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Studies towards the Synthesis of Bridged Fullerenes

Masterarbeit

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(Institut für Organische Chemie)

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“Maximus honor almae matri decet,

quia lucem in obscuritatem mentis generis humani apportat.”

Die vorliegende Arbeit wurde unter der Betreuung von Prof. Dr. Rolf Breinbauer in der Zeit von März 2014 bis November 2014 im Fachbereich Chemie am Institut für Organische Chemie der Technischen Universität Graz angefertigt.

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1. Introduction

Evolution taught humanity, that survival will be much easier, if people are smarter than animals in wild nature. This is the reason why people lived in groups, learned to make fire and made tools. Humans acquired their knowledge about their enemies in nature and became the dominant species on earth.

Few centuries ago different sciences separated from each other and natural science was born. At this time scientists explored properties and processes, which people nowadays sense as natural, for example gravity. Furthermore, physics bothered with state-properties and alchemy tried to convert several materials into gold. Various experiments with the purpose to establish gold failed, but other things were discovered this way.

Many inventions and achievements are due to the childish curiosity of scientists. These individuals have the ambition to acquire more knowledge about state and activity. A wise man, ALFRED NOBEL, created a price to honour humans, who achieved a great gain for humanity. The biggest honour for scientists is to be awarded the 'NOBEL PRICE'. To be rewarded for one's work is a further goal for everyone.

During the decades many different intelligent people contributed their knowledge to the common knowledge of mankind. But there is still a lot to do for all people with an inquisitive mind. This is the reason why thousands of men and women work in research-groups all over the world. This work attends to basic research in terms of chemistry and continuing to physics. We would like to place a further piece of a puzzle into the existing work of humanity. In fact, the goal of this work is to produce a non-existing molecule, which could have special physical properties, which could be processed on industrial scale for special applications.

2. Theory

2.1. Fullerenes

Fullerenes **1** are molecules, which only consist of carbon-atoms, like graphite or diamonds. All of the different fullerene molecules consist of carbon pentagons and hexagons, which are connected to each other to form three dimensional closed compounds. The nomenclature of fullerenes describes which atoms and how many of them are involved in this molecule, for example C_{60} fullerenes consist of 60 carbon atoms (Figure 1). Because of the high symmetry of the C_{60} fullerenes these molecules are named after the American architect BUCKMINSTER FULLER. In 1966 D. E. H. JONES was the first person, who predicted, the existence of convolute graphite-layers. Approximately 20 years later, H. W. KROTO *et al.* produced tiny amounts of C_{60}-fullerenes for the first time. In 1990 W. KRÄTSCHMER and F. FOSTIROPOLOUS made C_{60}-fullerenes out of graphite in ponderable amounts. In 1996 R. F. CURL, H. W. KROTO and R. M. SMALLEY were awarded for the NOBEL PRICE for the isolation of $C_{60,}$ C_{70}, C_{76}, C_{78} and C_{84} fullerenes.[1]

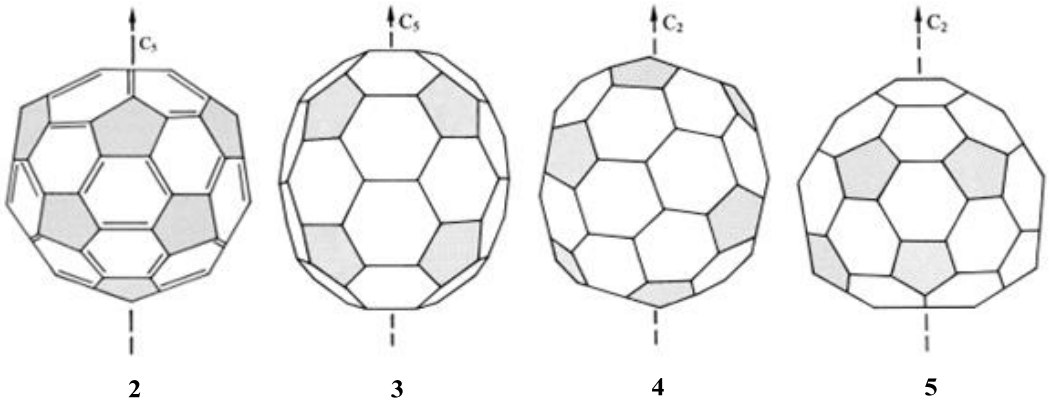


Figure 1: BUCKMINSTER-fullerene (**2**), D_{5h}-C_{70}-fullerene (**3**), D_2-C_{76}-fullerene (**4**), C_{2v}-C_{78}-fullerene (**5**), picture taken from[1]

To connect two five-membered aromatic systems along a common edge is thermodynamically disfavoured. Therefore, in fullerene molecules every pentagonal unit is surrounded by hexagonal units (isolated pentagon rule). The smallest fullerene molecule, which complies this rule, is the BUCKMINSTER fullerene C_{60} (**2**). All of the classic fullerenes consist of

pentagonal and hexagonal units. Instead of classic fullerenes the non-classic fullerenes are built up by tetragonal and heptagonal units.[1]

Like other unsaturated and conjugated systems fullerenes also show π-electron-delocalisation, but the distinctive feature of these molecules is, that this electron-delocalisation is not planar (three dimensional aromaticity). Annulenes are aromatic systems, if they obey the HÜCKEL-rules. Such molecules have to exhibit $(4n + 2)$ π-electrons. In contrast fullerenes are aromatic, if they own $2(n + 1)^2$ π-electrons. The BUCKMINSTER fullerene (**2**) possesses 30 π-bonds, therefore it has 60 molecular orbitals consisting of 30 bonding and 30 antibonding orbitals. These 30 bonding orbitals are filled with 60 electrons. The energy-difference between the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) is approximately 2 eV. The BUCKMINSTER fullerenes have five energetic identically HOMOs and three energetic identically LUMOs (Figure 2).[1]

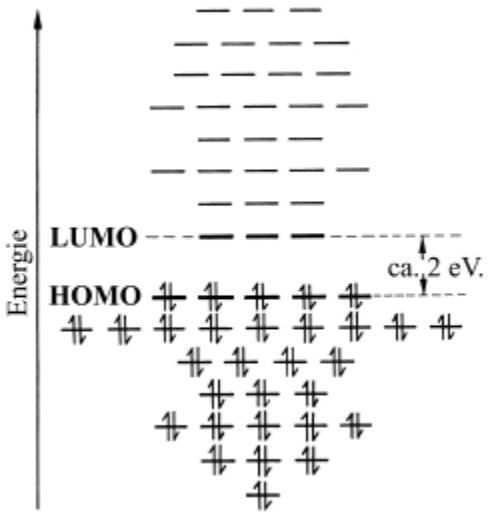
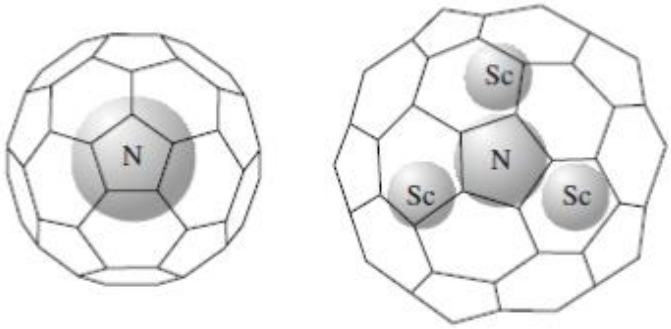


Figure 2: Molecular orbital schema of BUCKMINSTER-fullerene (**2**), picture taken from[1]

In solution the π-electron systems of fullerene molecules **1** interact with π-electron systems of solvent molecules (e. g. benzene, or toluene). These π-π* interactions are the reason why solutions of fullerenes are very colorful. The color of the solution depends on which type of fullerene molecule interacts. The solution of BUCKMINSTER fullerenes (**2**) is violet, C_{76} (**4**) otherwise is greenish using toluene as solvent. A further specific feature of fullerenes is, that they can enclose one or more atoms in their cage. Such molecules are called endohedral fullerene complexes. In most cases metal ions are captured in the carbon cage, but in some cases gases, especially nobel gases are encapsulated. A @-symbol advises in elemental

formula, that an endohedral fullerene complex is existent (e. g. $N@C_{60}$ (**6**), $Sc_3N@C_{80}$ (**7**)) (Figure 3). [1]



6 **7**

Figure 3: $N@C_{60}$ (**6**), $Sc_3N@C_{80}$ (**7**), picture taken from [1]

2.1.1. Reactions with fullerenes

2.1.1.1. Hydrogenation of fullerenes

Hydrides of fullerene are produced by reaction of fullerenes with nascent hydrogen (BIRCH reduction) or with a 120-fold excess of dihydroanthracene at 350 °C. In this reaction a mixture of reduced fullerenes are generated (from $C_{60}H_{18}$ to $C_{60}H_{36}$). In the fullerenehydride molecule $C_{60}H_{36}$ all of the double bounds, which are involved in twelve pentagonal units are reduced. Another way to produce fullerenehydrides is by diimide reduction. [1]

2.1.1.2. Halogenated fullerene compounds

If fullerene molecules are subjected to gaseous fluorine, a mixture of fluorinated fullerenes from $C_{60}F_2$ to $C_{60}F_{48}$ (**8**) is generated. Further fluorination of $C_{60}F_{48}$ does not lead to $C_{60}F_{60}$. In this case the cage of the fullerene compound will break up. In the $C_{60}F_{48}$ molecule all double bonds are fluorinated except one double bond of six pentagonal units. Analogous chlorinated and brominated fullerene compounds could be generated (Figure 4).[1]

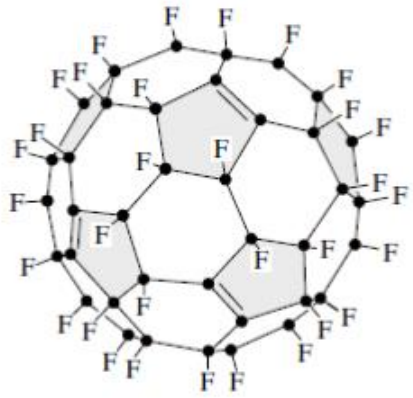


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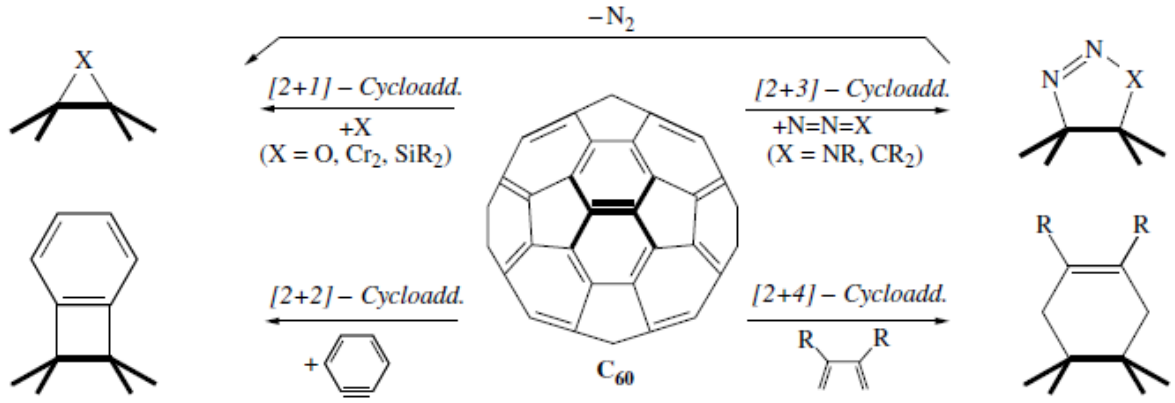
Figure 4: $C_{60}F_{48}$ (**8**), picture taken from [1]

2.1.1.3. Oxygenated fullerene compounds

$C_{60}O$ is generated, if fullerene is exposed to UV-radiation in oxygen containing benzene. In these $C_{60}O$ molecules the oxygen atom bridges two hexagonal units over their common edge like an epoxide. Fullereneacids ($C_{60}(OH)_{24}$, $C_{60}(OH)_{25}$, $C_{60}(OH)_{26}$) are produced by reactions with a fullerene benzene solution and caustic soda with traces of $Bu_4N^+OH^-$. Another option to generate fullerene acids is by hydroboration. A further special feature of fullerenes is, that they catalyze the transformation of triplett oxygen to singlet oxygen.[1]

2.1.1.4. Cycloaddition products of fullerenes

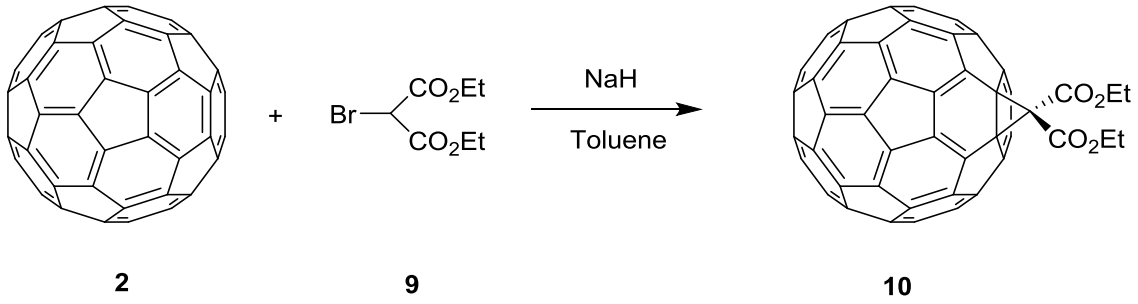
Fullerenes usually act as an *En* in pericyclic reactions. They can undergo [*2+1*], [*2+2*], [*2+3*], [*2+4*], [*2+6*] or [*2+8*] cycloaddition, but the [*2+4*] cycloaddition or DIELS-ALDER reaction is the most explored one of those, which are mentioned before.[1-3] In such reactions the double bond along the common edge of hexagonal units reacts with an appropriate reactant, e. g. carbenes, arynes, or dienes (Scheme 1).



Scheme 1: Cycloadditions of fullerenes **1**, picture taken from [1]

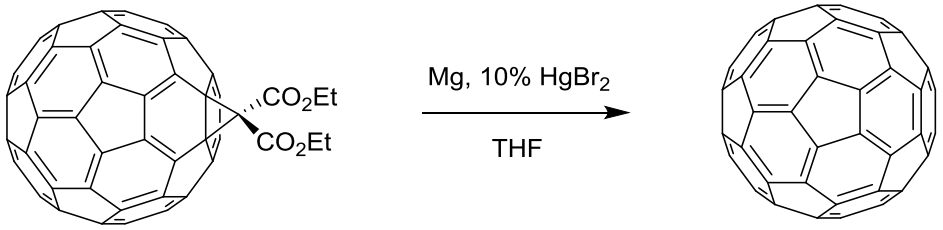
2.1.1.4.1. [*2+1*]- Cycloadditions of fullerenes

One of the first reactions to modify fullerenes was a cyclopropanation or [*2+1*]-cycloaddition, which was explored by BINGEL. In this reaction a carbon nucleophile, which also has a leaving group (e. g. diethyl bromomalonate (**9**), or ω-chloroacetophenone) does the cyclopropanation with fullerene (Scheme 2). Such a cycloaddition could happen more than once on the surface of a fullerene molecule.[4,5] The bis(alkoxycarbonyl)methano group can also be seen as a protecting group for fullerene molecules. The removal of the protecting groups is performed by electrochemical means. The best way to remove BINGEL adducts is obtained by amalgamation of Mg powder with 10% $HgBr_2$ in THF as solvent (Scheme 3).[6]



2 **9** **10**

Scheme 2: Cyclopropanation of diethyl bromomalonate (**9**) with C_{60} (**2**)[4]

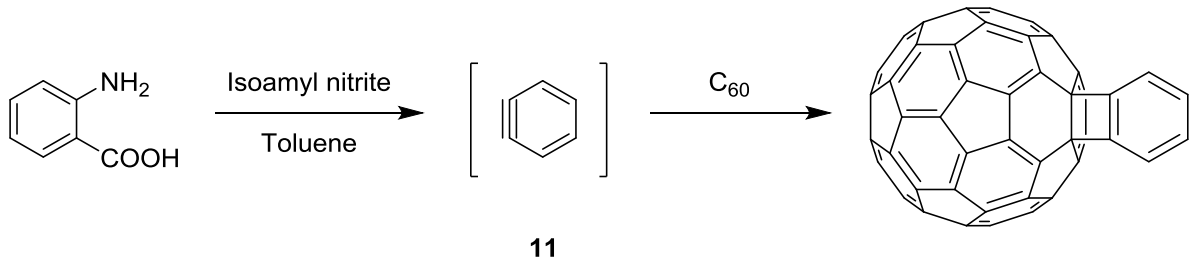


10 **2**

Scheme 3: Retro BINGEL reaction of bis(diethoxycarbonyl)methanofullerene (**10**)[6]

2.1.1.4.2. [*2+2*]- Cycloadditions of fullerenes

The reaction of C_{60}-fullerenes (**2**) with benzyne (**11**) does not lead to a DIELS-ALDER cycloadduct as expected but to a [*2+2*]-cycloaddition product (Scheme 4). The DIELS-ALDER product is energetically disfavoured, because the double bond of a common edge of a pentagonal and hexagonal unit has to react. The [*2+2*]-cycloaddition can occur more than once on the surface of a fullerene molecule, like a BINGEL reaction.[7-9]

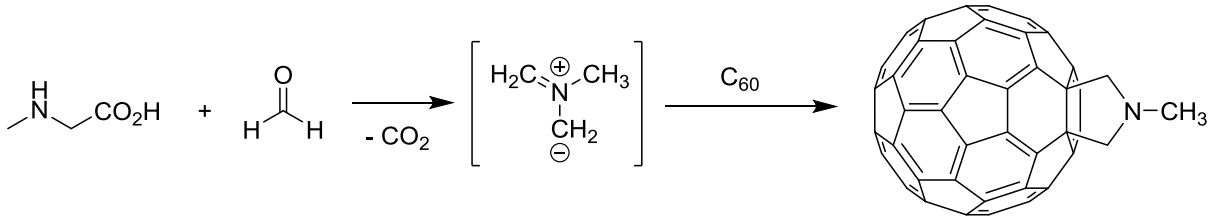


11

Scheme 4: [*2+2*]-Cycloaddition of C_{60} (**2**) and benzyne (**11**)[8]

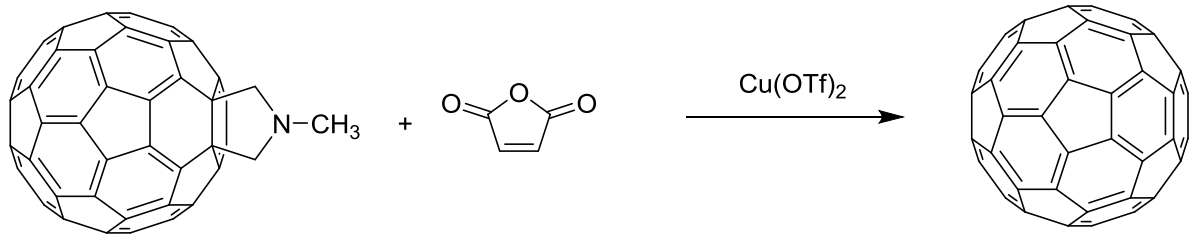
2.1.1.4.3. [*3+2*]- Cycloadditions of fullerenes

In 1993 M. PRATO developed another method to modify fullerenes **1**. In this reaction 1,3-dipoles react in a cycloaddition. The first reaction was performed with azomethine ylides (**12**). These azomethine ylide-intermediates can be formed in several different ways. An easy way to generate such an intermediate is by decarboxylation. The cycloaddition products, which are formed in these reactions, are substituted pyrrolidines (Scheme 5). The pyrrolidinofullerenes **13** are very stable cycloadducts, but it is possible to reverse these [*3+2*]-cycloadditions. The retro-cycloaddition is catalyzed by a LEWIS-acid (copper(II)triflate). An excess of maleic anhydride (**14**) traps the generated ylides, which are produced in the retro-PRATO-reaction (Scheme 6).[11-13]



12 **13**

Scheme 5: PRATO-reaction with BUCKMINSTER-fullerene (**2**)[11]



13 **14** **2**

Scheme 6: Retro-PRATO-reaction of pyrrolidinofullerene **13**[12]

2.1.1.4.4. [*4+2*]- Cycloadditions of fullerenes

The classic DIELS-ALDER reaction works in fullerene chemistry as well as in traditional chemistry. Therefore the HOMO of the diene interacts with the LUMO of the ene, generates an aromatic transition state and forms a ring. The smaller the gap between HOMO and LUMO is, the easier both reactants interact (Figure 5). One advantage of the DIELS-ALDER reaction with fullerene is, that the BUCKMINSTER-fullerene (**2**) itself has an energetically low

lying LUMO. The [*4+2*]-cycloaddition is a powerful method to introduce diverse functionalities on the surface of fullerenes (e. g. nitrile, esters, nitro groups) (Scheme 7).[14]

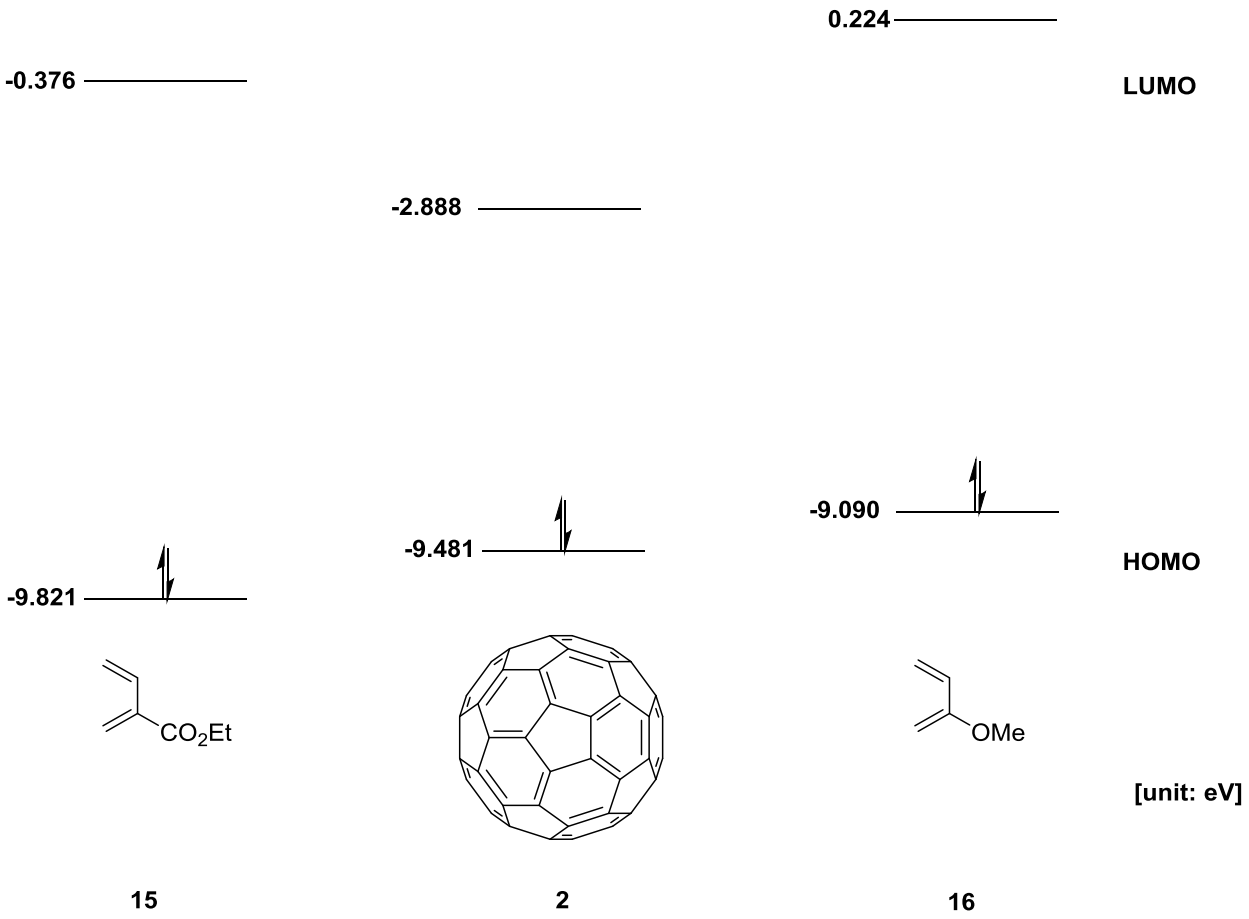
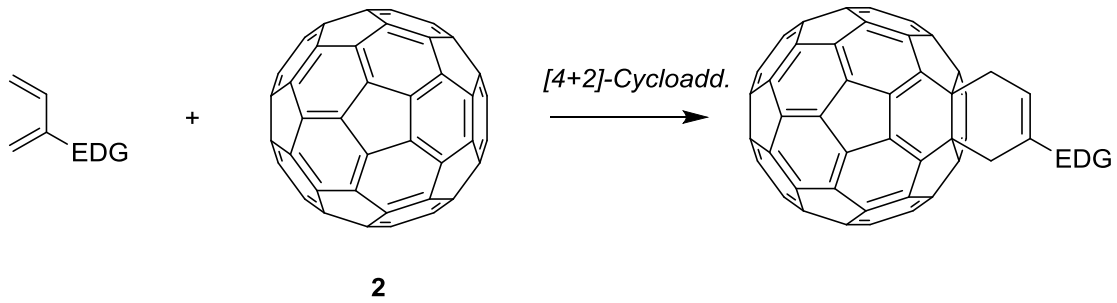


