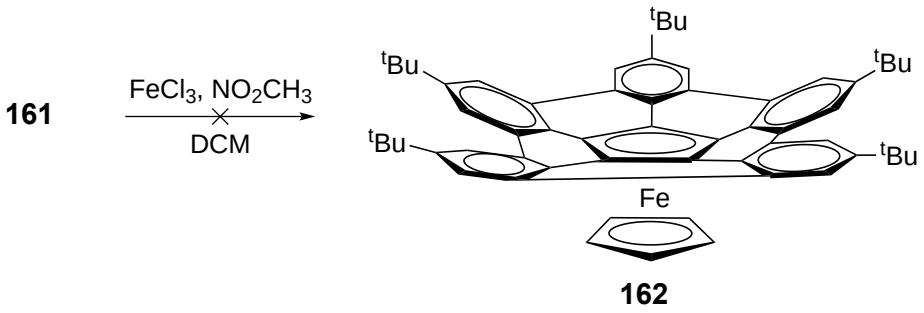


154 **155**

Method I: In a two necked flask under inert atmosphere the complex **154** (0.05 g, 0.088 mmol) was dissolved in DCM (8.83 ml). At 0 °C, DDQ (0.120 g, 0.530 mmol) was added. The reaction mixture immediately turned to a deep red colour. After stirring at 0 °C during 20 minutes (start at 9h40), the stirring was continue for 3 hours. A TLC with pentane/dcm 7:3 as eluent showed no more starting material. the stirring was continued for 2 hours. Then sat.$NaHCO_3$ was added. After extraction with DCM, drying over $MgSO_4$ and concentration, only the reduced Fe(I) compound (50% of the starting material mass) was observed. The rest was lost during the work up (certainly in the aqueous phase).

Method II:In a three necked flask under inert atmosphere equipped to bubble Ar during all the reaction, a solution of iron(III) chloride (2 g, 12.33 mmol) in nitromethane (13.62 ml) was dropwise added (40 ml/h) to a 40 °C solution of cyclopenta-2,4-dien-1-yl(1,2,3,4,5-pentaphenylcyclopenta-2,4-dien-1-yl)iron (0.135 g, 0.238 mmol) in DCM (34.0 ml). After 5 hours at 40 °C, the black reaction mixture was cooled down to rt and cold methanol (50 ml) was added. The black material obtained was filtrated, rinsed with cold methanol and dried under vacuum. A blue fluorescence was detected in solution, but a very small solubility was observed in common solvents. The NMR spectrum (1H and 13C) gave no product peaks. MALDI-MS showed only the starting complex.

4.13 Oxidation of the 1,2,3,4,5-(4-tert-butylpentaphenyl)ferrocene



In a three necked flask under inert atmosphere equipped to bubble Ar during all the reaction, A solution of iron(III) chloride (1 g, 6.17 mmol) in nitromethane (6.75 ml) was dropwise added (40 ml/h) to a 40 °C solution of cyclopenta-2,4-dien-1-yl(1,2,3,4,5-pentakis(4-(tert-butyl)phenyl)cyclopenta-2,4-dien-1-yl)iron (0.1 g, 0.118 mmol) in DCM (16.87 ml). After 6 hours at 40 °C, the black reaction mixture was cooled down to rt and cold methanol (50 ml) was added. The black material obtained was filtrated, rinsed with cold methanol and dried under vacuum. The obtained brown solid was insoluble in all common solvents, and therefore only MALDI-MS was recorded, showing the starting complex and other impurities.

VI. Bibliography

1 Bibliography

1 Website, www.gov.gg/ccm/cms-service/download/asset/?asset_id=11488047.

2 Total primary energy supply © OECD/IEA **2010**.

3 Share of total primary energy supply in 2008 © OECD/IEA **2010**.

4 H. Akasaka, T. Takahata, I. Toda ,H. Ono, S. Ohshio, S. Himeno, T. Kokubu, H. Saitoh *Int. J. Hydrogen Energy* **2011**, *36*, 580 - 585.

