Molecular Receptors Based on Bridged Corannulenes

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"It is a capital mistake to theorize before you have all the evidence. It biases the judgment."

Sir Arthur Conan Doyle (The Adventures of Sherlock Holmes "A Scandal in Bohemia")

Publications

Conference Lectures:

A. M. Meyer, D. Lentz, Workshop Anorganische Chemie an der FU, May 2013, Berlin (Germany).

A. M. Meyer, D. Lentz, at the 33th Meeting of the Graduate School "Fluorine as the Key Element", November 2013, Berlin, Germany.

A. M. Meyer, D. Lentz, 16th Deutscher Fluortag, September 2014, Schmitten (Germany).

Conference Posters:

B. M. Schmidt, A. K. Meyer, B. Topolinski, D. Lentz, at the 2nd CSI General Meeting of the Center for Supramolecular Interactions, March 2011, Berlin (Germany).

A. M. Meyer, B. M. Schmidt, D. Lentz, at the 2nd Berliner Chemie Symposium (BCS), April 2012, Berlin (Germany).

A. M. Meyer, D. Lentz, at the 5th Meeting of the European Association of Chemical and Molecular Sciences (EuCheMS), August 2014, Istanbul (Turkey).

All my friends for their patience and understanding when I cancelled meetings because I again lost track of time.

And most of all, I want to thank my family, for their help, their encouragement, their understanding, their motivation, their trust in me and being there for me through it all.

Contents

1. Introduction

1.1. Buckybowls

Corannulene is a polycyclic aromatic hydrocarbon (PAH) which consists of one five-membered ring surrounded by five six-membered rings (figure 1.1). The term corannulene is derived from the Latin word for heart *cor* and *annulus* which can be translated to ring. The IUPAC name is dibenzo[ghi,mno]fluoranthene but it is also known as [5]circulene. As the smallest still curved fragment of C_{60} fullerene it has a C_{5v} symmetry. The unique bowl shaped surface makes it a member of the buckybowl family which was named after the buckyball C_{60}. The second smallest bowl-shaped fragment of C_{60} is sumanene.
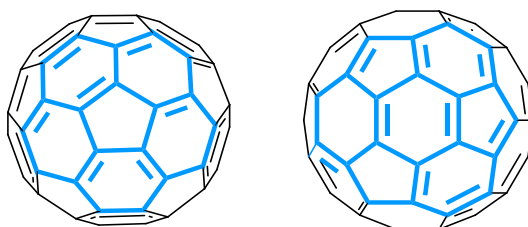
Figure. 1.1: Corannulene (left) and sumanene (right).

Corannulene is a nonrigid molecule, undergoing a bowl-to-bowl inversion with an inversion barrier of 42.7 kJ/mol (10.2 kcal/mol) at - 64 °C[1]. That means the bowl inverts over 200,000 times per second at room temperature *via* a planar transition state. The value was determined by temperature dependent NMR spectroscopy of substituted corannulenes. Sumanene is more rigid than its cousin because of the three benzylic positions. The barrier can be determined from pristine sumanene with a value of 82 kJ/mol (19.6 kcal/mol) at 140 °C[2]. Because of its flexibility the corannulene bowl is slightly more shallow with 0.87 Å than that of sumanene (1.11 Å)[3].

The interest in buckybowls grew since the Buckminsterfullerene was first synthesized in 1985[4]. The discovery was awarded with a noble prize in 1996 and it has been found in a young planetary nebula in outer space in 2010[5]. The bowl-shaped appearance of corannulene and sumanene makes them excellent systems to understand the reactivity and properties of fullerenes especially the, in fullerenes, very hard to access endo side. But the synthesis of the buckybowls is by no means an easy feat. The first to succeed in producing corannulene were Barth and Lawton in 1966[6], nineteen years prior to the syntheses of C_{60} fullerene, *via* a linear 17-step reaction pathway (scheme 1.1). Sadly, the overall yield was under one percent and no further studies were preformed aside from the determination of the bowlshaped structure[7].
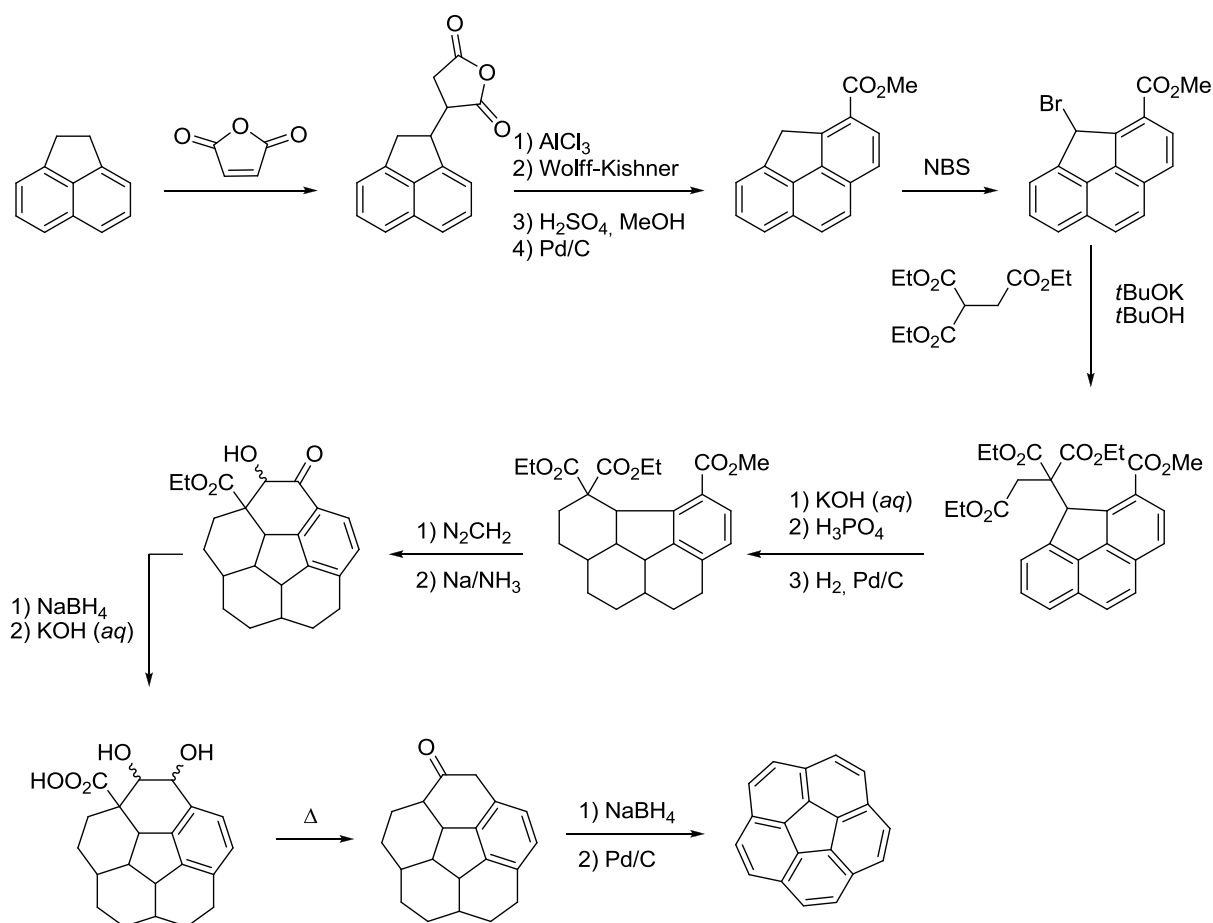
Scheme 1.1: First synthesis of corannulene by Bath and Lawton.

The synthesis starts with a naphthalene derivate and then one ring after the other is successfully added. In the last step the curvature and aromaticity of the molecule is introduced by dehydrogenation using palladium on carbon.

The increased interest in and demand for buckybowls called for an improved synthesis. In 1991 a new approach was introduced by Scott *et al.*[8] which was based on a flash vacuum pyrolysis (FVP) to conduct the final ring closure. This principle is used in a variety of larger aromatic systems like the first rational pathway for the formation of the Buckminsterfullerene in isolable quantities[9]. This corannulene synthesis starts with acenaphthenequinone which can be bought and then transformed to a fluoranthene derivative. From the fluoranthene the chlorovinyl precursor is synthesized using phosphorus pentachloride. The reaction consists of only three steps and has a much better yield of up to 30 %[10]. While this is a huge improvement from the first established synthesis there are still some major disadvantages occuring because of the FVP (scheme 1.2).
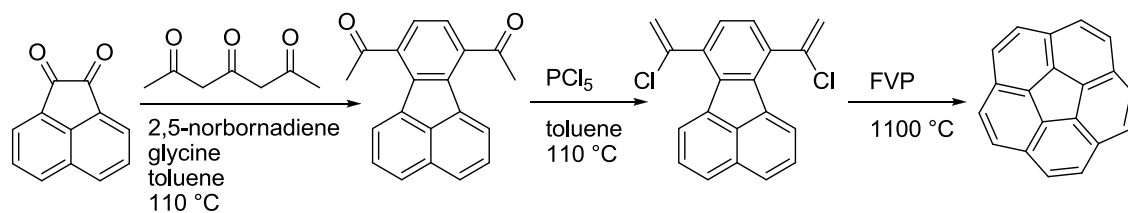
Scheme 1.2: Corannulene synthesis *via* FVP.

For example the low functional group tolerance, low yields for larger products than pristine corannulene[11], the necessary pyrolysis apparatus that can only be scaled up to a certain point because of technical difficulties, undesired side products or rearrangements and a small amount of monochlorocorannulene which is always formed during the pyrolysis.
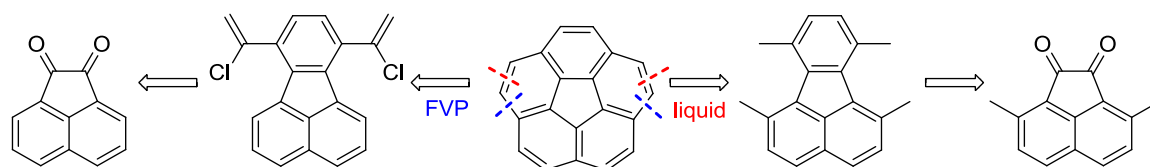
Scheme 1.3: Retrosynthetic approach of the FVP (blue) and liquid (red) synthesis of corannulene.

Considering the above mentioned problems it is generally agreed upon that a liquid synthesis is the more favorable one. The retrosynthetic approach for a liquid synthesis differs from that of the pyrolysis (scheme 1.3) but both precursors are members of the fluoranthene family and both synthetic routes are bilateral. The difference is in the formation of the final bond to the pristine corannulene. In case of the FVP the last bond formed is a flank carbon-carbon bond, for the liquid synthesis it is one of the rim bonds.

The first attempts at a liquid synthesis were made by the Siegel group[12] and start from cheap commercially available materials but using toxic reagents as well as having 13-steps made this particularly cascade of reactions a lengthy and time-consuming affair. With the very important discovery of Sygula and Rabideau[13] that the dehalogenation of octabromofluoranthene leads to the formation of tetrabromocorannulene, a new synthetic pathway opened up. In 2012 Siegel *et al.[14]* published a synthesis which, for the first time, allowed the preparation of corannulene on a kilogram scale (scheme 1.4). It is an eight step synthetic route, with an overall yield of 7.4 %, and is now the go-to method for the production of the buckybowl.
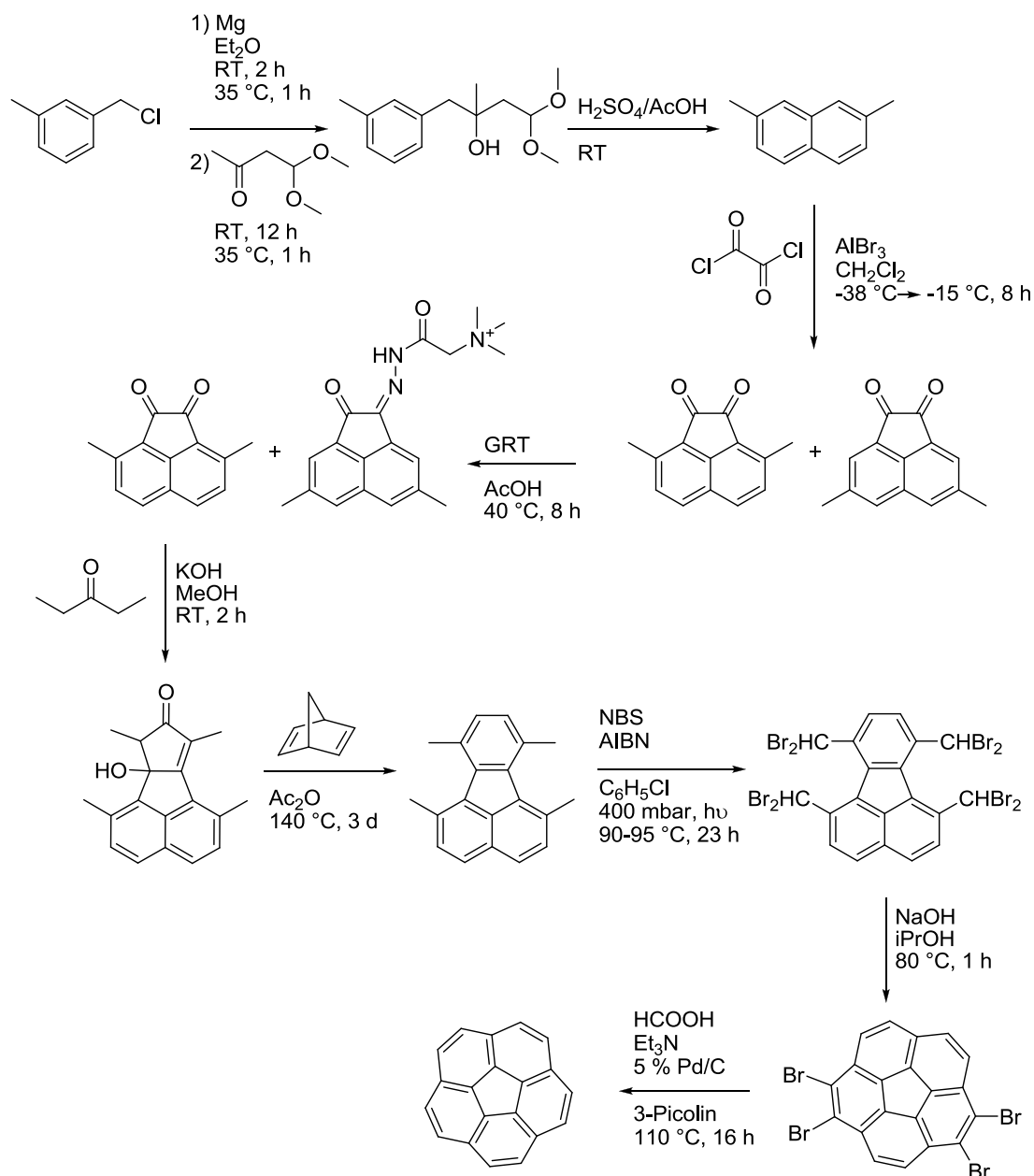
Scheme 1.4: Kilogramm synthesis as published by the Siegel group.

In contrast to the first synthesis, the bowl shape is introduced in the second to last step. The synthesis starts from readily available and cheap materials and the key intermediate is the octabromofluoroanthene derivate. This molecule is so remarkable and important because of the internal steric strain. The large steric demand of the side chains forces the aromatic six-membered rings out of one plane so that they are slightly twisted against each other. The high internal strain makes it an excellent precursor for the ring closure to tetrabromocorannulene. On one hand the reduction in energy due to the aromatization of the molecule favors the conversion. On the other hand the energy gained due to the curvature decreases it. Tetrabromocorannulene is, in the last step, dehalogenated to the pristine corannulene by the usage of palladium on carbon.

1.2. Applications of Corannulene

While corannulene is used to investigate basic principles of fullerenes it has additional interesting properties. It has been used in a variety of different applications ranging from bluelight emitters[15], sensing and identification of nitro-aromatic explosives[16], to liquid crystals[17]. It can also be utilitiezed as a precursor for the synthesis of a carbon nanotube endcap (CNT)[18] because of the already present curvature (figure 1.2). With such a template CNTs with a single-chirality can be constructed.
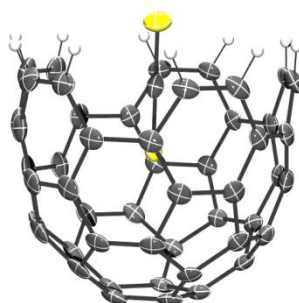
Figure 1.2: Molecular structure of the carbon nanotube endcap with an encapsulated carbon disulfide molecule synthesized by the group of Scott[18].

Corannulene has also very unique electronic properties. It can, for example, take up to four electrons (figure 1.3)[19]. The reduction is performed with lithium at -78 °C. Over the period of several days three color changes can be observed, from green to purple to a brownish-red indicating the formation of different anions. The tetraanion[20] is surprisingly stable due to the formation of a supramolecular sandwich complex with five cations between two bowls[21]. One more lithium cation is bound to each of the external surfaces of the two corannulene bowls. The remaining cation is removed from the surface and solvent-separated. When potassium is used as the reducing agent the reaction stops at the dianion stage even with an excess of metal.
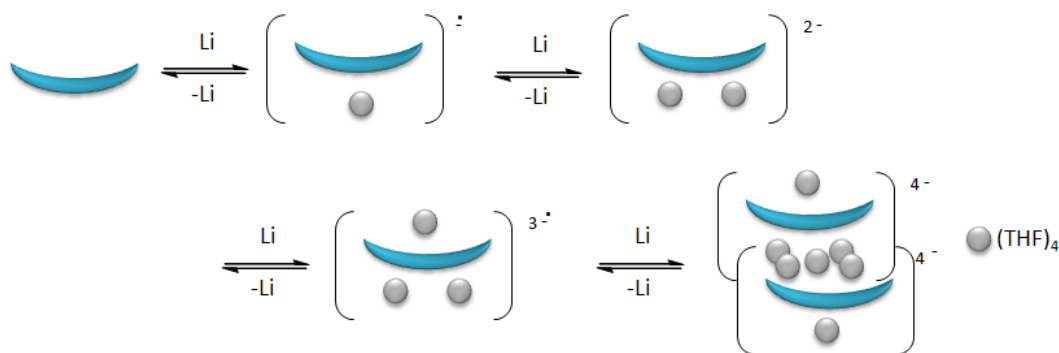
Figure 1.3: Reduction of corannulene with elemental lithium (blue bowls= corannulene anions, grey balls= lithium cations).

Because of these interesting electronic properties buckybowls are investigated for their application as molecular wires[22]. Another unique feature, making them even more interesting for this subject, is their tendency to stack in the solid phase forming molecular columns *via* π-π interactions. Pristine sumanene already shows this packing behavior in its crystal structure[3] but unsubstituted corannulene shows no such ordering[23]. Introducing electron withdrawing substituents at the corannulene rim[24], like trifluoromethyl groups[25], leads to the formation of the desired columns (figure 1.4) in the solid state. These columns have a high charge carrier mobility.
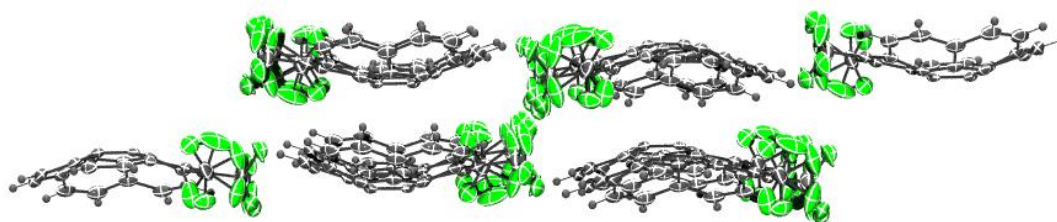
Figure 1.4: A section of the columnar stacking of disubstituted trifluoromethyl corannulene (the trifluoromethyl groups are disordered).

Like other aromatic compounds it is possible for corannulene to form organometallic complexes with corannulene as one of the ligands[26]. The first one was synthesized 1997 and the bowl is η^6 coordinated[27]. The full structural characterization was published later in 2004[28] and showed the coordination of the ruthenium centers to the opposite faces of corannulene which flattens the bowl (figure 1.5). Other bonding modes could be utilized as well but still a general preference for the bonding to the exo surface of corannulene is observed[29].

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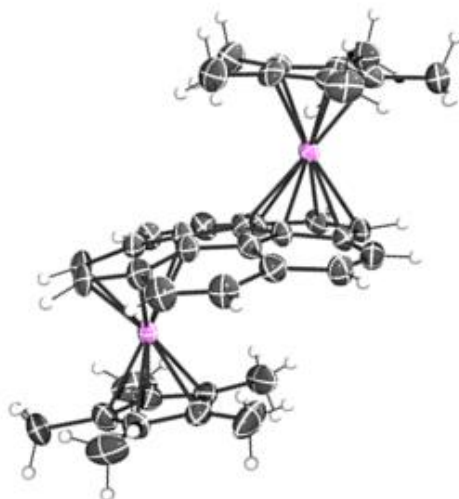
Figure 1.5: Molecular structure of the ruthenium complex[27] (anions and solvent molecules are omitted for clarity).

The most recent successes in corannulene chemistry include the selective cleavage of a rim carbon-carbon bond reported by the Shionoya group[30] resulting in a new flat type of aromatic hydrocarbons. Another working group from the University of Tokyo was able to introduce, for the first time, a hetero atom into the corannulene bowl[31] (figure 1.6).
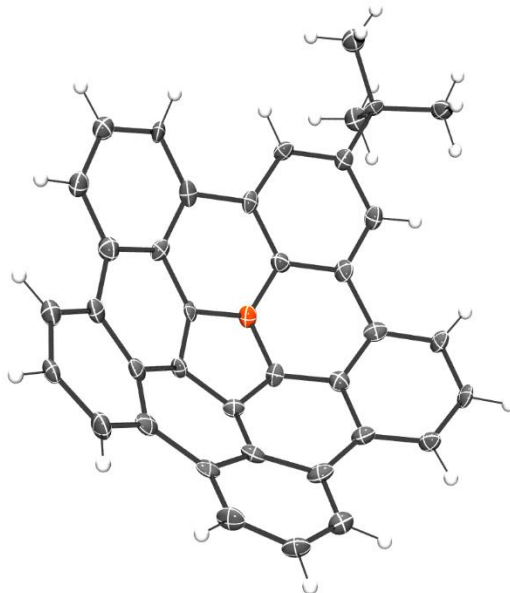
Figure 1.6: Molecular structure of the azocorannulene[31].

One of the most interesting properties of corannulene is without a doubt the supramolecular interaction with fullerenes. Corannulene as a fragment of the buckyball is able to form a supramolecular complex with the Buckminsterfullerene stabilized by convex-concave π-π

interactions. They act like a ball and socket leading to a maximum amount of π-π interaction between the bowl and the fullerene. Trying to observe the formation of the supramolecular complex between pristine corannulene and C_{60} by NMR spectroscopy is not possible but in 2012 Scott *et al.*[32] managed to co-crystallize them out of a 1:1 mixture proofing that indeed the supramolecular complex of the two compounds is formed. The great disordering of the fullerene observed in the crystal structure suggest that there are very little interactions between the guest and host explaining the NMR spectroscopic results. The first to detect a supramolecular complex of a corannulene derivative and the Buckminsterfullerene was the group of Scott using corannulene derivatives substituted with sulfide tentacles or flaps (figure 1.7)[33].
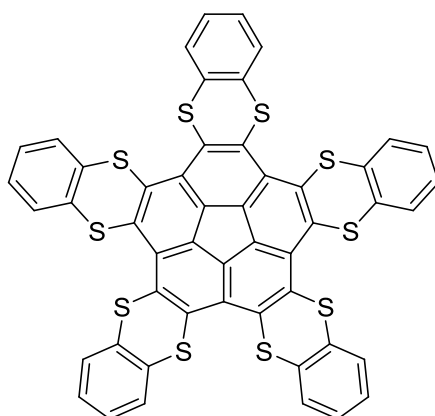
Figure 1.7: Schematic drawing of a corannulene derivative with sulfide flaps.

This molecule forms a 1:1 complex with C_{60} and C_{70} fullerenes with binding constants of $1420 \pm 64\ M^{-1}$ and $1110 \pm 92\ M^{-1}$ respectively in carbon disulfide. No interactions could be observed in toluene.

An interesting system was introduced 2007 by Sygula *et al.* and termed Buckycatcher[34] (figure 1.8). It consists of two corannulene bowls which are connected by a spacer. It was possible to obtain a crystal structure of the supramolecular complex which clearly shows the buckyball between the two corannulenes thus erasing all doubts of the exact positioning of the fullerene.
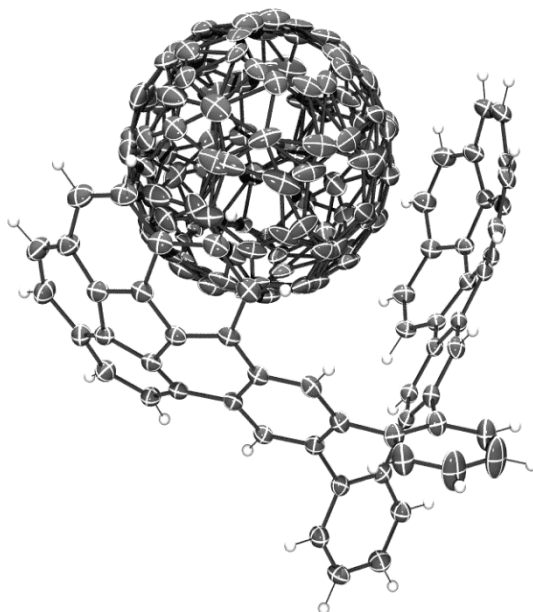
Figure 1.8: Crystal structure of the Buckycatcher (the fullerene and part of the spacer are disordered).

The binding constant for this system in toluene is 8600 ± 500 M^{-1} which is at the upper limits for the determination of binding constants *via* NMR titration. This molecule and the supramolecular complex was used as a reference in serval publications trying to create a reliable system for the determination of binding constants of corannulene based systems by theoretical calculation[35]. The group of Sygula published recently a second system with a norbornadiene as the spacer with even higher binding constants[36].

With this breakthrough a lot of other systems were introduced like a platinum complex with two corannulenes bound to the metal center over an acetylene group[37]. This molecule has a binding constant of 4600 ± 10 M^{-1} for the Buckminsterfullerene and a more than three times larger one (20700 ± 600 M^{-1}) for C$_{70}$. Polymers also can be used as hosts for the intercalation of fullerenes by corannulene bowls[38]. These structures can be fine-tuned with different monomers which link the corannulene units. Even Corannulene bound onto the surface of Cu (110) was found to show the desired interactions with the Buckminsterfullerene[39].

1.3. Molecular Tweezers, Clips and Receptors

Systems like the Buckycatcher are called molecular tweezers. Molecular clefts, clips or tweezers describe systems that can interact with a guest through noncovalent interactions. These can be electrostatic in nature (ion-ion, ion-dipole, dipole-dipole), π-π interactions, hydrogen bonding, hydrophobic or solvatophobic effects and van der Waals forces. The term "molecular tweezer" was first introduced by Whitlock *et al.* in 1978[40] and describes a noncyclic receptor system which is capable of reversibly incorporating a guest molecule (figure 1.9).
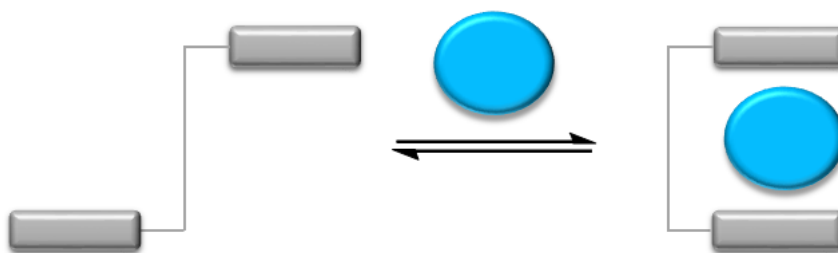
Figure 1.9: Principle of a molecular tweezer.

A lot of effort was invested into the construction and understanding of these clips as they can mimic biological processes and are part of the synthesis of molecular machines. These devices function due to host-guest recognition which induce molecular motions by external stimuli[41]. The pincers and spacer of the host molecules vary depending on the guest which should be incorporated. Different types of clips are known which incorporate all kinds of guests. In this brief overview only those hosting neutral guests are considered.

Generally, one can distinguish between two different variants of spacers. First, the rigid, preorganized type which possess an already formed cavity and second flexible spacers which adjust to the type and size of the substrate. An example for rigid systems, other than the Buckycatcher, are clips based on a glycoluril scaffold. Those go back to the ground breaking work of Nolte *et al.*[42] who discovered that the reaction of formaldehyde with diphenylglycoluril leads to an u-shaped tweezer with a rigid cavity (figure 1.10).
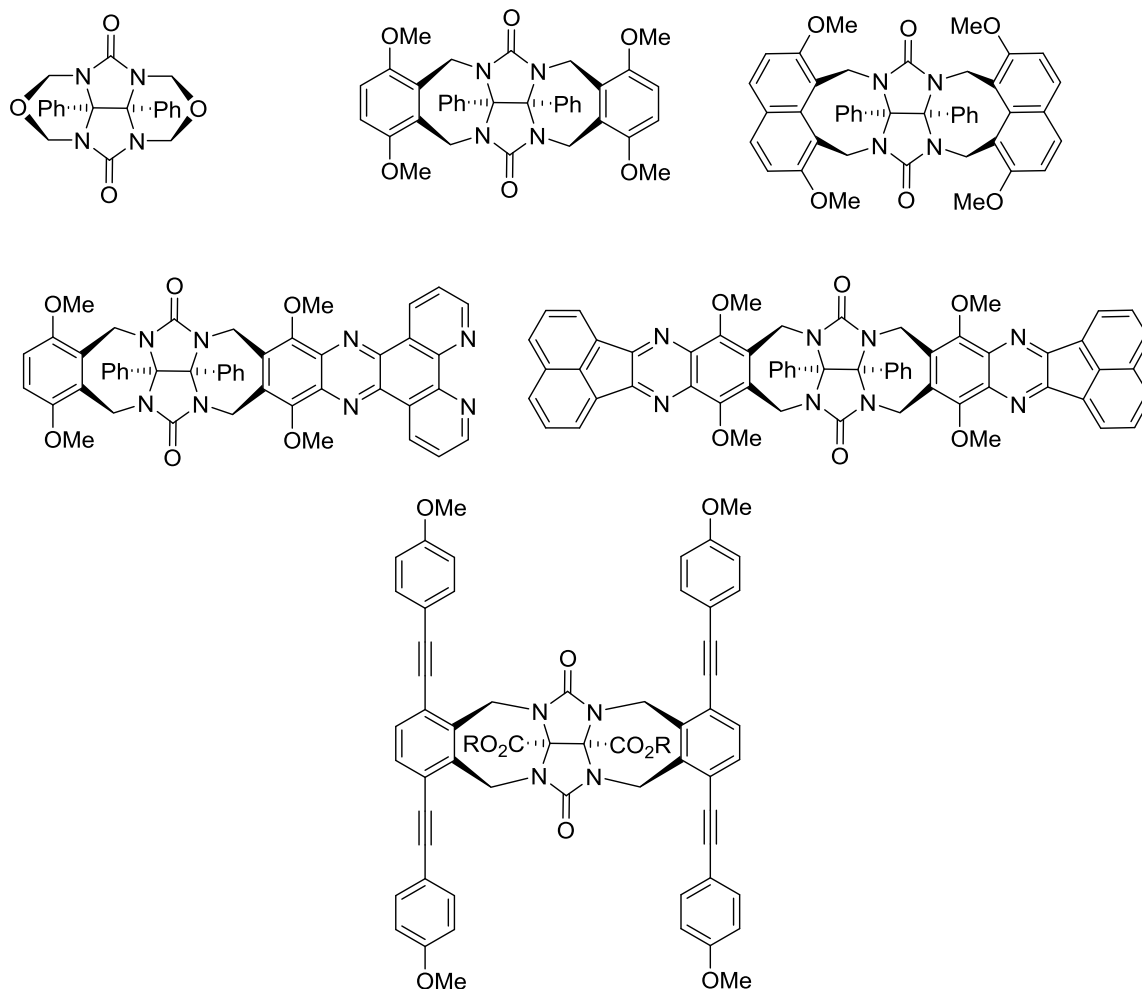
Figure 1.10: Molecular tweezers based on the glycoluril scaffold.

