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Towards $[0_n]$Paracyclophanes as Templates for the Synthesis of Nanotubes

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"Tu peux tout accomplir dans la vie si tu as le courage
de le rêver, l'intelligence d'en faire un projet réaliste,
et la volonté de voir ce projet mené à bien."
SIDNEY A. FRIEDMAN

À Arthur, Augustin et Marie-Paule
mes enfants et ma femme

À ma famille

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Résumé

Aujourd'hui, la nanotechnologie est une réalité qui touche quasiment toutes les sciences. En effet, les nanoparticules et nanosystèmes sont pourvus de propriétés inédites et prometteuses pour de nombreuses applications. La chimie est non négligeable dans l'approche de systèmes à l'échelle du nanomètre car elle permet une construction atome par atome. Dans cette optique, la synthèse rationnelle de nanotubes de carbone a été envisagée suite à la découverte de Raemy, concernant la fabrication de structures graphitiques à partir d'acétylène, et au travers de l'utilisation de segments de nanotubes du type $[0_\mathrm{n}]$paracyclophanes qui pourraient servir de point de départ pour la polymerisation.

Le but premier de ce travail est la synthèse de cycles $[0_\mathrm{n}]$paracyclophanes, basée sur le concept des charnières et des coudes. En effet, ces composés polyaromatiques sont trop tendus et doivent contenir des parties flexibles pour être cyclisés avant leur aromatisation. Pour ce faire, le motif *cis*-1,4-diphénylcyclohexane a été préparé selon quatre chemins synthétiques différents permettant d'obtenir trois charnières utilisables pour la préparation de précurseurs. A partir de tels composés, les stratégies utilisant la réaction de Diels-Alder, des homocouplages ou la réaction de McMurry ont été étudiées. Cette dernière, appliquée à des précurseurs pentacycliques d'une nouvelle famille de composés, constitués d'unités phényle et d'unités cyclohexyle alternées, a permis la préparation d'un macrocycle intermédiaire au $[0_5]$paracyclophane désiré. La caractérisation complète de ce produit n'a pas été faite car la basse sélectivité de la réaction a posé des problèmes d'isolation.

Des travaux préliminaires ont également été effectués concernant l'obtention de segments de nanotubes via la dégradation contrôlée de fullerènes ou de nanotubes de carbone à simple paroi, mais ces travaux n'ont pas donné le succès escompté. La poursuite de ce travail pourrait déboucher sur une synthèse rationnelle de nanotubes à partir de l'acétylène et de segments définis.

Summary

Today, nanotechnology has found a great interest in research areas of different scientific fields. Indeed, nanoparticles and nanodevices possess new and promising properties for a lot of applications. Chemistry is useful in preparation of such nanometer sized systems because she allows a construction atom by atom, also called "bottom-up" approach. A rational synthesis of carbon nanotubes was therefore considered by following the discovery of Raemy concerning the production of graphitic structures from acetylene through the use of segments of nanotubes such as $[0_n]$paracyclophanes acting as template for the carbon nanotube growing process.

The first challenge of this work is the synthesis of $[0_n]$paracyclophane cycles, based on the hinge and bend concept. Indeed, such polyaromatic compounds are strained and must contain flexible parts to allow for the possibility of a cyclization. Full aromatization must follow in a subsequent step. *cis*-1,4-Diphenylcyclohexane patterns were prepared according to four different synthetic strategies, involving three type of hinges in the preparation of precursors. On these compounds, processes using the Diels-Alder reaction, metal mediated homocoupling reactions or McMurry reaction were studied. The latter, applied to a pentacyclic precursor of a new family of compounds consisting of alternate phenyl and cyclohexyl rings, allowed the preparation of an intermediate macrocycle of the desired $[0_5]$paracyclophane. Due to the low selectivity during the cyclization reaction, full characterization of this product was prevented.

Preliminary attempts to get nanotube segments from controlled degradation of fullerenes or single-walled carbon nanotubes were likewise not successful so far. This work must be continued in order to allow for the possibility of a rational synthesis of nanotubes via template assisted polymerization of acetylene.

Contents

List of Abbreviations

Ac : acetyl
AFM : atomic force microscopy
APT : attached test proton
Ar : aryl
Bu : butyl
CNT : carbon nanotube
COSY : correlation spectroscopy
Cp : cyclopentadienyl
CVD : chemical vapor deposition
DBU : 1,8-diazabicyclo[5.4.0]undec-7-ene
DDQ : 2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DIBAH : diisobutylaluminumhydride
DME : dimethoxyethane
DMF : N,N-dimethylformamide
DMI : N,N'-dimethylimidazolidinone
DMPD : 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine
dmpe : 1,2-bis(dimethylphosphino)ethane
DMSO : dimethylsufoxide
dppb : 1,4-bis(diphenylphosphino)butane
dppe : 1,2-bis(diphenylphosphino)ethane
dppf : 1,1'-bis(diphenylphosphino)ferrocene
dppm : bis(diphenylphosphino)methane
dppp : 1,3-bis(diphenylphosphino)propane
EI : electron ionization
ESI : electrospray ionization
Et : ethyl
FAB : fast atom bombardment
FET : field effect transistor
FVP : flash vacuum pyrolysis
GC : gas chromatography

GPC	:	gel permeation chromatography
HETCOR	:	heteronuclear correlation
HiPco	:	high-pressure CO conversion
Me	:	methyl
MS	:	mass spectrometry
MWNT	:	multi-walled carbon nanotube
NBS	:	N-bromosuccinimide
NED	:	nano emissive display
NMR	:	nuclear magnetic resonance
ORTEP	:	oak ridge thermal ellipsoid plot
PAH	:	polycyclic aromatic hydrocarbon
Ph	:	phenyl
PIFA	:	[bis(trifluoroacetoxy)iodo]benzene
PLV	:	pulsed laser vaporization
Pr	:	propyl
rt	:	room temperature
SEM	:	scanning electron microscopy
STM	:	scanning tunneling microscopy
SWNT	:	single-walled carbon nanotube
TBAI	:	tetrabutylammonium iodide
TBDMS	:	*tert*-butyldimethylsilyl
TBDMSCl	:	tert-butyldimethylsilyl chloride
TCDI	:	thiocarbonyldiimidazole
TEM	:	transmission electron microscopy
Tf	:	triflate
TFA	:	trifluoroacetic acid
TGA	:	thermogravimetric analysis
THF	:	tetrahydrofuran
TLC	:	thin layer chromatography
TMS	:	trimethylsilyl or tetramethylsilane (NMR standard)
TMSA	:	trimethylsilyl acetylene
TMSCl	:	trimethylsilyl chloride
Ts	:	tosyl
TSA	:	toluenesulfonic acid

Part I

Theoretical background

Chapter 1

Introduction

The field of nanotechnology consists of preparation, characterization and application of devices and materials on the nanoscale. Nanotechnology concerns many different disciplines, such as biology, physics, chemistry or other scientific fields. Two main approaches are used in nanotechnology: one is a "bottom-up" approach where materials and devices are built up atom by atom; this approach is used in chemistry. Indeed, chemists generally work with molecules of Å or at most some nanometer size. The other method is the "top-down" approach, which consists of the preparation of nanodevices by removing existing material from larger entities, corresponding to a microtechnology based approach.

The actual interest for nanotechnology is due to the very interesting properties displayed by nanoparticles and nanodevices. Indeed, this field of sciences has an increased ratio of surface area to volume, opening new possibilities in surface-based science. Other phenomena become pronounced as the size of the system becomes smaller, in terms of statistical mechanical effects or quantum mechanical effects. Nanoscaled materials can show properties very different from macro scale materials. For instance, copper particles become colorless at the nanoscale, but gold becomes colored.

The study of these fields of sciences was possible only with the development of new analytical tools such as atomic force microscopy (AFM) or scanning tunneling microscopy (STM). Indeed, the characterization of nanodevices can be problematic with usual analytical methods.

In life science, most phenomena involve nanoscaled systems, in fact which inspires the scientific community. Indeed, the imitation of nature in nanotechnology is an important part of the actual research. Chemists successfully demonstrated that synthetically fabricated molecular machines can function, as for instance a rotating molecular motor [1] or a molecular actuator [2], but chemistry is also present in different other important subjects in nanotechnology. Functionalization of nanoparticles and carbon nanotubes represents, with colloid science and self-assembled devices, the most active research fields today.

Chapter 2

Carbon nanotubes

2.1 Type and nomenclature

Since their discovery in 1991 by Iijima [3], carbon nanotubes (CNTs) have become a major research subject in nanoscience and nanotechnology. Their particular structure and 1D geometry is promising for many applications in different fields of sciences, due to their interesting mechanical and electronic properties. CNTs could have different conductivities, depending on the geometry, length and other parameters.

The first CNTs observed possessed several graphitic shells as if the tubes were nested one in the other and are named multi-walled carbon nanotubes (MWNTs). A new kind of CNT, having very small diameters and constituted with only a single atomic layer thick wall, was discovered simultaneously in 1993 by Klang [4] and Iijima [5]. These tubes are known as single-walled carbon nanotubes (SWNTs).

SWNTs are representative of a unit for all CNTs and consist of cylindrical shaped tubules, like rolled-up cylinders of graphene sheets of sp^2 bonded carbon atoms, with caps at each end. The two caps, also called tips, can be joined together to form a fullerene. The three geometry types of SWNT, "zig-zag", "armchair" and "chiral" (figure 2.1) can be distinguished by the fundamental parameters of CNT. Indeed, to obtain the diameter of nanotube d_t or the chiral angle θ, the cylinder is unrolled to obtain a representative graphene sheet (figure 2.2) [6] on which vectors, integers and lengths can be found (Hamada's notation [7]). Table 2.1 summarizes the parameters with their respective formulas. The geometry depends on the chiral angle θ. Indeed, when this is a 0° angle, the CNT is in "zig-zag" configuration and the integers are given as (n,0). "Armchair" CNT have a chiral angle of 30° with integers $n = m$. When $0^\circ \leq |\theta| \leq 30^\circ$, $m \neq 0$ and $m \neq n$, the chiral vector corresponds to a chiral nanotube. For naming a specific SWNT, the notation will be "(n,m)-geometry", for example (5,5)-armchair.

Conductivity of CNTs depends on the geometry. All "armchair" nanotubes have metallic properties and are conductors. It is more complicated for "zig-zag" CNTs, for which conductivity is symmetry dependent. Band degeneracy occurs for different Fermi level energy bands and when integer n is a multiple of 3, tubules with metallic conduction can be observed. In the other cases, "zig-zag" CNTs are semiconductors. With regard to chiral CNTs, the conductivity depends on the chiral vector.

Name	Symbol	Formula	Value
C-C distance	a		1.421 Å
Length of unit vector	a_{C-C}	$\sqrt{3}a_{C-C}$	2.46 Å
Unit vector	a_1	$\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right)a$	coord. (x,y)
Unit vector	a_2	$\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)a$	coord. (x,y)
Chiral vector	C_h	$na_1 + ma_2 \equiv (n, m)$	$n, m =$ integers
Circumference	L	$\lvert C_h \rvert = a\sqrt{n^2 + m^2 + nm}$	$0 \leq \lvert m \rvert \leq n$
Diameter	d_t	$\frac{L}{\pi} = \frac{\sqrt{n^2+m^2+nm}}{\pi}a$	
Chiral angle	θ	$sin\theta = \frac{\sqrt{3}m}{2\sqrt{n^2+m^2+nm}}$	$0° \leq \lvert\theta\rvert \leq 30°$

Table 2.1: Basic parameters of CNT [6].

2.2 Preparation of CNTs

The first CNTs were prepared by using an arc-discharge evaporation method, a similar one used for mass production of fullerene [3], but only a small amount was recovered. The observed CNTs were multi-walled nanotubes with a diameter between 4 and 30 nm and up to 1 μm in length. A lot of methods were thereafter developed for large-scale synthesis and for length and diameter control.

The arc-discharge method was optimized by Ebbesen [8] to allow a large-scale preparation. By increasing the helium pressure inside the reactor, the major part (75 %) of the consumed carbon electrode gave MWNTs with a diameter from 2 to 20 nm and with a lengths of several μm. This progress in CNTs production increased intensively the research in this field of material science, but this method was rapidly modified by Klang [4] who used powder cobalt filled electrodes instead of classical graphite ones, giving, as a surprising result, SWNTs with a diameter of 1.2 nm. Cobalt played a special role in catalyzing the formation of these SWNTs and

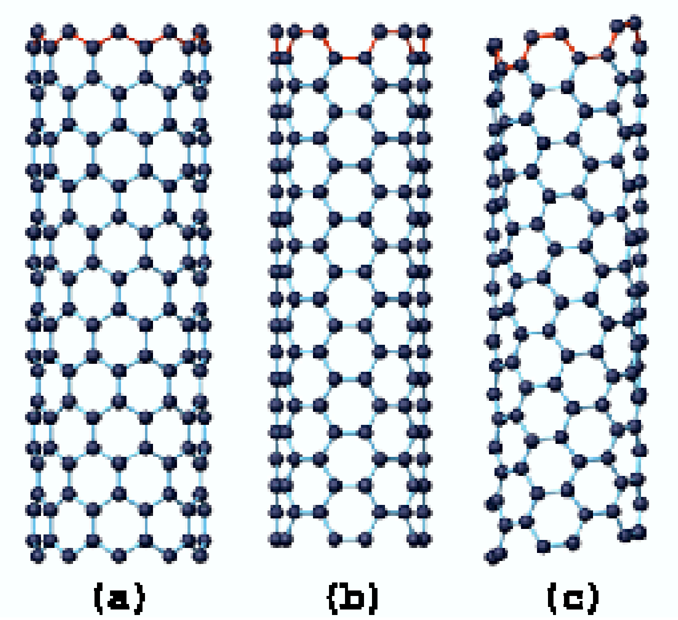


Figure 2.1: The different types of SWNTs in a) "zig-zag", b) "armchair" and c) "chiral" geometries.

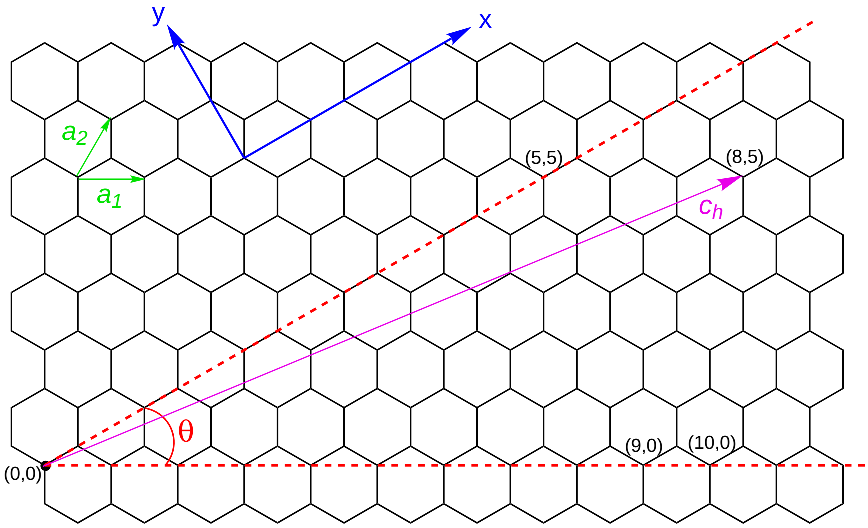


Figure 2.2: Hamada notation [7]. 2D graphene sheet, showing the honeycomb lattice of graphitic structure, unit vector a_1 and a_2, chiral vector C_h and chiral angle θ.

a specific nucleation process occurs, which was responsible for their uniform diameter. Iijima [5] described the same discovery at the same time, but using graphitic cathode including an iron piece, in an experiment carried out in a methane/argon gas mixture. The diameters of these SWNTs ranged from 0.8 to 1.35 nm. Unfortunately, these two procedures have only led to low yields, but the replacement of iron or cobalt catalyst by mixtures such as Ni-Co, Co-Y or Ni-Y [9] gave better results, going until 80 % yield for a Ni-Y mixture, allowing the synthesis of gram quantity of well-defined SWNTs with a diameter of around 1.4 nm.

The pulsed laser vaporization (PLV) of metal-doped carbon target, a method used for the first time in 1996 by Smalley [10], produced SWNTs of 1.4 nm in 70 % yield. The sample was prepared by laser vaporization of graphite rods doped with a 1.2 atomic % 1:1 Ni/Co mixture, at 1200 °C and under an argon atmosphere.

Decomposition of carbon-containing molecules on supported metal particles is a well-developed process for CNTs production. This method is known as chemical vapor deposition (CVD). In 1996, Smalley [11] described disproportion of CO on alumina-supported molybdenum catalyst, affording SWNTs and a small amount of double-walled carbon nanotubes. The experiment was carried out at 1200 °C and with a carbon monoxide pressure of 100 Torr above atmospheric pressure, giving tubules with a diameter from 1 to 5 nm. On its side, Peigney [12] developed a similar method using alumina-supported iron particles and CH_4 gas as the carbon source, but unfortunately, the obtained CNTs were a mixture of SWNTs and MWNTs. This process was improved [13] and high-quality SWNTs were found during a large-scale synthesis, using CO or C_2H_2 gases and Fe-Mo catalyst on alumina. Gas-phase decomposition of CO or high-pressure CO conversion (HiPco) method is a modified version of this method, with a working CO pressure until 10 atm [14]. The diameter of the obtained SWNTs was as small as 0.7 nm. Alumina-supported Fe_2O_3 was used for CVD of methane, yielding high quality SWNTs [15].

A large amount of CNTs production methods were developed by scientists, like, for example, self-catalytic behavior of CNTs [16]. MWNTs nucleation process was catalyzed by shorts, cuts MWNTs, which were acting as template during the growth mechanism. Cyclohexane was used as the carbon source and the reaction was carried out by detonation of picric acid.

Today, no mild conditions are known for CNTs production, but the chancy discovery of a acetylene polymerization by an iron/DIBAH catalyst yielding graphitic material, could offer a unique possibility to produce CNTs in solution. Preliminary tests were done by Raemy [17], who obtained graphitic material in a poly-acetylene coating. The question therefore is, whether a template as for example $[0_n]$paracyclophane, could be used to force the graphitic material to grow in a tube-like shape.

2.3 Purifications of SWNTs

Preparation of CNTs is done under very harsh conditions. Laser ablation, arc-discharge or CVD methods are yielding tubes contaminated with a large number of impurities, decreasing the overall yield of usable material. Impurities, including transition metal catalysts, such as Fe, Co and Ni as well as carbonaceous species such as amorphous carbon, fullerenes, multishell carbon nanocapsules, and nanocrystalline graphite should be removed to obtain high purity SWNTs. Different methods are available for purifying CNTs, as liquid and gas phase oxidation, chemical functionalization, filtration, chromatography and microwave heating. The choice of the method is depending of the preparation process, because impurities are not the same after a CVD or a PLV run. The most used methods are the oxidative ones, because they have the potential of large scale purification [18]. It is frequent that several methods are sequentially applied on a same sample to obtain the desired purity level.

Analytical methods are very important in this field of CNT science to control the efficiency of the applied procedure and, for this purpose, scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), thermogravimetric analyses (TGA), Raman spectroscopy and visible-NIR spectroscopy can be used. Electron microscopy techniques can not be used as quantitative evaluation of the purity level, due to the small sample volume analyzed and the lack of algorithms to convert images to numerical data [19].

2.3.1 Oxidative methods

Purification of CNTs by oxidative treatments is easy and convenient, but the main disadvantage is that nanotubes can be destroyed or damaged during the process. Oxygen-containing functional groups are often observed as a result of these experiments. Liquid phase oxidation can be realized by room temperature stirring or refluxing in acid solutions, such as HNO_3 or HCl and with mixture such as H_2SO_4-$KMnO_4$ or Caro's acid, but the most used acidic oxidant is HNO_3. In a typical run [20], for PLV produced SWNTs, nanotubes were refluxed in 2.6 M HNO_3 for 45 hours and then recovered by centrifugation and several water washings of the residue. Arc-discharge SWNTs can be purified by similar techniques as those used for laser ablation growth, but it is a more difficult task due to the large metal and impurities content. Catalysts are almost completely removed after refluxing in diluted HNO_3 and successive filtration steps [21], but nanocapsules are still present.

Gas phase oxidation can be carried out by using O_2 and air. They work as selective oxidation processes, since carbonaceous species are oxidized more quickly as the SWNTs. Treatment with H_2 is possible too. Whereas in H_2 reduction the amorphous carbon is transformed in CH_4, it is converted in CO_2 when using air or O_2 oxidation [22]. Gaseous treatment involving Cl_2 and HCl were developed [23], but the purity level of the resulting CNTs was not sufficient, leaving a large amount of metallic impurities.

A representative three-step oxidation process applied to arc-discharge nanotubes prepared with Ni-Y catalyst [22] can be described as follows: the as-synthesized SWNTs were refluxed with 3 M HCl for 18 h, treated by CO_2 at 800 $^\circ$C for 12 h and by acid washing. The last step was the hydrogen treatment at 1200 $^\circ$C for 5 h. Figure 2.3 shows TEM pictures of the SWNTs after the different treatments. The amount of impurities (spherical particles) is decreasing after each purification procedure.

The mechanism of impurity oxidation is not well known, but it is believed that oxidants break the carbon shell and then oxidize the catalysts to the corresponding metal hydroxide or oxide [24].

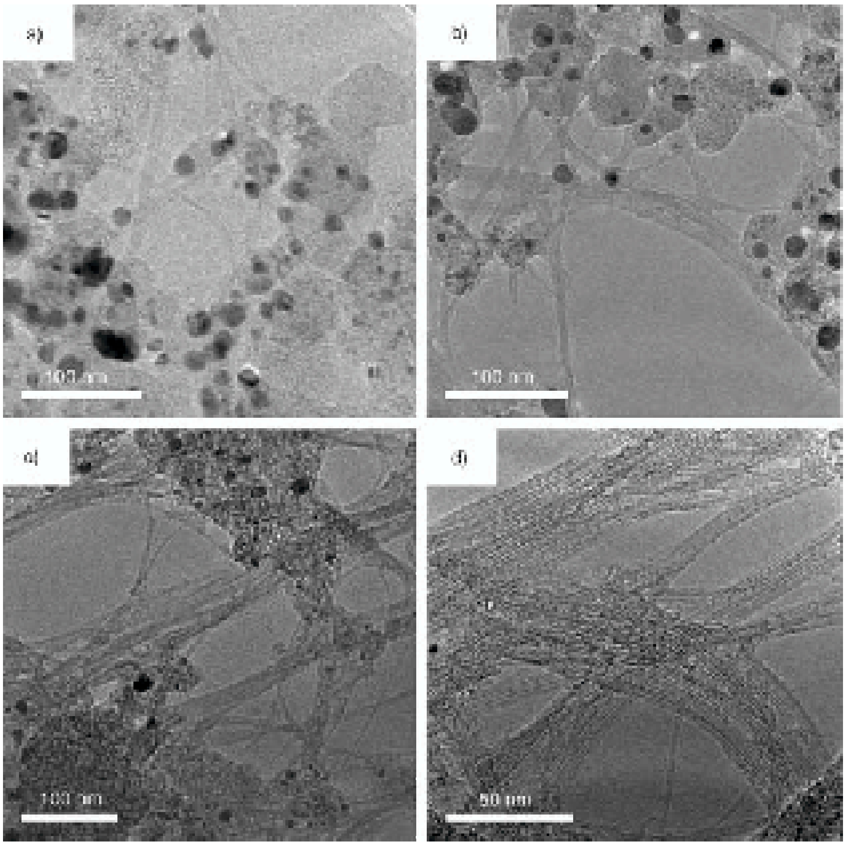


Figure 2.3: TEM pictures of a) as-synthesized SWNTs, b) acid-refluxed SWNTs, c) after CO_2 treatment and acid washing and d) SWNTs treated by H_2 [22].

2.3.2 Alternative methods

Chemical functionalization is a useful and reliable method for purification of nanotubes, but the number of steps and their complexity can be a disadvantage. For these reasons, use of such methods is limited. Developed methods are focused on solubilizing SWNTs, by adding different functional groups on the surface of the tubule. In general, carboxylic acid functionalities found at SWNTs open ends and defects sites can easily be modified with different substituents. Amide bond formation with octadecylamine after derivatization with thionylchloride gave CS_2 soluble SWNTs [25]. Such modified tubes can be use for HPLC [26] applications as purification method. Carboxylate SWNTs/ammonium derivative zwitterionic complexes were used for the purification of SWNTs by GPC [27].

The microfiltration method, based on size separation, is a fully physical-based purification technique, where no chemical treatment is required. The major advantage of such a procedure is the low level of sample loss and damaged SWNTs, but the number of successive filtration necessary to get the desired purity is less attractive. Microfiltration of a PLV produced SWNT suspension including a cationic surfactant affords the separation of metal and carbon nanoparticles from nanotubes [28].

The last kind of purification is based on microwave heating, which must be coupled with an acid treatment to achieve the purification. Microwave heating in air raises significantly the local temperature of encapsulated catalyst particles, leading to oxidation of the metal and of the carbon shells [29]. A mild acid oxidation is then sufficient to remove the residual catalyst. An other approach of microwave application for CNTs purification was developed, by using a SWNTs suspension in diluted HNO_3 [30]. This procedure was completed by an air oxidation at 300 $^\circ$C. The main advantage of this method is the reduction of the operation times as compared to the conventional acidic oxidation procedures.

2.4 Selected applications

Scientists have proposed many potential applications for CNTs, like sensors, carbon nanotube composites, hydrogen storage, field emission or electronic devices. Some of these applications are now realized, but different parameters, as cost or polydispersity in the nanotube type, are barriers for a large scale use.

A field-effect transistor (FET) (figure 2.4) was built using CNTs as a gate. The two ends of a semiconductor tubule were connected with a metallic source and, respectively, a metallic drain. CNTs were positioned on a silicon substrate using AFM tips [31] and the electrodes were connected to a CNT by lithography. Such transistors may or may not work, depending of the type of nanotube, metallic or semiconductor, over which the operator has no control. Such devices are several hundreds of nanometers big, not radically smaller than silicon-based FET, but advances in microlithography techniques could leed to improving these CNT-FETs.

More recently, the method for preparing nanotube FETs was improved. Indeed, a novel selective placement of functionalized CNTs on Al/Al_2O_3 was developed [32]. The CNTs can be strongly bonded with the metal oxide surfaces, but not with the silicon dioxide, allowing the deposition of the nanotubes exclusively on the prepared Al/Al_2O_3 zones, showing a tendency to align on narrow features. After removing the functional groups, the electrodes were made from palladium by lithography.

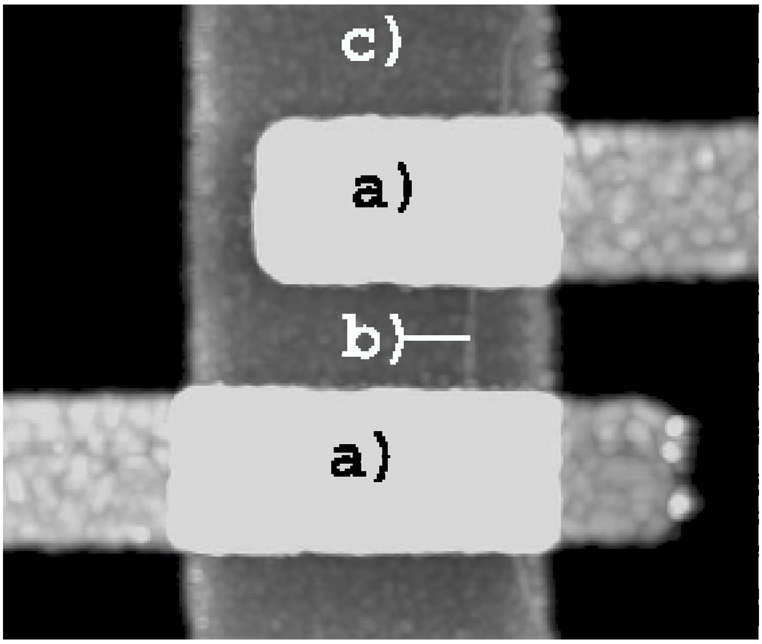


Figure 2.4: Scanning tunneling microscopy (STM) picture of a CNT-FET. a) Source and drain in gold, b) CNT and c) aluminum oxide support [33].

Focus in field emission electron source, such as flat panel displays, is a principal research subject in CNT applications. A potential applied between a surface coated with CNTs and an anode produce high local fields due to field enhancement, causing electron tunneling from the carbon nanotube tip into the vacuum. Such devices are relatively easy to manufacture as compared to tungsten or molybdenum tip displays [34]. The other advantages of CNTs devices are longer lifetimes, low emission threshold potentials and stable emission [35]. In 2001, a flat panel display made from CNTs was presented by Samsung [36] (figure 2.5).

The development of a competitive flat panel display was made by Motorola Labs with their nano emissive display (NED) technology, a scalable method of growing

CNTs directly on glass substrate. This cost-effective process offers the potential to create longer-lasting NED flat panel displays with high brightness, excellent uniformity and color purity [37].

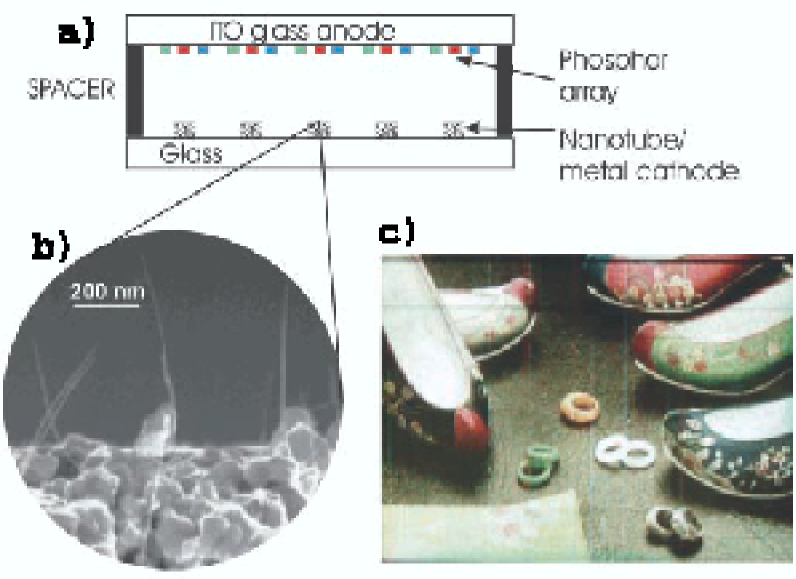


Figure 2.5: a) Shematic CNTs flat panel display, b) SEM picture of an electron emitter and c) a photograph of a 5 inch CNT field emission display [38].

Asymmetrically functionalized SWNTs have been prepared by a covalent reaction of an 11-mercaptoundecanol-modified Au surface with oxidized SWNTs cylinders. While one end of the tubes was attached to gold substrate via ester groups, then the free carboxylic substituents on the other end were deprotonated, creating a donor-acceptor asymmetric SWNT. Study of the SWNT monolayer conductance in Hg drop junction showed diode properties [39]. Figure 2.6 shows the details of this Au-SWNT-Hg diode. When the terminal carboxylic groups were derivatized as alkyl ester, SWNT becomes symmetric and the device lost the diode junction properties.

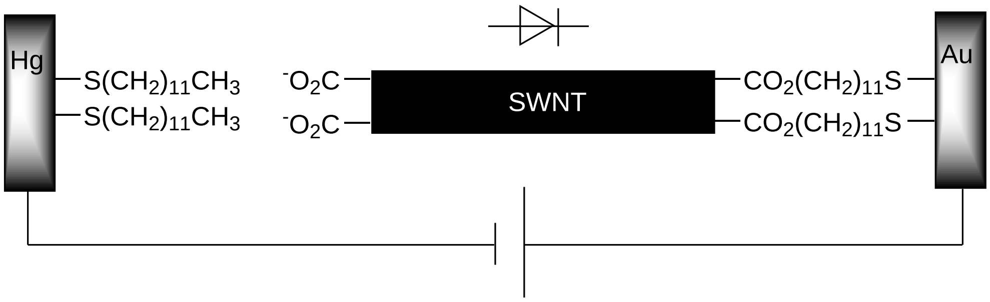


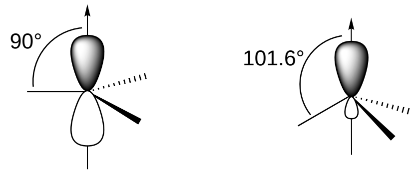
Figure 2.6: Donor-acceptor asymmetric SWNT junction, a CNTs-diode [39].

Since their discovery, CNTs are providing a lot of possibilities in the nanotechnology field and very different applications are in development. Future of nanotechnology and of many areas will be built on a carbon nanotubes science foundation. First examples of electronic devices will be further improved in order to allow high technology commercial products, replacing current ones.

Chapter 3

Curved polyaromatic molecules

Polycyclic aromatic hydrocarbons (PAHs) are non classical aromatic systems, in which sp^2-hybridized carbons present a pyramidalization angle. In general, a sp^2 carbon atom prefer to form planar framework with its neighbors, living the p orbital perpendicular to the ring plane, but in PAHs, as fullerene C_{60}, the sp^2-hybridized carbon atoms are pyramidalized, involving an angle larger than 90 ° between the p orbital and the σ bonds. The pyramidalization angle θ_p is defined as the angle between the p orbital and the σ bonds, minus 90 ° (figure 3.1) [40]. This angle of a carbon atom in a curved carbon surface is a good measure for the curvature-induced local weakening of π-conjugation.



a) b)

Figure 3.1: Pyramidalization angle θ_p for a) an planar sp_2-hybridized carbon ($\theta_p = 0^\circ$) and b) a nonplanar sp_2-hybridized carbon in C_{60} fullerene ($\theta_p = 11.6^\circ$) [40].

The p orbitals of a polyaromatic system are perpendicular with respect to the surface, which means that for a cylinder as CNT, the inner part of the p orbitals point towards the axis of the tube (figure 3.2) [41]. Planar pyrene (**1**) has p orbitals perpendicular one to the others, while systems as pyrenophane **2** and the "interesting synthetic target" **3** proposed by Vögtle [42, 43] are curved.

The majority of synthetic routes for the preparation of such curved PAHs employ pyrolitic techniques, such as flash vacuum pyrolysis (FVP), but others strategies without thermal treatment are available. A large amount of syntheses was done with C_{60} fullerene fragments, such as corannulene (**6**) or sumanene (**14**).

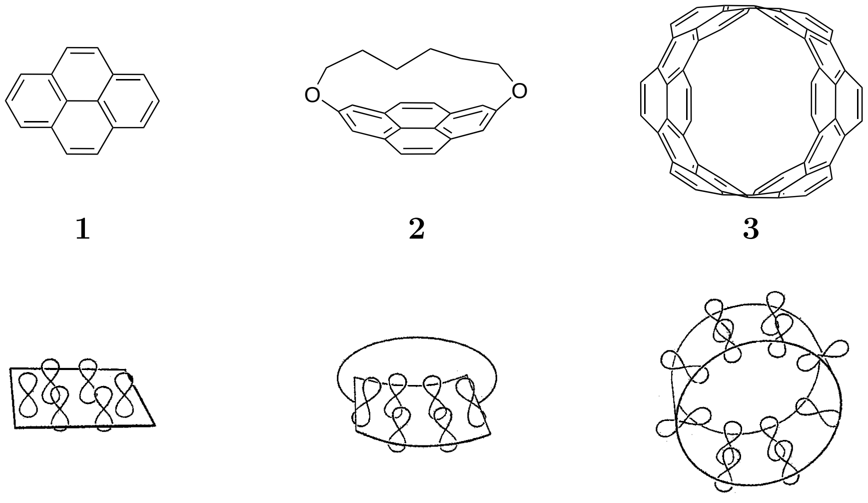
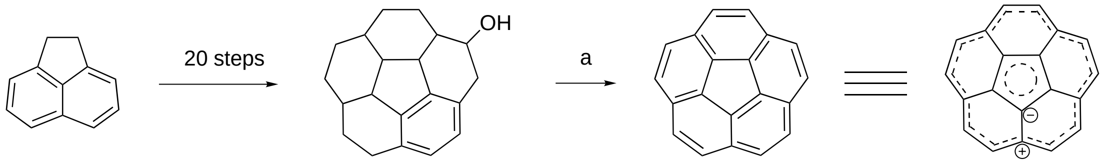


Figure 3.2: Three polyaromatic molecules with the representation of their p orbitals.