5 P. Atkins, L. Jones *CHIMIE molécules, matières, métamorphose*, trad. de la 3ème Ed., DeBoeck Université, **1998**.

6 Website, www.dlr.de/en/desktopdefault.aspx/tabid-1/86_read-14380/.

7 A. Currao *Chimia* **2007**, *61*, 815 - 819.

8 F. E. Osterloh *Chem. Mater.* **2008**, *20*, 35–54.

9 Website, http://www.biopetroleo.com/.

10 Y. Yürüm, A. Taralp, T. N. Veziroglu *Int. J. Hydrogen Energy* **2009**, *34*, 3784 - 3798.

11 C. Davis, B. Edelstein, B. Evenson, A. Brecher, D. Cox *Hydrogen Fuel Cell Vehicle Study*,**1993**, Report Prepared for the Panel on Public Affairs (POPA), American Physical Society.

12 K. Atkinson, S. Roth, M. Hirscher, W. Grünwald *Fuel Cells Bulletin* **2001**, *4*, 9 - 12.

13 Y. Wu *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **2003**, *48*, 940.

14 L. J. Murray, M. Dinca, J. R. Long *Chem. Soc. Rev.* **2009**, *38*, 1294 - 1314.

15 S. S. Kaye, A. Dailly, O. M. Yaghi, J. R. Long *J. Am. Chem. Soc.* **2007**, *129*, 14176 - 14177.

16 M. Dinca , A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann, J. R. Long *J. Am. Chem. Soc.* **2006**, *128*, 16876 - 16883.

17 A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. s. Bethune, M. J. Heben *Nature* **1997**, *386*, 377 - 379.

18 L. G. Scanlon, P. B. Balbuena, Y. Zhang, G. Sandi, C. K. Back, W. A. Feld, J. Mack, M. A. Rottermayer, J. L. Riepenhoff *J. Phys. Chem. B* **2006**, *110*, 7688 - 7694.

19 L. Schlapbach, A. Züttel *Nature* **2002**, *414*, 353 - 358.

20 Florian-Patrice Nagel, *DISS. ETH NO. 17856*, **2008.**

21 James Larminie, Andrew Dicks, *Fuel Cell Systems Explained 2nd Ed.*, **2003**, Wily.

22 Anne-Claire Dupuis *Pro. Mater. Sci.* **2011**, *56*, 289 - 327.

23 S. J. Peighambardoust, S. Rowhanazamir, M. Amjadi *Int. J. Hydorgen Energy* **2010**, *35*, 9349 - 9384.

24 Jochen Meier-Haack et al. *Sep. Purif. Technol.* **2005**, *41*, 207 - 220.

25 I. Kim, O. H. Han, S. A. Chae, Y. Paik, S.-H. Kwon, K.-S. Lee, Y.-E. Sung, H. Kim *Angew. Chem. Int. Ed.* **2011**, *50*, 2270 - 2274.

26 S. Thiers *Cours de piles a combustible, EPF - 5ème année*, **2009**.

27 A. Biyikoglu *Int. J. Hydrogen Energy* **2005**, *30*, 1181 - 1212.

28 C. He, S. Desai, G. Brown, S. Bollepalli *The Electrochemical Society Interface* **2005**, 41 - 44.

29 T. R. Ralph, M. P. Hogarth *Platinum Metal Rev.* **2002**, *46*, 117 - 135.

30 Erich Gülzow *J. Power Sources* **1996**, *61*, 99 - 104.

31 T. Alleau *Mémento de l'Hydrogène FICHE 5.2.5,* rév. **2004**.

32 S. Banerjee, D. E. Curtin *J. Fluorine Chem.* **2004**, *125*, 1211 - 1216.

33 Q. Li, R. He, J. O. Jensen, N. J. Bjerrum *Chem. Mater.* **2003**, *15*, 4896-4915.

34 B. Wahdame, D. Candusso, X. François, F. Hare, M.-C. Péra, D. Hissela, J.-M. Kauffmann *Int. J. Hydorgen Energy* **2007**, *32*, 4523 - 4536.