Depending on the chosen pincers the receptors can be fine-tuned to accompany the guest molecule. If there are two substituted benzene molecules instead of the ether groups, the electron rich spacer and the two hydrogen bond acceptors enable the incorporation of phenols, dihydroxybenzene and dihydroxynaphthalene derivatives[43]. When exchanging the benzene pincers with naphthalene the molecular clip can bind dicyanobenzene[44]. Creating an unsymmetrical tweezer with one side being a phenanthroline derivative allows for the binding of olivetol[45]. The symmetrical clip with the two fluoranthenes can even bind resorcinol[46]. Changing the backbone from phenyl substituents to ethyl ester groups and the pincers to extended *o*-xylenes allows for the complexation of nitrophenol[47].

Another way of creating a rigid spacer is connecting polyarenes in such a way that they are kept in a *syn* conformation as shown for the Buckycatchers. Those types of clips can have a belt like appearance creating a concave-convex topography allowing for multiple π-π and CH-π interactions with aromatic guests. They can be fine-tuned by varying the number and size of the arenes on the pincers[48].

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These tweezers are connected over a non-rigid spacer allowing flexibility to the pincers that often leads to a non-cofacial positioning. Thus they have a variety of possible guests while the rigid tweezers target only one guest. But the binding of a guest requires large reorganization energies because the pincers have to rearrange themselves into cofacial postion. This leads to a decline in the binding constant compared to rigid tethers.
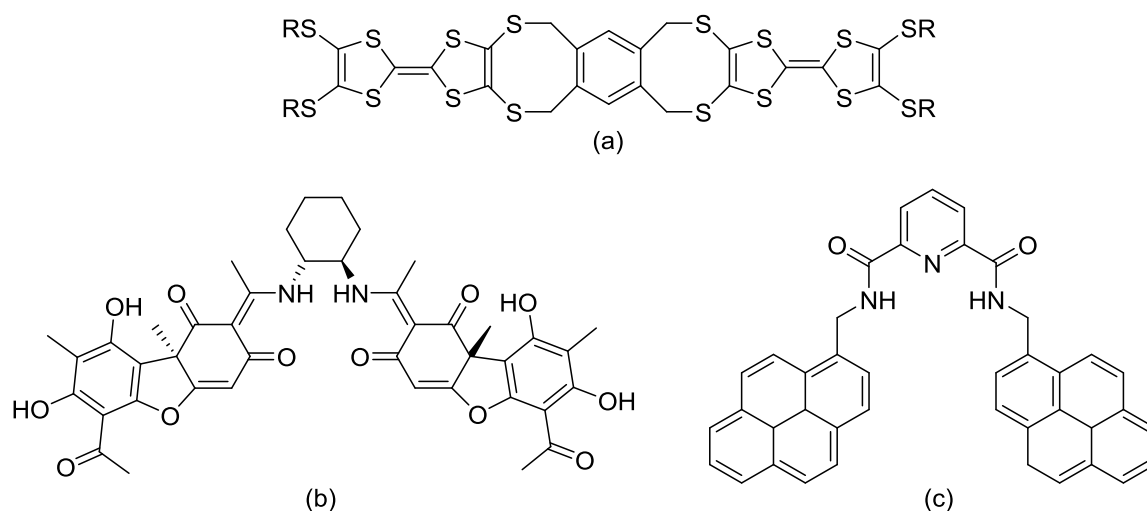
Figure 1.11: Three examples for non-rigid spacers ((a) tweezer with TTF based pincers, (b) = usnic acid tweezer, (c) = pyridine dicarbonyl tweezer).

An example for a flexible host uses usnic acids as pincers[49] (b) it is able to incorporate trinitrofluorenone creating a charge-transfer complex. Another approach uses conformation isomers like the bis-TTF based molecule[50] (a). This molecule can only form a host-guest complex when it adopts the *cis boat-boat* conformation. A direct synthesis produces receptors based on an isophthaloyl or pyridine dicarbonyl moiety[51] (c). Those can encapsulate macrocyclic derivatives based on naphthalenediimides with high association constants (figure 1.11).

While the thus far described molecular tweezers and clips are mostly 1:1 host guest systems there are a lot of examples for receptors with stoichiometries such as 1:2[52] and 2:1[36, 53]. There are even higher binding ratios like the polymeric corannulene chains mentioned in the previous chapter.

Krätschmer *et al.*[54] discovered that fullerenes can be extracted from soot by the usage of toluene receptors. Thus the merging of supramolecular chemistry, fullerenes, and carbon nanotubes started. Traditional host molecules with electron-rich arenes such as calix[n]arenes, cyclotriverarylenes (CTV) or oxacalix[3]arenes only bind the fullerenes in the solid state[55]. Two strategies were employed to further improve the binding. First, the host molecules were

decorated with electron-rich aromatic units as appendance[56]. Second, two host molecules were connected over a spacer[57] (figure 1.12.).
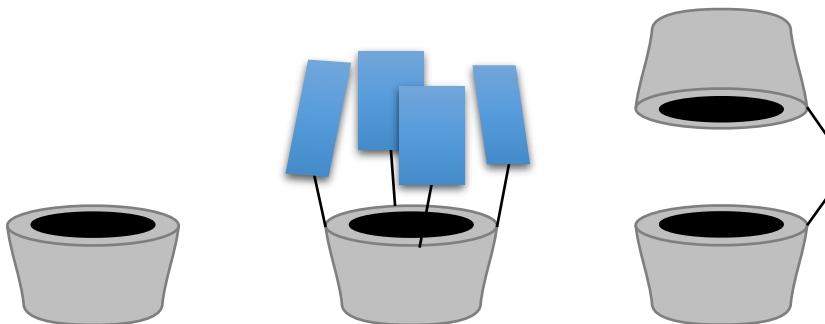
Figure 1.12: Left: traditional host, middle: traditional host decorated with electron rich aromatics, right: two traditional hosts connected over a spacer.

Also, new receptor molecules were designed to form stronger interactions with the curved surface of the guest molecules like corannulenes, extended TTF (exTTF) and "carbon nanorings". These molecules have their curved π-surfaces in common which can form strong interactions with the guests.

Corannulene based-systems, which were introduced in the previous chapter, are either hard to synthesize, even excluding the synthesis of corannulene itself, like the Buckycatcher. Or they depend on noble metals and are thus quite expensive and/or are missing substituents that allows them to be attached to a surface for their use as a stationary phase for the separation of fullerenes. All of the above described system for the incorporation of fullerenes also fall in the category of rigid spacers, making them inflexible and their great potential to bind fullerenes may hinder the release of the latter from the solid phase. The aim of this work was to construct a molecular system on the base of corannulene that can incorporate fullerenes, has flexible pincers and a possible point of attachment for immobilization (figure 1.13).
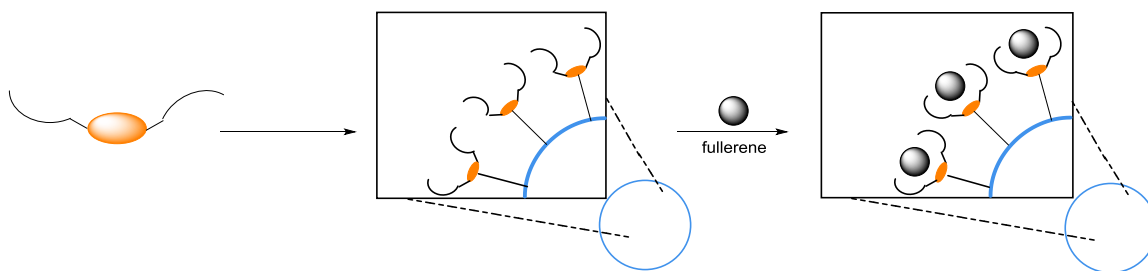
Figure 1.13: Schematic illustration of the attachment of the molecular receptors on a stationary phase.

There are many methods to connect two corannulene bowls. In this project three were investigated (figure 1.14). First, a perfluorinated four-membered ring was envisioned by polymerizing two trifluorovinyl corannulenes (1) (chapter 3.1.). The resulting corannulene derivative should not only be able to incorporate fullerenes but also have interesting electronic properties.
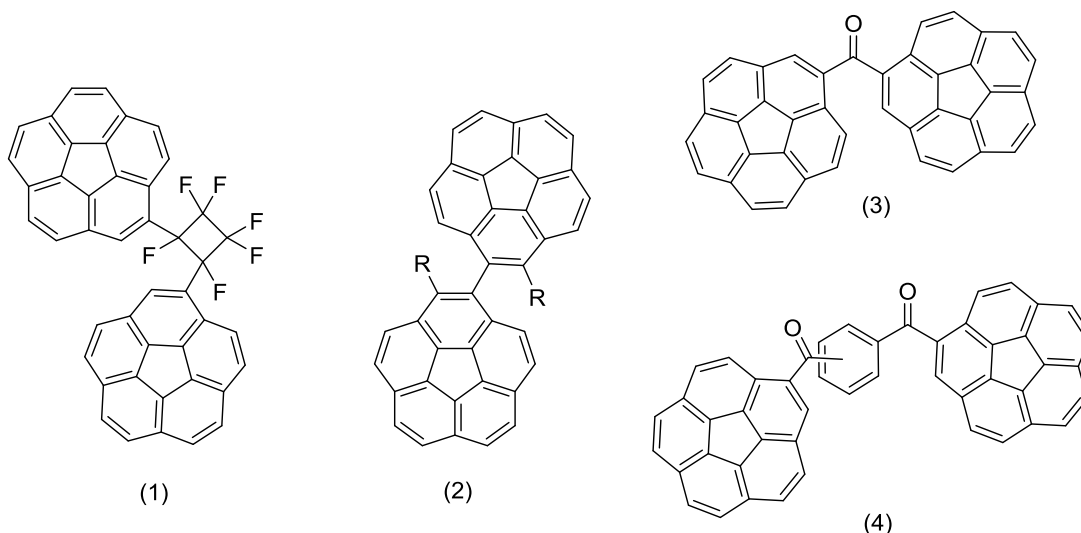
Figure 1.14: Investigated methods of connecting two corannulenes bowls (1) perfluorinated four membered ring, (2) covalent bond, (3) carbonyl group, (4) diketone.

Second, two corannulenes should be directly connected by a covalent bond (2). Introducing sterically demanding substituents next to the bridging bond should enlarge the cavity in which guests can incorporated (chapter 4.). The third option was the connection over a carbonyl group. This method allows for two binding motives, either by connecting the two corannulenes directly over one carbonyl group (3) (chapter 5.2.) or over two carbonyl groups (4) by introducing an aryl spacer in between the two polycyclic aromatic hydrocarbons (chapter 5.3.). The latter type of carbonyl spacer is an often used motive in supramolecular chemistry[51, 58]. The resulting receptors (1-4) should then be tested for their ability to bind monocyclic, polycyclic and geodesic aromatic guests. To investigate if the non-rigid spacers allow incorporation of aryl compounds besides fullerenes.

2. General remarks

2.1. Nomenclature

2.1.1. Corannulene

Following the general literature suggestions[59] the different carbons of corannulene **1** bonds are labelled, hub for the inner five-membered ring, spoke for the outer quaternary carbon atoms and rim for the tertiary carbon atoms. Carbon atoms that bear a substituent other than a hydrogen atom are called ipso (figure 2.1).

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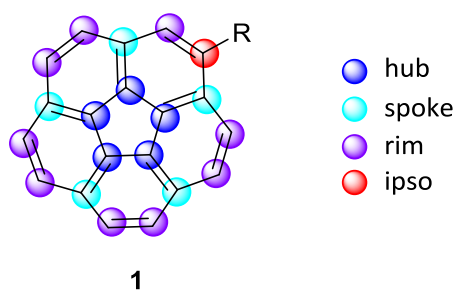
Figure 2.1: Labelling of the C-C bonds in corannulene.

The bowl depth of the buckybowls is defined by the distance between the plane formed by the rim carbon atoms and the plane from the hub atoms (figure 2.2).
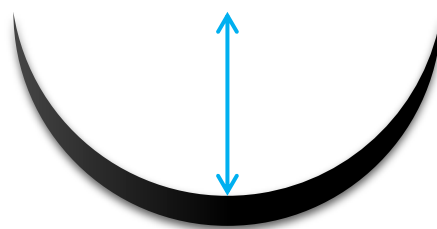
Figure 2.2: Bowldepth of the corannulene bowl.

2.1.2. Isophthalic Acid Derivatives

The numbering of the carbon atoms of the benzene ring in the isophthaloyl derivatives starts with the left carbonyl group and then moves clockwise around the benzene ring (figure 2.3).
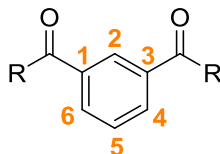
Figure 2.3: Numbering of the carbon atoms for the isophthaloyl compounds.

3. Modifications of the Corannulene Synthesis

The pristine corannulene **1** used in this thesis was synthesized following the procedure of the Siegel group[14]. Modifications to the scale of the protocol had to be made since the original synthesis was designed for a pilot plant. Thus the work-up methods and reaction conditions had to be adjusted.

The first step was scaled down and product **2** was extracted from the quenched reaction mixture. For the synthesis of the dimethylnaphthalene **3,** the Siegel group proposes the use of conc. sulfuric acid instead of hydrogen bromide. It is favored as it corrodes the steel vessel less than the hydrogen bromide solution. However, the reaction yield drops by 16 %. Therefore the hydrogen bromide option was used. The dimethylnaphthalene **3** had to be purified by sublimation after the recrystallization because a brown oily side product sticked to the crystals. This was ignored in the kilogram-scale production. To ensure the optimal temperature control for formation of the diketone **4a** a three neck double walled 2L-flask was constructed. The isomers **4a** and **4b** can be separated with GRT. However a highly viscose side product sticks to the isolated isomer **4a** and therefore has to be removed either by column chromatography or recrystallization from toluene. Because of the much smaller scale the work-up of the intermediate **6** according to literature was not possible. Instead of separating product **6** by filtration it was extracted with dichloromethane.
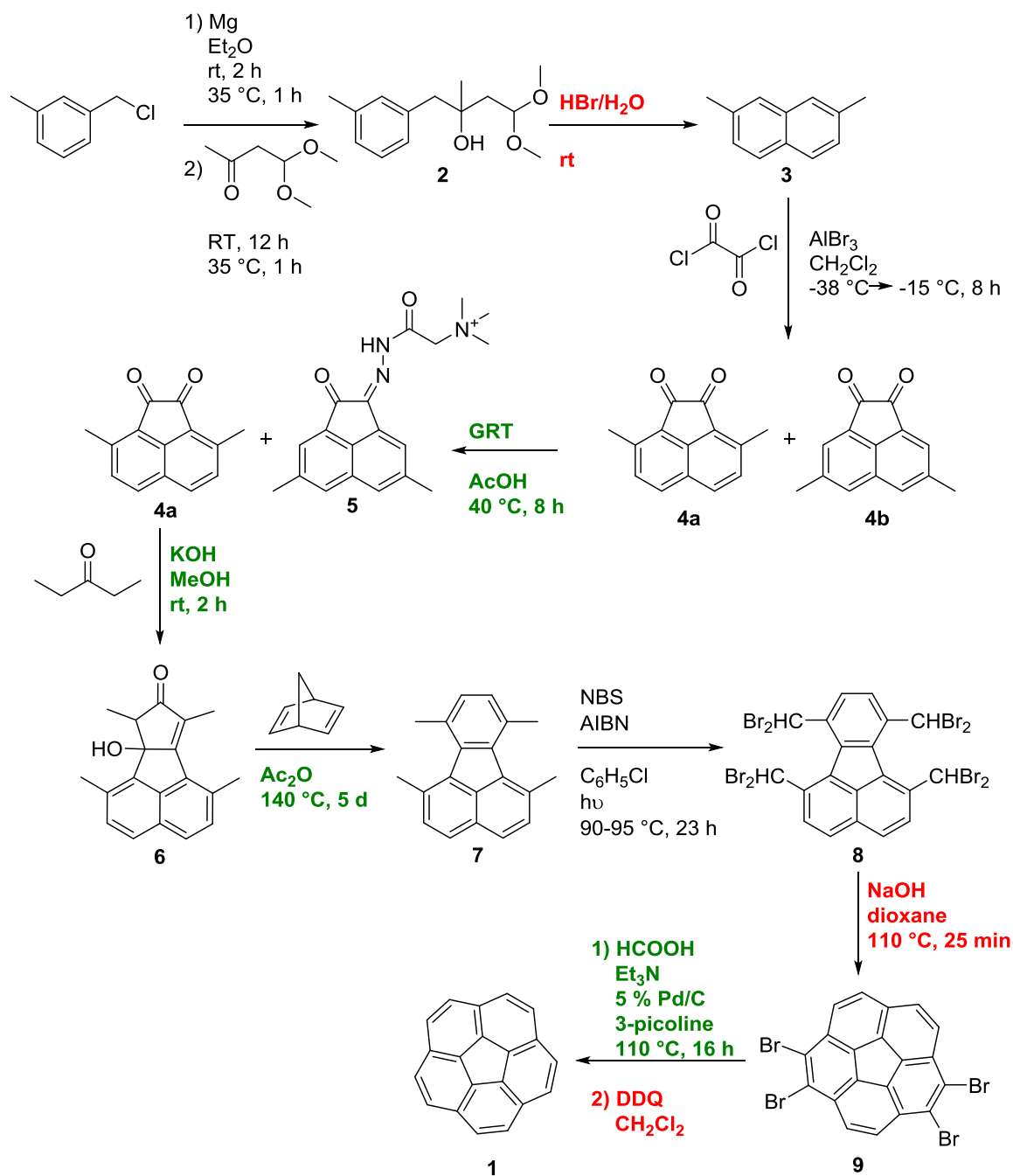
Scheme 3.1: Modified corannulene **1** synthesis for laboratory scale (red = changed reaction conditions, green= changed work-up routine).

Tetramethylfluoranthene **7** was synthesized according to literature procedure but was isolated by flash column chromatography using *n*-pentane as the mobile phase. Bromination of compound **7** used NBS in tetrachloromethane or monochlorobenzene with the respective radical starter. Although both versions are viable tetrachloromethane falls under the Montreal protocol making it difficult to acquire and quite costly. So the reaction was carried out in the aromatic solvent. The ring closure to tetrabromocorannulene **9** was performed in dioxane instead of isopropanol. The

alcohol led to a mixture of brominated corannulenes instead of one single product. For the final step, the paper proposes the use of picoline or pyridine. In both cases, side products could be detected. When pyridine was chosen as the solvent more unwanted products formed. The most likely explanation is the difference in reaction temperatures. Picoline boils at 140 °C while pyridine has a boiling point of just 115 °C. This hypothesis was further reinforced when a magnetic stirrer malfunctioned and the reaction temperature was kept at 40 °C for the complete duration of the experiment. After work-up no corannulene **1** could be found. In cases were corannulene **1** was synthesized, a few minor impurities could be removed by column chromatography and one of them identified as bicorannulenyl. It probably formed by a palladium catalyzed homocoupling reaction. Nevertheless, the major impurity could not be removed. Sublimation, crystallization from a variety of solvents, and addition of activated carbon failed to remove the impurity. Examining the ^{1}H NMR spectrum revealed a signal at 3.37 ppm indicating a hydrogen positioned at a sp^3-hybridized carbon atom.

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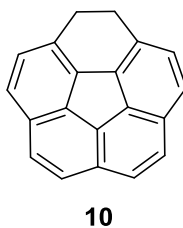
Figure 3.1: Hydrogenated corannulene.

This leads to the assumption that a hydrogenated corannulene **10** was formed (figure 3.1). This hypothesis was supported by finding lot of signals around the same region in the mixture produced by the reaction with the malfunctioning stirrer. Both mixtures were dissolved in dichloromethane and treated with DDQ. In both cases pristine corannulene **1** could be isolated after an aqueous work-up and a flash column chromatography (scheme 3.1). The reaction was monitored by ^{1}H NMR spectroscopy and clearly showed the disappearance of the signals in the aliphatic region and the corresponding aromatic protons, leaving only one singlet for corannulene (figure 3.2).
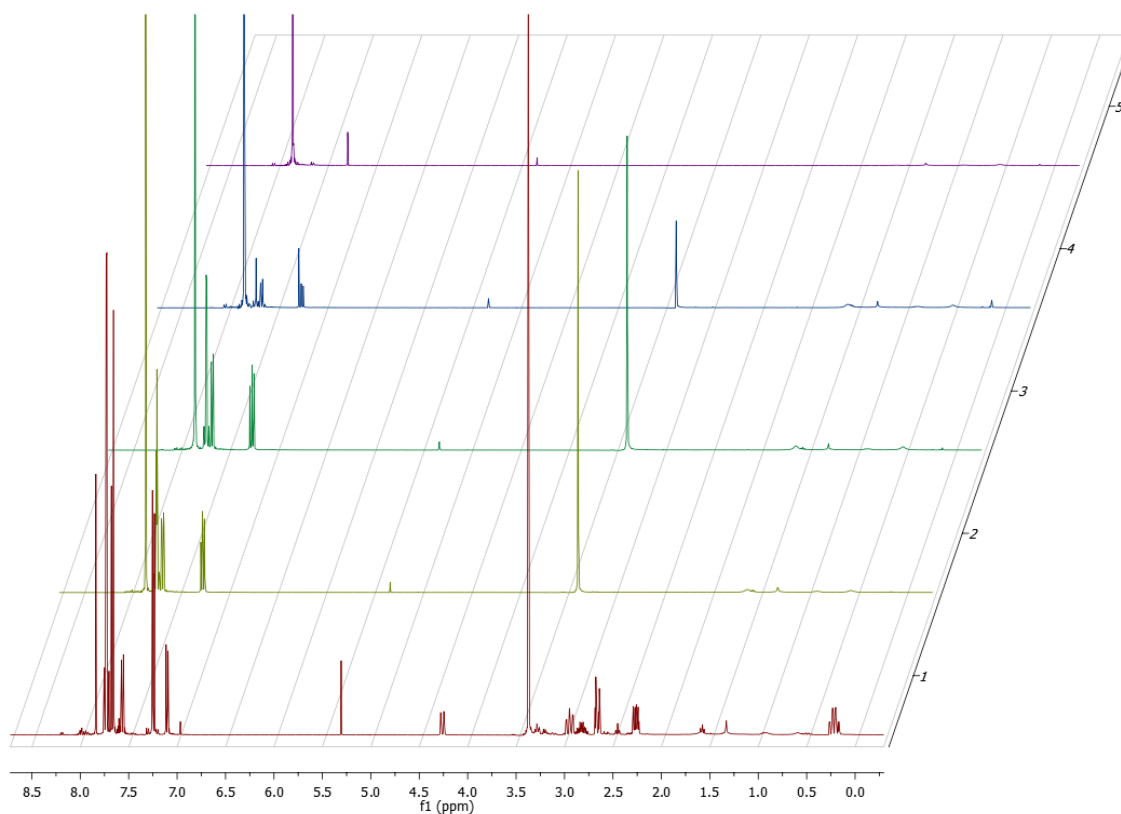
Figure 3.2: Reaction mixture (red), after steering with DDQ in dichloromethane for 6 d (yellow green), 8 d (green), 15 d (blue) and 20 d (violet).

Since the degree of hydrogenation depends strongly on the reaction temperature, it can be assumed that only a small amount of the nearly insoluble tetrabromocorannulene **9** is in solution and can react. Therefore, a large amount of the hydrogen produced in situ is left unreacted. Since the reaction is performed in a closed vessel it is not removed from the reaction and reacts with corannulene **1** leading to the hydrogenated side product **10**.

4. Trifluorovinyl corannulenes

The first attempt to construct a molecular tweezer is based on the dimerization of trifluorovinyl corannulene **11**. This particular reaction has already been investigated for ferrocene derivatives[60]. It proceeds in good yields and is a fast way to connect two molecules.
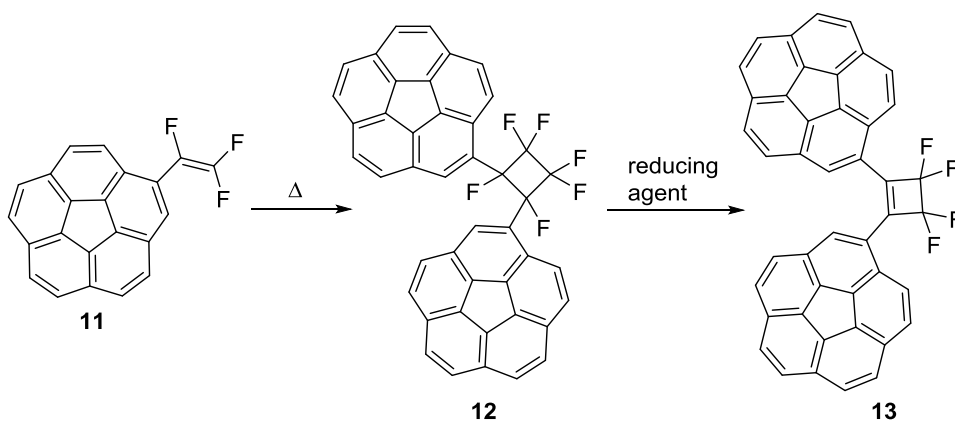
Scheme 4.1: Synthesis of two corannulene containing receptors **12** and **13**.

The perfluorinated four membered ring can be further reduced in one step to form the unsaturated analog making it possible to create two potential tweezers from the same educt **11** (scheme 4.1). Those, derivatives **12** and **13**, are also interesting candidates for possible columnar stacking in the solid state and thus potential nanowires.

4.1. Monotrifluorovinylcorannulene

To synthesize monotrifluorovinylcorannulene **11**, monoiodcorannulene **14** is needed as a starting material. This molecule can be synthesized following the protocol from Wang *et al.*[61]. They use corannulene **1**, N-iodosuccinimide in stoichiometrical amounts and gold(III)-chloride as a catalyst (scheme 4.2).
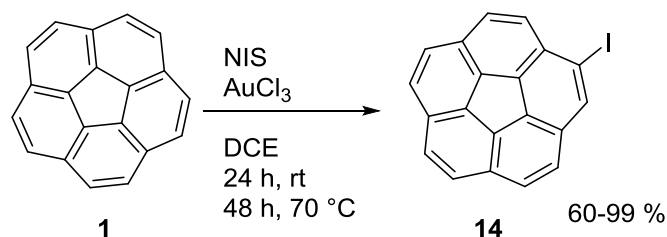
Scheme 4.2: Synthesis of monoiodocorannulene **14**.

The major drawback of this synthesis is the inconsistency of the yield with fluctuating values from 60 % up to 99 %. If unreacted corannulene **1** is still present after the reaction, it cannot be separated from product **14**. If the educt-product mixture is used in the next reaction step, the synthesized monotrifluorovinylcorannulene **11** cannot be isolated from educt **1** either. Thus a different synthetic route using a Sandmeyer type of reaction (scheme 4.3) was envisioned. For this route aminocorannulene **15** is required.
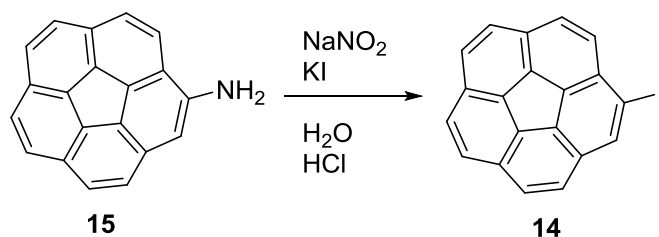
Scheme 4.3: Different approach to synthesize monoiodocorannulene **14**.

Derivative **15** is already described in the literature[62]. The synthesis requires nitrocorannulene **16**, which can be produced from pristine corannulene **1** by treatment with nitric acid. Product **16** can be easily separated from educt **1** *via* column chromatography excluding the problem of remaining corannulene **1**.
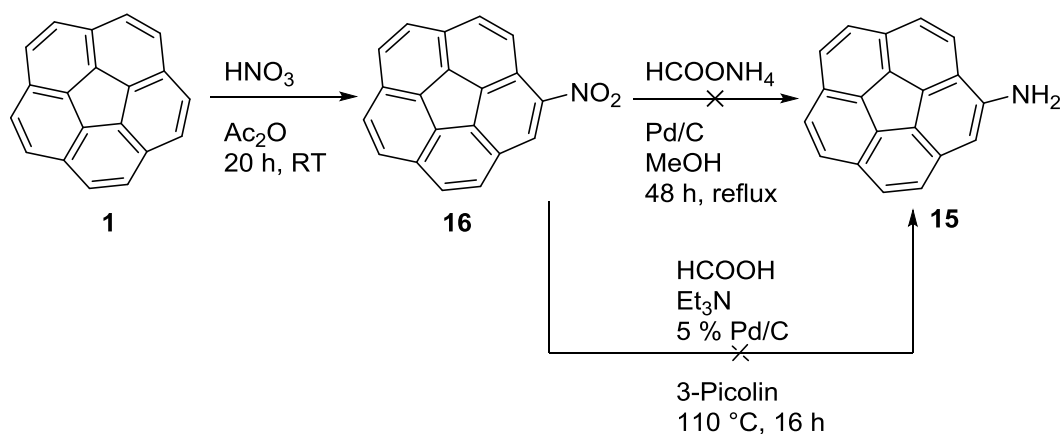
Scheme 4.4: Attempts to generate aminocorannulene **15**.