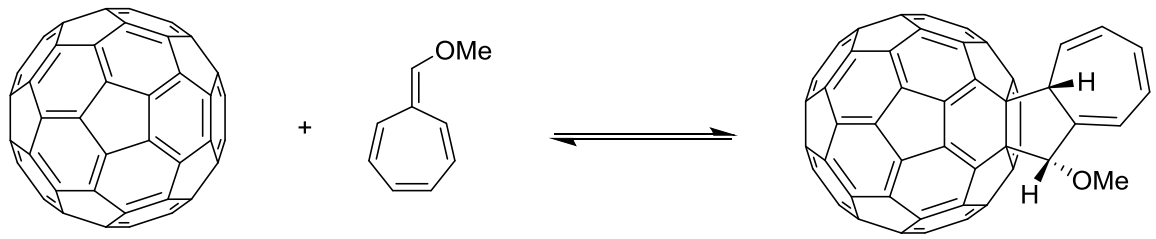
Figure 5: HOMOs and LUMOs of 2-ethoxycarbonyl-1,3-butadiene (**15**), C_{60} (**2**) and 2-methoxy-1,3-butadiene (**16**)[14]



Scheme 7: DIELS-ALDER reaction with C_{60} (**2**)[14]

3.1.1.5.1. [*8+2*]- Cycloaddition of fullerene

One unusual cycloaddition of fullerenes is the [*8+2*]-cycloaddition. In this specific reaction 8-methoxyheptafulvene (**17**) reacts with C_{60}-fullerene (**2**) to a tetrahydroazulene-cycloadduct **18** (Scheme 8). This product is instable at r.t. and does the retro-cycloaddition at these conditions.[15]



2 **17** **18**

Scheme 8: [*8+2*]-Cycloaddition of BUCKMINSTER-fullerene (**2**) and 8-methoxyheptafulvene (**17**) to tetrahydroazulenofullerene (**18**)[15]

2.1.2. Fullerenes in Organometallic Chemistry

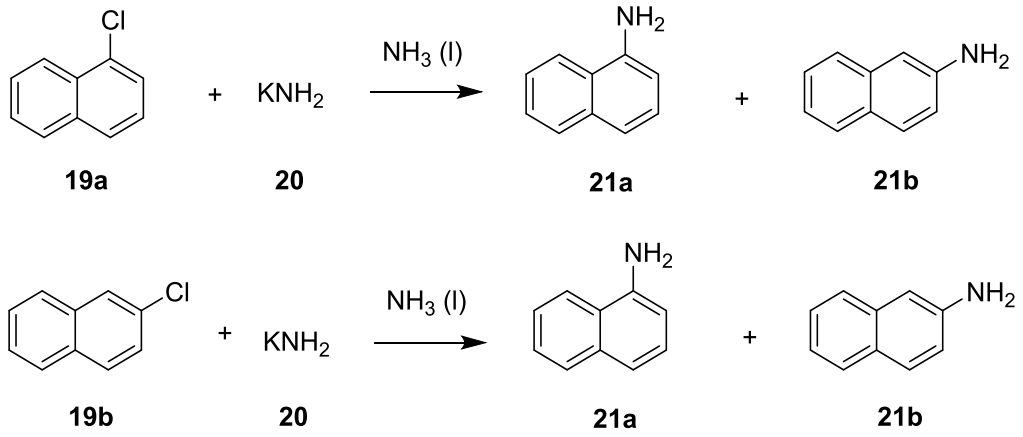
Fullerenes **1** are sometimes used as ligands in Organometallic Chemistry because of their large delocated π-electronsystem and enormous sterical hindrance. Several fullerene complexes are known today. One of the first metalcomplexes with fullerene as ligand was [η^2, η^2, η^2, η^2, η^2, η^2,-C_{60}{$Pt(PEt_3)_2$}$_6$]. Again all of the ligands bind *side-on* (η^2) at the double bond of the common edge of two hexagonal units. The same complex can be formed with palladium or nickel as metal atoms. In this complex the six metal compounds are arranged to form an octahedral complex. Furthermore, some other complexes with rhenium, osmium and iridium are known.[1]

2.2. Aryne-Intermediates

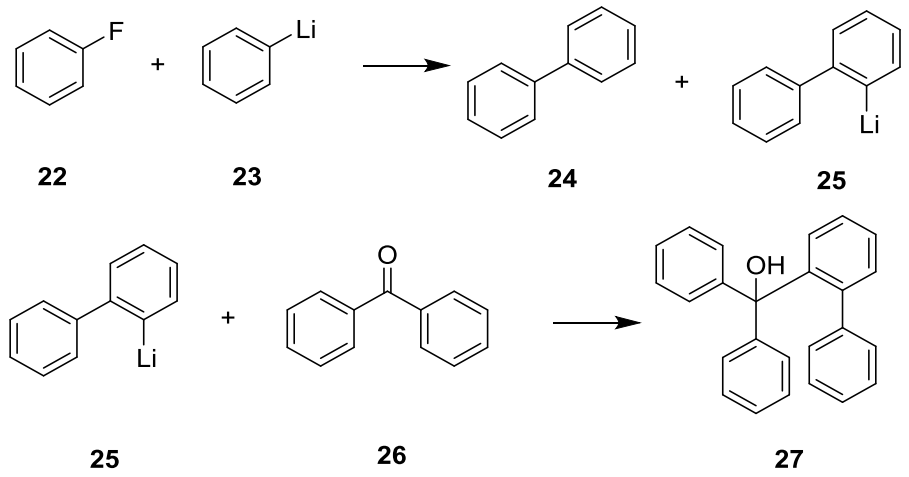
2.2.1. Benzyne-intermediate

In the 1940's scientists performed the reaction in which 1- and 2-chloronaphthalene (**19a, 19b**) had to react with potassium amide (**20**) in liquid ammonia and they observed α- and β-naphthylamine (**21a, 21b**) in the same ratio (Scheme 9). At this time that phenomenon could not be explained. 15 years later WITTIG analyzed this circumstance and performed an experiment in which fluorobenzene (**22**) and phenyllithium (**23**) reacted to diphenyl (**24**) and *o*-lithiumdiphenyl (**25**). WITTIG added some benzophenone (**26**) to the product mixture and

[1,1'-biphenyl]-2-yldiphenylmethanol (**27**) was detected (Scheme 10). After the detection of the formed carbinol (**27**) the existence of *o*-lithiumdiphenyl (**25**) was indisputable.[16]

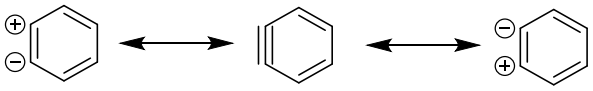


Scheme 9: Reaction of 1- and 2-chloronaphthalene (**19a, 19b**) and potassiumamide to α- and β-naphthylamine (**21a, 21b**)[16]



Scheme 10: Reaction of fluorobenzene (**22**) and phenyllithium (**23**) to diphenyl (**24**) and o-lithiumdiphenyl (**25**) and further conversion of *o*-lithiumdiphenyl with benzophenone (**26**) to [1,1'-biphenyl]-2-yldiphenylmethanol (**27**)[16]

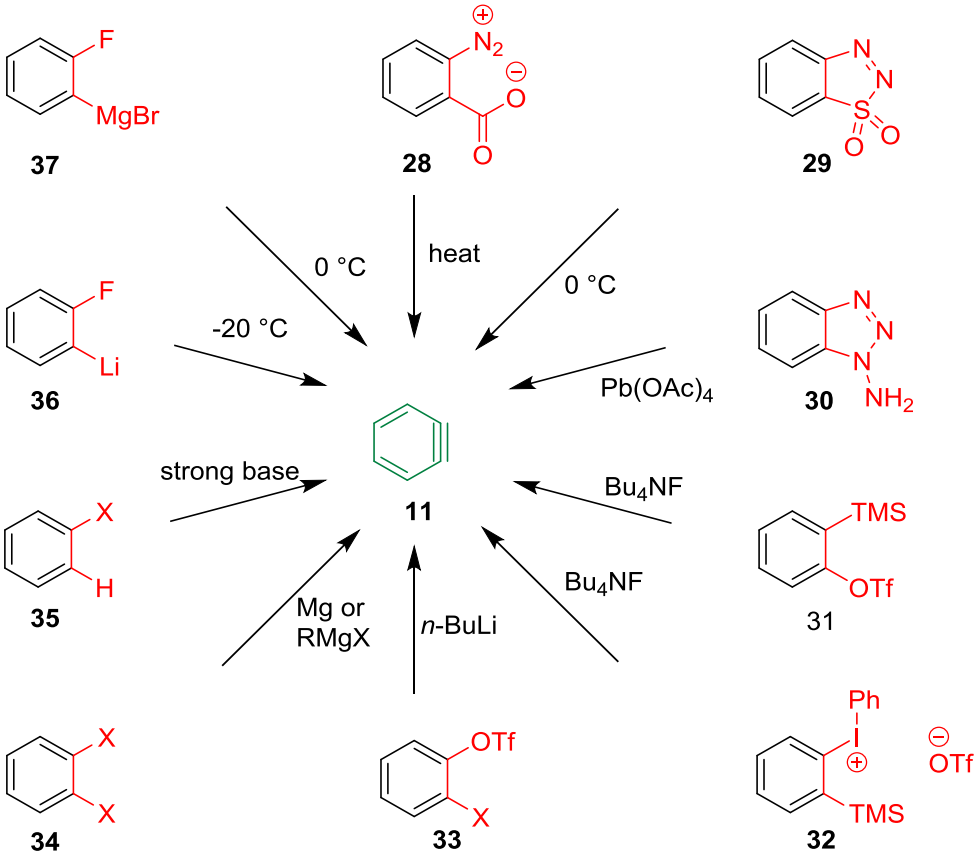
After further experiments WITTIG came to the conclusion that the important intermediate, which was formed in those reactions, had to be a cyclohexandienine (**11**), which he called dehydrobenzene. Nowadays this intermediate is named benzyne. The mesomeric resonance structure is shown in Scheme 11.



11

Scheme 11: Mesomeric resonance structure of benzyne (**11**)[16]

Of course the benzyne intermediate (**11**) is not a stable molecule, because it has a high ring-strain caused by the deformed triple bond. The molecule itself wants to relieve this strain. Nowadays this intermediate can be produced by many different ways.

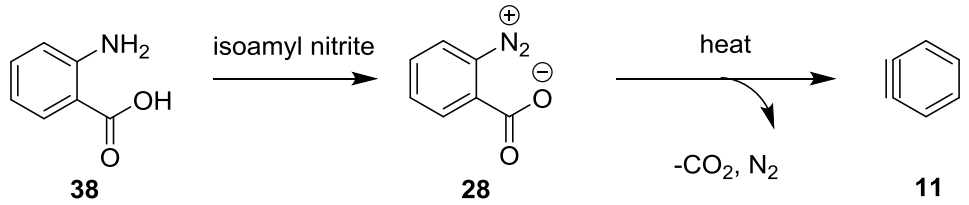


Scheme 12: Generation of benzyne (**11**) by different options[17-24]

The important thing to generate an aryne-system is having an aromatic system with two functional groups. The first should donate its electron pair, somehow, and in *ortho* position to this electron donating moiety there must be a leaving group. The generation of the triple bond can be performed either by adding an organometallic compound (e. g. *n*-BuLi), or by adding a fluoride, or in special cases by adding an oxidizing agent, or by thermal treatment (Scheme 12).[17-23]

2.2.1.1. Diazonium-carboxylate precursor for benzyne generation

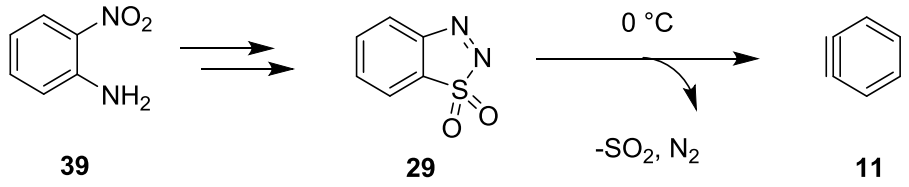
In this variant of benzyne generation aminocarboxylic acids (e. g. anthranilic acid (**38**)) are used as substrate. By treating this kind of molecules with a reagent with a nitrogroup (e. g. $NaNO_2$ or isoamylnitrite) the diazonium salt is formed *in situ*. Afterwards the benzyne intermediate (**11**) can be formed by treating these diazoniumcarboxylates **28** at higher temperatures (Scheme 13).[17]



Scheme 13: Preparation of benzyne (**11**) using diazonium-carboxylate (**28**) as precursor[17]

2.2.1.2. Benzothiadiazol-1,1-dioxide precursor for benzyne generation

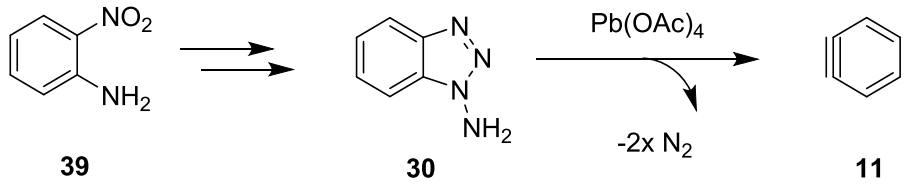
Similar to the variant with diazonium-carboxylate **28** a precursor molecule is generated, which can release gaseous molecules to produce the benzyne intermediate (**11**). After several reactions using 2-nitroaniline (**39**) as substrate benzothiadiazol-1,1-dioxide (**29**) can be produced. In contrast to the reaction with diazonium-carboxylate **28** sulfurdioxide and nitrogen leave the benzothiadiazol-1,1-dioxide at 0 °C and generate benzyne (**11**) (Scheme 14).[18]



Scheme 14: Preparation of benzyne (**11**) using benzothiadiazol-1,1-dioxide (**29**) as precursor[18]

2.2.1.3. 2-Aminobenzotriazole precursor for benzyne generation

In the last variant forming the benzyne intermediate by decomposition 2-nitroaniline (**39**) is used as commercial available substrate. After four reactions 2-aminobenzotriazole (**30**) can be produced. This molecule is stable and can be isolated, but when it is treated with an oxidizing agent (e. g. $Pb(OAc)_4$) a nitrene will be generated followed by the generation of the benzyne intermediate. Two molecules of nitrogen will be released in this reaction (Scheme 15).[19]



Scheme 15: Preparation of benzyne (**11**) using 2-aminobenzotriazole (**30**) as precursor[19]

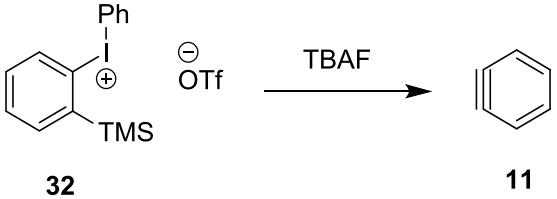
2.2.1.4. 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate precursor for benzyne generation

Another route to benzyne-formation is by treating a silylgroup with a fluoride. The simplest silylgroup is the trimethylsilylgroup. Of course bigger silylgroups can be used in this way of benzyne generation, but there is no necessity to use more sterically demanding silylgroups. In this case trifluoromethanesulfonate is the leaving group. As fluoride source usually tetrabutylammonium fluoride or potassium fluoride are used (Scheme 16).[20]

Scheme 16: Preparation of benzyne (**11**) using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**31**) as precursor[20]

2.2.1.5. 2'-(Trimethylsilyl)diphenyliodonium trifluoromethanesulfonate precursor for benzyne generation

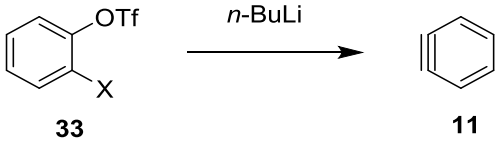
According to the previous benzyne generation method, this reaction processes the same way. The only difference is the switch of the leaving group. The hypervalent iododine species is the best leaving group, which can be used. Therefore 2'-(trimethylsilyl)diphenyliodonium trifluoromethanesulfonate (**32**) is treated with a fluoride to produce benzyne (**11**) (Scheme 17).[21]



Scheme 17: Preparation of benzyne (**11**) using 2'-(trimethylsilyl)diphenyliodonium trifluoromethanesulfonate (**32**) as precursor[21]

2.2.1.6. 2-Halophenyl trifluoromethanesulfonate precursor for benzyne generation

A further possibility to produce a benzyne (**11**) intermediate is using a 2-halophenyl trifluoromethanesulfonate (**33**) as substrate and treat that molecule with *n*-butyllithium. In this reaction a halogen-lithium exchange occurs, the triple bond will be generated and lithium trifluoromethanesulfonate leaves the ring system. The mechanism of the halogen-lithium exchange depends on the character of the electrophile. In the case of aryl iodides or bromides a nucleophilic mechanism via an "-ate-complex" was proposed and in 1986 verified by FARNHAM after the isolation of a hypervalent iodine species (Scheme 18).[22, 25]



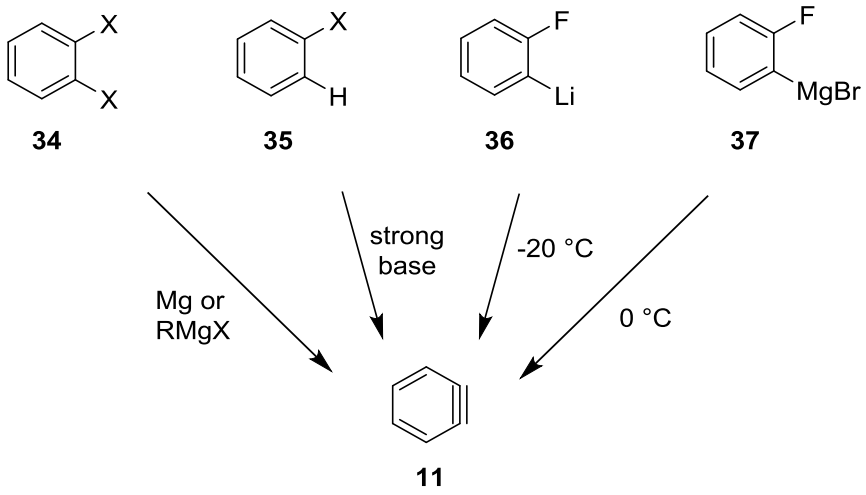
Scheme 18: Preparation of benzyne (**11**) using 2-halophenyl trifluoromethanesulfonate (**33**) as precursor[22]

2.2.1.7. Benzyne generation using lithium or magnesium reagents

In this variant to generate benzyne (**11**) the harshest conditions are needed. Strong bases or GRIGNARD-reagents are used. In the 1950's WITTIG used fluorobenzene (**35**) as substrate and phenyllithium as reagent. In this reaction *ortho*-fluorophenyllithium (**36**) is produced *in situ*, the triple bond is generated and lithiumfluoride leaves the system (Scheme 10, 19).[16,24] Such a strong base is necessary, because the pK_a value of this compounds is approximately 40. Furthermore fluoride is not the best leaving group, but it can stand those unpleasant conditions.

A further possibility of benzyne (**11**) generation is using *ortho*-bromofluorobenzene (**34**) and treat it with magnesium. In this classical GRIGNARD-reaction *ortho*-fluorophenylmagnesium-bromide (**37**) is formed and the triple bond is generated by releasing magnesium bromide fluoride out of the ringsystem (Scheme 19).[23, 24]

In both cases many functional groups are not tolerated, because of the harsh conditions. Moreover, the ratio of unwanted byproducts is quite high.



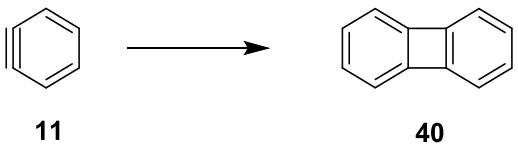
Scheme 19: Generation of benzyne (**11**) using organolithium or GRIGNARD reagents[16, 23, 24]

2.2.2. Reactions with benzyne

Reactions with benzyne (**11**) can result in a wild mixture of products. Because of its high reactivity benzyne reacts within few seconds. Furthermore it can react with polar reagents (e. g. water) or with olefins via cycloaddition (Scheme 11).

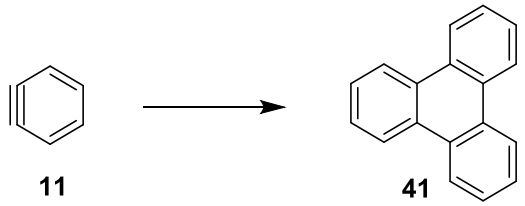
2.2.2.1. Benzyne without any reagent

If benzyne (**11**) does not find any reaction-partner it will react with one or two of itself to generate a polycyclic ringsystem. In the simplest case diphenyl (**24**) is produced (Scheme 10).[16] It is also possible that diphenylene (**40**) is produced, if two benzyne intermediates hit each other (Scheme 20).[26]



Scheme 20: Reaction of benzyne (**11**) to diphenylene (**40**)[26]

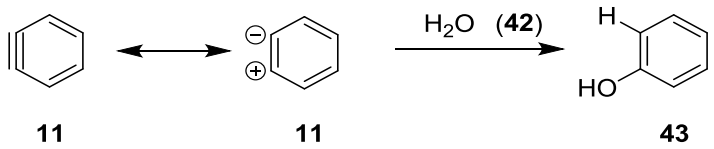
In 1927 BACHMANN reported that triphenylene (**41**) is formed, if three of the benzyne (**11**) intermediates hit each other (Scheme 21).[27]



Scheme 21: Reaction of benzyne (**11**) to triphenylene (**41**)[27]

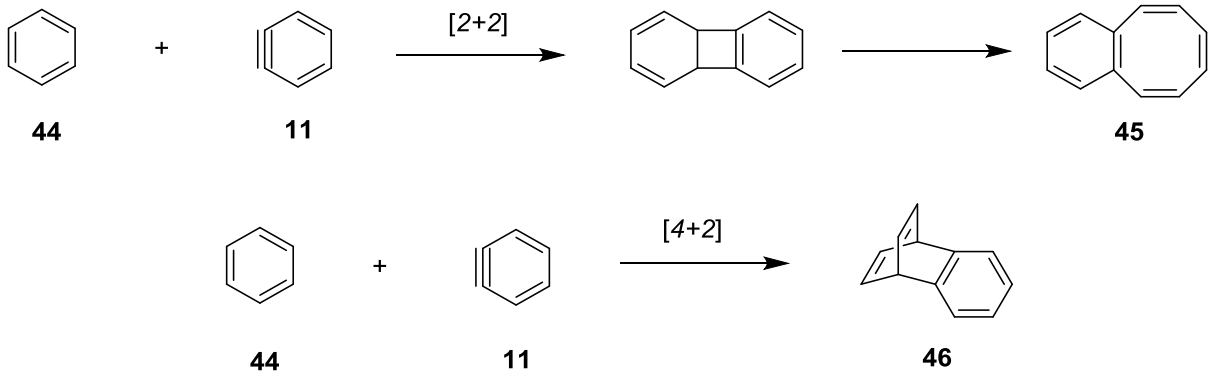
2.2.2.2. Reaction of benzyne with solvents

Because of the high reactivity of benzyne (**11**), it will not wait to find the best reaction partner. If there is an opportunity to react with solvent molecules, arynes will do that. Therefore it is important to choose the right solvent for the upcoming reaction. Furthermore, the solvent has to be absolute dry, because the benzyne intermediate reacts with water (**42**) and produces phenol-derivates (**43**) (Scheme 22).