35 EG&G Technical Services, Inc. *Fuel Cell Handbook, 7th Ed.*, **2004**.

36 Honda *Press Information Honda Fuel Cell Power FCX* **2004**.

37 Website, http://www.kkg.ch/fr/i/intro.html.

38 Website, http://www.ballard.com/Default.aspx.

39 G. Crawley, Proton Exchange Membrane (PEM) Fuel Cell, *Fuel Cell Today* **2006**.

40 K. D. Kreuer, S. J. Paddison, E. Spohr, M. Schuster *Chem Rev* **2004**, *41*, 104, 4638 - 4678.

41 N. W. Deluca, Y. A. Elabd J. Polym. Sci. Part B Polym. Phys. 2006, 41, 2201 - 2225.

42 R. Souzy, B. Ameduri *Prog. Polym. Sci.* **2005**, *30*, 644 - 687.

43 K. A. Mauritz, R. B. Moore *Chem. rev.* **2004**, *104*, 4535-4585.

44 F. Toulgoat, B. R. Langlois, M. Médebielle, J.-Y. Sanchez *J. Org. Chem.* **2007**, *72*, 9046 - 9052.

45 G. Gebel *Polymer* **2000**, **41**, 5829 - 5838.

46 Carla Heitner-Wirguin, *J. Membrane Sci.* **1996**, *120*, 1 - 33.

47 T. A. Zawodzinski, J. Davey, J. Valerio, S. Gottesfled *Electrochem. Acta*, **1995**, *40*, 297 - 302.

48 C. R. Greaves, S. P. Bond, W. R. McWhinne *Polyhedron*, **1995**, *14*, 3635 - 3639.

49 T. Sancho, J. Soler, M.P. Pina *J. Power Sources* **2007**, *169*, 92 - 97.

50 C. Chen, T. F. Fuller *Polym. Degrad. Stab.* **2009**, *94*, 1436 - 1447.

51 C. Chen, G. Levitin, DW. Hess, TF. Fuller *J. Power Sources* **2007**, *169*, 288 - 295.

52 J. Qiao, M. Saito, K. Hayamizu, T. Okada *J. Electrochem. Soc.* **2006**, *153*, A967 - 74.

53 M. Danilczuk, F. D. Coms, S. Schlick *J. Phys. Chem. B* **2009**, *113*, 8031 - 8042.

54 A. F. Parsons *An introduction to free radical chemistry* **2000**, Ed. Blackwell Science.

55 L. Ghassemzadeh, K.-D. Kreuer, J. Maier, K. Müller *J. Phys. Chem. C* **2010**, *114*, 14635 - 14645.

56 D. E. Curtin, R. D. Lousenberg, T. J. Henry, P. C. Tangeman, M. E. Tisack *J. Power Sources* **2004**, *131*, 41 - 48.

57 L. Akbarian-Feizi, S. Mehdipour-Ataei, H- Yeganeh *Int. J. Hydrogen Energy* **2010**, *35*, 9385- 9397.

58 Y. Yin, O. Yamada, K. Tanaka, and K.-I. Okamoto *Polym J.* **2006**, *38*, 197 - 219.

59 T. Higashihara, k. Matsumoto, M. Ueda *Polymer*, **2009**, *50*, 5341 - 5357.

60 K. Nakabayashi, K. Matsumoto, M. Ueda *J. Polym. Sci. Part A Polym. Chem.* **2008**, *46*, 3947 - 57.

61 S. Matsumura, A. R. Hlil, C. Lepiller, J. Gaudet, D. Guay, Z. Shi, A. S. Hay et al. *Macromolecules* **2008**, *41*, 281 - 284.

62 S. Matsumura, A. R. Hlil, C. Lepiller, J. Gaudet, D. Guay, Z. Shi, A. S. Hay et al. *Macromolecules* **2008**, *41*, 277 - 280.

63 S. Matsumura, A. R. Hlil, N. Du, C. Lepiller, J. Gaudet, D. Guay, Z. Shi, A. S. Hay et al. *J. Polym. Sci. Part A Polym. Chem.* **2008**, *46*, 3860 - 3868.

64 S. Matsumura, A. R. Hlil, A. S. Hay *J. Polym. Sci. Part A Polym. Chem.* **2008**, *46*, 6365 - 6375.

65 M. Schuster, C. C. de Araujo, V. Atanasov, H. T. Andersen Macromolecules 2009, 42, 3129-3137.

66 Klaus-Dieter Kreuer,*,‡ and Joachim Maier

67 S. M. Haile, D. A. Boysen, C. R. I. Chisholm, R. B. Merle *Nature*, **2001**, *410*, 910 - 913.

68 C. Laberty-Robert, K. Vallé, F. Pereira, C. Sanchez *Chem. Soc. Rev*. **2011**, *40*, 961 - 1005.

69 Y. Ye, C. C. Ahn, C. Witham, B. Fultz, J. Liu, A. G. Rinzler, D. Colbert, K. A. Smith, R. E. Smalley *Appl. Phys. Lett.* **1999**, *74*, 2307 - 2309.