3.1 Fullerene fragments

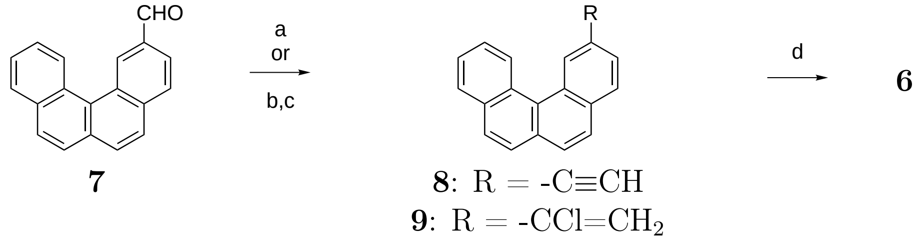
Corannulene (**6**), constituted of five six-membered rings around a central five-membered ring, is of interest because of its strained nature and curved structure, and its unique electronic distribution. Indeed, this bowl-shaped structure forms two concentric conjugated systems. Molecule **6** was first prepared by a 21 steps rational synthesis starting from acenaphthene (**4**), where the last step was a dehydrogenation process of the tetradecahydrocorannulene derivative **5** (figure 3.3) [44, 45]. Thereafter, other approaches were conceived with pyrolysis often used as an efficient method during the last step of the preparation. The following strategy involves benzo[c]phenantrenes derivatives **8** or **9**. These two precursors were prepared by a five and six steps sequences, respectively, involving benzo[c]phenanthrene-2-carbaldehyde (**7**) as an advanced intermediate (figure 3.4) [46]. Formation of **6** was achieved by FVP, giving a 2-4 % and 8 % yield, respectively, of isolated product.



4 **5** **6**

Figure 3.3: Key step of the first corannulene (**6**) synthesis [44, 45]. a) 5 % Pd/C, N_2, 110 °C to 275 °C.

Sumanene (**14**), constituted of a six-membered ring surrounded by six alternated six-membered and five-membered rings, was prepared first by Sakurai and Hirao [47] (figure 3.5), after first exploring different routes without success [48, 49, 50].



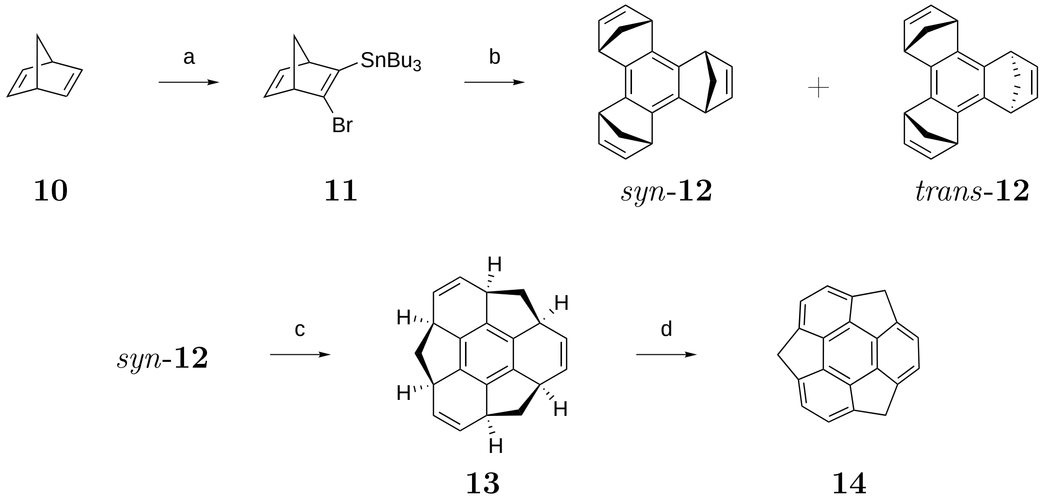
7

8: R = -C≡CH
9: R = -CCl=CH$_2$

Figure 3.4: Syntheses of corannulene (**6**) by FVP [46]. a) R = -C≡CH: $ClCH_2PPh_3^+Cl^-$, *t*-BuOK; b) R = -CCl=CH$_2$: CH_3MgI, THF, then PCC, CH_2Cl_2 c) R = -CCl=CH$_2$: PCl_5, benzene; d) FVP, 1200 °C, N_2, 0.5 torr.

The preparation of **14** involves only four steps and starts with 2,5-norbornadiene (**10**), which was stannated to give intermediate **11**. Trimerization of **11** gives in a second step a mixture of *syn*- and *trans*-benzotris(norbornadiene) (**12**) in a 1:3 ratio. This mixture of diastereoisomers was resolved by chromatography. An alkene ring exchange was achieved by a tandem ring-opening and ring-closing metathesis of *syn*-**12** under an ethylene atmosphere, yielding the key intermediate hexahydrosumanene **13**. Dehydrogenation of **13** was achieved by DDQ oxidation, giving **14**.

Molecules **6** and **14** show a bowl-to-bowl inversion at room temperature, which is rapid for corannulene (**6**) [51], but much slower for sumanene (**14**).



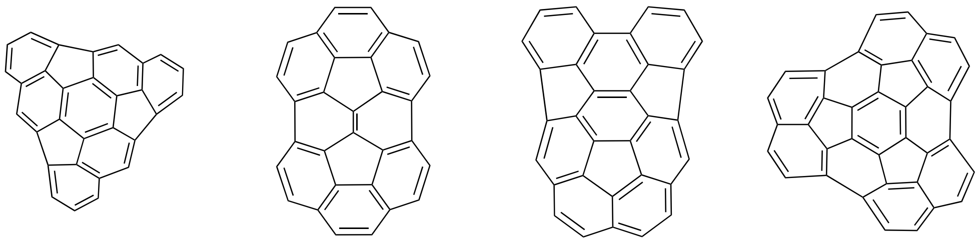
10 **11** *syn*-**12** *trans*-**12**

syn-**12**

13 **14**

Figure 3.5: Synthesis of sumanene (**14**) by Sakurai and Hirao [47]. a) *n*-BuLi, *t*-BuOK, then $BrCH_2CH_2Br$, THF, -78 °C to -45 °C, then Bu_3SnCl, rt; b) Cu(2-$C_4H_3SCO_2$), 1-methyl-2-pyrrolidinone, -20 °C to rt; c) 10 mol% $[P(C_6H_1 1)_3]_2RuCl_2$=CHPh, ethylene, toluene, -78 °C to rt; d) DDQ, toluene, 110 °C.

In the aim of a chemical synthesis of fullerene, larger bowl-shaped hydrocarbons were prepared. Indeed, PAHs **15** [52], **16** [52, 53], **17** [54] and **18** [55] (figure 3.6) are all fullerene C_{60} fragments, which can be prepared by FVP of their respective precursors.



15 **16** **17** **18**

Figure 3.6: Structures of some PAHs. All are C_{60} fullerene fragments.

3.2 Pyrenophanes

Syntheses of (2,7)pyrenophanes as **2** were developped by Bodwell [56, 57, 58, 59]. This new synthetic route provided 2,7-bridged pyrene units in which the PAH was curved over the entire aromatic surface. The strategy is based upon a valence isomerization of [2.2]metacyclophane-1,9-diene, followed by a dehydrogenation of the generated dihydropyrene. The presence of an aliphatic tether bridge between the positions 2 and 7 of the pyrene, forces the PAH system to be curved. The influence of the distortion of the pyrene unit upon the π-electron delocalization was investigated with two different measures of aromaticity, based on magnetism and on geometry. As a result of this study it was found, that the π-electron system was almost untouched and the aromaticity only slightly decreased as a function of the distortion angle.

In a general procedure [57] for the preparation of a tether-bridged pyrenophane (figure 3.7), two molecules of 5-hydroxyisophthalic acid dimethyl ester (**19**) were bridged by a double Williamson etherification to give **20**. Compound **20** was then reduced to the tetrabromobenzyl analog **21**. [2.2]Metacyclophane-1,9-diene **23** was obtained by a two step conversion of the dithiacyclophane **22**, prepared by nucleophilic substitution of **21**. Compound **23** showed a valence isomerization with 10b,10c-dihydropyrene **24**. Finale oxidation with DDQ gave 1,9-dioxa[9](2,7)pyrenophane (**25**). This strategy was applied for bridges having a carbon chain constituted of 7 to 10 methylene units. Fully carbonated bridges were prepared too, with chains containing between 7 to 9 methylene groups [58]. The preparation of the latter changes only during the early steps, where the tether chain must be replaced by an aliphatic one, directly linked to the aromatic rings. Synthesis of [7](2,7)-pyrenophane (**29**) is based on the precursor **28**, which was prepared as follows (figure 3.8): compound **19**

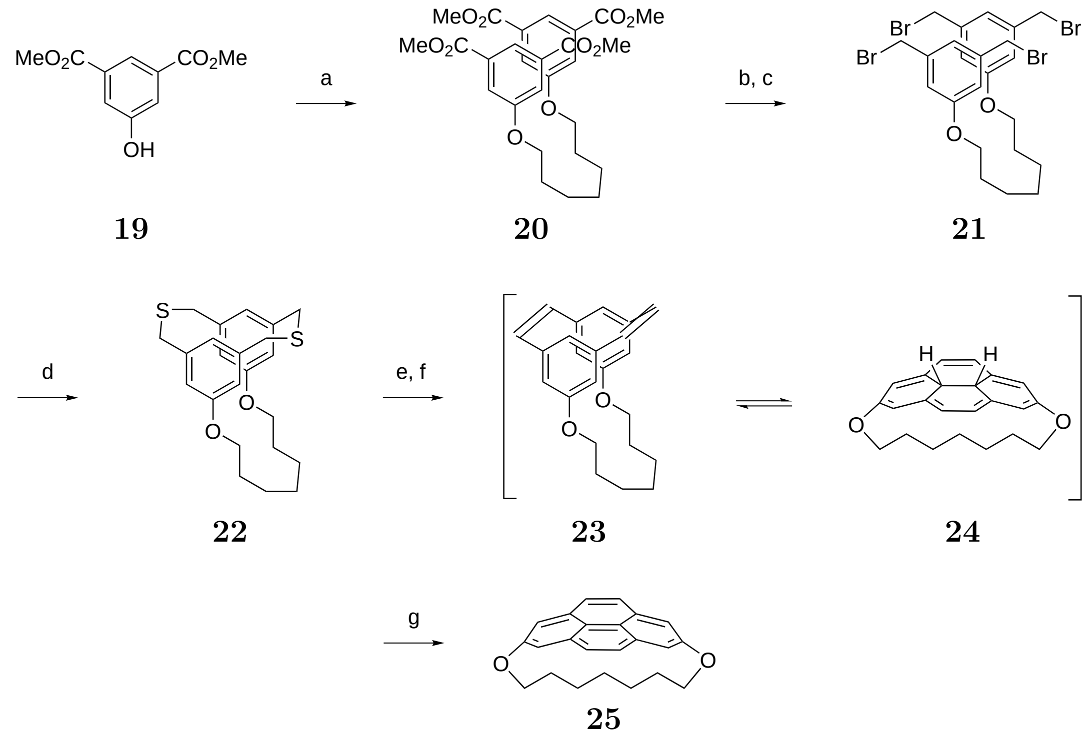


Figure 3.7: Synthesis of 1,9-dioxa[9](2,7)pyrenophane (**25**) [58]. a) NaH, 1,7-dibromoheptane, TBAI, THF, relfux; b) $LiAlH_4$, THF, rt; c) 48 % HBr/H_2SO_4 2:1, 70 to 90 $^\circ$C; d) Na_2S/Al_2O_3, 18 % CH_2Cl_2/EtOH, rt; e) $(MeO)_2CHBF_4$, CH_2Cl_2, rt, then *tert*-BuOK, THF, rt; f) $(MeO)_2CHBF_4$, CH_2Cl_2, rt, then *tert*-BuOK, THF/*tert*-BuOH, rt; f) DDQ, benzene, reflux.

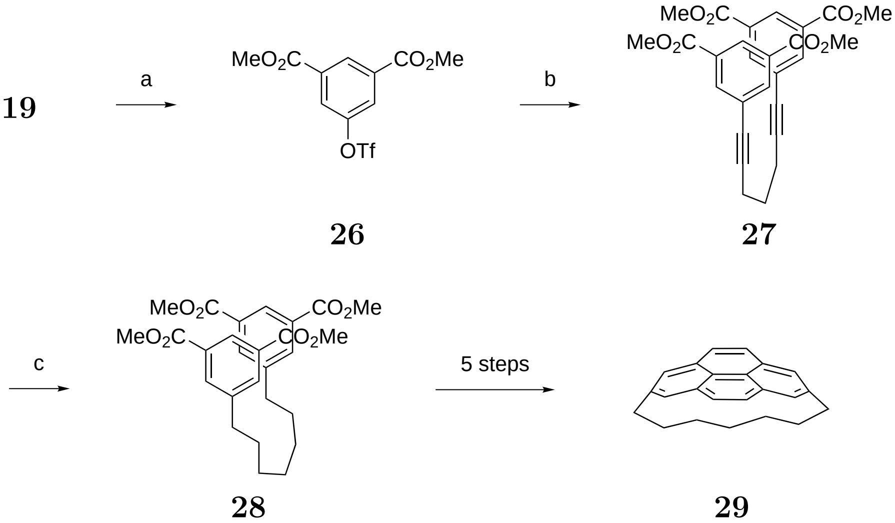
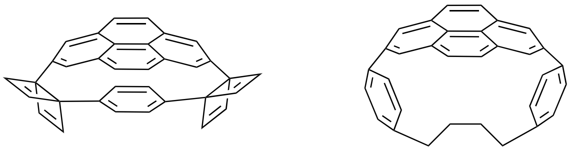


Figure 3.8: Synthesis of [7](2,7)pyrenophane (**29**) [57]. a) Tf_2O, pyridine CH_2Cl_2, 0 $^\circ$C; b) 1,6-heptadiyne, $Pd(PPh_3)_2Cl_2$, CuI, DBU, benzene, rt; c) H_2, Pd(OH)/C, AcOEt, rt.

was transformed to the triflate derivative **26**. A double Sonogashira reaction on **26** using the 1,6-heptadiyne gave the bridged diacetylenic product **27**, which was hydrogenated to yield **28** (figure 3.8). The continuation of this synthesis corresponds to the one described in figure 3.7.



30 **31**

Figure 3.9: Structures of pyrenophanes **30** and **31**, two possible precursors for an aromatic belt [59].

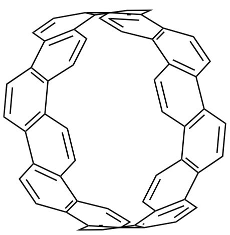
A large family of bridged pyrenophanes was prepared with variations on the bridge, like a central ether function or a *para*-linked phenyl unit [59]. Access to these bent pyrenes opens the possibility of synthesizing cyclic fullerene fragments. For this purpose, pyrenophane precursors **30** and **31** (figure 3.9) were proposed by Bodwell [59], but there synthesis was not achieved until now.

Chapter 4

Aromatic belts

4.1 Belts in fullerenes and SWNTs

A single-walled carbon nanotube consists of many assembled aromatic macrocycles, such as stacked rings, where each ring is an incremental part of a given SWNT. Figure 4.1 shows different conjugated belts coming from (7,7)-armchair (**32**), (12,0)-zigzag (**33**) and (9,1)-chiral (**34**) nanotubes.



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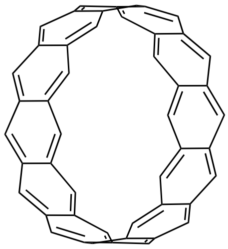

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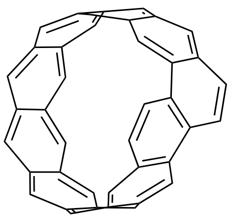

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Figure 4.1: Exemple of fully conjugated rings, coming from (7,7)-armchair (**32**), (12,0)-zigzag (**33**) and (9,1)-chiral (**34**) nanotubes.

This kind of conjugated belts can be found in the different type of fullerenes too. C_{60} and C_{70} contain both a (5,5)-armchair type conjugated belt, acting as an equatorial ring. [10]Cyclophenacene (**35**) (figure 4.2) is a 40 π-electron structure, which represents the shortest (5,5)-armchair CNT.

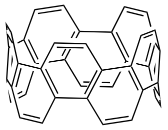

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Figure 4.2: [10]Cyclophenacene (**35**), the shortest (5,5)-armchair CNT.

In 2003, Nakamura has presented [10]cyclophenacene derivatives as the firsts hoop-shaped cyclic benzenoid compounds, prepared by dearomatization of C_{60} fullerene [60] (figure 4.3). The first step was carried out using an organocopper reagent to afford pentamethylated C_{60} **37**, a 50 π-electron structure. Masking of the cyclopentadiene hydrogen by a cyano group was introduced to prevent cyclopentadienyl anion formation, which is an unreactive species for further substitutions. Protected compound **38** can be converted to **39** by phenyl substitution, using the same kind reaction as the first one. Obtained product **39** was reduced to **40** by treatment with lithium naphtalenide. X-ray crystallographic analysis provided high precision structural data sets. On the basis of these results, it was proved that such chemically stable **35** derivatives are aromatics, a property which was predicted by theoretical studies [61].

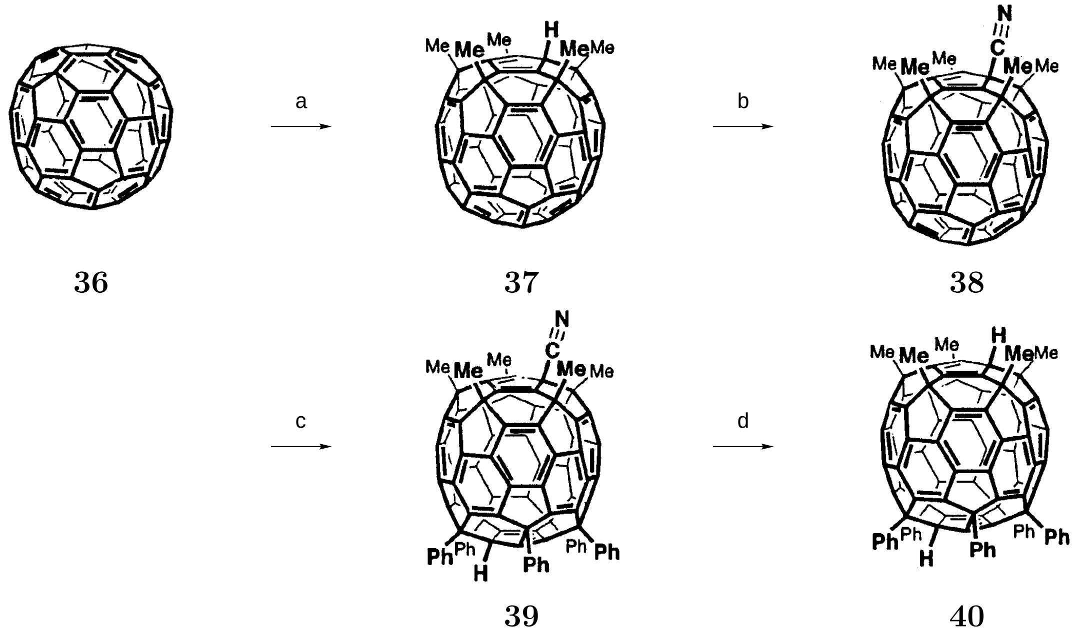
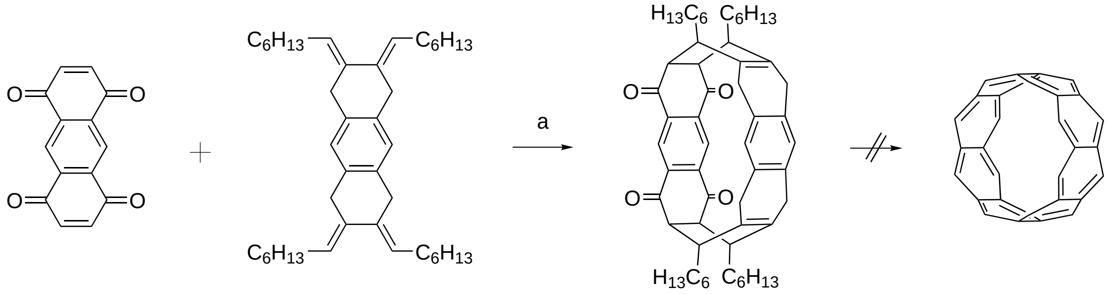


Figure 4.3: Synthesis of a [10]cyclophenacene derivative (**40**) starting from C_{60} fullerene (**36**). Molecules **37** and **38** are 50 π-electrons systems [60]. a) MeMgBr, $CuBr{\cdot}Me_2S$, DMI, THF/*o*-dichlorobenzene, rt; b) *tert*-BuOK, THF, then TsCN, PhCN, rt; c) PhMgBr, $CuBr{\cdot}Me_2S$, DMI, THF/*o*-dichlorobenzene, rt; d) $Li^+[C_{10}H_{10}]^-$, PhCN, rt.

4.2 Cyclacenes

One of the synthetic challenges in fully conjugated belt is the synthesis of cyclacenes, i.e. the (n,0)-zigzag unit of CNTs. Cory and Stoddard, among other researchers, have tried to pick up this challenge, but unfortunately, neither one nor the other have achieved the aromatization of their respective cyclic precursors. Synthetic attempt of [8]cyclacene (**44**) by Cory [62, 63] involved stereospecific double Diels-Alder macroannulation. Starting materials were the rigid planar bisdienophile diquinone **41** and the flexible non-planar bisdiene **42**. Flexibility of **42** is very important for the success of this macrocyclization, because of the relative shortness of **41**. The reaction was carried out by a slow and simultaneous addition of **41** and **42** solutions, yielding 69 % of cyclophane **43**, but unfortunately, only partial oxidation of **43** was possible, even if different methods were tested, no desired **44** was observed.



41 **42** **43** **44**

Figure 4.4: Synthetic approach of [8]cyclacene (**44**) made by Cory [62, 63]. a) dioxane, reflux.

On his side, Stoddard has presented a different strategy to get [12]cyclacene (**48**) and has proposed different synthetic ways to produce **47**, one of his macrocyclic precursors [64, 65, 66], with a large range of yields between 4 and 69 % for the ring closure reaction. Each route was using a diastereoselective Diels-Alder reaction sequence. The best method (figure 4.5), gave 69 % of **47** after the cycloaddition of 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane (**46**) with bisdienophile **45**, itself prepared by a Diels-Alder sequence. The obtained macrocycle **47** was then used for different oxidation attempts, but unfortunately only partial aromatization occured and no desired **48** was found.

4.3 Benzoannulenes

Patterns of the type *all-Z*-benzoannulene are found in all armchair carbon nanotubes. *All-Z*-tribenzo[12]annulene (**52**) was synthesized by Iyoda [67] and Vollhardt [68], using two different strategies. The first one was a nickel-catalyzed cyclotrimerization of 1,2-dibromo-1,2-dihydrobenzocycloobutene **49**. The reaction (figure 4.6) was carried out in DMF in the presence of $NiBr_2(PPh_3)_2$ and PPh_3, yielding 38 % of **50** and 4 % of **51**. Thermal treatment of **51** in refluxed *o*-dichlorobenzene afforded **52** in 90 % yield. The thermal ring-opening process retains the configuration of the starting material **51**, presumably due to the rigidity of its molecular framework [69].

The second strategy (figure 4.7) was involving tris(benzocyclobutadieno)benzene

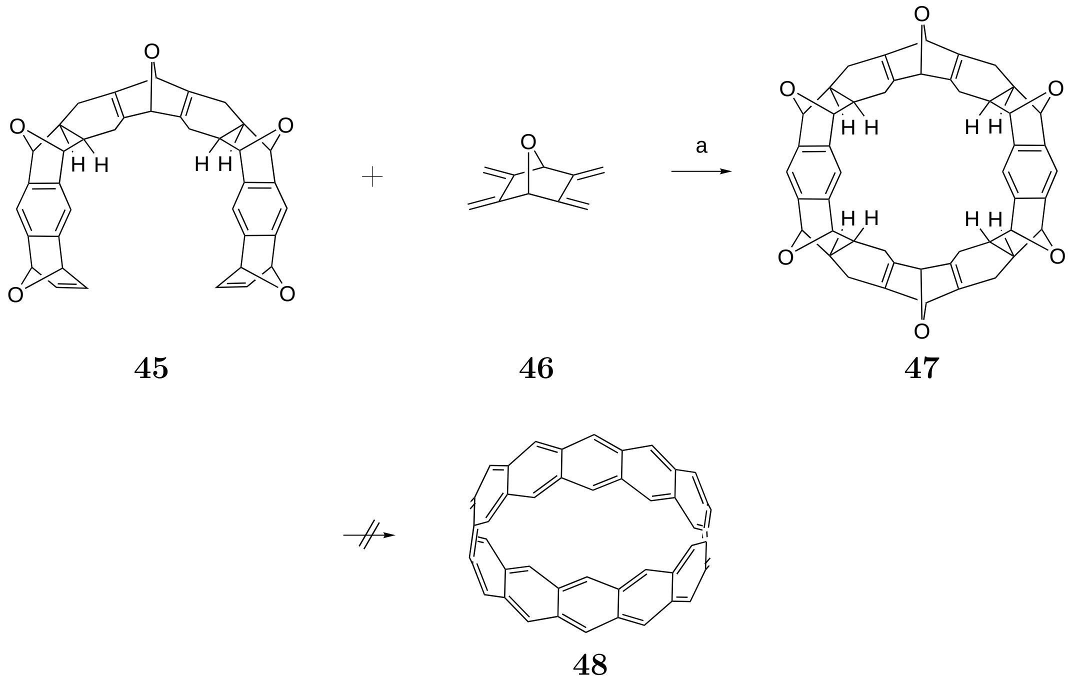


Figure 4.5: Synthetic approach of [12]cyclacene (**48**) made by Stoddard [65]. a) toluene, reflux.

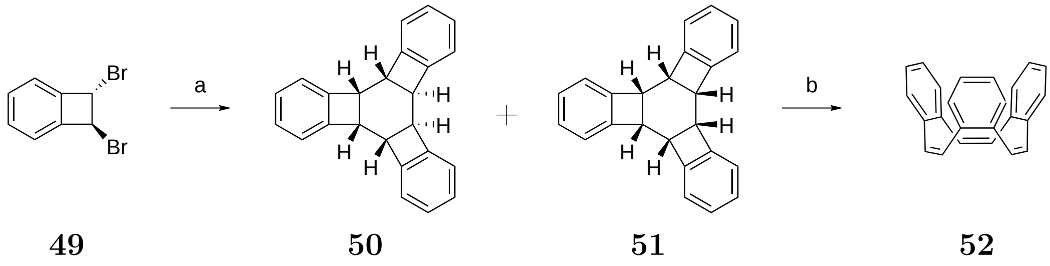
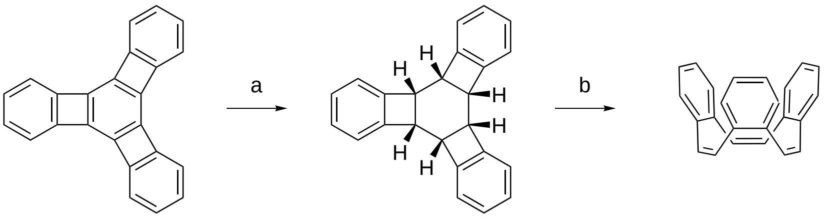


Figure 4.6: Synthesis of *all*-*Z*-benzo[12]annulene (**52**) by Iyoda [67]. a) $NiBr_2(PPh_3)_2$, PPh_3, DMF, rt; b) Δ, *o*-dichlorobenzene.

(**53**) [70], which was selectively reduced with soft hydrogenation conditions, giving the cyclohexane derivative **51** in a 87 % yield. This method allorwed to increase drastically the yield obtained by Iyoda. Retrocyclization of **51** at 125-160 °C gave the desired *all*-*Z*-tribenzo[12]annulene in a 95 % yield. Molecular models showed that **52** has a crown-like, rigid structure with a C_{3v} symmetry. This benzoannulene was used as ligand for the formation of Ag^+ (**54**) or Cu^+ (**55**) in a 1:1 ratio complexes (figure 4.8) [71].



53 **51** **52**

Figure 4.7: Synthesis of *all*-*Z*-tribenzo[12]annulene (**52**) by Vollhardt [68]. a) H_2 (1 atm), Pd/C, THF, rt; b) C_6D_6, 125-160 °C.

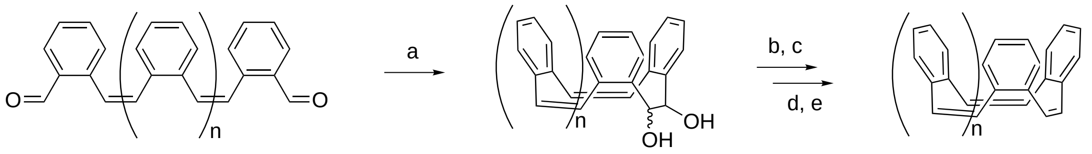
54 **55**

Figure 4.8: Complexes of Ag-**52** and Cu-**52**

Higher rings size of benzoannulene were synthesized (figure 4.9), as *all*-*Z*-tetrabenzo[16]annulene (**58**) and *all*-*Z*-pentabenzo[20]annulene (**61**) [72]. These macrocycles were prepared by a VCl_3/Zn-mediated cyclization of the corresponding dialdehydes **56** and **59**. Obtained *cis* and *trans* mixtures of diols **57** and **60**, respectively, were submitted to a stereochemical conversion to afford *cis*-diols only. Further olefination with the Corey-Winter method gave the benzoannulene **58** and **61**, respectively. Molecule **58** exhibits at room temperature a fast equilibrium between its two C_{2v} symmetrcal conformations (figure 4.10).

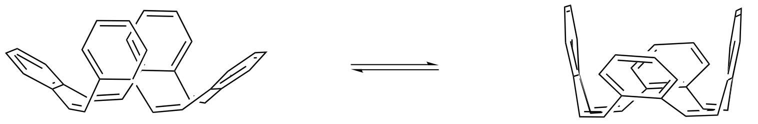
4.4 [0_n]Paracyclophanes

Paracyclophanes are cyclic molecules of *para*-linked phenyl or phenyl derivative units. The nomenclature of such a system is defined by giving the number and the length of each linker. A [2.2]paracyclophane (**62**) is a two phenyl unit compound,



56: n = 2 **57**: n = 2 **58**: n = 2
59: n = 3 **60**: n = 3 **61**: n = 3

Figure 4.9: Syntheses of *all*-*Z*-tetrabenzo[16]annulene (**58**) and *all*-*Z*-pentabenzo-[20]annulene (**61**) [72]. a) $VCl_3(THF)_3$, Zn, DMF, CH_2Cl_2, rt; b) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; c) $NaBH_4$, MeOH, CH_2Cl_2, 0 °C; d) TCDI, toluene, reflux; e) DMPD, benzene, reflux.

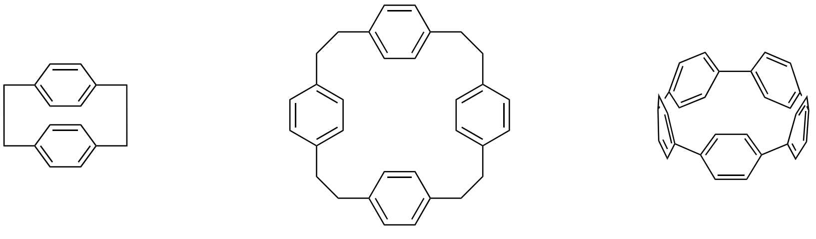


58 **58**

Figure 4.10: The two conformation of **58** at room temperature.

which contain two bridges composed of two carbon atoms each, while [2.2.2.2]paracyclophane (**63**) contains four phenyls linked with four bridges of two carbons (figure 4.11). When all bridges of a paracyclophane are equivalent, the notation can be modified to [2_2]paracyclophane for **62** and [2_4]paracyclophane for **63**, where the first number is the length of the bridge and the index number the number of units.

In the armchair CNT pattern, [0_n]paracyclophanes are found as a tube segment. For example, [0_5]paracyclophane (**64**), consisting of five phenyls directly *para*-linked together, is a subunit of a (5,5)-armchair SWNT.



62 **63** **64**

Figure 4.11: Structures of [2_2]paracyclophane (**62**), [2_4]paracyclophane (**63**) and [0_5]paracyclophane (**64**).

Syntheses of [0_n]paracyclophane are not yet achieved, but a lot of synthetic approaches were done, using different strategies for macrocycle formation and aromatization processes of the precursors. Due to the high rigidity of aromatic patterns, benzene ring formation must be done after macrocycle ring closure, which must contain flexible parts of preformatted benzene as, for example, saturated six-membered rings or butadiene patterns.

4.4.1 Cyclohexane hinges

A large number of precursors of **64**, or related products, containing cyclohexane rings were synthesized, but different strategies for macrocyclization were used or attempted, as McMurry olefination or carbon cross-coupling.

McMurry reaction was used in the syntheses of macrocycles **73** [73, 74] and **74** [75] (figure 4.12), constituted of cyclohexane rings joined together by double bonds. The use of an olefin is an advantage during such a synthesis, because it prevents formation of *cis* and *trans* mixtures. Phosphonohydrazone **65**, made by Horner-Emmons condensation of diethylphosphonohydrazate [76] with the corresponding ketone, was used to form azine **66**. This molecule was transformed to **67** by H_2S addition, followed by an oxidation. Precursors **69** and **71** were prepared by a similar synthetic sequence. After removal of the ketal protecting groups, N_2 extrusion and desulphurization, macrocycles **73** and **74** were closed by a McMurry reaction, but for molecules **73** and **74** being too small for a paracyclophane preparation, no aromatization attempt were done and **74** was used as ligand in Ag^+ complex preparation. Based on this synthetic route, Vögtle [77] has synthesized the penta-membered diketone precursor **72**, but the low obtained overall yield (0.7 %) did not offer the possibility of synthesizing the corresponding penta-membered ring **75** in useable quantity. Only traces of the desired product **75** were detected by mass spectrometry.

A similar approach was done by Cory, who had presented the tree-membered precursor **79** (figure 4.13) [78]. The synthesis involved 1,4-dilithiobenzene (**76**), obtained by a double lithiation of 1,4-dibromobenzene. This compound **76** was used as nucleophile in carbonyl attack of two 1,4-cyclohexanedione monoethylene ketal molecules (**77**). The benzylic alcohols of the obtained **78** were eliminated and the carbonyl protections removed by a one pot TFA treatment, giving **79**. McMurry conditions were then applied for a self-coupling of this compound, but unfortunatly, no $[0_6]$paracyclophane precursor **80** was obtained.

The following strategy, proposed by Vögtle [77], involving cyclohexane as an articulation, was using carbon homocoupling for ring formation attempt. Flexible *cis*-1,4-bis(4-iodophenyl)cyclohexane **81** was transformed to a double Grignard substrate, before being coupled with $CuCl_2$ (figure 4.14). Desired $[0_6]$paracyclophane precursor **82** was not formed and only oligomers were found. The observation of iodoaryl molecules after the coupling reaction shows that the first stage, the Grignard formation, was not completed.