Scheme 5: Reaction of benzyne (**11**) and water (**42**) to phenol (**43**)

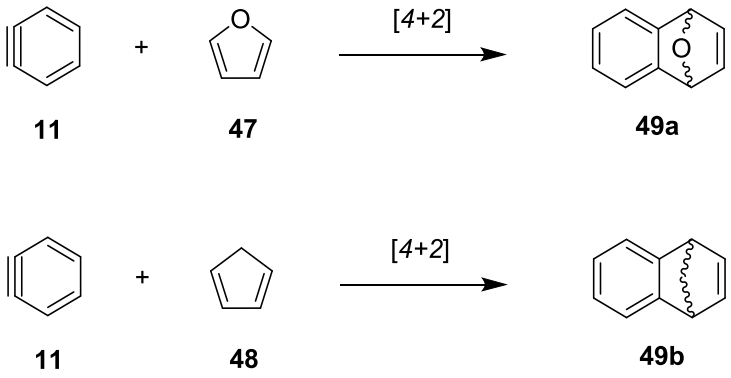
In 1963 MILLER *et. al*. found out, that benzyne (**11**) also reacts with benzene (**44**) via cycloaddition. This is the reason why three other byproducts are generated using benzene as solvent. One product of the reaction of benzyne (**11**) with benzene (**44**) is diphenyl (**24**) shown in Scheme 10. It is also possible to do a [*2+2*]-cycloaddition of benzyne with benzene. After an isomerization reaction benzocyclooctatetraene (**45**) is generated. Another sidereaction, which can occur is a [*4+2*]-cycloaddition. In this case the bicyclic system benzobicyclo [2.2.2]-octatriene (**46**) is produced (Scheme 23).[28]



Scheme 23: Cycloadditions of benzyne (**11**) with benzene (**44**)[28]

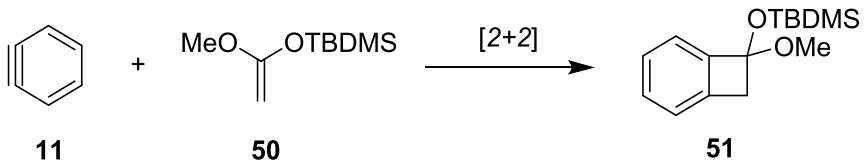
2.2.2.3. Reaction of benzyne with arynophiles

In most cases the benzyne (**11**) intermediate is treated with dienes to do a cycloaddition reaction. Dienes, which have energetically high HOMOs (e. g. furan (**47**), cyclopentadiene (**48**)) are gladly used, but dienes, which do not have best requirements will also react to bicyclic systems **49**, because of the high reactivity of the benzyne (Scheme 24).[18,29]



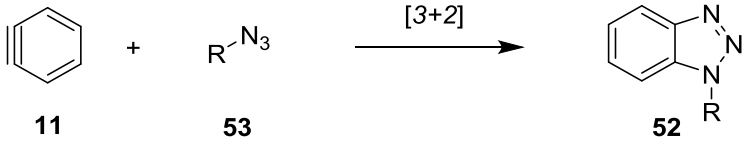
Scheme 24: Reaction of benzyne (**11**) with furan (**47**) to 1,4-dihydro-1,4-epoxynaphthalene (**49a**) and benzyne (**11**) with cyclopentadiene (**48**) to 1,4-dihydro-1,4-methanonaphthalene (**49b**)[18]

Another commonly used reaction is the [*2+2*]-cycloaddition. If the benzyne (**11**) intermediate is treated with enolesters **50** it would do such a [*2+2*]-cycloaddition to reduce the ring-strain. In this reaction substituted benzocyclobutene **51** is produced (Scheme 25).[30]



Scheme 25: [*2+2*]-Cycloaddition of benznye (**11**) with 1-(*tert*-butyldimethylsilyloxy)-1-methoxyethene (**50**) to 1-(*tert*-butyldimethylsilyloxy)-1-methoxy-benzocyclobutene (**51**)[30]

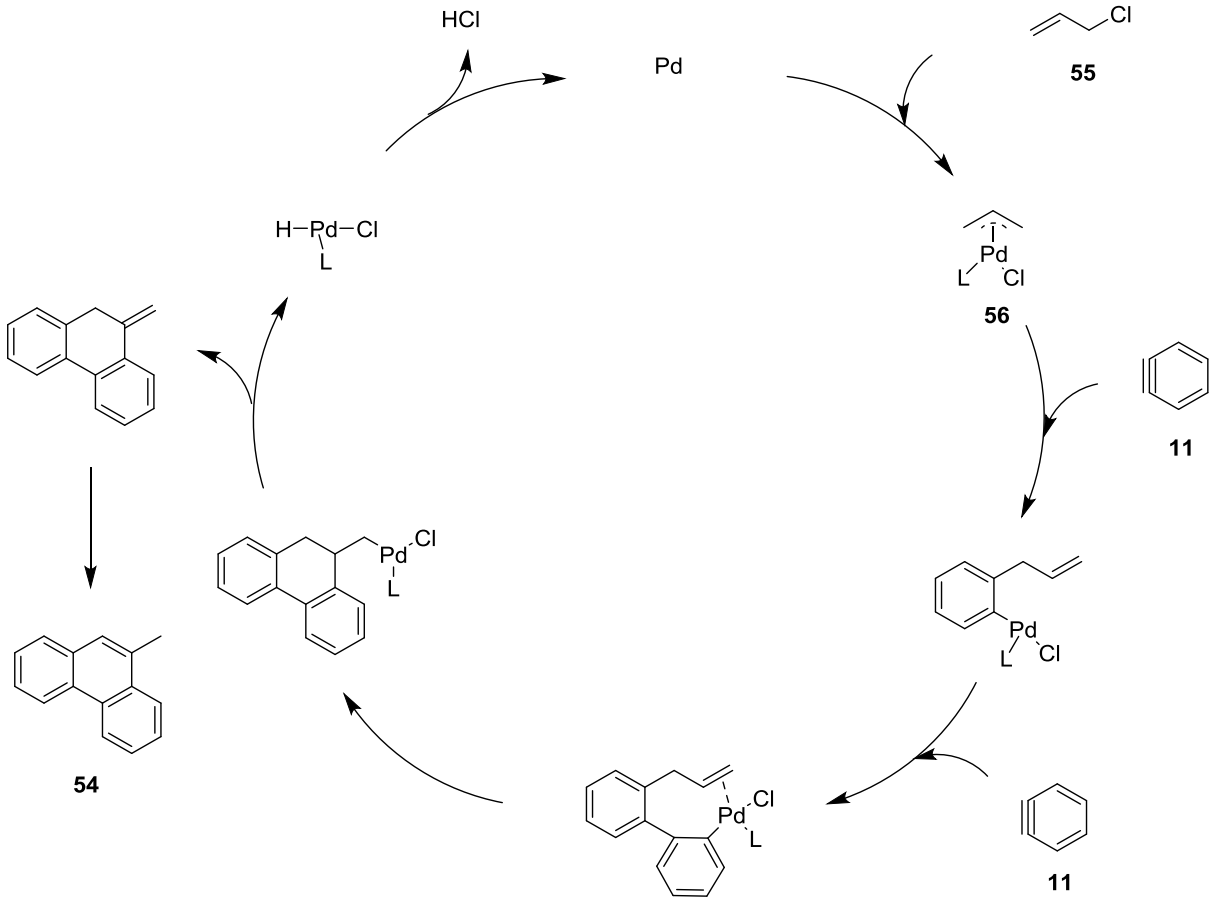
An elegant way to synthesize benzotriazoles **52** is by modified CLICK-chemistry. Therefore an azide-moiety **53** is also needed like in traditional CLICK-chemistry, but instead of an alkyne benzyne (**11**) is used. A further difference to the traditional alternative is, that those reactions with benzyne do not have to be copper catalyzed (Scheme 26).[31]



Scheme 26: Generation of modified benzotriazoles **52** by benznye (**11**) and azides **53**[31]

2.2.2.4. Phenanthrene synthesis

An easy way to build up a phenanthrene **54** skeleton is by palladium catalysis. In such a reaction benzyne (**11**) and allylchloride **55** are used as substrates. In this catalytic cycle palladium in the oxidation state 0 is needed to start the cycle. First of all a π-allyl palladium complex **56** is formed. After that, benzyne inserts twice followed by a β-H-elimination. The formed product tautomerizes to the modified phenanthrene **54** and the palladium catalyst is recycled by reductive elimination (Scheme 27).[32]



Scheme 27: Palladium catalyzed phenanthrene **54** formation using benzyne (**11**) and allylchloride **55** as substrate[31]

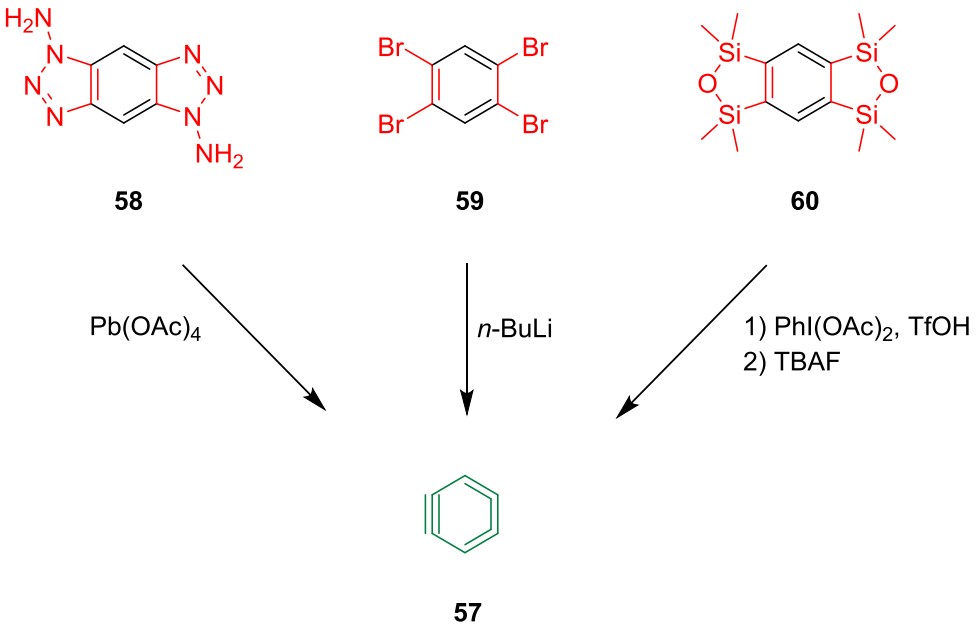
2.2.3. 1,4-Benzdiyne intermediate

Similar to the benzyne (**11**) formation processes are the benzdiyne (**57**) formation. The precursor molecules must have an electron donating group in *ortho* position to a leaving group into an aromatic system again, but in this case two sets of these functional groups are needed. The lifetime of the formed up benzdiyne is very short. Therefore these benzdiyne intermediates decompose to more stable C_6H_2-structures (Figure 6).[33]

57

Figure 6: Structure of 1,4-benzdiyne (**57**)

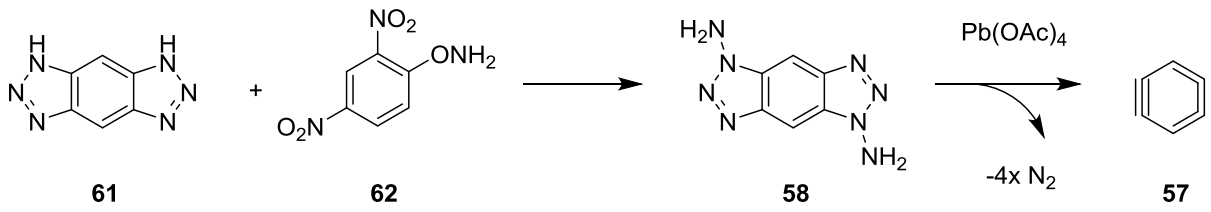
In principle the formation of the precursor molecules of the 1,4-benzdiyne (**57**) intermediate are identical to the formation of the benzyne (**11**) precursors. In literature three options to synthesize these precursor molecules are commonly used (Scheme 28).



Scheme 28: Generation of 1,4 benzdiyne (**57**) by different options[34-36]

2.2.3.1. Benzo[1,2-*d*:4,5-*d*']bis[(1,2,3]triazole)-1,5-diamine precursor for benzdiyne generation

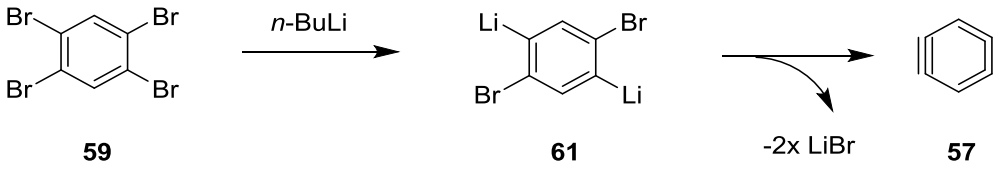
Benzo[1,2-*d*:4,5-*d*']bis([1,2,3]triazole)-1,5-diamine (**58**) can be easily prepared using benzo[1,2-*d*:4,5-*d*']bis[1,2,3]triazole (**61**) and 2,4-dinitrophenoxyamine (**62**) as substrates. After that benzo[1,2-*d*:4,5-*d*']bis([1,2,3]triazole)-1,5-diamine can be oxidized by $Pb(OAc)_4$ to generate two nitrenes, which decompose to the corresponding 1,4-benzdiyne (**57**) and released in this process four molecules of nitrogen (Scheme 29).[34]



Scheme 29: Preparation of 1,4-benzdiyne intermediate (**57**) using benzo[1,2-*d*:4,5-*d*']bis[(1,2,3]triazole)-1,5-diamine (**58**) as precursor[34]

2.2.3.2. 1,2,4,5-Tetrabromobenzene precursor for benzdiyne generation

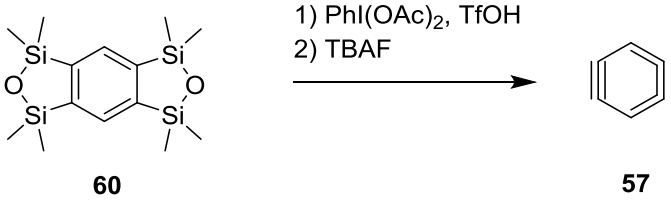
In this variant of 1,4-benzdiyne (**57**) generation harsh reaction conditions are used. 1,2,4,5-Tetrabromobenzene (**59**) is treated with organolithium reagents (e. g. *n*-BuLi) or GRIGNARD-reagents to generate a dimetalodibromobenzene (**61**) species, which eliminates metal bromide salts and forms the triple bond twice (Scheme 30).[35]



Scheme 30: Preparation of 1,4-benzdiyne intermediate (**57**) using 1,2,4,5-tetrabromobenzene (**59**) as precursor[35]

2.2.3.3. 1,1,3,3,5,5,7,7-Octamethyl-5,7-dihydro-1*H*,3*H*-benzo[1,2-*c*:4,5-*c*']bis([1,2,5]oxadisilole) precursor for benzdiyne generation

In this reaction 1,1,3,3,5,5,7,7-octamethyl-5,7-dihydro-1*H*,3*H*-benzo[1,2-*c*:4,5-*c*']bis-([1,2,5]oxadisilole) (**60**) acts as precursor molecule, which is treated with (diacetoxyiodo)benzene and trifluoromethanesulfonic acid to generate *in situ* two hypervalent iodine species. After that, these molecules are transformed with fluoride-anions (e. g. TBAF) to the benzdiyne (**57**) intermediate (Scheme 31).[36]

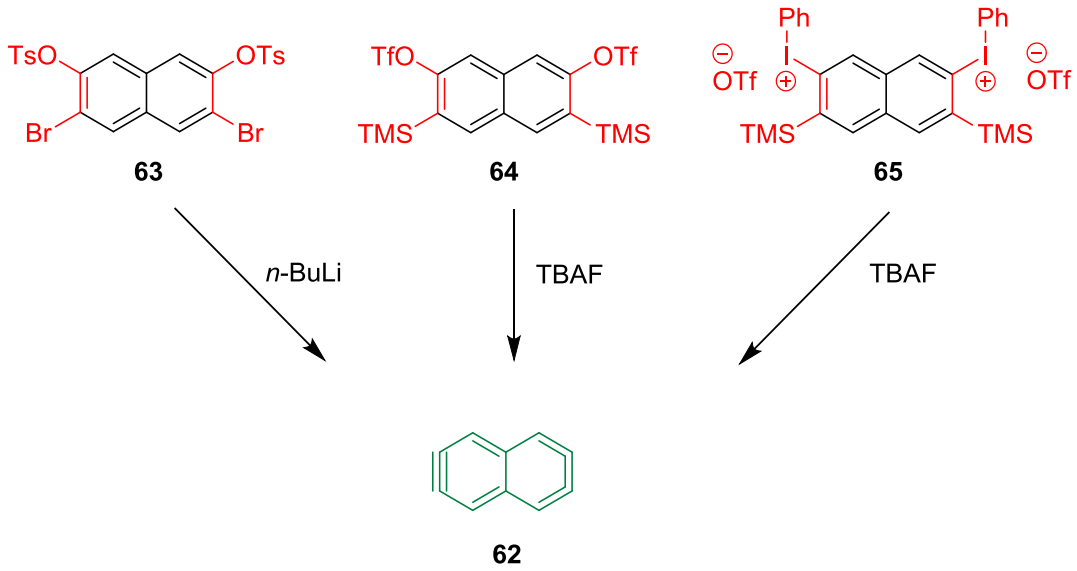


Scheme 31: Preparation of 1,4-benzdiyne intermediate (**57**) using 1,1,3,3,5,5,7,7-octamethyl-5,7-dihydro-1*H*,3*H*-benzo[1,2-*c*:4,5-*c*']bis([1,2,5]oxadisilole) (**60**) as precursor[36]

The generated benzdiyne (**57**) could be used for different reactions like the benzyne (**11**) intermediate, which was described in chapter 2.2.2..

2.2.4. 2,6-Naphthodiyne intermediate

The triple bond formation in aromatic systems is not limited to benzene derivatives. It is also possible to generate such a triple bond in bigger aromatic systems (e.g. naphthalenes). These aryne formation in modified naphthalenes proceeds the same way as the triple bond generation in benzene systems. Therefore naphthalene systems with two different functional groups are needed. One, which can deliver electrons to the ring system and the other should be a leaving group. With this it is also possible to introduce two triple bonds into the naphthalene system. In this case the cyclic molecules, which consist of one or two triple bonds want to release their ring-strain. This is the reason, why naphthodiynes (**62**) are quite unstable molecules like benzynes (**11**) and benzdiynes (**57**). The generation of naphthodiyne intermediates can be performed by different variants as in the case of benzyne and benzdiyne (Scheme 32).[37-39]

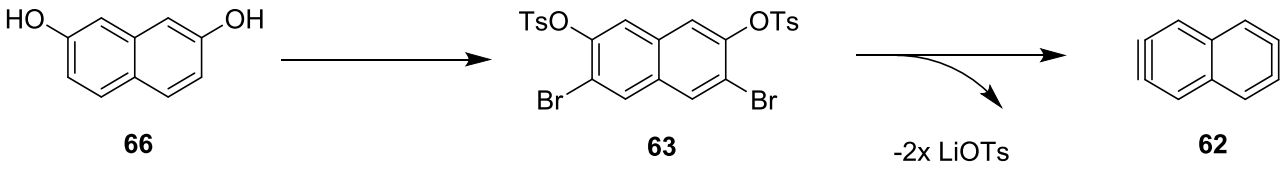


Scheme 32: Generation of 2,6-naphthodiyne (**62**) by different routes.[37-39]

2.2.4.1. 3,6-Dibromonaphthalene-2,7-diyl bis(4-methylbenzenesulfonate) precursor for 2,6-naphthodiyne generation

In this variant of naphthodiyne (**62**) formation 2,7-dihydroxynaphthalene (**66**) is used as substrate. In two reactions the naphthodiyne precursor molecule is constructed and can be used for aryne generation. Therefore 3,6-dibromonaphthalene-2,7-diyl bis(4-methylbenzenesulfonate) (**63**) is treated with *n*-BuLi. In this reaction at first a metal-halogen

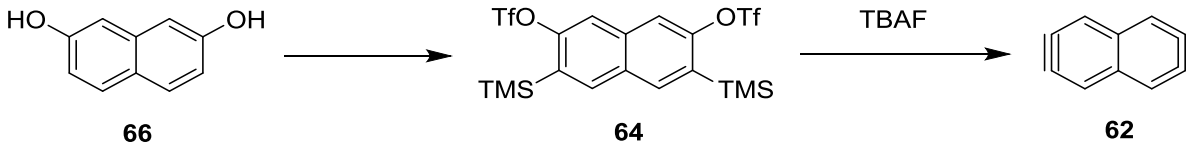
exchange occurs, followed by the triple bond formation and discharge of lithiumtosylate (Scheme 33).[37]



Scheme 33: Preparation of 2,6-naphthodiyne (**57**) using 3,6-dibromonaphthalene-2,7-diyl bis(4-methylbenzenesulfonate) (**63**) as precursor[37]

2.2.4.2. 3,6-Bis(trimethylsilyl)naphthalene-2,7-diyl bis(trifluoromethanesulfonate) precursor for 2,6-naphthodiyne generation

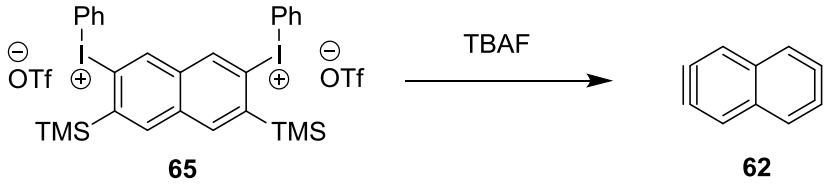
The next route of naphthodiyne (**62**) generation uses naphthalene-2,7-diole (**66**) as substrate. In this case four reactions are needed to produce the desired 3,6-bis(trimethylsilyl)naphthalene-2,7-diyl bis(trifluoromethanesulfonate) (**64**), which can be used for naphthodiyne generation. But in this case TBAF is required to form the triple bonds (Figure 40).[37]



Scheme 34: Preparation of 2,6-naphthodiyne (**57**) using bis(trimethylsilyl)naphthalene-2,7-diyl bis(trifluoromethanesulfonate) (**64**) as precursor[38]

2.2.4.3. (3,6-Bis(trimethylsilyl)naphthalene-2,7-diyl) bis(phenyliodonium) trifluoromethanesulfonate precursor for 2,6-naphthodiyne generation

A further option of a naphthodiyne (**62**) precursor is the exchange of the trifluoromethanesulfonic acid moieties of bis(trimethylsilyl)naphthalene-2,7-diyl bis(trifluoromethanesulfonate) (**64**) to hypervalent iodine species. These hypervalent iodine species are better leaving groups than trifluoromethanesulfonantes. The naphthodiyne intermediate is generated by treating (3,6-bis(trimethylsilyl)naphthalene-2,7-diyl)bis(phenyliodonium) trifluoromethanesulfonate (**65**) with TBAF like in the case of bis(trimethylsilyl)naphthalene-2,7-diyl bis(trifluoromethanesulfonate) (Scheme 35).[39]



65 **62**

Scheme 35: Preparation of 2,6-naphthodiyne (**57**) using (3,6-bis(trimethylsilyl)naphthalene-2,7-diyl)bis(phenyliodonium) trifluoromethanesulfonate (**65**) as precursor[38]

The generated naphthodiyne (**62**) intermediate could be used for different reactions like the benzyne (**11**) intermediate, which was described in chapter 2.2.2..