Aminocorannulene **15** can be generated using ammonium formiate and palladium on carbon. The reaction was carried out six times using the described reaction conditions but product **15** did not form. After correspondence with the authors, the nitrocorannulene **16** was purified by pecipitation from a *n*-pentane:dichloromethane solution. However, still no desired reaction product **15** could be obtained. After applying the conditions of the last step of the corannulene synthesis[14], just corannulene **1** could be isolated (scheme 4.4). Since aminocorannulene **15** cannot be synthesized easily and it is not clear if iodocorannulene **14** can be generated through a Sandmeyer reaction, the compound **14** was eventually generated using the standard synthesis described above (scheme 4.2).

To synthesize trifluorovinylcorannulene **11**, iodocorannulene **14** is reacted with an organometallic reagent bearing a trifluorvinylgroup in a palladium catalyzed corss-coupling reaction. Possible trifluorovinyl donors are trifluorvinylzinc chloride, tri-*n*-butyltrifluorovinyl stannane and lithium trimethoxy(trifluorovinyl)borate. The first reacts in a Negishi type fashion, the second in a Stille like coupling and the last one in a Suzuki-Miyaura cross-coupling reaction. For the synthesis of trifluorovinyl compound **11** the zinc reagent **17** was chosen. Since it is not stable when isolated, it is stored as a stock solution in THF at -60 °C.
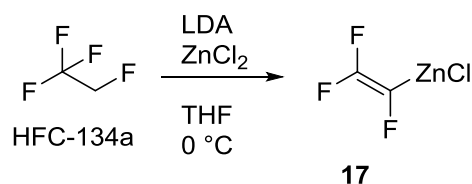
Scheme 4.5: Synthesis of trifluorovinylzinc chloride **17**.

Trifluorovinylzinc chloride **17** is generated by an *in-situ* metalation-trans metalation procedure published by Raghavanpillai and Burton[63] starting from the cheap gas HFC-134a (scheme 4.5). The trifluorovinylzinc chloride solution was reacted with monoiodocorannulene **14** using a palladium(II) catalyst and triphenyl phosphine (scheme 4.6).

22
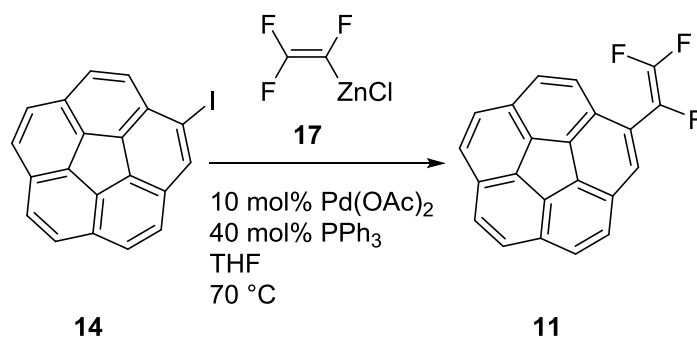
Scheme 4.6: Synthesis of trifluorovinyl corannulene **11**.

After seven hours a ^{19}F NMR spectra of the solution was measured showing the signals of residual HFC-134a from the synthesis of trifluorovinylzinc chloride **17** and of unreacted triflurovinylzinc chloride stock solution which was used in excess. A third set of signals was found matching those expected for product **11** (figure 4.1).
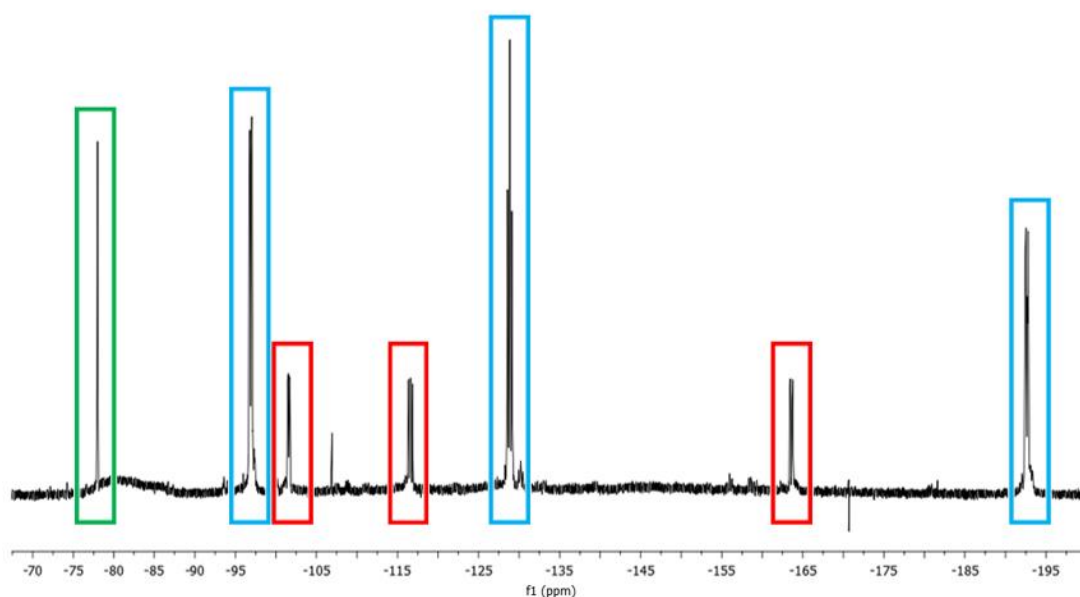
Figure 4.1: ^{19}F NMR spectrum of the reaction mixture (red= monotrifluorovinylcorannulene **11**, green= HFC-130a, blue= trifluorovinylzinc chloride **17**).

Work-up of the reaction mixture removes the traces of the residue gas and zinc chloride **17** but also leads to a new set of signals. These probably correspond to the reaction product of the excess amount of **17** and dichloromethane which was used in the work-up (figure 4.2).

23
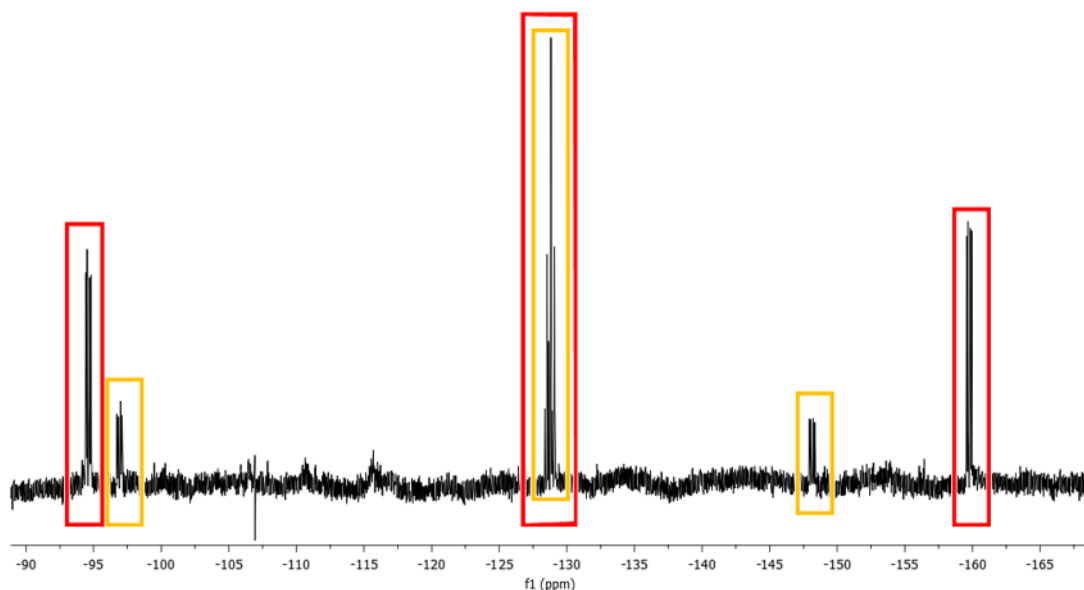
Figure 4.2: ^{19}F NMR spectrum of the reaction mixture (red= monotrifluorovinylcorannulene, orange= impurity).

Separation of the undesired compound and the product by column chromatography was not successful. In fact, no product or side product could be detected at all after the purification effort. Most likely, both products polymerized when concentrated or on the silica gel of the column.

4.2. Interlude: Higher substituted corannulenes

To investigate if the decomposition of trifluorovinyl corannulene **11** is a general problem of this class or specific for the monosubstituted derivative **11**, the synthesis of higher substituted analogs was attempted. While those are not prime precursors for the construction of molecular tweezers, they are believed to have very interesting electronic properties.
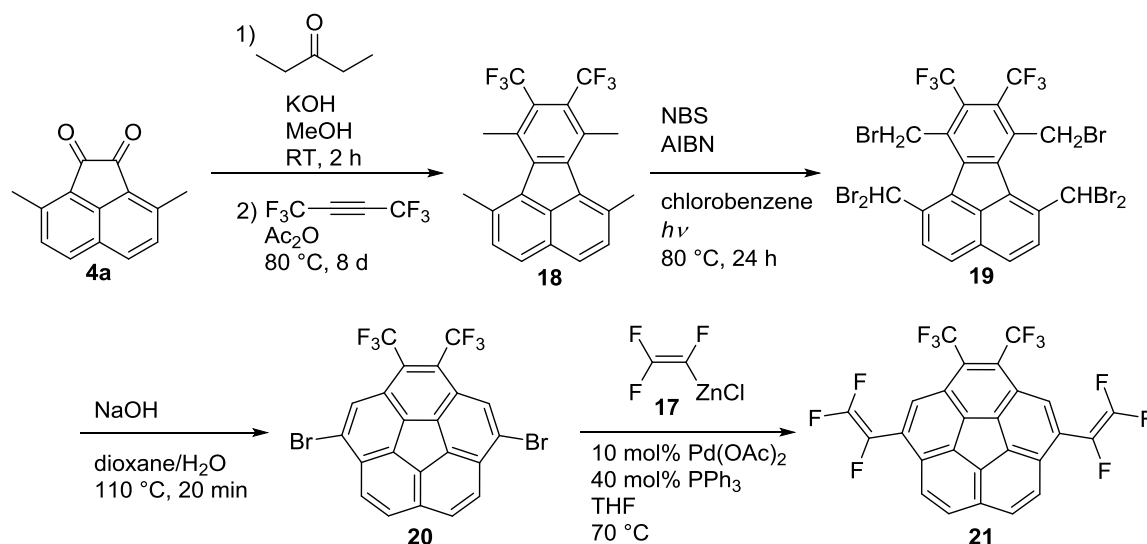
Scheme 4.7: Synthesis of bis(trifluorovinyl)corannulene **21**.

After the formation a selective halogenation of the corannulene core is challenging. A more viable approach is to influence the number of possible substituents before the formation of the core. One key step of the original synthesis is the Diels-Alder reaction of dienone **6**, with norbornadiene. Replacing this reagent with suitable substituted alkynes allows the introduction of substituents in ortho position. Extremely useful for this purpose are acetylenes bearing one or two trifluoromethyl groups. They are chemically inert and sterically demanding enough to have the desired effect. For the synthesis of dibromocorannulene **20**, hexafluorobutyne was used as dienophile (scheme 4.7). The crystal structure of the fluoranthene was already published by the Lentz group[25b]. The Diels-Alder reaction product **18** is then brominated with AIBN as the radical initiator and chlorobenzene as the solvent analog to the procedure of the Siegel group[14]. Brominated derivative **19** can then be cyclized and the formed dibromo compound **20** reacted through the Negishi procedure mentioned above. Following the reaction process with ^{19}F NMR spectroscopy the formation of a new compound bearing a trifluorovinyl group could be detected (figure 3.3).
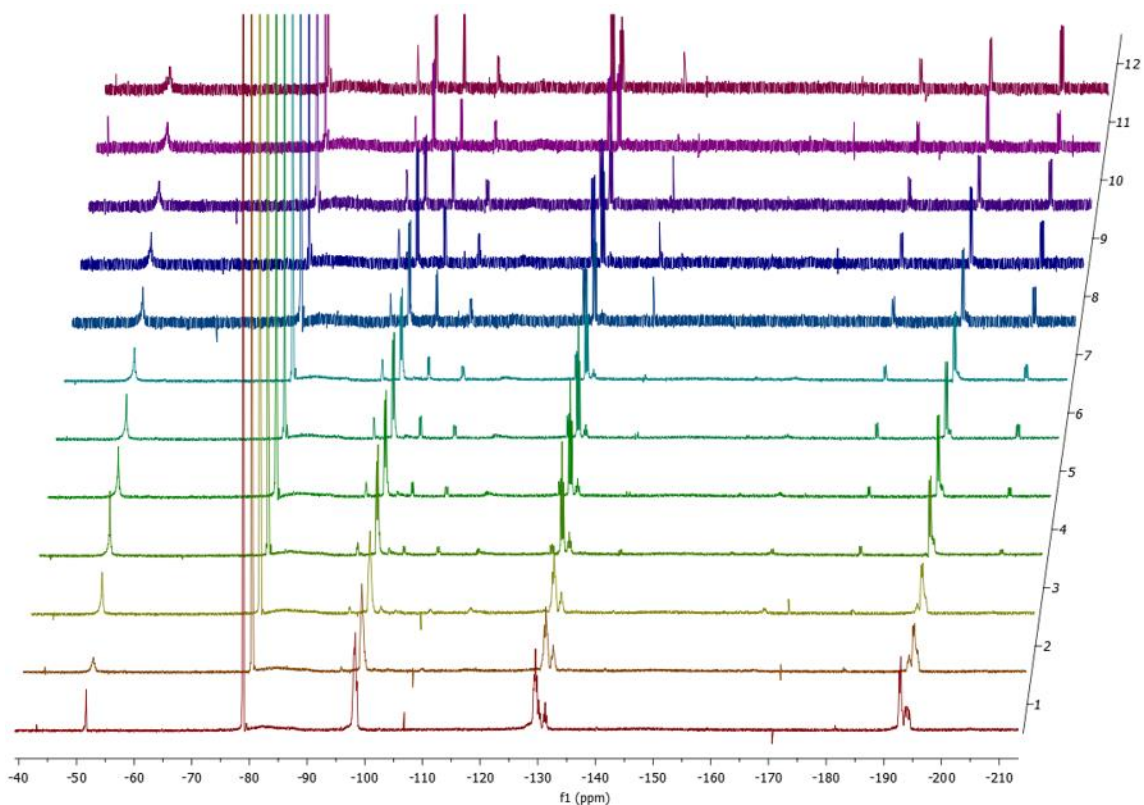
Figure 4.3: ^{19}F NMR spectra of the reaction process of **21** (1 = 0 min, 2 = 25 min, 3 = 30 min, 4 = 1 h, 5 = 1.5 h, 6 = 2 h, 7 = 2.5 h, 8 = 3 h, 9 = 4 h, 10 = 5 h, 11 = 6 h, 12 = 3 d).

Even after preparing the sample and measuring the first spectra small signals next to the educt **17** at -194 ppm, -131 ppm and -99 ppm indicate the possible formation of the monosubstituted product. These signals slowly decrease over the course of the study. After 25 min, small signals appear at -95 ppm, -103 ppm and -182 ppm. They most likely belong to the product since their intensity gradually increases over the course of the experiment. After approximately one hour, part of the organozinc compound **17** starts to hydrolyze and trifluoroethene is formed as a side product (-109 ppm, -128 ppm, -206 ppm). The signal of the trifluoromethyl groups broadens during the course of the reaction but does not shift (figure 4.4).
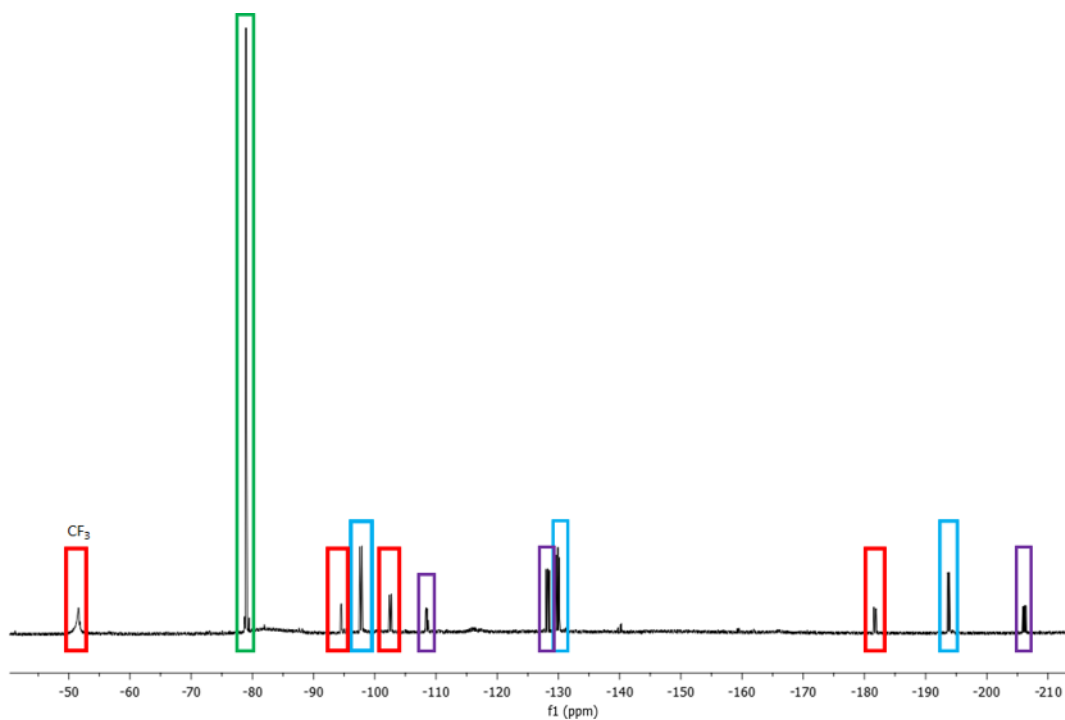
Figure 4.4: ^{19}F NMR spectrum of the reaction mixture of **21** (red= ditrifluorovinylcorannulene **21**, green= HFC-134a, blue= trifluorovinylzinc chloride **17**, violet= trilfuoroethene).

Unfortunately, no product **21** could be detected after concentrating the reaction mixture.

The utilized dienophile is the only difference between the synthesis of dibromocorannulene **20** and tribromocorannulene **24**. For the synthesis of tribromo compound **24** trifluoropropyne was used (scheme 4.8).
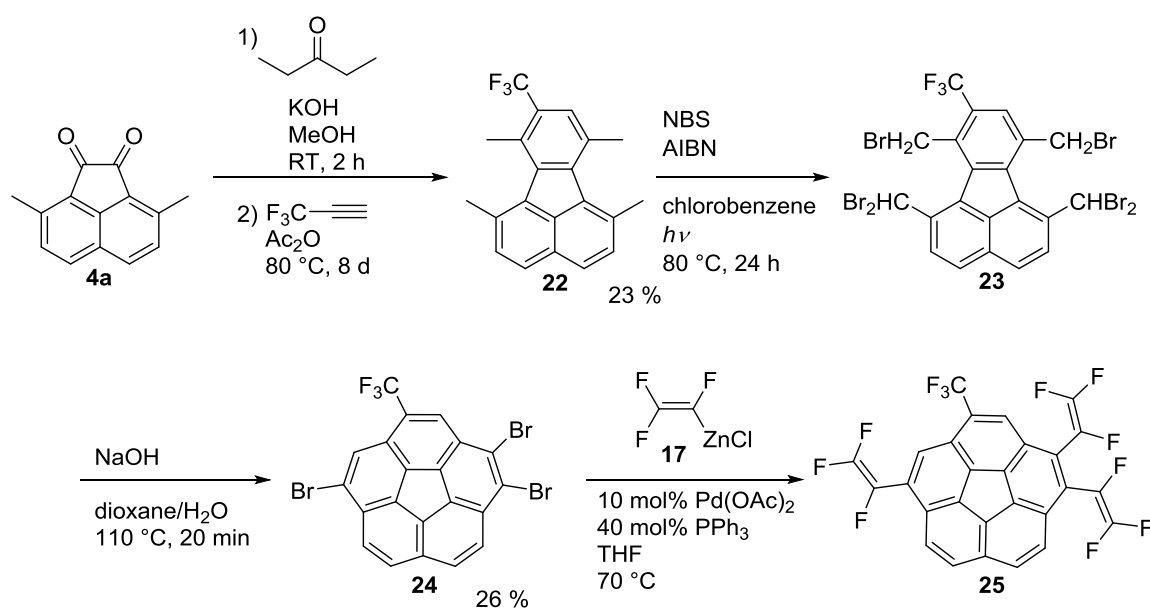
Scheme 4.8: Synthesis of tris(trifluorovinyl)corannulene **25**.

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It was possible to obtain crystals of molecule **22** with a sufficient quality for single crystal X-ray diffraction. The resulting crystal structure shows two molecules in the asymmetric unit which is in contrast to disubstituted derivative **18** (figure 4.5).
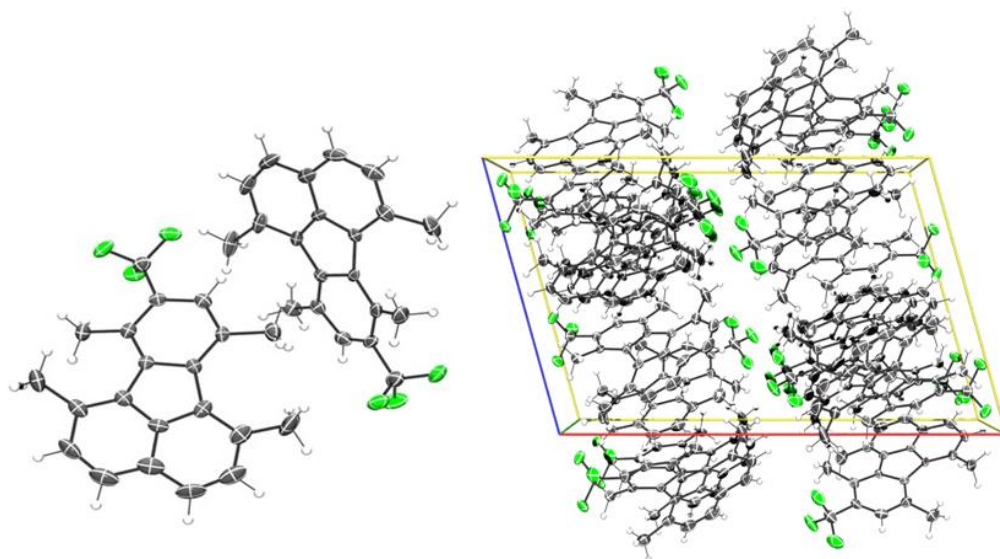
Figure 4.5: Molecular structure of the monosubstituted derivative **22** (left: asymmetric unit, right: packing pattern).

While both substances crystallize in a monocline space group their packing motive is very different. The disubstituted molecule **18** forms head-to-head dimers which are arranged in alternating columns. The packing of the monosubstituted product **22** is influenced by C-C (3.373-3.397 Å), C-H (2.829-2.850 Å), H-F (2.546-2.875 Å) and F-F (2.835 Å) interactions which result in the formation of strands. Both molecules **18** and **22** exhibit the same C_2-twist conformation. Therefore the upper fluorine containing part is not in the same plane as the naphthalene part, resulting in high internal strain.

Monosubstituted product **22** was further brominated and cyclized to tribromo corannulene **24**. When attempting to react it with trifluorovinyl zinc chloride **17**, no product **25** could be isolated. Similar observations were made for tetrakis(trifluorovinyl) corannulene **26** (scheme 4.9). In this case educt **9** is part of the synthesis of pristine corannulene **1** and thus it requires no additional effort to produce it.
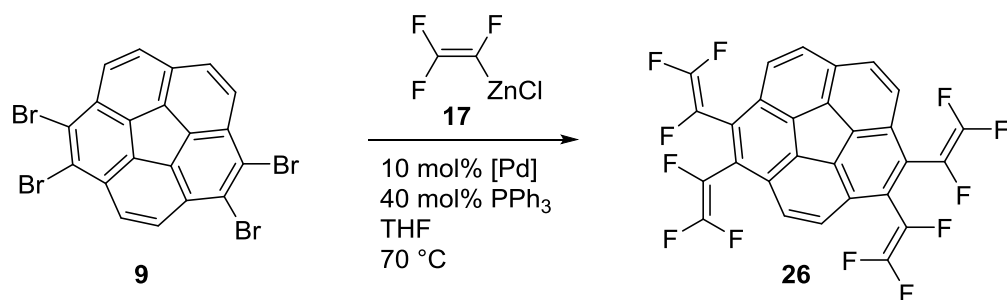
Scheme 4.9: Synthesis of bis(trifluorovinyl)corannulene **26**.

In conclusion, none of the synthesized trifluorovinyl corannulenes could be isolated. They can be observed in ^{19}F NMR spectra but they decompose, probably due to polymerization, during the reaction work-up.

This interlude proved that the troubles with the isolation of the trifluorovinyl corannulenes **11**, **21**, **25** and **26** is a general problem of this class of compounds and not restricted to the monosubstituted derivative **11**.

5. Biscorannulenyls

As described in the previous chapter, the selective functionalization of corannulene **1** poses a challenge because of the ten chemically identical hydrogen atoms at the rim. While there are some known protocols for higher substitution grades, like penta and deca substitution, the difficulty increases when decreasing the amount of substituents. It is often a better choice to introduce the substituent already on the fluoranthene stage. One possible approach is to use electron deficient dienophiles like the trifluoromethyl acetylenes used in the synthesis of the trifluorovinyl corannulenes. There are already some examples for this published but none using diacetylenes.

The synthesis of diacetylene **28** follows the route of Li *et al.* starting from the acetylene monomer **27**. Which is then reacted under the conditions established by the Siegel group[14], except that intermediate **6** is used in excess (scheme 5.1).
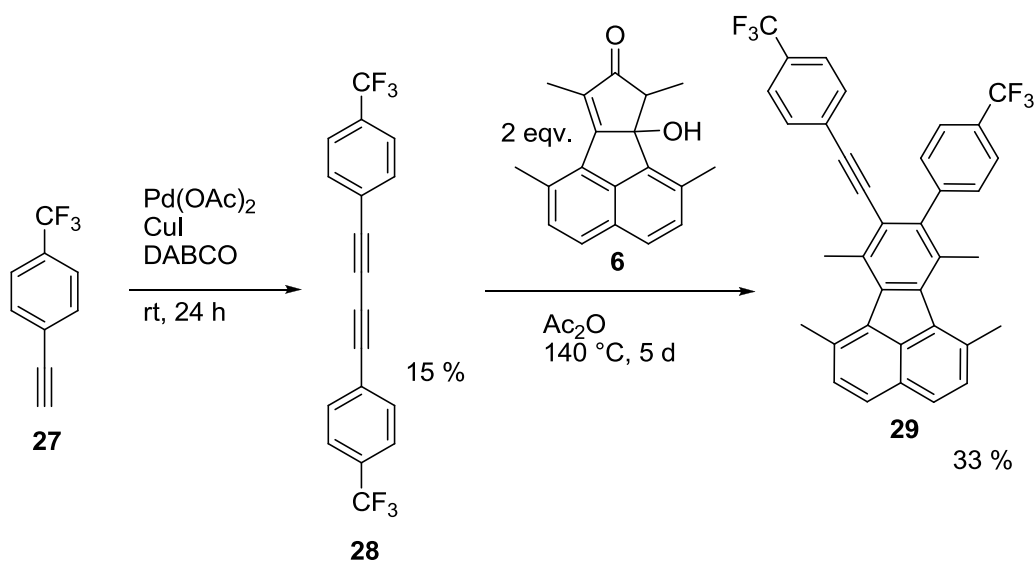
Scheme 5.1: Reaction to the fluoranthene derivative **29**.

Unfortunately, only monosubstituted derivative **29** could be isolated when two equivalent of **6** were used. While the derivative is interesting by itself, it serves no purpose for the construction of a receptor for the binding of fullerenes. Nevertheless, it was possible to obtain a solvent free single crystal which could be used for a structure determination by X-ray diffraction (figure 5.1).
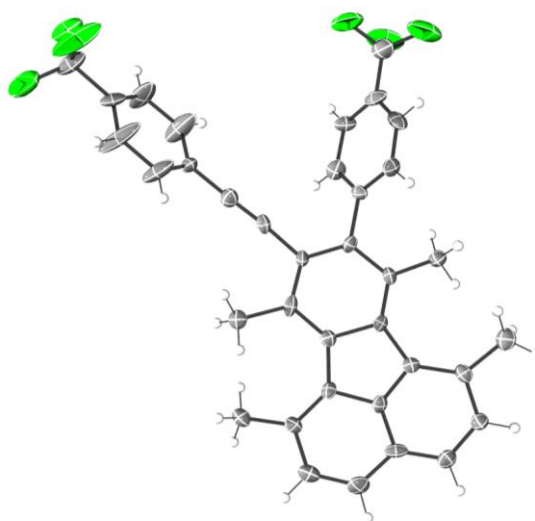
Figure 5.1: Molecular structure of the fluoranthene derivative **29**.

The previously described twisting of the naphthalene and benzene part of the molecule can be clearly observed making it a possible precursor for the synthesis of a substituted corannulene.

When isolating the compound by column chromatography a fraction was isolated containing product **29** and a side product in small amounts. EI mass spectrometry showed almost no signals belonging to monosubstituted product **29**. The observed fragmentation corresponds to the disubstituted product **30** that must have formed as a minor product during the reaction.

Form this observation it was concluded that increasing the equivalents of intermediate **6** may lead to an increased formation of the disubstituted product **30**. This hypothesis was confirmed when using 6 equivalents of **6** produced disbustituted molecule **30** as the main product (scheme 5.2).
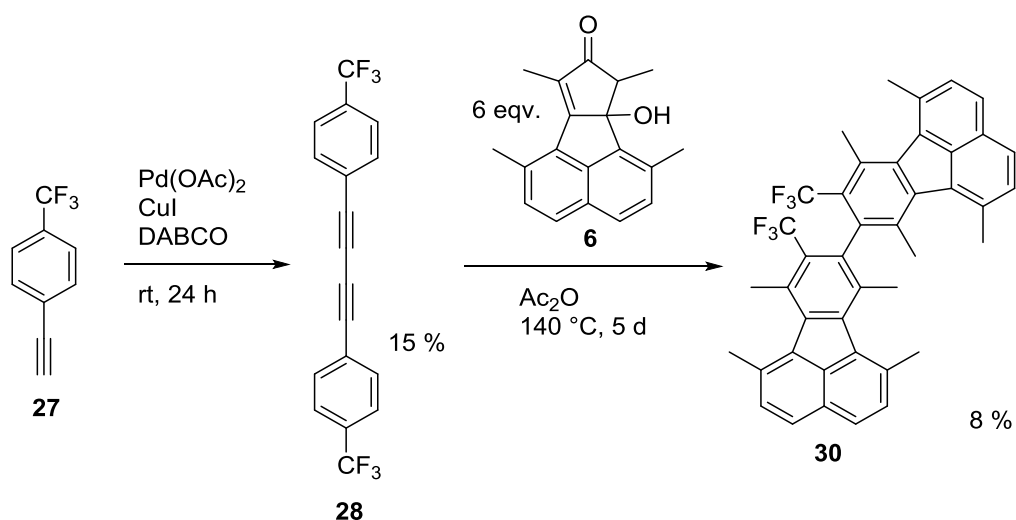
Scheme 5.2: Reaction to the fluoranthene derivative **30**.