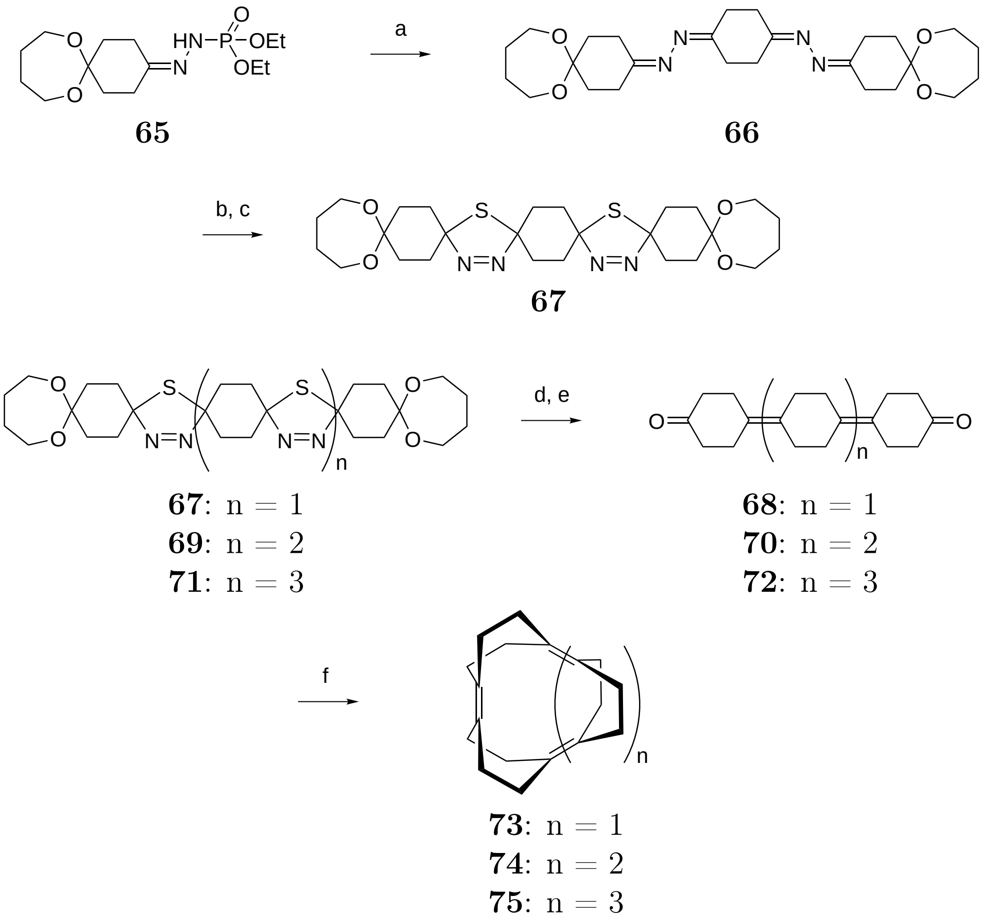


Figure 4.12: Syntheses of **73**, **74** and **75**. a) NaH, ketone, THF, rt; b) H_2S, MeCN, rt; c) $Pb(OAc)_4$, $CaCO_3$, CH_2Cl_2, rt; d) 37 % HCl, H_2O CH_2Cl_2, rt; e) toluene reflux, then $P(OEt)_3$ reflux; f) $TiCl_3$, Zn(Cu), DME, 68 °C.

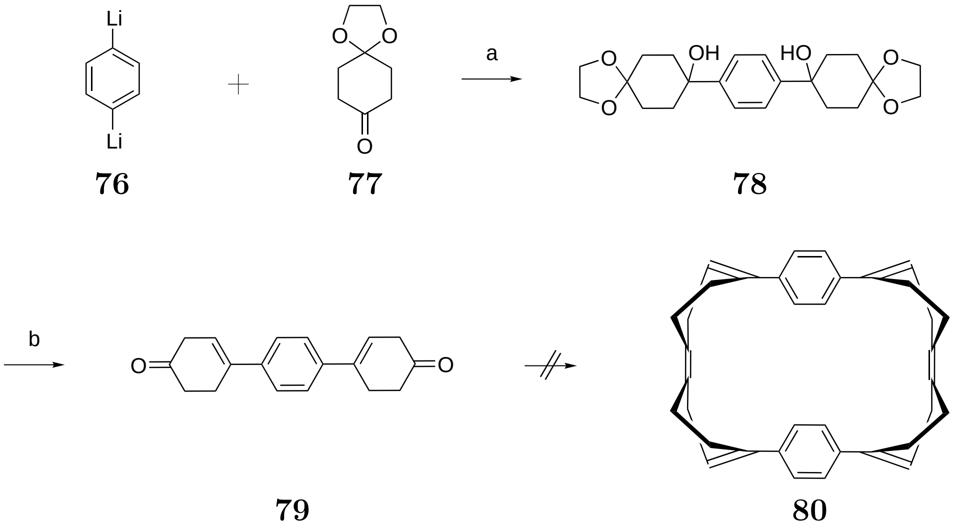
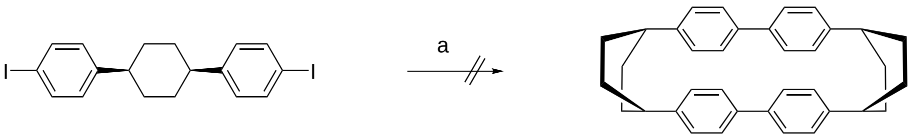


Figure 4.13: Synthesis of **79** made by Cory [78]. a) THF, rt; b) TFA, CH_2Cl_2, rt.

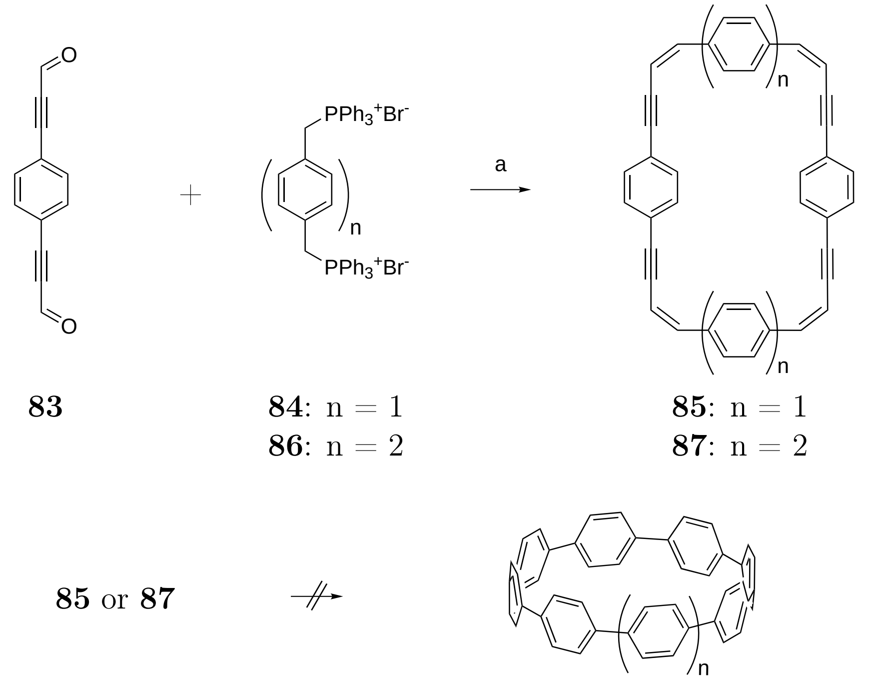


81 **82**

Figure 4.14: Synthetic attempt of [0_6]paracyclophane precursor **82**. a) Mg, THF, 70 °C, then $CuCl_2$.

4.4.2 Butenyne hinges

Macrocycles **85** and **87** were prepared [77] with the method used by Tanner [79] for the synthesis of [4.4.4.4]paracyclophane, containing four *E,Z*-butadiene bridges. Unfortunately, such butadiene isomers are not suitable for Diels-Alder reaction. For this reason, in each bridge of **85** and **87**, a double bond was replaced by an alkyne functional group. Their syntheses involved a multi-Wittig reaction between **84** or **86** and **83** (figure 4.15), but the formed macrocycles can not be aromatized by Diels-Alder reactions using the dienophile phenyl vinyl sulfoxide, a method conveniently used in the [1.1.1.1]paracyclophane preparation [80].



83

84: n = 1
86: n = 2

85: n = 1
87: n = 2

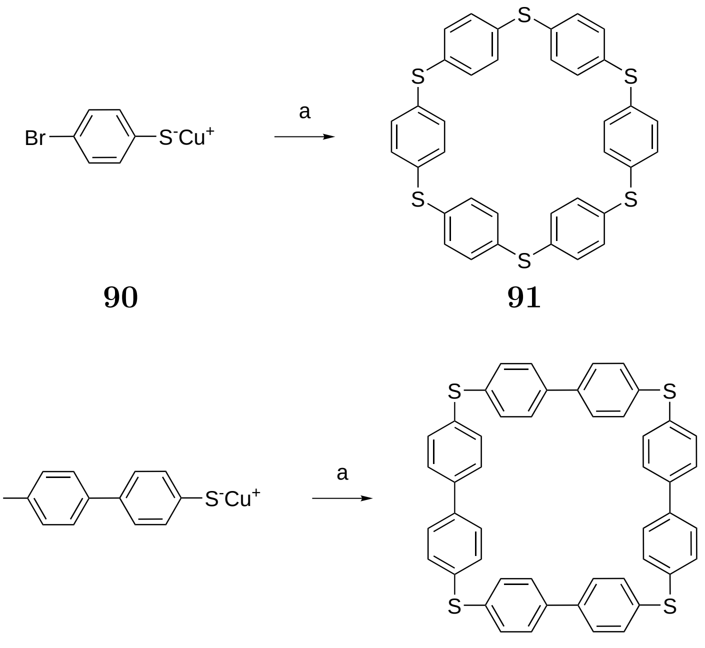
85 or **87**

88: n = 1
89: n = 3

Figure 4.15: Syntheses of macrocycles **88** and **89** [77]. a) EtOLi, DMF, -40 °C.

4.4.3 Sulfide and sulfur oxide hinges

Aryl sulfides and sulfones can be used as hinges in $[0_n]$paracyclophane precursor preparation. Aromatization could be achieved by known catalytic pyrolysis of such sulfides or sulfones, which affords aryl-aryl bonds [81]. Cyclic hexa-*p*-phenylenesulfide (**91**) and tetra-4,4'-biphenyldiylsulfide (**93**) were prepared in up to 62 % yield by oligomerization of the corresponding copper thiophenolates **90** and **92**, respectively [82]. The major difficulty of the synthetic route is the sulfide elimination. When processed with pyrolysis in presence of a Raney nickel catalyst, a mild detonation occurred, which shows limits in the synthetic control in this strategy.



90 **91**

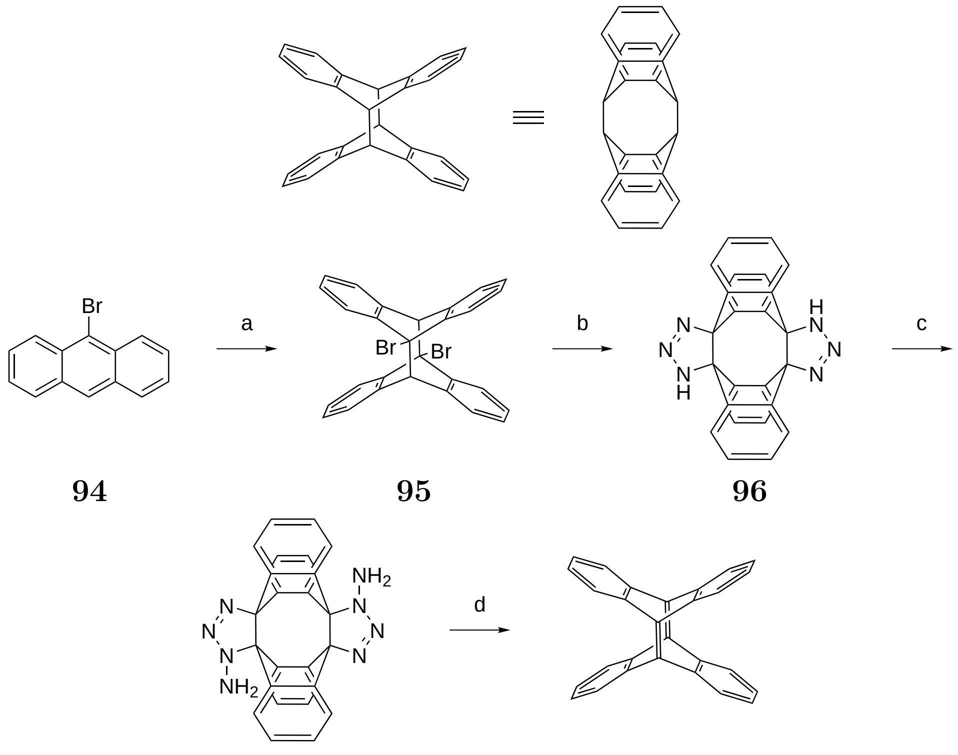
92 **93**

Figure 4.16: Syntheses of macrocycles **91** and **93** [82]. a) chinoline, pyridine, reflux.

4.4.4 9,9',10,10'-Tetradehydrodianthracene

9,9',10,10'-Tetradehydrodianthracene (**98**), prepared by Greene [83], corresponds to a tetrabenzo analog of $[0_2]$paracyclophane. The synthesis used for the preparation of **98** involved first a photodimerization of 9-bromoantracene (**94**), followed by a double elimination of bromohydric acid on dimer **95** (figure 4.17). Double bonds being very reactive were trapped *in situ* during the elimination by the addition of azide and regenerated under non-nucleophilic conditions, involving the formation of the intermediates **96** and **97**. The geometry of the olefinic carbons of **98** is far from a classical double bond and possesses a pyramidalization angle of 35 °, a property which increases the reactivity towards electrophiles and generated an unusually enhanced reactivity towards nucleophiles too. Compound **98** reacts as an electron-deficient dienophile with tetrazenes, via a [4+2] cycloaddition reaction with inverse electron demand [84]. Photochemically-induced [2+2] cycloaddition with ethylene gives the cyclobutane derivative **99**, which can be opened by a retro-cycloaddition, affording **100** (figure 4.18) [85]. In the case of [2+2] cycloaddition of cyclic olefins, the reaction gives directly the opened product, without the possibility of a cyclobutane derivative isolation. Fully conjugated belt derivatives of **98** can be obtained by metathesis with annulenes, benzene or α-pyrone, giving **101** [86] and **103**, respectively [87] (figure 4.19). The isolation of the intermediate product was only achieved for **102**, the precursor of **103**.

Compound **98** reacts with itself, forming a tube-like structure in a ring enlargement dimerization metathesis carried out by photochemistry, yielding picotube **104** in 35 % yield, an octabenzo analog of [0_4]paracyclophane (figure 4.20) [88]. Oxidation attempts were made, but no (4,4)-armchair nanotube segments were detected.



94 **95** **96**

97 **98**

Figure 4.17: Synthesis of 9,9',10,10'-tetradehydrodianthracene (**98**). a) hν, toluene, rt; b) *tert*-BuOK, NaN_3, DMSO, rt; c) *tert*-BuOK, mesityl-SO_2-ONH_2, rt; d) $Pb(OAc)_4$, benzene, rt.

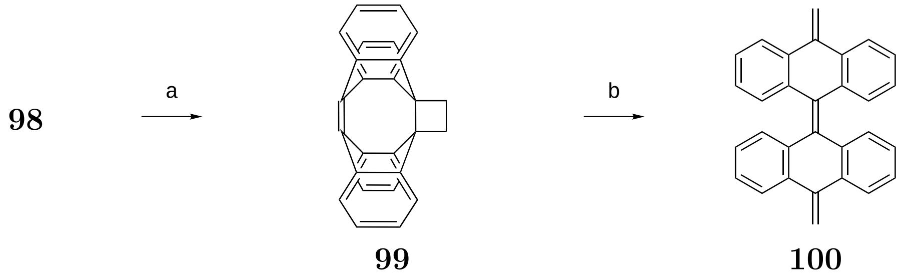


Figure 4.18: Reaction of **98** with ethylene, followed by retrocyclization [85]. a) C_2H_4, hν, benzene, rt; b) toluene, 110 °C.

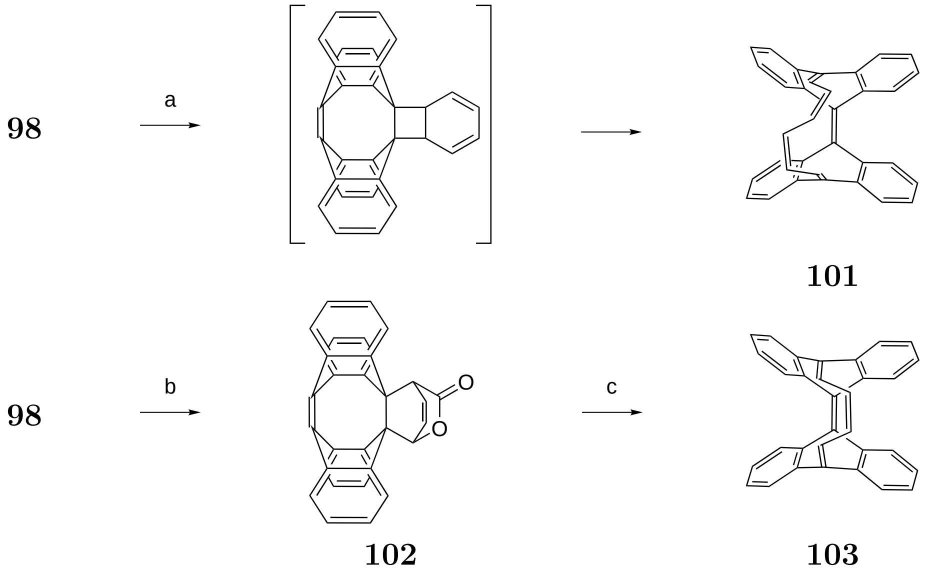


Figure 4.19: Formation of annulenes **101** [86] and **103** [87]. a) benzene hν; b) α-pyrone, toluene, 100 °C; c) xylene, 140 °C.

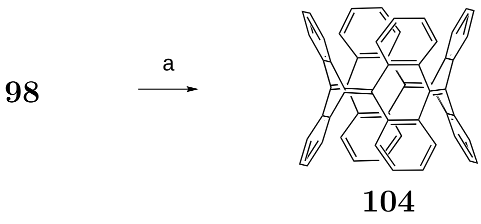


Figure 4.20: Synthesis of picotube **104** [88]. a) benzene hν.

Part II

Aim and methodology

Chapter 5

Aim of the work

This work is based on the results found by Manuel Raemy [17] during his PhD thesis, where iron(0)/DIBAH catalysts, tested for polymerization of acetylene, were found to produce graphitic material under mild conditions. The polymeric bulk, supported by an iron foil (figure 5.1), was produced in a reaction mixture, containing DIBAH as a co-catalyst and placed under 0.5 bars of acetylene, was carried out in benzene at room temperature. A Raman analysis of the coated foil revealed resonances corresponding to *trans*-polyacetylene, but the layer close to the metallic surface showed graphitic structures (figure 5.2).

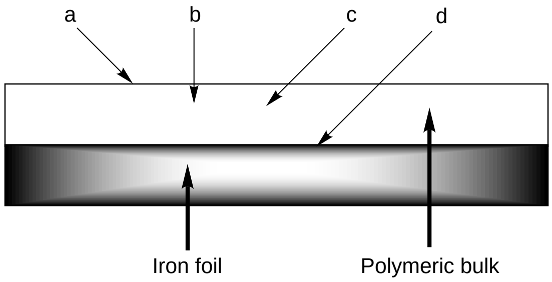


Figure 5.1: Scheme of the iron foil bearing the polymeric bulk. Arrows a,b,c and d are indicating the spots analyzed by Raman spectroscopy (see figure 5.2).

In his outlook Raemy proposed to use these results to produce SWNT under mild conditions. The ability of the catalyst to promote the formation of graphite from acetylene being demonstrated, the problem to force the sheet to adopt a tube-like shape could be solved by using a defined circular template (figure 5.3). With such an approach, a chemical synthesis of carbon nanotubes, with given diameter and geometry, could be realized. This proposal includes two challenges:

1. The synthesis of a $[0_n]$paracyclophane macrocycle, as proposed in the conclusion written by Raemy, is the first aim. Indeed, no $[0_n]$paracyclophane synthesis was reported so far in the chemical literature. On the other hand several

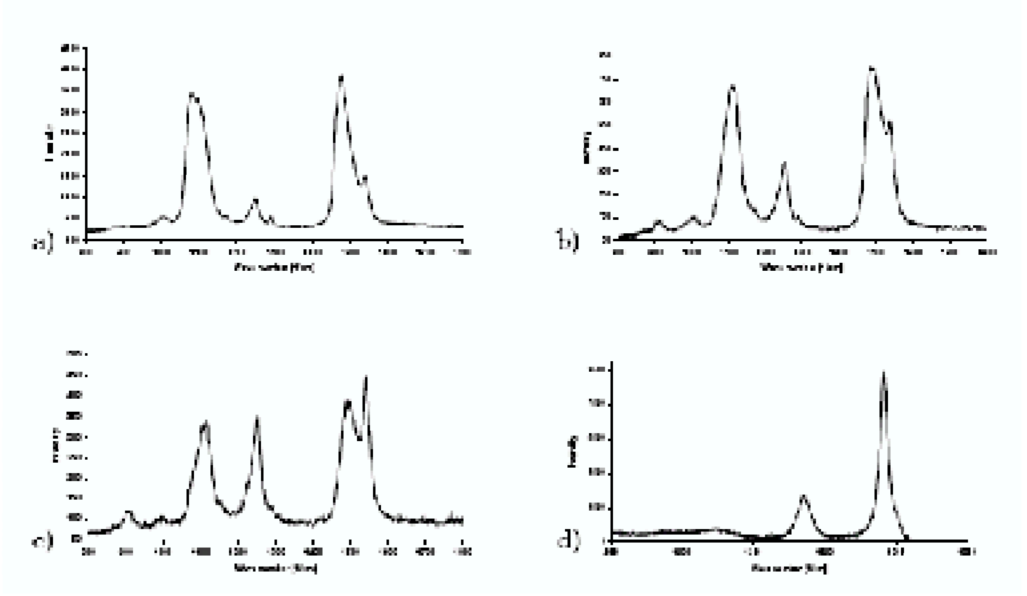


Figure 5.2: Raman spectra of polymeric bulk. a) at the surface; b) and c) inside layers; d) layer close to the iron foil.

articles concerning the modelization of such a cycle were published [89, 90] and it was demonstrated [90] that the selected macrocycle geometry consist of the most stable template for armchair SWNT production. Among the different possibilities for the paracyclophane diameter, the work was concentrated for the most part to the synthesis of [0_5]paracyclophane, corresponding to the (5,5)-SWNT, the smallest one found in the carbon nanotube bulk produced by physical techniques.

2. The second aim is to test the catalyzed polymerization and dehydrogenation of acetylene process on a curved polyaromatic template. Indeed, it is not clear if the iron(0)/DIBAH system works for extending polyaromatic compounds and hence offers the possibility of CNT growing using a short cut carbon nanotube or a hemi-fullerene. These templates are one possibility to test the catalytic system.

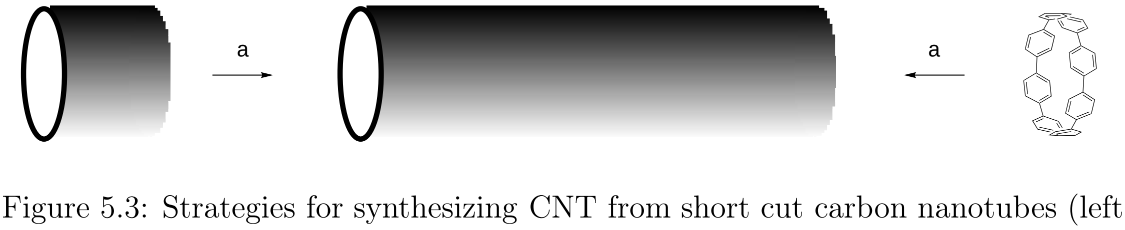


Figure 5.3: Strategies for synthesizing CNT from short cut carbon nanotubes (left) or [0_n]paracyclophane (right) template. a) iron precursor, DIBAH, 0.5 bars acetylene, benzene, rt.

Chapter 6

Methodology: the hinge and bend concept

Benzene rings have a rigid and planar geometry, but the target compounds of this work are macrocycles containing curved phenyl units. By using directly aromatic rings for the preparation of the precursors, the macrocyclic ring closure would not be possible. The solution is to use hinges and bends prior to the ring closing procedure, which can be removed afterwards or transformed to aromatic rings.

6.1 Prearomatic hinges and bends

The use of aromatic precursors allowing for flexibility or using precursors preset at fixed angles are needed for the ring closure reaction. These precursors must have the possibility to be transformed in a phenyl unit during subsequent steps.

6.1.1 Cyclohexane

Cyclohexane, substituted in positions 1 and 4, in a *cis* configuration, is a hinge which can adopt a large range of angles between the two substituents, as shown for chair, twist and boat conformations (figure 6.1). The advantages of this precursor are its high flexibility and the allready existing six-membered ring. Oxidation can be achieved by DDQ treatment, but additional functional groups, such as alcohols, can be useful. Indeed, elimination of such groups offers a more advanced oxidation state of the ring, equivalent to a cyclohexene or cyclohexadiene unit. The oxidation of *cis*-1,4-diphenylcyclohexane by DDQ [91] (figure 6.2) was realized in order to test the ability of such a pattern to be oxidized into a phenyl unit. The reaction, carried out in benzene, gave 85 % of *para*-terphenyl (**106**) starting from precursor **105**. The obtained product was characterized by comparison with a commercial source. This experiment showed how easy this oxidation is achieved, but in the case of the $[0_n]$paracyclophanes, the curvature of the resulting compound should be considered. It was not yet demonstrated, however, that such reaction works on strained molecules, such as cyclacenes (see section 4.2).

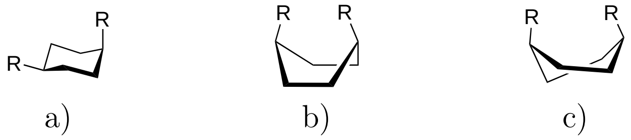
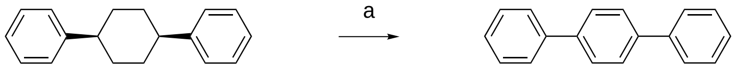


Figure 6.1: The three conformations of *cis*-1,4-disubtituted cyclohexane. a) chair; b) boat; c) twist.



105 **106**

Figure 6.2: Oxidation of **105** by DDQ [91]. a) DDQ, benzene, reflux, 20 h, 85 %.

6.1.2 Dewar benzenes

Dewar benzene corresponds to an isomer of classical benzene. Indeed, the bonding sequence gives a different geometry to the molecule, corresponding of two four-membered cycles, linked by a common single bond with an angle of approximately 80 ° . Valence isomerization of such molecules is a useful reaction for generating structurally distorted benzene derivatives. Dewar benzenes were used for the preparation of small [n]paracyclophanes and larger ring systems. The synthesis presented in figure 6.3 shows the preparation of a 2,5-disubstitued Dewar benzene derivative, corresponding to a 1,4-disubstituted benzene unit. The target compound **112** was obtained with its isomer **113** after a four steps synthesis [92]. The Dewar benzene skeleton **109** was first obtained by a double cycloaddition reaction between dimethylacetylenedicarboxylate (**107**) and 1,2-dichloroethylene (**108**). Compound **109** was then protected as a ketal (**111**) after being reduced to the diol **110**. Dewar benzene derivatives **112** and **113** were finally obtained by a double HCl elimination in an equimolar ratio.

6.1.3 Butadienes

Butadiene patterns such as *E,E*-1,4-disubstituted butadienes, pyridazines, 2-pyrones or furans can be used as non-planar precursors of benzene rings. Indeed, a cycloaddition [4+2] with such compounds can produce directly six-membered rings or bridged bicycles bearing leaving groups or weak bonds. In the case of *E,E*-1,4-disubstituted butadiene, the obtained product is an oxidated derivative of cyclohexane, namely

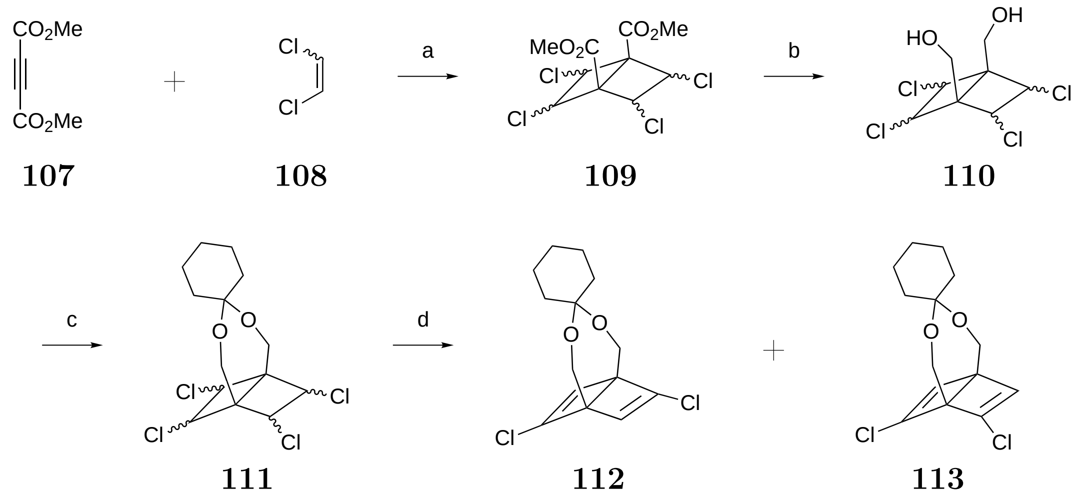
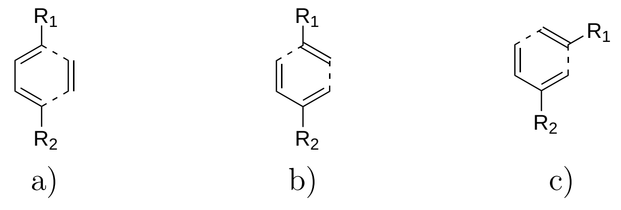


Figure 6.3: Synthesis of Dewar benzene derivatives **112** and **113** [92]. a) hν, -10 °C, 12 h, 35 %; b) $LiAlH_4$, Et_2O, reflux, 2 h, 89 %; c) 1,1'-dimethoxycyclohexane, TsOH, benzene, reflux, 68 %; d) *tert*-BuOK, 0 °C to rt, 3 h, 35 % (**112**) and 35 % (**113**).

cyclohexene, but contrary to the cyclohexane unit, butadiene allows, before cycloaddition, its incorporation in a less strained macrocycle. This property is an advantage for the macrocycle formation, but such conjugated systems are more difficult to be synthesized because of their *E,E*-configuration needed for the Diels-Alder reaction. An other possibility for a [4+2] cycloaddition reaction involving mono-substituted butadiene and a dienophile bearing the other substituents, but in this case, the selectivity of the reaction needs to be controled to get the 1,4-disubstituted compound instead of the 1,3-one (figure 6.4).



a) b) c)

Figure 6.4: [4+2] Cycloadditions of a butadiene unit. a) 1,4-disubtituted butadiene, b) monosubstituted butadiene giving the 1,4-benzene precursor and c) monosubstituted butadiene giving the undesired 1,3-compound.

Compounds as pyridazine, 2-pyrone or furan are cyclic equivalents of an *E,E*-butadiene unit. To obtain a *para*-substituted benzene, two possibilities are available for the functional groups positions (figure 6.5). If the cycle is linked two times with the other parts of the molecule, as in 2,5-disubstituted pyridazine, 3,6-disubstituted-2-pyrone or 2,5-disubstituted furan, the selectivity of the Diels-Alder reaction is easier controled, but the flexibility of the pattern is less attractive for such bicycles bearing functional groups on the bridge heads. Indeed, if the cycloaddition reaction happens before the macrocycle ring closure, the angle between the two substituents is too much open with respect to the desired articulation (see table 6.1). In the case of 2,5-disubstituted pyridazine, the elimination of the nitrogen happens in general during the Diels-Alder addition, allowing only the possibility of a cycloaddition used for the macrocycle formation.

The other possibility with these patterns is the use of mono-substituted dienes, as for instance 3-substituted furan, 4- or 5-substituted-2-pyrone and 3-substituted pyridazine, which can react with the substituted dienophile. The choice of this route is more convenient, because of the better adjusted angle available with molecules bearing substituents on the bridge heads (see table 6.1), but the selectivity of the reaction is more complex because of the attack, which can give two different isomers for acetylenic dienophiles. For olefinic dienophiles, the *endo/exo* orientation gives more products, which are not important for bicycles with substituents on the bridge heads.

Oxidation of these precursors to a phenyl unit can be achieved by opening the bicycle (furan) or by the elimination of a small molecule such as N_2 (pyridazine) or CO_2 (2-pyrone).

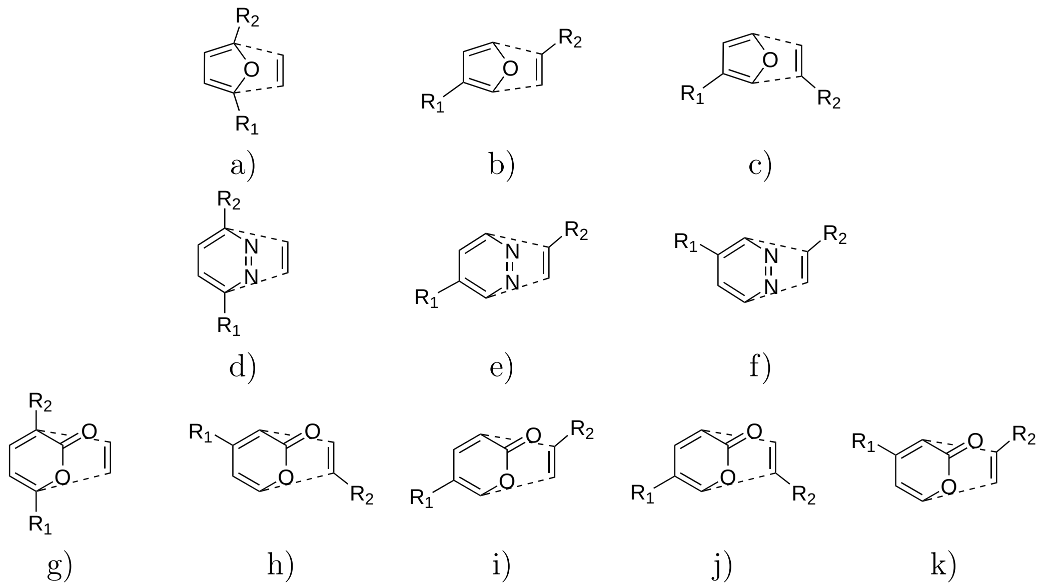
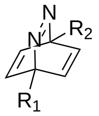
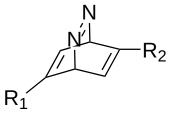
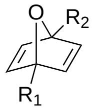
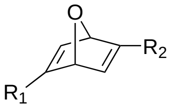
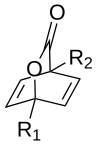
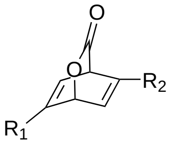
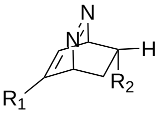
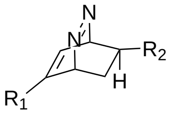
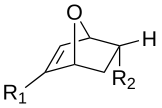
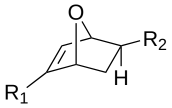
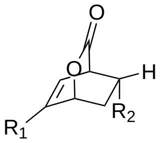
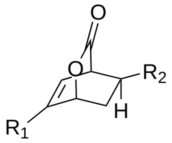


Figure 6.5: The different possibilities obtained after a Diels-Alder reaction involving furan (a-c), pyridazine (d-f) or 2-pyrone (g-k). The dienophile are presented as olefines, but they can be acetylene derivative too.

Pattern	Angle^{a} [$^\circ$]	Pattern	Angle^{a} [$^\circ$]
Acetylenic dienophiles			
	180		56
	141		69
	180		57
Olefinic dienophiles^{b}			
	81		156
	85		152
	81		154

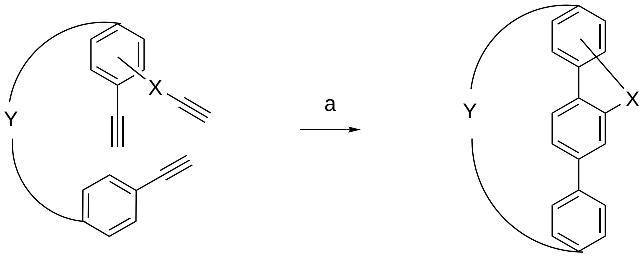
a) These angles, given only as information, were calculated from ACD/3D, Chem3D or directly measured on real molecular models; b) Compounds bearing substituents on bridge's head were omitted, due to the low variation with obtained with acetylenic dienophiles.