70 M. Shiraishi, T. Takenobu, A. Yamada, M. Ata, H. Kataura *Chem. Phys. Lett.* **2002**, *358*, 213 - 218.

71 Website, nanopedia.case.edu.

72 A. Fujiwara, K. Ishii, H. Suematsu, H. Kataura, Y. Maniwa, S. Suzuki, Y. Achiba *Chem. Appl. Lett.* **2000**, *336*, 205.

73 W. E. Barthe, R. G. Lawton *J. Am. Chem. Soc.* **1966**, *88*, 380 - 381.

74 R. G. Lawton, W. E. Barthe *J. Am. Chem. Soc.* **1971**, *93*, 1730 - 1745.

75 L. T. Scott, M. M. Hashemi, D. T. Meyer, H. B. Warren *J. Am. Chem. Soc.* **1991**, *113*, 7082 - 7084.

76 T. J. Seiders, K. K. Baldridge, J. S. Siegel *J. Am. Chem. Soc.* **1996**, *118*, 2754 - 2755.

77 V. M. Tsefrikas, L. T. Scott *Chem. Rev.* **2006**, *106*, 4868–4884.

78 L. T. Scott, M. M. Boorum, B. J. McMahon, S. Hagen, J. Mack, J. Blank, H. Wegner, A. de Meijere *Science* **2002**, *295*, 1500.

79 A. Sygula, P. W. Rabideau *J. Am. Chem. Soc.* **1999**, *121*, 7800 - 7803.

80 a) T. J. Seiders, K. K. Baldridge, E. L. Elliott, G. H. Grube, J. S. Siegel *J. Am. Chem. Soc.* **1999**, *121*, 7439–7440; b) T. J. Seiders, E. L. Elliott, G. H. Grube, J. S. Siegel *J. Am. Chem. Soc.* **1999**, *121*, 7804–7813.

81 Y.-T. Wu, J. S. Siegel *Chem. Rev*. **2006**, *106*, 4843–4867.

82 A. Sygula *Eur. J. Org. Chem.* **2011**, 1611 - 1625.

83 F. J. Lovas, R. J. McMahon, J.-U. Grabow, M. Schnell, J. Mack, L. T. Scott, R. L. Kuczkowski *J. Am. Chem. Soc.* **2005**, *127*, 4345 - 4349.

84 H. Becker, G. Javahery, S. Petrie, P.-C. Cheng, H. Schwarz, L. T. Scott, D. K. Bohme *J. Am. Chem. Soc.* **1993**, *115*, 11636 - 11637.

85 a) J. S. Siegel, K. K. Baldridge, A. Linden, R. Dorta *J. Am. Chem. Soc.* **2006**, *128*, 10644 - 10645; b) H. B. Lee, P.l R. Sharp *Organometallics*, **2005**, *24*, 4875 - 4877.

86 L. G. Scanlon, P. B. Balbuena, Y. Zhang, G. Sandi, C. K. Back, W. A. Feld, J. Mack, M. A. Rottmayer, J. L. Riepenhoff *J. Phys. Chem. B* **2006**, *110*, 7688 - 7694.

87 M. A. Petrukhina, K. W. Andreini, J. Mack, L. T. Scott *J. Org. Chem.* **2005**, *70*, 5713 - 5716.

88 Y.-T. Wu, D. Bandera, R. Maag, A. Linden, K. K. Baldridge, J. S. Siegel *J. Am. Chem. Soc*. **2008**, *130*, 10729 - 10739.

89 Y. Zhang, L. G. Scanlon, M. A. Rottmayer, P. B. Balbuena *J. Phys. Chem. B* **2006**, *45*, 22532 - 22541.

90 S. Banerjee, C. G. S. Pillai, C. Majumder *Int. J. Hydrogen Energy*, **2011**, *36*, 4976 - 4983.

91 A. C. Grimsdale, K. Müllen *Angew. Chem. Int. Ed,* **2005**, *44*, 4428 - 4432.

92 A. Soncini, E. Steiner, P. W. Fowler, R. W. A. Havenith, L. W. Jenneskens *Chem., Eur. J.* **2003**, *9*, 2974 - 2981.