3. Goals

In 2012 P.-T. CHIANG *et. al.* published the production of a molecular car in nanoscale. The wheels of this car consist of caboranes, which are connected via a molecular axis. These axis in turn consist of a linear carbon structure, which are connected via a nanoengine with each other (Figure 7). The nanocar could be set in motion by terminal or electrical force. The movement on a metallic surface is followed by scanning tunnelling microscopy.[40]

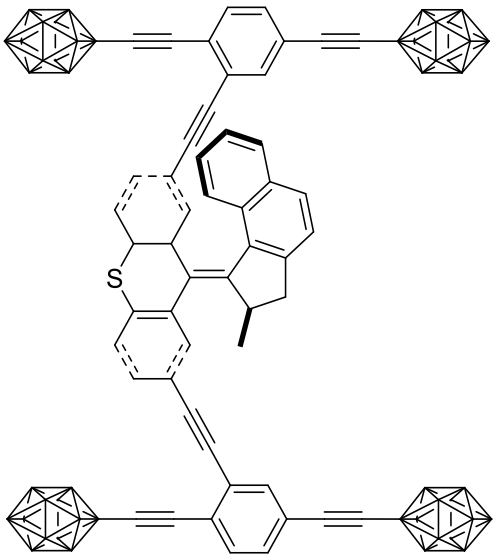
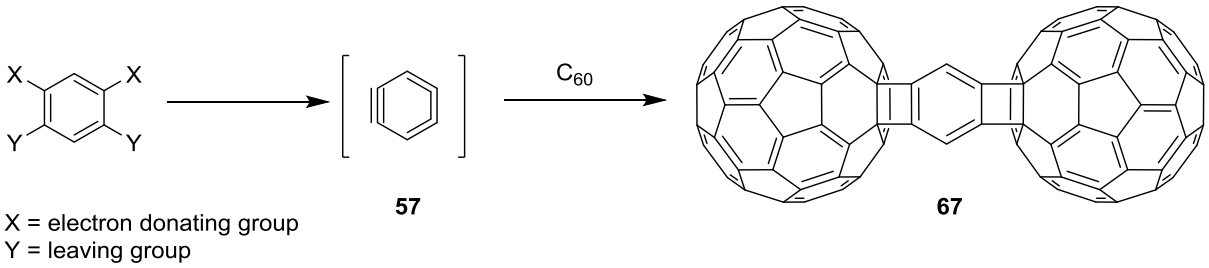


Figure 7: Existing nanocar, consisting of axles, tires and engine in molecular size[40]

In the nineties of the last century, cycloaddition reactions were performed in which benzyne (**11**) intermediates were treated with C_{60}-fullerenes.[8] The goal of this master thesis is the combination of both topics. A bigger part of the nanocar (axis with connected tires) should be prepared. In contrast to the work of CHIANG, those parts have to be prepared by aryne-chemistry. Therefore two aryne species have to be generated and coupled to fullerenes **1** (Scheme 36). The biggest difficulty of that reaction is that cycloadditions with fullerenes give quite low yield of product formation. Proper reaction conditions have to be found to maximize the product generation and minimize the side product generation, because the aryne intermediate is highly reactive. After the accomplishment of the generation of the nanocar parts, those parts should be connected via an engine to produce another type of car on molecular scale.

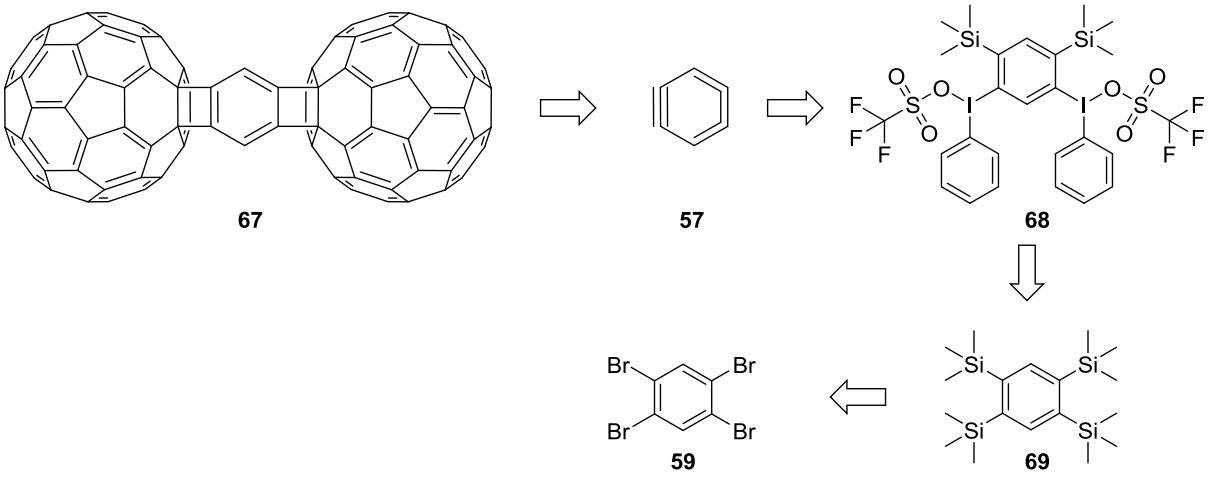


Scheme 36: Generation of bridged fullerenes

Subsequently physical experiments could be done with that molecular car. That movement could be detected either by scanning tunnelling microscopy on a metallic surface or single-molecule fluorescence microscopy on a glass surface like it was done in the work of CHIANG.

4. Results and Discussion

The aim of this master thesis is the preparation of bridged fullerenes **1** via an aromatic system. The key fragment in this synthesis is the aryne-intermediate. Therefore benzdiyne (**57**) or naphthodiyne (**62**) have to be generated *in situ* and further coupled via a [*2+2*]-cycloaddition with C_{60}-fullerene (**2**) (Scheme 37). In these reactions attention has to be paid on the proper ratio of substrates and reagents to prevent side products and maximize the product formation.



Scheme 37: Retrosynthesis of bridged fullerenes **67** via an aromatic system

In the course of the production of bridged fullerenes several pre-experiments were performed. To become familiar with fullerene-chemistry reactions to connect one fullerene to a benzene ring were executed. Therefore several precursor molecules for the benzyne (**11**) intermediate were also formed by different reactions (Figure 8). After the formation of the different precursor molecules screening experiments were conducted to find the best method for the cycloaddition reaction of the desired target molecules. For the pre-experiments furan (**47**) was used as diene for the cyclisation. After accomplishment of the cyclized product via aryne intermediate the reaction partner was exchanged to BUCKMINSTER-fullerene (**2**).

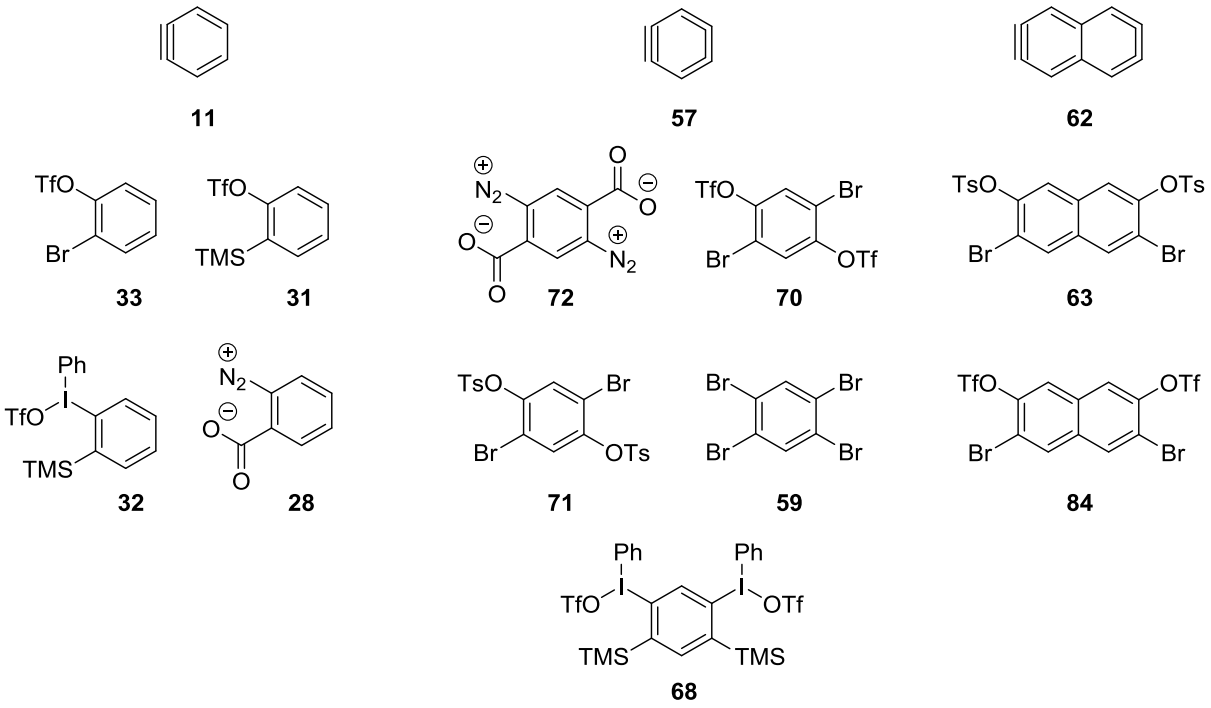
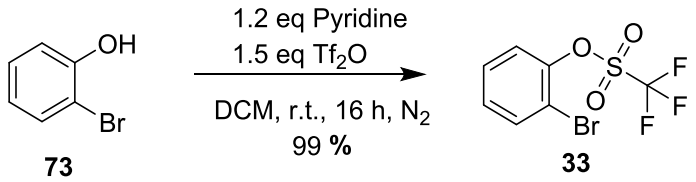


Figure 8: Aryne-intermediates (**11**, **57**, **62**) and their produced precursor molecules (**28**, **31**, **32**, **33**, **59**, **63**, **68**, **70**, **71**, **72, 84**)

4.1. Precursor molecules for benzyne generation

The simplest way to produce the benzyne (**11**) intermediate is using 1,2-dibromobenzene (**34**) as substrate and treatment of this molecule with *n*-butyllithium.[16] Cyclisation experiments using furan (**47**) as diene were not performed, because that reaction is known in literature.

4.1.1. Preparation of 2-bromophenyl trifluoromethanesulfonate

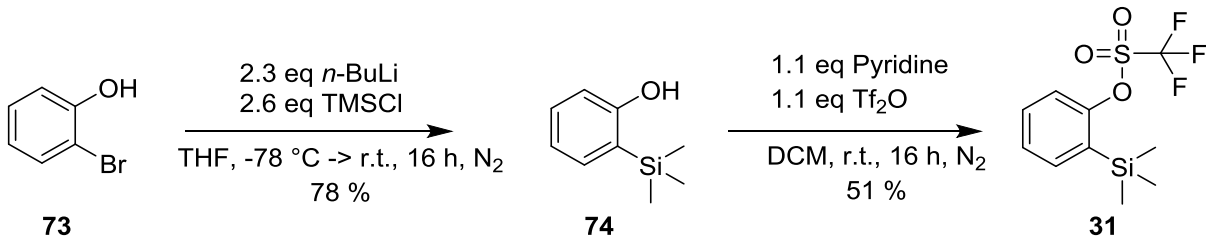


Scheme 38: Generation of 2-bromophenyl trifluoromethanesulfonate (**33**) using 2-bromophenol (**73**) as substrate

The exchange reaction of an alcohol moiety to a trifluoromethanesulfonate moiety is known in literature and is often performed in lab-courses, because of its simplicity and the nearly quantitative product formation and isolation. In this case 2-bromophenol (**73**) is used as substrate. In this experiment 1.2 eq of a softer base (pyridine) are used to activate the reagent trifluoromethanesulfonic anhydride and build up an active ammonium-species. Subsequently

that activated species could be attacked by the alcohol without deprotonation of the alcohol moiety.[41] The dropwise addition of 1.5 eq of trifluoromethanesulfonic anhydride was performed at 0 °C, because this reaction is quite exothermic. This reaction normally should be finished after 2 h, but in some cases it takes a little bit longer. In the work-up the organic phase was washed with 1 M hydrochloric acid-solution to protonate the rest of the pyridine. MATSUMURA *et. al.* achieved in this reaction 97 % yield. The yield of the performed experiment was a little bit better and reached 99 % (Scheme 38).

4.1.2. Preparation of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate



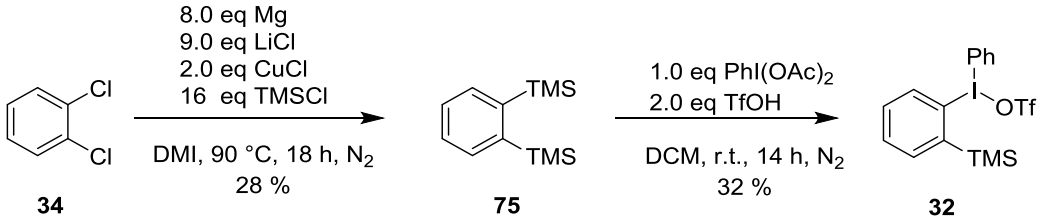
73 **74** **31**

Scheme 39: Generation of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**33**) using 2-bromophenol (**73**) as substrate

In this experiment 2-bromophenol (**73**) was used as substrate again, but this time the desired product was generated by two subsequent reactions. In the first reaction the bromine moiety was exchanged to a trimethylsilyl moiety. First 2.3 eq of *n*-BuLi were added to the mixture of 2-bromophenol. Thereby the first equivalent of *n*-BuLi was required to deprotonate the hydroxyl group of the phenol. The second equivalent of the reagent underwent the lithium-halogen exchange reaction. After that 2.6 eq of trimethylsilyl chloride were added and both functional groups of the aromatic ring system got trimetylsilylated. The addition of both reagents had to be performed at -78 °C, because these reactions are exothermic. According to the work of NISHIDE *et. al.* the reaction mixture had to be stirred until no substrate was detectable by thin layer chromatography, which takes about 3-4 h. After that it was necessary to treat the reaction mixture with tetrabutylammonium fluoride to cleave off the trimethylsilyl group on the phenolic position. If the work-up was done with hydrochloric acid-solution instead of tetrabutylammonium fluoride the phenol moiety remained protected by a trimethylsilyl group.[42] To purify the crude product flash chromatography was required. The yield of this reaction should be up to 89 %, but in this work a yield of 78 % was achieved. Probably the loss in yield depends on the work-up or purification.

The subsequent transformation of the alcohol moiety to a trifluoromethanesulfonate moiety was performed as described by MATSUMURA *et. al.*.[40] In this reaction 1.0 eq 2-(trimethylsilyl)phenol (**74**) and 1.1 eq of pyridine were used. Pyridine activates trifluoromethanesulfonic anhydride to an activated ammonium species. 1.1 eq of trifluoromethanesulfonic anhydride were added dropwise at 0 °C to form the desired 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**33**). In this reaction it was important, that there is no water inside of the reaction mixture. Otherwise the trifluoromethanesulfonic anhydride would be quenched and no product is observable. Therefore absolute dichloromethane was used as solvent in this reaction. The crude product was difficult to purify this time. Therefore two purifications by flash column chromatography were necessary. The yield of this reaction was 51 %. The reason of the low yield originals from the purification, which unfortunately had to be done twice (Scheme 39).

4.1.3. Preparation of phenyl(2-(trimethylsilyl)phenyl)-λ^3-iodanyl trifluoromethanesulfonate



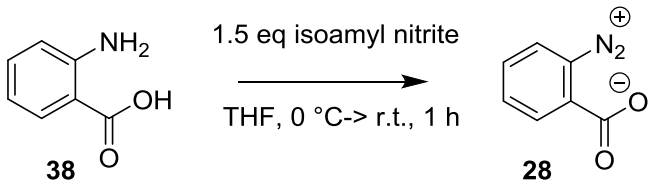
Scheme 40: Generation of phenyl(2-(trimethylsilyl)phenyl)-λ^3-iodanyl trifluoromethanesulfonate (**32**) using 1,2-dichlorobenzene (**34**) as substrate

The hypervalent iodinated benzyne precursor molecule **32** was produced in two steps. The first reaction was a copper(I) catalyzed GRIGNARD reaction. That not classical GRIGNARD-reaction needed a high load of reagents (8.0 eq magnesium, 9.0 eq lithium chloride, 2.0 eq copper(I) chloride and 16 eq trimethylsilyl chloride) and an extraordinary solvent (1,3-dimethyl-2-imidazolidinone (DMI)). This route of bis(trimethylsilyl)benzene (**75**) generation was first described by KITAMURA and had better yields than the conventional route.[43] In that route hexamethylphosphortriamide was used as solvent.[44] For safety reasons the option of bis(trimethylsilyl)benzene generation using DMI as solvent was chosen. Therefore 8.0 eq magnesium, 9.0 eq lithium chloride, 2.0 eq copper(I) chloride were dried in the vacuum of an oil pump. After that DMI and 16 eq trimethylsilyl chloride were added. Subsequently 1.0 eq of 1,2-dichlorobenzene was added dropwise. The reaction mixture was

heated to 90 °C for 16-17 h, as described by KITAMURA. Reaction control by GC-MS showed, that approximately 5 % of the product mixture consisted of mono(trimethylsilyl)benzene. The solvent is very hygroscopic and should be stored under inert atmosphere over molecular sieves. That could be the reason why one of the chloride moieties got exchanged to hydrogen. The crude product was purified by Kugelrohr-distillation. Because of the small reaction scale and the purification by a Kugelrohr-distillation the isolated yield was quite low at 28 %.

The second part of the phenyl(2-(trimethylsilyl)phenyl)-λ^3-iodanyl trifluoromethane-sulfonate (**32**) generation was the exchange reaction of one trimethylsilyl moiety to a hypervalent iodine species. That reaction was also described by KITAMURA and is easy to perform.[43] Therefore 1.0 eq of (diacetoxyiodo)benzene was treated with 2.0 eq of trifluoromethanesulfonic acid. After 2 h of stirring a solution of 1.0 eq bis(trimethylsilyl)-benzene (**75**) in dichloromethane was added. After 16 h of stirring at r.t. the solvent was removed and the resulting colorless crystalline solid could be used without further purification.[43] The crude product, which was produced in an experiment of this work, was a brown oil. After trituration with diethyl ether a brownish solid precipitated. According to the ^{1}H-NMR-spectra the product was contaminated with DMI, which was regarded as not problematic for subsequent reactions. The yield, which was achieved in this reaction, was 32 % (Scheme 40).

4.1.4. Preparation of 2-diazoniumbenzoic acid salt



Scheme 41: Generation of 2-diazoniumbenzoic acid salt (**28**) using 2-aminobenzoic acid (**38**) as substrate

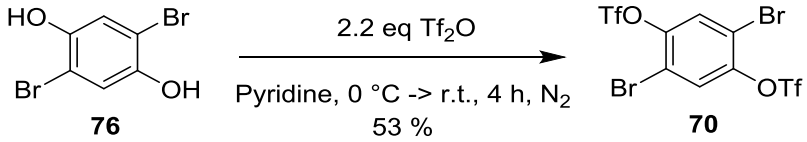
2-Diazoniumbenzoic acid salt (**28**) is highly explosive. Therefore it always is prepared *in situ* in the certain experiment. In such an experiment 1.0 eq of 2-aminobenzoic acid is treated with 1.5 eq of isoamyl nitrite and catalytic amounts of trichloroacetic acid in tetrahydrofuran at 0 °C. The reaction mixture is stirred for 1 h at r.t.. Thereby a colorless solid precipitates, which is then filtered off. It is important, that the collected solid is not allowed to get dry, because of the explosion risk. While the 2-diazoniumbenzoic acid salt is filtered the solvent is

exchanged to the solvent, which is used in the next experiment. The 2-diazoniumbenzoic acid salt suspension has to be used for the next experiment immediately (Scheme 41).[45]

4.2. Precursor molecules for benzdiyne generation

Like benzyne (**11**) generation the simplest production of benzdiyne (**57**) intermediate starts from 1,2,4,5-tetrabromobenzene (**59**) by treatment with *n*-butyllithium.[35] This time cyclisation experiments using furan (**47**) as diene were performed to have reference material and to compare the yield of different cyclisation experiments.

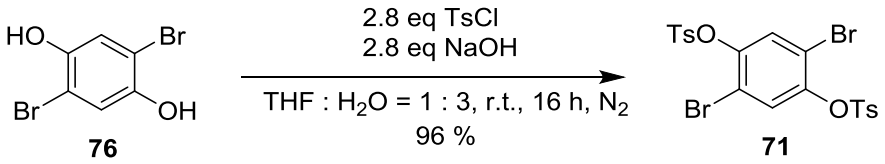
4.2.1. Preparation of 2,5-dibromo-1,4-phenylene bis(trifluoromethanesulfonate)



Scheme 42: Generation of 2,5-dibromo-1,4-phenylene bis(trifluoromethanesulfonate) (**70**) using 2,5-dibromohydroquinone (**76**) as substrate

This time two hydroxyl groups have to be transformed to leaving groups. 2,5-Dibromohydroquinone (**76**) was used as commercially available substrate. Instead of using dichloromethane as solvent, like it was described by MATSUMURA, dry pyridine was used as reagent and solvent.[41] Such an exchange reaction was described by ECHAVARREN.[46] Therefore 1.0 eq of 2,5-dibromohydroqinone was suspended in dry pyridine. Subsequently 2.2 eq of trifluoromethanesulfonic anhydride were added dropwise at 0 °C. Because of better solubility of 2,5-dibromo-1,4-phenylene bis(trifluoromethanesulfonate) (**70**) the solid of the reaction mixture disappeared, during the addition of trifluoromethanesulfonic anhydride. The disadvantage of using such a high amount of pyridine is the difficult purification. All of the pyridine could not be removed by acidic work-up. Therefore the crude product had to be purified by flash column chromatography. The yield of this reaction was 53 %. It might be, that the working procedure of MATSUMURA produces better yield, because the amount of pyridine is much smaller or that washing with aqueous $CuSO_4$-solution would improve the yield (Scheme 42).

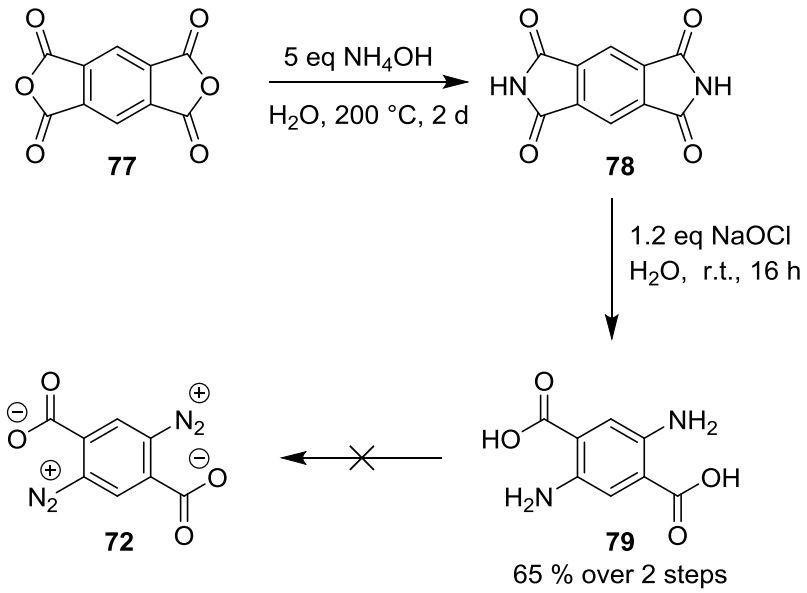
4.2.2. Preparation of 2,5-dibromo-1,4-phenylene bis(4-methylbenzenesulfonate)



Scheme 43: Generation of 2,5-dibromo-1,4-phenylene bis(trifluoromethanesulfonate) (**71**) using 2,5-dibromohydroquinone (**76**) as substrate

The goal of this experiment was to convert the alcohol moiety to a leaving group, but this time 4-methylbenzenesulfonate instead of trifluoromethanesulfonate. In this experiment a solvent mixture consisting of tetrahydrofuran and water in the ratio of 1 : 3 was used. This kind of option for a tosylation reaction was described by HEATHCOTE.[47] Therefore 1.0 eq of 2,5-dibromohydroquinone (**76**) was treated with 2.8 eq of sodium hydroxide and 2.8 eq of *p*-toluenesulfonyl chloride. The hydroxide deprotonated the phenol groups of the substrate and made the oxygen atom of the deprotonated phenol moiety more nucleophilic. After that the phenolate attacked the *p*-toluenesulfonyl chloride and product formation occurred. After 16 h of vigorously stirring the product was collected by filtration and washed with water. No further purification was necessary and the yield of this reaction was 96 %. Because of the very poor solubility of this product the analytical characterization was hard to achieve or impossible. Furthermore this product cannot be used for further experiments because it will not be dissolved in the proper solvent, which should be used for this kind of reaction (Scheme 43).