As expected the main side product in this case is monosubstituted derivative **29** which could not be separated by column chromatography from product **30**.

Nevertheless, it was possible to select a single crystal of compound **30** for X-ray diffraction. The molecule shows the characteristic deformation of this type of fluoranthenes (figure 5.2).
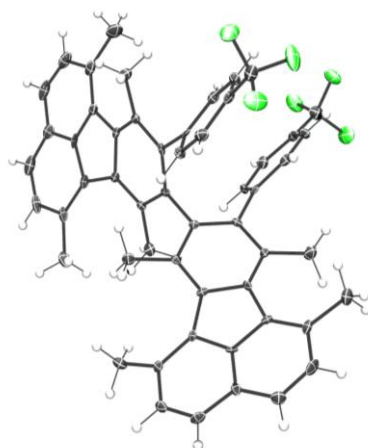
Figure 5.2: Molecular structure of the disubstituted fluoranthene derivative **30**.

Molecule **30** forms strands which are connected *via* F-F (2.935 Å), F-H (2.655 Å), C-C (3.370-3.398 Å), C-H (2.777-2.889 Å) and H-H (2.319-2.389 Å) interactions. There are no intramolecular interactions between the two identical halves of the fluoranthene **30** in the solid state. Leaving only packing and steric effects as reasons for the close proximity and almost planar arrangement of the two trifluoromethylated benzene rings.

The disubstituted fluoranthene **30** was treated according to the standard procedure described previously (scheme 5.3). Product **31** was directly cyclized to avoid polymerization reactions. A brown residues with low solubility in common organic solvents was isolated. It was subsequently debrominated to synthesize the corannulene derivative **32** with should have a higher solubility. Unfortunately, dehalogenated product **32** could not be isolated after column chromatography.
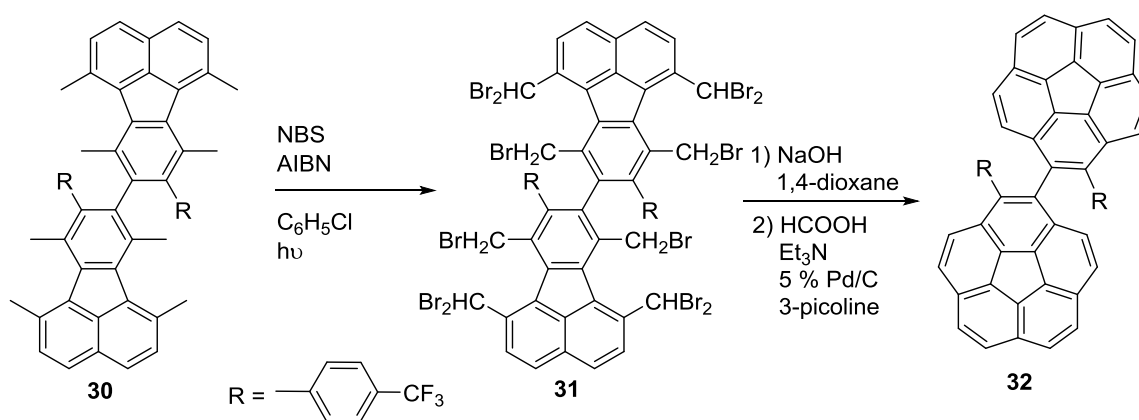
Scheme 5.3: Synthesis of biscorannulenyl **32**.

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6. Carbonyl Containing Corannulene Receptors by Friedel-Crafts Acylation

A major drawback of the two approaches described in chapter 3 and 4 are the complexe synthesis involved. Therefore a more straightforward procedure may lead to better results. One way might be the Friedel-Crafts acylation named after Charles Friedel and James Mason Craft. Typically, an aromatic system is reacted with an acid chloride using a Lewis acid as the catalyst, to form a ketone. The reaction is applied in the fine and pharmaceutical chemistry thus making it an important protocol for the synthesis of aromatic ketones.

In only one publication Friedel-Crafts acylations are performed with corannulene **1** [19b]. One is a reaction of corannulene with phthalic anhydride which leads to a carboxylic acid. Which is then further reacted with hydrogen iodide and red phosphorus to naphthocorannulene. For the other Friedel-Crafts acylation two equivalents of a benzoyl chloride derivative are reacted with the buckybowl **1** to give a mixture of two inseparable products. This mixture was pyrolysed in a FVP forming two diindenocorannulenes as the major products (scheme 6.1).
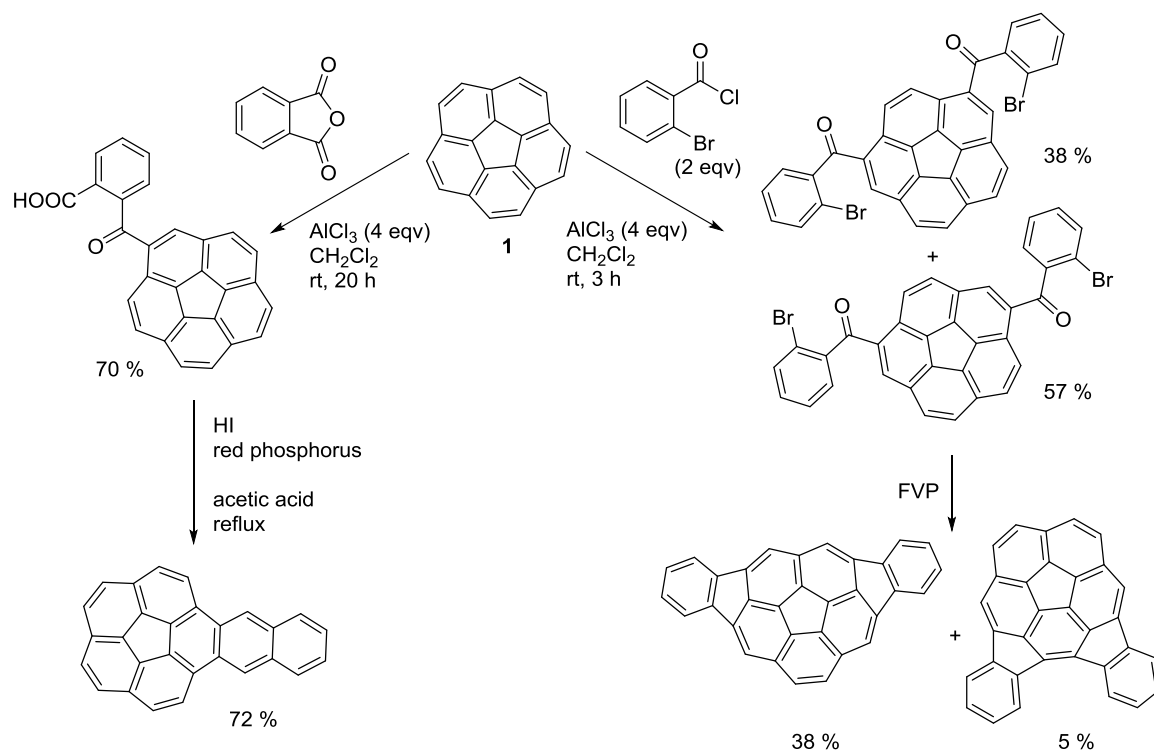
Scheme 6.1: Literature known Friedel-Crafts reaction of corannulene **1**.

Using a Friedel-Crafts acylation opens up two possible pathways for the construction of corannulene **1** containing receptors. In the first one, the corannulenes **1** are directly connected

over a carbonyl group. In the second one, a spacer is incorparated between the two bowls generating a diketone.

6.1. Benzoylchloride

The Friedel-Crafts reaction with the anhydride demonstrates that a mono substitution of corannulene **1** is possible. To investigate if the same applies to acid chlorides the simplest aromatic carboxylic acid chloride, benzoyl chloride, was reacted with corannulene **1**. Product **33** formed quite readily and in the moderate yield of 43 % (scheme 6.2).
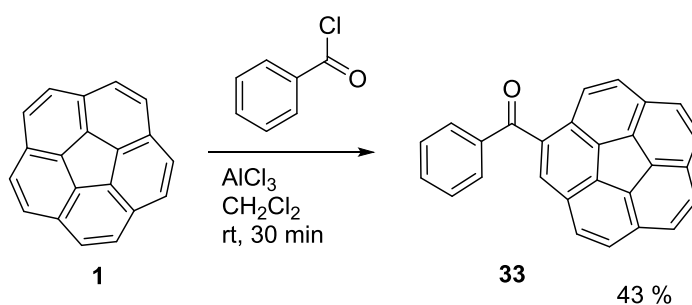
Scheme 6.2: Reaction of corannulene with one eqv. of benzoyl chloride.

Compound **33** is air and moisture stable and proves that indeed a mono substitution of the corannulene **1** bowl using Friedel-Crafts conditions is possible.

6.2. Bis(corannulene-1-yl)methanone

Having shown that aromatic acid chlorides react with corannulene **1** under Friedel-Crafts conditions it should be possible to connect two corannulenes *via* a carbonyl group using the acylation conditions. Using phosgene as the acid chloride could be one way to achieve this connection. However, the harsh reaction conditions, the high reactivity of the gas, the limitation in purchasing it as well as the involved safety regulations require an alternative synthetic route. It may be preferred to first generate the corannulene acid chloride **34** and the react it with corannulene **1** (scheme 6.3).
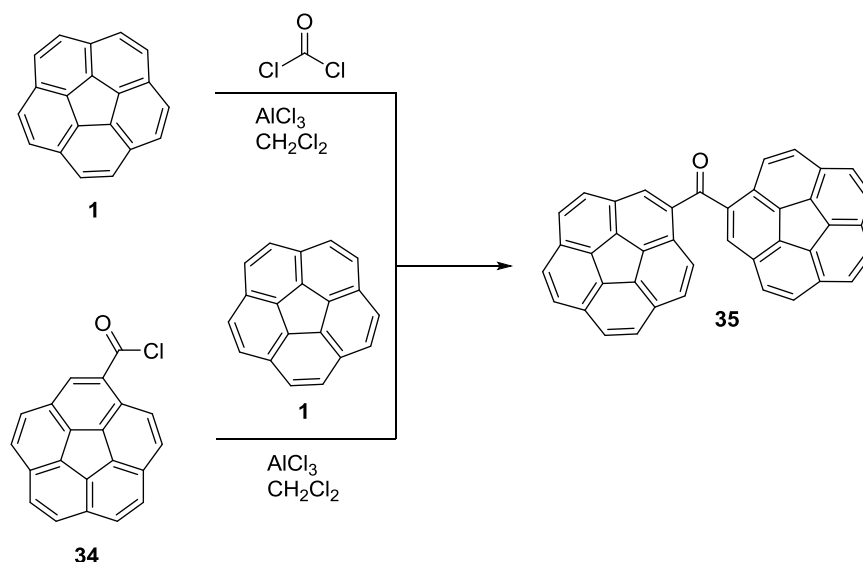
Scheme 6.3.: Two synthetic routes for the synthesis of **35**.

To synthesize the acid chloride **34,** the carboxylic acid derivative is needed as a precursor. The disubstituted acid has already been synthesized[64] but not the monosubstituted one. Therefore, the carboxylic group is introduced at the fluoranthene stage, for the same reason as described previously (scheme 6.4).
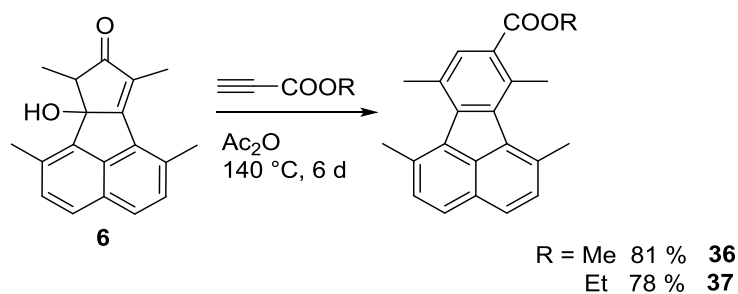
Scheme 6.4.: Generation of the fluoroanthene **36** and **37**.

When using methyl and ethyl propiolate as dienophiles, both products **36** and **37** could be generated in good yields. However, a side product formed in both cases which could not be separated from the products by column chromatography. It was possible to identify the side product by ^{1}H NMR spectroscopy (figure 6.1). The propiolate reacted either with the acetic anhydride or the acetic acid forming an unsaturated diester *in situ*. For the ethyl propiolate, an

unsaturated ethyl derivative was also generated, excluding the possibility of impurities in the used dienophiles.
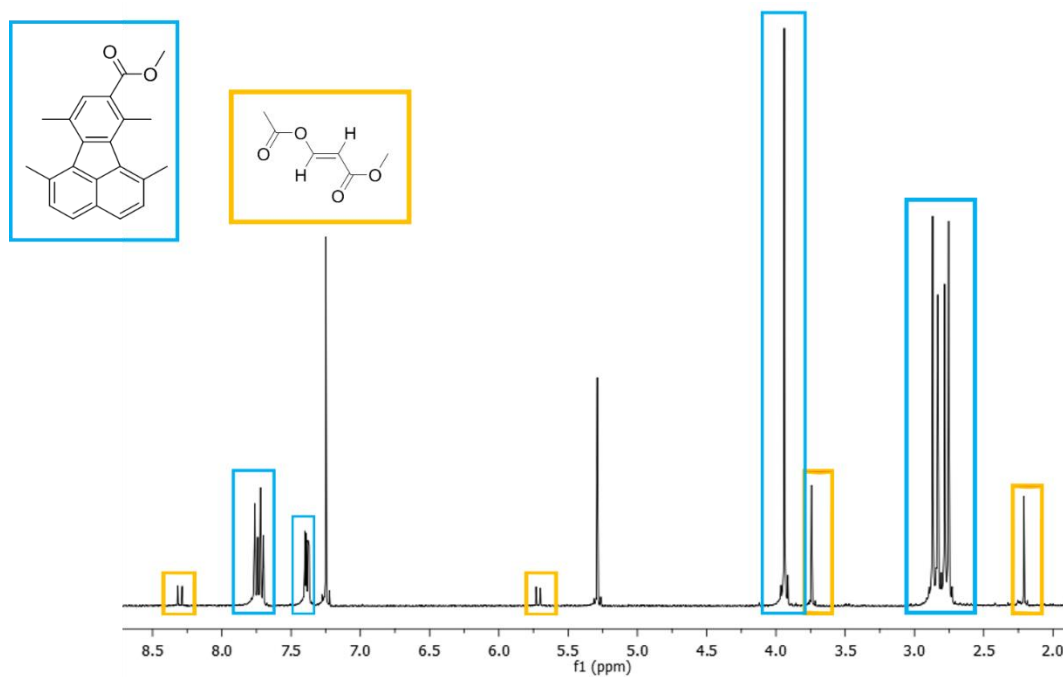
Figure 6.1: ¹H NMR spectrum of the methyl ester **36** and the generated side product.

When melting the mixtures in high vacuum a gas evolution started as soon as they turned liquid. After no more evolution could be detected the mixture was cooled to room temperature and a ¹H NMR spectrum confirmed that the side product was completely removed.

Single crystals of **36** could be obtained from a saturated dichloromethane solution (figure 6.2).
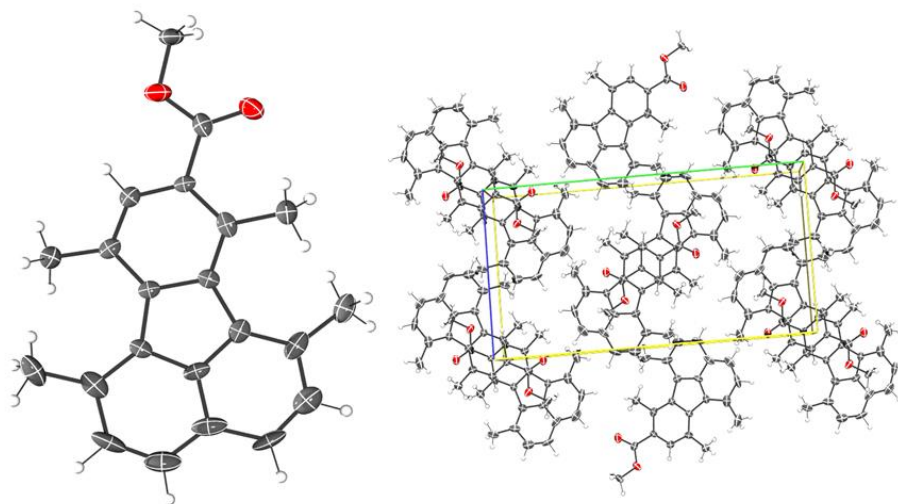
Figure 6.2: Molecular structure of **36** (left: asymmetric unit, right: packing pattern).

The asymmetric unit of the structure contains one molecule that shows the internal strain between the benzene and the naphthalene part of the molecule. In the solid state the molecules form layers which are stabilized by H-H (2.311-2.354 Å), C-H (2.667-2.892 Å) and O-H (2.395-2.639 Å) interactions.

Ethyl ester **37** was brominated using the standard conditions and subsequently, deviating from the standard protocol, cyclized to the corannulene bowl using nickel powder (scheme 6.5). This deviation was proposed in literature for the dicarboxylic compound claiming it improved the yield from 20 % to 60 %.
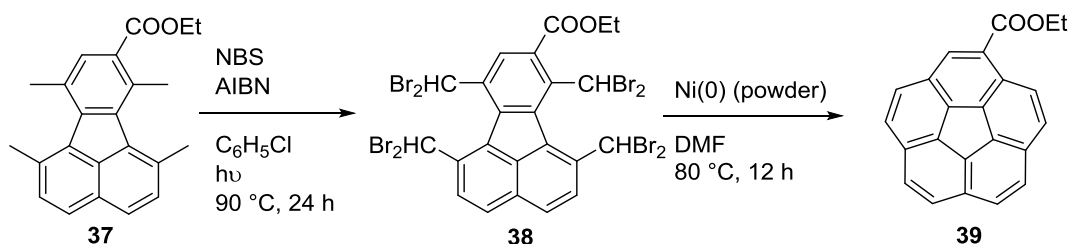
Scheme 6.5.: Synthesis of the corannulene **39**.

However in this case, the product was contaminated by a side product which could not be identified or separated from the desired product **39**. Therefore, for methyl derivative **41** the conditions were changed back to the ones used for the generation of pristine corannulene **1** (scheme 6.6).
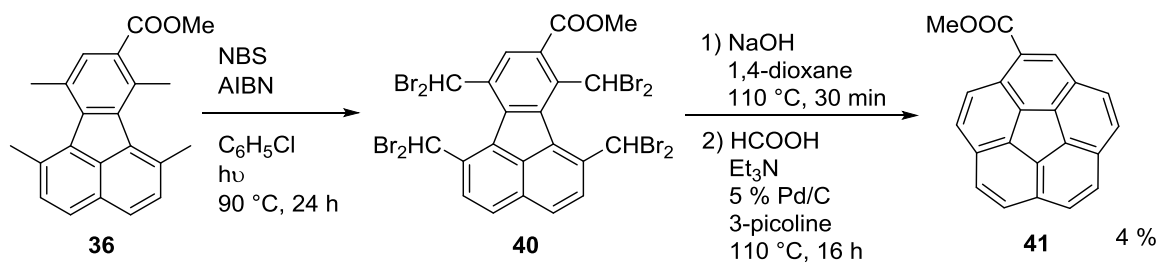
Scheme 6.6.: Synthesis of the corannulene derivative **41** starting from the methyl ester **36.**

Under these conditions the product **41** could be isolated but only in a very low yield. Perhaps part of the methyl ester is cleaved due to the alkaline conditions of the cyclisation and forms the carboxylic acid which then is removed during aqueous work-up.

Since **39** and **41** were either just formed in low yields or could not be purified, the focus on creating new corannulene materials containing carbonyl groups switched to the usage of aromatic spacers.

6.3. Ortho-, Meta-, Para-Derivatives

In order to synthesis ortho, meta, and para substituted spacers phthaloyl, isophthaloyl and terephthaloyl dichloride were used (scheme 6.7). While both of the latter reacted with corannulene **1** in good yields, phthaloyl chloride did not lead to any product **42** formation. Instead, an insoluble black substance formed whose composition could not be determined.
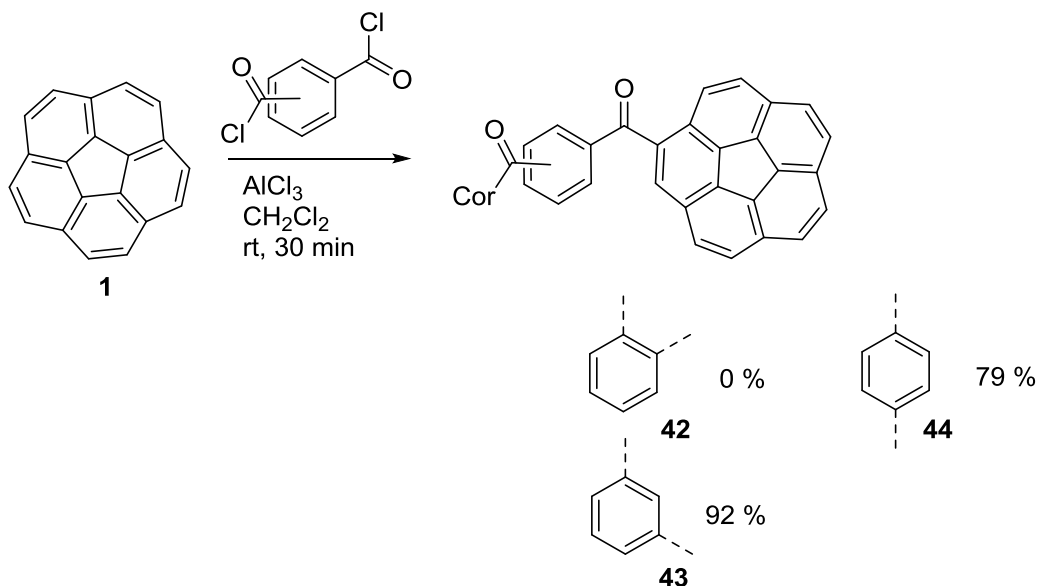
Scheme 6.7: Synthesis of the meta **43** and para **44** derivative and the attempted synthesis of the ortho **42** derivative.

Due to the close proximity of the two acid chloride functions the phthaloyl chloride forms a cyclic intermediate **47** which has a different reactivity than the acid chloride (scheme 6.9). If benzene is used as the arene compound, an anthraquinone forms in a 1,4-cycloacylation. Product **49,** however, could not be found in case of corannulene **1**.
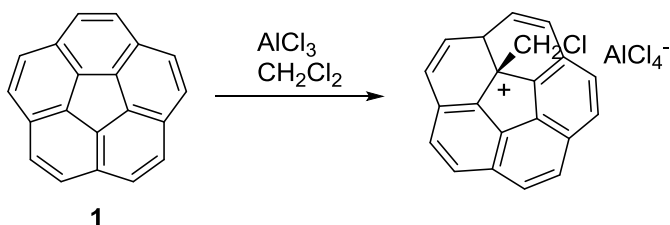
Scheme 6.8: Possible side reaction during the Friedel-Crafts acylation.

One reason for this observation could be, that the hub carbon atoms of corannulene is attacked by a complex formed by aluminum chloride and dichloromethane (scheme 6.8)[65]. This leads to

the formation of a cationic corannulene species with different reactivity than the parent compound **1**. Another reason could be one of the intermediates formed during the synthesis of **48.** The anthraquinone is produced from intermediate **48** which can either form by an aluminum-chloride-promoted "ring-chain tautomerism" after the acid chloride is reacted once with a benzene ring of the corannulene in a Friedel-Crafts acylation. The other possible route involves the formation of cyclic dichloride **47** induced by the same Lewis acid promoted ring-chain isomerization as in the first pathway. Dichloride **47** then reacts with corannulene **1** to form the intermediate **48**. The latter route is supported by ^{13}C NMR studies which clearly show the formation of the cyclic dichloride **47** upon treatment of phthaloyl chloride with aluminum(III) chloride. Considering the structure of intermediate **48** and the reactivity of corannulene **1** the latter will probably polymerize and/or decompose, explaining the insoluble residue which was isolated after the reaction.
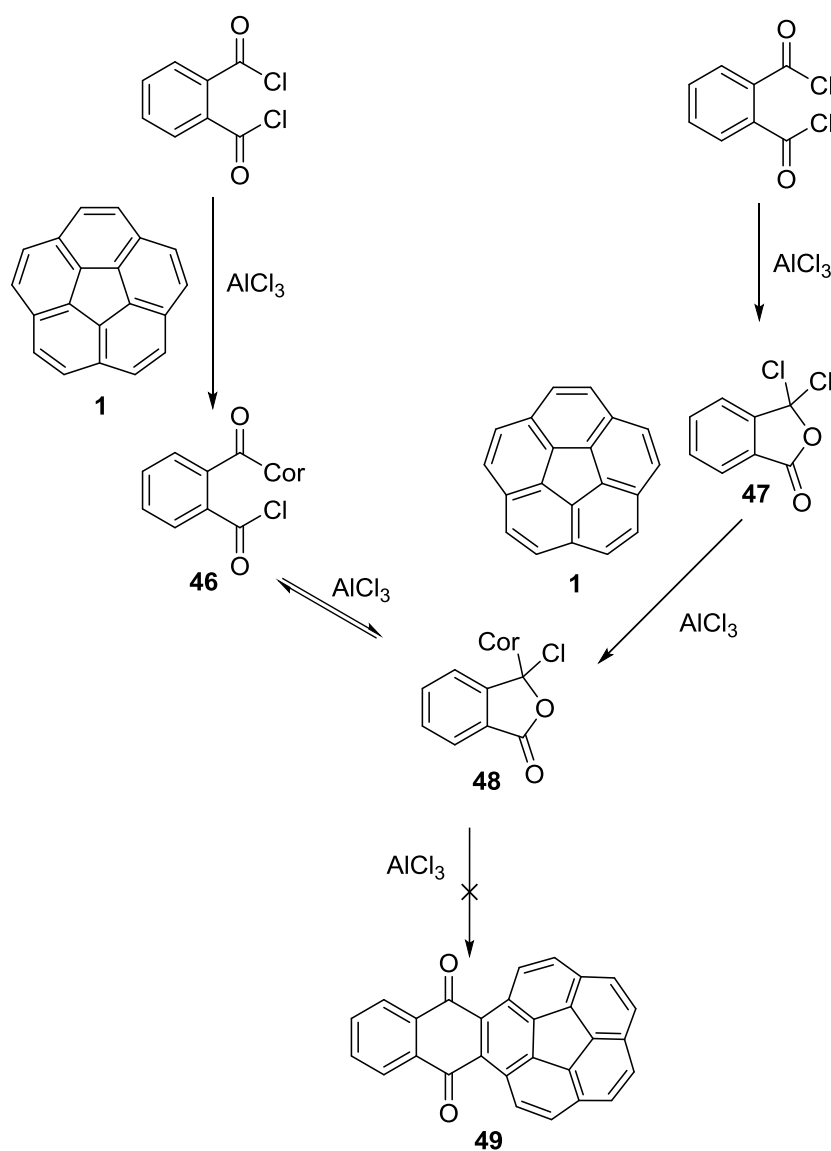
Scheme 6.9: Theoretically possible side reactions by the acylation of corannulene **1** with phthalic acid dichloride.

Meta-substituted corannulene derivative **43** was further investigated through NMR spectroscopy. The aromatic region of the ^{1}H NMR spectrum (figure 6.3) of the isophthalic derivative **43** is characteristic for all synthesized diketones. The four rim positions of the corannulene moiety that bear two protons split into AB patterns. The one closest to the carbonyl group has a large distance between the two doublets, while the rest of the AB signals all occur in the region from 7.7 to 7.9 ppm. All of the [3]J coupling constants of the doublets are approximately 8.8 Hz which is typical for the vicinal coupling of aromatic protons.
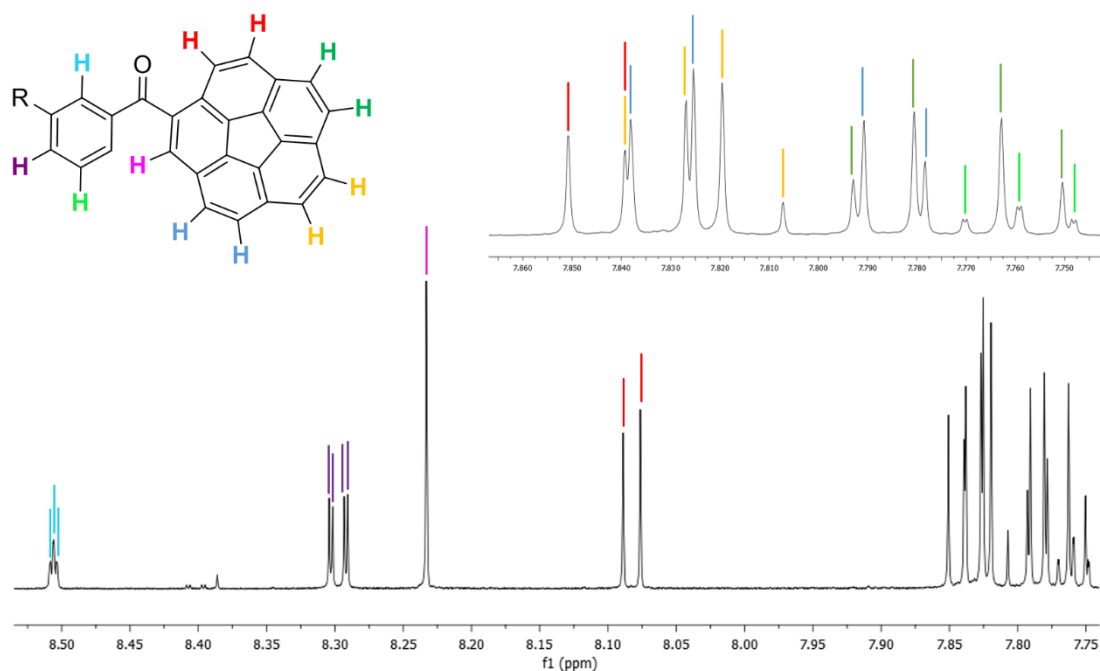
Figure 6.3: Aromatic region of the ^{1}H NMR (700 MHz) spectrum of compound **43** in d-chloroform (the symmetric part of the pictured molecule was omitted for clarity).