93 W. Pisula, M. Kastler, D. Wasserfallen, M. Mondeshki, J. Piris, I. Schnell, Klaus Müllen *Chem. Mater.* **2006**, *18*, 3634 - 3640.

94 A. M. van de Craats, J. M. Warman, A. Fechtenkötter, J. D. Brand, M. A. Harbison and K. Müllen *Adv. Mater.* **1999** *11*, 1469 - 1472.

95 X. Feng, W. Pisula, K. Müllen *Pure Appl. Chem.* **2009**, *81*, 2203 - 2224.

96 B. Alameddine, O. F. Aebischer, W. Amrein, B. Donnio, R. Deschenaux, D. Guillon,§ C. Savary, D. Scanu, O. Scheidegger, T. A. Jenny *Chem. Mater.* **2005**, *17*, 4798-4807.

97 O. F. Aebischer, P. Tondo, B. Alameddine, T. A. Jenny *Synthesis*, **2006**, *17*, 2891–2896.

98 Jean G. Riess *Tetrahedron* **2002,** *58*, 4113-4131.

99 David F. Eaton, Bruce E. Smart *J. Am. Chem. Soc.* **1990,** *112*, 2821-2823.

100 B. Alameddine *Thesis No 1440,* Universtié de Fribourg, **2004**.

101 O. F. Aebischer, *Thesis No 1575*, Université de Fribourg, **2007**.

102 B. T. King, J. Kroulik, C. R. Robertson, P. Rempala, C. L. Hilton, J. D. Korinek, L. M. Gortari *J. Org. Chem* **2007**, *72*, 2279 - 2288.

103 L. Zhai, R. Shukla, R. Rathore *Org. Lett.* **2009**, *11*, 3474-3477.

104 M. S.-O. Yusybov, V. D. Filimonov *Synthesis* **1991**, 131 - 132.

105 Anuja De Silva, Jin-Kyun Lee, Xavier André, Nelson M. Felix, Heidi B. Cao, Hai Deng, Christopher K. Ober *Chem. Mater.* **2008,** *20*, 1606-1613.

106 Klaus Schwetlick, *Organikum*. 21st ed.; WILEY-VCH: Weinheim, 2001.

107 Sumita Bhandaria, Suprabhat Raya *Synth. Commun.* **1998,** *28*, 765 - 771.

108 G. Gambaretto, L. Conte, G. Fornasieri, C. Zarantonello, D. Tonei, A. Sassi, R. Bertani *J. Fluorine Chem.* **2003,** *121*, 57-63.

109 Shunji Ito, Mike Wehmeier, J. Diedrich Brand, Christian Kübel, Rebekka Epsch, Jürgen P. Rabe, Klaus Müllen *Chem. Eur. J.* **2000,** *6*, 4327-4342.

110 M. Miura, S. Pivsa-Art, G. Dyker, J. Heiermann, T. Satoh, M. Nomura *Chem. Comm.* **1998**, 1889 - 1890.

111 P. Mazerolles, P. Boussaguet, V. Huc *Org. Synth.* **1999,** *76*, 221.

112 Mate Erdelyi, Adolf Gogoll *J. Org. Chem.* **2001,** *66*, 4165-4169.

113 B. Alameddine, *Synthesis and investigation of new large self-assembled supramolecules as potential electron emitters*, **2004**, Thesis No 1440, University of Fribourg.

114 Changming Hu, Fengling Qing *J. Org. Chem.* **1991,** *56*, 6348-6351.

115 Jean Boivin, Béatrice Quiclet-Sire, Laure Ramos, Samir Z. Zard *Chem. Comm.* **1997**, 353 - 354.

116 Hai-Ping Cao, Quig-Yun Chen *J. Fluorine. Chem.* **2007,** *128*, 1187 - 1190.

117 C. K. Luscombe, S. Proemmel, W. T. S. Huck, A. B. Holmes, H. Fukushima *J. Org. Chem.* **2007,** *72*, 5505-5513.

118 G. Johansson, V. Percec, G. Ungar, J. P. Zhou *Macromolecules* **1996,** *29*, 646-660.

119 James H. Babler, Nancy Casey Malek, Michael J. Coghlan *J. Org. Chem.* **1978,** *43*, 1821-1823.

120 1.Y. Shirai, A. J. Osgood, Y. Zhao, Y. Yao, L. Saudan, H. Yang, C. Yu-Hung, L. B. Alemany, T. Sasaki, J. F. Morin, J. M. Guerrero, K. F. Kelly, J. M. Tour *J. Am. Chem. Soc.* **2006,** *128*, 4854-4864.