4.2.3. Preparation of 2,5-bis(diazonium)terephthalic acid disalt



Scheme 44: Generation of 2,5-bis(diazonium)terephthalic acid disalt (**72**) using 1,2,4,5-benzenetetracarboxylic anhydride (**77**) as substrate

In these reactions a product should be formed, which could be used for benzdiyne (**57**) generation by decomposition. For the production of 2,5-bis(diazonium)terephthalic acid disalt (**72**) three steps were necessary. The commercially available substrate, which was used in these reactions, is 1,2,4,5-benzenetetracarboxylic anhydride (**77**). In the first reaction 1.0 eq of 1,2,4,5-benzenetetracarboxylic anhydride (**77**) was treated with 5.0 eq of ammonium hydroxide. After 1 d of heating under reflux, the solvent was removed and the crude product was further heated without any solvent to 200 °C for 1 d. Subsequently the crude product was purified by recrystallization from *N*,*N*-dimethylformamide. This reaction was described by HOJO.[48] Unfortunately the desiccation of the product was quite hard, because of the high boiling point of the used solvent. The mother liquor was also dried, because after the next reaction a mixture of two diamino terephthalic acids were produced. Therefore the substrate has not to be a pure substance.

The second reaction is a classical HOFMANN degradation reaction. This reaction was also described by HOJO.[48] Therefore 1.0 eq of 1,2,4,5-benzenetetracarboxylic diimide (**78**) was treated with 1.2 eq of sodium hypochlorite. Thereby the color of the solid changed from yellow to colorless and after 16 h of vigorously stirring at r.t. the solid was collected by filtration and recrystallized from water. Because of the higher symmetry 2,5-diamino terephthalic acid (**79**) was obtained after recrystallization. The 2,5-diamino terephthalic acid is

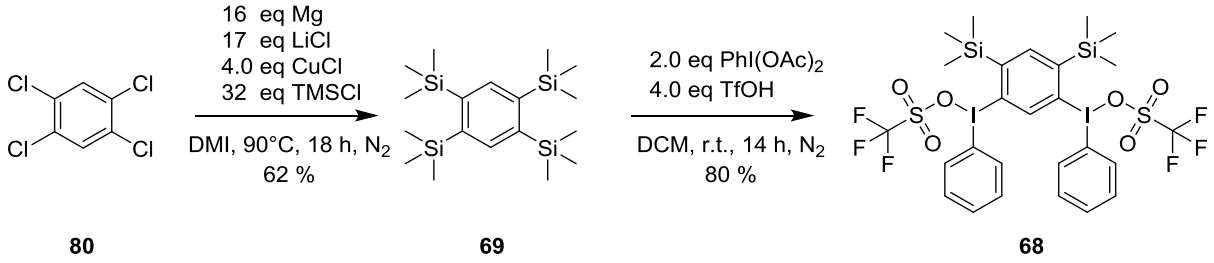
very insoluble in many different solvents. It is only soluble via addition of a huge amount of acid or base in polar solvents correlated to the product. That product could also be zwitterionic. That could be the reason why it is quite insoluble in many solvents without any additive. The yield over these two steps was 65 %, which also could be higher. Because of recrystallization purification, which was done twice, there is some loss of product possible (Scheme 44).

The last reaction to produce the benzdiyne (**57**) intermediate was to generate the diazonium moieties out of the amino moieties. Because of the rather good yield of the 2-diazoniumbenzoic acid salt (**28**) that experiment was also tried according to the procedure of LOGULLO *et. al.*.[45] However, the explosion risk in this case is much bigger, because this time four gaseous molecules could be generated. That experiment was tried for several times with different reagents and in different solvents, but unfortunately no product formation could be observed (Table 1).

Table 1: Different attemts of 2,5-bis(diazonium)terephthalic acid disalt (**72**) formation

entry	2,5-diamino terephthalic acid (79) [eq]	Isoamyl nitrite [eq]	*tert*-Butyl nitrite [eq]	Sodium nitrite	additive	solvent
1	1.0	3.0	-	-	Trichloroacetic acid	THF
2	1.0	3.0	-	-	Trifluoroacetic acid	THF
3	1.0	3.0	-	-	Excess Trifluoroacetic acid	Trifluoro-ethanol
4	1.0	3.0	-	-	Trifluoroacetic acid	Dimethoxy-ethane
5	1.0	-	3.0	-	Trichloroacetic acid	THF
6	1.0	-	-	3.0	Hydrochloric acid	Water

4.2.4. Preparation of (4,6-bis(trimethylsilyl)-1,3-phenylene)bis(phenyl- λ^3-iodanediyl) bis(trifluoromethanesulfonate)



Scheme 45: Generation of (4,6-bis(trimethylsilyl)-1,3-phenylene)bis(phenyl- λ^3-iodanediyl) bis(trifluoromethanesulfonate) (**68**) using 1,2,4,5-tetrachlorobenzene (**80**) as substrate

The last option of benzdiyne (**57**) precursor molecule generation, which was done in this work, was the preparation of (4,6-bis(trimethylsilyl)-1,3-phenylene)bis(phenyl-λ^3-iodanediyl) bis(trifluoromethanesulfonate) (**68**). The reaction to produce 1,2,4,5-tetrakis(trimethylsilyl)-benzene (**69**) is known in the literature and is described by KITAMURA.[43] The subsequent reaction to exchange two of the trimethylsilyl moieties to hypervalent iodine species is not known in literature, but a similar reaction is also described by KITAMURA.[44] In the first reaction 1.0 eq of 1,2,4,5-tetrachlorobenzene (**80**) is treated with 16 eq of magnesium, 17 eq of lithium chloride, 4.0 eq of copper(I) chloride and 32 eq of trimethylsilyl chloride to do a modified GRIGNARD reaction. In this reaction the use of 1,3-dimethyl-2-imidazolidinone (DMI) was preferred to the harmful hexamethylphosphortriamide, as it was done in the preparation of phenyl(2-(trimethylsilyl)phenyl)-λ^3-iodanyl trifluoromethanesulfonate (**32**). After the 16 h of heating to 90 °C under inert atmosphere the reaction control via GC-MS showed, that there was no substrate remaining, but unfortunately approximately 40 % of the product mixture consisted of tris(trimethylsilyl)benzene. Probably the reduction of one chlorine moiety depended on the hygroscopic properties of DMI. Therefore DMI should always be stored under inert atmosphere over molecular sieves. Fortunately the separation of tris- and tetrakis(trimethylsilyl)benzene (**69**) was quite easy. Because of the higher symmetry tetrakis(trimethylsilyl)benzene crystallizes selectively in acetone. The yield of this reaction was 62 %, which could even be higher because there was already some product in the mother liquor, which could not be collected.

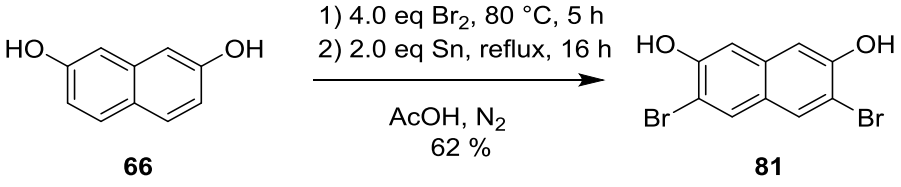
In the second reaction two of the trimethylsilyl moieties have to be exchanged to hypervalent iodine species. Therefore 2.0 eq of (diacetoxyiodo)benzene were treated with 4.0 eq of

trifluoromethanesulfonic acid in absolute dichloromethane under inert atmosphere. Because of decomposition reactions of aromatic iodine molecule initiated by light, the reaction vessel was covered with aluminium foil to protect the content from light. After 16 h of stirring a solution consisting of 1.0 eq of tetrakis(trimethylsilyl)benzene (**69**) in absolute dichloromethane was added dropwise at 0 °C to the reaction mixture. The reaction mixture was stirred for further 16 h at 0 °C. If the stirring of the reaction was performed at r.t. or at 0 °C without light protection the product decomposes and the yield decreases. Work-up was also performed at 0 °C and with protection from light. Therefore the solvent was removed in the vacuum of an oil pump at 0 °C. The crude product was purified by trituration in pentane, but all of the impurities could not be seperated. The yield of this reaction was 80 %, but there were still impurities left in this material. It is also a possibility that there is product inside, which has the hypervalent iodine and trimethylsilyl moieties in *para* position. Because of the electron withdrawing group properties the major product must be (4,6-bis(trimethylsilyl)-1,3-phenylene)bis(phenyl-λ^3-iodanediyl) bis(trifluoromethanesulfonate) (**68**) (Scheme 45).

4.3. Precursor molecules for 2,6-naphthodiyne generation

Of course it is possible to expand the aromatic system of aryne chemistry. Therefore some experiments were done on the aromatic system of naphthalene to produce some precursor molecules, which could be used for 2,6-naphthodiyne (**62**) generation. Unfortunately 2,3,6,7-tetrahalonaphthalene is very expensive, therefore the starting material of all reactions, which were performed on the naphthalene-core, was 2,6-dihydroxynaphthalene (**66**).

4.3.1. Preparation of 3,6-dibromonaphthalene-2,7-diol



Scheme 46: Generation of 3,6-dibromonaphthalene-2,7-diole (**81**) using 2,6-dihydroxynaphthalene (**66**) as substrate

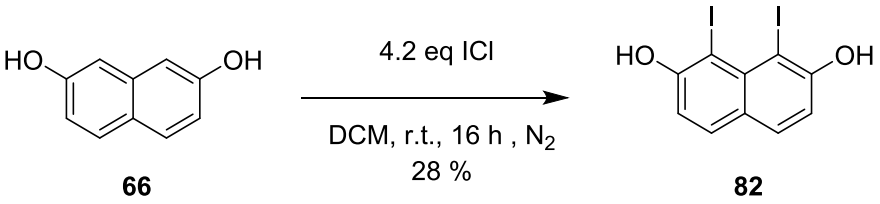
In this reaction elementary bromine is used as bromination reagent. In some cases *N*-bromosuccinimide is used to avoid too high local bromine concentrations, but in this case it does not matter which bromine source is used. This reaction is performed in acetic acid as solvent and was described by MENG.[49] Therefore 1.0 eq of 2,6-dihydroxynaphthalene is

treated with 4.0 eq of bromine solution in acetic acid under inert atmosphere. While bromine was added a huge amount of solid precipitated. Hence mechanical stirrers should be used in this reaction. After heating for a period of 1 h under inert atmosphere 2.0 equivalents of tin were added in small portions. Tin is added in this reaction, because in this time the reaction mixture consists of 1,3,6-tribromonaphthalene-2,7-diol to some part. The tin removes the unwanted bromine moiety in the 1-position selectively. Therefore the reaction was heated for 16 h under inert atmosphere. During the heating process the precipitated solid disappeared. Just tin remained as solid in the reaction mixture. After work-up and purification by recrystallization a yield of 62 % was obtained (Scheme 46).

4.3.2. Iodinated 2,6-dihydroxynaphthalene compounds

The aim of the precursor molecules is to generate 2,6-naphthodiyne (**62**). In this route of 2,6-naphthodiyne generation the aryne intermediate is produced via lithium-halogen exchange reaction. Iodinated compounds for this kind of reaction are better than brominated compounds. That is the reason why in this work some diiodinated naphthalene-2,6-diole compounds are produced. The products, which are generated by two different experiments are not known in literature.

4.3.2.1. Preparation of 1,8-diiodonaphthalene-2,7-diol

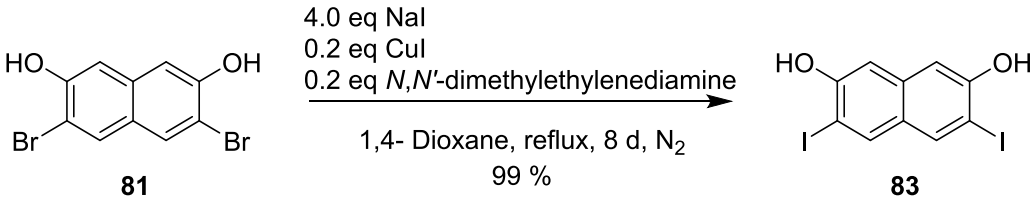


Scheme 47: Generation of 1,8-diiodonaphthalene-2,7-diole (**82**) using 2,6-dihydroxynaphthalene (**66**) as substrate

In order to access 3,6-diiodonaphthalene (**83**) 2,6-dihydroxynaphthalene (**66**) was treated with iodine monochloride. This reagent was preferred to molecular iodine, because the iodine-atom in this molecule is positively charged because of its lower electronegativity. So the aromatic system should selectively attack the iodine and get iodinated like in the case of preparation of 3,6-dibromonaphthalene-2,7-diol, in which that substrate got brominated. Hence 1.0 eq of naphthalene-2,7-diol was treated with 4.2 eq of iodine monochloride, which was dissolved in absolute dichloromethane. After the dropwise addition of the iodine monochloride solution, the reaction mixture was stirred for 16 h at r.t. under inert atmosphere. After work-up and

purification by recrystallization 28 % yield were obtained. But the characterization of that product showed, that the iodine atoms were attached in a position different from the one expected. So in this experiment a regioselective iodination was performed, which is extremely kinetically disfavoured. Furthermore iodination on aromatic systems were often performed by functional group exchange reaction. So this reaction is unique, because iodine atoms were introduced into an aromatic system without functional group exchange reaction and the product, which is formed, has an extremely high internal strain, because of the *peri*-direction of the iodine moieties (Scheme 47).

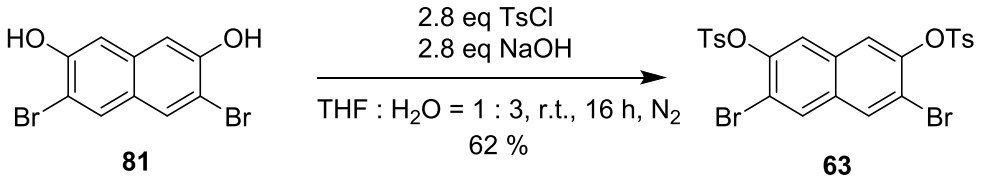
4.3.2.2. Preparation of 3,6-diiodonaphthalene-2,7-diol



Scheme 48: Generation of 3,6-diiodonaphthalene-2,7-diol (**83**) using 3,6-dibromonaphthalene-2,7-diole (**81**) as substrate

To achieve the desired regioselectivity of the iodinated naphthalene-2,7-diole for 2,6-naphthodiyne (**62**) generation another route of synthesis had been chosen. BUCHWALD *et. al.* described a method, which can selectively exchange a bromine moiety into an iodine moiety on an aromatic system. This modified FINKELSTEIN reaction is copper(I) catalyzed and a special ligand is needed to activate the copper ion.[50] In this experiment 1.0 eq of 3,6-dibromonaphthalene-2,7-diol (**81**) is treated with 4.0 eq sodium iodide, 0.2 eq of copper(I) iodide and 0.2 equivalents of *N,N'*-dimethylethylenediamine. In this reaction dry 1,4-dioxane is used as solvent. The reaction mixture is heated under reflux for 8 d under inert atmosphere. Here it is important that there are no traces of oxygen inside the reaction flask. Therefore the reaction mixture should be flushed with inert gas for at least 15 min. It is also possible to add substoichiometric amount of sodium ascorbate to avoid the oxidation of copper(I). After work-up and purification via recrystallization quantitative yield was obtained. This iodinated product is also unknown in literature (Scheme 48).

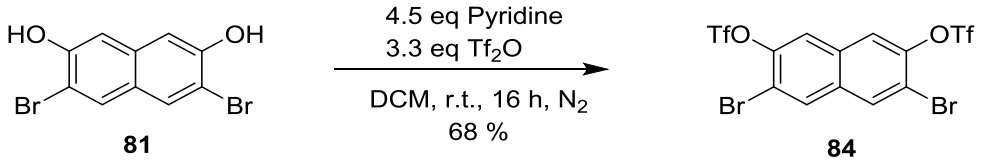
4.3.3. Preparation of 3,6-dibromonaphthalene-2,7-diyl bis(4-methylbenzenesulfonate)



Scheme 49: Generation of 3,6-dibromonaphthalene-2,7-diyl bis(4-methylbenzenesulfonate) (**63**) using 3,6-dibromonaphthalene-2,7-diol (**81**) as substrate

The goal of this experiment was to transform the phenol moieties to leaving groups to prepare a precursor molecule, which could be used for 2,6-naphthodiyne (**62**) generation. In this experiment a solvent mixture consisting of tetrahydrofuran and water in the ratio of 1 : 3 was used. This kind of option for a tosylation reaction was describes by HEATHCOTE.[47] Therefore 1.0 eq of 3,6-dibromonaphthalene-2,7-diol (**81**) was treated with 2.8 eq of sodium hydroxide and 2.8 eq of *p*-toluenesulfonyl chloride. The hydroxide deprotonated the phenol moieties of the substrate and made the oxygen atom of the deprotonated phenol moieties more nucleophilic. After that the phenolates attacked the *p*-toluenesulfonyl chloride and the product formation occurred. After 16 h of vigorously stirring the product was collected by filtration and washed with water. After work-up the crude product was purified by recrystallization from toluene. The yield of this reaction was 62 %, which could be higher, because some loss of product via recrystallization could not be avoided (Scheme 49).

4.3.4. Preparation of 3,6-dibromonaphthalene-2,7-diyl bis(trifluoromethanesulfonate)



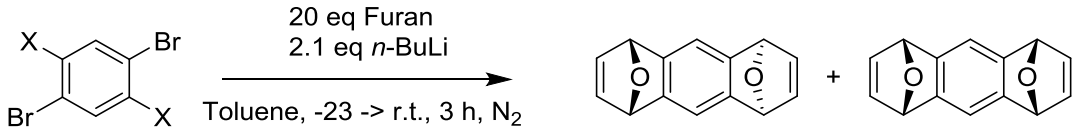
Scheme 50: Generation of 3,6-dibromonaphthalene-2,7-diyl bis(trifluoromethanesulfonate) (**84**) using 3,6-dibromonaphthalene-2,7-diol (**81**) as substrate

Again a precursor molecule should be prepared, which could be used for 2,6-naphthodiyne (**62**) generation. But this time leaving groups are trifluoromethanesulfonates instead of 4-methylbenzenesulfonates. In this case 3,6-dibromonaphthalene-2,7-diol (**81**) was used as substrate. In this experiment 4.5 eq of a softer base (pyridine) were used to activate

the trifluoromethanesulfonic anhydride. The activated ammonium species could be attacked by the phenol without deprotonation.[41] The dropwise addition of 3.3 eq of trifluoromethane-sulfonic anhydride was performed at 0 °C, because this reaction is quite exothermic. This reaction normally should be finished after 2 h, but in some cases it takes a little bit longer. In the work-up the organic phase was washed with 1 M hydrochloric acid-solution to protonate the rest of the pyridine and isolate the product from the reagents. After work-up the crude product was purified via flash column chromatography. The yield of this reaction was 68 %, which could be higher, because there is often some loss of product via column chromatography. (Scheme 50).

4.4. *In situ* generation of benzdiyne and 2,6-naphthodiyne intermediate and subsequent cycloaddition using furan as diene

In this chapter preexperiments were performed, in which the aryne intermediates benzdiyne (**57**) and 2,6-naphthodiyne (**62**) are produced *in situ*. Because of the very high reaction potential and the intrinsic instability of the aryne intermediates the experiments were performed in toluene with a 20-fold excess of a diene (furan (**47**)) corresponding to the substrate to perform the [*4+2*]-cycloadditions and produce 1,4,5,8-tetrahydro-1,4:5,8-diepoxyanthracene (**85**). In these experiments 1.0 eq of an aromatic precursor molecule, which contains two bromine moieties (**59**, **70**, **71**), was treated with 2.1 eq of *n*-BuLi in a solvent mixture, which consists of toluene and 20 eq of furan (**47**) (Scheme 51).



X = Br 59
X = OTf 70
X = OTs 71

85a **85b**

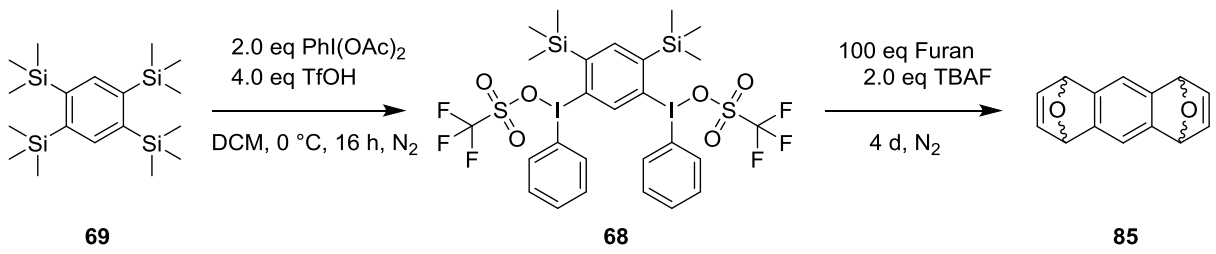
Scheme 51: [*4+2*]-Cycloaddition with furan (**47**) using different precursor molecules (**59**, **70**, **71**)

The *n*-butyllithium solution was added dropwise at -23 °C under inert atmosphere to the reaction mixture. After the addition of *n*-BuLi the reaction mixture was allowed to reach r.t. and was stirred for 3 h at r.t. under inert atmosphere. After work-up the product mixture was purified via flash column chromatography. Using this purification method the separation of the desired stereoisomer was possible (*anti* = **85a**, *syn* = **85b**). Isolated yields of the different reactions are listed in Table 2.

Table 2: Screening reactions to produce 1,4,5,8-tetrahydro-1,4:5,8-diepoxyanthracene (**85**) using 1,2,4,5-tetrabromobenzene (**59**), 2,5-dibromo-1,4-phenylene bis(trifluoromethanesulfonate) (**70**), 2,5-dibromo-1,4-phenylene bis(4-methylbenzenesulfonate) (**71**) as substrate substrates

entry	substrate	isolated yield *anti*-product in % (85a)	isolated yield *syn*-product in % (85b)
1	**59**	28	25
2	**70**	15	18
3	**71**	-	-

In this part of the chapter the *in situ* generation of benzdiyne (**57**) via *in situ* generation of (4,6-bis(trimethylsilyl)-1,3-phenylene)bis(phenyl-λ^3-iodanediyl) bis(trifluoromethane-sulfonate) (**68**) and further coupling with furan (**47**) is discussed. In all of these experiments 2.0 eq of (diacetoxyiodo)benzene were treated with 4.0 eq of trifluoromethanesulfonic acid in absolute dichloromethane under inert atmosphere. Because of the light sensitive aromatic iodine species the reaction flask always was protected from light. After at least 4 h of vigorously stirring a solution of 1.0 eq of 1,2,4,5-tetrakis(trimethylsilyl)benzene (**69**) in absolute dichloromethane was added dropwise over a period of 15 min at 0 °C under inert atmosphere. After the addition of 1,2,4,5-tetrakis(trimethylsilyl)benzene the reaction mixture was stirred for 16 h at 0 °C under inert atmosphere. After that 4.1 eq of 2,6-di *tert*-butylpyridine were added in just one experiment and the reaction mixture was further stirred for 15 min. The solvent was removed by reduced pressure at 0 °C, because it is likely, that the generated hypervalent iodine species degrades at higher temperatures. Subsequently approximately 100 eq of furan (**47**) and 2.0 eq of TBAF were added at different temperatures under inert atmosphere (Scheme 52, Table 3).