Table 6.1: Calculated angles between substituents R_1 and R_2 in disubstituted bicycles made from pyrone, furan and pyridazine.

6.1.4 Cyclotrimerization of acetylene

Cyclotrimerization of acetylene is an other possibility for forming a benzene ring, but this method is not very attractive. Indeed, this reaction has a low selectivity and it will be a hard task to obtain a 1,4-disubstituted benzene ring. Moreover, this aromatic ring formation would only be possible as the macrocyclization key step.

The following proposal (figure 6.6), extrapolated from [7]helicene-like molecules syntheses [93], is one possibility to get the selectivity in such a trimerization. The macrocycle precursor **114** could be functionalized with three acetylenes groups, one of them linked via a labile bridge to the position 2 or 3 of a terminal aromatic ring. The bridge (X on figure 6.6) could be removed from **115** in a subsequent step. The Y part corresponds to the flexible part of the macrocyclic precursor. In the major part of cyclotrimerization reactions, $Co_2(CO)_8$ or $CoCp(CO)_2$ are used as catalyst [94], but Si_2Cl_6 [95], a less employed cyclotrimerization agent, offers a larger selectivity. Unfortunately, no specific catalyst is available to obtain 1,4-disubstituted benzene.



114 **115**

Figure 6.6: Proposed strategy for trimerization of acetylene derivatives with a 1,4-selectivity. X = labile bridge and Y = flexible part of the precursor. a) [Co] or Si_2Cl_6.

6.2 Others hinges and bends

Non-aromatic hinges could be used for the formation of strained *para*-linked polyaromatic macrocycles. They consist of heteroatoms placed between two phenyl units. The angle of the hinge can be fixed or variable, depending of the element used. Onece the macrocycle is closed, the inserted heteroatom could be removed providing the biaryl pattern.

6.2.1 Platinum bend

Formation of square planar platinum(II) complexes, bearing two aryl ligands in *cis* geometry imposed by a bidentate bis-phosphine ligand equivalents a rigid hinge, set at a fixed angle. Molecular modeling of $PtAr_2(Ph_2P\text{-}(CH_2)_n\text{-}PPh_2)$ complexes allow for calculation of the corresponding Ar-Pt-Ar angle (table 6.2). Macrocycles containing platinum complexes as bends can be oxidized giving the aryl-aryl coupling product by reductive elimination of the residual metallic complex. Such a method was employed by Bäuerle for the synthesis of a strained polythiophene macrocycle [96] (see section 8.2).

Ligand name	n	Ar-Pt-Ar angle[a] [°]
dppm	1	115
dppe	2	78
dppp	3	68
dppb	4	63

a) Calculated with Chem3D.

Table 6.2: Calculated angles of Ar-Pt-Ar of $PtAr_2(Ph_2P\text{-}(CH_2)_n\text{-}PPh_2)$ complexes with different biphosphine ligands.

6.2.2 Sulfur hinge

The sulfur hinge is more flexible than the Pt one. The use of such a pattern was already attempted for the formation of polyaromatic strained cycles (see section 4.4.3). The main advantage of this kind of articulation between two existing phenyl units is that no C-C bond should be formed to obtain a strained macrocycle. Extrusion is in general achieved by thermal treatment or photolysis of the corresponding sulfone, but unfortunately sulfur extrusion between two aromatic rings is not very efficient giving low yields. In comparison, sulfone extrusion [97] between to benzyl groups is better and allows for medium to good yields. Moreover, thermal extrusion is not a clean reaction and selectivity can not be guaranteed for such process, giving a lot of side products.

Part III

Results and discussion

Chapter 7

1,4-Diphenylcyclohexane pattern synthesis

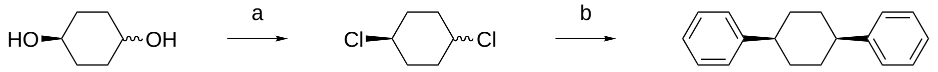
The choice of the *cis*-1,4-diphenylcyclohexane pattern as starting point for the different strategies presented below was made for different reasons. Firstly, the *cis*-1,4-disubstituted cyclohexane offers a good hinge, a quality which was discussed in section 6.1.1. An other advantage of *cis*-1,4-diphenylcyclohexane is the rich chemistry in *para* of the phenyls, provided by the activation effect of the cyclohexane substituent. Finally, this pattern is known and has already been prepared by different methods [77, 98].

On the other hand, the main disadvantage of the *cis*-1,4-diphenylcyclohexane is the presence of the *trans* isomer, which must be removed from the mixture before going on to further steps, but in general, the separation is not difficult and gives the *cis* form in high purity.

7.1 Synthesis of *cis*-1,4-diphenylcyclohexane derivatives

One of the procedures used for synthesizing *cis*-1,4-diphenylcyclohexane (**105**) [98] consists to a double $AlCl_3$ catalyzed Friedel-Crafts acylation on benzene with an epimeric mixture of 1,4-dichlorocyclohexane (**117**), which was previously produced at 53 % yield by a nucleophilic substitution reaction of a *cis* and *trans* mixture of 1,4-cyclohexanediol (**116**) in refluxing concentrated HCl [99]. The Friedel-Crafts reaction was carried out at room temperature for 2 hours, yielding 32 % of the *cis* isomer after a purification made by vacuum distillation and the separation of the *trans* isomer by crystallization of this latter from ethanol (figure 7.1). The oily product contained in the mother liquor is the *cis* form [100]. The quality of the separation was controlled by GC-MS analysis.

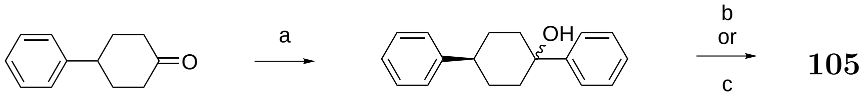
The other approach for synthesizing **105** consists in using 4-phenylcyclohexanone



116 **117** **105**

Figure 7.1: Synthesis of *cis*-1,4-diphenylcyclohexanol (**105**) by Friedel-Crafts reaction [99, 98]. a) 37 % HCl, 100 ˚C, 18 h, 53 %; b) benzene, $AlCl_3$, rt, 2 h, 32 %.

(**118**) as the substrate. The carbonyl was attacked by a phenylmagnesium bromide reagent in a 4 hours reaction carried out in THF and at room temperature. The *cis* and *trans* mixture of the obtained benzylic alcohols **119** was then treated to remove the hydroxyl group. The first procedure which was used consists in an elimination of the alcohol by hydrogenation under 3 bars in ethanol in presence of 10 % of Pd/C, yielding 29 % of pure *cis* isomer. The choice of the solvent is very important in this reaction. Indeed, since the byproduct *trans*-1,4-diphenylcyclohexane is insoluble in ethanol, it can be easily removed by filtration during the work-up procedure. The second method used for the reduction of the benzylic alcohol of **119** involved Raney-nickel as the reducing agent. The mixture was treated at room temperature in ethanol for two days. The washing of the nickel slurry at the end of the reaction gave a mixture of **105** and its *trans* isomer, which were separated as previously described by crystallization (figure 7.2).



105

118 **119**

Figure 7.2: Synthesis of *cis*-1,4-diphenylcyclohexanol (**105**) by Grignard reaction, followed by an alcohol elimination with H_2 or Raney-nickel. a) C_6H_5MgBr, THF, rt, 4 h, 91 %; b) H_2 3 bars, EtOH, rt, 3 d, 29 %; c) Ni, EtOH, rt, 2 d, 41 %.

To confirm the attribution of the structure of the two epimers, the solid one was crystallized and submitted to an X-ray analysis. These results are in agreement with [100]. Figure 7.3 shows the structure of *trans*-1,4-diphenylcyclohexane.

The synthesis of derivatives of **105** (figure 7.4) bearing functional groups in the *para* position of the aromatic rings and in the two benzylic positions was an other starting point. The strategy was a double carbonyl attack of 1,4-cyclohexanedione with a mono-lithiated derivative of 1,4-dibromobenzene (**120**). The halogen exchange with *tert*-BuLi is easy for the first bromide, but harsher conditions are needed for the second one. This property affords the mono-lithiated compound, avoiding oligomerization or polymerization processes. As described above, the dou-

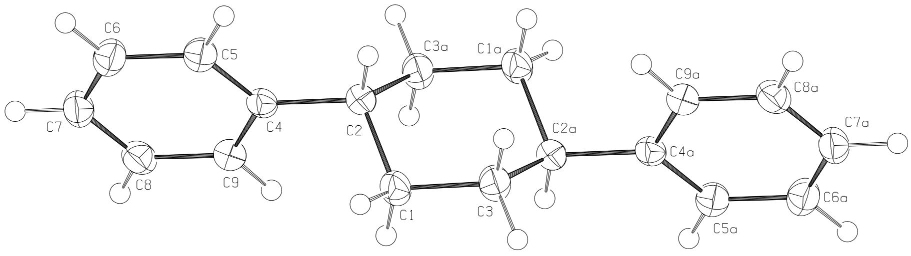
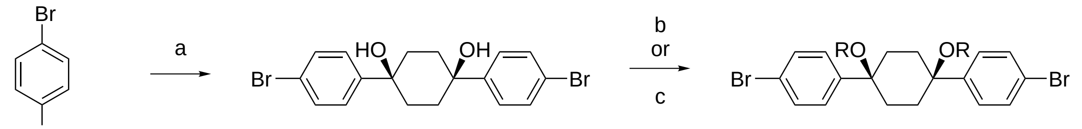


Figure 7.3: ORTEP presentation of *trans*-1,4-diphenylcyclohexane.

ble reaction on 1,4-cyclohexanedione gave epimeric mixtures of diol **121**. The reaction involves first the formation of the lithio derivative in THF at -78 °C. The 1,4-cyclohexanedione was then added and the temperature directly rose to 35 °C. Indeed, the ratio *cis/trans* is at the maximum at this temperature. At lower or higher temperature the *trans* isomer becomes the major product. The two epimers have distinct physical properties due to the hydrogen bonding found in the *cis* form, which does not exist for the other form. The separation was done by column chromatography, yielding 32 % of pure **121**. The last step in the preparation of theses derivatives is the protection of the alcohol groups. Different methods were tested, giving TMS protected and methylated compounds. The trimethyl silyl protection was carried out in THF in presence of imidazole as a base, yielding 87 % of product after 4 hours at room temperature. The obtained derivative **122** was purified by column chromatography. The methoxy protection was made by using NaH and MeI in refluxing THF, yielding 95 % of derivative **123**. Crystallization of the *cis* isomer allowed the confirmation of the attribution of the *cis* and *trans* products obtained in the previous step (figure 7.5). Compound **123** was already published [77], but its previous synthesis involved 5 steps instead of two.

The replacement of the TMS or Me groups by a more bulky protecting group,such as TBDMS, could have the advantage to force the cyclohexane unit to take a boat conformation. But unfortunately, all the attempts using TBDMSCl as reagent gave no results.



120 **121** **122**: b, R = TMS
123: c, R = Me

Figure 7.4: Synthesis of compounds **122** and **123**. a) *tert*-BuLi, THF, -78 °C, 45 min, then 1,4-cyclohexanedione, 35 °C, 5 h, 32 %; b) imidazole, TMSCl, THF, rt, 4 h, 87 %; c) NaH, MeI, THF, reflux, 23 h, 95 %.

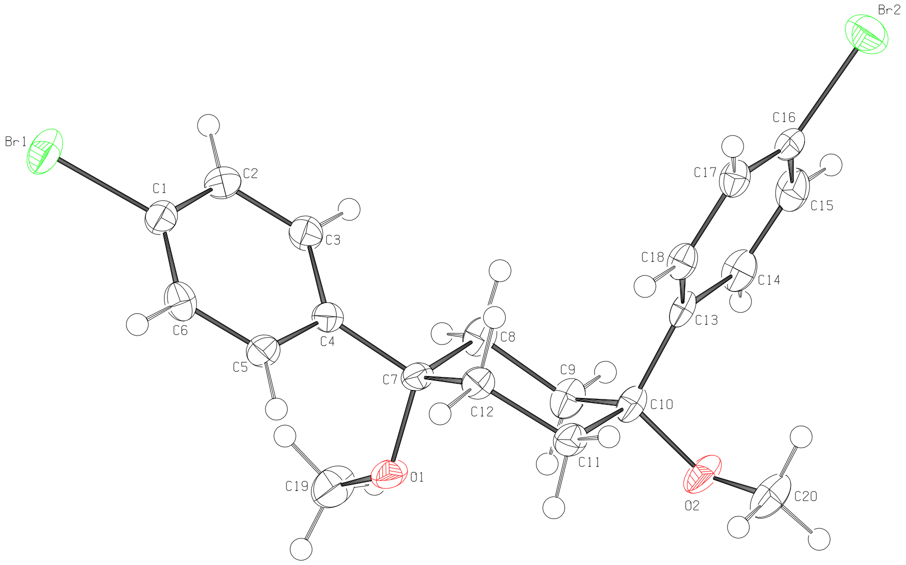


Figure 7.5: ORTEP presentation of **123**.

Chapter 8

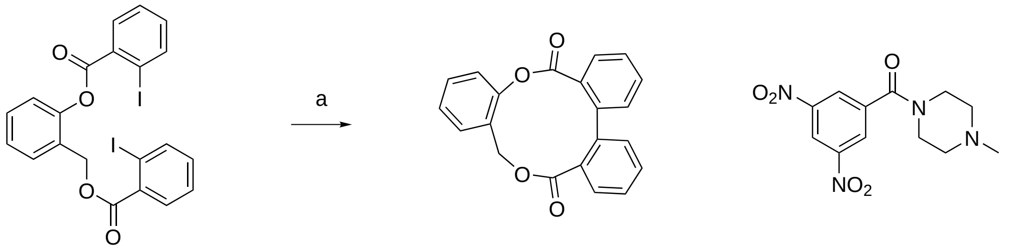
Homocoupling of the 1,4-diphenylcyclohexane pattern

Homocoupling of 1,4-diphenylcyclohexane patterns such as **105**, **122** and **123** is one possibility to get a $[0_6]$paracyclophane precursor.

8.1 Copper bromide mediated coupling

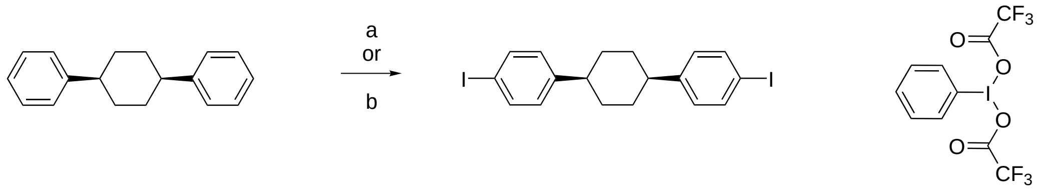
The strategy for coupling **105** was already proposed by Vögtle [77] (see section 4.4.1), but the tools available at that time were not sufficient to get the desired product. For this reason, a recent procedure was tested on the *cis*-1,4-bis(4-iodophenyl)cyclohexane (**81**). It consists in a $CuBr{\cdot}Me_2S$ mediated coupling of arylmagnesium chloride, followed by the elimination of the metallic center with an oxidant. This method, developed by Spring [101], was successfully used for the closure of highly strained macrocycles such as **125** (figure 8.1). In this example, the ring closure occurred after transmetallation with isopropylmagnesium chloride on the precursor **124**, followed by the addition of the copper reagent. The oxidant used in this reaction was the (3,5-dinitrophenyl)-(4-methylpiperazin-1-yl)methanone (**126**) instead of *meta*-dinitrobenzene, a more classical oxidant, but which involves a more difficult purification process.

In the case studied in this work, compound **105** musts be first functionalized by iodine in *para* position of both aromatic rings. The two methods used afforded **81** between 48 and 54 % yield (figure 8.2). The first one, already described [77], was using AgTfO and elemental iodine. The second one was using a more recent reagent [102], [bis(trifluoroacetoxy)iodo]benzene (also called PIFA) (**127**), and iodine. In both cases, purification of the crude product was done by recrystallization in EtOH, giving white crystals. Similar reactions were attempted by replacing I_2 by Br_2 in the aim to obtain the brominated aryl, but no purification procedures were found to separate the different isomers obtained.



124 **125** **126**

Figure 8.1: Synthesis of a strained macrocyle by Spring [101]. a) *iso*-PrMgCl, THF, -20 °C, 10 min, then CuBr·Me_2S, 30 sec, then **126**, rt, 20 min, 85 %.



105 **81** **127**

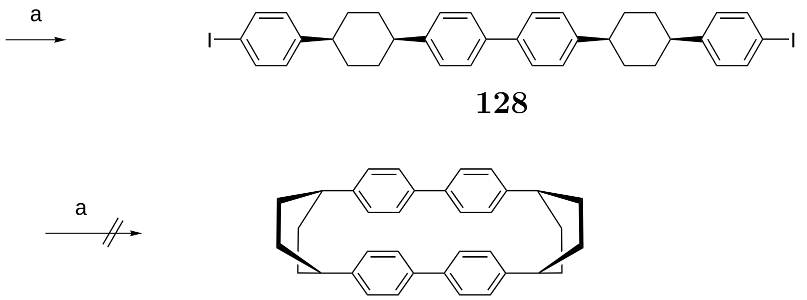
Figure 8.2: Synthesis of *cis*-1,4-bis(4-iodophenyl)cyclohexane (**81**). a) I_2, AgOTf, $CHCl_3$, 0 °C to rt, 2 h, 54 %; b) **127**, I_2, $CHCl_3$, rt, 2 h, 48 %.

Homocoupling of **81** with Spring's method was attempted in a two step procedure (figure 8.3). The first reaction consists of coupling two molecules of **81** to give the linear hexa-cyclic compound **128** and the second reaction would be the cyclization attempt. Formation of the mono-Grignard derivative of **81** was not efficient. Indeed, after the three stages, the major part of the starting material was found in the crude mixture, indicating that the first step did not work correctly, probably due to the low solubility of the substrate at low temperatures. After a separation of the crude mixture by chromatography, 9 % of the desired compound **128** was isolated. But the second Spring reaction gave only pure starting material. In this case, the Grignard formation did not work at all.

8.2 Platinum mediated coupling

An effective method for the synthesis of conjugated macrocycles was described by Bäuerle [96]. Indeed, an octa-membered thiophene ring, the cyclo[8]thiophene (**130**), was prepared via double platinum complexes (figure 8.4). The use of a dppp ligand offers a *cis* square planar platinum complex, which provides a perfect hinge. The elimination of the two metal centers afforded the macrocycle, which was then aromatized.

81

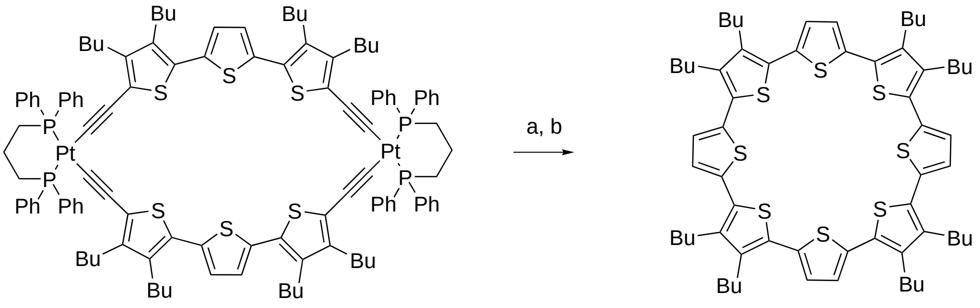


128

82

Figure 8.3: Synthetic attempt for the preparation of **82**. a) *iso*-PrMgCl, THF, -18 °C, 20 min, then CuBr·Me_2S, 30 sec, then **126**, rt, 20 min, 9 % (for **128**).

This novel and effective procedure for the synthesis of conjugated macrocycles in which conveniently accessible diyne building blocks and transition metal precursor complexes form a stable coordinatively bound metallo-macrocycle. Importantly, the transition metal units are expelled under simultaneous formation of C-C bonds leading to the conjugated macrocycle.



129 **130**

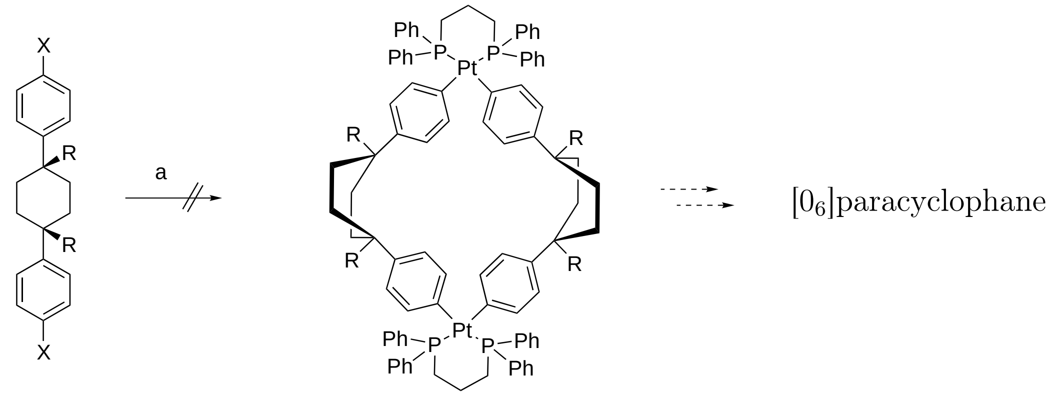
Figure 8.4: Synthesis of cyclo[8]thiophene (**130**) [96]. a) I_2, THF, 60 °C, 24 h, 54 %; b) $Na_2S \cdot H_2O$, xylene, $MeOCH_2CH_2OH$, 140 °C, 24 h, 19 %.

In our work, for the homocoupling of **81**, the platinum centers should be directly linked to the aryl units, without acetylene bridges. For this purpose, a procedure published in [103] was used, affording complexes of the kind $PtAr_2$(dppp), prepared from the aryl lithium derivative of the aromatic ligand. The starting complex $PtCl_2$(dppp) (**131**) was beforehand made by a known procedure from K_2Cl_4Pt and 1,5-bis(diphenylphosphano)pentane(dppp) [104]. Compound **81** was first transformed to its dilithio derivative, using *tert*-BuLi as lithiation reagent. This reaction was carried out at -50 °C, instead of the more classical -78 °C. Indeed, by raising the temperature by 20 °C, the halogen-lithium exchange on **81** was much more efficient. Like described in section 8.1, the lithiated precursor is only slightly soluble at low temperature. $PtCl_2$(dppp) was then added, but in spite of different conditions applied, no desired complex **132** was detected. In the contrary, PtI_2(dppp) was isolated, crystallized and analyzed by X-ray diffraction (figure 8.6). Compound **123** was used as a ligand too, but the results were identical as those obtained with **81**: no complex **133**. Table 8.1 summarizes the conditions used for the reactions.

Ligand	**131** [eq]	^{t}BuLi [eq]	Add.	Solvent	Temp. [°C]	Time [h]
81	1	4	-	THF	-50 to 20	24
81	1	4	-	PhMe/THF	-50 to 20	48
81	1	4	CuI^a	THF	-50 to 20	72
123	1	4	-	Et_2O/THF	-78 to 20	20
123	1	4	-	PhMe	-78 to 20	20

a) 2 equivalents

Table 8.1: Conditions used for the attempted synthesis of **132** and **133**.



81: R = H, X = I
123: R = OMe, X = Br

132: R = H
133: R = H

Figure 8.5: Attempted syntheses of bis-platino complexes **132** and **133**. a) see table 8.1.

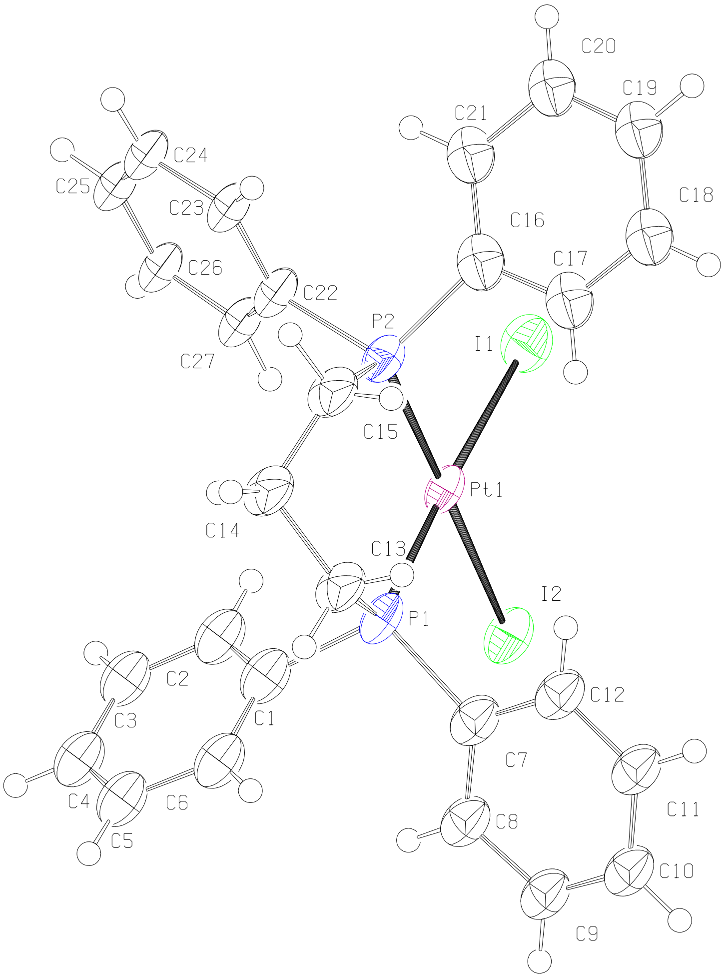


Figure 8.6: ORTEP structure of PtI_2(dppp) complex.

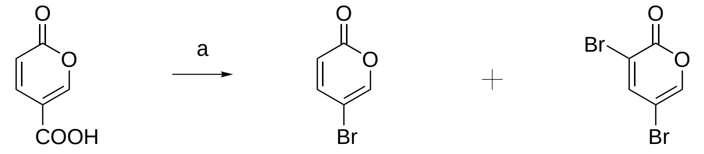
Chapter 9

Diels-Alder approach

As described previously (see section 6.1.3), cycloadditions are an other possible approach for aromatic ring preparation. Based on this idea, the different precursors derived from 1,4-diphenylcyclohexane were modified with different functional groups in the aim of a further Diels-Alder reaction.

9.1 α-Pyrone derivatives

α-Pyrone consists formally of a diene closed by an ester bridge. Such compounds, and their derivatives can be used for a Diels-Alder reaction, giving a bicyclic compound. Coumalic acid (**134**) was used as starting material for the preparation of α-pyrone derivative of **123**. Synthesis of 5-bromo-2-pyrone (**135**) was done by treating **134** with NBS, in presence of LiOAc (figure 9.1). Unfortunately, this procedure, described in literature [105, 106], gave only low yield (12 %), due to the low conversion of **134** and the formation of 3,5-dibromo-2-pyrone (**136**) in 9 % yield. Compound **135** can be coupled to **123** by a Suzuki reaction. For this purpose, the tricyclic precursor was first derivatized by two boronic ester functional groups, via the dilithio derivative, giving **137** [107]. The double Suzuki reaction gave the desired compound **138** (figure 9.2) [108].



134 **135** **136**

Figure 9.1: Synthesis of **135** [105, 106]. a) NBS, LiOAc·$2H_2O$, MeCN, H_2O, rt, 4 d, 12 % (for **135**) and 9 % (for **136**).

In parallel with the preparation of **138**, several Diels-Alder attempts were made with **135** and **134** as the diene and *para*-divinylbenzene and 4-bromostyrene as the

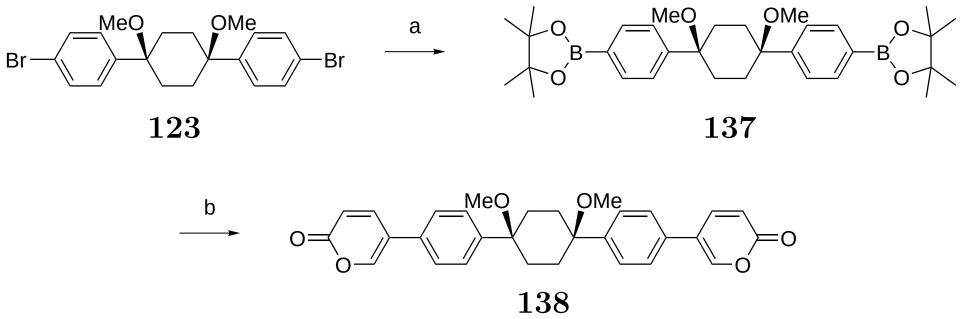


Figure 9.2: Synthesis of **138**. a) *tert*-BuLi, THF, -78 ° C, 45 min, then $B(OMe)_3$, rt, 3 h, then pinacol, rt, 15 min, 83 %; b) **135**, $PdCl_2(dppf)\cdot CH_2Cl_2$, K_3CO_3, DMF, 60 ° C, 24 h, 40 %.

dienophile. But unfortunately, no bicyclic compounds were obtained after these reactions. In one case, a byproduct was isolated, consisting to a dimer of 4-bromostyrene. Due to these results, this synthetic route was stopped. With a double Diels-Alder involving *para*-divinylbenzene or 4,4'-divinylnaphtalene, compound **138** could have formed a $[0_6]$paracyclophane or $[0_7]$paracyclophane precursor, respectively.

Within the same synthetic strategy, a divinyl derivative of **122** was prepared. After a first attempt of a double Kumada coupling which failed [109], an other procedure was used for producing 1,4-bis(4-vinylphenyl)-1,4-bis-trimethylsilanyloxycyclohexane (**139**). It consists in a $NiCl_2$(dmpe) [110] catalyzed Kumada reaction, involving vinylmagnesium bromide (figure 9.3) [111]. Traces of the desired compound were detected by ^1H NMR, but no yield was calculated.

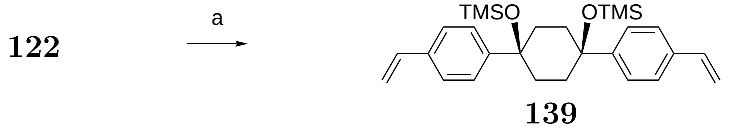


Figure 9.3: Synthesis of 1,4-bis(4-vinylphenyl)-1,4-bis-trimethylsilanyloxycyclohexane (**139**). a) $CH_2CHMgBr$, $NiCl_2$(dmpe), THF, rt, 4 d, traces.

The failure of this approach was probably due to the wrong choice of 2-pyrone and dienophile derivatives. Indeed, Diels-Alder reactions involving 2-pyrone units work with inverse electron demand, and in this case, a phenyl substituted dienophile was used for the attempts, which corresponds only to a weak donor. An alternative would have been a substitution of the vinyl by a stronger donor and of 2-pyrone by a stronger attractive group such as bromine. A study of this reaction with different reagents would have allowed probably the right choice of substituents for the diene and the dienophile. This work was not undertaken, because in case of a successful Diels-Alder reaction, a new synthetic problem would appear: removal the substituent at the end of the paracyclophane preparation, which is not necessary an easy task.

9.2 Diacetylene derivative

In the aim of forming an 7-oxabicyclo[2.2.1]hepta-2,5-diene pattern, a bicycle which is a hinge with a predefined angle of 69 ° (see table 6.1) and a prearomatized cycle, Diels-Alder reactions involving acetylene and furan derivatives were attempted in different conditions. Precursors **141** and **143** were synthesized in the goal of forming a macrocycle, a precursor of $[0_5]$paracyclophane. Compound **140** was obtained in 62 % yield by a Sonogashira reaction using **122** and TMSA (figure 9.4). Isolation of the pure compound was done by silica gel column chromatography. Purification of deprotected **140** was more difficult, due to the presence of byproducts created by OTMS eliminations. Only 9 % of pure compound **141** were recovered, while a lot material was contaminated by different byproducts. In the same time, preparation of known **143** [112] was performed from 3-bromofuran (**142**) (figure 9.5). The product obtained in this reaction was very sensitive. After purification by sublimation under vacuum, the obtained white compound rapidly decomposes, even if it was stored at low temperature under an argon atmosphere.

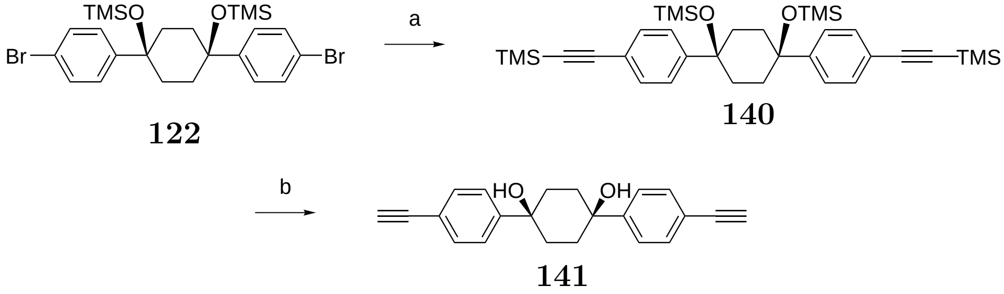
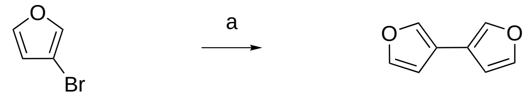


Figure 9.4: Synthesis of **141**. a) PPh_3, TMSA, CuI, $PdCl_2(PPh_3)_2$, piperidine, 80 °C, 21 h, 62 %; b) K_2CO_3, THF, MeOH, reflux, 18 h, 9 %.



142 **143**

Figure 9.5: Synthesis of 3,3'-bifuran (**143**) [112]. a) *tert*-Buli, $CuCl_2$, Et_2O, THF, -70 to -20 °C, 3 h, 8 %.

In parallel, Diels-Alder attempts were made with furan (**144**) and 1-bromo-4-ethynylbenzene (**145**), obtained from the TMS protected compound. Table 9.1

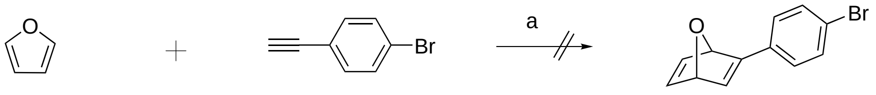
summarizes the conditions used for these experiments. The last attempt, using $AlCl_3$ as additive gave no desired product, but 1,3,5-tri(4-phenyl)benzene was isolated as a byproduct.

Furan [eq]	Solvent	Additive	Temp. [° C]	Time [h]
2	CH_2Cl_2	-	20	24
2	toluene	-	100	20
4	toluene	-	160[a]	7
4	toluene	-	200[a]	18
4	toluene	-	230[a]	20
4	CH_2Cl_2	$AlCl_3$[b]	40	2

a) autoclave

b) 1 equivalent

Table 9.1: Conditions used for the attempted Diels-Alder reaction involving furan (**144**) and 4-bromoethynylbenzene (**145**).



144 **145** **146**

Figure 9.6: Model reaction Diels-Alder attempts. a) see table 9.1 for conditions.

In this approach, the failure is probably due to the same trouble as discussed in section 9.1. Indeed, the absence of influencing functional groups, electron rich or poor substituents, probably prohibits a cycloaddition reaction.

Chapter 10

Carbonyl olefination of diketone precursors and metathesis

10.1 The McMurry reaction

The McMurry reaction was discovered in 1973 simultaneously by Mukaiyama [113] and the tandem Tyrlik-Wolochowicz [114]. The first one got a reductive coupling of aromatic aldehydes and ketones, using the $TiCl_4$-Zn system. Benzaldehyde and acetophenone were selectively transformed to their respective pinacols and alkene dimers. The second discovery was the observation of tetramethyl-ethylene after the treatment of acetone by $TiCl_3$-Mg. In this case, it was suggested that dimerization occurs with two carbene species, generated by the deoxygenation of the ketone. The two mechanisms proposed are showed in figure 10.1.