121 Y. Rubin, C. B. Knobler, F. Diederich *J. Am. Chem. Soc.* **1990**, *112*, 1607 - 1617.

122 1.Jianwei Sun, Yanmei Dong, Liya Cao, Xinyan Wang, Shaozhong Wang, Yuefei Hu *The Journal of Organic Chemistry* **2004,** *69*, 8932-8934.

123 Milco van Leeuwen, Alexander McKillop *J. Chem. Soc., Perkin Trans. 1* **1993**, 2433 - 2440.

124 B. Mohr, V. Enkelmann, G. Wegner *J. Org. Chem.* **1994**, *59*, 635-638.

125 Yoshihiro Kikuzawa, Tomohiko Mori, Hisato Takeuchi *Org. Lett.* **2007,** *9*, 4817-4820.

126 John D. Tovar, Norbert Jux, Thibaut Jarrosson, Saeed I. Khan, Yves Rubin *J. Org. Chem.* **1997**, *62*, 3432-3433.

127 H. Nam, M. Granier, B. Boury, S. Y. Park *Langmuir* **2006,** *22*, 7132-7134.

128 Mu-Fa Zou, Theresa Kopajtic, Jonathan L. Katz, Sara Wirtz, Joseph B. Justice, Amy Hauck Newman *J. Med. Chem* **2001,** *44*, 4453-4461.

129 Shakiru O. Alapafuja, Spyros P. Nikas, Vidyanand G. Shukla, Ionnis Papanastasiou, Alexandros Makriyannis *Tetrahedron Lett.* **2009,** *50*, 7028 - 7031.

130 G. Dyker, J. Heiermann, M. Miura, J.-I Inoh, S. Pivsa-Art, T. Satoh, M. Nomura *Chem. Eur. J.* **2000,** *6*, 3426 - 3432.

131 G. D. Dennis, D. Edwards-Davis, L. D. Field, A. F. Masters, T. Maschmeyer, A. J. Ward, I. E. Buys, P. Turner *Aust. J. Chem.* **2006,** *59*, 135 - 146.

132 William F. Bailey, Mark R. Luderer, Kevin P. Jordan *J. Org. Chem.* **2006,** *71*, 2825-2828.

133 Emilie V. Banide, Bevin C. Molloy, Yannick Ortin, Helge Müller-Bunz, Michael J. McGlinchey *Eur. J. Org. Chem.* **2007,** *2007*, 2611-2622.

134 B. Martin-Matute, M. Edin, K. Bogar, F. B. Kaynak, J.- E. Backvall *J. Am. Chem. Soc.* **2005,** *127*, 8817-8825.

135 G. Vives, G. Rapenne *Tetrahedron* **2008,** *64*, 11462 - 11468.

136 Yan Li, Zhaohui Wang *Org. Lett.* **2009,** *11*, 1385-1387.

137 L. Liu, B. Yang, T. J. Katz, M. K. Poindexter *J. Org. Chem.* **1991**, *56*, 3769 - 377.

138 M. Kanthak, E. Muth, G. Dyker *Eur. J. Org. Chem.* **2010**, 6084 - 6091.

139 R. A. Brown, S. I. S. Fernando and R. M. G. Roberts *J. Chem. Soc. Perkin Trans. 1* **1994**, 197 - 201.

140 S. McVey, P. L. Pauson *J. Chem. Soc.* **1965**, 4312 - 4318.

141 L. D. Field, T. W. Hambley, C. M. Lindall, A. f. Maters *Polyhedron* **1989,** *8*, 2425 - 2430.

142 Kylie N. Brown, Leslie D. Field, Peter A. Lay, Charles M. Lindall, Anthony f. Masters *J. Chem. Soc., Chem. Commun.* **1990**, 408 - 410.