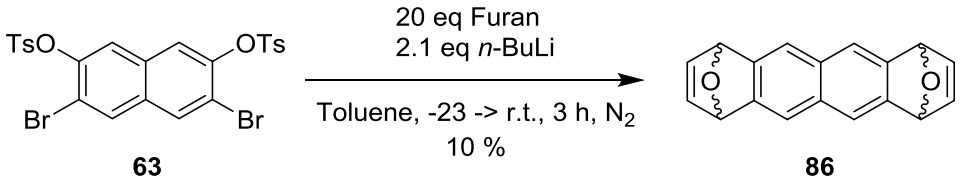
Scheme 53: [*4+2*]-Cycloaddition with furan (**47**) using (4,6-bis(trimethylsilyl)-1,3-phenylene)bis(phenyl- λ^3-iodanediyl) bis(trifluoromethanesulfonate) (**68**) as substrate

Table 3: Screening reactions to produce 1,4,5,8-tetrahydro-1,4:5,8-diepoxyanthracene (**85**) using (4,6-bis(trimethylsilyl)-1,3-phenylene)bis(phenyl- λ^3-iodanediyl) bis(trifluoromethanesulfonate) (**68**) as substrate

entry	reagent	temperature	additive	product yield [%]
1	TBAF	r.t.	-	-
2	abs. TBAF	-30	-	-
3	abs. TBAF	-10	2,6-di *tert*-butylpyridine	-

Unfortunately no product formation was obtained using the different reaction conditions. Only little amounts of monocycloaddition product were detected by GC-MS.

The same experiment was performed using 3,6-dibromonaphthalene-2,7-diyl bis(4-methylbenzenesulfonate) (**63**) as substrate. Again 1.0 eq of 3,6-dibromonaphthalene-2,7-diyl bis(4-methylbenzenesulfonate) was treated with 2.1 eq of *n*-BuLi in a solvent mixture of toluene with 20 eq furan. The *n*-butyllithium solution was added dropwise at -23 °C under inert atmosphere to the reaction mixture. After the addition of *n*-BuLi the reaction mixture was allowed to reach r.t. and was stirred for 3 h at r.t. under inert atmosphere. After work-up the product mixture was purified via flash column chromatography, but this time the stereoisomers could not be separated. The yield in this reaction was 10 %, but this experiment shows, that it is also possible to produce an aryne intermediate using a poor leaving group, like in this case 4-methylbenzenesulfonate (Scheme 54).

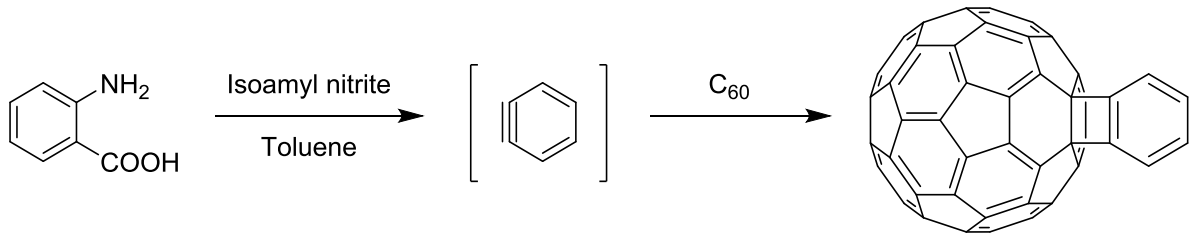


63 **86**

Scheme 54: Preparation of 1,4,7,10-tetrahydro-1,4:7,10-diepoxytetracene (**86**) using 3,6-dibromonaphthalene-2,7-diyl bis(4-methylbenzenesulfonate) (**63**) as substrate

4.5. *In situ* generation of benzyne intermediate and subsequent cycloaddition using BUCKMINSTER-fullerene as arynophile

To become familiar using C_{60}-fullerene (**2**) as reagent the benzyne adduct was generated. After accomplishment of the generation of the triple bond the aryne intermediate should react with BUCKMINSTER-fullerene via [*2+2*]-cycloaddition. Such a reaction is known in literature and was described by HOKE II *et. al.*.[8] This reaction was performed, to learn about the behaviour of fullerenes in solution and find the best solvent and reaction conditions, which should be used in fullerene-chemistry. Hence, 1.7 eq of anthranilic acid (**87**) were treated with 1.7 eq of isoamyl nitrite in the presence of 1.0 eq of C_{60}-fullerene (**2**) in toluene under inert atmosphere. The amount of toluene was quite high, because solubility of C_{60}-fullerene in toluene is 2.8 mg/mL.[51] After vigorously stirring for 3 d at r.t. the product mixture was subjected to purification. Because of the very apolar behaviour of the substrate and of the product as well, it was very hard to purify the product mixture. Normally the purification in fullerene-chemistry is performed with preparative HPLC using a special separation column, which has a high affinity to fullerenes. Unfortunately such a separation system was not available, therefore the purification had to be done by a different purification method. It was accomplished to purify [1,2]benzeno-C_{60}-fullerene (**88**) via preparative thin layer chromatography. The yield of this reaction was extremely low with 7 % (Scheme 55).



87 **11** **88**

Scheme 55: Generation of [1,2]benzeno-C_{60}-fullerene (**88**) using anthranilic acid (**87**) as substrate

After the characterization of the desired product several experiments were performed using different substrates, reagents stoichiometries and solvents. The results of these screening experiments are shown in Table 4.

Table 4: Screening reactions to produce [1,2]benzeno-C_{60}-fullerene (**88**) using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**31**), phenyl(2-(trimethylsilyl)phenyl)-λ^3-iodanyl trifluoromethanesulfonate (**32**), 2-bromophenyl trifluoromethanesulfonate (**33**), 1,2-dibromobenzene (**34**), anthranilic acid (**87**) as substrates

entry	C_{60}-fullerene (2) [eq]	substrate [eq]	reagent [eq]	solvent	product yield [%]
1	1.0	anthranilic acid (**87**) [1.7]	isoamyl nitrite [1.7]	toluene	7
2	1.0	1,2-dibromobenzene (**34**) [1.6]	*n*-BuLi [1.7]	toluene	-
3	1.0	2-bromophenyl trifluoromethanesulfonate (**33**) [1.9]	*n*-BuLi [2.0]	toluene	-
4	5.4	2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**31**) [1.0]	TBAF [1.1]	toluene	-
5	5.6	phenyl(2-(trimethylsilyl)phenyl)-λ^3-iodanyl trifluoromethanesulfonate (**32**) [1.0]	TBAF [1.1]	*o*-dichlorobenzene	4

Product formation could only be obtained in the case using the hypervalent iodine species as leaving group in *o*-dichlorobenzene as solvent. In the case of using furan (**47**) as scavenger reagent of the aryne intermediate using the hypervalent iodine precursor achieved quantitative yield, using a trifluoromethanesulfonate as leaving group instead the obtained product formation is 61 %.[44] It is also possible, that the reaction is too diluted using toluene as solvent. The solubility of fullerene in *o*-dichlorobenzene is approximately 10 times higher with 27 mg/mL.[51] So the possibility of a reaction between benzyne (**11**) and C_{60}-fullerene (**2**) is much higher in the case of using *o*-dichlorobenzene as solvent.

In the case using *n*-BuLi as reactant no product formation was observed. Maybe another reaction is preferred, hence the triple bond formation could never occur. The addition of organolithium reagents or GRIGNARD reagents onto the surface of BUCKMINSTER-fullerenes (**2**) is known in literature and was describe by HIRSCH.[52] So it is possible that the

reaction of fullerene with *n*-BuLi favoured the formation of an alkly adduct over the aryne generation and that could be the reason why no product was detected.

5. Summary and Outlook

The aim of this work was to synthesize substructures, which could be used as a part for the construction of a car on molecular scale. In detail, two BUCKMINSTER-fullerenes (**2**) should be connected with each other over an aromatic system. The common intermediate, which was generated in each reaction, was an aryne intermediate. Because of the instability and the resulting high reactivity, the aryne intermediates had to be generated *in situ*. Hence precursor molecules had to be produced, which should generate the aryne intermediates by different methods (Figure 9).

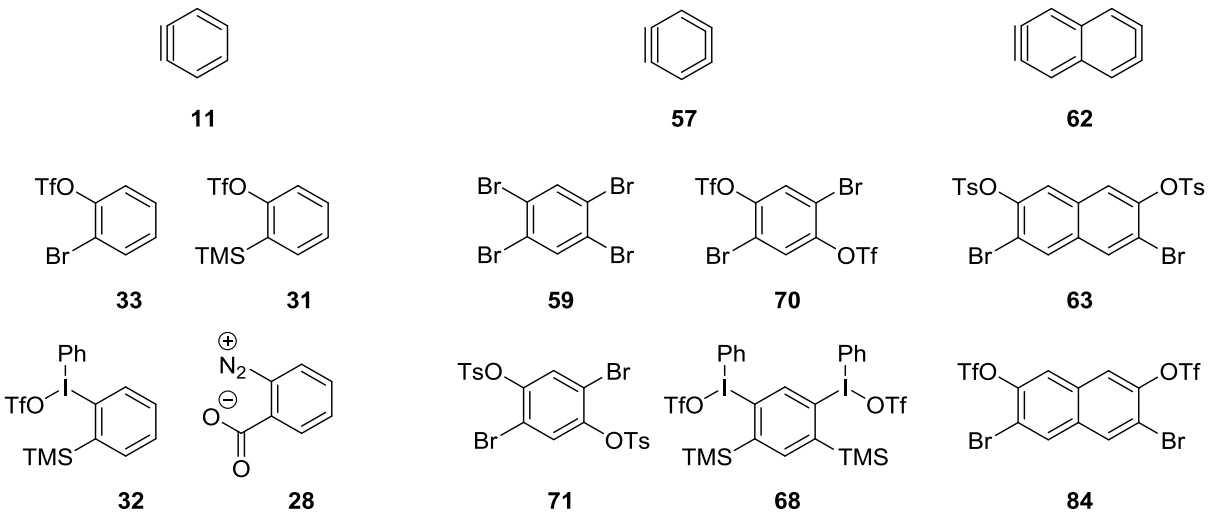


Figure 9: Isolated precursor molecules, which can be used for aryne generation

All of the molecules, which are shown in Figure 9, were synthesized and characterized, except 1,2,4,5-tetrabromobenzene (**59**), which was purchased from Alfa Aesar.

During the preparation of some precursor molecules, which could be used for 2,6-naphthodiyne (**62**) generation, two iodinated molecules were synthesized, which have not been described in literature before (Figure 10).

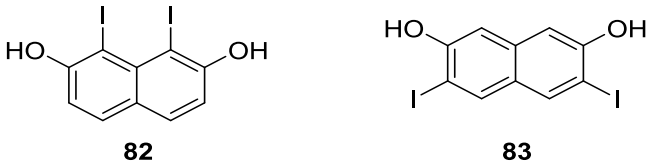
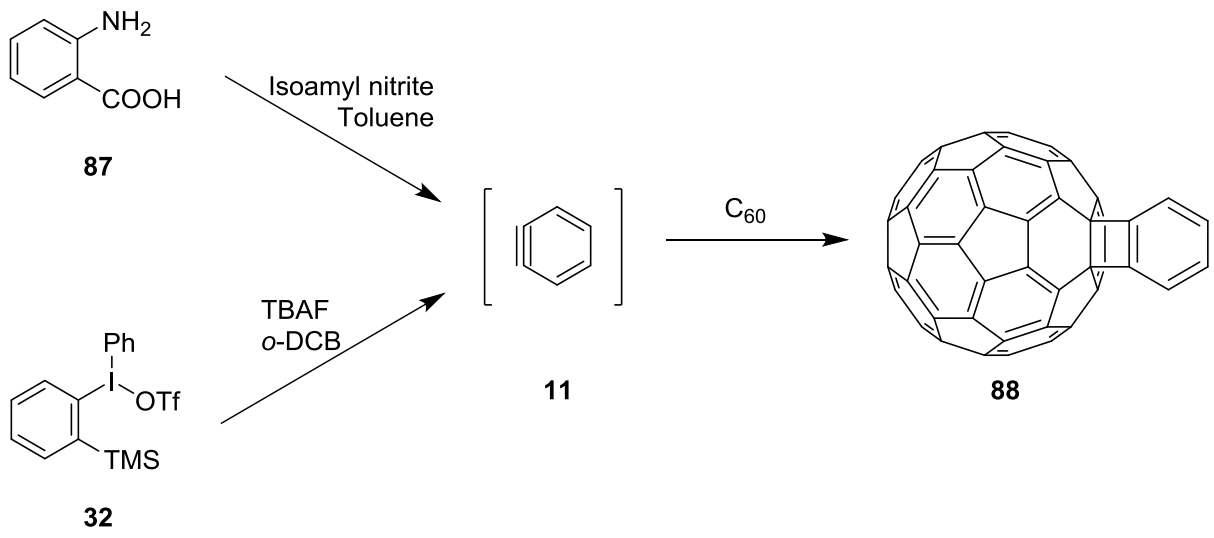


Figure 10: 1,8-Diiodonaphthalene-2,7-diol (**82**), 3,6-diiodonaphthalene-2,7-diol (**83**)

It is impressive, that the isolated product **82** after recrystallization consisted of two iodine moieties which are in *peri*-position. Such an arrangement of newly introduced functional groups is extremely kinetically disfavoured. So in this work a reaction was performed, which could selectively introduce iodine moieties into aromatic systems, which are in *peri*-position to each other. 3,6-Diiodonaphthalene-2,7-diole was synthesized from the corresponding 3,6-dibromonaphthalene-2,7-diol. These two iodinated naphthalenedioles were identified and characterized.

The synthesis of [1,2]benzeno-C_{60}-fullerene (**88**) via aryne generation was accomplished using anthranilic acid (**87**) as substrate, which was described by HOKE II *et. al.*[8] and using phenyl(2-(trimethylsilyl)phenyl)-λ^3-iodanyl trifluoromethanesulfonate (**32**) as substrate (Scheme 56).



Scheme 56: Preparation of [1,2]benzeno-C_{60}-fullerene (**88**) using different substrates for benzyne (**11**) generation

It is still a long way to go to achieve the desired goal. Therefore some experiments have to be done in future, which should optimize the cycloaddition reaction, because the yield in these experiments is extremely low. Maybe another route to generate the aryne intermediate is better and achieves higher yields. The connection of the second fullerene-tire has to be done, too. To accomplish bridged fullerenes over an aromatic system would be a milestone in this research and size exclusion chromatography might be suited to address the challenge of purification of those molecules.

6. Experimental

6.1. General Aspects, Material and Methods

Standard Schlenk technique was used for all synthesis and screening-experiments, if it is not otherwise noted. Therefore the glassware was evacuated and heated with a heat gun. After cooling the glassware was purged with inert gas (nitrogen or argon). Absolute solvents were obtained by different methods, which are noted in 6.1.1.2.. Reaction control was either performed by TLC, GC-MS, or HPLC (6.1.2.2., 6.1.2.4., 6.1.2.6.). For screening via GC-MS or HPLC, 5 droplets of each reaction mixture were distributed between ethyl acetate and saturated ammonium chloride-solution (1 mL). Subsequently the organic phase was filtered through a silica gel and $MgSO_4$ filled Pasteur pipette.

6.1.1. Materials

6.1.1.1. Chemicals

All chemicals for synthesis were purchased from ABCR Chemicals, Acros Organics, Alfa Aesar, Carl Roth, EGA Chemie, Fisher Scientific, Fluka, Merck, Sigma Aldrich and VWR Chemicals. These chemicals were used without further purification, unless noted in the experimental procedures.

6.1.1.2. Solvents

3 Å and 4 Å molecular sieves (MS) were dried at 150 °C by heating in a heating mantle and oil pump vacuum at 10^{-3} mbar for 2 d. Subsequently the molecular sieves were cooled to r.t. and stored under argon atmosphere.

Cyclohexane: Cyclohexane with a minimum amount of 99.99 % was purchased in 5 L plastic cans from Fisher Scientific.

Tetrahydrofuran (THF): Tetrahydrofuran with a minimum amount of 99 % was purchased from VWR Chemicals. It was distilled to remove the stabilizer 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) and stored in a 2.5 L dark Schlenk bottle over potassium hydroxide.

Tetrahydrofuran (THF) dry: Tetrahydrofuran was dried by heating under reflux over sodium under argon atmosphere. Dryness indication was performed by the addition of

benzophenone via formation of the ketyl-radical (deep blue). After distillation THF was stored under argon with 4 Å MS in a 2.5 L dark Schlenk bottle.

Ethyl acetate: Ethyl acetate with a minimum amount of 99.99 % was purchased in 5 L plastic cans from Fisher Scientific.

1,2-Dichlorobenzene: 1,2-Dichlorobenzene with a minimum amount of 99 % was purchased in 1 L darkened glass bottles from EGA Chemie.

1,2-Dichlorobenzene dry: 1,2-Dichlorobenzene was dried over 4 Å MS under nitrogen atmosphere.

Dichloromethane (DCM): Dichloromethane with a minimum amount of 99.99 % was purchased in 5 L plastic cans from Fisher Scientific.

Dichloromethane (DCM) dry: First dichloromethane was dried over phosphorus pentoxide, then over calciumhydride. After that it was distilled into a 1 L dark Schlenlk bottle and stored under argon atmosphere over 4 Å MS.

Diethyl ether: Diethyl ether with a minimum amount of 99 % was purchased from VWR Chemicals. It was distilled to remove the stabilizer 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) and stored in a 2.5 L dark Schlenk bottle over potassium hydroxide.

1,3-Dimethyl-2-imidazolidinone (DMI): 1,3-Dimethyl-2-imidazolidinone was purchased from Alfa Aesar.

Acetone: Acetone was purchased from Brenntag and purified by distillation.

Pyridine dry: Dry pyridine was purchased from Sigma Aldrich (99.8 %, anhydrous, under argon atmosphere).

***N*,*N*-Dimethylformamide (DMF):** *N*,*N*-Dimethylformamide with a minimum amount of 99.8 % was purchased from Carl Roth.

Toluene dry: Dry toluene was generated via a drying alox column apparatus. It was stored in a 2.5 L dark Schlenk bottle under argon atmosphere over 4 Å MS.

Furan: Furan was purchased from Fluka and purified by distillation.

1,4-Dioxane dry: 1,4-Dioxane was dried by heating under reflux over sodium under argon atmosphere. Dryness indication was performed by the addition of benzophenone via formation of the ketyl-radical (deep blue). After distillation 1,4-dioxane was stored under argon over 4 Å MS in a 2.5 L dark Schlenk bottle.

Saturated aqueous ammonium chloride: Ammonium chloride was added to distilled water under stirring until ammonium chloride precipitated.

Saturated aqueous sodium bicarbonate: Sodium bicarbonate was added to distilled water under stirring until sodium bicarbonate precipitated.

Saturated aqueous sodium chloride: Sodium chloride was added to distilled water under stirring until sodium chloride precipitated.

Saturated aqueous sodium thiosulfate: Sodium thiosulfate was added to distilled water under stirring until sodium thiosulfate precipitated.

Saturated aqueous sodium bisulfite: Sodium bisulfite was added to distilled water under stirring until sodium bisulfite precipitated.

6.1.1.3. Reagents

***n*-Butyllithium (*n*-BuLi):** *n*-Butyllithium was purchased from Sigma Aldrich as a 2.5 M solution. The concentration was determined by titration according to the method by W. G. KOFRON *et. al.*.[53] Therefore an oven dried 10 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 250.0 mg diphenylacetic acid and 10 mL dry tetrahydrofuran. The reaction mixture was stirred vigorously, while the *n*-BuLi solution was added via a 1 mL syringe until the color of the reaction mixture changed to yellow. The added amount of *n*-BuLi corresponds to the weighted amount of diphenylacetic acid. The concentration of *n*-BuLi was determined as the average value of at least three assignments.

Tetrabutylammonium fluoride (TBAF) dry: Tetrabutylammonium fluoride trihydrate was purchased from Sigma Aldrich. It was dried after the procedure of D. P. COX *et. al.*.[54] Therefore an oven dried 10 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with tetrabutylammonium fluoride trihydrate. Afterwards the TBAF was heated to 40 °C in the vacuum of an oil pump at 10^{-3} mbar for 3 d. Thereby the crystals disappeared and the TBAF got amorphous.

6.1.2. Analytical Methods

6.1.2.1. Flash Chromatography

60 Å silica gel with a particle size between 35 - 70 µm, which was purchased from Acros Organics, was used for column chromatography. Applied pressure and amount of silica gel (20 - 100 fold) depended on the separation problem.

6.1.2.2. Thin Layer Chromatography (TLC)

Thin layer chromatography silica gel on aluminium foil (60 F_{254}) was used for reaction control. Detections were carried out with UV-light (254 nm).

6.1.2.3. Preparative Thin Layer Chromatography (prep. TLC)

Preparative thin layer chromatography silica gel on glass plates with a silica gel thickness of 2 mm (60 F_{254}) were used for purification. The product mixture was dispersed in 4 mL toluene and applied to the surface of the silica gel plate by a TLC pipetting device. Detections were carried out with UV-light (254 nm).

6.1.2.4. Gas Chromatography Mass Spectrometry (GC-MS)

An Agilent Technologies 7890A equipped with a polar Agilent Technologies J&W HP 5MS capillary (30 m x 0.25 mm x 0.25 µm film (5 % phenyl)methylpolysiloxane) in spilt mode with carrier gas (He 5.0) was used for analytical gas chromatography. The injection was performed by an Agilent Technologies 7683 autosampler. Methanol and dichloromethane were used to wash the needle of the autosampler before and after injection. Ionization was achieved via Electron Impact Ionization (EI, E = 70 eV). Masses were analyzed through Mass analyzer 5975C with MSD and triple axis detector. In the associated experiments retention time t_R, basic peak (BP) and molecular peak (relative intensity to the basic peak (BP)) are listed. Because of no use of an internal standard the intensities of the different peak can only be seen as relative.

CL_50_S: 50 °C 1 min, ramp 40 °C/min linear to 300 °C, 5 min.

6.1.2.5. High Resolution Mass Spectrometry (HR-MS)

High resolution mass spectrometry was performed on a Waters GCT premier micromass. The products were ionized by an Electron Impact Ionization (EI)-source with 70 eV. Probes were

either injected via an Agilent Technologies GC 7890A with capillary column (DB-5MS, 30 m x 0.25 mm x 0.25 µm film) or via direct inlet. Micromass Tofspec 3E spectrometer with matrix assisted laser desorption ionization (MALDI) was used for the analysis of heavier molecules, *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile as matrix, sodium trifluoroacetate as sodium source and a time of flight mass analyzer (TOF).

6.1.2.6. High Performance Liquid Chromatography (HPLC)

All analytical HPLC measurements were performed on a Shimadzu Nexera Liquid Chromatograph with thermostatically controlled column oven. The separation of the analytes was carried out using a C-18 reversed-phase column of the type Poroshell® 120 SB-C18, 3.0 x 100 mm, 2.7 µm by Agilent Technologies. Detection of the substances was accomplished with a Shimadzu SPD-M20A Prominence Diode Array Detector at a wavelength of $\lambda = 254$ nm. As eluents acetonitrile and water with 0.01 % formic acid as additive were used.

allgemein 30zu100: 0.0-0.5 min 30 % acetonitrile and 70 % water, 0.5-6.5 min linear to 100 % acetonitrile, 6.5-7.2 min 100 % acetonitrile, 7.2-7.3 min linear to 30 % acetonitrile and 70 % water; 0.70 mL/min, 40 °C

6.1.2.7. Nuclear Magnetic Resonance Spectroscopy (NMR)

All measured NMR-spectra were recorded on a Bruker Avance III 300 MHz FT NMR spectrometer with autosampler (300.36 MHz (^{1}H-NMR); 75.53 MHz (^{13}C-NMR)). Chemical shifts δ are referenced to the residual protonated solvent signals as internal standard. ^{13}C and APT spectra were proton decoupled. Signal multiplicities *J* are abbreviated as s (singlet), d (doublet), dd (doublet of doublet), t (triplet), dt (doublet of triplet) and m (multiplet). For the correct assignment of the signals HH-COSY and HSQC experiments were recorded if necessary. Moreover, the deuterated solvent, the chemical shifts δ in ppm (parts per million), the coupling constant *J* in Hertz (Hz) and the integral and assignment of the respective signals are given.

6.1.2.8. IR-Spectroscopy

A Bruker Tensor 37 with a Standard Pike ATR cell was used to perform FT-IR-spectroscopy. It is equipped with a room temperature detector, mid IR source (4000 - 400 cm^{-1}). Before every measurement of a product background spectra were performed. 16 scans were executed per analytical measurement in a range of 4000-600 cm^{-1}.