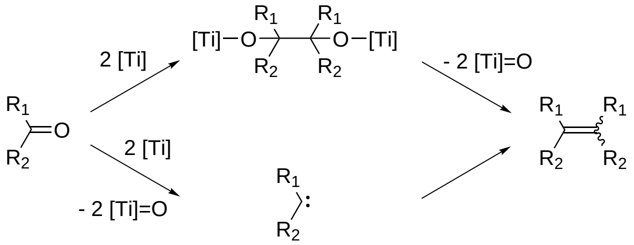


Figure 10.1: The mechanism proposed by Mukaiyama (top) and by Tyrlik-Wolochowicz (bottom) [115].

One year later, McMurry and Fleming, with a $TiCl_3$-$LiAlH_4$, showed that metallo-pinacol intermediates are formed during the reaction. Until this discovery, a large number of McMurry couplings, involving a lot of different conditions were reported in the literature. This reaction, where the driving force is the formation of strong titanium-oxygen bonds, gives the possibility to couple ketones, aldehydes, acylsilanes, keto esters and oxoamides in intermolecular, intramolecular or mixed reactions. The major advantage of the McMurry reaction is the possibility to form strained or sterically hindered olefins, macrocycles, and heterocycles.

On the other hand, the formation of low-valent titanium species is difficult. Indeed, the selection of the reducing agent and of the titanium source is crucial, a choice to be optimized for each specific substrate. The table 10.1 summarizes the different reducers, solvents and additives compatible with for a specific titanium source and a specific substrate.

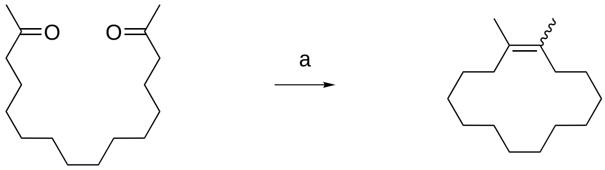
Ti source	Red. Agent	Solvent	Additive	Substrate class[a]
$TiCl_3$	Zn(Cu)	DME	-	A,B,F,I,J,K,L,P
$TiCl_3$	K	THF	-	A
$TiCl_3$	$LiAlH_4$	THF	-	A,C,F,H,J,K,L
$TiCl_4$	Zn	THF	pyridine	A,B,E,G,K,P
$TiCl_4$	Zn	THF/CH_2Cl_2	-	B
$TiCl_4$	Zn	THF	-	B,C,E,F,G,H,I,J,K,M,N,O
$TiCl_4$	Zn	DME	-	C,I,K
$TiCl_3$	Zn(Cu)	THF	-	D
$TiCl_4$	$LiAlH_4$	THF	-	D,H,I
$TiCl_3$	$LiAlH_4$	THF	pyridine	E
$TiCl_3$	Zn(Cu)	DME	pyridine	F,H
$TiCl_4$	Zn	dioxane	pyridine	F
$TiCl_3$	Li	DME	-	G,H,I,J
$TiCl_3$	$Na(Al_2O_3)$	THF	-	G
Ti	-	DME	TMSCl	G
$TiCl_3$	Na	dioxane	-	I
$TiCl_3$	Zn	THF	-	J,K
$TiCl_3$	$LiAlH_4$	DME	-	J
$TiCl_4$	Zn(Cu)	DME	-	K
$TiCl_4$	Mg(Hg)	THF	-	K
$TiCl_3$	C_8K	THF	-	M
$TiCl_4$	Zn	PhMe/THF	-	M
$TiCl_4$	Zn(Cu)	THF	pyridine	M,O

a) A: saturated aldehydes and ketones; B: unsaturated aldehydes and ketones; C: ketones and aldehydes with halides groups; D: ketones and aldehydes with acetals, toluenesulfonates, esters and ethers groups; E: ketones and aldehydes with sulfides groups; F: ketones and aldehydes with amines groups; G: ketones and aldehydes with phospholes, alkyl- and arylsilanes and ketones groups; H: organometallic aldehydes and ketones; I: intermolecular cross-coupling products; J: preparation of cycloalkenes and cyclopolyenes; K: preparation of cyclophanes and calixarenes; L: preparation of phenantrenes, helicenes and circulenes; M: preparation of crownophanes, crown ether-calixarenes and polyepoxyannulenes, N: thiophenes and selenophenes; O: porphyrins; P: Ferrocenophanes.

Table 10.1: Summary of the McMurry regents used for carbonyl olefination of different classes of compound.

The list cited in table 10.1 is not exhaustive (see [115] and references cited therein for full details), but shows the diversity of the conditions used for the McMurry reaction. It is interesting to see that four systems ($TiCl_3/Zn(Cu)/DME$, $TiCl_3/LiAlH_4/$-THF, $TiCl_4/Zn/THF/pyridine$ and $TiCl_4/Zn/THF$) were used for a large variety of substrates, with yields ranging between 3 and 99 %.

The yield or the success of the reaction is depending of the quality of the reagents and the ability of the operator. A failure can not always be totally explained. For example, the synthesis of 1,2-dimethylcyclotetradecene (**148**) from hexadecane-2,15-dione (**147**) by slow addition (figure 10.2), reported in [116], was reproduced during this work, but the desired product was obtained only after three attempts, using the same conditions at each time. This experiment shows, how the McMurry reaction is difficult to perform.



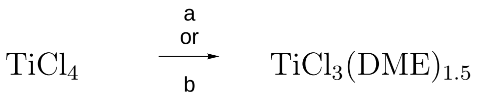
147 **148**

Figure 10.2: Synthesis of 1,2-dimethylcyclotetradecene (**148**) [116]. a) Zn(Cu), $TiCl_3(DME)_{1.5}$, DME, reflux, 48 h, 76 % (mixture of isomers).

10.2 Titanium sources and reducing agents preparation

As shown in section 10.1, the two majors titanium sources are $TiCl_3$ and $TiCl_4$, but only $TiCl_3$ was used in this work. Indeed, the best results observed in literature for the synthesis of strained cycles were using this source. Unfortunately, titanium(III) chloride is very sensitive and reacts quickly with the moisture of air and its purification is very difficult. Presence of aluminum chloride in $TiCl_3$, coming from the reduction process, is a persistant problem in titanium(III) chloride. Samples formation of ethereal complexes of DME or THF allows to solubilize the aluminum complex, which is then easily removed from the solid $TiCl_3(ROR)_3$ by filtration and washings. This procedure is very delicate because the success depends of different factors such as stirring or dryness of solvents.

It is possible to get $TiCl_3(ROR)_3$ commercially or by reduction of $TiCl_4$ in an ethereal solution, using aluminum or titanium metallic powder (figure 10.3). Table 10.2 summarizes the different procedures used for the preparation of such complexes. The quality of the obtained $TiCl_3(ROR)_3$ was determined on the basis of the color. Indeed, the formation of degradation products causes a brown-green coloration of the solid. The more the solid is blue, the less impurities are present in the product. Green titanium(III) complexes obtained by reduction with Ti (entry 4) and turquoise ones (entries 3 and 5) were not sufficiently efficient for the McMurry coupling of ketones as described in figure 10.2, which was used as a test for regents.



$$TiCl_4 \xrightarrow[\text{b}]{\text{a or}} TiCl_3(DME)_{1.5}$$

Figure 10.3: Synthesis of the $TiCl_3(DME)_{1.5}$ complex. a) Ti, DME, reflux, 24 h, 89 %; b) Al, DME, relfux, 24 h, 80 %.

Entries	Ti source	Ether	Red. Agent	Yield [%]	Color[a]	Ref.
1	$TiCl_3(THF)_3$	-	-	-	+++	-
2	$TiCl_3$	DME	-	79	+++	[116]
3	$TiCl_4$	DME	Al	80	++	-
4	$TiCl_4$	DME	Ti	89	+	[117]
5	$TiCl_4$	THF	Al	86	++	[118]

a) +++ = pure blue; ++ = turquoise; + = green

Table 10.2: Conditions used for the preparation of titanium(III) chloride ethereal complexes.

Preparation of the Zn(Cu) couple, used for the reduction to low-valent titanium species, was prepared as described in [116], by adding $CuSO_4$ to ground Zn. To get a better reducing agent, powdered Zn was used, but unfortunately, this slurry was not efficient. This result is probably due to the larger zinc oxide content of this fine zinc powder.

10.3 Synthesis of diones precursors of $[0_5]$paracyclophane

Products showed in this section were prepared for the first time as precursors of $[0_5]$para-cyclophane. The idea was to use the same strategy as used by McMurry for the formation of **73** and **74** (see section 4.4.1), but with intercalated phenyl units between the different cyclohexane cycles. With this trick, the solubility problems mentioned in [77] for the five-membered linear precursor were resolved. Indeed, presence of theses aryls decreases the intermolecular interactions which are strong for linear multi-linked cyclohexanes.

Compound **151** was prepared from **123**. In a first attempt, 1,4-cyclohexanedione was used as cyclohexane source, but only dehalogenated **123** was recovered after the reaction. This result is probably due to the enolization of 1,4-cyclohexanedione as studied in [119] by Imamoto. The use of cerium chloride would have possibly allowed to limit this side reaction, but the following three step route was chosen to get the desired compound (figure 10.4). The first reaction consists in a carbonyl attack of 1,4-cyclohexanedione monoethylene ketal by dilithio derivative of **123**, yielding 93 % of **149**. The halogen-metal exchange was performed by using two equivalents of *tert*-BuLi. The two new benzylic alcohols were then protected by treatment with MeI and NaH, giving **150** in 92 % yield. The last step of this preparation is the removal of the two ketal protective groups performed by an acidic hydrolysis, yielding **151** (^{1}H NMR spectra is shown in figure 10.5). A similar approach was done with **122** (figure 10.6), giving **152** in 73 % yield, but TMS protective groups did not support conditions used to remove ketals.

McMurry conditions were applied (see section 10.4) to this precursor but no results were obtained. This failure is not yet explained, but the hypothesis which was kept is the interference of the four methyl ether functional groups with the oxophilic titanium reagent. This result has implied the preparation of **155** from **81**, a similar compound without methyl ether groups.

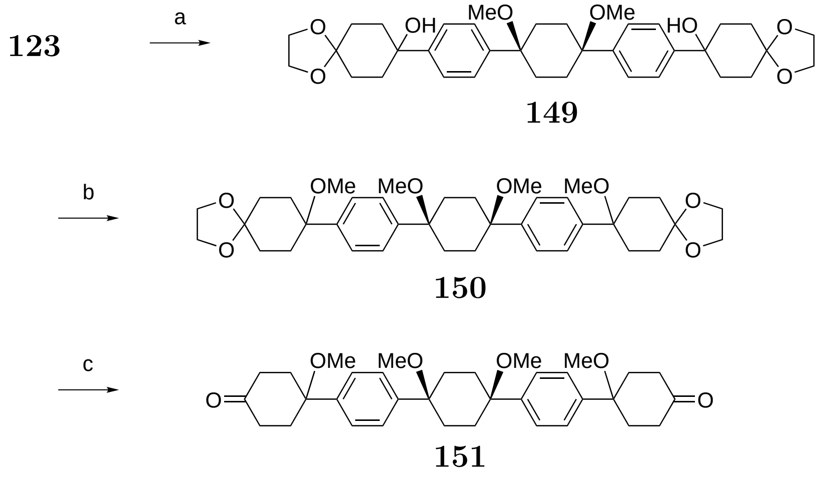


Figure 10.4: Synthesis of **151**. a) *tert*-BuLi, THF, -78 °C, 50 min, then 1,4-cyclohexanedione monoethylene ketal, rt, 3.5 d, 93 %; b) NaH, MeI, THF, reflux, 46 h, 92 %; c) *p*-TSA, acetone, water, reflux, 17 h, 64 %.

Preparation of **155** is similar, but two different routes were developed for the synthesis of this compound. Indeed, the first strategy (figure 10.7) gave no satisfactory yield for the hydrogenation step. The intermediate **153** was made as previously described for **149**. The preparation of the lithiated regent with *tert*-BuLi was carried

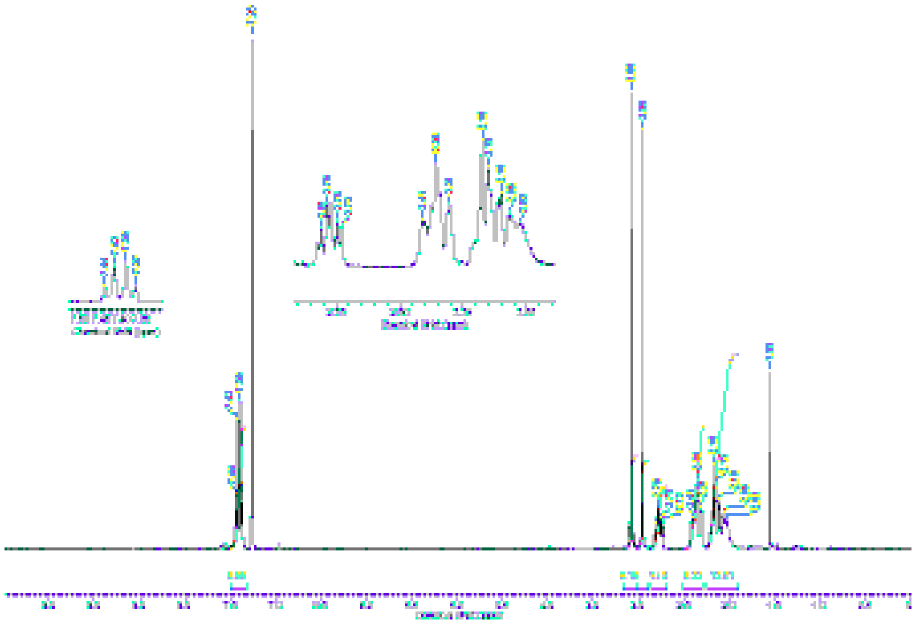


Figure 10.5: ^{1}H NMR spectra of **151**, 360 MHz, $CDCl_3$, rt.

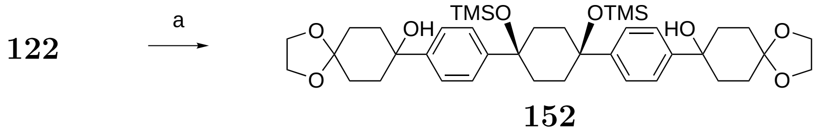


Figure 10.6: Synthesis of **152**. a) *tert*-BuLi, THF, -78 °C, 1 h, then 1,4-cyclohexanedione monoethylene ketal, rt, 4 d, 73 %

out at -50 ° C (see section 8.2). Deprotection of carbonyl groups and elimination of benzylic alcohols was done in a one pot reaction, using a 1:5 TFA/CH_2Cl_2 mixture to give **154** (^{1}H NMR spectra is shown in figure 10.8) in 98 % yield. This compound was then hydrogenated over Pd/C, but side reactions gave a lot of byproducts, yielding only 35 % of the desired compound **155** (^{1}H NMR spectra is shown in figure 10.9) after preparative TLC. Indeed, enolization of the ketone can inhibit the hydrogenation process of the β,γ-olefin and create different rearrangement products.

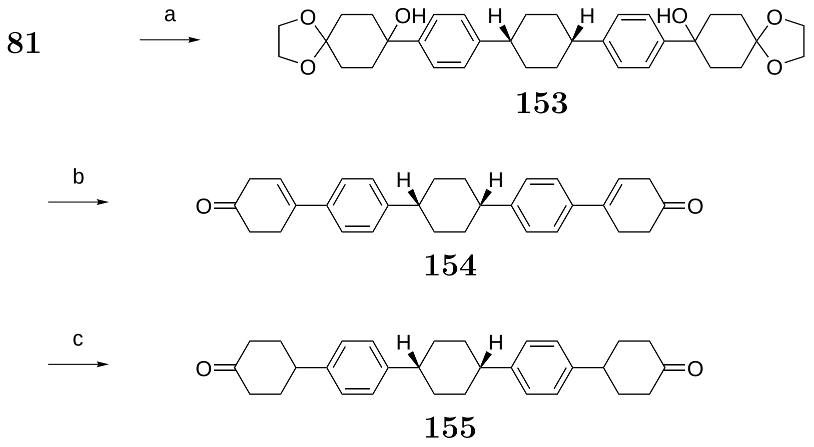


Figure 10.7: Synthesis of macrocycle precursor **155** via the first route. a) *tert*-BuLi, THF, -50 ° C, 20 min, then 1,4-cyclohexanedione monoethylene ketal, rt, 20 h, 70 %; b) TFA, CH_2Cl_2, rt, 6 h, 98 %; c) Pd/C, H_2 3 bars, CH_2Cl_2/EtOH, rt, 1.5 h, 35 %.

The following strategy (figure 10.10) was developed to perform elimination of the benzylic alcohols and hydrogenation of the resulting double bonds before removing the two ketal groups. The elimination process was carried out in a Dean-Stark apparatus, using benzene as solvent in presence *p*-toluenesulfonic acid and a large excess of ethylene glycol. With these conditions, no deprotection of the carbonyl group was observed and 86 % of the desired compound **156** were obtained. In this reaction, it is not clear whether the ethylene glycol part of the molecule was exchanged with free ethylene glycol of the mixture. Indeed, the water is rapidly eliminated via the azeotropic distillation, but a reaction with isotope labelled diol would be interesting to explain the phenomenon. The hydrogenation of **156** was then carried out over Pd/C in a CH_2Cl_2/EtOH mixture under 3 bars of H_2, yielding 100 % of **157**. The two protective groups were then removed by classic acidic treatment, giving 96 % of the target compound **155**. With this route, the overall yield was 83 %, instead of the 34 % from the first strategy.

In an attempt to get **157** directly from **153** by a Raney-Nickel reduction, monobenzylic derivative **158** was obtained in 57 % yield (figure 10.11) [120] after purification

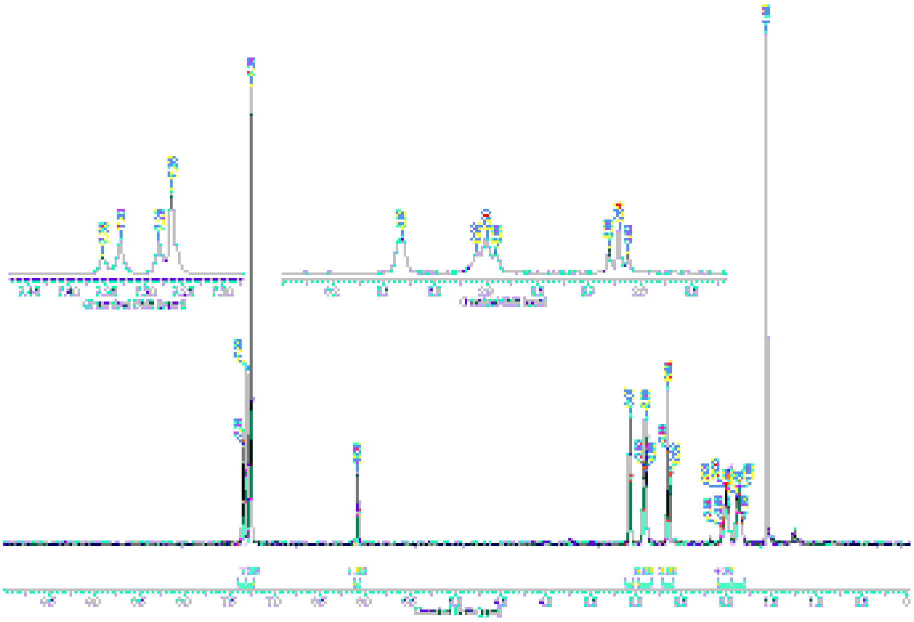


Figure 10.8: ^{1}H NMR spectra of **154**, 360 MHz, $CDCl_3$, rt.

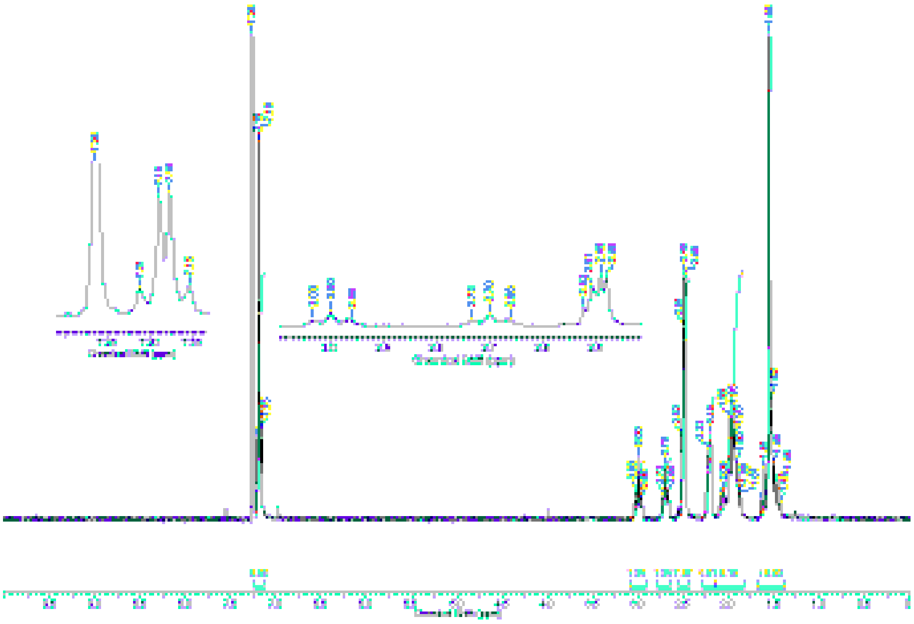


Figure 10.9: ^{1}H NMR spectra of **155**, 360 MHz, $CDCl_3$, rt.

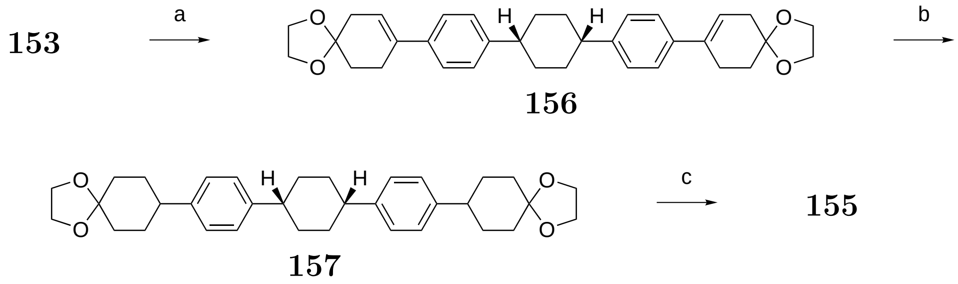


Figure 10.10: Synthesis of macrocyclic precursor **155** via the second approach. a) *p*-TSA, benzene, ethylene glycol, reflux, 68 h, 86 %; b) Pd/C, H_2 3 bars, CH_2Cl_2/EtOH, rt, 2.5 h, 100 %; c) HCl 37 %, acetone, water, reflux, 20 h, 96 %.

by column chromatography. The mass balance was completed by the starting material, but no **157** was found.

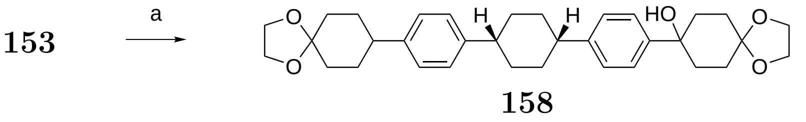


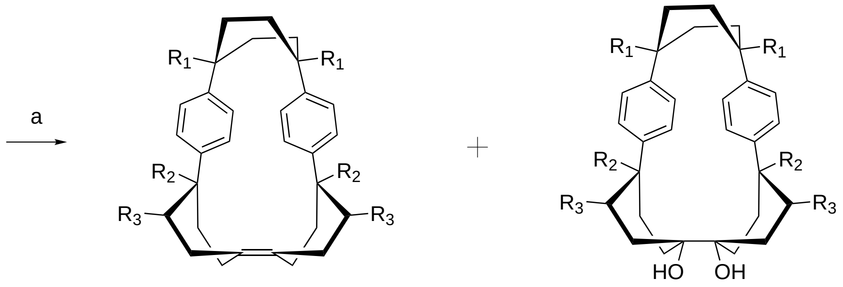
Figure 10.11: Synthesis of **158**. a) Ni, EtOH, rt, 3.5 d, 57 %.

10.4 Macrocyclization attempts

Compound **151**, **154** and **155** were used as starting materials for the macrocyclization attempts (figure 10.12). The conditions employed are summarized in table 10.3. The reactions were carried out in general two times with these different substrates. Solvents used in these experiments were alox dried THF and toluene, as well as potassium dried DME. The drying of DME was carried out using benzophenone as ketyl radical indicator.

In the cases shown in entries 8 and 9, the classical $TiCl_3(ROR)_3$ complex was replaced by a $TiCl_3$ source. Indeed, this regent was commercially available with a grade of 99.999 % in gram quantity. This product was transferred to a Schlenk tube under a laminar flow of nitrogen to get the lowest amount possible of titanium oxide in the sample. During the first reaction performed with the conditions of entry 9, traces of the macrocyclic pinacol **160** were found by positive ESI-MS analysis. To confirm this result, bicyclohexyl-1,1'-diol (**165**) obtained from [121] (figure 10.14) was analyzed by mass spectrometry under the same conditions as used for **160**. The result was similar. Indeed, the peak corresponding to the molecular mass was not visible in both cases and an intense one was present for M-OH at 413.4 for **160**

155
or
154
or
151



159 $R_1 = R_2 = R_3 = H$ **160**
161 $R_1 = H$; R_2-R_3 **162**
163 $R_1 = R_2 = OMe$; $R_3 = H$ **164**

Figure 10.12: Attempted syntheses of macrocycles **159**, **160**, **161**, **162**, **163**, **164**. a) see table 10.3.

(figure 10.13) and 181.3 at for the reference compound **165**. Unfortunately, as in such reactions, a lot of byproducts such as oligomers and reduced starting material were contaminating the sample, and no additional analyses were recorded. In a second attempt done under the same conditions, no fraction containing the pinacol macrocycle was detected, proving the difficulty of the McMurry reaction.

The ethereal complexes, available in larger quantity as compared to $TiCl_3$, and the reducing agents were quickly weighed in air before being transfered to in the Schlenk tube.

Entry 10 shows the use of the $VCl_3(THF)_3$ complex, which is commercially available.

10.5 Metathesis approach

An other approach, using similar compounds as the ones developed for the McMurry strategy, was attempted. It consists of the synthesis of compound **168** the reaction of the organolithium derivative of **122** and two molecules of 4-methylenecyclohexanone (**167**), giving 77 % of the desired product (figure 10.15). The carbonyl compound was previously obtained by a two steps procedure from 1,4-cyclohexanedione monoethylene ketal, the first step being a Wittig reaction and the second one the removal the ketal protection.

Compound **168** was submitted to metathesis conditions, with 1^{st} generation Grubbs catalyst and 2^{nd} generation Hoveyda-Grubbs catalyst, but the bulky methylenecyclohexane units prevented a ring closure. This failure can be explained by the distance between the two carbons and the additional ring strain in the formation of the transition four-membered metallic species. Indeed, the carbons should be relatively close to allow for the bonding, what is not the case with precursor **168** (figure 10.16).

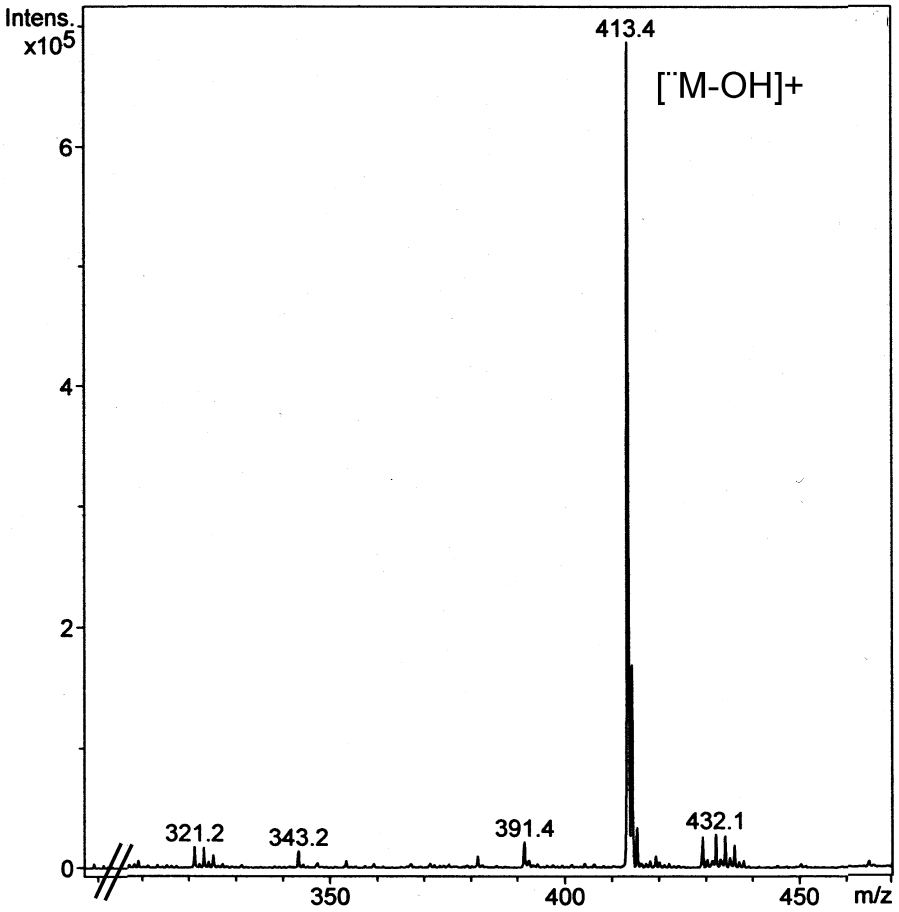
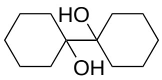


Figure 10.13: Positive ESI-MS of the crude product containing **160**. The peak corresponds to [M-OH]$^+$.



165

Figure 10.14: Structure of bicyclohexyl-1,1'-diol (**165**) obtained from [121].

	Subst.	Ti source	Red. agent	Solvent	Conc.[a] [mol/l]	Time[b] [h]			Temp. [° C]	Yield[c]
						1	2	3		
11	**151**	$TiCl_3(DME)_{1.5}$	Zn(Cu)	DME	$6.4 \cdot 10^{-3}$	5	35	8	reflux	-/-
1	**154**	$TiCl_3(DME)_{1.5}$	Zn(Cu)	DME	$6.2 \cdot 10^{-3}$	5	42	6	reflux	-/-
2	**154**	$TiCl_3(DME)_{1.5}$	Zn(Cu)	DME	$1.1 \cdot 10^{-2}$	5	72	8	reflux	-/-
3	**154**	$TiCl_3(THF)_3$	Zn(Cu)	DME	$5.9 \cdot 10^{-3}$	5	26	15	95	-/-
4	**155**	$TiCl_3(THF)_3$	Zn(Cu)	DME	$8.8 \cdot 10^{-3}$	5.5	-[d]	42	reflux/rt/57[e]	-/-
5	**155**	$TiCl_3(DME)_{1.5}$	Zn(Cu)	DME/THF	$5.8 \cdot 10^{-3}$	1[f]	40	5	80	-/-
6	**155**	$TiCl_3(DME)_{1.5}$	Zn(Cu)	DME/THF	$3.6 \cdot 10^{-3}$	1[f]	38	5	80	-/-
7	**155**	$TiCl_3(DME)_{1.5}$	Zn(Cu)	PhMe/DME	$4.7 \cdot 10^{-3}$	4[g]	35	28	80	-/-
8	**155**	$TiCl_3$[h]	Zn(Cu)	PhMe/DME	$5.8 \cdot 10^{-3}$	4	29	40	80/85[i]	-/-
9	**155**	$TiCl_3$	Zn(Cu)	PhMe/DME	$5.3 \cdot 10^{-3}$	4	27	40	80/85[i]	-/traces
10	**155**	$VCl_3(THF)_3$[j]	Zn	CH_2Cl_2	$7.0 \cdot 10^{-3}$	0.5	16	2	rt	-/-

a) calculated at the end of the addition; b) 1 = low-valent Ti formation, 2 = slow addition, 3 = post-addition; c) olefine/pinacol; d) quick addition of the solid substrate; e) low-valent Ti formation/for 20 hours/for 22 hours; f) in ultrasonic bath; g) 1 hour in ultrasonic bath; h) in presence of dry pyridine [116, 122]; i) low-valent Ti formation/reaction; j) pinacol formation (see [123]).

Table 10.3: Conditions used for the attempted macrocyclizations of precursors **151**, **155** and **154** via a McMurry reaction.

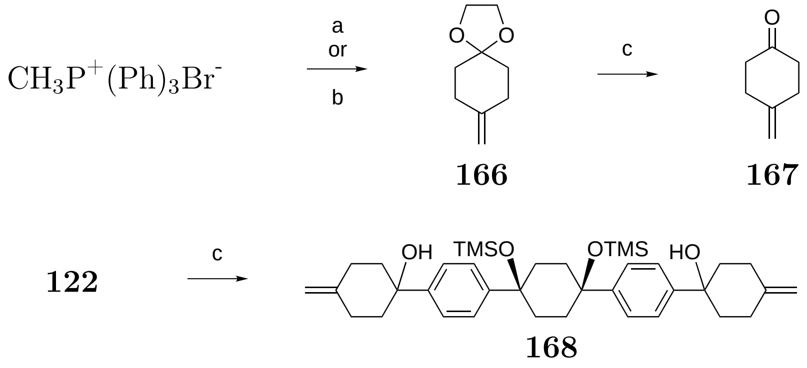


Figure 10.15: Synthesis of **168**. a) NaH, THF, reflux, 2 h, then 1,4-cyclohexane monoethylene ketal, rt, 2 h, 71 %; b) *tert*-BuLi, THF, 0 °C, 20 min, then 1,4-cyclohexane monoethylene ketal, rt, 2 h, 92 %; c) HCl 2M, THF, reflux, 4 h, 53 %; c) *tert*-Buli, THF, -78 ° C, 1 h, then **167**, rt, 6 d, 77 %.

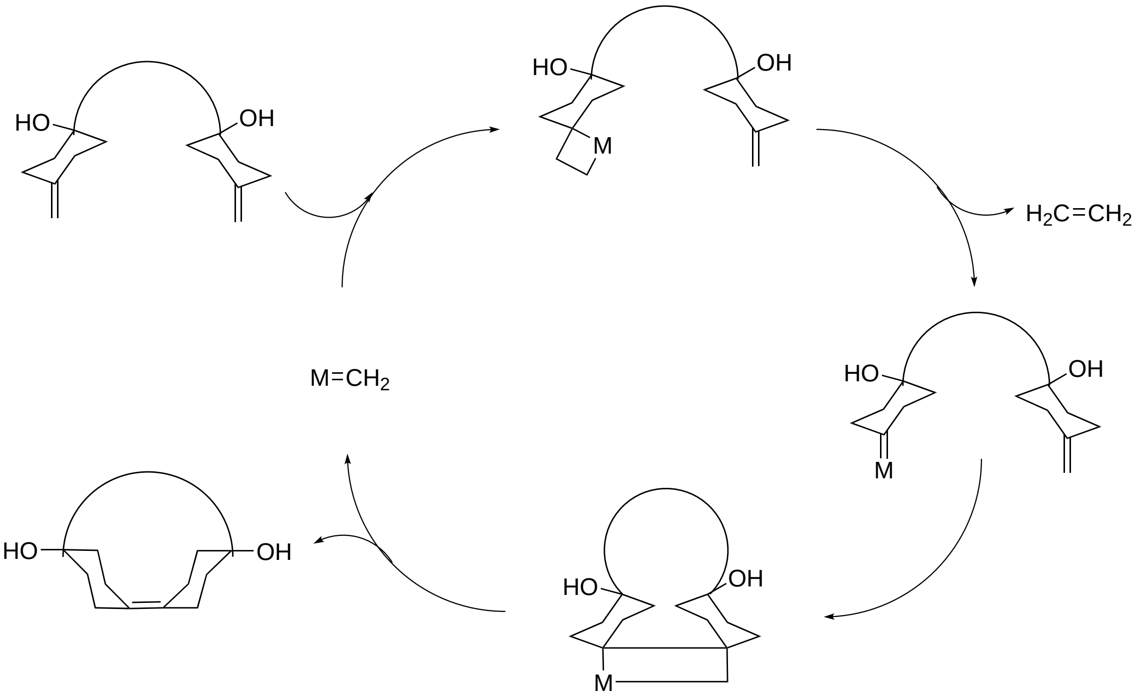


Figure 10.16: Reaction mechanism of a ring closure metathesis involving **168**.