The single corannulene proton next to the carbonyl group corresponds to a singlet at 8.22 ppm. This is the corannulene signal that is shifted the most towards low field. The signal of the spacer proton in five position at 7.76 ppm splits into a triplet of doublets with a [3]J coupling of 7.8 Hz for the adjacent protons and a [5]J coupling of 0.6 Hz to the hydrogen between the carbonyl groups. This proton appears as triplet of doublets at 8.53 ppm in the low field of the NMR. The [4]J coupling of 1.7 Hz to the next two protons is typical for aromatic protons, the same applies for the [5]J coupling of 0.5 Hz. The last protons of the spacer split into a doublet of doublets at 8.29 ppm with a [3]J coupling of 7.7 Hz and a [4]J coupling of 1.8 Hz to the other spacer protons.
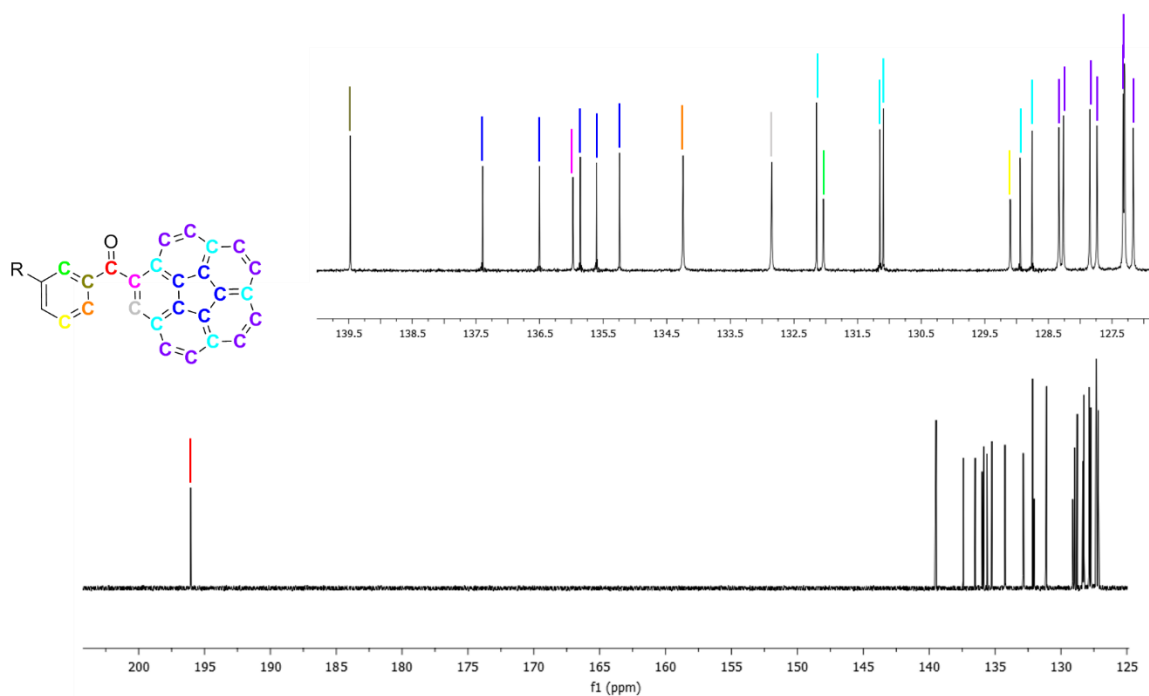
Figure. 6.4: ^{13}C NMR (700 MHz) spectrum of compound **43** in d-chloroform (the symmetric part of the pictured molecule was omitted for clarity).

The ^{13}C NMR spectrum (figure 6.4) of the molecule exhibits one signal at 196 ppm corresponding to the carbonyl carbon atoms. The remaining resonances appear between 127-140 ppm. The assignment of these was only possible with the help of HMBC, HMQC and DEPT spectra. The eight rim carbon atoms of the corannulene appear between 127-129 ppm. The two ipso carbon atoms appear at 133 and 136 ppm respectively. Two of the five spoke atoms are observed next to the eight rim carbons at roughly 129 ppm the other are located between 131 and 132 ppm. The five hub carbons appear between 134 and 138 ppm. The resonances for the spacer carbon atoms are mixed with those of the corannulene. The resonance at 128 ppm is assigned to the five position and that at 132 ppm to the carbon atom between the two carbonyl. The spacer ipso carbon is located at 140 ppm, leaving the last signal at around 134 ppm for the remaining carbon atoms close to the carbonyl group.

Measuring compound **43** in different deuterated solvents showed similar chemical shifts for d-chloroform, d-methylene chloride and d-THF. While some of the resonances shifted, the overall spectra looked almost identical. However, changing the solvent to d-toluene shifted all signals (table 6.1), while the coupling constants stayed the same. The only explanation is that the interaction between **43** and the aromatic solvent is completely different compared to those of the other three solvents (figure 6.5).
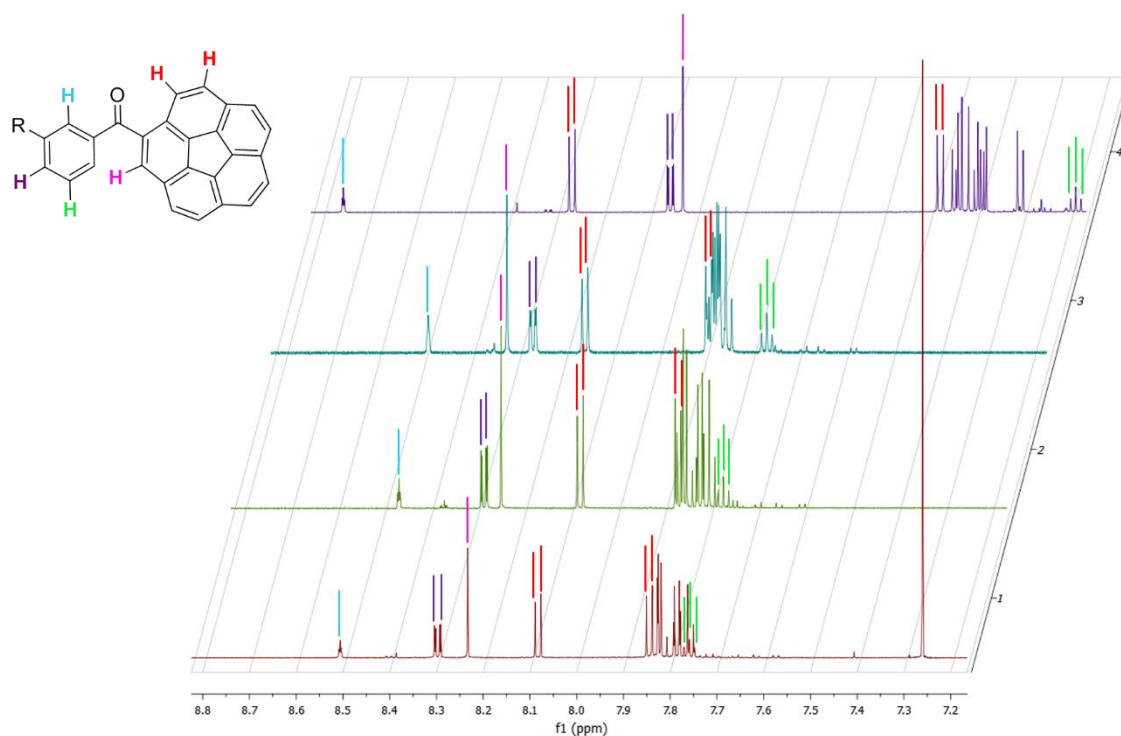
Figure 6.5: 700-MHz ^{1}H NMR spectra of compound **43** in d-chloroform (dark red), d-dichloromethane (green), d-THF (turquoise) and d-toluene (violet), the symmetrical part of the pictured molecule is omitted for clarity.

Considering that toluene is an aromatic compound, π-π stacking forces can occur between the tweezers and the solvent making both, face-to-face and edge-to-face interactions possible. This changes the environment of the protons resulting in the differences observed in the spectra.

Table 6.1: Different chemical shifts [ppm] of selected protons.

	H [ppm]	H [ppm]	H [ppm]	H [ppm]	H [ppm]
CDCl$_3$	8.51	8.30	8.23	8.08/7.84	7.76
CD$_2$Cl$_2$	8.47	8.28	8.25	8.08/7.87	7.77
d-THF	8.26	8.26	8.32	8.15/7.89	7.76
d-Toluene	8.75	8.05	8.03	8.27/7.48	7.19

To investigate a possible interaction between the carbonyl groups of the receptor and the fullerenes the carbonyl carbon atoms were labeled with ^{13}C. The synthesis follows the same procedure as described previously producing derivative **50** in 78 % yields. The ^{1}H NMR spectrum is almost identical to compound **43** just showing the additional couplings with the ^{13}C labeled nuclei for all protons close to the carbonyl groups (figure 6.6).
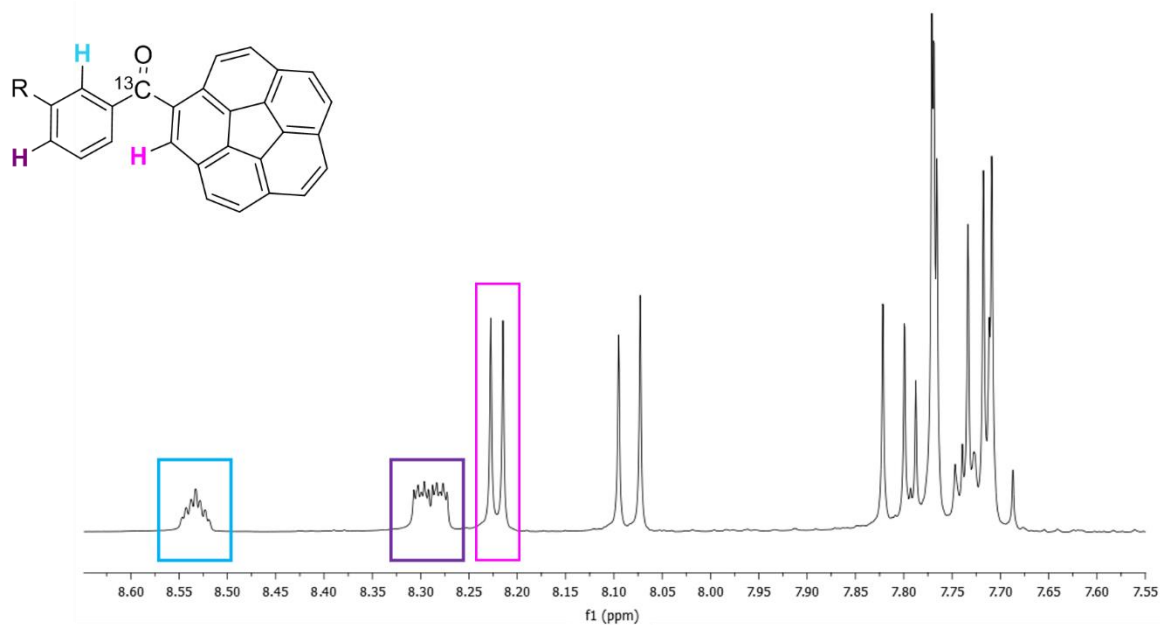
Figure 6.6: ¹H NMR spectrum of the ¹³C labeled derivative **50**; resonances showing additional couplings are marked.
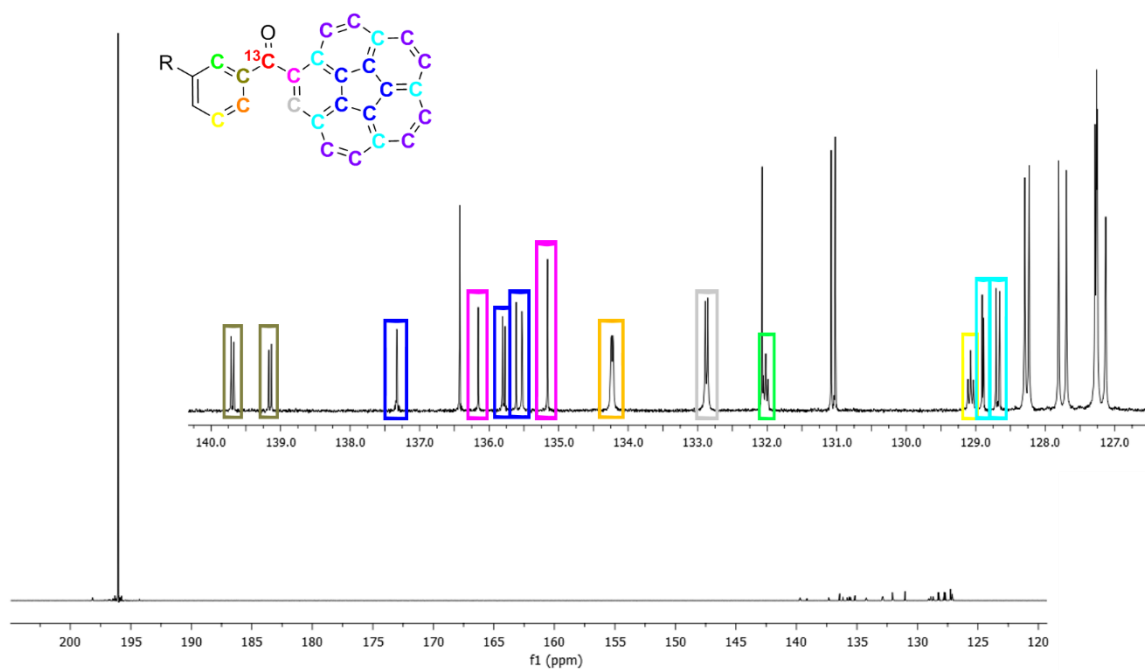
Figure 6.7: ¹³C NMR spectrum of the ¹³C labeled derivative **50**; resonances showing additional couplings are marked (¹³C-¹³C Coupling constants in Hz from left to right: 3.9 (olive-green), 0.8 (blue), 54.9 (pink), 3.7 (blue), 0.8 (blue), 2.6 orange), 3.7 (grey), 3.2 (green), 4.0 (yellow), 2.1 (cyan), 5.0 (cyan).

The ^{13}C NMR spectrum (figure 6.7) is dominated by the peak at 196 ppm corresponding to the carbonyl groups. Again, the spectrum is identical to that of compound **43** except for the carbon atoms closest to the ^{13}C enriched carbonyl groups which show coupling with the labeled nuclei.

From the three tested diacid chlorides the isophtalic acid chloride showed the most potential. Since the phthaloyl receptor could not be synthesized it is easily excluded as a potential motive. The terephthalic dichloride derivative could be generated but in a lower yield than the isophthalic receptor **43**. It was also possible to synthesize the ^{13}C marked isophtalic derivative **50** allowing to observe a possible complex formation between the receptors and the fullerenes by ^{13}C NMR spectroscopy.

6.4. Isophthaloylic Spacer

Since the isophthalic acid spacer had the highest yield and is the easiest to introduce a single substituent to it was chosen as the motive of choice for the investigation of possible methods to modify the spacer. In this work the modifications of the spacers were attempted in two and five position.

6.4.1. Isophthaloyl Derivatives Substituted in Five Position

To synthesize a library of in five position substituted isopththaloyl receptors the substituted acid chlorides were reacted with corannulene **1**. A variety of functional groups were chosen. For example a substituent which can act as a leaving group is of great interest because the receptors should be able to be immobilized on a solid phase. Others were selected to study the influence of different electronic and steric effects on the association with potential guests. An overview of all substitueted derivatives is given in scheme 6.10.
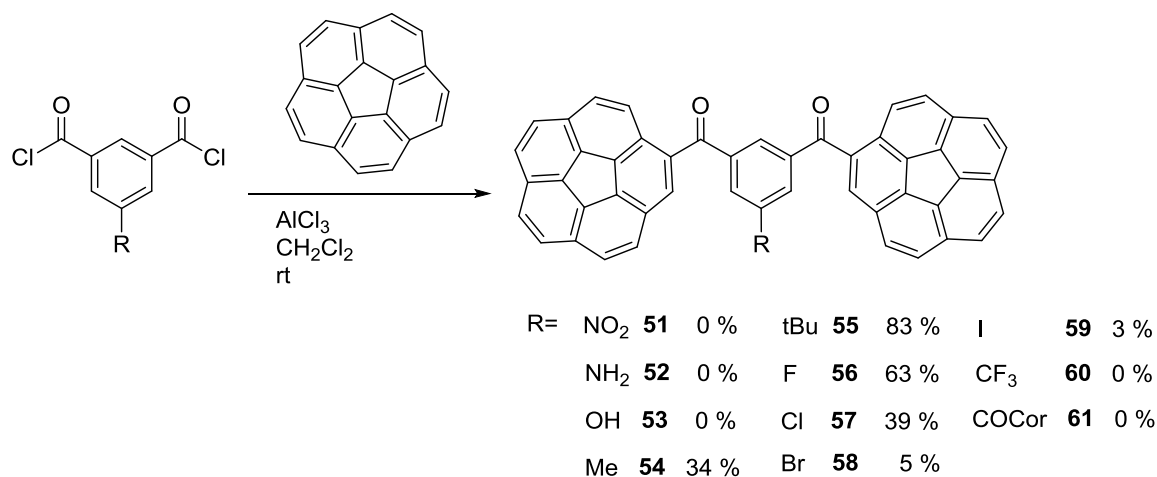
Scheme 6.10: Synthesis of the isopthalic acid derivatives.

R=								
NO$_2$	**51**	0 %	tBu	**55**	83 %	I	**59**	3 %
NH$_2$	**52**	0 %	F	**56**	63 %	CF$_3$	**60**	0 %
OH	**53**	0 %	Cl	**57**	39 %	COCor	**61**	0 %
Me	**54**	34 %	Br	**58**	5 %			

Since all the NMR spectra of the derivatives substituted in five position are very similar to those of compound **43**, they are summarized in the experimental part and will not be discussed in the following chapters.

6.4.1.1 Alkyl Substituents

Two different alkyl substituents were chosen to investigate the effect of a positive mesomeric and positive inductive effect. These groups are very stable and are most likely not attacked during the reaction which decreases the chance of potential side reactions. In addition, both groups are sterically demanding which should force the carbonyl groups in a position that is favorable for the incorporation of a guest molecule. While the methyl derivative **53** only forms in a moderate yield of 34 %, the *tert*-butyl one **55** can be isolated with yield of 83 %. An explanation for the lower yield of methyl compound **54** could be the low solubility in common organic solvents which makes the work-up difficult.

6.4.1.2 Substituents with a Negative Mesomeric Effect

Using spacers with easily abstractable hydrogen atoms, for example aniline **52** or phenol **53** derivatives, does not result in the formation of the target compounds (scheme 6.7). Instead, only an insoluble black solid can be isolated. Since these derivatives are quite interesting for a possible immobilization on a stationary phase, a different synthetic route was envisioned using nitro compound **50** (scheme 6.11) and Sandmeyer conditions.

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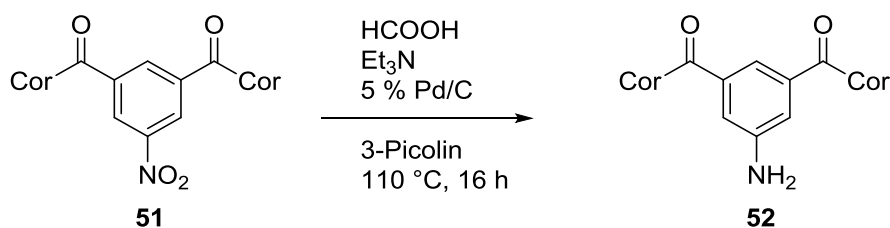
Scheme 6.11: Synthesis of aniline derivative **52** starting from nitro compound **51**.

However, it is not possible to introduce a nitro group to the spacer. That is surprising, because nitrobenzene is used as a solvent in Friedel-Crafts acylations[66]. Therefore the functional group should be stable under the applied conditions. However changing the reaction conditions and the work-up procedure did not lead to product **51**. The reaction was repeated with pentamethylbenzene as the aryl compound showing a similar outcome. To determine if the nitro group is the limiting factor for this reaction a benzoyl derivative bearing one nitro group in meta position was reacted with corannulene **1**. Product **63** formed in moderate yields of 50 % (scheme 6.12) proving that a nitro group is not the sole reason that product **64** did not form.
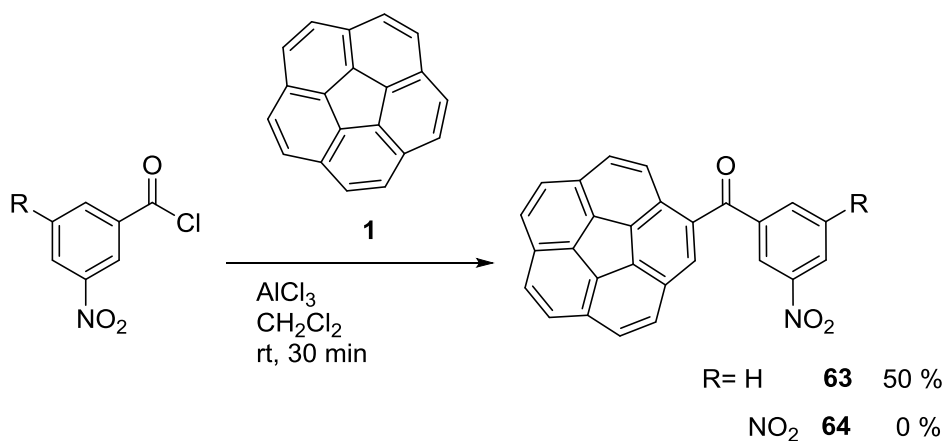
Scheme 6.12: Synthesis of the nitrobenzoyl derivatives **63** and **64**.

Introducing a second nitro group to the benzoyl ring **64** resulted in an insoluble residue. This was again verified by reaction with pentamethylbenzene **65** giving the same results.
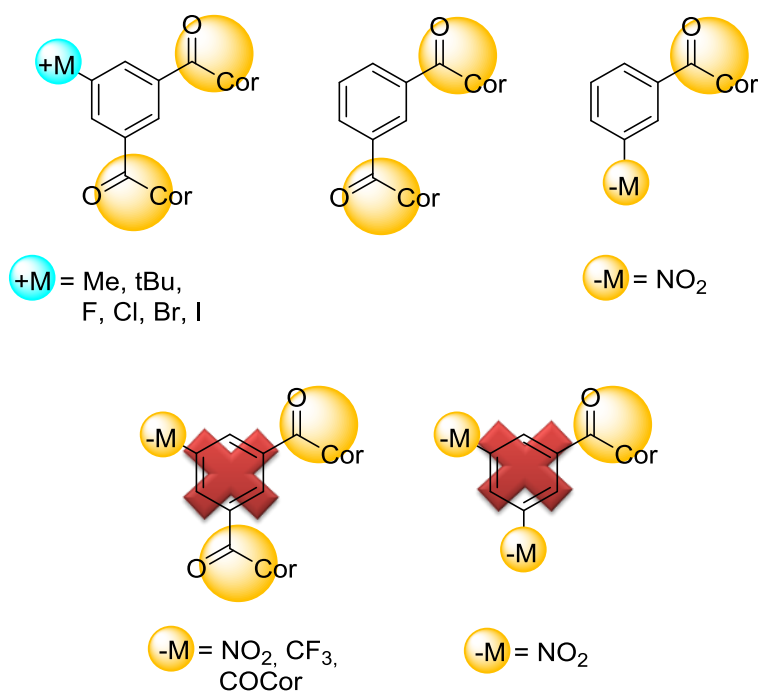
Figure 6.8: Implication of the mesomeric effects on the formation of the products (orange circles = -M effects, cyan circles = +M effects).

In summary, three or more negative mesomeric effects on the spacer prevent the formation of the molecule or it slowly decomposes after being formed (figure 6.8). The inductive effect does not seem to have any influence on the stability since both the halogen (negative inductive effect) and the alkyl substituents (positive inductive effect) can be synthesized.

The trifluoromethyl derivative did not form either in the case of corannulene **60** or pentamethylbenzene **66**. When trying to introduce a third ketogroup **61** to the spacer the compound decomposed after a few hours at room temperature or when trying to isolate it by column chromatography. Synthesizing the pentamethyl analog **67** yielded a diketone with a carboxyl group in five position **68**. Most likely only two of the three acid chlorides reacted and the last one was quenched in the reaction work-up (scheme 6.13). No triketone **67** could be detected.
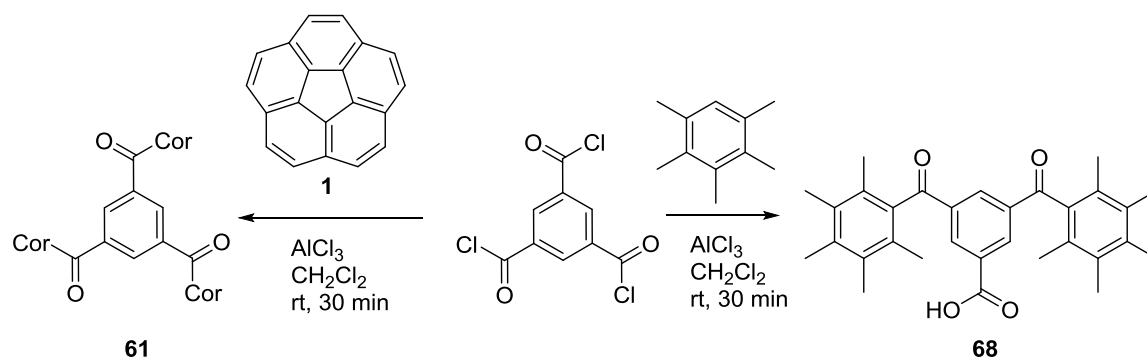
Scheme 6.13: Synthesis of ketone derivatives **61** and **67**.

Fortunately, an EI mass spectrum of corannulene derivative **61** could be obtained proving the existence of the triketone **61**.

6.4.1.3 Halogen Derivatives

It was possible to synthesize halogen derivatives **56** - **59** (scheme 6.10). These compounds are excellent precursors for further derivatization like a Suzuki-Miyaura cross coupling reaction.

The solubility of the halogen derivatives **56** - **59** decreases as the atomic number of the halogen substituent increases. Fluorine derivative **56** can be generated in 63 % yield and is well soluble in dichloromethane, chloroform, THF and toluene. Chlorine compound **57** can only be synthesized with 39 % yield and, while soluble in dichloromethane, chloroform and THF, shows a poor solubility in toluene. The bromide and iodine compound can only be isolated in low yields and have a very poor solubility in common organic solvents making the work-up challenging. Investigating if the decrease in yields is a general trend or a corannulene specific phenomenon the chlorine **68** and bromine pentamethyl derivatives **69** were synthesized. The yields are very similar with 43 % for **67** and 12 % for **68** proving the existence of a general trend which is most likely dictated by the halogen substituents of the acid chlorides.
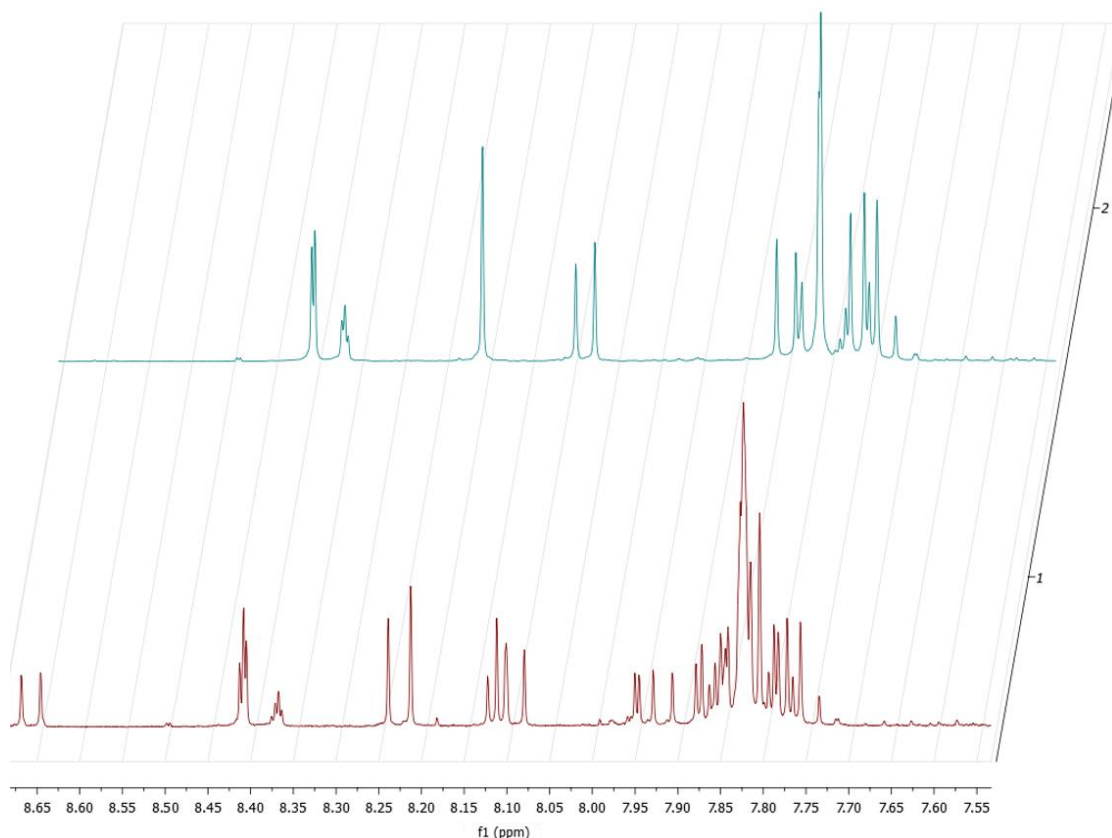
Figure 6.9: ^{1}H NMR spectra of the bromine derivative **58** (top) and the mixture of **58** with an unidentified side product (bottom).

The low yield for bromine compounds **58** and **69** can be explained by the formation of a side product that can be only be separated from the main product by preparative TLC. Column chromatography and precipitation from a *n*-pentane:dichloromethane solution was not successful, indicating that the retention time and the solubility of the two compounds is quite similar. The same similarity can be observed in the ^{1}H NMR spectrum (figure 6.9). The unknown side product features the typical NMR shifts observed for the corannulene or pentamethyl derivatives respectively but it is neither the monosubstituted compound, nor the hydrogen **43** or chlorine derivative **57**. Mass spectra showed only the signals of bromine compound **58** making it thus far impossible to identify the side product.

Creating an electron-deficient spacer with a substituent in five position was not possible (chapter 6.4.1.2). However, a fluorine substituent is tolerated. Therefore, a perfluorinated aromatic spacer should be enough to generate a similar system. To clarify if a perfluorinated spacer survives the reaction conditions, a perfluorinated benzoyl derivative was reacted with corannulene **1** forming product **70** in 42 % yield (scheme 6.14).
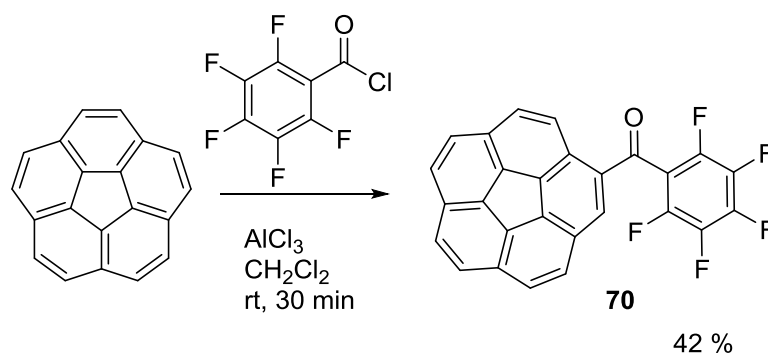
Scheme 6.14: Synthesis of perfluorinated derivative **70**.