143 H. Schumann, A. Lentz, R. Weimann, J. Pickardt *Angew. Chem.* **1994**, *106*, 1827 - 1829.

144 Skoog, West, Holler *Chimie analyitque, trad. 7ème Ed.,* **1997**, Ed. de Boeck.

145 Website, http://www.societechimiquedefrance.fr/produit-du-jour/ferrocene.html.

146 Rajendra Rathore, Carrie L. Burns *J. Org. Chem.* **2003,** *68*, 4071-4074.

147 M. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518-1520.

VII. Curriculum Vitae

Nicolas Fragnière

Adresse : Route du Centre Sportif 7 - 1625 Sâles (Fribourg)
Téléphone : +41 79 364 69 79
E-mail : nicolas.fragniere2@unifr.ch

Naissance : 11 septembre 1982
Nationalité : Suisse
Etat civil : Marié, un enfant
Militaire : Obligations militaires terminées

Formation

2007 - 2011 Doctorat en chimie organique - Groupe du Prof. Titus A. Jenny - Université de Fribourg

- New Polycondensed aromatic compounds for applications in the hydrogen cycle

2002 - 2007 Master in Science - Université de Fribourg

- Travail de Master : « Synthesis and Investigation of New Triaryl Amine Compounds »

1998 - 2002 Maturité gymnasiale - Collège du Sud - Bulle

- Option spécifique : Biologie/Chimie

Expérience professionnelle

2007 - 2011 Responsable de différents travaux pratiques pour les étudiants - Université de Fribourg

- Laboratoires de chimie organique et analytique
- Formation HPLC-ESI-MS pour étudiants Master
- Supervision d'étudiants Master pour des travaux pratiques de synthèse

2004 - 2006 Stagiaire chez Dupont Polymer Powders à Bulle (environ 1100 heures)

- Mise à jour des P&ID des lignes de dissolution/distillation
- Rédaction des modes opératoires des installations de production en collaboration avec les opérateurs
- Rédaction de procédures concernant la sécurité, l'hygiène et l'environnement
- Participation et préparation d'audits (PSM et ISO)

Formation complémentaire

09.2009 - 01.2010 Cours d'entreprenariat « Venture Challenge » avec projet de start-up : « Molésonde, your specialist in microwave synthesis »

Organisation : Commission pour la Technologie et l'Innovation - Haute Ecole de Gestion - Fribourg

Posters et présentations

Mars 2011	Présentation d'un poster « Synthesis of New Functionnalized HBC » - Congrès international « Hybrid Materials » - Strasbourg
2008	Présentation orale « Synthesis of New Functionalized Perfluoralkylated HBC Derivatives » lors du Graduate Students Symposium - Université de Berne

Techniques scientifiques particulières

Synthèse	Micro-ondes, atmosphère inerte, photochimie, boite à gants, scale-up (réacteur de 5 l)
Analyse	GC-MS, HPLC-MS, ESI-MS, MS-MS, NMR, FT-IR, UV-Vis, Fluorimetrie, SEM, ICP

Langues

Français	Langue maternelle
Allemand	Bonnes connaissances parlées et écrites
Anglais	Très bonnes connaissances parlées et écrites

Connaissances informatiques

Chimie	ChemOffice, ChemSketch, ACD-LABS, SciFinder, Reaxys
Autre	Microsoft Office, Photoshop, Illustrator, Framemaker

Activités parallèles

Sports d'endurance	Course à pieds, ski alpinisme, vélo - Participation à plusieurs Patrouilles des Glaciers, Sierre-Zinal, marathon de Zermatt
Football	Entraîneur juniors de 1999 à 2008, joueur jusqu'en mai 2011
Emplois divers	Manœuvre dans des entreprises de charpenterie de 1998 à 2003 - Vial Frère SA - Le Crêt - Marc Descloux - Maules

Centres d'intérêt et loisirs

Sport, montagne, guitare

Références

Prof. Titus A. Jenny	Directeur de thèse - Chemin du Musée 9 - 1700 Fribourg +41 26 300 8778 - titus.jenny@unifr.ch
Dr. Philippe Menoud	Dupont Polymer Powders - Rue St-Joseph 25 - 1630 Bulle 1, Switzerland - +41 26 913 0 930 - philippe.menoud@che.dupont.com