Chapter 11

Tubular templates

The second aim of this work was to test the acetylene polymerization on a curved polyaromatic template. Due to the unavailability of a $[0_n]$paracyclophane template, other templates were sought to attempt the test of the catalytic system of Raemy [17]. It is obvious that geometry and diameter are not important points for testing the idea. $[0_n]$Paracyclophane could advantageously be replaced by less defined tubules such as short cut SWNTs or decapitated fullerenes (figure 11.1).

Figure 11.1: Strategies for synthesizing CNT from short cut carbon nanotube (left) or decapitated fullerenes (right) template. a) iron(0), DIBAH, 0.5 bars acetylene, benzene, rt.

11.1 Short cut carbon nanotubes

Several methods were developed for shortening carbon nanotubes, which can be grouped in two different families. The first one is using mechanical methods, whereas the second one is using a chemical or thermal cutting. Such strategies were and are actually developed because the chemistry of short CNTs seams to be much richer than that the one with longer CNTs.

11.1.1 Mechanical methods

Several procedures were published for shortening SWNTs [124] or MWNTs [125] by mechanical breaking, affording tubules with a length between 60 and 600 nm. The main advantage of such a method is that no oxygen containing functional groups are formed during the process. On the other hand and despite of the apparent facility, such procedures gave no reproducible results.

In this work, a sample of commercial SWNT with a purity of 50-70 % was submitted to soft grinding in a γ-cyclodextrine matrix for 2 hours. After the removing of the matrix by water washing and centrifugation, the black residual solid was suspended by sonication in ethanol and deposited by spraying the solution on a small silicon wafer. An other sample was prepared with as-received SWNTs by the same method. SEM pictures were then taken for analyzing the concept of carbon nanotubes. The picture taken after the treatment shows no longer the presence of CNT, whereas the commercial sample contains SWNTs (figure 11.2). However, new attempts should be done with high purity SWNT to increase the chance to get short CNT pieces.

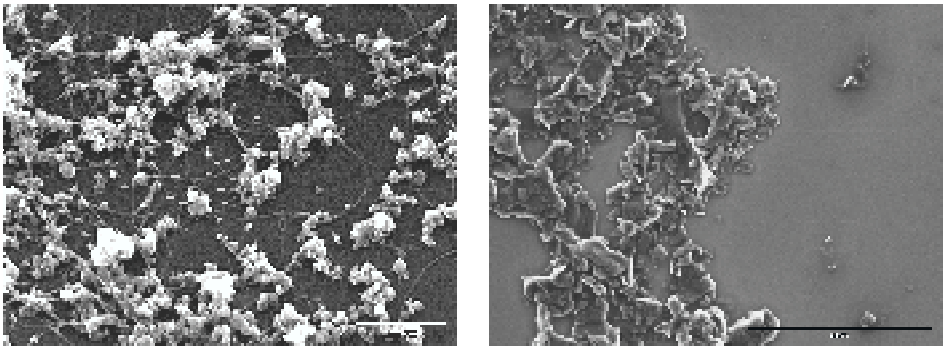


Figure 11.2: SEM micrographies of a commercial sample of SWNTs (left) and of the residue found after the cutting process [124] (right). On the left picture, small spheres correspond to amorphous carbon and catalytic particles.

11.1.2 Chemical methods

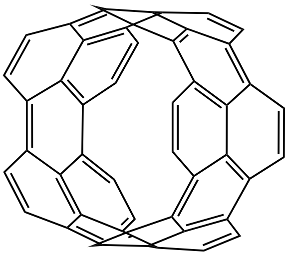
Chemical methods were not tested in this work. Indeed, the formation of oxygen containing functional groups (mainly carboxylic acids) at the ends of shortened CNTs is a major problem for the continuation of the experiment, i.e. the polymerization/dehydrogenation of acetylene. It is imperative that the part to be used for the growing process bears no functionalization.

Among the most used chemical methods, etching of previously damaged CNTs gave nanotubes around 100 nm length [126]. The first step consists to break some C-C bonds constituting the wall of a nanotube by fluorination/defluorination of the surface. Then, the damages can be exploited to cut the tubule by oxidation with Caro's acid or nitric acid.

11.2 Decapping fullerenes

Until now, only few selective chemical routes were developed to open fullerene cages [127] or to dearomatize C_{60} fullerene caps (see section 4.1), but no oxidative removal of caps was reported. It is known that fullerene and CNT caps are more sensitive to oxidation that other positions on the surface. A controlled oxidation could be used to decappe fullerene and some attempts were realized to test this idea.

Fullerene C_{70} was chosen because of the larger aromatic belt as compared to the C_{60} one. Indeed, the macrocycle constituting the equatorial belt of C_{70} is alternatingly made of five naphtalene and five phenyl rings (figure 11.3), equivalent to a very short (5,5)-armchair SWNT (**169**). With the hypothesis concerning the reactivity of the different curvatures, it was supposed that the chance to preserve the tubular part of this fullerene was bigger than in the case of C_{60}.



169

Figure 11.3: Structure of the equatorial ring of C_{70} fullerene.

The choice of the oxidant is important too. As it was already discussed that strong oxidants such as nitric acid etch nanotubes and form carboxylic acids. Hence, a reported procedure [128], concerning decapitation of closed CNTs, was selected. It was reasoned, that removing of -COOH functions should be relatively easy.

Fullerene C_{70} was refluxed at 140 °C for 30 minutes. The color of the reaction mixture rapidly changed from black to pale yellow. The reaction mixture was then diluted and extracted with organic solvents, but ESI-MS analyses gave no results. Indeed, due to the large number of carboxylic acids on the expected compound, its solubility is high in the aqueous phase. The excess of nitric acid was therefore evaporated to dryness and the colorless residue was submitted to LC-MS analysis, but actually no results were obtained.

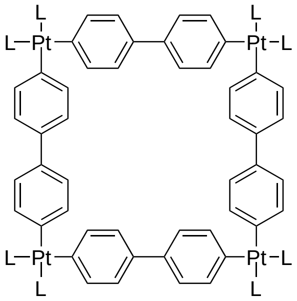
Chapter 12

Conclusion and perspectives

The hinge and bend concept was used in this work for the synthetic approach of $[0_n]$paracyclophanes, especially for the case $n = 5$ and $n = 6$. The different new strategies developed and presented here are based on molecular patterns containing bends, or hinges, or both, in the aim to provide enough flexibility for closing a strained polyaromatic macrocycle. Although this goal was not reached, some important results were obtained trough the different experiments and syntheses realized.

Firstly, a new synthetic route for the production of **123** was developed, allowing to increase the overall yield as compared to the published strategy [77]. From this compound, a new family of compounds was synthesized. These pentacyclic precursors (**154**, **151** and **155**) of $[0_5]$paracyclophane consist of alternate phenyl and cyclohexyl rings, functionalized at the ends by carbonyl groups. Whereas the intramolecular McMurry carbonyl coupling failed for the most part of these precursors, the compound **155** void of substituent gave a pinacolic cycle **160**, intermediate of the desired olefin. To get this result, screening and optimization of McMurry conditions for cyclization of strained ketones was performed, using different reagents and procedures. The best reaction conditions were found in the use of commercial $TiCl_3$ of highest purity and a Zn-Cu couple made from ground zinc and a 1:1 toluene/DME solvent mixture. The obtained compound was detected by ESI-MS in a complex product mixture and must still be isolated and converted to the corresponding olefin before it oxidation.

With the bend concept, Diels-Alder based strategies gave no satisfactory results and were given up, but the platinum bend bearing precursors seem to be promising, although only preliminary tests were done. New ligands should be tested to get a macrocyclic precursor of $[0_n]$paracyclophane as for example compound **170** (figure 12.1).

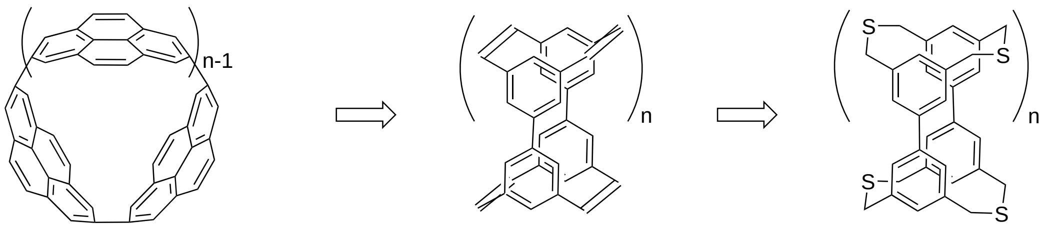


170

Figure 12.1: Structure of a tetra platinum complex as precursor for the synthesis of $[0_8]$paracyclophane. L = bidentate phosphine.

The acetylene polymerization/dehydrogenation process could not be tested on an appropriate template. It remains therefore unknown, whether the catalyst would be able to form curved graphitic structures and CNT growing. Ideas and preliminary attempts discussed in chapter 11 should be continued.

Finally, as they provide a new approach to the problem different polyaromatic belts can be imagined, starting from know procedures such as Dewar benzenes or pyrenophanes, already used to create curved aromatic patterns. The synthetic route sketched in figure 12.2 could provide a viable solution, but for this purpose, a step by step oxidation should be needed. Indeed, a one step aromatization is not a good strategy due to high sterical constraints.



171 **172** **173**

Figure 12.2: Proposed retrosynthesis of an aromatic belt corresponding to a (6,6)-SWNT piece, inspired by [58].

Part IV

Experiment

Chapter 13

General considerations

13.1 Chromatography techniques

Thin layer chromatography (TLC) analyses were performed on Merck aluminum sheets coated with silica gel 60 F_{254} and were revealed by spraying a $KMnO_4$ solution or under UV-light at 254 nm. Column chromatographies were carried out at atmospheric pressure or under N_2 pressure on Merck silica gel 60 (0.040-0.063 mm).

13.2 Mass spectrometry

Mass spectrometry (MS) analyses were recorded on a HP 5988A Quadrupol spectrometer (EI ionization), a Vacuum Generators Micromass VG 70/70E spectrometer (FAB ionization), a FT/ICR mass spectrometer Bruker 4.7T Bioapex II spectrometer (ESI ionization) or Bruker Daltonics Esquire HCT spectrometer (ESI ionization). Analysis of volatile compounds were carried out on a Thermoquest Finnigan Voyager GC-MS Trace GC 2000 series equipped with a Zebron ZB1 capillary column (30 m L x 0.25 mm ID x 0.25 μmdf, 100% methyl polysiloxane) (EI ionization).

13.3 Nuclear magnetic resonance

NMR analyses were recorded either on a Bruker Avance DRX-500 (^1H: 500 MHz and ^{13}C: 125 MHz), on a Bruker DPX-360 (^1H: 360 MHz and ^{13}C: 91 MHz) and on a Varian Gemini 200 (^1H: 200 MHz and ^{13}C: 50 MHz). Chemical shifts are given in ppm relative to tetramethylsilane (TMS) or to the residual proton signal of the deuterated solvent. The NMR signals were assigned using APT, HETCOR and COSY techniques.

13.4 X-ray diffraction

The X-ray analyses were performed at the University of Neuchâtel by Prof. Dr. Helen Stoeckli- Evans. The structures were solved by direct methods using the program SHELXS-97[1] and refined by full matrix least squares F^2 with SHELXL-97.

13.5 Solvents and chemicals

Technical solvents were distilled prior to use and dry solvents were obtained by classical distillation over sodium or potassium or by drying with the solvents purification system on activated basic aluminum oxide (THF, Et_2O, toluene, pentane and CH_2Cl_2) [129]. Chemical products and regents were provided by Merck, Fischer Scientific, Fluka, Aldrich, Acros, Riedl-de-Haën or Strem and were used without further purification. Titanium(III) chloride was purchased by Aldrich.

13.6 Reactions

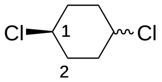
Sensitive reactions were carried out in oven and vacuum dried glassware, under argon 48 or nitrogen 45 (both from Carbagas). Otherwise, no particular precautions were employed. Reactions carried out at low temperature were cooled with an acetone/liquid nitrogen or with a cryostat Julabo FT901 immerged in an acetone bath. Reactions or distillations needing temperature higher than 180 °C were heated with a graphite bath (flakes, Aldrich).

Chapter 14

Syntheses

14.1 *cis*-1,4-Diphenylcyclohexane pattern

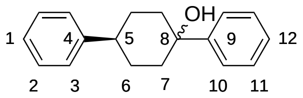
1,4-Dichlorocyclohexane (117)



117

A solution of 45.00 g (0.38 mol) of a *cis* and *trans* mixture of 1,4-cyclohexanediol in 270 ml of 37 % HCl was heated at 100 °C for 18 h. After cooling, the layers were separated and the aqueous phase was extracted with 3 x 200 ml of Et_2O, diluted with 200 ml of water and re-extracted with 2 x 200 ml of Et_2O. The joined organic layers were dried over Na_2SO_4 and the solvent was removed by evaporation. The crude product was purified by distillation (14 mmHg, 72-74 °C) to give 29.00 g (0.19 mol, 49 %) of **117** as colorless liquid and white solid *cis* and *trans* mixture.
TLC (SiO_2, pentane): $R_f = 0.61$.
^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 4.17 (br s, 2H, HC(1)) ; 2.32-2.24 (m, 4H, $H_aC(2)$) ; 1.83-1.70 (m, 4H, $H_bC(2)$).
^{13}C NMR (50 MHz, $CDCl_3$) δ_C: 57.9 ; 57.5 ; 35.0 ; 32.3.
EI-MS *m/z* (%): 115.8 (8) ; 87.7 (9) ; 82.2 (10) ; 81.0 (100) ; 79.9 (84) ; 78.8 (51) ; 76.8 (21) ; 74.8 (17) ; 66.8 (20) ; 64.9 (8) ; 61.9 (9) ; 55.0 (14) ; 54.0 (14) ; 53.0 (19) ; 51.0 (10).

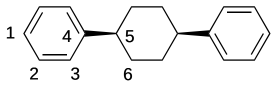
1,4-Diphenylcyclohexanol (119)



119

Under inert atmosphere and at 0 ° C, 6.3 ml (18.9 mmol) of 3 M solution of phenylmagnesium bromide in Et_2O was added carefully to a solution of 2.00 g (11.5 mmol) of 4-phenylcyclohenanone in 50 ml of dry Et_2O. The reaction mixture was stirred at room temperature for 4 h and quenched with 50 ml of a saturated solution of NH_4Cl. The layers were separated and the aqueous phase was extracted with 2 x 20 ml of Et_2O. The joined organic phases were dried over Na_2SO_4 and the solvent was evaporated to give 2.75 g (10.9 mmol, 91 %) of **119** as a white solid constituted as a epimeric mixture. The product was used without further purifications.
Analyses correspond to the epimeric mixture, no attribution was made.
^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.57 (t, J = 8.1 Hz, 2H) ; 7.42-7.12 (m, 8H) ; 2.61-2.53 (m, 1H) ; 2.08-1.83 (m, 6H) ; 1.63-1.56 (m, 2H).
^{13}C NMR (50 MHz, $CDCl_3$) δ_C: 149.3 ; 147.1 ; 146.0 ; 144.6 ; 128.6 ; 128.4 ; 128.3 ; 127.5 ; 126.9 ; 126.8 ; 126.2 ; 126.0, 125.9 ; 124.4 ; 73.2 ; 72.5 ; 43.6 ; 42.8 ; 39.1 ; 38.0 ; 30.9 ; 29.6.
EI-MS m/z (%): 234.1 (21) ; 142.9 (6) ; 132.9 (22) ; 129.3 (100) ; 114.9 (19) ; 103.7 (26) ; 90.9 (12) ; 76.8 (10) ; 76.7 (12).

cis-1,4-Diphenylcyclohexane (105)



105

Method A (from **117**): Under inert atmosphere, 29.00 g (0.19 mol) of **117** were added carefully to a a suspension of 6.32 g (0.05 mol) of $AlCl_3$ in 360 ml of dry benzene. The reaction mixture was stirred at room temperature for 2 h and quenched with ice. The layers were separated and the aqueous phase was extracted with 3 x 150 ml of Et_2O. The joined organic phases were dried over Na_2SO_4 and the solvents were removed by evaporation. The crude mixture was purified by distillation (14 mmHg, 190-192 ° C) to give the *cis* and *trans* mixture, which was resolved by two crystallization of the trans isomer at room temperature, giving 14.31 g (0.06 mol, 32 %) of **105** as a colorless liquid.
Method B (from **119**): A suspension of 58 mg (10 %) of Pd/C and 585 mg (2.32 mmol) of **119** in 10 ml of EtOH was placed under 3 bars of H_2. The reaction

mixture was stirred at room temperature for 3 days and filtered via a cannula. The crude product was purified by silica gel column chromatography (eluent: pentane) to give 160 mg (0.7 mmol, 29 %) of **105** as a colorless liquid.
Method C (from **119**): Under inert atmosphere, a solution of 5.00 g (19.8 mmol) of **119** in 100 ml of absolute EtOH was added with 60 ml of a Raney-Nickel suspension. The reaction mixture was stirred at room temperature for 2 days. The mixture was filtered via cannula without washing and the solvent was evaporated, giving 1.93 g (8.2 mmol, 41 %) of **105** as a colorless liquid.

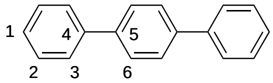
TLC (SiO_2, pentane): $R_f = 0.45$.

^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.30-7.24 (m, 6H, HC(1,3)) ; 7.19-7.13 (m, 4H, HC(2)) ; 2.89-2.87 (m, 2H, HC(5)) ; 2.04-1.96 (m, 4H, $H_aC(6)$) ; 1.86-1.79 (m, 4H, $H_bC(6)$).

^{13}C NMR (50 MHz, $CDCl_3$) δ_C: 147.0 (C(4)) ; 128.2 (C(2)) ; 127.2 (C(3)) ; 125.6 (C(1)) ; 40.2 (C(5)) ; 29.9 (C(6)).

EI-MS *m/z* (%): 236.2 (71) $M^{+\bullet}$; 193.0 (8) ; 157.8 (8) ; 144.8 (85) ; 142.7 (7) ; 132.1 (9) ; 131.0 (20) ; 129.9 (5) ; 129.0 (12) ; 127.7 (12) ; 118.1 (21) ; 116.9 (53) ; 115.0 (33) ; 105.1 (14) ; 103.7 (100) ; 92.1 (32) ; 90.9 (92).

Synthesis of *para*-terphenyl 106



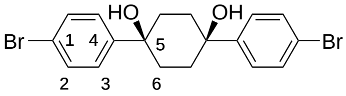
106

Under inert atmosphere, a solution of 50 mg (0.21 mmol) of **105** in 5 ml of benzene and 154 mg (0.68 mmol) of DDQ was refluxed for 20 h. The reaction mixture was filtered over a basic alox plug. The solvent was evaporated and the crude product was purified by recristallisation in cyclohexane to give 41 mg (0.18 mmol, 85 %) of **106** as a white solid.

^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.70 (s, 4H, HC(6)) ; 7.67-7.65 (m, 4H, HC(3)) ; 7.48 (t, $J = 7.5$ Hz, 4H, HC(2)) ; 7.38 (t, $J = 7.3$ Hz, 2H, HC(1)).

EI-MS *m/z* (%): 230.0 (100) $M^{+\bullet}$; 228.1 (13) ; 227.1 (4) ; 226.0 (8) ; 201.9 (6) ; 151.9 (7) ; 115.0 (11) ; 28.0 (6).

Synthesis of 121



121

Under inert atmosphere and at -78 °C, 15.5 ml (26.6 mmol) of a 1.7 M *tert*-BuLi solution in pentane was added dropwise to a solution of 5.00 g (21.2 mmol) of 1,4-dibromobenzene in 50 ml of dry THF. The reaction mixture was stirred at this temperature for 45 minutes. Then, a solution of 1.13 g (10.0 mmol) of 1,4-cyclohexanone in 20 ml of dry THF was added dropwise and the mixture was heated immediately at 35 °C for 5 hours. The reaction mixture was quenched with 50 ml of water and extracted with 3 x 50 ml of Et_2O. The joined organic layers were dried over Na_2SO_4 and the solvents were removed by evaporation. The crude product was purified by silica gel column chromatography (eluent: pentane/AcOEt 1:3) to give 1.37 g (3.2 mmol, 32 %) of **121** as a white solid.

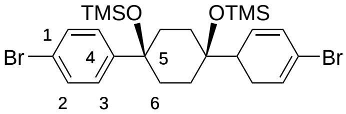
TLC (SiO_2, pentane/AcOEt 1:3): $R_f = 0.35$.

^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.48 (d, J = 8.6 Hz, 4H, HC(2)) ; 7.34 (d, J = 8.6 Hz, 4H, HC(3)) ; 2.08 (s, 8H, $H_2C(6)$) ; 1.71 (s, 2H, OH).

^{13}C NMR (50 MHz, $CDCl_3$) δ_C: 144.6 (C(4)) ; 131.6 (C(2)) ; 127.2 (C(3)) ; 121.4 (C(1)) ; 72.3 (C(5)) ; 35.2 (C(6)).

ESI-MS m/z: 449.0 $[M+Na]^+$; 874.9 $[2M+Na]^+$.

Synthesis of 122



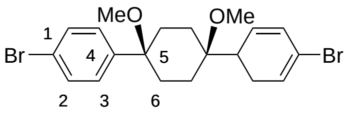
122

Under inert atmosphere, a solution of 1.00 g (2.3 mmol) of **121**, 0.64 g (9.4 mmol) of imidazole and 1.02 g (9.4 mmol) of TMSCl in 60 ml of dry THF was stirred at room temperature for 16 hours. The reaction mixture was quenched with 50 ml of water and extracted with 3 x 50 ml of Et_2O. The joined organic layers were dried over Na_2SO_4 and the solvents were removed by evaporation. The crude product was purified by silica gel plug filtration (eluent: CH_2Cl_2) to give 1.17 g (2.1 mmol, 91 %) of **122** as a white solid. This product can be recrystallized in hot EtOH with the addition of some drop of water.

TLC (SiO_2, CH_2Cl_2): $R_f = 0.80$.

^{1}H NMR (360 MHz, CD_2Cl_2) δ_H: 7.42 (d, J = 8.6 Hz, 4H, HC(2)) ; 7.32 (d, J = 8.6 Hz, 4H, HC(3)) ; 2.18 (br s, 4H, $H_aC(6)$) ; 1.96 (br s, 4H, $H_bC(6)$) ; -0.07 (s, 18H, OTMS).
^{13}C NMR (50 MHz, $CDCl_3$) δ_C: 144.9 (C(4)) ; 131.2 (C(2)) ; 128.0 (C(3)) ; 121.1 (C(1)) ; 74.6 (C(5)) ; 35.6 (C(6)) ; 2.2 (OTMS).
ESI-MS m/z: 593.1 $[M+Na]^+$; 1163.1 $[2M+Na]^+$.

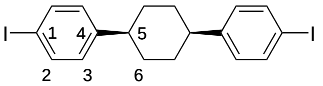
Synthesis of 123



123

Under inert atmosphere, a suspension of 750 mg (1.76 mmol) of **121**, 211 mg (5.28 mmol) of a 60 % NaH suspension and 999 mg (7.04 mmol) of MeI in 50 ml of dry THF was heated at reflux for 23 h. The reaction mixture was quenched with 50 ml of water and extracted with 3 x 50 ml of Et_2O. The joined organic phases were dried over Na_2SO_4 and the solvents were evaporated. The crude mixture was purified by silica gel plug filtration (eluent: CH_2Cl_2/AcOEt 95:5) to give 757 mg (1.67 mmol, 95 %) of **123** as a white solid.
TLC (SiO_2, CH_2Cl_2): $R_f = 0.21$.
^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.46 (d, J = 8.6 Hz, 4H, HC(2)) ; 7.28 (d, J = 8.6 Hz, 4H, HC(3)) ; 2.95 (s, 6H, OMe) ; 2.15-2.09 (m, 4H, $H_aC(6)$) ; 1.96 (br s, 4H, $H_bC(6)$).
^{13}C NMR (50 MHz, $CDCl_3$) δ_C: 141.6 (C(4)) ; 131.4 (C(2)) ; 128.6 (C(3)) ; 121.4 (C(1)) ; 74.6 (C(5)) ; 49.7 (OMe) ; 31.5 (C(6)).
ESI-MS m/z: 477.0 $[M+Na]^+$.

cis-1,4-bis(4-Iodophenyl)cyclohexane (81)



81

Method A: A solution of 1.00 g (4.23 mmol) of **105** and 2.64 g (10.27 mmol) of AgOTf in 60 ml of $CHCl_3$ was cooled at 0 °C. A solution of 2.18 g (8.59 mmol) of I_2 in 60 ml of $CHCl_3$ was added for 30 minutes and the reaction mixture was stirred at room temperature for 2 h. The precipitate was removed by filtration and the filtrate was washed with 3 x 50 ml of a 10 % $Na_2S_2O_3$ solution. The organic phase was dried over Na_2SO_4 and the solvent was evaporated. The crude mixture was recrystallized in EtOH to give 920 mg (1.88 mmol, 45 %) of **81** as a white solid. In some cases, a few drops of $CHCl_3$ were needed for the recrystallization. The mother liquor was concentrated and gave additionnal 180 mg (0.37 mmol, 9 %) of desired product.

Method B: Under inert atmosphere, a solution of 14.31 g (60.55 mmol) of **105**, 15.37 g (60.55 mmol) of I_2 and 31.24 g (72.66 mmol) of PIFA in 50 ml of $CHCl_3$ was stirred at room temperature for 2 h. The mixture was washed with 3 x 50 ml of a 10 % $Na_2S_2O_3$ solution and the organic phase was dried over Na_2SO_4. The solvent was evaporated and the crude product was recrystallized in EtOH, giving 14.19 g (29.06 mmol, 48 %) of **81** as a white solid. In some cases, a few drops of $CHCl_3$ were needed for the recrystallization.

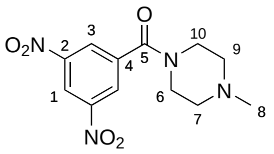
TLC (SiO_2, pentane): $R_f = 0.35$.

^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.61 (d, J = 8.7 Hz, 4H, HC(2)) ; 7.02 (d, J = 8.6 Hz, 4H, HC(3)) ; 2.83 (br s, 2H, HC(5)) ; 1.96-1.77 (m, 8H, $H_2C(6)$).

^{13}C NMR (50 MHz, $CDCl_3$) δ_C: 146.6 (C(4)) ; 137.4 (C(2)) ; 128.9 (C(3)) ; 91.0 (C(1)) ; 44.1 (C(5)) ; 33.5 (C(6)).

EI-MS m/z (%): 488.5 (30) $M^{+\bullet}$; 362.2 (5) ; 229.9 (27) ; 217.0 (26) ; 207.0 (100) ; 191.0 (6) ; 129.0 (13) ; 127.9 (25) ; 126.8 (31) ; 117.0 (10) ; 116.0 (21) ; 115.0 (34) ; 103.0 (15) ; 90.9 (27).

Synthesis of 126



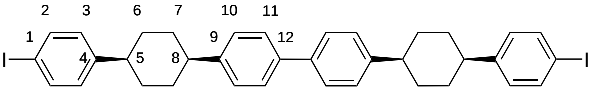
126

A suspension of 12.20 g (0.1 mol) of 3,5-dinitrobenzoic acid in 100 ml of $SOCl_2$ was refluxed for 10 hours. Thionyl chloride was then removed by evaporation and two times by azeotropic vacuum distillation with 25 ml of toluene. The residue was dissolved with 200 ml of $CHCl_3$ and added dropwise to a mixture of 12.00 g (0.12 mol) of 1-methylpiperazine and 14.00 g (0.1 mol) of K_2CO_3 in 200 ml of $CHCl_2$ at 0 ° C. The reaction mixture was stirred at room temperature for 1 hour and washed with 3 x 400 ml of water. The organic layer was dried over Na_2SO_4 and the solvent was removed by evaporation. The crude product was purified by precipitation of a hot $CHCl_3$ solution by addition of hot hexane to give 20.20 g (68.7 mmol, 69 %) of **126** as a yellow solid.

^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 9.11 (s, 1H, HC(1)) ; 8.60 (s, 1H, HC(3)) ; 3.86 (br s, 2H, $H_aC(6,10)$) ; 3.45 (br s, 2H, $H_bC(6,10)$) ; 2.55 (br s, 2H, $H_aC(7,9)$) ; 2.42 (br s, 2H, $H_bC(7,9)$) ; 2.36 (s, 3H, $H_3C(8)$).

^{13}C NMR (90 MHz, CDCl$_3$) δ_C: 165.1 (C(5)) ; 148.4 (C(2)) ; 139.1 (C(4)) ; 127.4 (C(3)) ; 119.6 (C(1)) ; 54.9 (C(7)) ; 54.3 (C(9)) ; 47.8 (C(8)) ; 45.9 (C(6)) ; 42.5 (C(10)).
ESI-MS *m/z*: 295.1 [M+H]$^+$.

Synthesis of 128

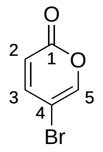


128

Under inert atmosphere and at -18 °C, 0.5 ml (1.0 mmol) of a 2 M isopropylmagnesium chloride solution were added to a solution of 0.49 g (1.0 mmol) of **81** in 3 ml of dry THF. The reaction mixture was stirred at this temperature for 20 minutes and then, 0.10 g (0.5 mmol) of CuBr·Me$_2$S were added. After 30 seconds of stirring, a solution of 0.29 g (1.0 mmol) of **126** in 3 ml was added. The reaction mixture was stirred at room temperature for 20 minutes and then filtered over a silica gel plug (eluent: pentane/AcOEt 1:1) and the solvents were removed by evaporation. The crude product was purified by silica gel chromatography (eluent: cyclohexane/AcOEt 100:0 ; 95:5) to give 60 mg (0.03 mmol, 17 %) of **128** as a white solid.
TLC (SiO$_2$, cyclohexane): R$_\mathrm{f}$ = 0.12.
^{1}H NMR (360 MHz, CDCl$_3$) δ_H: 7.61 (d, J = 8.2 Hz, 4H, HC(2)) ; 7.51 (d, J = 8.2 Hz, 4H, HC(11)) ; 7.29 (d, J = 8.2 Hz, 4H, HC(10)) ; 7.01 (d, J = 8.2 Hz, 4H, HC(3)) ; 2.77-2.65 (m, 4H, HC(5,8)) ; 2.10-1.93 (m, 8H, H$_\mathrm{a}$C(6,7)) ; 1.66-1.40 (m, 8H, H$_\mathrm{b}$C(6,7)).
^{13}C NMR (90 MHz, CDCl$_3$) δ_C: 146.9 (C(9)) ; 145.9 (C(4)) ; 138.8 (C(2)) ; 137.3 (C(12)) ; 129.0 (C(3)) ; 127.1 (C(10)) ; 127.0 (C(11)) ; 90.9 (C(1)) ; 44.2 (C(7)) ; 44.1 (C(5)). 33.7 (C(6)) ; 33.7 (C(8)).
EI-MS *m/z* (%): 722.0 (59) M$^{+\bullet}$; 596.2 (21) ; 451.1 (23) ; 230.0 (27) ; 217.0 (100).

14.2 Diels-Alder precursors

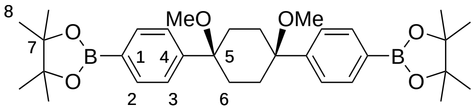
5-Bromo-2-pyrone (135)



135

A solution of 2.00 g (14.28 mmol) of coumalic acid and 2.91 g (28.55 mmol) of LiOAc·$2H_2O$ in 110 ml of MeCN and 22 ml of water was stirred at room temperature for 5 minutes. Then, 5.08 g (28.55 mmol) of NBS were added and the reaction mixture was stirred for 4 days. The reaction was quenched with 50 ml of water and extracted with 3 x 50 ml of CH_2Cl_2. The joined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The crude mixture was purified by silica gel column chromatography (eluent: pentane/Et_2O 100:0; then 90:10; 80:20; 75:25) to give 270 mg (1.54 mmol, 11 %) of **135** as a white solid.
TLC (SiO_2, pentane/Et_2O 50:50): $R_f = 0.40$.
^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.58 (s, 1H, HC(5)) ; 7.34 (d, J = 10.0 Hz, 1H, HC(3)) ; 6.30 (d, J = 10.0 Hz, 1H, HC(2)).
EI-MS m/z (%): 174.4 (63) $M^{+\bullet}$; 173.4 (6) ; 163.4 (18) ; 161.5 (17) ; 149.5 (6) ; 148.5 (92) ; 147.4 (9) ; 146.4 (100) ; 120.4 (17) ; 119.5 (30) ; 118.5 (19) ; 117.4 (31) ; 95.5 (10) ; 81.4 (14) ; 79.4 (13).

Synthesis of 137

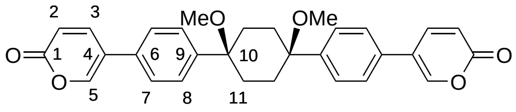


137

Under inert atmosphere and at -78 °C, 1 ml (1.65 mmol) of a 1.7 M *tert*-BuLi solution in pentane was added to a solution of 250 mg (0.55 mmol) of **123** in 10 ml of dry THF. The reaction mixture was stirred at this temperature for 45 minutes and 126 mg (1.21 mmol) of $B(OMe)_3$ were added. The mixture was stirred 3 h at room temperature and 325 mg (2.75 mmol) of pinacol were added. The reaction was quenched after 15 minutes by the addition of 40 drops of concentrated AcOH and filtered over celite. After several washings with Et_2O, the solvents were evaporated and the crude product was purified by silica gel column chromatography (eluent: CH_2Cl_2/AcOEt 70:30) to give 251 mg (0.46 mmol, 83 %) of **137** as a white solid.
TLC (SiO_2, CH_2Cl_2/AcOEt 85:15): $R_f = 0.44$.

^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.78 (d, J = 7.7 Hz, 4H, HC(2)) ; 7.41 (d, J = 7.7 Hz, 4H, HC(3)) ; 2.95 (s, 6H, OMe) ; 2.18-2.11 (m, 4H, $H_aC(6)$) ; 2.05 (br s, 4H, $H_bC(6)$) ; 1.34 (s, 12H, $H_3C(8)$).
ESI-MS m/z: 571.3 $[M+Na]^+$.

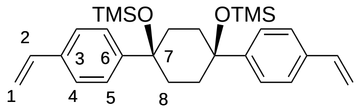
Synthesis of 138



138

Under inert atmosphere, a solution of 200 mg (0.36 mmol) of **137**, 140 mg (0.80 mmol) of **135** and 30 mg (0.04 mmol) of $PdCl_2(dppf){\cdot}CH_2Cl_2$ in 10 ml of degased DMF was prepared. Then, 619 mg (2.92 mmol) of K_3PO_4 were added and the reaction mixture was refluxed for 24 h. The solvent was removed by evaporation and the residual material was dissolved in CH_2Cl_2. A prepurification was done by silica gel filtration (eluent: AcOEt). Purification by silica gel column chromatography (eluent: CH_2Cl_2/AcOEt) gave 69 mg (0.14 mmol, 40 %) of **138** as a white solid.
TLC (SiO_2, CH_2Cl_2/AcOEt 50:50): R_f = 0.41.
^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.69 (br s, 2H, HC(5)) ; 7.62 (dd, J = 9.5 Hz, J = 7.2 Hz, 2H, HC(3)) ; 7.49 (d, J = 8.2 Hz, 4H, HC(8)) ; 7.36 (d, J = 8.2 Hz, 4H, HC(7)) ; 6.45 (d, J = 9.5 Hz, 2H, HC(2)) ; 2.99 (s, 6H, OMe) ; 2.22-2.12 (m, 4H, $H_aC(11)$) ; 2.05 (br s, 4H, $H_bC(11)$).