6.1.2.9. Melting Point

Melting points were determined with a Mel Temp melting point apparatus with integrated microscopical support from Electrothermal in open capillary tubes. The temperature was measured using a mercury thermometer. Melting points were not corrected.

6.2. Experimental Procedures

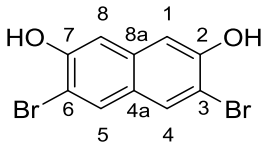
6.2.1. General Cyclisation Reaction with Furan

An oven dried 20 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 0.25 mmol (1.0 eq) benzdiyne-precursor, which contains bromine moieties, 370 µL (5.11 mmol, 20 eq) furan and 4 mL absolute toluene under inert atmosphere. The reaction mixture was cooled in an acetone/dry-ice bath to -25 °C and stirred for 15 min. Subsequently 230 µL (0.53 mmol, 2.1 eq) 2.3 M *n*-butyllithium-solution were added dropwise over a period of 10 min at -25 °C under inert atmosphere to the reaction mixture. Then the acetone/dry-ice bath was removed and reaction control was performed by TLC.

6.2.2. General Cyclisation Reaction with Fullerene

An oven dried 100 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 50.0 mg (0.69 mmol, 5.5 eq) C_{60}-fullerene, 250 µL (0.13 mmol, 1.0 eq) 0.05 M benzyne-precursor-solution, which contains a trimethylsilyl moiety and 8 mL absolute 1,2-dichlorobenzene under inert atmosphere. The deep violet reaction mixture was flushed with inert gas for 15 min, while it was treated with ultrasonic sound. Subsequently 130 µL (0.13 mmol, 1.1 eq) 0.1 M dry tetrabutylammonium fluoride-solution were added dropwise over a period of 10 min at r.t. under inert atmosphere to the reaction mixture. Reaction control was performed by TLC.

6.2.3. 3,6-Dibromonaphthalene-2,7-diole (81)



An oven dried 500 mL three-neck round-bottom flask equipped with a Teflon-coated magnetic stir bar, a reflux condenser, a glass stopper and a nitrogen inlet was charged with 10.0 g (62.4 mmol, 1.0 eq) 2,7-dihydroxynaphthalene and 100 mL glacial acetic acid under nitrogen atmosphere. The suspension consisting of a green liquid and a grey solid was stirred for 15 min at r.t.. Afterwards an oven dried 100 mL Schlenk flask was charged with 12.8 mL (250 mmol, 4.0 eq) bromine and 70 mL glacial acetic acid. The glass stopper of the three-neck round-bottom flask was exchanged with a dropping funnel. The dropping funnel was filled with the prepared bromine solution in acetic acid under inert atmosphere. The bromine solution was added dropwise over a period of 30 min. Thereby the color of the solution changed from green into dark brown. After the addition of 60 mL of the bromine solution a bright orange solid appeared. The reaction mixture was heated to 80 °C for 1 h under nitrogen. Subsequently the reaction mixture was allowed to cool down to r.t. and was diluted with 30 mL distilled water and 30 mL of acetic acid. The reaction control was done by GC. 14.8 g (125 mmol, 2.0 eq) tin were added to the reaction mixture at r.t.. After that the reaction mixture was heated to 150 °C for 24 h. After a heating period of 15 min the orange solid disappeared. Subsequently the acetic acid was removed under reduced pressure and a yellow solid precipitated. The yellow solid was treated with 100 mL of water and was collected by filtration. The crude product was dissolved in 50 mL ethyl acetate, washed with saturated sodium thiosulfate solution (3 x 30 mL), dried over sodium sulfate and filtered through cotton. Finally the solvent was removed under reduced pressure and the bright brown solid was dried in oil pump vacuum at 10^{-3} mbar.

Yield: 12.7 g (39.8 mmol, 62 % o. th.) bright brown solid

$C_{10}H_6Br_2O_2$ [317.96 g/mol]

R_f = 0.33 (cyclohexane/ethyl acetate = 2:1 (v/v), 254 nm)

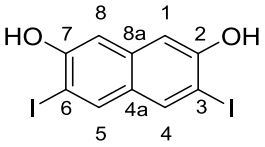
GC-MS (CL_50_S): t_R = 7.69 min; *m/z* = 318 (100 %, MP, BP).

mp: 184 °C

^{1}H-NMR: (300.36 MHz, Methanol d_4): δ = 7.86 (s, 2H, H-4, H-5), 7.00 (s, 2H, H-1, H-8).

^{13}C-NMR (75.53 MHz, Methanol d_4): δ = 153.7 (C-2, C-7), 136.0 (C-8a), 131.9 (C-4, C-5), 126.2 (C-4a), 111.3 (C-3, C-6), 109.3 (C-1, C-8).

6.2.4. 3,6-Diiodonaphthalene-2,7-diole (83)



An oven dried 20 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 6.9 mg (0.04 mmol, 0.2 eq) copper(I) iodide and 97.3 mg (0.63 mmol, 4.0 eq) sodium iodide. The salt mixture was dried in the vacuum of an oil pump at 10^{-3} mbar for 30 min. Another oven dried 20 mL Schlenk flask was charged with 49.9 mg (0.16 mmol, 1.0 eq) 3,6-dibromonaphthalene-2,7-diole, 4.1 µL (0.04 mmol, 0.2 eq) *N,N'*-dimethyl-ethylenediamine and 1 mL of absolute 1,4-dioxane. The brown reaction solution was flushed with inert gas, while it was treated with ultrasonic sound for 30 min. After that the brown mixture, which consisted of 3,6-dibromonaphthalene-2,7-diole, *N,N'*-dimethylethylendiamine and 1,4-dioxane, was added dropwise via a syringe over a period of 10 min to the Schlenk flask filled with copper(I) iodide and sodium iodide. Subsequently the brown reaction mixture was dissolved with 2 mL of absolute 1,4-dioxane, heated to 135 °C and stirred at 135 °C for 8 d. The reaction control was performed by HPLC. After complete conversion the 1,4-dioxane was removed under reduced pressure and the remaining reaction mixture was dissolved in 10 mL of ethyl acetate. The reaction mixture was transferred into an extraction funnel. The phases were separated, the organic phase was washed with saturated ammonium chloride-solution (2 x 10 mL) and water (1 x 10 mL). The aqueous phase was reextracted with ethyl acetate (2 x 20 mL). Subsequently the organic phase was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The product was purified by recystallization from 5 mL cyclohexane.

Yield: 65 mg (0.16 mmol, 99% o. th.), red-brown solid

$C_{10}H_6I_2O_2$ [411.96 g/mol]

HR-MS (EI: [M]) [*m/z*]: calculated: 411.8457, found: 411.8447

mp: 172 °C

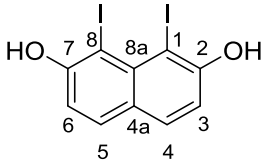
R_f = 0.31 (cyclohexane/ethyl acetate = 2:1 (v/v)), (254 nm)

HPLC-UV-Vis (allgmein 30zu100): t_R = 4.09 min, (254 nm).

^{1}H-NMR: (300.36 MHz, Methanol d_4): δ = 8.08 (s, 2H, H-4, H-5), 6.93 (s, 2H, H-1, H-8).

^{13}C-NMR (75.53 MHz, Methanol d_4): δ = 155.8 (C-2, C-7), 138.8 (C-4, C-5), 137.5 (C-8a), 127.9 (C-4a), 107.7 (C-1, C-8), 84.8 (C-3, C-6).

6.2.5. 1,8-Diiodonaphthalene-2,7-diole (82)



An oven dried 10 mL one-neck round bottom flask equipped with a Schlenk adapter and a Teflon-coated magnetic stir bar was charged with 49.7 mg (0.31 mmol, 1.0 eq) 2,7-dihydroxynaphthalene and 3 mL absolute dichloromethane. Further, an oven dried 10 mL Schlenk flask was charged with 221 mg (1.36 mmol, 4.2 eq) iodine monochloride and 4 mL absolute dichloromethane. The dark red iodine monochloride-solution was added dropwise via a syringe over a period of 15 min under inert atmosphere at r.t. to the yellowish-green reaction mixture, which consisted of 2,7-dihydroxynaphthalene and dichloromethane. Thereby the color of the reaction mixture changed from yellowish-green to dark red. The round bottom flask was covered with aluminium foil to protect the reaction mixture from light. Subsequently the reaction mixture was stirred for 16 h at r.t.. Thereby the reaction control was performed by TLC. The reaction mixture was transferred into a separation funnel and washed with saturated sodium bisulfite-solution (2 x 10 mL) and brine (1 x 10 mL). The aqueous phase was reextracted with dichloromethane (2 x 10 mL), the combined organic phases were dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The product was purified by recystallization from 5 mL cyclohexane.

Yield: 36 mg (0.09 mmol, 28% o. th.), red-brown solid

$C_{10}H_6I_2O_2$ [411.96 g/mol]

HR-MS (EI: [M]) [*m/z*]: calculated: 411.8457, found: 411.8466

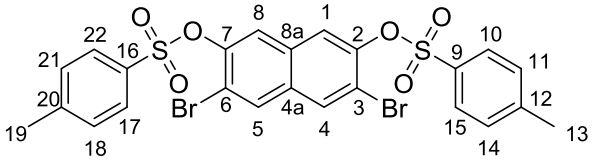
mp: 164 °C

R_f = 0.27 (cyclohexane/ethyl acetate = 5:1 (v/v)), (254 nm)

^{1}H-NMR: (300.36 MHz, Methanol d_4): δ = 7.57 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H-4, H-5), 7.02 (s, $^3J_{HH}$ = 8.8 Hz, 2H, H-3, H-6).

^{13}C-NMR (75.53 MHz, Methanol d_4): δ = 154.7 (C-2, C-7), 130.6 (C-8a), 130.2 (C-4, C-5), 127.2 (C-4a), 116.4 (C-3, C-6), 112.7 (C-1, C-8).

6.2.6. 3,6-Dibromonaphthalene-2,7-diyl bis(4-methylbenzenesulfonate) (63)



An oven dried 100 mL one-neck round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with 1.00 g (3.15 mmol, 1.0 eq) 3,6-dibromo-2,7-dihydroxynaphthalene, 1.68 g (8.83 mmol, 2.8 eq) *p*-toluenesulfonylchloride and 353 mg (8.83 mmol, 2.8 eq) sodium hydroxide. The solids were treated with 10 mL of tetrahydrofuran. The yellow suspension was stirred for 15 min at r.t.. Then 30 mL of water were added and the solids dissolved. After 1 min of vigorously stirring a pale yellow solid precipitated. The reaction mixture was stirred for 16 h at r.t.. TLC was used for reaction control. Tetrahydrofuran was removed under reduced pressure. The product was extracted with dichloromethane (3 x 15 mL), dried over sodium sulfate, filtered, the solvent was removed under reduced pressure and finally recrystallized from 20 mL toluene.

Yield: 1.24 g (1.98 mmol, 62 % o. th.), colorless solid

$C_{24}H_{18}Br_2O_6S_2$ [626.33 g/mol]

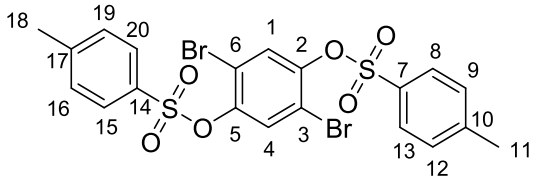
R_f = 0.68 (cyclohexane/ethyl acetate = 2:1 (v/v), 254 nm)

mp: 155 °C

^{1}H-NMR: (300.36 MHz, $CDCl_3$): δ = 7.92 (s, 2H, H-4, H-5), 7.83 (d, $^3J_{HH}$ = 8.2 Hz, 4H, H-10, H-15, H-17,H-22), 7.74 (s, 2H, H-1, H-8), 7.35 (d, $^3J_{HH}$ = 8.2 Hz, 4H, H-11, H-14, H-18, H-21), 2.48 (s, 6H, H-13, H-19).

^{13}C-NMR (75.53 MHz, $CDCl_3$): δ = 146.2 (C-2, C-7), 145.2 (C-12, C-20), 132.7 (C-8a), 131.8 (C-4, C-5), 131.7 (C-9, C-16), 131.5 (C-4a), 130.1 (C-11, C-14, C-18, C-21), 128.9 (C-10, C-15, C-17, C-22), 121.5 (C-1, C-8), 116.9 (C-3, C-6), 21.96 (C-13, C-19).

6.2.7. 2,5-Dibromo-1,4-phenylene bis(4-methylbenzenesulfonate) (71)



An oven dried 100 mL one-neck round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with 1.00 g (3.73 mmol, 1.0 eq) 2,5-dibromo-1,4-dihydroxybenzene, 2.00 g (10.5 mmol, 2.8 eq) *p*-toluenesulfonylchloride and 421 mg (10.5 mmol, 2.8 eq) sodium hydroxide. The solids were treated with 10 mL of tetrahydrofuran. The colorless suspension was stirred for 15 min at r.t.. Then 30 mL water were added and the solids dissolved. After 1 min of vigorously stirring a colorless solid appeared. The reaction mixture was stirred for 16 h at r.t.. TLC was used for reaction control. Tetrahydrofuran was removed under reduced pressure. The product was collected by filtration and dried in the vacuum of an oil pump for 2 d.

Yield: 2.07 g (3.59 mmol, 96 % o. th.), colorless solid

$C_{20}H_{16}Br_2O_6S_2$ [576.27 g/mol]

HR-MS (EI: [M]) [*m/z*]: calculated: 573.8755, found: 573.8763

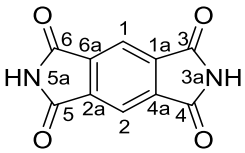
R_f = 0.70 (cyclohexane/ethyl acetate = 2:1 (v/v), 254 nm)

mp: 218 °C

IR (cm^{-1}): 3101 (C-H stretch, aromatic), 1383 (R-SO_2-OR'), 1088 (Aryl-Br frame oscillation).

^{1}H-NMR: (300.36 MHz, DMSO d_6): δ = 7.71 (d, $^3J_{HH}$ = 8.2 Hz, 4H, H-8, H-13, H-15, H-20), 7.46 (s, 2H, H-1, H-4), 7.45 (d, $^3J_{HH}$ = 8.2 Hz, 4H, H-9, H-12, H-16, H-19), 2.37 (s, 6H, H-11, H-18).

6.2.8. Benzene-1,2,4,5-tetracarboxylic diimide (78)



An oven dried 100 mL one-neck round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with 36 mL (231 mmol, 5.0 eq) 25 % solution of ammonium hydroxide in water. The reaction vessel was cooled in an ice-water bath and 10.0 g (46.0 mmol, 1.0 eq) of benzene-1,2,4,5-tetracarboxylic dianhydride were added in small portions, while the reaction mixture was stirred vigorously. During the addition of benzene-1,2,4,5-tetracarboxylic dianhydride a colorless solid precipitated. The reaction mixture was heated to 165 °C for 16 h. The reaction mixture was cooled in an ice-water bath for 20 min and the aqueous phase was treated with 1 M HCl until pH 2 was reached. The colorless solid was collected by filtration and washed with 40 mL cold water. A 100 mL one-neck round-bottom flask was charged with the collected colorless solid and heated to 200 °C for 24 h. The color of the solid turned into bright yellow. The bright yellow solid was recrystallized from 100 mL *N*,*N*-dimethylformamide and dried in the vacuum of an oil pump for 2 d.

Yield: 2.14 g (9.90 mmol, 21 % o. th.), bright yellow solid

$C_{10}H_4N_2O_4$ [216.15 g/mol]

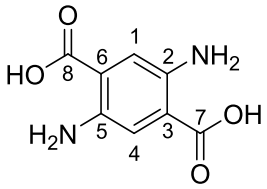
mp: > 360 °C

^{1}H-NMR: (300.36 MHz, DMSO d_6): δ = 11.82 (s, 2H, H-3a, H-5a), 7.95 (s, 2H, H-1, H-2).

^{13}C-NMR (75.53 MHz, DMSO d_6): δ = 167.6 (C-3, C-4, C-5, C-6), 137.9 (C-1a, C-2a, C-4a, C-6a), 117.2 (C-1, C-2).

IR (cm^{-1}): 3514 (N-H stretch, imide), 3446 (N-H bend, imide), 1740 (C=O-amide valence oscillation), 1544 (cyclic 5-membered imide).

6.2.9. 2,5-Diaminoterephthalic acid (79)



An oven dried 10 mL one-neck round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with 1.0 g (3.96 mmol, 1.0 eq) benzene-1,2,4,5-tetracarboxylic diimide and 2.5 mL of water. The reaction vessel was cooled in an ice-water bath and the reaction mixture was stirred for 10 min, while it was treated with ultrasonic sound. Subsequently 2.28 mL (4.77 mmol, 1.2 eq) 13 % solution of sodium hypochlorite in water were added dropwise via a syringe. During the addition of sodium hypochlorite a colorless solid precipitated. Then the reaction mixture was stirred at r.t. for 16 h. The reaction mixture was treated with 80 mg sodium sulfite. The colorless solid was collected by filtration and recrystallized from 50 mL water and dried in the vacuum of an oil pump for 2 d.

Yield: 2.14 g (9.90 mmol, 21 % o. th.), bright yellow solid

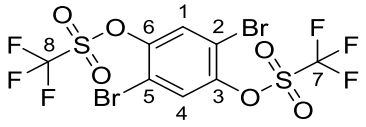
$C_8H_8N_2O_4$ [196.16 g/mol]

mp: > 320 °C

^{1}H-NMR: (300.36 MHz, D_2O): δ = 7.82 (s, 2H, H-1, H-4).

^{13}C-NMR (75.53 MHz, D_2O): δ = 176.7 (C-7, C-8), 137.9 (C-2, C-5), 126.0 (C-1, C-2).

6.2.10. 2,5-Dibromo-1,4-phenylene bis(trifluoromethanesulfonate) (70)



An oven dried 25 mL one-neck round bottom flask equipped with a Schlenk adapter and a Teflon-coated magnetic stir bar was charged with 500 mg (1.81 mmol, 1.0 eq) 2,5-dibromohydroquinone and 10 mL absolute pyridine. The colorless reaction mixture was cooled in an ice-water bath and stirred at 0 °C for 15 min. Then 670 µL (3.98 mmol, 2.2 eq) trifluoromethanesulfonic anhydride were added dropwise via a syringe over a period of 10 min. Thereby the colorless solid disappeared and the color of the liquid changed to green-brownish. Subsequently the reaction mixture was stirred at 0 °C for 5 min, before the ice-water bath was removed. The reaction mixture was stirred at r.t. for 4 h and the reaction control was performed by TLC. The reaction mixture was diluted with 25 mL of ethyl acetate and transferred to an extraction funnel. The phases were separated and the organic phase was washed with water (3 x 15 mL). The aqueous phase was reextracted with ethyl acetate (2 x 20 mL). Then the combined organic phases were washed with 1 M hydrochloric acid (2 x 10 mL) and brine (1 x 10 mL). Subsequently the organic phase was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The product was purified via flash column chromatography (30 g SiO_2 150 x 20 mm, eluent: cyclohexane/ethyl acetate = 4:1, fraction size: 20 mL, detection: 254 nm).

Yield: 510 mg (0.96 mmol, 53% o. th.), bright yellow needle-shaped crystals

$C_8H_2Br_2F_6O_6S_2$ [532.02 g/mol]

mp: 108 °C

HR-MS (EI: [M]) [*m/z*]: calculated: 529.7563, found: 529.7589

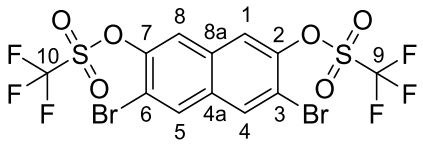
R_f = 0.70 (cyclohexane/ethyl acetate = 2:1 (v/v)), (254 nm)

GC-MS (CL_50_S): t_R = 5.94 min; *m/z* = 532 (32 %, MP), 399 (23 %, M* - CF_3O_2S), 69 (100 %, BP, CF_3*).

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ = 7.69 (s, 2H, H-1, H-4).

^{13}C-NMR (75.53 MHz, $CDCl_3$): δ = 146.3 (C-3, C-6), 128.2 (C-1, C-4), 118.7 (J_{CF} = 320 Hz, C-7, C-8), 116.1 (C-2, C-5).

6.2.11. 3,6-Dibromonaphthalene-2,7-diyl bis(trifluoromethane-sulfonate) (84)



An oven dried 100 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 513 mg (1.61 mmol, 1.0 eq) 2,6-dibromonaphthalene-2,7-diol, 580 µL (7.19 mmol, 4.5 eq) absolute pyridine and 15 mL absolute dichloromethane. The solution was cooled in an ice-water bath and stirred at 0 °C for 15 min. Then 880 µL (5.23 mmol, 3.3 eq) trifluoromethanesulfonic anhydride were added dropwise via a syringe over a period of 10 min. Thereby the color of the solution changed to green-brownish. Subsequently the reaction mixture was stirred at 0 °C for 5 min, before the ice-water bath was removed. The reaction mixture was stirred at r.t. for 16 h and the reaction control was performed by TLC. Then, the reaction mixture was diluted with 25 mL of dichloromethane and transferred into an extraction funnel. The phases were separated and the organic phase was washed with water (3 x 15 mL). The aqueous phase was reextracted with dichloromethane (2 x 20 mL). Then the combined organic phases were washed with 1 M hydrochloric acid (1 x 20 mL) and brine (1 x 20 mL). Subsequently the organic phase was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The product was purified via flash column chromatography (30 g SiO_2 300 x 20 mm, eluent: cyclohexane/ethyl acetate = 250:3, fraction size: 20 mL, detection: 254 nm).

Yield: 640 mg (1.10 mmol, 68 % o. th.), colorless solid

$C_{12}H_4Br_2F_6O_6S_2$ [582.08 g/mol]

mp: 118 °C

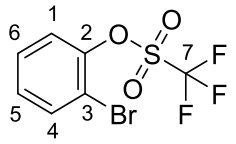
R_f = 0.75 (cyclohexane/ethyl acetate = 2:1 (v/v)), (254 nm)

GC-MS (CL_50_S): t_R = 7.61 min; *m/z* = 582 (47 %, MP), 449 (100 %, BP, M* - CF_3O_2S), 69 (100 %, BP, CF_3*).

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ = 8.18 (s, 2H, H-4, H-5), 7.85 (s, 2H, H-1, H-8).

^{13}C-NMR (75.53 MHz, $CDCl_3$): δ = 145.6 (C-2, C-7), 132.7 (C-4, C-5), 132.3 (C-8a), 131.7 (C-4a), 120.9 (C-1, C-8), 118.7 (J_{CF} = 320 Hz, C-9, C-10), 116.3 (C-3, C-6).

6.2.12. 2-Bromophenyl trifluoromethanesulfonate (33)



An oven dried 100 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 188 µL (1.61 mmol, 1.0 eq) 2-bromophenol, 150 µL (1.86 mmol, 1.2 eq) absolute pyridine and 10 mL absolute dichloromethane. The solution was cooled in an ice-water bath and stirred at 0 °C for 15 min. Then 413 µL (2.45 mmol, 1.5 eq) trifluoromethanesulfonic anhydride were added dropwise via a syringe over a period of 10 min. Thereby a colorless solid precipitated. Subsequently the reaction mixture was stirred at 0 °C for 5 min, before the ice-water bath was removed. The reaction mixture was stirred at r.t. for 16 h and the reaction control was performed by TLC. Then, the reaction mixture was diluted with 15 mL of dichloromethane and transferred into an extraction funnel. The phases were separated and the organic phase was washed with 1 M hydrochloric acid (3 x 10 mL). The aqueous phase was reextracted with dichloromethane (2 x 10 mL). Then the combined organic phases were washed with brine (2 x 10 mL). Subsequently the organic phase was dried over sodium sulfate, filtered, and the solvent was removed under reduced pressure at 15 mbar for 12 h.

Yield: 488 mg (1.59 mmol, 99% o. th.), colorless solid in viscous liquid

$C_7H_4BrF_3O_3S$ [305.07 g/mol]

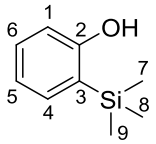
R_f = 0.81 (cyclohexane/ethyl acetate = 2:1 (v/v)), (254 nm)

GC-MS (CL_50_S): t_R = 4.80 min; *m/z* = 306 (73 %, MP), 171 (100 %, BP, M* - CF_3O_2S), 143 (98 %, M* - $C_2HF_3O_3S$).