Unfortunately, as a second acid chloride moiety was introduced into the system, side reactions started to occur. The reaction with pentamethylbenzene (scheme 6.15) produced a mixture of fluorinated products. Thus no further studies with corannulene **1** as the aryl compound were attempted.
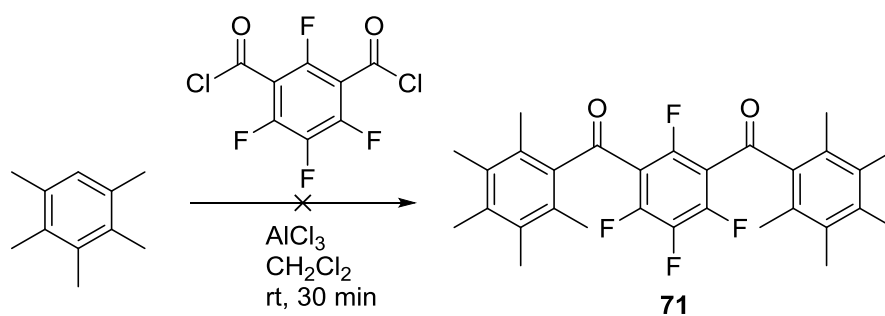
Scheme 6.15: Synthesis of tetrafluoro derivative **71**.

6.4.2. Different Reaction Conditions

It appears that there are some major side reactions occurring during the synthesis of the dicarbonyl compounds, which create impurities that make it hard to isolate the products. So a variety of changes were made to some of the reaction parameters.

First the reaction was found to be completed in 30 min instead of 3 h or even 20 h as applied in literature[19b]. That allowed for the formation of less side products but still some impurities were detected when using corannulene **1** as an educt. One major problem seemed to be a Friedel-Crafts alkylation between corannulene **1** and dichloromethane promoted by aluminum(III) chloride. This reaction occurs if pristine corannulene **1** has prolonged contact with the Lewis acid producing a buckybowl which is substituted at a hub carbon atom (scheme 6.8)[65].

To avoid side reactions different Lewis acids, titanium(IV) chloride and boron trifluouride diethyl etherate, were tested as catalysts. The fluorinated isophthaloyl derivative was chosen as the acid dichloride to observe the reaction progress by ^{19}F NMR[10]. To be able to detect any corannulene specific problems the reaction behavior of the different Lewis acids was studied with pentamethylbenzene as the starting material, as well (scheme 6.16).
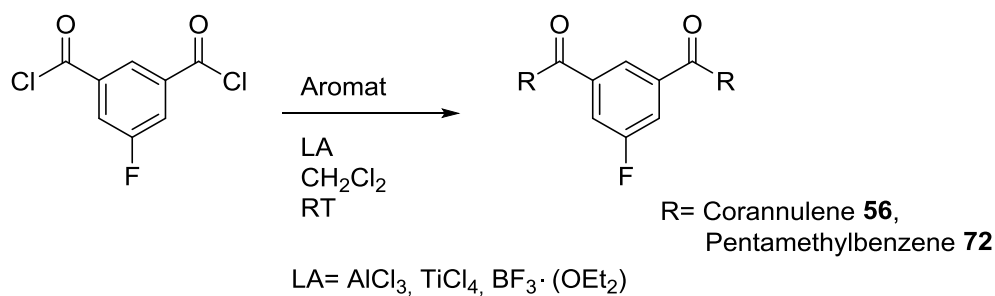
Scheme 6.16: Trial systems for the determination of the most efficient catalyst.

^{19}F NMR spectra were measured at certain times to observe the progress of the reaction (see chapter 10.6.5.6.). The samples with the aluminum catalyst already showed a large shift of the fluorine signals for both aromatic systems in the first measurement which was collected half an hour after the initial preparation of the samples. This indicates that the reaction was already complete at this point. Almost no change of the position of the fluorine signals could be detected for the other two catalysts and after quenching no product **56** could be obtained.

After five days no signal in the ^{19}F NMR for the reaction of corannulene with aluminum trichloride could be detected in contrast to all other samples which still showed signals. The reaction product **56** probably decomposed reinforcing the need for shorter reaction times.

Because the Lewis acids described previously, except aluminum(III) chloride, were not able to catalyze the system a different reaction protocol was applied. Metal triflates can be used as catalysts in Friedel-Crafts acylations. One of the earliest studies reports the use of boron, aluminum and gallium triflates[67]. The triflates have the advantage that they can be applied in catalytical amounts and are less corrosive. This makes them favorable for industrial applications. Hafnium triflate is in particularly known for catalyzing even reactions with unactivated aromatic substrates like monochloro- or monofluorobenzene. Still no reaction occurred with either isophthalic dichloride or the iodine derivative even with the addition of cocatalysts like lithium perchlorate or trifluoromethanesulfonic acid (scheme 6.17). The most likely explanation is that corannulene **1** is barely soluble in nitromethane and thus no reaction can take place.
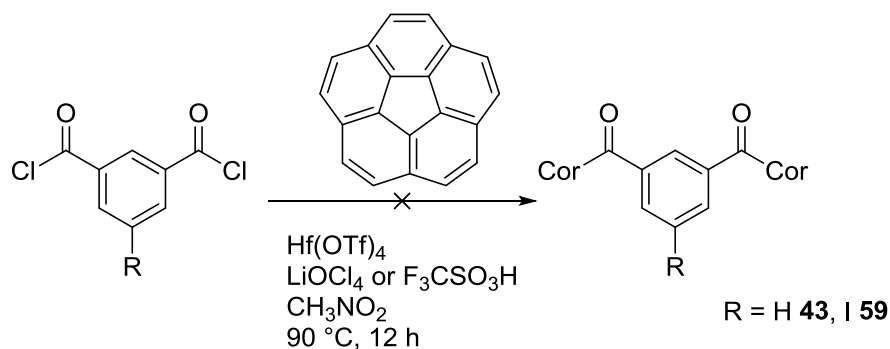
Scheme 6.17: Synthesis of **43** and **59** with hafnium(IV) triflate as the catalyst and lithium perchlorate or trifluoromethanesulfonic acid as cocatalysts.

After discovering that an exchange of Lewis acids is not possible, a change of the solvent to prevent the alkylation reaction was the next choice. A fluorinated solvent in theory, should not be attacked by aluminum(III) chloride. Unfortunately, again corannulene **1** did not dissolve making a reaction impossible.

Given the poor solubility of corannulene the usage of other solvents than dichloromethane does not seem viable. The same applies for the usage of other catalysts than aluminum(III) chloride. That leaves only the reaction time to improve the yields.

6.4.3. Substituent in Two Position

To investigate the importance of a hydrogen atom in two position between the two carbonyl groups, a molecule was synthesized bearing a methyl group in this position (scheme 6.18). Because of the steric hindrance there were concerns if a substituent can be introduced in this position. To test this, benzoylic derivatives **73** and **74** were synthesized in 67 % and 39 % yield, respectively. Since both compounds could be easily generated the synthesis of the isophthaloyl derivatives **75** and **76** was attempted.
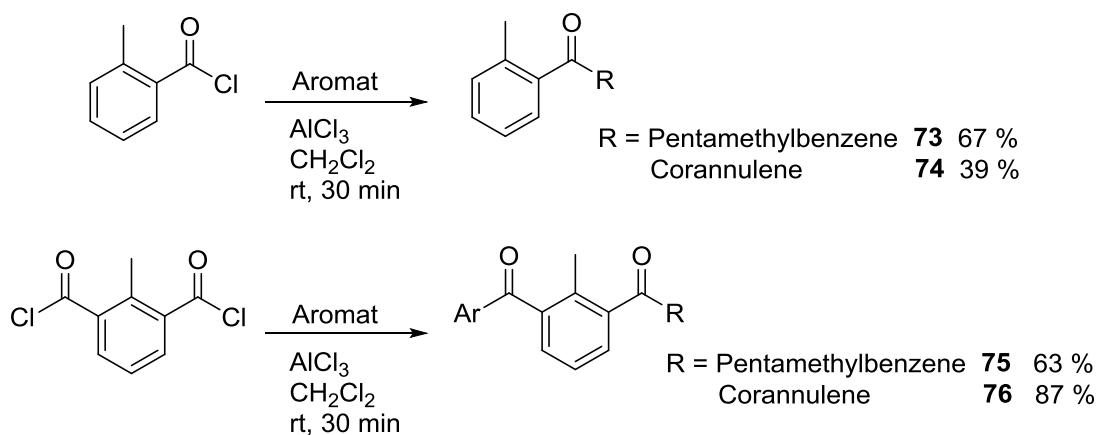
Scheme 6.18: Synthesis of methyl derivatives **73,74,75** and **76**.

Unexpectedly, the yield (87 %) for methyl derivative **76** is much higher compared to the in five position substituted compound **54** (34 %). A reason for that might be the much higher solubility of **76** in common organic solvents.
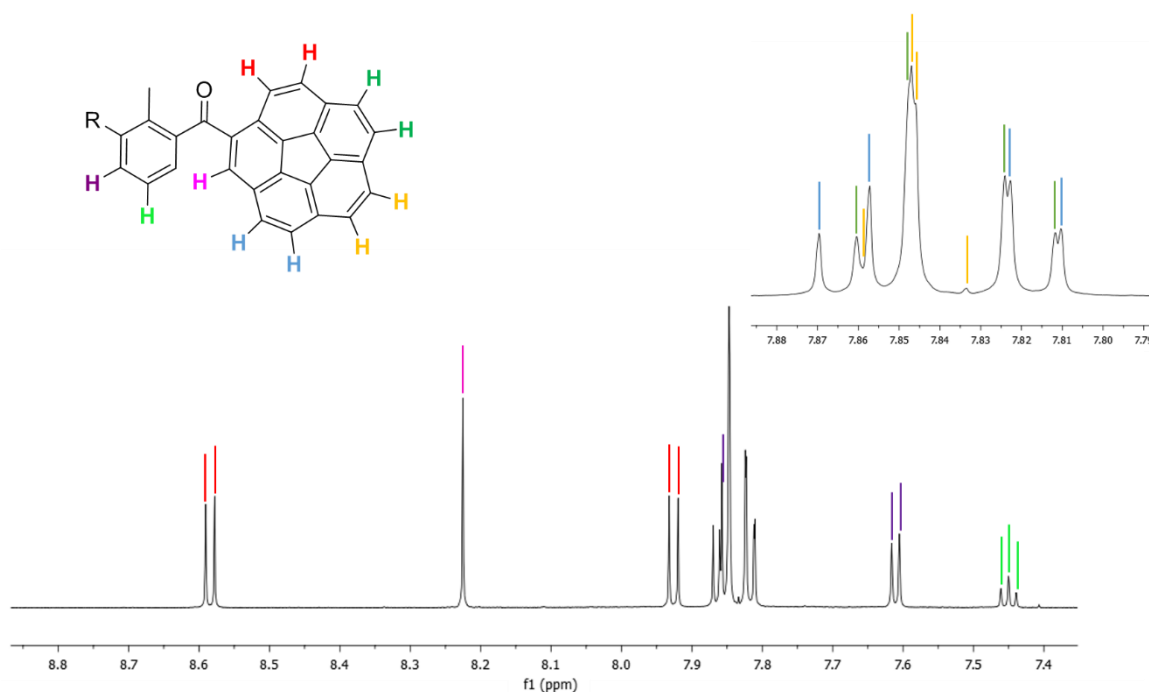
Figure 6.10: Aromatic region of the ^{1}H NMR spectrum of compound **76** (the chemical equivalent protons in the pictured molecule are omitted for clarity).

The ^{1}H NMR spectrum (figure 6.10) of compound **76** looks at first glance less complicated than those of the other derivatives. But three of the AB patterns of the corannulene bowl (7.8-7.9 ppm)

are overlapping making it difficult to distinguish between them. As the ^{13}C NMR spectrum is very similar to that of **43**, it is summarized in the experimental part.

The EI mass spectrum of the derivative with only one corannulene moiety **74** has an interesting fragmentation pathway compared to all other synthesized derivatives. The most stable cationic species generated has a mass difference of 17 to the molecular peak which can only be explained by the loss of a hydroxide radical while the benzyl ring forms a quinone like structure. Disubstituted **76** and pentamethyl derivative **75** show the same fragmentation but it is not the main fragmentation pathway. For corannulene derivative **76,** the generation of a corannulene cation is more favorable and for the pentamethyl derivative **75** the loss of a methyl group is more prominent.

6.5. Elongation of the Alkylchain

Until now the focus for possible substitutions was on the benzene ring of the spacer. However, there are other possible options, like increasing the length of the alkylic chain connecting spacer and bowl.
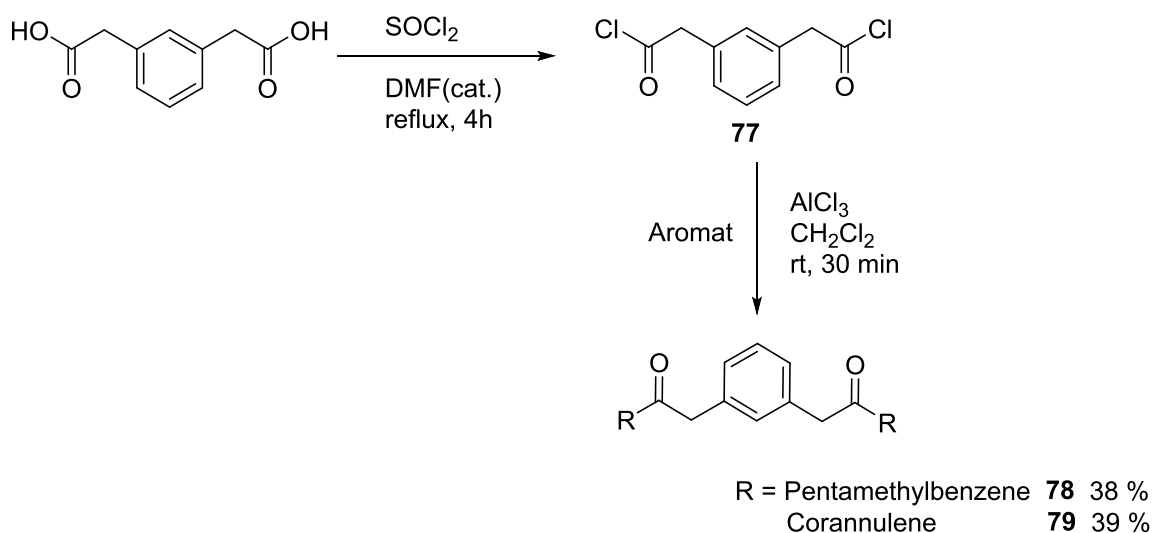
Scheme 6.19.: Synthesis of **77**, **78** and **79**.

Suprisingly, the reaction product **77** of the acid chloride synthesis is black (scheme 6.19). All other synthesized or bought acid chlorides are either colorless liquids or crystalline compounds. Since all acid chlorides were sublimated or distillated after the synthesis to remove possible impurities

the same was done with the black residue of the above mentioned substance **77**. After sublimation, pure product **77** was isolated in a low yield as an off-white crystalline substance. Considering this it is apparent that **77** is quite sensible to harsh reaction conditions. In contrast to all other acid chlorides **77** turned black in contact with anhydrous aluminum(III) chloride even in the glove box and no further reaction with corannulene **1** took place. Changing the reaction conditions and dissolving acid chloride **77** and the arene together in a different flask than aluminum(III) chloride and just adding the acid chloride solution to the suspension right before the reaction gave product **78** in 38 % yield and product **79** in an almost identical yield.
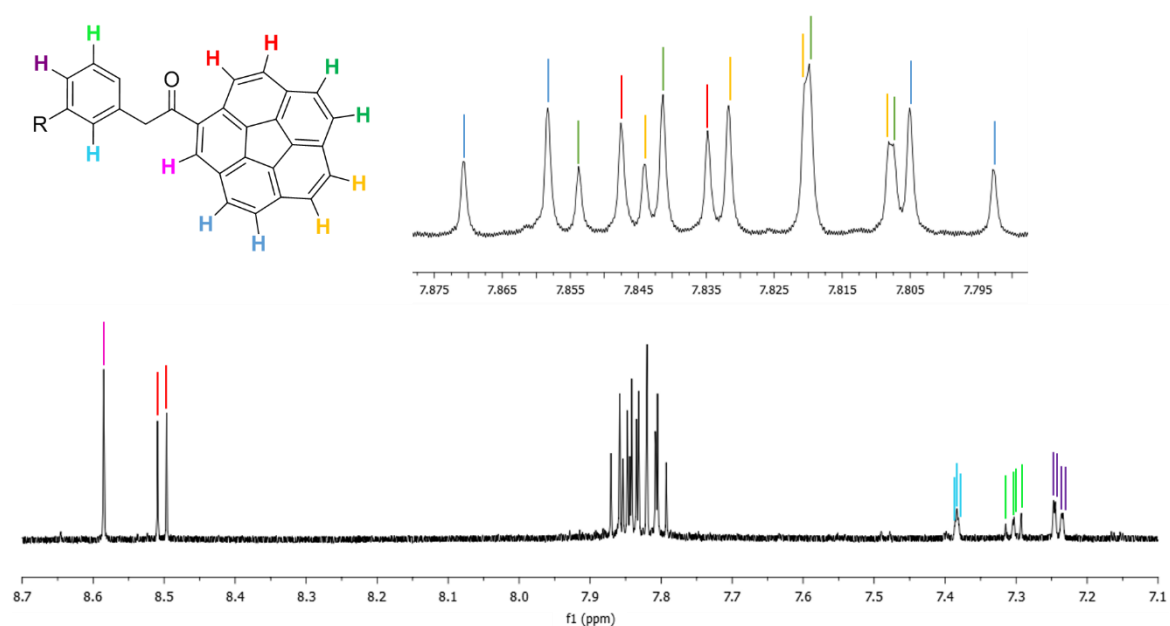
Figure 6.20: Aromatic region of the ^{1}H NMR spectrum of compound **79** in d-dichloromethane (the chemical equivalent protons in the pictured molecule are omitted for clarity).

compound **79** has, after iodine compound **59**, the lowest solubility in common organic solvents. For example, less than 0.1 mg of **79** are soluble in 1.0 mL toluene. In the ^{1}H NMR spectrum (figure 6.20) of product **79** the common pattern for the signals can be observed. The AB pattern for the closest corannulene proton to the carbonyl group is shifted to the downfield (7.84 and 8.50 ppm) and the spacer protons moved to the highfield (7.2-7.4 ppm) compared to compound **43**. This is the only dicarbonyl compound where the singlet for the proton next to the carbonyl group shifts (8.20 ppm to 8.59 ppm). The reason for that is probably that the carbonyl group is no longer directly connected to the aromatic system of the spacer.

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6.6. Functionalizing the Carbonyl Group

It was possible to synthesize isophthaloyl diketones that have a substituent in the five position, one that has a methyl group in two position **76** and one with an increased distance between the spacer and the corannulene bowls **79** (scheme 6.21). Another possible point of variation is the carbonyl group. While it was not possible to reduce them to the corresponding alcohol as hydrogenation of the corannulenes occurs, it was possible to obtain thioketal **80** in high yield (74 %).
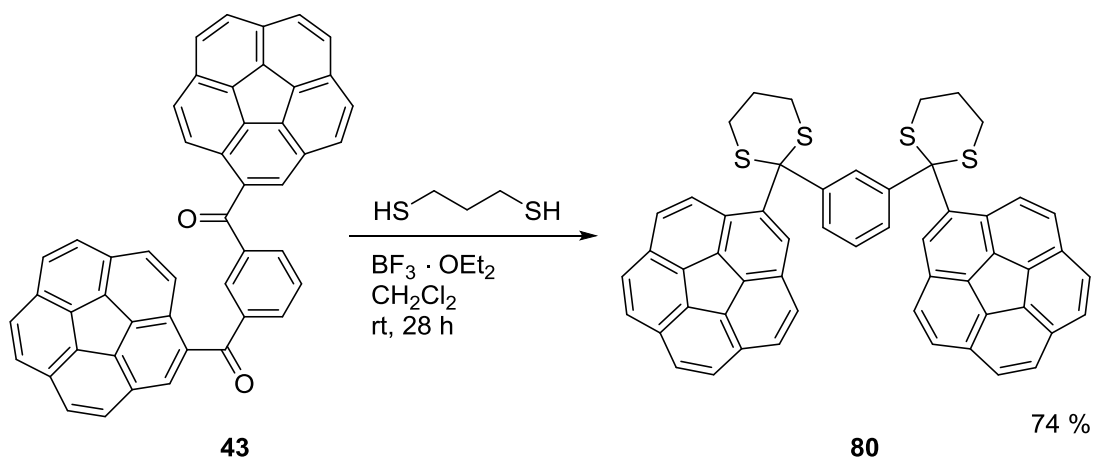
Scheme 6.21.: Generation of the thioketal **80**.

Propanedithiol was chosen as the sulfur compound because it forms a six membered cyclic ketal under acidic conditions. This results in a symmetric molecule which makes it much easier to interpret the NMR spectra. The aromatic region of the ^{1}H NMR spectrum (figure 6.11) is similar to the carbonyl compounds but the signals are shifted highfield because of the less electron withdrawing effects of the thioketals. Again, four AB patterns and one singlet (8.23 ppm) can be observed for the corannulene moiety. All the protons which are close to the saturated six-membered sulfur containing rings are broadened because of the alternation between several conformations. The spacer protons are shifted the most compared to the parent compound **43**. The proton located between the two bridges is shifted 0.4 ppm and the signal for the two chemical equivalent protons of the spacer relocated 1 ppm to the highfield. The proton in the five position is mixed with the three AB patterns in educt **43** but it is now shifted to 7.06 ppm and no longer part of those patterns.
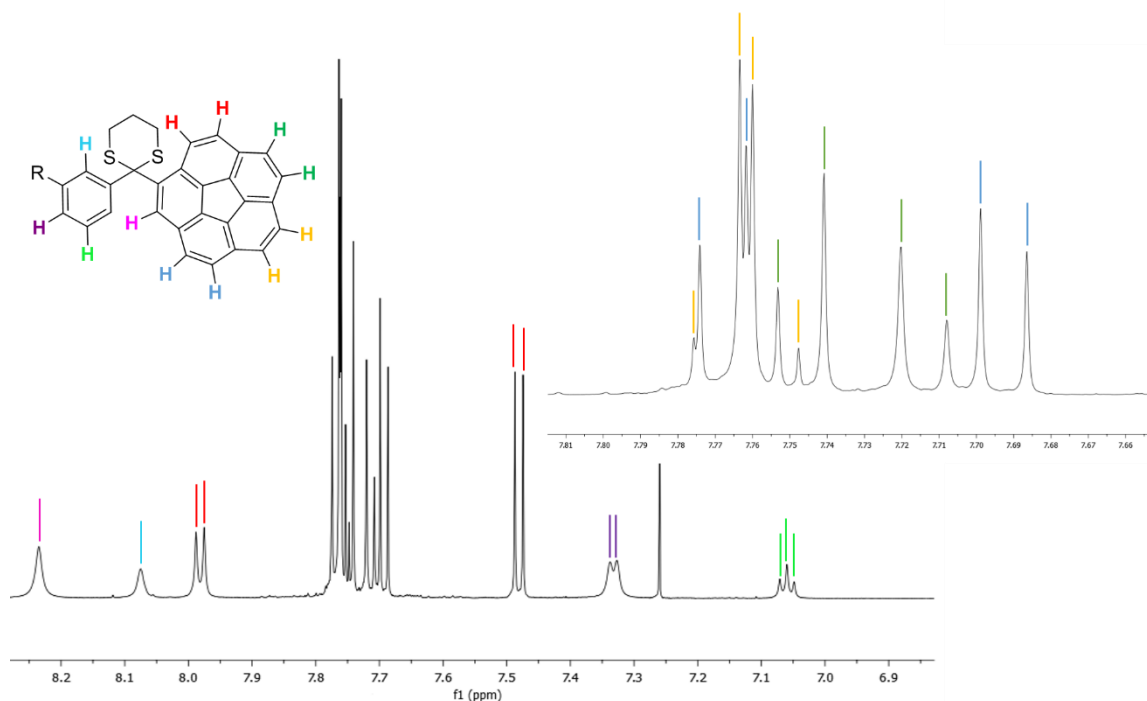
Figure 6.11: ^{1}H NMR spectrum of the aromatic region of **80** (the identical half of the molecule is omitted for clarity).

The ^{13}C NMR spectrum of **80** is again very similar to that of the carbonyl compounds and thus summarized in the experimental part.

The thioketal opens up further routes for substitutions like the introduction of fluorine with Olah's reagent or the creation of a methylene group with Raney nickel.

6.7. Crystal Structures of the Carbonyl Compounds

To compare the molecular structures of the different derivatives determined by X-ray diffraction all ketone compounds are discussed in this chapter. It was possible to obtain single crystals for corannulene derivatives **33** and **43** and pentamethyl derivatives **45**, **75** and **78**.

The structure (figure 6.12) of compound **33** shows that the phenyl ring and the corannulene are not in one plane thus preventing conjugation between the two parts of the system. The phenyl ring is positioned *exo* to the open face of the corannulene bowl.
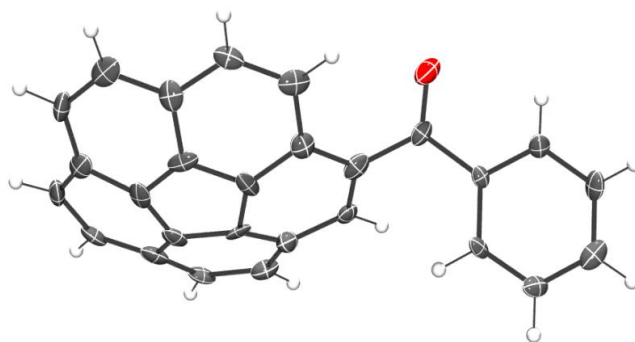
Figure 6.12: Asymmetric unit of **33**.

Due to the introduction of the carbonyl group the rim bonds are elongated while some of the flank bonds are shortened compared to pristine corannulene (table 5.2). The spoke and hub bonds are shortened or elongated depending on their position towards the carbonyl group. Comparing the bowl depth of the ketone to that of corannulene **1** reveals only a slight difference of 0.015 Å. The dihedral angle between the two aryl groups is 45.0(8)°. The bond lengths of the carbon carbon bonds in the six-membered benzoyl ring are similar and comparable to benzene. Overall, the benzoyl ring shows almost no difference to the pristine counterpart but the corannulene bowl is slightly distorted as a result of the substitution. This distortion is reflected in the slightly different bowl depth of benzoyl derivative **33**.

Table 6.2: Bond length of the benzoyl derivative **33** and corannulene **1**.

	Benzoyl Derivative **33**	Corannulene **1**
Rim bonds	1.411(9) - 1. 450(9)	1.337(2)-1.387(2)
Flanks bonds	1.403(9) - 1. 451(9)	1.441(2)-1.450(2)
Spoke bonds	1.368(9) - 1.415(9)	1.376(2)-1.381(2)
Hub bonds	1.375(9) - 1.432(9)	1.411(2)-1.417(2)
Benzoyl bonds	1.381(9) - 1.400(8)	-
Bowl depth	0.863	0.878
Dihedral angle	45.0(8)	-

The packing in the crystal structure is dominated by H-π interactions. While π-π forces are present, they have no major contribution to the overall packing motif. One benzoyl group points directly into the bowl of a second molecule forming a clam like structure (figure 6.13).
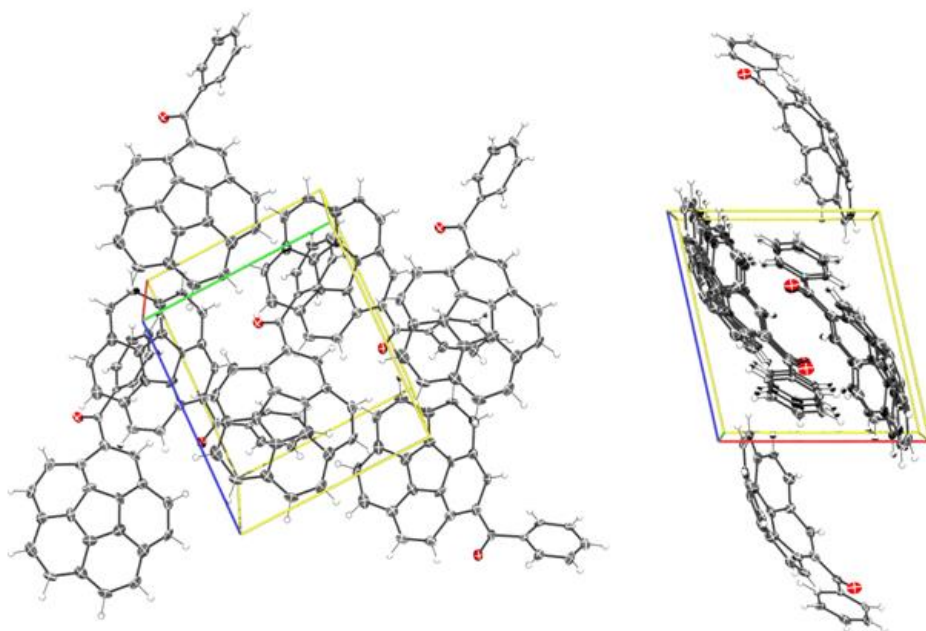
Figure 6.13: Packing of **33** in the solid state.

It was possible to obtain a single crystal of **43** by slow evaporation of a chloroform solution. The quality of the crystal was sufficient for X-ray diffraction. The resulting structure shows one molecule of diketone **43** and one chloroform in the asymmetric unit (figure 6.14). Interestingly enough, both corannulene bowls and both carbonyl groups point in the same direction.
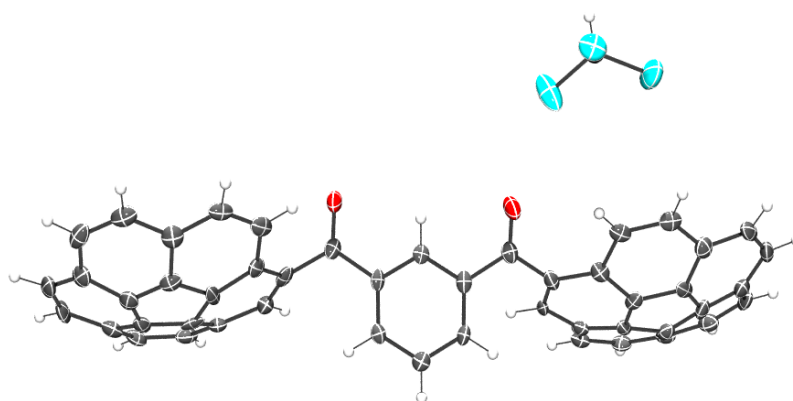
Figure 6.14: Asymmetric unit of **43** with a chloroform molecule.