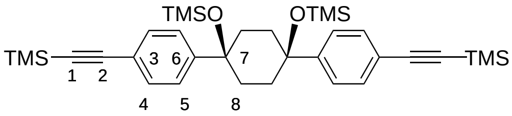
Synthesis of 139



139

Under inert atmosphere, 0.85 ml (0.82 mmol) of a 1 M vinylmagnesium bromide solution in THF were added to a solution of 195 mg (0.34 mmol) of **122** and 9.5 mg (0.03 mmol) of $NiCl_2$(dmpe) in 10 ml of dry THF. The reaction mixture was stirred at room temperature for 4 days and quenched with 10 ml of water. The mixture was extracted with 3 x 10 ml of Et_2O. The joined organic phases were dried over Na_2SO_4 and the solvents were evaporated. The crude product was not purified and traces were detected by ^{1}H NMR analysis.

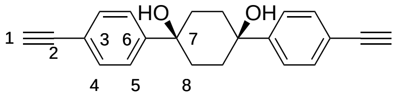
Synthesis of 140



140

Under inert atmosphere, a solution of 100 mg (0.2 mmol) of **122**, 5.5 mg (21 μmol) of triphenylposphine, 4.0 mg (21 μmol) of CuI and 7.4 mg (11 μmol) of Pd(PPh$_3$)Cl$_2$ in 10 ml of argon purged piperidine was heated at 80 $^\circ$C. With a syringe, 45 mg (0.5 mmol) of TMSA were added and the reaction mixture was heated at 80 $^\circ$C for 21 hours. The mixture was quenched with 10 ml of a saturated NH$_4$Cl solution and extracted with 3 x 10 ml of CH$_2$Cl$_2$. The joined organic layers were dried over Na$_2$SO$_4$ and the solvent was removed by evaporation. The crude product was purified by silica gel column chromatography (eluent: pentane/CH$_2$Cl$_2$ 85:15) to give 67 mg (0.1 mmol, 62 %) of **140** as a white solid.
TLC (SiO$_2$, pentane/CH$_2$Cl$_2$ 85:15): R$_f$ = 0.18.
^{1}H NMR (360 MHz, CD$_2$Cl$_2$) δ_H: 7.39 (d, J = 8.6 Hz, 4H, HC(5)) ; 7.34 (d, J = 8.6 Hz, 4H, HC(4)) ; 2.18-2.13 (m, 4H, H$_a$C(8)) ; 1.94 (br s, 4H, H$_b$C(8)) ; 0.24 (s, 18H, TMS) ; -0.10 (s, 18H, OTMS).
^{13}C NMR (50 MHz, CDCl$_3$) δ_C: 146.3 (C(6)) ; 131.7 (C(4)) ; 126.1 (C(5)) ; 121.7 (C(3)) ; 104.9 (C(2)) ; 94.1 (C(1)) ; 74.7 (C(7)) ; 35.6 (C(8)) ; 2.2 (OTMS) ; 0.0 (TMS).
ESI-MS m/z: 627.3 [M+Na]$^+$.

Synthesis of 141

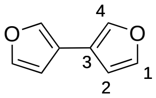


141

A suspension of 100 mg (0.17 mmol) of **140** and 73 mg (0.53 mmol) of K$_2$CO$_3$ in 10 ml of a 1:1 THF/MeOH mixture was refluxed for 18 h. The reaction mixture was quenched with 10 ml of water and extracted with 3 x 10 ml of CH$_2$Cl$_2$. The joined organic phases were dried over Na$_2$SO$_4$ and the solvents were evaporated. The crude product was purified by silica gel column chromatography (eluent: CH$_2$Cl$_2$/AcOEt 30:70) to give 7 mg (15 μmol, 9 %) of **141** as a white solid.
TLC (SiO$_2$, CH$_2$Cl$_2$/AcOEt 30:70): R$_f$ = 0.28.
^{1}H NMR (360 MHz, CD$_2$Cl$_2$) δ_H: 7.48 (d, J = 8.2 Hz, 4H, HC(5)) ; 7.43 (d, J = 8.2 Hz, 4H, HC(4)) ; 3.08 (s, 2H, HC(1)) ; 2.09 (s, 8H, H$_2$C(8) ; 1.71 (s, 2H, OH).

^{13}C NMR (50 MHz, $CDCl_3$) δ_C: 146.3 (C(6)) ; 132.3 (C(4)) ; 125.4 (C(5)) ; 121.2 (C(3)) ; 83.3 (C(2)) ; 77.5 (C(1)) ; 72.5 (C(7)) ; 35.1 (C(8)).
ESI-MS m/z: 281.3 $[M-H_2O-OH]^+$.

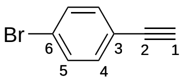
Synthesis of 143



143

Under inert atmosphere and at -70 °C, 4.0 ml (6.8 mmol) of a 1.7 M *tert*-BuLi solution in pentane were added to a solution of 1.00 g (6.8 mmol) of 3-bromofuran in 5 ml of dry THF and 15 ml of dry Et_2O. The reaction mixture was stirred at this temperature for 30 minutes and then, 1.102 g (8.2 mmol) of $CuCl_2$ were added. The mixture was stirred at -70 °C for 1 hour and at -20 °C for 2 hours. The reaction was quenched with 10 ml of a saturated aqueous solution of glycine and extracted with 2 x 20 ml of $CHCl_3$. The combined organic layers were carefully evaporated and the crude product was purified by sublimation to give 37 mg (0.1 mmol, 8 %) of **143** as a white solid. The product was kept in freezer and degraded after a few hours.
^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.58 (s, 2H, HC(4)) ; 7.44 (s, 2H, HC(1)) ; 6.52 (s, 2H, HC(2)).

1-Bromo-4-ethynylbenzene (145)



145

To a solution of 1.61 g (6.3 mmol) of (4-bromophenylethynyl)trimethylsilane in 20 ml of THF and 15 ml of MeOH, 1.40 g (10.1 mmol) of K_2CO_3 were added. The reaction mixture was stirred at room temperature for 18 hours, quenched with 20 ml of water and extracted with 3 x 10 ml of CH_2Cl_2. The joined organic layers were dried over Na_2SO_4 and the solvents were removed by evaporation. The crude product was purified by sublimation to give 0.91 g (5.0 mmol, 80 %) of **145** as a white solid.
TLC (SiO_2, pentane): $R_f = 0.69$.
^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.46 (d, J = 8.6 Hz, 2H, HC(5)) ; 7.35 (d, J = 8.6 Hz, 2H, HC(4)) ; 3.13 (s, 1H, HC(1)).
^{13}C NMR (90 MHz, $CDCl_3$) δ_C: 133.5 (C(5)) ; 131.6 (C(4)) ; 123.1 (C(6)) ; 121.0 (C(3)) ; 82.5 (C(2)) ; 78.3 (C(1)).
EI-MS m/z (%): 180 (100) $M^{+\bullet}$; 101 (12) $C_8H_5^{+\bullet}$.

14.3 McMurry regents

Synthesis of $TiCl_3(ROR)_3$

Method A (from $TiCl_3$, ROR = DME): Under inert atmosphere, a solution of 5.00 g (32.4 mmol) of $TiCl_3$ in 70 ml of dry DME was refluxed for 2 days. The mixture was cooled and filtered under argon via a cannula. The crude material was washed with dry pentane and vacuum dried to give 7.41 g (25.5 mmol, 79 %) of $TiCl_3(DME)_{1.5}$ as a blue solid.

Method B (from $TiCl_4$ and Al, ROR = DME): Under inert atmosphere, 2.8 ml (4.88 g, 25.7 mmol) of $TiCl_4$ were added carefully to a suspension of 223 mg (8.27 mmol) of powdered Al in 70 ml of dry DME was refluxed for 2 days. The mixture was cooled and filtered under argon via a cannula. The crude material was washed with dry pentane and vacuum dried to give 5.97 g (20.6 mmol, 80 %) of $TiCl_3(DME)_{1.5}$ as a turquoise solid.

Method C (from $TiCl_4$ and Ti, ROR = DME): Under inert atmosphere, 8.5 ml (14.63 g, 77.1 mmol) of $TiCl_4$ were added carefully to a suspension of 1.19 g (24.8 mmol) of powdered Ti in 200 ml of dry DME and refluxed for 2 days. The mixture was cooled and filtered under argon via a cannula. The crude material was washed with dry pentane and vacuum dried to give 25.85 g (68.6, 89 %) of $TiCl_3(DME)_{1.5}$ as a green solid.

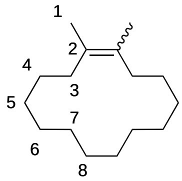
Method D (from $TiCl_4$ and Al, ROR = THF): Under inert atmosphere, 6.7 ml of dry THF were added slowly to a solution of 2.0 ml (3.47 g, 18.3 mmol) of $TiCl_4$ in 33 ml of dry pentane. After 10 minutes of stirring the solvent was filtered off via cannula, then 50 ml of dry THF and 157 mg (5.8 mmol) of powdered Al were added to the residue. TRhe reaction mixture was refluxed for 24 h, giving 5.83 g (15.7 mmol, 86 %) of $TiCl_3(THF)_3$ as a turquoise solid.

Synthesis of Zn(Cu)

A suspension of 9.80 g (0.15 mol) of ground zinc in 40 ml of nitrogene-purged water was purged with N_2 for 15 minutes and then 0.75 g (4.70 mmol) of $CuSO_4$ were added . The black slurry was filtered under nitrogen via a cannula and washed with nitrogen-purged water, acetone and Et_2O. The Zn(Cu) couple was vacuum dried to give 9.67 g of a black powder.

14.4 McMurry precursors and reactions

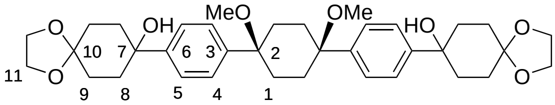
1,2-Dimethylcyclotetradecene (148)



148

Under inert atmosphere, a mixture of 2.30 g (7.85 mmol) of $TiCl_3(DME)_{1.5}$ and 1.55 g (23.80 mmol) of Zn(Cu) in 75 ml of dry DME. The mixture was refluxed for 5 h. A solution of 250 mg (0.98 mmol) of 2,15-hexadecanedione in 25 ml of dry DME was then added by syringe pump over a period of 35 h at 80 °C and the mixture was stirred an additional 8 h after the end of the addition. The reaction mixture was cooled and 75 ml of pentane were added. The crude material was filtered over Florisil and the solvents were evaporated to give 166 mg (7.47 mmol, 76 %) of a *cis* and *trans* mixture of 1,2-dimethylcyclotetradecene (**148**).
TLC (SiO_2, CH_2Cl_2): $R_f = 0.70$.
^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 2.42 (t, $J = 7.5$ Hz, 4H, $H_2C(3)$) ; 2.14 (s, 6H, $H_3C(1)$) ; 1.58-1.13 (m, 20H, $H_2C(4,5,6,7,8)$).
EI-MS m/z (%): 179.3 (6) ; 138.2 (5) ; 125.1 (8) ; 123.1 (11) ; 109.1 (15) ; 97.2 (13) ; 96.2 (6) ; 95.1 (18) ; 85.1 (7) ; 83.0 (19) ; 81.0 (13) ; 71.0 (51) ; 69.0 (18) ; 67.0 (12) ; 59.1 (14) ; 57.9 (76) ; 55.1 (32) ; 43.0 (100) ; 41.1 (15) ; 32.1 (7) ; 29.2 (8) ; 28.1 (36) ; 27.1 (6).

Synthesis of 149

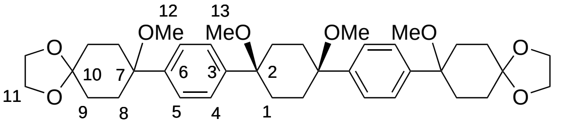


149

Under inert atmosphere and at -78 °C, 5.2 ml (9.69 mmol) of a 1.7 M *tert*-BuLi solution in pentane were added to a solution of 1.00 g (2.20 mmol) of **123** in 25 ml of dry THF. The reaction was stirred for 50 minutes and a solution of 712 mg (4.62 mmol) of 1,4-cyclohexanedione monoethylene ketal in 10 ml of dry THF was added. The reaction mixture was stirred at room temperature for 3.5 days and quenched with 15 ml of water. The layers were separated and the aqueous phases was extracted with 3 x 30 ml of Et_2O. The joined organic phases were dried over $MgSO_4$ and the solvents were evaporated. The crude material was purified by silica

gel column chromatography (eluent: CH_2Cl_2/AcOEt 50:50; 0:100) to give 1.25 g (2.05 mmol, 93 %) of **149** as a white solid.
TLC (SiO_2, AcOEt): $R_f = 0.40$.
^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.47 (d, J = 8.2 Hz, 4H, HC(4)) ; 7.38 (d, J = 8.2 Hz, 4H, HC(5)) ; 4.01-3.96 (m, 8H, $H_2C(11)$) ; 2.95 (s, 6H, OMe) ; 2.20-1.99 (m, 16H, $H_aC(1,8)$ and $H_2C(9)$) ; 1.83-1.79 (m, 4H, $H_bC(1)$) ; 1.71-1.68 (m, 4H, $H_bC(8)$) ; 1.48 (s, 2H, OH).
^{13}C NMR (50 MHz, $CDCl_3$) δ_C: 147.4 (C(6)) ; 141.0 (C(3)) ; 126.7 (C(5)) ; 124.4 (C(4)) ; 108.4 (C(10)) ; 76.8 (C(2)) ; 72.1 (C(7)) ; 64.3 (C(11)) ; 49.6 (C(OMe)) ; 36.4 (C(9)) ; 31.5 (C(1)) ; 30.7 (C(8)).
ESI-MS m/z: 631.3 $[M+Na]^+$.

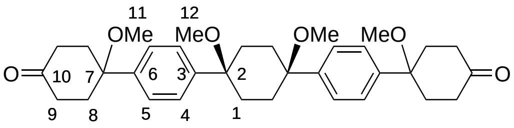
Synthesis of 150



150

Under inert atmosphere, a suspension of 1.105 g (1.82 mmol) of **149**, 221 mg (3.18 mmol) of a 60 % NaH suspension in parafin and 1.03 g (7.26 mmol) of MeI in 60 ml of dry THF was refluxed for 46 h. The reaction mixture was carefully quenched with 40 ml of water and the layers were separated. The aquouse phase was extracted with 3 x 30 ml of Et_2O. The joined organic phases were dried over $MgSO_4$ and the solvents were evaporated. The residu was purified by silica gel column chromatography (eluent: CH_2Cl_2/AcOEt 50:50) to give 1.06 g (1.66 mmol, 92 %) of **150** as a white solid.
TLC (SiO_2, CH_2Cl_2/AcOEt): $R_f = 0.36$.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.37 (s, 8H, HC(4,5)) ; 4.00-3.94 (m, 8H, $H_2C(11)$) ; 2.99 (s, 6H, $H_3C(12)$) ; 2.95 (s, 6H, $H_3C(13)$) ; 2.18-2.14 (m, 4H, $H_aC(1)$) ; 2.06-1.80 (m, 16H, $H_bC(1)$, $H_aC(8)$ and $H_2C(9)$) ; 1.71-1.68 (m, 4H, $H_bC(8)$).
^{13}C NMR (125 MHz, $CDCl_3$) δ_C: 143.7 (C(3,6)) ; 126.7 (C(4)) ; 125.9 (C(5)) ; 108.5 (C(10)) ; 76.8 (C(2)) ; 76.4 (C(7)) ; 64.2 (C(11)) ; 50.1 (C(12)) ; 49.6 (C(13)) ; 32.7 (C(9)) ; 31.6 (C(1)) ; 30.5 (C(8)) .
ESI-MS m/z: 659.4 $[M+Na]^+$.

Synthesis of 151



151

A solution of 500 mg (0.79 mmol) of **150** and 15 mg (0.08 mmol, 10 mol%) of *p*-TSA·H_2O in 24 ml of a 10:2 acetone/water mixture was refuxed for 17 h. To the reaction mixture, 20 ml of a saturated $NaHCO_3$ solution were added and the acetone was evaporated. The precipitate was filtered over Büchner funnel. The obtained solid was washed 2 times with water in ultrasonic irradiations and dried under vacuum, giving 276 mg (0.50 mmol, 64 %) of **151** as a white solid.

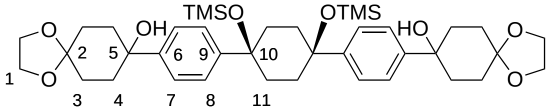
TLC (SiO_2, CH_2Cl_2/AcOEt 95:5): $R_f = 0.26$.

^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.43 (d, J = 8.1 Hz, 4H, HC(4)) ; 7.38 (d, J = 8.1 Hz, 4H, HC(5)) ; 3.08 (s, 6H, $H_3C(11)$) ; 2.96 (s, 6H, $H_3C(12)$) ; 2.82-2.73 (m, 4H, $H_aC(8)$) ; 2.41-2.30 (m, 8H, $H_bC(8)$ and $H_aC(1)$) ; 2.21-1.97 (m, 12H, $H_bC(1)$ and $H_2C(9)$).

^{13}C NMR (90 MHz, $CDCl_3$) δ_C: 211.3 (C(10)) ; 142.3 (C(3,6)) ; 127.0 (C(4)) ; 125.9 (C(5)) ; 78.7 (C(7)) ; 76.0 (C(2)) ; 50.4 (C(11)) ; 49.7 (C(12)) ; 37.0 (C(9)) ; 34.9 (C(1)) ; 31.6 (C(8)) .

ESI-MS m/z: 571.3 $[M+Na]^+$.

Synthesis of 152



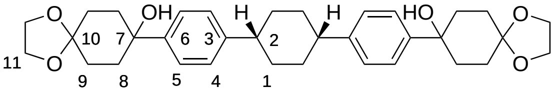
152

Under inert atmosphere and at -78 °C, 1.7 ml (2.8 mmol) of a 1.7 M *tert*-BuLi solution in pentane were added to a solution of 0.40 g (0.7 mmol) of **122** in 20 ml of dry THF. The mixture was stirred at this temperature for 1 hour and then, 0.23 g (1.5 mmol) of 1,4-cyclohexanedione monoethylene ketal in 5 ml of dry THF were added. The reaction mixture was stirred at room temperature for 4 days, quenched with 10 ml of a saturated NH_4Cl solution and extracted with 3 x 10 ml of Et_2O. The joined organic layers were dried over $MgSO_4$ and the solvents were removed by evaporation. The crude product was purified by silica gel chromatography (eluent: CH_2Cl_2/AcOEt 70:30 ; 50:50) to give 373 mg (0.5 mmol, 73 %) of **152** as a white solid.

TLC (SiO_2, CH_2Cl_2/AcOEt 70:30): $R_f = 0.17$.

^{1}H NMR (360 MHz, CDCl$_3$) δ_H: 7.41 (s, 8H, HC(7,8)) ; 4.02-3.94 (m, 8H, H$_2$C(1)) ; 2.23-1.97 (m, 16H, H$_a$C(4,11) and H$_2$C(3)) ; 1.80-1.78 (m, 4H, H$_b$C(11)) ; 1.66-1.40 (m, 4H, H$_b$C(4)) ; -0.12 (s, 18H, OTMS).
^{13}C NMR (125 MHz, CDCl$_3$) δ_C: 147.2 (C(6,9)) ; 126.2 (C(7)) ; 124.2 (C(8)) ; 108.4 (C(2)) ; 74.7 (C(10)) ; 72.2 (C(5)) ; 64.3 (C(1)) ; 36.5 (C(11)) ; 35.6 (C(3)) ; 30.7 (C(4)) ; 2.1 (C(OTMS)).
ESI-MS m/z: 747.39 [M+Na]$^+$.

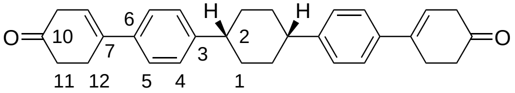
Synthesis of 153



153

Under inert atmosphere and at -50 °C, 12 ml (20.40 mmol) of a 1.7 M *tert*-BuLi solution in pentane were added to a solution of 2.15 g (4.40 mmol) of **81** in 50 ml of dry THF. The reaction was stirred for 20 minutes and 2.76 g (17.67 mmol) of 1,4-cyclohexanedione monoethylene ketal were added. The reaction mixture was stirred at room temperature for 20 h and quenched with 20 ml of water. The layers were separated and the aqueous phase was extracted with 3 x 20 ml of Et$_2$O. The joined organic phases were dried over Na$_2$SO$_4$ and the solvents were evaporated. The crude material was purified by silica gel column chromatography (eluent: CH$_2$Cl$_2$/AcOEt 50:50) to give 1.69 g (3.08 mmol, 70 %) of **153** as a white solid.
TLC (SiO$_2$, CH$_2$Cl$_2$/AcOEt 50:50): R$_f$ = 0.34.
^{1}H NMR (360 MHz, CDCl$_3$) δ_H: 7.44 (d, J = 7.7 Hz, 4H, HC(5)) ; 7.22 (d, J = 7.7 Hz, 4H, HC(4)) ; 4.02-3.95 (m, 8H, H$_2$C(11)) ; 2.74-2.68 (m, 2H, HC(2)) ; 2.20-1.95 (m, 12H, H$_a$C(1) and H$_2$C(8)) ; 1.82-1.47 (m, 8H, H$_b$C(1), H$_2$C(9) and OH).
^{13}C NMR (50 MHz, CDCl$_3$) δ_C: 146.0 (C(3)) ; 145.8 (C(6)) ; 126.6 (C(4)) ; 124.5 (C(5)) ; 72.2 (C(7)) ; 64.3 (C(11)) ; 44.1 (C(2)) ; 36.5 (C(9)) ; 33.6 (C(8)) ; 30.7 (C(1)).
ESI-MS m/z: 571.3 [M+Na]$^+$.

Synthesis of 154



154

A solution of 237 mg (0.43 mmol) of **153** and 2 ml (2.98 g, 26.14 mmol) of TFA in 10 ml of CH$_2$Cl$_2$ was stirred at room temperature for 6 h. The reaction mixture was quenched with a saturated $NaHCO_3$ solution until it was alkaline and extracted with 2 x 20 ml of CH_2Cl_2. The joined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by silica gel filtration (eluent: CH_2Cl_2) to give 180 mg (0.42 mmol, 98 %) of **154** as a white solid.

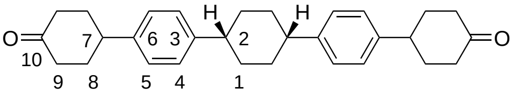
TLC (SiO_2, CH_2Cl_2/AcOEt 95:5): $R_f = 0.55$.

^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.34 (d, J = 8.2 Hz, 4H, HC(5)) ; 7.23 (d, J = 8.2 Hz, 4H, HC(4)) ; 6.07 (br s, 2H, HC(8)); 3.07-3.06 (m, 4H, $H_2C(9)$) ; 2.91-2.88 (m, 4H, H_2C(11 ou 12)) ; 2.76-2.70 (m, 2H, HC(2)) ; 2.66-2.62 (m, 4H, H_2C(11 ou 12)); 2.10-1.96 (m, 4H, $H_aC(1)$) ; 1.68-1.44 (m, 4H, $H_bC(1)$).

^{13}C NMR (50 MHz, $CDCl_3$) δ_C: 199.4 (C(10)) ; 145.3 (C(3)) ; 138.0 (C(6)) ; 137.4 (C(7)) ; 127.3 (C(4)) ; 125.0 (C(5)) ; 120.2 (C(8)) ; 39.9 (C(10)) ; 39.8 (C(2)) ; 38.7 (C(11)) ; 29.8 (C(1)) ; 27.8 (C(12)).

ESI-MS m/z: 447.2 $[M+Na]^+$.

Synthesis of 155



155

Method A (from **154**): A mixture of 168 mg (0.40 mmol) of **154** and 34 mg (20 wt%) of 10 % Pd/C in 15 ml of a 2:1 CH_2Cl_2/EtOH mixture was placed under 3 bars of H_2. The reaction mixture was stirred for 90 minutes and the catalyst was removed by filtration. The crude product was purified by silica gel TLC (eluent: CH_2Cl_2/AcOEt 94:6) to give 60 mg (0.14 mmol, 35 %) of **155** as a white solid.

Method B (from **157**): To a suspension of 5.05 g (9.77 mmol) of **157** in 360 ml of acetone and 40 ml of water, 0.2 ml of 37 % HCl were added. The reaction mixture was refluxed for 20 h and then cooled. The precipitate was filtered over Büchner funnel and washed twice with a 1:1 acetone/water mixture. The product was vacuum dried to give 4.01 g (9.36 mmol, 96 %) of **155** as a white solid.

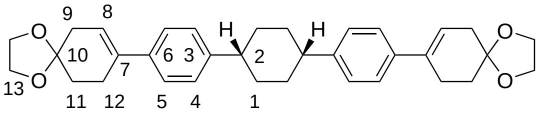
TLC (SiO_2, CH_2Cl_2/AcOEt 95:5): $R_f = 0.23$.

^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.21-7.15 (m ou q, 8H, HC(4,5)) ; 3.04-2.96 (m, 2H, HC(7)) ; 2.73-2.66 (m, 2H, HC(2)) ; 2.52-2.48 (m, 8H, $H_2C(9)$) ; 2.23-2.19 (m, 4H, $H_aC(8)$); 2.09-1.87 (m, 8H, $H_aC(1)$ and $H_bC(8)$) ; 1.64-1.42 (m, 4H, $H_bC(1)$).

^{13}C NMR (90 MHz, $CDCl_3$) δ_C: 211.4 (C(10)) ; 145.5 (C(3)) ; 142.3 (C(6)) ; 127.0 (C(4)) ; 126.6 (C(5)) ; 44.2 (C(7)) ; 42.3 (C(2)) ; 41.4 (C(9)) ; 34.0 (C(8)) ; 33.7 (C(1)) .

ESI-MS m/z: 429.3 $[M+H]^+$.

Synthesis of 156



156

In a Dean-Stark apparatus, a solution of 6.38 g (11.63 mmol) of **153** and 500 mg (20 mol%, 2.63 mmol) of *p*-TSA·H_2O in 25 ml of ethylene glycol and 250 ml of dry benzene was refluxed for 68 h. The reaction mixture was cooled and 150 ml of a saturated $NaHCO_3$ solution were added. The layers were separated and the aqueous phase was extracted with 2 x 150 ml of CH_2Cl_2. The joined organic phases were dried over Na_2SO_4 and the solvents were evaporated. The crude material was purified by silica gel filtration (eluent: CH_2Cl_2/AcOEt 95:5) to give 5.15 g (10.05 mmol, 86 %) of **156** as a white solid.

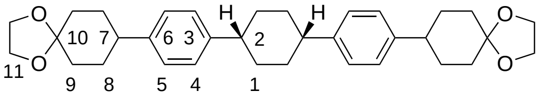
TLC (SiO_2, CH_2Cl_2/AcOEt 95:5): $R_f = 0.53$.

^{1}H NMR (360 MHz, $CDCl_3$) δ_H : 7.32 (d, J = 7.7 Hz, 4H, HC(5)) ; 7.17 (d, J = 8.2 Hz, 4H, HC(4)) ; 5.94 (br, 2H, HC(8)) ; 4.02 (s, 8H, $H_2C(13)$) ; 3.72 - 2.63 (m, 6H, $H_2C(9)$ and HC(2)) ; 2.46 (br, 4H, $H_2C(12$; 2.08 - 1.89 (m, 4H, $H_2C(11)$) ; 1.65 - 1.42 (m, 4H, $H_2C(1)$).

^{13}C NMR (90 MHz, $CDCl_3$) δ_C : 145.9 (C(3)) ; 139.2 (C(6)) ; 136.1 (C(7)) ; 126.6 (C(4)) ; 125.2 (C(5)) ; 120.8 (C(8)) ; 107.8 (C(10)) ; 64.5 (C(13)) ; 44.2 (C(2)) ; 36.1 (C(9)) ; 33.7 (C(1)) ; 31.4 (C(11)) ; 26.8 (C(12)).

ESI-MS *m/z*: 535.3 $[M+Na]^+$.

Synthesis of 157



157

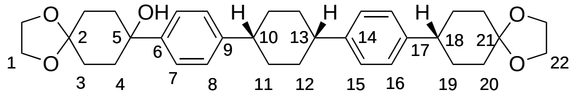
A mixture of 5.15 g (10.05 mmol) of **156** and 515 mg (10 mol%) of 10 % Pd/C in 140 ml of a 1:1 CH_2Cl_2/EtOH mixture was placed under 3 bars of H_2. The reaction mixture was stirred for 2.5 h and filtered by cannula. The residue was washed with 2 x 20 ml of CH_2Cl_2 and the solvents were evaporated, to give 5.18 g (10.05 mmol, 100 %) of **157** as a white solid.

TLC (SiO_2, CH_2Cl_2): $R_f = 0.17$.

^{1}H NMR (360 MHz, $CDCl_3$) δ_H : 7.16 (s, 8H, HC(4,5)) ; 3.98 (br s, 8H, $H_2C(11)$; 2.71-2.67 (m, 2H, HC(1)) ; 2.55-2.48 (m, 2H, HC(7)) ; 2.05-1.41 (m, 24H, $H_2C(1,8,9)$.

^{13}C NMR (50 MHz, $CDCl_3$) δ_C : 145.0 (C(3)) ; 144.0 (C(6)) ; 126.8 (C(4)) ; 126.7 (C(5)) ; 108.6 (C(10)) ; 64.2 (C(11)) ; 44.2 (C(7)) ; 42.9 (C(2)) ; 35.1 (C(8)) ; 33.7 (C(9)) ; 31.6 (C(1)).
ESI-MS m/z: 539.3 $[M+H]^+$.

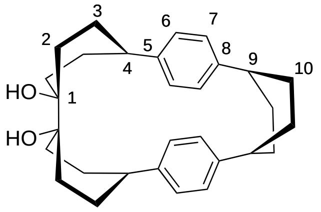
Synthesis of 158



158

Under inert atmosphere, 10 ml of a 50 % water suspension of Raney nickel were added to a solution of 400 mg (0.73 mmol) of **153** in 20 ml of ethanol. The reaction mixture was stirred at room temperature for 3.5 days and 20 ml of CH_2Cl_2 were added. The mixture was filtered via cannula and the nickel slurry was washed with 3 x 20 ml of CH_2Cl_2. The solvents were removed by evaporation and the product was purified by silica gel column chromatography (eluent: CH_2Cl_2/AcOEt 50:50) to give 222 mg (0.42 mmol, 57 %) of **158** as a white solid.
TLC (SiO_2, CH_2Cl_2): $R_f = 0.55$.
^{1}H NMR (500 MHz, $CDCl_3$) δ_H : 7.44 (d, J = 8.5 Hz, 2H, HC(7)) ; 7.44 (d, J = 8.5 Hz, 2H, HC(16)) ; 7.17 (s, 4H, HC(8,15)) ; 4.01-3.95 (m, 8H, H_2C1,22) ; 2.74-2.66 (m, 2H, HC(10,13)) ; 2.56-2.50 (m, 1H, HC(18)) ; 2.19-2.07 (m, 6H) ; 1.99-1.96 (m, 2H) ; 1.86-1.74 (m, 8H) ; 1.71-1.63 (m, 4H) ; 1.61-1.55 (m, 2H) ; 1.52-1.44 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ_C : 146.0 (C(9)) ; 145.9 (C(6)) ; 144.9 (C(14)) ; 144.1 (C(17)) ; 126.8 (C(8)) ; 126.7 (C(15)) ; 126.6 (C(16)) ; 124.5 (C(7)) ; 108.5 (C(21)) ; 108.4 (C(2)) ; 72.2 (C(5)) ; 64.3 (C(1)) ; 64.2 (C(22)) ; 44.1 (C(10,13)) ; 42.9 (C(18)) ; 42.1 ; 36.5 ; 35.1 ; 33.7 ; 31.6 ; 30.7 ; 26.9.
ESI-MS m/z: 555.3 $[M+Na]^+$.

Synthesis of 160



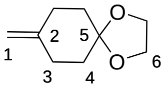
160

Under inert atmosphere, a suspension of 507 mg (3.29 mmol) of $TiCl_3$ and 642 mg (9.86 mmol) of a Zn-Cu couple in 40 ml of a 1:1 dry toluene/dry DME mixture was

heated at 80 °C for 4 hours. The temperature was raised to 85 °C and a solution of 178 mg (0.42 mmol) of **155** in 38 ml of a 1:1 dry toluene/dry DME mixture was added for 27 hours (1.4 ml/h) along the glass wall. The reaction mixture was heated for additional 40 hours and then opened and cooled for 18 hours under stirring. The crude mixture was filtered on a silica gel plug (eluent: THF) and the solvents were evaporated. The residue was fractioned by silica gel column chromatography (eluent: CH_2Cl_2/AcOEt 98.5:1.5, then 50:50; 0:100). ESI-MS of the more polar fraction showed traces of **160**.
ESI-MS m/z : 413.4 $[M\text{-}OH]^+$.

14.5 Metathesis precursor

4-Methylenecyclohexanone ethylene ketal 166

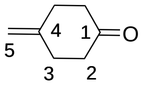


166

Method A: Under inert atmosphere, a mixture of 6.00 g (16.8 mmol) of methyltriphenylphosphonium bromide and 1.01 g (25.2 mmol) of a NaH (60 % suspension in mineral oil) in 35 ml of dry THF was refluxed for 2 hours. The reaction mixture was cooled down and filtered via cannula on a solution of 2.62 g (16.8 mmol) of 1,4-cyclohexanedione monoethylene ketal in 15 ml of dry THF. The reaction mixture was stirred at room temperature for 2 hours, quenched with 50 ml of water and extracted with 3 x 50 ml of Et_2O. The joined organic layers were dried over Na_2SO_4 and the solvents were removed by evaporation. The crude product was purified by silica gel column chromatography (eluent: PE/Et_2O 8:2) to give 1.84 g (11.9 mmol, 71 %) of **166** as a colorless liquid.
Method B:Under inert atmosphere and at 0 °C, 5.0 ml (8.5 mmol) of a 1.7 M *tert*-BuLi solution in pentane were added dropwise to a suspension of 3.00 g (8.4 mmol) of methyltriphenylphosphonium bromide in 20 ml of dry THF. The reaction mixture was stirred for 20 minutes and a solution of 1.31 g (8.4 mmol) of 1,4-cyclohexanedione monoethylene ketal in 10 ml of dry THF was added. The mixture was stirred at room temperature for 2 hours, quenched with 30 ml of water and extracted with 3 x 30 ml of Et_2O. The joined organic layers were dried over Na_2SO_4 and the solvents were removed by evaporation. The crude product was purified by silica gel column chromatography (eluent: PE/Et_2O 8:2) to give 1.18 g (7.7 mmol, 92 %) of **166** as a colorless liquid.
TLC (SiO_2, PE/Et_2O 8:2): $R_f = 0.30$.

^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 4.68 (s, 2H, $H_2C(1)$) ; 3.97 (s, 4H, $H_2C(6)$) ; 2.29 (t, J = 6.3 Hz, 4H, HC(3)) ; 1.71 (t, J = 6.3 Hz, 4H, HC(4)).
^{13}C NMR (50 MHz, $CDCl_3$) δ_C: 147.3 (C(2)) ; 108.5 (C(1)) ; 108.2 (C(5)) ; 64.3 (C(6)) ; 35.8 (C(4)) ; 31.9 (C(3)).
EI-MS m/z (%): 154 (100) $M^{+\bullet}$; 139 (59) ; 125 (70) ; 109 (12) ; 99 (42) ; 86 (35) ; 81 (12) ; 67 (8) ; 55 (5).