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ = 7.69 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H-4), 7.39 (m, 2H, H-1, H-5), 7.26 (dt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.9 Hz, 1H, H-6).

^{13}C-NMR (75.53 MHz, $CDCl_3$): δ = 147.2 (C-2), 134.6 (C-4), 129.6 (C-1), 129.2 (C-5), 123.1 (C-6), 118.7 (J_{CF} = 321 Hz, C-7), 116.2 (C-2).

6.2.13. 2-(Trimethylsilyl)phenol (74)



An oven dried 100 mL two-neck round bottom flask equipped with a Schlenk adapter and a Teflon-coated magnetic stir bar was charged with 1.35 mL (11.3 mmol, 1.0 eq) 2-bromophenol and 30 mL absolute tetrahydrofuran. The bright yellow solution was cooled in an acetone-dry ice cooling-bath and stirred at -70 °C for 15 min. Then 11.8 mL (26.0 mmol, 2.3 eq) 2.21 M *n*-butyllithium were added dropwise via a syringe over a period of 30 min. Subsequently the reaction mixture was stirred at -70 °C for 50 min, before 3.85 mL (30.1 mmol, 2.6 eq) trimethylsilyl chloride were added dropwise via a syringe at -70 °C over a period of 30 min. The colorless reaction mixture was allowed to warm to r.t. and was stirred for 16 h. The reaction control was performed by TLC. Then 3.30 g (10.5 mmol, 0.9 eq) tetrabutylammonium fluoride trihydrate were added to the reaction mixture. Thereby the colorless solid got dissolved. After 2 h of vigorously stirring, the reaction mixture was diluted with 25 mL ethyl acetate and transferred into an extraction funnel. The phases were separated and the organic phase was washed with saturated ammonium chloride-solution (2 x 10 mL). The aqueous phase was reextracted with ethyl acetate (2 x 10 mL). Then the combined organic phase was washed with brine (1 x 15 mL). Subsequently the organic phase was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The product was purified via flash column chromatography (30 g SiO_2 300 x 20 mm, eluent: cyclohexane/ethyl acetate = 50:1, fraction size: 20 mL, detection: 254 nm).

Yield: 1.46 g (8.77 mmol, 78% o. th.), yellow viscous liquid

$C_9H_{14}OSi$ [166.29 g/mol]

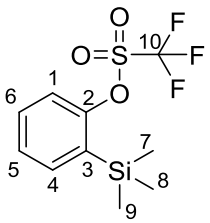
R_f = 0.72 (cyclohexane/ethyl acetate = 2:1 (v/v)), (254 nm)

GC-MS (CL_50_S): t_R = 4.94 min; *m/z* = 166 (24 %, MP), 151 (100 %, BP, M* - CH_3), 123 (76 %, C_6H_7OSi*).

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ = 7.42 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H-4), 7.28 (dt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H-6), 6.97 (t, $^3J_{HH}$ = 7.3 Hz, 1H, H-5), 6.71 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H-1), 0.36 (s, 9H, H-7, H-8, H-9).

^{13}C-NMR (75.53 MHz, $CDCl_3$): δ = 160.5 (C-2), 135.4 (C-4), 130.8 (C-6), 125.5 (C-3), 120.6 (C-5), 114.6 (C-1), 0.8 (C-7, C-8, C-9).

6.2.14. 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (31)



An oven dried 100 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 400 mg (2.40 mmol, 1.0 eq) 2-(trimethylsilyl)phenol, 215 µL (2.66 mmol, 1.1 eq) absolute pyridine and 11 mL absolute dichloromethane. The reaction mixture was cooled in an ice-water bath and stirred at 0 °C for 15 min. Then 440 µL (2.61 mmol, 1.1 eq) trifluoromethanesulfonic anhydride were added dropwise via a syringe over a period of 30 min. Thereby a bright yellow solid precipitated. Subsequently the reaction mixture was stirred at 0 °C for 90 min. The reaction control was performed by GC-MS. Then the reaction mixture was diluted with 10 mL dichloromethane and transferred into an extraction funnel. The phases were separated and the organic phase was washed with brine (2 x 10 mL). The aqueous phase was reextracted with dichloromethane (3 x 10 mL). Then the combined organic phases were washed with brine (1 x 20 mL). Subsequently, the organic phase was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The product was purified via flash column chromatography (60 g SiO_2 300 x 20 mm, eluent: cyclohexane, fraction size: 20 mL, detection: 254 nm).

Yield: 365 mg (1.22 mmol, 51% o. th.), yellow viscous liquid

$C_{10}H_{13}F_3O_3SSi$ [298.35 g/mol]

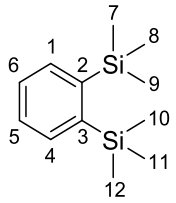
R_f = 0.55 (cyclohexane), (254 nm)

GC-MS (CL_50_S): t_R = 4.93 min; *m/z* = 283 (100 %, BP, M* - CH_3), 150 (74 %, $C_8H_{10}O$*).

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ = 7.55 (dd, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H-4), 7.46 (dt, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, H-6), 7.35 (m, 2H, H-1, H-5), 0.38 (s, 9H, H-7, H-8, H-9).

^{13}C-NMR (75.53 MHz, $CDCl_3$): δ = 155.3 (C-2), 136.4 (C-4), 132.7 (C-3), 131.4 (C-6), 127.6 (C-5), 119.7 (C-1), 118.7 (J_{CF} = 320 Hz, C-10), 0.8 (C-7, C-8, C-9).

6.2.15. 1,2-Bis(trimethylsilyl)benzene (75)



An oven dried 100 mL three-neck round-bottom flask equipped with a Teflon-coated magnetic stir bar, a reflux condenser, a glass stopper and a nitrogen inlet was charged with 1.24 g (51.1 mmol, 8.0 eq) magnesium, 2.54 g (59.9 mmol, 9.0 eq) dry lithium chloride, 1.23 g (12.4 mmol, 2.0 eq) copper(I) chloride and 45 mL 1,3-dimethyl-2-imidazolidinone under nitrogen atmosphere. The suspension consisting of a green liquid and a grey solid was stirred for 15 min at r.t.. Afterwards the glass stopper of the three-neck round-bottom flask was exchanged with a dropping funnel. The dropping funnel was filled with 13.0 mL (102 mmol, 16.0 eq) trimethylsilyl chloride under inert atmosphere. Then, the trimethylsilyl chloride was added dropwise over a period of 30 min. Thereby the color of the suspension changed from green into orange. After the addition of trimethylsilyl chloride 725 µL (6.41 mmol, 1.0 eq) 1,2-dichlorobenzene were added dropwise via a syringe over a period of 15 min under inert atmosphere. Then the reaction mixture was heated to 90 °C for 16 h under inert atmosphere. Thereby the color of the suspension changed from orange via yellow and colorless into grey. The reaction control was done by GC. Subsequently the reaction mixture was poured onto a mixture of 5 g crushed ice, 20 mL saturated sodium bicarbonate and 20 mL cyclohexane. Thereby an orange-red solid precipitated. The solid was filtered off. The filtrate was transferred into an extraction funnel, the phases were separated and the aqueous phase was extracted with cyclohexane (3 x 20 mL). The combined organic phases were washed with brine (3 x 20 mL), dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. Finally the product was purified via Kugelrohr-destillation at 2.67 mbar and 85 °C.

Yield: 400 mg (1.80 mmol, 28 % o. th.), colorless liquid

$C_{12}H_{22}Si_2$ [222.48 g/mol]

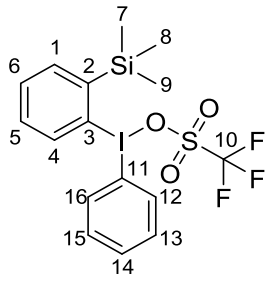
GC-MS (CL_50_S): t_R = 5.34 min; *m/z* = 222 (7 %, MP), 207 (65 %, M* - CH_3), 191 (100 %, BP, M* - C_2H_6), 73 (27 %, C_3H_9Si*).

bp: 85 °C (2.67 mbar/2.00 torr)

^{1}H-NMR: (300.36 MHz, $CDCl_3$): δ = 7.67 (dd, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 3.4 Hz, 2H, H-1, H-4), 7.32 (dd, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 3.4 Hz, 2H, H-5, H-6), 0.36 (s, 18H, H-7, H-8, H-9, H-10, H-11, H-12).

^{13}C-NMR (75.53 MHz, $CDCl_3$): δ = 146.2 (C-2, C-3), 135.3 (C-5, C-6), 127.9 (C-1, C-4), 2.1 (C-7, C-8, C-9, C-10, C-11, C-12).

6.2.16. Phenyl(2-(trimethylsilyl)phenyl)-λ^3-iodanyltrifluoromethane-sulfonate (32)



An oven dried 20 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 522 mg (1.62 mmol, 1.0 eq) (diacetoxyiodo)benzene and 3 mL absolute dichloromethane. The reaction mixture was cooled in an ice-water bath and stirred at 0 °C for 15 min. Then 144 µL (1.62 mmol, 1.0 eq) trifluoromethanesulfonic acid were added in one portion via a syringe. Thereby a bright yellow solution appeared. Subsequently the reaction mixture was stirred at r.t. for 2 h. Another oven dried 20 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 400 mg (1.62 mmol, 1.0 eq) 1,2-bis(trimethylsilyl)benzene and 2 mL absolute dichloromethane. The 1,2-bis(trimethyl-silyl)benzene-solution was added dropwise via a syringe to the hypervalent iodine-solution over a period of 10 min under inert atmosphere. The reaction mixture was stirred at r.t. for 16 h. The reaction control was performed by ^{1}H-NMR. Then the solvent of the orange reaction mixture was removed under reduced pressure and the crude product was triturated with diethyl ether (5 x 1 mL). Finally the product was dried under the vacuum of an oil pump at 10^{-3} mbar.

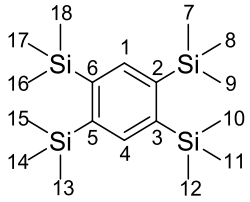
Yield: 230 mg (0.46 mmol, 30 % o. th.), orange solid

$C_{16}H_{18}F_3IO_3SSi$ [503.36 g/mol]

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ = 8.13 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H-4), 7.80 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H-12, H-16), 7.67 (m, 2H, H-5, H-6), 7.57 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H-14), 7.51 (m, 3H, H-1, H-13, H-15) 0.41 (s, 9H, H-7, H-8, H-9).

^{13}C-NMR (75.53 MHz, $CDCl_3$): δ = 147.4 (C-2), 139.2 (C-4), 138.6 (C-5), 133.6 (C-1), 133.4 (C-12, C-16), 132.6 (C-13, C-15), 132.5 (C-6), 132.3 (C-14), 121.9 (C-3), 120.3 (J_{CF} = 320 Hz, C-10), 114.0 (C-11), 0.2 (C-7, C-8, C-9).

6.2.17. 1,2,4,5-Tetrakis(trimethylsilyl)benzene (69)



An oven dried 100 mL three-neck round-bottom flask equipped with a Teflon-coated magnetic stir bar, a reflux condenser, a glass stopper and a nitrogen inlet was charged with 1.98 g (81.6 mmol, 16 eq) magnesium, 1.98 g (20.1 mmol, 4.0 eq) copper(I) chloride, 3.69 g (87.0 mmol, 17 eq) dry lithium chloride and 20 mL 1,3-dimethyl-2-imidazolidinone under inert atmosphere. The suspension consisting of a green liquid and a grey solid was stirred for 15 min at r.t.. Afterwards the glass stopper of the three-neck round-bottom flask was exchanged with a dropping funnel. The dropping funnel was filled with 21.0 mL (164 mmol, 32 eq) trimethylsilyl chloride under inert atmosphere. The trimethylsilyl chloride was added dropwise over a period of 30 min. Thereby the color of the suspension changed from green into orange. After the addition of trimethylsilyl chloride 1.11 g (5.12 mmol, 1.0 eq) 1,2,4,5-tetrachlorobenzene were added in small portions over a period of 15 min under inert atmosphere. Then the reaction mixture was heated to 90 °C for 16 h under inert atmosphere. Thereby the color of the suspension changed from orange via yellow and colorless into grey. The reaction control was done by GC. Subsequently the reaction mixture was poured onto a mixture of 10 g crushed ice, 25 mL saturated sodium bicarbonate and 25 mL cyclohexane. Thereby an orange-red solid precipitated. The solid was filtered off. The filtrate was transferred into an extraction funnel, the phases were separated and the aqueous phase was extracted with cyclohexane (3 x 20 mL). The combined organic phases were washed with

brine (3 x 20 mL), dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. Finally the product was purified via recrystallization from 4 mL acetone.

Yield: 330 mg (39.8 mmol, 62 % o. th.), colorless cuboid-shaped crystals

$C_{18}H_{38}Si_4$ [366.84 g/mol]

R_f = 0.79 (Cyclohexane), (254 nm)

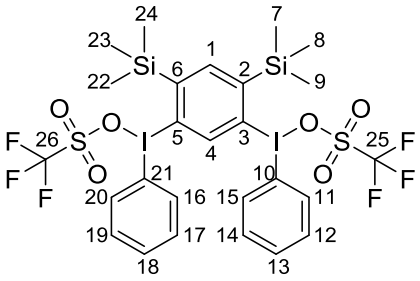
GC-MS (CL_50_S): t_R = 6.76 min; *m/z* = 366 (32 %, MP), 351 (100 %, BP, M* - CH_3), 335 (85 %, M* - C_2H_6), 263 (51 %, $C_{13}H_{23}Si_3$*).

mp: 165 °C

^{1}H-NMR: (300.36 MHz, $CDCl_3$): δ = 7.97 (s, 2H, H-1, H-4), 0.37 (s, 36H, H-7, H-8, H-9, H-10, H-11, H-12, H-13, H-14, H-15, H-16, H-17, H-18).

^{13}C-NMR (75.53 MHz, $CDCl_3$): δ = 144.9 (C-2, C-3, C-5, C-6), 141.7 (C-1, C-4), 2.0 (C-7, C-8, C-9, C-10, C-11, C-12, C-13, C-14, C-15, C-16, C-17, C-18).

6.2.18. (4,6-Bis(trimethylsilyl)-1,3-phenylene)bis(phenyl- λ^3-iodanediyl) bis(trifluoromethanesulfonate) (68)



An oven dried 20 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 87.7 mg (0.27 mmol, 2.0 eq) (diacetoxyiodo)benzene and 0.5 mL absolute dichloromethane. The reaction mixture was cooled in an ice-water bath and stirred at 0 °C for 15 min. The Schlenk flask was protected from light by covering with aluminium foil. Then 48.8 µL (0.55 mmol, 4.0 eq) trifluoromethanesulfonic acid were added in one portion via a syringe. Subsequently the reaction mixture was stirred at r.t. for 2 h. Another oven dried 20 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 50 mg (0.14 mmol, 1.0 eq) 1,2,4,5-tetrakis(trimethylsilyl)benzene and 0.5 mL absolute dichloromethane. The 1,2,4,5-tetrakis(trimethylsilyl)benzene-solution was added dropwise via

a syringe to the hypervalent iodine-solution over a period of 10 min at 0 °C under inert atmosphere. The reaction mixture was stirred at 0 °C for 16 h. The reaction control was performed by ^{1}H-NMR. Then the solvent of the yellow reaction mixture was removed under reduced pressure at 0 °C and the crude product was triturated with pentane (5 x 1 mL). Finally the product was dried under the vacuum of an oil pump at 10^{-3} mbar.

Yield: 100 mg (0.11 mmol, 80% o. th.), bright yellow solid

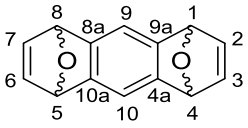
$C_{26}H_{30}F_6I_2O_6S_2Si_2$ [926.61 g/mol]

HR-MS (MALDI: [M+Na]) [*m/z*]: calculated: 948.891, found: 948.992

^{1}H-NMR (300.36 MHz, Acetonitrile d_3): δ = 8.23 (s, 1H, H-4), 7.98 (s, 1H, H-1), 7.88 (t, $^{3}J_{HH}$ = 6.9 Hz, 4H, H-11, H-15, H-16, H-20), 7.69 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, H-13, H-18), 7.55 (t, $^{3}J_{HH}$ = 7.7 Hz, 4H, H-12, H-14, H-17, H-19), 0.38 - 0.40 (m, 18H, H-7, H-8, H-9, H-22, H-23, H-24).

^{13}C-NMR (75.53 MHz, Acetonitrile d_3): δ = 146.9 (C-2, C-6), 144.0 (C-1), 142.4 (C-4), 133.6 (C-11, C-15, C-16, C-20), 131.8 (C-13, C-18), 131.5 (C-12, C-14, C-17, C-19), 121.6 (C-3, C-5), 121.6 (J_{CF} = 320 Hz, C-25, C-26), 117.0 (C-10, C-21), 0.0 (C-7, C-8, C-9, C-22, C-23, C-24).

6.2.19. 1,4,5,8-Tetrahydro-1,4:5,8-diepoxyanthracene (85)



An oven dried 20 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 98.4 mg (0.25 mmol, 1.0 eq) 1,2,4,5-tetrabromobenzene, 370 µL (5.11 mmol, 20 eq) furan and 4 mL absolute toluene under inert atmosphere. The reaction mixture was cooled in an acetone/dry-ice bath to -25 °C and stirred for 15 min. Subsequently 230 µL (0.53 mmol. 2.1 eq) 2.3 M *n*-butyllithium-solution were added dropwise over a period of 10 min at -25 °C under inert atmosphere to the reaction mixture. The acetone/dry-ice bath was removed and reaction control was performed by TLC. After 3 h 0.5 mL diethyl ether were added. Thereby a brown solid precipitated. The reaction mixture was transferred into an extraction funnel and was washed with water (2 x 4 mL) and brine (1 x 4 mL). The organic phase was dried over sodium sulfate, filtered and the solvent was removed under reduced

pressure. The product was purified via flash column chromatography (10 g SiO_2 100 x 10 mm, cyclohexane/dichloromethane/diethyl ether = 5:2:1, fraction size: 8 mL, detection: 254 nm).

Yield: 26.8 mg (0.13 mmol, 51% o. th.), pale yellow solid

$C_{14}H_{10}O_2$ [210.23 g/mol]

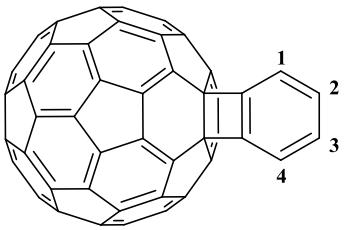
R_f^{anti} = 0.35 (cyclohexane/ethyl acetate = 2:1 (v/v), 254 nm)

R_f^{syn} = 0.28 (cyclohexane/ethyl acetate = 2:1 (v/v), 254 nm)

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ = 7.20^{anti}, 7.19^{syn} (s, 2H, H-9, H-10), 7.02 (s, 4H, H-2, H-3, H-6, H-7), 5.63 (s, 4H, H-1, H-4, H-5, H-8).

^{13}C-NMR (75.53 MHz, $CDCl_3$): δ = 148.0 (C-4a, C-8a, C-9a, C-10a), 143.5^{anti} (C-2, C-3, C-6, C-7), 114.2^{anti} (C-9, C-10), 82.5 (C-1, C-4, C-5, C-8).

6.2.20. [1,2]Benzeno-C_{60}-fullerene (88)



An oven dried 100 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was charged with 50.0 mg (0.69 mmol, 5.5 eq) C_{60}-fullerene, 250 µL (0.13 mmol, 1.0 eq) 0.05 M phenyl(2-(trimethylsilyl)phenyl)-λ^3-iodanyl trifluoromethanesulfonate and 8 mL absolute 1,2-dichlorobenzene under inert atmosphere. The deep violet reaction mixture was flushed with inert gas for 15 min, while it was treated with ultrasonic sound. Subsequently 130 µL (0.13 mmol, 1.1 eq) 0.1 M dry tetrabutylammonium fluoride-solution were added dropwise over a period of 10 min at r.t. under inert atmosphere to the reaction mixture. Reaction control was performed by TLC. After 16 h the solvent was removed under reduced pressure. Finally the crude product was purified by prep. TLC (cyclohexane/ 1,2-dichlorobenzene = 25:1, detection: 254 nm).

Yield: 1.0 mg (1.2 µmol, 2 % o. th.), dark brown solid

$C_{66}H_4$ [794.74 g/mol]

R_f = 0.72 (cyclohexane/1,2-dichlorobenzene = 25:1 (v/v), 254 nm)

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ = 7.60 (dd, $^3J_{HH}$ = 5.4 Hz, $^4J_{HH}$ = 3.0 Hz, 2H, H-1, H-4), 7.36 (dd, $^3J_{HH}$ = 5.4 Hz, $^4J_{HH}$ = 3.0 Hz, 2H, H-2, H-3).

^{13}C-NMR (75.53 MHz, $CDCl_3$): δ = 155.5 (C_{aro}), 149.7 (C_{aro}), 147.3 (C_{aro}), 147.0 (C_{aro}), 146.6 (C_{aro}), 145.9 (C_{aro}), 145.1 (C_{aro}), 143.5 (C_{aro}), 143.4 (C_{aro}), 142.9 (C_{aro}), 142.7 (C_{aro}), 141.0 (C_{aro}), 139.5 (C_{aro}), 130.8 (C_{aro}), 124.3 (C_{aro}).

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8. Abbreviation List

8.1. Analytical Methods

^{1}H-NMR	proton NMR
^{13}C-NMR	carbon NMR
APT	Attached Proton Test
BP	basic peak
C_{aro}	aromatic carbon
d	doublet
dd	doublet of doublet
dt	doublet of triplet
ESI	electrospray ionization
EDG	electron donating group
eV	electron volt
GC	gas chromatography
GC-MS	gas chromatography mass spectrometry
HPLC-MS	high performance liquid chromatography mass spectrometry
HR-MS	high resolution mass spectrometry
Hz	Hertz
IR	infra red
J	signal multiplicity
η^2	hapto (*side on*)
m	multiplet

m/*z*	mass/charge-ratio
M^+	molecule peak
MHz	megahertz
mp	melting point
NMR	nuclear magnetic resonance
ppm	parts per million
R_f	retention factor
s	singlet
t	triplet
TLC	thin layer chromatography
t_R	retention time
UV	ultraviolet
δ	chemical shift

8.2. Chemical Abbreviations

AcOH	acetic acid
$CDCl_3$	deuterated dichloromethane
$Cu(OTf)_2$	copper(II) trifluoromethanesulfonate
DCM	dichloromethane
DME	1,2-dimethoxyethane
DMF	*N*,*N*-dimethylformamide
DMI	1,3-dimethyl-2-imidazolidinone
DMSO-d_6	deuterated dimethylsulfoxide
eq	equivalent

HOMO	highest occupied molecular orbital
L	ligand
LUMO	lowest unoccupied molecular orbital
m	*meta*
n-BuLi	*n*-butyllithium
o	*ortho*
pH	logarithm of the reciprocal of the hydrogen ion activity
$PhI(OAc)_2$	(diacetoxyiodo)benzene
$Pb(OAc)_4$	lead(IV) acetate
TBDMS	*tert* butyldimethylsilyl
TBAF	tetrabutylammonium fluoride
Tf	trifluoromethanesulfonate
TfOH	trifluoromethanesulfonic acid
Tf_2O	trifluoromethanesulfonic anhydride
THF	tetrahydrofuran
TMS	trimethylsilyl
TMSCl	trimethylsilylchloride
Ts	*p*-toluenesulfonate

8.3. Others

(v/v)	volume/volume
°C	Celsius
cycloadd.	cycloaddition
Å	Ångström

d	day/-s
e. g.	exempli gratia (lat.: for example)
EI	electron impact ionization
eq	equivalents
et al.	*et alii* (lat.: and co-workers)
g	gram
h	hour/-s
L	litre
m	meter
M	molar (mol/L)
mmol	millimole/-s
min	minute/-s
mL	milliliter
mm	millimeter
nm	nanometer
ppm	parts per million
r.t.	room temperature
sat.	saturated
λ	wavelength
µL	microliter
µm	micrometer
o. th.	of theory

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