Examining the packing (figure 6.15) reveals the reason behind the orientation of the corannulenes. They form columns where the bowls stack but are slightly displaced against each other. The chloroform fills the cavities created by this arrangement. This so called "slipped" stacking was

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already observed when introducing a fluorine or chlorine substituent at the rim. In these cases, the columns alternate between "up" and "down" and do not point in the same direction. While there is a likeness to already known structures there is no similarity between these columns and the packing of benzoyl derivative **33**.
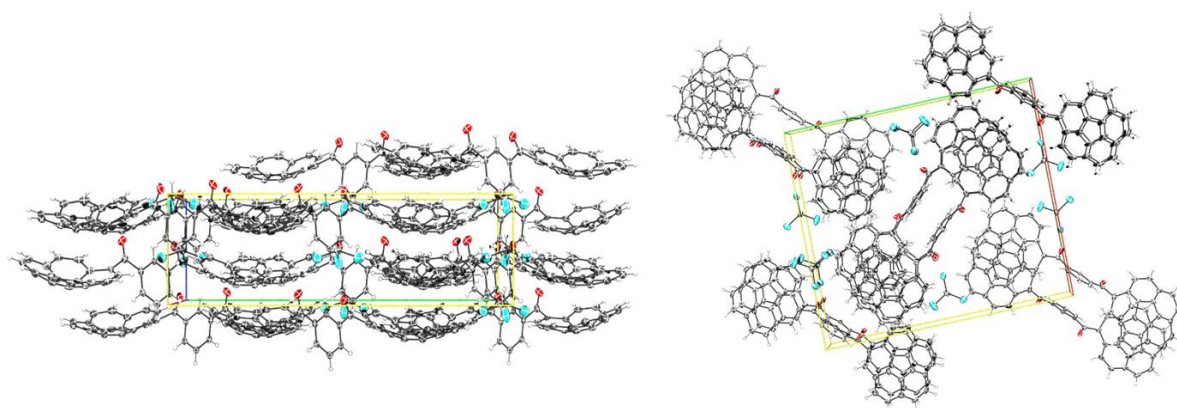
Figure 6.15: Packing of the molecule **43** in the solid state.

It was not only possible to obtain a single crystal of a chloroform but also of a toluene solvate. Considering the difference in the NMR spectra one would expect a deviation of the packings in the solid state. Surprisingly, that is not the case since the toluene fills the same pores as the chloroform, while the bowls show the "slipped" stacking motif (figure 6.16). This confirms that the observed diffenrence of the chemical shits in the NMR spectra is a solvation effect. Even the cell constants of both solvates are quite similar to each other (see part 10.2.).
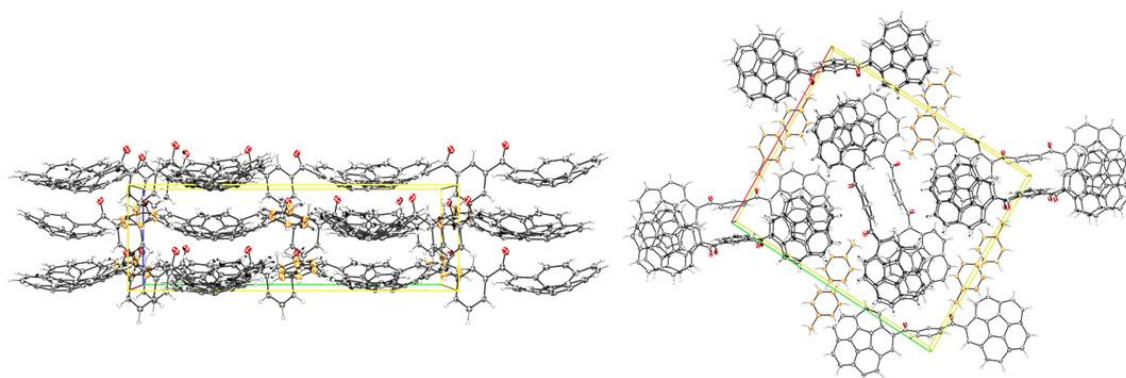
Figure 5.16: Packing of the molecule **43** and toluene in the solid state (the toluene was colored orange for clarity).

The bond lengths are similar to that of benzoyl derivative **33** and pristine corannulene **1**. In comparison to the latter, again the bonds are slightly distorted (table 6.3). The dihedral angles are both larger than that of compound **33**, probably due to the different packing motive of **43**. The corannulene bowl of the toluene solvate is closer to the incorporated solvent molecule and thus has a slightly bigger angle. This is due to interactions between the closest carbonyl group and the solvent molecule.

Table 6.3: Bond lengths of the diketone derivative **43** and corannulene **1**.

	Diketone **43** (CDCl$_3$)	Diketone **43** (d-Toluene)	Corannulene **1**
Rim bonds	1.40(1)-1.427(9)	1.383(4)-1.407(4)	1.337(2)-1.387(2)
Flanks bonds	1.40(1)-1.453(8)	1.430(4)-1.459(4)	1.441(2)-1.450(2)
Spoke bonds	1.368(8)-1.423(9)	1.371(4)-1.390(4)	1.376(2)-1.381(2)
Hub bonds	1.354(1)-1.460(1)	1.393(4)-1.430(4)	1.411(2)-1.417(2)
Benzoyl bonds	1.387(1)-1.400(1)	1.389(4)-1.398(5)	-
Bowl depth	0.877	0.868	0.878
Dihedral angle	50.5(8)°	60.6(4)°	-
	-69.6(8)°	-53.0(4)°	-

It was possible to generate the pentamethylbenzene equivalent **45** of isophthaloyl derivative **43** and to crystallize it. The asymmetric unit includes only half a molecule and no solvent molecule is incorparated (figure 6.17).
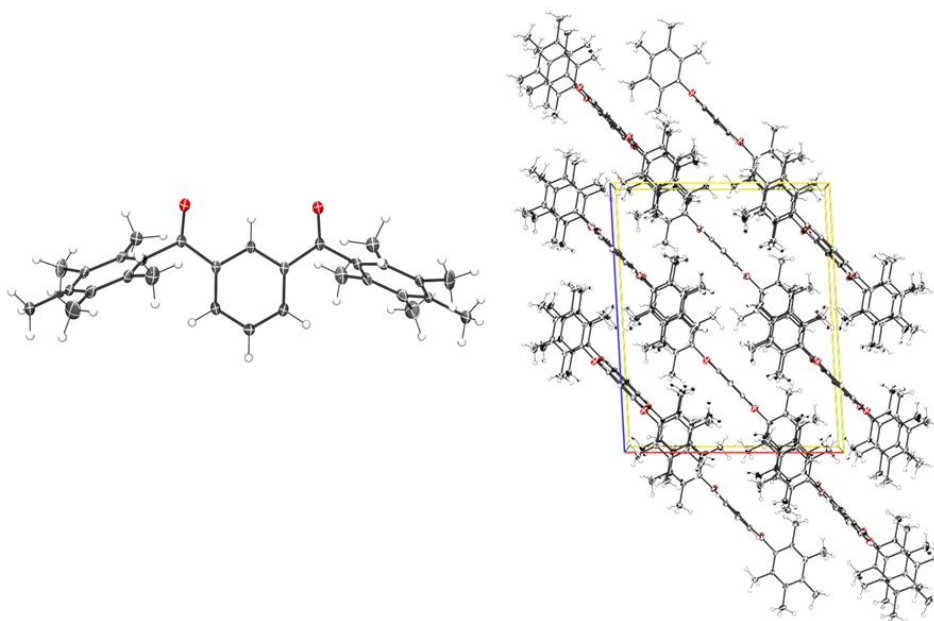
Figure 6.17: Left: Molecular structure of molecule **45**, right: Packing diagram of **45** along 010.

Pentamethylbenzene derivative **45** forms columns as well but these alternate in directions like the chloro- and fluorocorannulene. Therefore, the tendency to build these strands is not unique to diketone corannulene derivative **43** but stacking in only one direction is. The dihedral angle of the pentamethylbenzene ring and the spacer is -78.4(2)° and thus a little larger than that of the corannulene derivative **43** probably due to the sterical strain of the methyl groups.

Most of the corannulene derivatives, with the exception of **33** and **43,** did not crystallize. However, their pentamethyl analogs did. In case of in two position substituted compound **75** the asymmetric unit contains one molecule of **75** with both pentamethylbenzene groups pointing in the same direction (figure 6.18). The carbonyl groups are not in the same plane as the benzene ring of the spacer resulting in a dihedral angle of - 78.6(2)° and 83.3(2)° respectively. The different position of the carbonyl groups compared to derivative **45** is mostly likely to avoid steric strain between methyl and carbonyl groups. Again, compound **75** prefers a column like stacking with alternating strands.
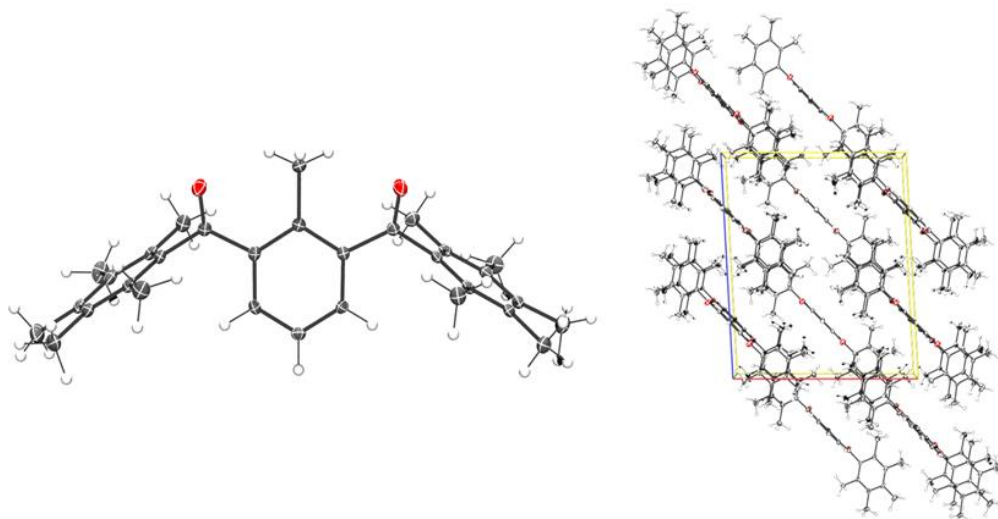
Figure 6.18.: Asymmetric unit of compound **75** (left) and the packing pattern (right).

Corannulene compound **79** does not form crystals in the solid state but pentamethyl derivative **78** crystallized as a single crystal with sufficient quality for X-ray diffractometry (figure 6.19) from a dichloromethane *n*-pentane mixture.
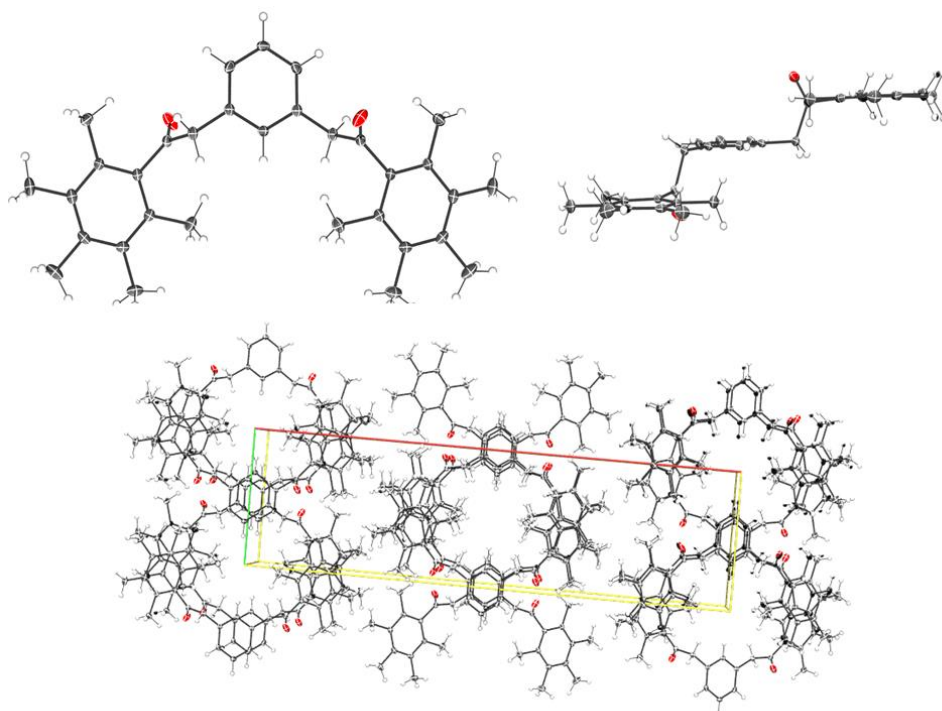
Figure 6.19.: Molecular structure of molecule **78** birds view (first row, left) and side-on (first row, right) and the packing pattern (second row).

The structure of the asymmetric unit is different from the other crystallized pentamethyl derivatives. The carbonyl groups point in two different directions forcing the aromatic rings in planes that are parallel to each other leading to a "steps" like appearance. The packing is dominated by the π-π interactions of the pentamethylbenzene rings while the position of the spacers alternate. The dihedral angle between the pentamethyl benzene and the methylene bridge is 80.1(2)° and thus very similar to that of the methyl derivative **45**.

As mentioned previously, corannulene derivatives **33** and **43** crystallized as single crystals with a sufficient quality for X-ray diffractometry. The other synthesized derivatives are amorphous powders and thus could not be investigated by this method. The corannulene bowl of both carbonyl derivatives is slightly different to that of pristine corannulene **1**. Compound **33** shows a "clam"-like packing behavior, in contrast to derivative **43** which forms a slipped stacking of the corannulene bowls, independent of the solvent. A columnar packing can also be observed for the structures of **75** and **45**. Pentamethylbenzene compound **78** forms an entirely different structure with the two carbonyl groups pointing in opposite directions.

7. Determination of Possible Guests and Binding Constants

Besides fullerenes, which are already known to form supramolecular complexes with corannulene **1**, a variety of other guests were screened to explore if other molecules are complementary to the receptors. As guests, monocyclic (figure 7.1), polycyclic (figure 7.2) and curved aromatic compounds (figure 7.3) were chosen.
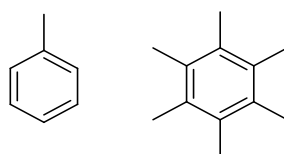
Figure 7.1: Monocyclic aromatic guests: toluene (left), hexamethylbenzene (right).

Toluene was suspected to interact with the receptors and thus was investigated towards its binding to the receptors in low concentration. Hexamethylbenzene was selected because it is a relatively small but highly activated aromatic compound and should be able to form π-π interactions with the corannulene bowls.
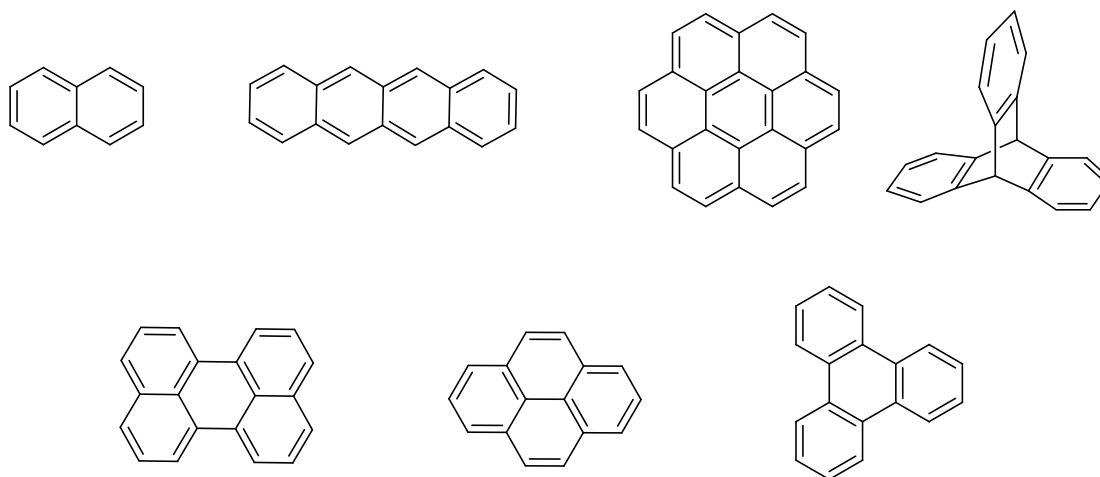
Figure 7.2: Polycyclic aromatic guests: naphthalene (first row left), tetracene (first row second to left), coronene (first row second to right), tryptycene (first row right), perylene (second row left), pyrene (second row middle), triphenylene (second row right).

The wide cavity of the receptors may prevent a successful incorporation of small molecules. Therefore a variety of polycyclic aromatic compounds ranging from small to large planar systems up to enormous curved systems like C_{70} fullerenes were screened. Planar molecules are less likely to be incorporated because the favorable convex-concave interactions cannot be formed. In contrast, geodesic aromatic molecules should be optimal for binding into the cavity formed by the two corannulene moieties.
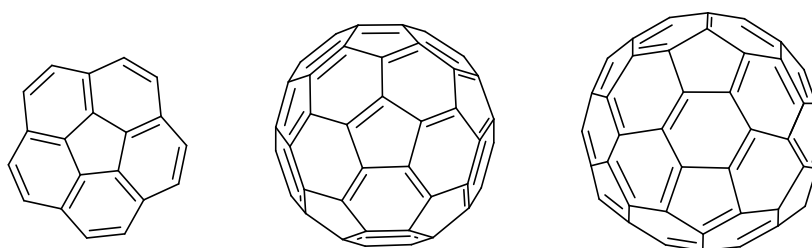
Figure 7.3: Polycyclic curved aromatic guest corannulene (left), C_{60} (middle), C_{70} (right).

7.1. Screening of Potential Guests

Neither all host molecules, nor all guest molecules were soluble in toluene. Therefore, d-chloroform was chosen as a second solvent.

The screening was carried out by preparing a stock solution of the molecular receptors in the respective solvent and adding it to a NMR tube. If the host molecule contained a fluorine atom (**55**),

a capillary containing pentafluorobutane was added as a standard. A ^{1}H NMR spectrum and in the relevant cases a ^{19}F or ^{13}C NMR spectrum of the solution was measured. Afterwards five equivalents of the guests were added to the tubes and another set of spectra were recorded.

Table 7.1: Shifts of the NMR signals of the receptors dissolved in either d-chloroform or d-toluene with the potential guests.

Host	Solvent	Toluene	Hexamethylbenzene	Naphthalene	Coronene	Corannulene	Benzanthracene	Perylene	Pyrene	Triphenylene	Triptycene	C_{60}	C_{70}
43	Chloroform	-	+	+	+	+	-	-	-	+	+	X	X
	Toluene	X	-	-	+	+	-	+	+	+	-	+	+
50	Chloroform	-	+	+	+	+	-	+	-	+	+	X	X
	Toluene	X	-	-	+	+	-	-	+	+	-	+	+
54	Chloroform	-	+	+	+	+	-	-	+	+	+	X	X
	Toluene	X	-	-	+	+	-	-	+	+	-	+	+
55	Chloroform	-	-	+	+	+	-	+	+	+	+	X	X
	Toluene	X	-	-	+	+	-	+	+	+	+	+	+
56	Chloroform	-	-	+	+	+	-	-	+	+	+	X	X
	Toluene	X	-	-	+	+	-	+	-	-	-	+	+
57	Chloroform	-	-	+	+	+	-	+	+	+	+	X	X
	Toluene	X	-	-	+	+	-	+	+	+	-	+	+
58	Chloroform	-	+	+	+	+	-	-	-	+	+	X	X
	Toluene	X	-	-	+	-	-	-	+	-	-	+	+
76	Chloroform	-	-	+	+	+	-	-	+	+	+	X	X
	Toluene	X	+	+	+	+	-	-	+	+	-	+	+
79	Chloroform	-	+	+	+	-	-	-	-	+	+	X	X
	Toluene	X	-	+	+	-	-	-	-	-	-	+	+
80	Chloroform	-	+	+	+	-	-	-	+	+	-	X	X
	Toluene	X	-	-	+	-	-	-	+	-	-	+	+

X (the guest was not tested in the solvent), - (no shifting of the NMR peaks, after the addition of a potential guest, could be detected), **+** (a shifting of the signals was observed after the addition of a potential guest)

All observations are summarized in table 7.1. Toluene induced no shifts of the NMR signals in d-chloroform but that does not exclude the possibilty that there are interactions in higher concentration. Hexamethylbenzene showed for the most parts only interactions in d-chloroform, the same is true for triptycene. Naphthalene, coronene, corannulene, pyrene and triphenylene

show an interaction with almost every host molecule in both solvents, while for benzanthracene no change of the chemical shifts could be detected. As expected, the biggest changes in the NMR spectra for all the receptors could be detected in the case of the fullerenes. The ^{19}F NMR spectra showed most of the time the same type of shifting as the ^{1}H NMR spectra but the capillary decreased the quality of the spectra and it was laborious to get sufficient shimming. While the ^{13}C NMR spectra of the marked compound **49** does not require a standard, only fullerenes changed the carbonyl resonance. But even then they the changes were small.

Summarizing all the host-guest screening results, it is clear that a larger π-system is more likely to show interactions with the receptors. The chosen solvents have an influence on the binding abilities of the host and guests. All of the tested guests show mostly very little or no differences in their chemical shifts. Only in case of the fullerenes noticeable shifts could be observed indicating that the corannulene hosts, as expected, favor the interaction with the ball shaped molecules.

7.2. Receptors and Fullerenes

Since the fullerenes showed the most potential of the tested guests, all further investigations of the supramolecular complex formation are based on them.

7.2.1. Job's Plots

A Job's plot or the "Method of Continuous Variation" was executed to determine the stoichiometry of the supramolecular complex **43**⊂C_{60} in solution. During the experiment, the total mole fraction of the host and guest is kept constant while the ratio is varied. The observed difference of the chemical shift multiplied with the mole fraction of the host against the mole fraction of the host results in a parable with the maxima at 0.5 for a 1:1 complex and at 0.33 for a 1:2 complex.
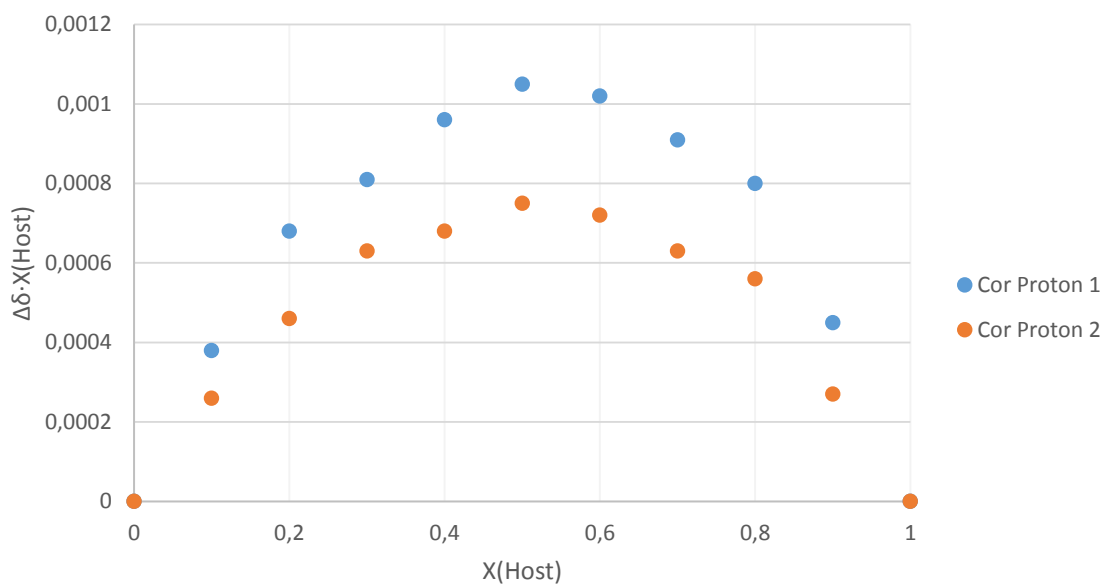
Figure 7.4: Job's Plot of the complexation of the host **43** and C_{60} for the two signals with the biggest difference of the chemical shift.

The Job's Plot of molecule **43** and C_{60} (figure 7.4) has a maxima at 0.5 indicating that indeed a 1:1 complex forms. The data was verified with a second Job's Plot using the same conditions yielding indentical results. The same analysis was preformed with the C_{70} fullerene, again resulting in a maxima at 0.5 (figure 7.5).
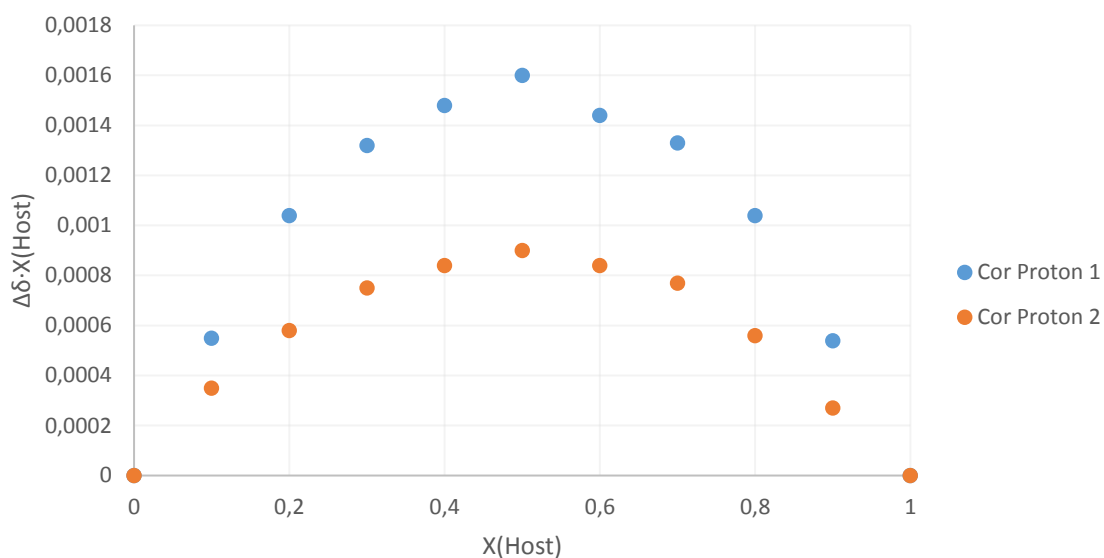
Figure 7.5: Job's Plot of the complexation of the host **43** and C_{70} for the two signals with the biggest difference of the chemical shift.

7.2.2. Temperature Dependents

The first experiment for assigning a binding constant of a supramolecular complex is to determine if the formation is fast or slow on the NMR timescale. If the exchange is slow, one set of signals belonging to the free host and one for the complex can be observed. The binding constant can then simply be determined with the help of the integrals. If the exchange is fast, only one set of signals belonging to both species, the free host and the complex, can be detected and the determination of the binding constant is more complex.
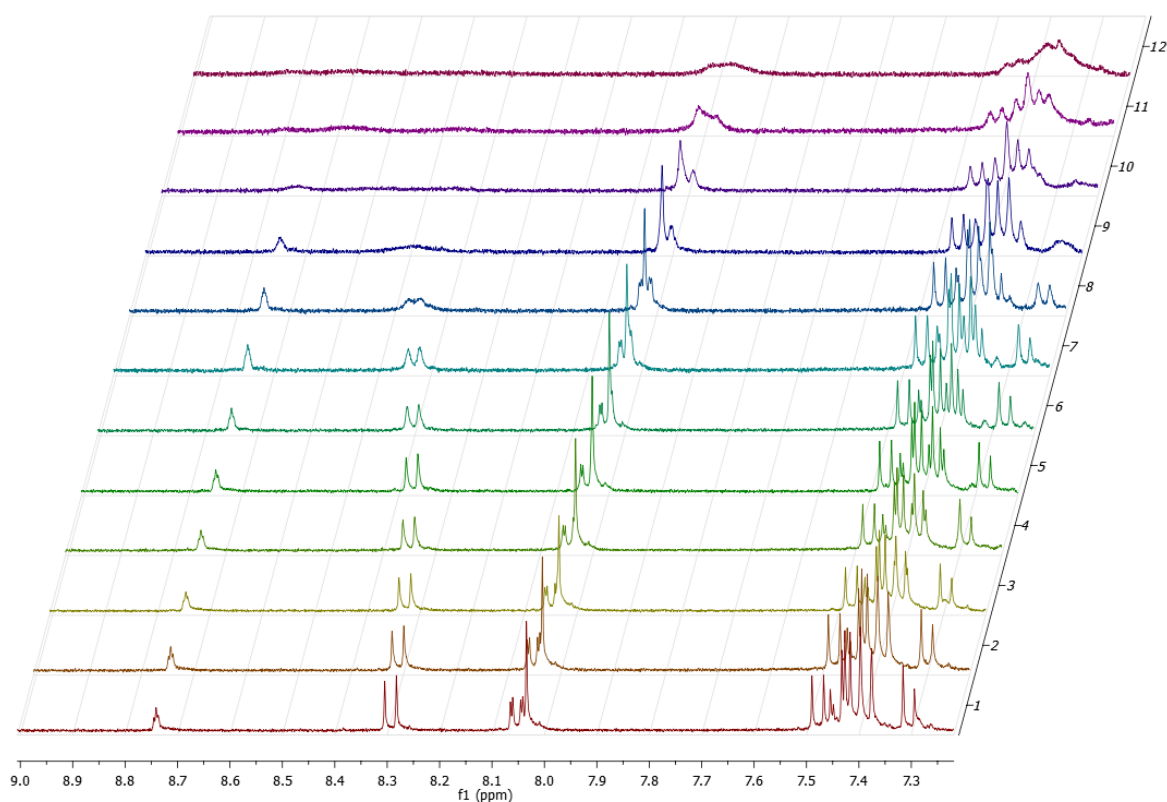
Figure 7.6: Temperature depending ^{1}H NMR spectra of **43** and C_{60} in d-toluene: (20 °C (1), 10 °C (2), 0 °C (3), -10 °C (4), -20 °C (5), -30 °C (6), -40 °C (7), -50 °C (8), -60 °C (9), -70 °C (10), -80 °C (11), -90 °C (12).

A stock solution of host **43** and C_{60} in d-toluene was prepared. The solution was placed in a NMR tube and cooled, in 10 °C steps, to -90 °C. A ^{1}H NMR was measured in between every step. While some shifts of the signals can be observed they do not split into two independent sets proving that the complex formation is fast on the NMR timescale (figure 7.6). Nevertheless a broadening of the signals at lower temperature can be observed. This indicates a coalescence of the signals but the low-temperature limiting spectrum cannot be observed. Since the binding constant cannot be determined with the measured spectra, more complex NMR experiments were necessary.