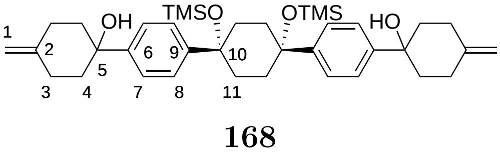
4-Methylenecyclohexanone 167



167

A solution of 1.84 g (11.9 mmol) of **166** in 20 ml of a 2 M HCl aqueous solution and 20 ml of THF was refluxed for 4 hours. The reaction mixture was extracted with 3 x 20 ml of Et_2O. The joined organic layers were dried over Na_2SO_4 and the solvents were carefully removed by evaporation. The crude product was purified by vacuum distillation (56 °C, 15 mmHg) to give 693 mg (6.3 mmol, 53 %) of **167** as a colorless liquid. The product should be stored in the freezer.
^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 4.89 (s, 2H, $H_2C(5)$) ; 2.53 (t, J = 6.8 Hz, 4H, $H_2C(3)$) ; 2.44 (t, J = 6.8 Hz, 4H, $H_2C(2)$).
^{13}C NMR (90 MHz, $CDCl_3$) δ_C: 210.9 (C(1)) ; 144.4 (C(4)) ; 107.8 (C(5)) ; 41.6 (C(2)) ; 33.2 (C(3)).
EI-MS m/z (%): 110.0 (54) $M^{+\bullet}$; 81.9 (54) ; 80.9 (38) ; 68.0 (25) ; 66.9 (100) ; 55.0 (20) ; 54.0 (50) ; 53.0 (35) ; 51.0 (10).

Synthesis of 168



168

Under inert atmosphere and at -78 °C, 1.7 ml (2.8 mmol) of a 1.7 M *tert*-BuLi solution in pentane were added dropwise to a solution of 400 mg (0.7 mmol) of **122** in 10 ml of dry THF. The reaction mixture was stirred at this temperature for 1 h. Then, 178 mg (1.6 mmol) of **167** were added with a syringe and the mixture was stirred at room temperature for 6 days. The reaction mixture was quenched with 10 ml of water and extracted with 3 x 10 ml of Et_2O. The joined organic layers were dried over Na_2SO_4 and the solvents were removed by evaporation. The crude

product was purified by silica gel column chromatography (eluent: CH_2Cl_2/AcOEt 97.5:2.5) to give 342 mg (0.5 mmol, 77 %) of **168** as a white solid.
TLC (SiO_2, CH_2Cl_2/AcOEt 95:5): $R_f = 0.31$.
^{1}H NMR (360 MHz, $CDCl_3$) δ_H: 7.39 (s, 8H, HC(7,8)) ; 4.69 (s, 4H, $H_2C(1)$) ; 2.55 (dt, J = 12.7 Hz, J = 5.0 Hz, 4H, $H_aC(3)$) ; 2.24-1.84 (m, 20H, $H_bC(3)$ and $H_2C(4,11)$) ; 1.54 (s, 2H, OH) ; -0.12 (s, 18H, OTMS).
^{13}C NMR (90 MHz, $CDCl_3$) δ_C: 148.1 (C(2)) ; 147.4 (C(6,9)) ; 126.2 (C(7)) ; 124.1 (C(8)) ; 107.4 (C(1)) ; 74.7 (C(5)) ; 72.8 (C(10)) ; 40.0 (C(11)) ; 35.6 (C(4)) ; 30.6 (C(3)) ; -2.1 (TMS).
ESI-MS m/z : 655.36 $[M+Na]^+$.

Part V

Appendices

Appendix A

Crystallographic data for *trans*-1,4-diphenylcyclohexane

Crystal colour	colourless
Crystal size	0.50 x 0.50 x 0.50 mm
Empirical formula	$C_{18}H_{20}$
Formula weight	236.34 g·mol^{-1}
Crystal system	Monoclinic
Unit cell dimensions	a = 5.5414(7) Å alpha = 90 °
	b = 18.1015(18) Å beta = 109.544(14) °
	c = 7.0492(9) Å gamma = 90 °

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	7856(2)	-206(1)	3188(2)	28(1)
C(2)	8427(2)	610(1)	3764(2)	23(1)
C(3)	11282(2)	708(1)	4966(2)	29(1)
C(4)	7527(2)	1115(1)	1947(2)	23(1)
C(5)	5476(2)	1596(1)	1679(2)	27(1)
C(6)	4645(2)	2063(1)	21(2)	31(1)
C(7)	5861(2)	2059(1)	-1406(2)	30(1)
C(8)	7904(2)	1583(1)	-1166(2)	29(1)
C(9)	8723(2)	1115(1)	490(2)	26(1)
H(1A)	5994	-269	2492	34
H(1B)	8748	-352	2242	34
H(2A)	7447	746	4674	28
H(3A)	12301	595	4086	34
H(3B)	11610	1229	5403	34
H(5A)	4629	1605	2648	32
H(6A)	3240	2386	-134	37
H(7A)	5301	2378	-2538	36
H(8A)	8748	1577	-2138	35
H(9A)	10120	791	634	32

Angles [°]	
C(3)#1-C(1)-C(2)	111.63(9)
C(3)#1-C(1)-H(1A)	109.3
C(2)-C(1)-H(1A)	109.3
C(3)#1-C(1)-H(1B)	109.3
C(2)-C(1)-H(1B)	109.3
H(1A)-C(1)-H(1B)	108.0
C(4)-C(2)-C(3)	112.59(9)
C(4)-C(2)-C(1)	112.04(8)
C(3)-C(2)-C(1)	109.85(9)
C(4)-C(2)-H(2A)	107.4
C(3)-C(2)-H(2A)	107.4
C(1)-C(2)-H(2A)	107.4
C(1)#1-C(3)-C(2)	111.90(9)
C(1)#1-C(3)-H(3A)	109.2
C(2)-C(3)-H(3A)	109.2
C(1)#1-C(3)-H(3B)	109.2
C(2)-C(3)-H(3B)	109.2
H(3A)-C(3)-H(3B)	107.9
C(5)-C(4)-C(9)	117.77(10)
C(5)-C(4)-C(2)	120.93(10)
C(9)-C(4)-C(2)	121.30(10)
C(6)-C(5)-C(4)	121.32(10)
C(6)-C(5)-H(5A)	119.3
C(4)-C(5)-H(5A)	119.3
C(7)-C(6)-C(5)	120.13(11)
C(7)-C(6)-H(6A)	119.9
C(5)-C(6)-H(6A)	119.9
C(6)-C(7)-C(8)	119.40(11)
C(6)-C(7)-H(7A)	120.3
C(8)-C(7)-H(7A)	120.3
C(7)-C(8)-C(9)	120.27(11)
C(7)-C(8)-H(8A)	119.9
C(9)-C(8)-H(8A)	119.9
C(8)-C(9)-C(4)	121.11(10)
C(8)-C(9)-H(9A)	119.4
C(4)-C(9)-H(9A)	119.4

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z+1

Bond lengths [Å]	
C(1)-C(3)#1	1.5271(15)
C(1)-C(2)	1.5360(15)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(4)	1.5154(14)
C(2)-C(3)	1.5347(15)
C(2)-H(2A)	1.0000
C(3)-C(1)#1	1.5271(15)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.3938(15)
C(4)-C(9)	1.3960(16)
C(5)-C(6)	1.3899(16)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.3851(18)
C(6)-H(6A)	0.9500
C(7)-C(8)	1.3868(17)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.3897(16)
C(8)-H(8A)	0.9500
C(9)-H(9A)	0.9500

Torsion-angles [°]	
C(3)#1-C(1)-C(2)-C(4)	-178.80(9)
C(3)#1-C(1)-C(2)-C(3)	55.27(13)
C(4)-C(2)-C(3)-C(1)#1	178.96(9)
C(1)-C(2)-C(3)-C(1)#1	-55.42(13)
C(3)-C(2)-C(4)-C(5)	-124.52(11)
C(1)-C(2)-C(4)-C(5)	111.06(11)
C(3)-C(2)-C(4)-C(9)	55.31(13)
C(1)-C(2)-C(4)-C(9)	-69.11(13)
C(9)-C(4)-C(5)-C(6)	-0.10(16)
C(2)-C(4)-C(5)-C(6)	179.74(10)
C(4)-C(5)-C(6)-C(7)	-0.17(17)
C(5)-C(6)-C(7)-C(8)	0.22(17)
C(6)-C(7)-C(8)-C(9)	0.01(17)
C(7)-C(8)-C(9)-C(4)	-0.28(17)
C(5)-C(4)-C(9)-C(8)	0.33(16)
C(2)-C(4)-C(9)-C(8)	-179.51(9)

#1 -x+2,-y,-z+1

Appendix B

Crystallographic data for 123

Crystal colour	colourless
Crystal size	0.50 x 0.50 x 0.50 mm
Empirical formula	$C_{20}H_{22}Br_2O_2$
Formula weight	454.20 g·mol^{-1}
Crystal system	Orthorhombic
Unit cell dimensions	a = 13.9248(7) Å alpha = 90 °
	b = 13.5045(7) Å beta = 90 °
	c = 20.1106(12) Å gamma = 90 °

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	-5144(1)	4837(1)	6644(1)	36(1)
Br(2)	-4735(1)	5010(1)	880(1)	38(1)
O(1)	-2171(2)	2262(2)	4634(1)	26(1)
O(2)	-1650(2)	2066(2)	2490(1)	28(1)
C(1)	-4466(2)	4273(2)	5914(2)	22(1)
C(2)	-4962(2)	3810(2)	5418(2)	27(1)
C(3)	-4468(2)	3377(2)	4905(2)	23(1)
C(4)	-3473(2)	3394(2)	4882(2)	17(1)
C(5)	-2993(2)	3862(2)	5396(2)	21(1)
C(6)	-3476(2)	4307(2)	5913(2)	23(1)
C(7)	-2878(2)	2909(2)	4332(2)	18(1)
C(8)	-3484(2)	2351(2)	3821(2)	22(1)
C(9)	-2861(2)	1881(2)	3286(2)	23(1)
C(10)	-2274(2)	2657(2)	2904(2)	20(1)
C(11)	-1693(2)	3257(2)	3403(2)	21(1)
C(12)	-2286(2)	3690(2)	3968(2)	20(1)
C(13)	-2923(2)	3270(2)	2444(2)	18(1)
C(14)	-3488(2)	2785(2)	1979(2)	24(1)
C(15)	-4023(2)	3281(2)	1523(2)	26(1)

to be continued...

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Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(16)	-4011(2)	4307(2)	1529(2)	22(1)
C(17)	-3481(2)	4824(2)	1979(1)	21(1)
C(18)	-2927(2)	4297(2)	2432(2)	20(1)
C(19)	-2559(3)	1450(3)	4994(2)	40(1)
C(20)	-998(3)	2602(2)	2086(2)	35(1)
H(2A)	-5644	3785	5430	26(9)
H(3A)	-4812	3056	4558	22(8)
H(5A)	-2311	3875	5392	19(8)
H(6A)	-3136	4635	6258	23(8)
H(8A)	-3859	1826	4046	32(9)
H(8B)	-3942	2816	3610	23(9)
H(9A)	-3271	1509	2971	15(8)
H(9B)	-2415	1405	3497	40(11)
H(11A)	-1371	3806	3165	18(8)
H(11B)	-1187	2827	3593	7(7)
H(12A)	-2724	4200	3788	16(8)
H(12B)	-1851	4017	4290	18(8)
H(14A)	-3500	2081	1978	10(8)
H(15A)	-4400	2933	1206	25(9)
H(17A)	-3487	5527	1983	18(8)
H(18A)	-2544	4652	2742	6(7)
H(19A)	-2767	937	4681	56(13)
H(19B)	-3109	1671	5259	45(11)
H(19C)	-2064	1180	5289	53(12)
H(20A)	-537	2952	2369	68(14)
H(20B)	-1353	3082	1816	48(12)
H(20C)	-654	2143	1794	41(10)

Angles [°]	
C(19)-O(1)-C(7)	114.9(2)
C(20)-O(2)-C(10)	115.6(2)
C(2)-C(1)-C(6)	121.3(3)
C(2)-C(1)-Br(1)	119.7(2)
C(6)-C(1)-Br(1)	118.9(2)
C(1)-C(2)-C(3)	119.4(3)
C(1)-C(2)-H(2A)	120.3
C(3)-C(2)-H(2A)	120.2
C(4)-C(3)-C(2)	121.3(3)
C(4)-C(3)-H(3A)	119.1
C(2)-C(3)-H(3A)	119.6
C(3)-C(4)-C(5)	117.7(3)
C(3)-C(4)-C(7)	123.9(3)
C(5)-C(4)-C(7)	118.4(3)
C(6)-C(5)-C(4)	121.8(3)
C(6)-C(5)-H(5A)	119.1
C(4)-C(5)-H(5A)	119.0
C(5)-C(6)-C(1)	118.4(3)
C(5)-C(6)-H(6A)	120.8
C(1)-C(6)-H(6A)	120.8
O(1)-C(7)-C(4)	108.8(2)
O(1)-C(7)-C(8)	111.1(3)
C(4)-C(7)-C(8)	113.5(3)
O(1)-C(7)-C(12)	104.5(2)
C(4)-C(7)-C(12)	110.1(3)
C(8)-C(7)-C(12)	108.5(3)
C(9)-C(8)-C(7)	111.5(3)
C(9)-C(8)-H(8A)	109.1
C(7)-C(8)-H(8A)	109.7
C(9)-C(8)-H(8B)	109.3
C(7)-C(8)-H(8B)	109.3
H(8A)-C(8)-H(8B)	108.0
C(8)-C(9)-C(10)	111.9(2)
C(8)-C(9)-H(9A)	109.6
C(10)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.0
C(10)-C(9)-H(9B)	108.9
H(9A)-C(9)-H(9B)	107.9
O(2)-C(10)-C(11)	110.8(3)
O(2)-C(10)-C(13)	107.7(3)
C(11)-C(10)-C(13)	115.0(2)
O(2)-C(10)-C(9)	103.4(2)
C(11)-C(10)-C(9)	108.5(3)
C(13)-C(10)-C(9)	110.8(3)
C(10)-C(11)-C(12)	114.1(3)
C(10)-C(11)-H(11A)	108.7
C(12)-C(11)-H(11A)	108.6
C(10)-C(11)-H(11B)	108.7
C(12)-C(11)-H(11B)	108.8
H(11A)-C(11)-H(11B)	107.7
C(11)-C(12)-C(7)	112.7(3)
C(11)-C(12)-H(12A)	109.1
C(7)-C(12)-H(12A)	108.9
C(11)-C(12)-H(12B)	109.1
C(7)-C(12)-H(12B)	109.1
H(12A)-C(12)-H(12B)	107.8
C(18)-C(13)-C(14)	117.3(3)
C(18)-C(13)-C(10)	123.5(3)
C(14)-C(13)-C(10)	119.0(3)
C(15)-C(14)-C(13)	122.2(3)
C(15)-C(14)-H(14A)	118.8
C(13)-C(14)-H(14A)	119.0
C(14)-C(15)-C(16)	118.7(3)
C(14)-C(15)-H(15A)	120.8
C(16)-C(15)-H(15A)	120.5
C(17)-C(16)-C(15)	121.7(3)
C(17)-C(16)-Br(2)	119.2(2)
C(15)-C(16)-Br(2)	119.1(2)
C(16)-C(17)-C(18)	118.4(3)
C(16)-C(17)-H(17A)	120.9
C(18)-C(17)-H(17A)	120.8
C(17)-C(18)-C(13)	121.7(3)
C(17)-C(18)-H(18A)	118.9
C(13)-C(18)-H(18A)	119.4
O(1)-C(19)-H(19A)	109.3
O(1)-C(19)-H(19B)	109.9
H(19A)-C(19)-H(19B)	109.5
O(1)-C(19)-H(19C)	109.3
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(2)-C(20)-H(20A)	109.5
O(2)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(2)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Bond lengths [Å]	
Br(1)-C(1)	1.904(3)
Br(2)-C(16)	1.903(3)
O(1)-C(19)	1.420(4)
O(1)-C(7)	1.450(3)
O(2)-C(20)	1.417(4)
O(2)-C(10)	1.445(4)
C(1)-C(2)	1.364(4)
C(1)-C(6)	1.380(4)
C(2)-C(3)	1.372(4)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.387(4)
C(3)-H(3A)	0.9501
C(4)-C(5)	1.384(4)
C(4)-C(7)	1.529(4)
C(5)-C(6)	1.376(4)
C(5)-H(5A)	0.9500
C(6)-H(6A)	0.9501
C(7)-C(8)	1.528(4)
C(7)-C(12)	1.525(4)
C(8)-C(9)	1.520(4)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9901
C(9)-C(10)	1.536(4)
C(9)-H(9A)	0.9899
C(9)-H(9B)	0.9900
C(10)-C(11)	1.522(4)
C(10)-C(13)	1.536(4)
C(11)-C(12)	1.522(4)
C(11)-H(11A)	0.9899
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(18)	1.387(4)
C(13)-C(14)	1.386(4)
C(14)-C(15)	1.359(5)
C(14)-H(14A)	0.9501
C(15)-C(16)	1.386(4)
C(15)-H(15A)	0.9500
C(16)-C(17)	1.361(4)
C(17)-C(18)	1.388(4)
C(17)-H(17A)	0.9500
C(18)-H(18A)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9801
C(20)-H(20B)	0.9799
C(20)-H(20C)	0.9800

Torsion-angles [°]	
C(6)-C(1)-C(2)-C(3)	-0.5(5)
Br(1)-C(1)-C(2)-C(3)	-177.9(2)
C(1)-C(2)-C(3)-C(4)	0.4(5)
C(2)-C(3)-C(4)-C(5)	0.2(5)
C(2)-C(3)-C(4)-C(7)	178.8(3)
C(3)-C(4)-C(5)-C(6)	-0.6(5)
C(7)-C(4)-C(5)-C(6)	-179.4(3)
C(4)-C(5)-C(6)-C(1)	0.6(5)
C(2)-C(1)-C(6)-C(5)	0.0(4)
Br(1)-C(1)-C(6)-C(5)	177.4(2)
C(19)-O(1)-C(7)-C(4)	63.8(3)
C(19)-O(1)-C(7)-C(8)	-61.9(3)
C(19)-O(1)-C(7)-C(12)	-178.7(3)
C(3)-C(4)-C(7)-O(1)	-127.2(3)
C(5)-C(4)-C(7)-O(1)	51.5(4)
C(3)-C(4)-C(7)-C(8)	-3.0(4)
C(5)-C(4)-C(7)-C(8)	175.7(3)
C(3)-C(4)-C(7)-C(12)	118.9(3)
C(5)-C(4)-C(7)-C(12)	-62.5(4)
O(1)-C(7)-C(8)-C(9)	-56.9(3)
C(4)-C(7)-C(8)-C(9)	-179.9(2)
C(12)-C(7)-C(8)-C(9)	57.4(3)
C(7)-C(8)-C(9)-C(10)	-60.1(4)
C(20)-O(2)-C(10)-C(11)	-62.5(4)
C(20)-O(2)-C(10)-C(13)	64.1(3)
C(20)-O(2)-C(10)-C(9)	-178.5(3)
C(8)-C(9)-C(10)-O(2)	172.8(3)
C(8)-C(9)-C(10)-C(11)	55.1(3)
C(8)-C(9)-C(10)-C(13)	-72.0(3)
O(2)-C(10)-C(11)-C(12)	-165.1(3)
C(13)-C(10)-C(11)-C(12)	72.5(3)
C(9)-C(10)-C(11)-C(12)	-52.2(3)
C(10)-C(11)-C(12)-C(7)	53.8(4)
O(1)-C(7)-C(12)-C(11)	64.7(3)
C(4)-C(7)-C(12)-C(11)	-178.7(3)
C(8)-C(7)-C(12)-C(11)	-53.9(3)
O(2)-C(10)-C(13)-C(18)	-118.3(3)
C(11)-C(10)-C(13)-C(18)	5.8(4)
C(9)-C(10)-C(13)-C(18)	129.3(3)
O(2)-C(10)-C(13)-C(14)	56.7(3)
C(11)-C(10)-C(13)-C(14)	-179.2(3)
C(9)-C(10)-C(13)-C(14)	-55.7(4)
C(18)-C(13)-C(14)-C(15)	0.4(5)
C(10)-C(13)-C(14)-C(15)	-174.9(3)
C(13)-C(14)-C(15)-C(16)	-0.7(5)
C(14)-C(15)-C(16)-C(17)	-0.2(5)
C(14)-C(15)-C(16)-Br(2)	178.5(2)
C(15)-C(16)-C(17)-C(18)	1.3(5)
Br(2)-C(16)-C(17)-C(18)	-177.4(2)
C(16)-C(17)-C(18)-C(13)	-1.7(4)
C(14)-C(13)-C(18)-C(17)	0.9(5)
C(10)-C(13)-C(18)-C(17)	175.9(3)

Appendix C

Crystallographic data for PtI_2(dppp)

Crystal colour	colourless
Crystal size	0.20 x 0.10 x 0.05 mm
Empirical formula	$C_{27}H_{26}I_2P_2Pt$
Formula weight	861.31 g·mol^{-1}
Crystal system	Orthorhombic
Unit cell dimensions	a = 9.5788(14) Å alpha = 90 °
	b = 20.955(4) Å beta = 103.973(11) °
	c = 13.4323(19) Å gamma = 90 °

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	1360(20)	177(10)	2817(15)	47(2)
C(2)	150(20)	256(10)	2061(15)	47(2)
C(3)	-820(20)	-256(10)	1724(15)	47(2)
C(4)	-510(20)	-837(10)	2232(15)	47(2)
C(5)	650(20)	-926(10)	2954(15)	47(2)
C(6)	1680(20)	-424(9)	3285(15)	47(2)
C(7)	4388(19)	597(9)	3363(15)	43(2)
C(8)	4734(19)	48(9)	2881(15)	43(2)
C(9)	6213(19)	-81(9)	2957(14)	43(2)
C(10)	7290(20)	296(9)	3466(14)	43(2)
C(11)	6907(19)	840(9)	3928(14)	43(2)
C(12)	5471(19)	992(9)	3897(15)	43(2)
C(13)	2580(20)	841(10)	4646(14)	46(3)
C(14)	1200(20)	1113(9)	4884(15)	46(3)
C(15)	1220(20)	1835(9)	4849(14)	46(3)
C(16)	1520(20)	3007(9)	3923(15)	45(2)
C(17)	2990(20)	3080(9)	4253(14)	45(2)
C(18)	3630(20)	3660(9)	4560(14)	45(2)
C(19)	2740(20)	4190(10)	4532(14)	45(2)

to be continued...

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Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(20)	1270(20)	4141(10)	4212(14)	45(2)
C(21)	640(20)	3538(9)	3909(14)	45(2)
C(22)	-1062(17)	2215(9)	3128(14)	39(2)
C(23)	-1835(17)	2499(9)	3816(14)	39(2)
C(24)	-3359(17)	2519(9)	3453(14)	39(2)
C(25)	-4001(18)	2281(9)	2504(14)	39(2)
C(26)	-3236(17)	2009(8)	1887(15)	39(2)
C(27)	-1755(18)	1968(9)	2205(14)	39(2)
P(1)	2553(5)	837(3)	3300(4)	38(1)
P(2)	891(5)	2200(2)	3582(4)	37(1)
Pt(1)	1897(1)	1735(1)	2415(1)	34(1)
I(1)	1215(1)	2786(1)	1296(1)	51(1)
I(2)	2867(1)	1203(1)	909(1)	48(1)
H(2A)	-44	655	1754	57
H(3A)	-1632	-204	1187	57
H(4A)	-1161	-1172	2049	57
H(5A)	817	-1324	3263	57
H(6A)	2520	-493	3789	57
H(8A)	4019	-224	2524	52
H(9A)	6450	-445	2638	52
H(10A)	8247	196	3506	52
H(11A)	7630	1113	4271	52
H(12A)	5250	1353	4231	52
H(13A)	2724	407	4905	55
H(13B)	3399	1092	5009	55
H(14A)	363	955	4384	55
H(14B)	1129	973	5559	55
H(15A)	2154	1979	5245	55
H(15B)	505	1995	5188	55
H(17A)	3576	2724	4269	54
H(18A)	4627	3698	4778	54
H(19A)	3147	4586	4734	54
H(20A)	693	4500	4194	54
H(21A)	-358	3496	3704	54
H(23A)	-1366	2658	4455	47
H(24A)	-3919	2695	3861	47
H(25A)	-4996	2306	2275	47
H(26A)	-3710	1851	1248	47
H(27A)	-1234	1772	1789	47

Angles [$^\circ$]	
C(2)-C(1)-C(6)	120(2)
C(2)-C(1)-P(1)	121.7(17)
C(6)-C(1)-P(1)	118.3(16)
C(1)-C(2)-C(3)	122(2)
C(4)-C(3)-C(2)	117(2)
C(5)-C(4)-C(3)	122(2)
C(4)-C(5)-C(6)	122(2)
C(1)-C(6)-C(5)	117(2)
C(12)-C(7)-C(8)	120.0(16)
C(12)-C(7)-P(1)	117.1(14)
C(8)-C(7)-P(1)	122.8(15)
C(7)-C(8)-C(9)	117.8(19)
C(10)-C(9)-C(8)	123.5(18)
C(9)-C(10)-C(11)	117.2(17)
C(10)-C(11)-C(12)	122.4(19)
C(7)-C(12)-C(11)	119.1(18)
C(14)-C(13)-P(1)	113.7(14)
C(15)-C(14)-C(13)	110.0(14)
C(14)-C(15)-P(2)	116.6(14)
C(17)-C(16)-C(21)	119.0(18)
C(17)-C(16)-P(2)	115.8(15)
C(21)-C(16)-P(2)	125.2(15)
C(18)-C(17)-C(16)	122.7(19)
C(17)-C(18)-C(19)	117.8(19)
C(20)-C(19)-C(18)	121.7(19)
C(19)-C(20)-C(21)	119.4(19)
C(16)-C(21)-C(20)	119.5(18)
C(27)-C(22)-C(23)	121.8(16)
C(27)-C(22)-P(2)	122.3(12)
C(23)-C(22)-P(2)	115.9(14)
C(24)-C(23)-C(22)	115.8(17)
C(25)-C(24)-C(23)	120.0(15)
C(26)-C(25)-C(24)	122.4(16)
C(25)-C(26)-C(27)	120.1(19)
C(22)-C(27)-C(26)	119.8(16)
C(13)-P(1)-C(1)	102.7(9)
C(13)-P(1)-C(7)	100.0(9)
C(1)-P(1)-C(7)	109.0(9)
C(13)-P(1)-Pt(1)	117.7(7)
C(1)-P(1)-Pt(1)	112.4(7)
C(7)-P(1)-Pt(1)	113.8(6)
C(16)-P(2)-C(15)	100.5(9)
C(16)-P(2)-C(22)	108.6(9)
C(15)-P(2)-C(22)	104.6(8)
C(16)-P(2)-Pt(1)	114.0(6)
C(15)-P(2)-Pt(1)	117.5(6)
C(22)-P(2)-Pt(1)	110.6(6)
P(1)-Pt(1)-P(2)	96.12(17)
P(1)-Pt(1)-I(1)	176.80(11)
P(2)-Pt(1)-I(1)	86.97(14)
P(1)-Pt(1)-I(2)	86.96(12)
P(2)-Pt(1)-I(2)	174.86(14)
I(1)-Pt(1)-I(2)	90.01(5)

to be continued...

...continued from previous column

Bond lengths [Å]	
C(1)-C(2)	1.35(3)
C(1)-C(6)	1.41(3)
C(1)-P(1)	1.81(2)
C(2)-C(3)	1.42(3)
C(3)-C(4)	1.39(3)
C(4)-C(5)	1.30(3)
C(5)-C(6)	1.44(3)
C(7)-C(12)	1.38(3)
C(7)-C(8)	1.40(2)
C(7)-P(1)	1.811(17)
C(8)-C(9)	1.42(2)
C(9)-C(10)	1.35(3)
C(10)-C(11)	1.39(3)
C(11)-C(12)	1.40(2)
C(13)-C(14)	1.55(2)
C(13)-P(1)	1.802(18)
C(14)-C(15)	1.51(3)
C(15)-P(2)	1.822(18)
C(16)-C(17)	1.38(3)
C(16)-C(21)	1.39(3)
C(16)-P(2)	1.817(19)
C(17)-C(18)	1.38(2)
C(18)-C(19)	1.40(3)
C(19)-C(20)	1.37(3)
C(20)-C(21)	1.42(3)
C(22)-C(27)	1.36(3)
C(22)-C(23)	1.44(2)
C(22)-P(2)	1.822(17)
C(23)-C(24)	1.42(2)
C(24)-C(25)	1.37(2)
C(25)-C(26)	1.36(2)
C(26)-C(27)	1.38(2)
P(1)-Pt(1)	2.233(5)
P(2)-Pt(1)	2.251(4)
Pt(1)-I(1)	2.6571(16)
Pt(1)-I(2)	2.6644(13)

Torsion-angles [°]	
C(6)-C(1)-C(2)-C(3)	0(2)
P(1)-C(1)-C(2)-C(3)	-176.3(12)
C(1)-C(2)-C(3)-C(4)	3(2)
C(2)-C(3)-C(4)-C(5)	-3(2)
C(3)-C(4)-C(5)-C(6)	1(3)
C(2)-C(1)-C(6)-C(5)	-2(2)
P(1)-C(1)-C(6)-C(5)	174.3(12)
C(4)-C(5)-C(6)-C(1)	2(2)
C(12)-C(7)-C(8)-C(9)	0(3)
P(1)-C(7)-C(8)-C(9)	178.0(13)
C(7)-C(8)-C(9)-C(10)	0(3)
C(8)-C(9)-C(10)-C(11)	-1(3)
C(9)-C(10)-C(11)-C(12)	1(3)
C(8)-C(7)-C(12)-C(11)	1(3)
P(1)-C(7)-C(12)-C(11)	-177.2(13)
C(10)-C(11)-C(12)-C(7)	-2(3)
P(1)-C(13)-C(14)-C(15)	-78.8(19)
C(13)-C(14)-C(15)-P(2)	74.3(19)
C(21)-C(16)-C(17)-C(18)	-1(3)
P(2)-C(16)-C(17)-C(18)	-178.6(14)
C(16)-C(17)-C(18)-C(19)	0(3)
C(17)-C(18)-C(19)-C(20)	0(3)
C(18)-C(19)-C(20)-C(21)	0(3)
C(17)-C(16)-C(21)-C(20)	1(3)
P(2)-C(16)-C(21)-C(20)	178.9(14)
C(19)-C(20)-C(21)-C(16)	-1(3)
C(27)-C(22)-C(23)-C(24)	-2(3)
P(2)-C(22)-C(23)-C(24)	179.1(13)
C(22)-C(23)-C(24)-C(25)	0(3)
C(23)-C(24)-C(25)-C(26)	1(3)
C(24)-C(25)-C(26)-C(27)	0(3)
C(23)-C(22)-C(27)-C(26)	3(3)
P(2)-C(22)-C(27)-C(26)	-178.2(14)
C(25)-C(26)-C(27)-C(22)	-2(3)
C(14)-C(13)-P(1)-C(1)	-75.1(16)
C(14)-C(13)-P(1)-C(7)	172.7(14)
C(14)-C(13)-P(1)-Pt(1)	48.9(16)
C(2)-C(1)-P(1)-C(13)	122.1(15)
C(6)-C(1)-P(1)-C(13)	-54.5(15)
C(2)-C(1)-P(1)-C(7)	-132.5(14)
C(6)-C(1)-P(1)-C(7)	50.9(15)
C(2)-C(1)-P(1)-Pt(1)	-5.4(16)
C(6)-C(1)-P(1)-Pt(1)	178.1(11)
to be continued...	

...continued from previous column	
Torsion-angles [°]	
C(12)-C(7)-P(1)-C(13)	-60.5(17)
C(8)-C(7)-P(1)-C(13)	120.9(16)
C(12)-C(7)-P(1)-C(1)	-167.8(15)
C(8)-C(7)-P(1)-C(1)	13.7(18)
C(12)-C(7)-P(1)-Pt(1)	65.9(16)
C(8)-C(7)-P(1)-Pt(1)	-112.6(15)
C(17)-C(16)-P(2)-C(15)	72.5(15)
C(21)-C(16)-P(2)-C(15)	-105.1(17)
C(17)-C(16)-P(2)-C(22)	-178.0(14)
C(21)-C(16)-P(2)-C(22)	4.4(18)
C(17)-C(16)-P(2)-Pt(1)	-54.2(16)
C(21)-C(16)-P(2)-Pt(1)	128.2(14)
C(14)-C(15)-P(2)-C(16)	-164.5(13)
C(14)-C(15)-P(2)-C(22)	82.9(14)
C(14)-C(15)-P(2)-Pt(1)	-40.2(15)
C(27)-C(22)-P(2)-C(16)	126.2(16)
C(23)-C(22)-P(2)-C(16)	-54.6(15)
C(27)-C(22)-P(2)-C(15)	-127.1(16)
C(23)-C(22)-P(2)-C(15)	52.1(16)
C(27)-C(22)-P(2)-Pt(1)	0.4(18)
C(23)-C(22)-P(2)-Pt(1)	179.6(12)
C(13)-P(1)-Pt(1)-P(2)	-16.3(7)
C(1)-P(1)-Pt(1)-P(2)	102.7(6)
C(7)-P(1)-Pt(1)-P(2)	-132.8(8)
C(13)-P(1)-Pt(1)-I(1)	148(2)
C(1)-P(1)-Pt(1)-I(1)	-93(3)
C(7)-P(1)-Pt(1)-I(1)	32(3)
C(13)-P(1)-Pt(1)-I(2)	167.8(7)
C(1)-P(1)-Pt(1)-I(2)	-73.2(6)
C(7)-P(1)-Pt(1)-I(2)	51.3(7)
C(16)-P(2)-Pt(1)-P(1)	129.2(8)
C(15)-P(2)-Pt(1)-P(1)	11.9(8)
C(22)-P(2)-Pt(1)-P(1)	-108.1(7)
C(16)-P(2)-Pt(1)-I(1)	-50.0(8)
C(15)-P(2)-Pt(1)-I(1)	-167.2(8)
C(22)-P(2)-Pt(1)-I(1)	72.7(6)
C(16)-P(2)-Pt(1)-I(2)	-104.2(16)
C(15)-P(2)-Pt(1)-I(2)	138.6(15)
C(22)-P(2)-Pt(1)-I(2)	18.5(18)

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Curriculum Vitae

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EDUCATION

PhD in organic chemistry, "*Towards [0_n]Paracyclophanes as Templates for the Synthesis of Nanotubes*", done in the research group of Prof. Dr. Titus A. Jenny, University of Fribourg, Switzerland — Since 2003

Chemistry diploma, "*Activité Optique induite par un Ferrocène 1,3-Disubstitué : Premier Dendrimère Mésomorphe contenant une Chiralité Planaire*", done in the research group of Prof. Dr. Robert Deschenaux, University of Neuchâtel, Switzerland — 1998-2003

Federal maturity, type C (scientific), Gymnase Cantonal de Neuchâtel, Switzerland — 1994-1998

PROFESSIONAL EXPERIENCE

Assistant of chemistry, University of Fribourg, Switzerland — Since 2003

- "*Synthesis of retinoic acid derivatives*", project undergone for Helsinn Advanced Synthesis SA
- Supervisor for advanced practical work and Master thesis in organic chemistry
- Supervisor for the instrumental analysis and organic chemistry laboratory sessions for undergraduate students
- In charge of the new academic program (Bologna) for the instrumental analysis student's laboratory
- In charge of the quality analysis and the maintenance of the solvent purification system

Assistant of chemistry, University of Neuchâtel, Switzerland 2000-2002

- Preparation and maintenance of the student's laboratory equipment

Trainee in glue development, Asulab SA, Marin, Switzerland 2001

- Synthesis of monomers used in epoxy resin

Operator in microelectronics, EM Microelectronique-Marin SA, Marin, Switzerland Summer 1999

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- Photolithography
- Plating and galvanic baths
- Optical microscopy control

ADDITIONAL EXPERIENCE

Chief of ABC protection, Organisation de la Protection Civile du Littoral Centre, Neuchâtel since 2006

- Course for ABC protection officers, The Federal Office for Civil Protection, Spiez

Workshop "*Young Entrepreneur*", IVE Institute, Fribourg, Switzerland 2006

- First prize award for best business plan, sponsored by Credit Suisse SA

Assistant in a marketing department, Kelly Services (Suisse) SA, Neuchâtel, Switzerland 2001-2003

- Data treatment and statistical analysis

LANGUAGES AND COMPUTER KNOWLEDGE

French (mother tongue), English (good knowledge), German (basic)

Word, Excel, PowerPoint, LaTeX, ACDlabs, OpenOffice and ChemDraw