7.2.3. Concentration Dependents

Since the exchange is fast on the NMR timescale the best way to obtain the binding constant is by titration. The challenge hereby is that C_1-symmetric corannulene derivatives dimerize in solution[68] which can cause the same change in the observed physical properties as the complexation. Consequently the concentration of the host in solution had to be low enough that no dimer formation is possible. To determine the right concentration, a sample of molecule **54** was diluted sequentially three times and the ^{1}H NMR spectrum was measured in between each step while keeping the temperature constant. Comparing the spectra reveals that almost no difference between the signals can be observed (figure 7.7). Thus derivative **54** does not dimerize at the tested concentrations.
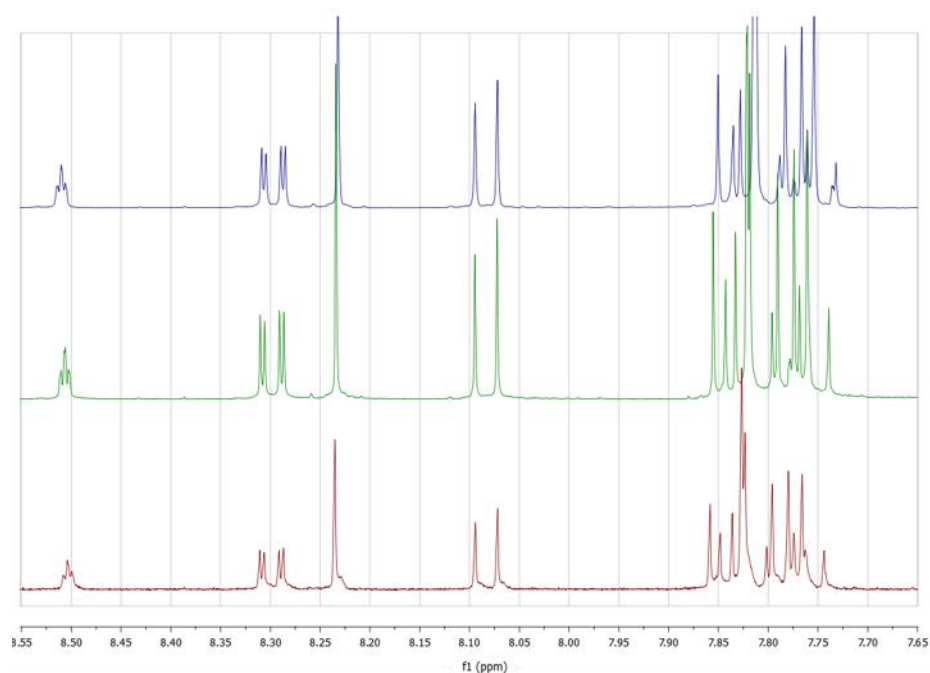
Figure 7.7: ^{1}H NMR spectra of **54** (top: 23 mM, middle: 12 mM, bottom: 2 mM).

To verify that the observed shifting under the condition used for a NMR titration is not depending on the concentration, an experiment was conducted in which a stock solution of host **43** was prepared and divided upon two NMR tubes. To one of the two a solution of C_{60} in d-toluene was added and to the other tube the same amount of d-toluene was added. For the first one, the typical difference of the chemical shift could be observed. If only toluene was added, no change could be detected (figure 7.8).
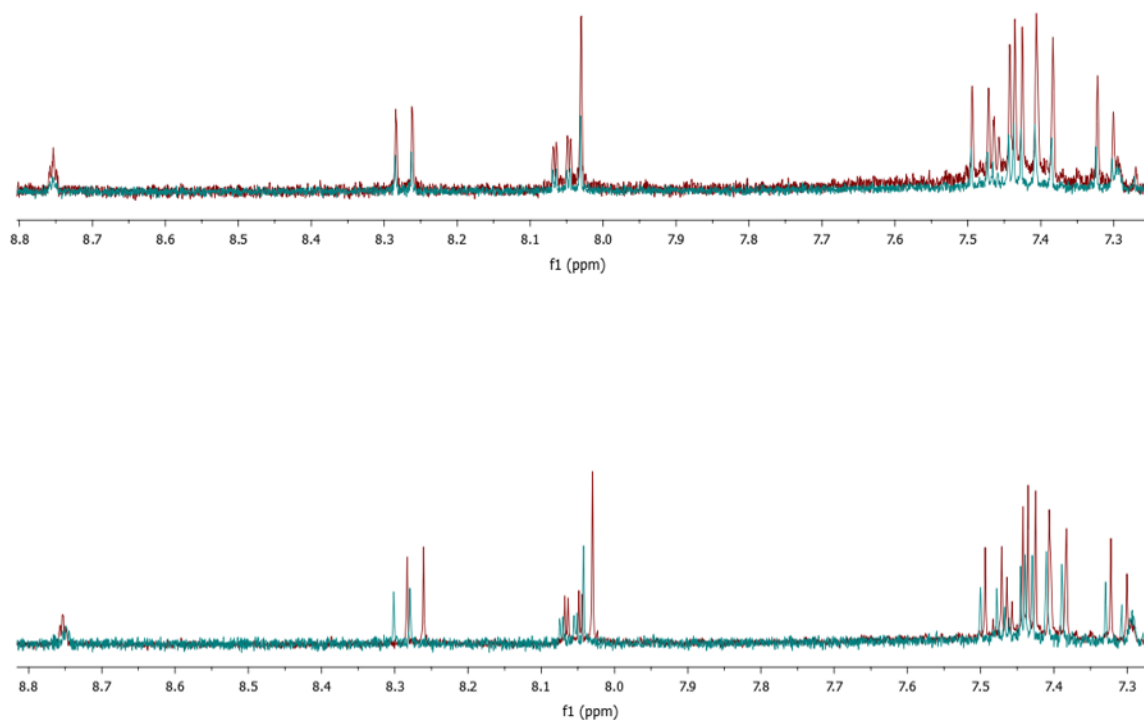
Figure 7.8: A Section of the aromatic region of the ^{1}H NMR spectra: Guest **43** solution to which was added toluene (top) and guest **43** solution to which was added a C_{60} solution (bottom).

Only in one case a noticeable difference between the two spectra can be observed. Thus the change of the chemical shifts under the condition of a NMR titration are caused by the formation of a supramolecular complex between the guest and host and not because of a dimerization of the receptors.

7.2.4. Titrations

There are a lot of possible ways to determine the binding constant of supramolecular complexes in solution. The most common ones are titrations. In principle, the change of a physical property of the host molecule caused by the complex formation is observed. Possible methods to observe these changes are UV-Vis, NMR or fluorescence spectroscopy. The fluorescence of the designed receptors is quite low and this technique was thus excluded from the possible methods. Both UV-Vis and NMR spectroscopy are possible and have been used for the determination of the binding constants.

For the NMR titration two stock solutions in d-toluene were prepared, one containing the host and the other the guest. The host solution was added to a NMR tube and a ^{1}H NMR spectrum was measured. Afterwards a small amount of the guest solution was added and another spectrum obtained. This was repeated serveral times. For the exact amounts added see experimental part (chapter 10.5). In the end, more than eleven equivalents of the guest were added to the tube.

To calculate the binding constants of a 1:1 complex, one first assumes that the supramolecular complex HG is in equilibrium with the guest G and host H (equation 1).

$$H + G \rightleftharpoons HG \qquad (1)$$

$$K_a = \frac{[HG]}{[H] \cdot [G]} \qquad (2)$$

The binding constant K_a is defined as the concentration of the complex $[HG]$ divided by the concentration of the host $[H]$ and the guest $[G]$ (equation 2).

If the formation and release of the supramolecular complex is fast, the observed chemical shift δ_{obs} is the weighted average between the free host δ_H and the formed complex δ_{HG}. Defining the initial host concentration as H_0 gives the equation (3).

$$\delta_{obs} = \frac{H_0 - [HG]}{H_0} \cdot \delta_H + \frac{[HG]}{H_0} \cdot \delta_{HG} \qquad (3)$$

A slight rearranging of the equation and the introduction of the term $\Delta\delta$, which equals the difference in chemical shift between the free and bound host (equation 4), leads to equation 5.

$$\Delta\delta = \delta_{HG} - \delta_H \qquad (4)$$

$$\delta_{obs} = \delta_H + \frac{[HG]}{H_0} \cdot \Delta\delta \qquad (5)$$

The concentration of the supramolecular complex $[HG]$ can be determined if the dissociation constant and the initial concentration of the host and guest are known (equation 7). The dissociation constant K_d is the inverse equilibrium constant (equation 6).

$$K_d = \frac{[H] \cdot [G]}{[HG]} = \frac{1}{K_a} \tag{6}$$

$$[HG] = \frac{1}{2}[K_d + H_0 + G_0] - \sqrt{(K_d + H_0 + G_0)^2 - 4H_0G_0} \tag{7}$$

Merging equation 5 and 7 gives the observed chemical shift as a function of the starting concentrations of guest and host, the dissociation constant, the change in the observed chemical shifts and the initial chemical shift of the host.

$$\delta_{obs} = \delta_s + \frac{\Delta\delta}{2G_0}\left[[K_d + H_0 + G_0] - \sqrt{(K_d + H_0 + G_0)^2 - 4H_0G_0}\right] \tag{8}$$

Equation 8 can be solved by common software packages like origin[69] with nonlinear regression methods given that the concentration of the host and guest are known.
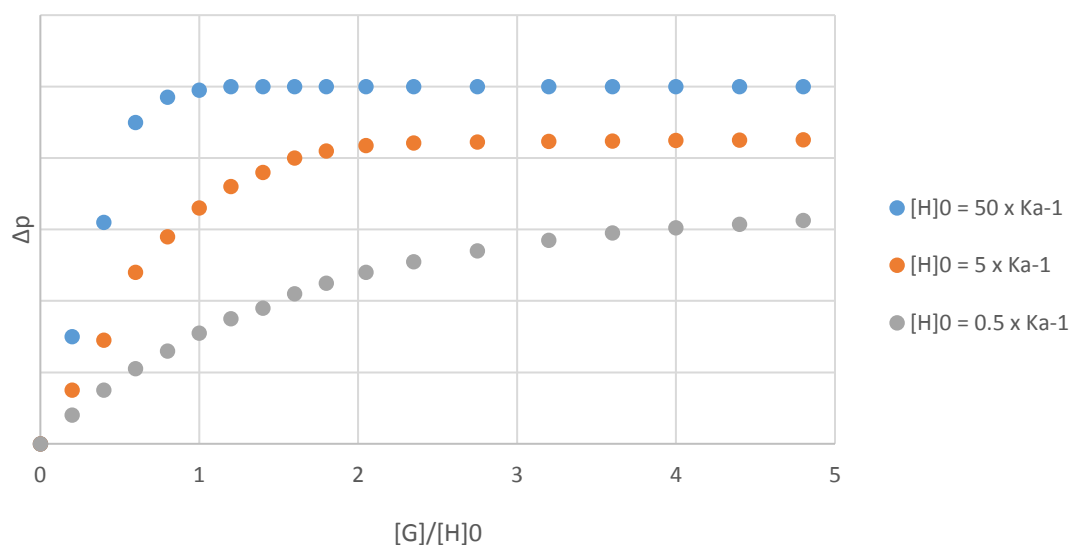
Figure 7.9: Typical graphs for a NMR titration (blue: very big binding constant, orange: big binding constant, green: small binding constant).

As can be observed in figure 7.9 if the binding constant is big (blue dots) the system reaches the equilibrium state fast and the graph evens out afterwards because no more changes in the chemical shift can be observed. Systems with a small binding constant need longer to reach an equilibrium so the graph only evens out slowly.
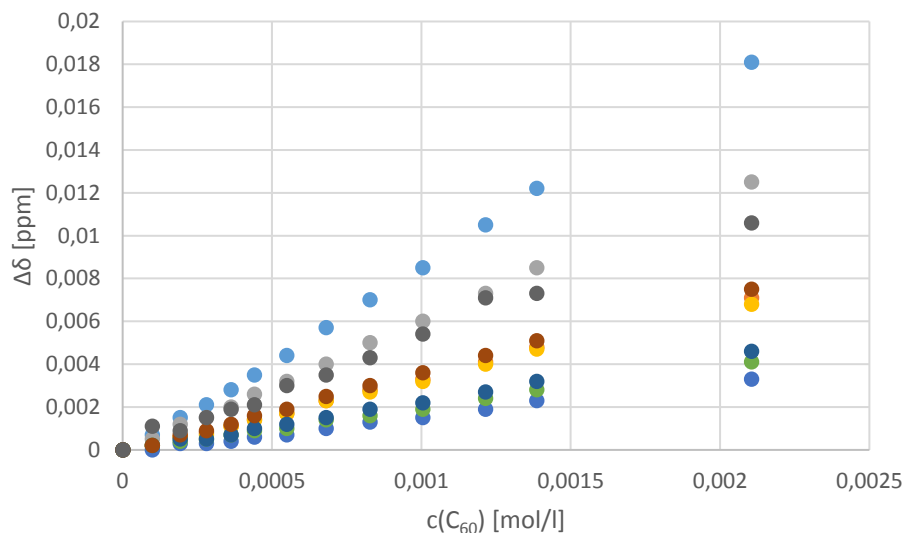
Figure 7.10: ^{1}H NMR titration of receptor 4**3** (1.6 mM) with C_{60} every color represents a different hydrogen atom of the receptor.

The line shape of the graph derived from the titration for receptor **43** is almost linear with no curvature (figure 7.10). As a consequence the program cannot converge the graph to equation 8. Besides experimental errors, one possibility for this observation could be that the binding constant is too small. The titration was repeated three times with the same results diminishing the chance of experimental errors. Other tested substrates like **53**, **54** and **75** showed the same linear graphs (see appendix). One possible method to determine small binding constants is to reduce the concentration of the host or increase the amount of guest added. The latter is not possible since the amount of C_{60} that is soluble in toluene is limited to 3 mg/mL at room temperature. Reducing the amount of host **43**, roughly by a factor of three, still led to the already observed straight line (figure 7.11).
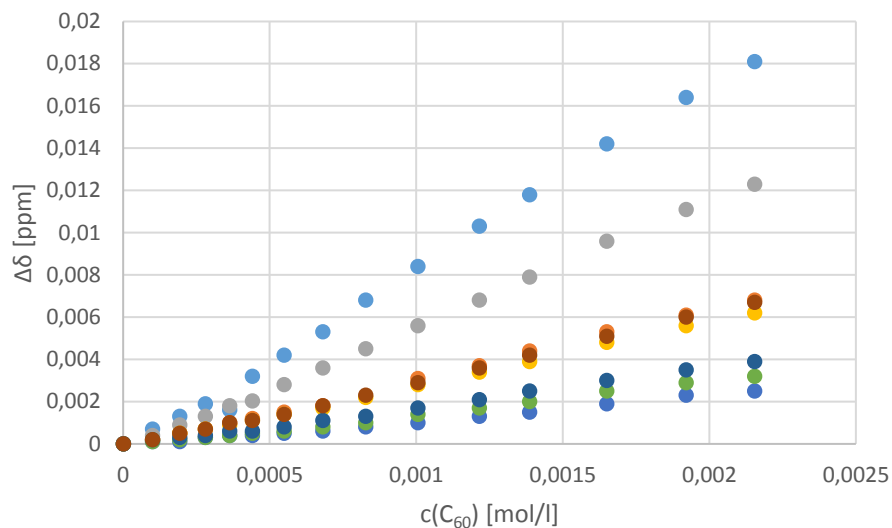
Figure 7.11: ^{1}H NMR titration of receptor **43** (0.6 mM) with C_{60} every color represents a different hydrogen atom of the receptor.

Again when the guest was changed from the Buckminster fullerene to C_{70} the program could not find a fit, even if the graph flatted somewhat at the end of the measurement (figure 7.12).
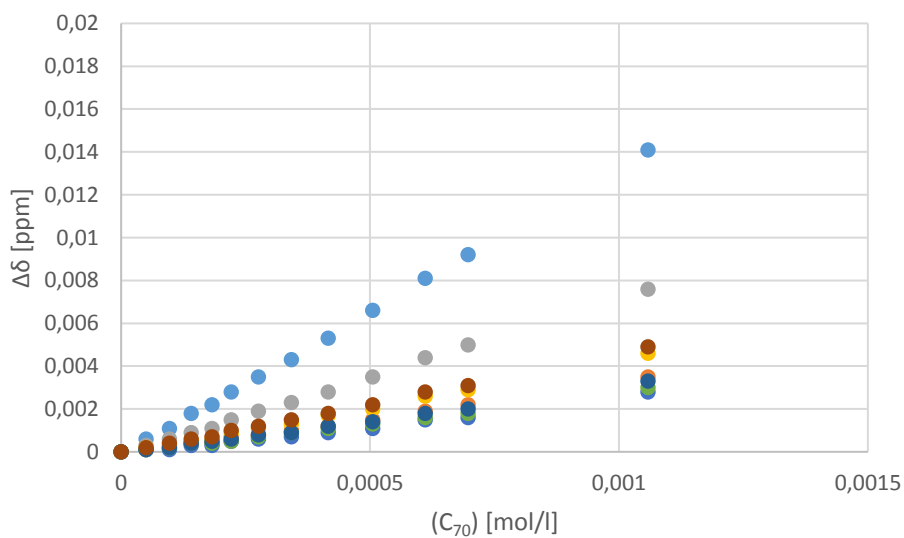
Figure 7.12: ^{1}H NMR titration of receptor **43** (1.3 mM) with C_{70} every color represents a different hydrogen atom of the receptor.

Since the problem, of fitting the data, does not depend on the fullerene, maybe changing the solvent would lead to better results. As already discussed, toluene may interact with the

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supramolecular complex, which could be the reason why it is not possible to determine the binding constant. The solvent was changed to a non-aromatic one to avoid the postulated interactions. However, fullerenes are not easily dissolved and it is especially difficult in non-aromatic solvents. Considering the possible solvents only two seemed viable: bromoform and carbon disulfide. According to literature, both dissolve C_{60} fullerene better than toluene. Bromoform has the benefit of possessing a hydrogen atom which can be exchanged for a deuterium atom to have an internal standard and lock signal for the NMR measurement. However, d-bromoform showed unsatisfactory results. The background of the spectrum was high and the signals very broad which prevented the assignments of the signals. Even the amount of fullerene which, according to literature, can be dissolved in bromoformcould not been reached. As a conclusion bromoform is not a suitable solvent for the NMR titrations.

Carbon disulfide does not have a hydrogen atom and thus an external standard has to be introduced into the system risking an interaction between the standard and the host or guest molecules. To avoid this problem altogether, a deuterated standard in a glass capillary was added to aid with the quality of the spectra by providing a lock signal. As potential deuterated substances DMSO, acetone, deuterium oxide and benzene were tested. The best results could be observed for deuterium oxide but the obtained titration data was not sufficient enough to determine a binding constant. Because of those unsatisfactory results the less preferred option of introducing a standard directly into the system had to be attempted. It was decided to use TMS since it provides a very sharp singlet which is per definition at 0 ppm. It is an inert, non-aromatic compound and thus should not interact with the receptor or the guest. While it was possible to obtain ^{1}H NMR spectra in good quality, just a very small change of the chemical shift could be observed during the titration. This is most likely because of the missing lock signal. Again it was impossible to obtain a binding constant.

Maybe NMR spectroscopy is the wrong method since it is not possible to exchange the solvent and the solubility of the guest in toluene is limited. If the binding constant is very small, the literature advices the use of either UV-Vis or fluorescence spectroscopy[70]. The latter method is not possible which is why UV-Vis spectroscopy was the method of choice. Determining the binding constant from the UV-Vis titration gave a value of over 200 000 M^{-1} which is completely unrealistic for this kind of non-rigid spacers (figure 7.13).
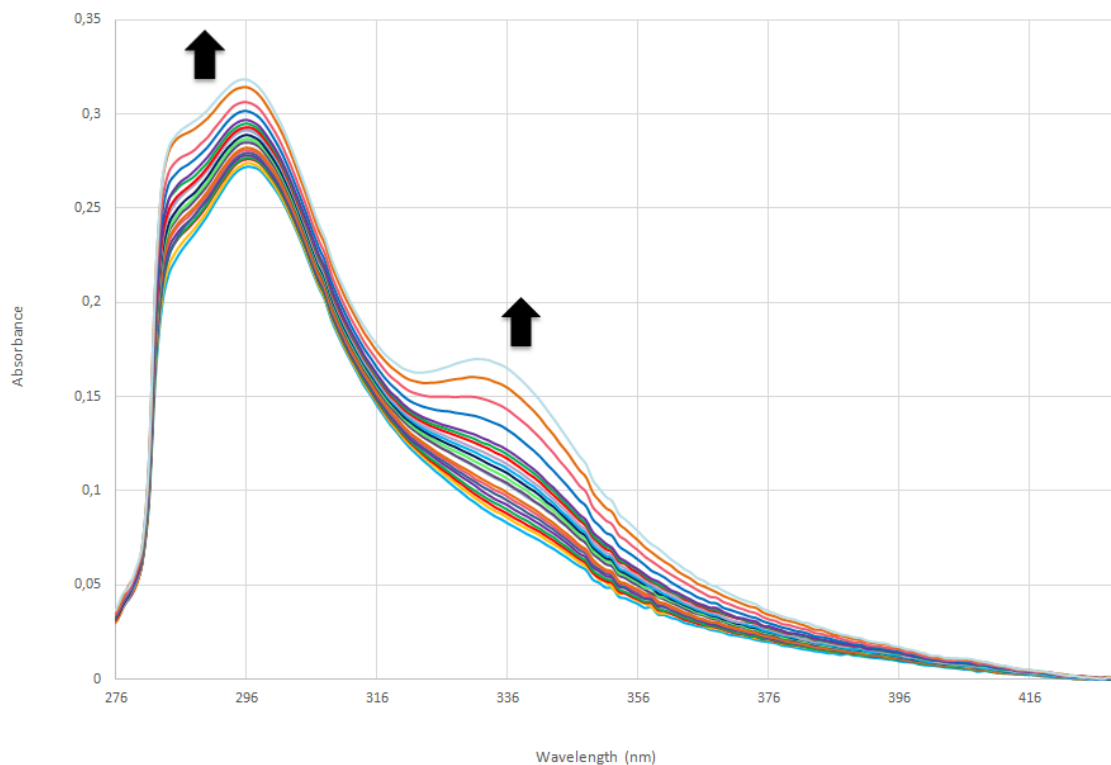
Figure 7.13: UV-vis titration with receptor **54**.

Since it was not possible to determine a reasonable binding constant it was considered that the assumption of a 1:1 stoichiometry may not be the correct one. Cases have been reported were the Job's Plot failed to describe the correct stoichiometry. For example if a 1:2 host guest system is formed, more than one host guest complex is likely depending on the saturation of the solution (equation 9).

$$H + G \leftrightharpoons HG + G \rightleftharpoons HG_2 \qquad (9)$$
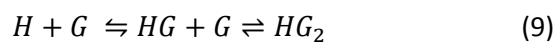
The Job's plot can predict a wrong stoichiometry if the formed complexes HG and HG_2 have different physical properties like different chemical shifts in the NMR spectrum. Therefore, assumeing that the dependence of these shifts is linear is not correct. Thus making the result of the Job's Plot incorrect.

An indication for the correct stoichiometry is the number of isosbestic points in an UV-Vis titration. As seen in figure 6.12, there are no isosbestic points for the UV-Vis titration of derivative **54**. Therefore a statement based on them is not possible. Another method to determine the stoichiometry is to fit the titration data against other possible stoichiometries and identify the fitting with the smallest error.

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To determine the equation which is needed for fitting the data for other stoichiometries than 1:1 is quite complicated. Since the stepwise binding of the receptors to the guest has to be taken into consideration. For a 1:2 system the binding constants K_a and K_2 are given by equation 2 and 10.

$$K_2 = \frac{[HG_2]}{[HG] \cdot [G]} \qquad (10)$$

The concentration of the guest $[G]$ can be solved from equations 2 and 11 as a function of $[G_g]$ and $[H_g]$ (equation 11).

$$K_a K_2 [G]^3 + K_a (2K_2[H_g] - K_2[G_g] + 1)[G]^2 + \qquad (11)$$
$$(K_a[H_g] - K_a[G_g] + 1)[G] - [G_g] = 0$$

The variables $[G_g]$ and $[H_g]$ are defined as the total concentration of the guest and host respectively (equation 12 and 13).

$$[G_g] = [G] + [HG] + 2[HG_2] \qquad (12)$$

$$[H_g] = [H] + [HG] + [HG_2] \qquad (13)$$

The cubic equation 11 has to be solved for multiple initial estimates of K_a and K_2 and for multiple $[G_g]$ and $[H_g]$s. Each solution for $[G]$ is used to obtain the concentrations $[HG]$ and $[HG_2]$ with the help of equations 14 and 15 respectively.

$$[HG] = \frac{K_a[H_g][G]}{K_a K_2 [G]^2 + K_a[G] + 1} \qquad (14)$$

$$[HG_2] = \frac{K_a[H_g][G]^2}{K_a K_2 [G]^2 + K_a[G] + 1} \qquad (15)$$

Given equation 14 and 15 the observed chemical shift δ_{obs} can be written as follows.

$$\delta_{obs} = \frac{[G]}{[G_g]}\delta_G + \frac{[HG]}{[G_g]}\delta_{HG} + \frac{2[HG_2]}{[G_g]}\delta_{HG_2} \qquad (16)$$

The difference of the chemical shifts $\Delta\delta$ can this time be defined as the difference of the observed chemical shift δ_{obs} and δ_G (equation 17).

$$\Delta\delta \ = \frac{[HG]}{[G_g]}\delta_{HG} + \frac{2[HG_2]}{[G_g]}\delta_{HG_2} \qquad (17)$$

The obtained results of equations 11, 14 and 15 can be substituted into 17 to obtain δ_{HG} and δ_{HG_2}. Those are in turn inserted into equation 16 and compared with the observed chemical shift δ_{obs} values to generate the standard deviation. The values of the two binding constants K_a and K_2 are varied until a minimum of the standard deviation is reached. The values for K_a, K_2, δ_{HG} and δ_{HG_2} corresponding to that minimum are the once generating the best fit for the data obtained by the titration.

The equations can be solved by common software packages like matlab[71] with nonlinear regression methods but writing the function files and implementing the necessary pathways is by no means a trivial matter. For that reason, a premade software package from the Australian Research Council Centre of Excellence in Covergent Bio-Nano Science and Technology (CBNS) was used[72].

Using the 1:2 stoichiometry significant binding constants could be obtained for some cases. For others the fit gives either values that are to big, up to 10^6 M^{-1}, or even negative (see appendix) which is by definition impossible. The fits were attempted with various starting values but the results did not change significantly. Even for three titrations that were done under the same conditions and with the same concentrations the results varied between 1001 and 4752 for K_a and -228 and 1036 for K_2. For receptor **43,** which was measured with two different concentrations, completely different values for each concentration were obtained (see appendix) giving the impression that neither the 1:1 nor the 1:2 stoichiometry describes the system correctly.

7.2.5. Crystallography: Supramolecular Complexes

The stoichiometry of the supramolecular complex between the corannulene derivatives and the fullerenes could not be determined by titration. An explanation for that phenomenon was derived from three crystal structures determined by X-ray diffraction.

Solvent-free single crystals were obtained after the slow evaporation of a 1:1 solution of C_{60} and **33** in toluene with a sufficient quality for X-ray structure determination (figure 7.14). No solvent molecules are present in the molecular structure which is seldom observed [36]. Because the solvent molecules play an important role in the formation and stabilization of fullerene containing cocrystals[73].
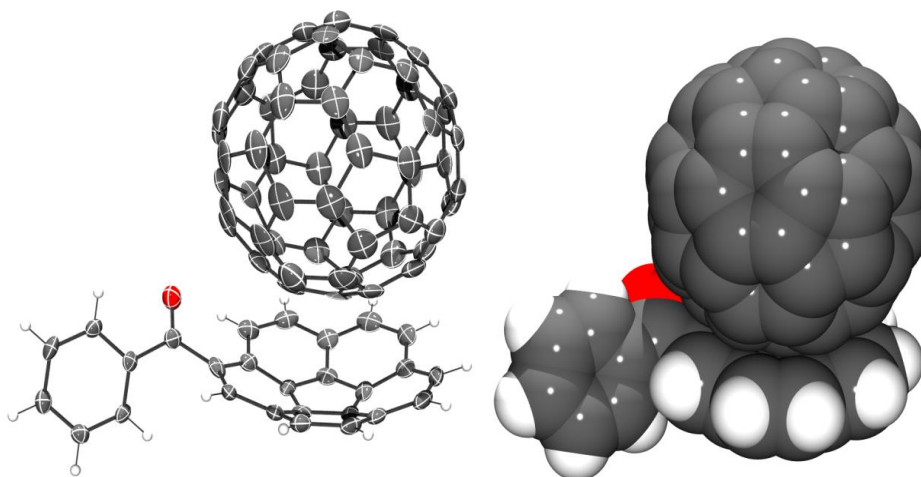
Figure 7.14: Molecular structure of **33** and C_{60} ellipsoid (left) and space filling (right).

As can be observed in figure 7.14 the Buckminsterfullerene is located in the corannulene bowl proving the desired complexation of the buckyball. The C_{60} has only a population parameter of 50 % because the 2-fold axes of the space group is not aligned with the 2-fold axes of the fullerene resulting in a disordered Buckminsterfullerene in the asymmetric unit (figure 7.15). Since there are two receptor molecules in the asymmetric unit the stoichiometry for the supramolecular complex of **33** and C_{60} is 2:1.
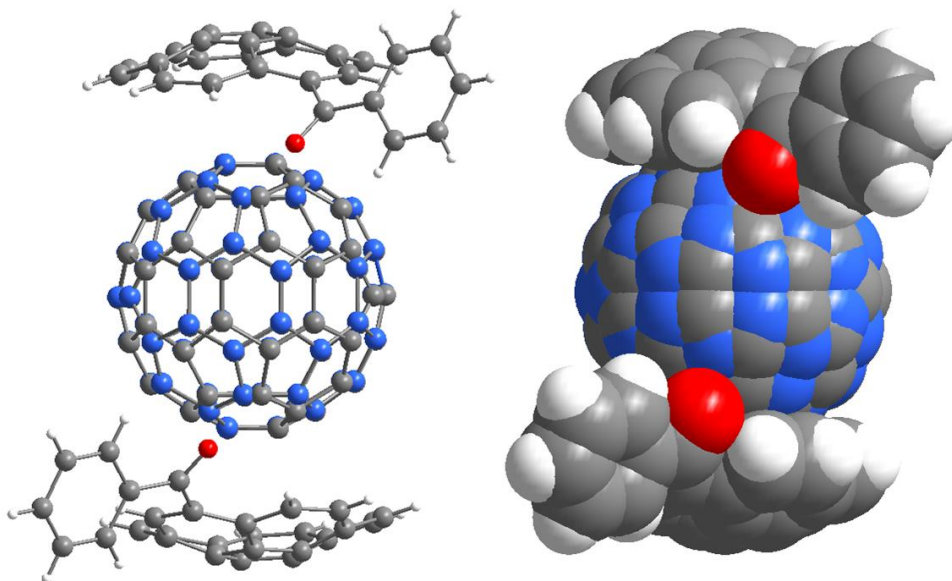
Figure 7.15: Asymmetric unit of the crystal structure of **33** and C$_{60}$ ball-and-stick (left) and space filling (right) the second fullerene is colored blue.

The bowl depth of the corannulene bowl is now 0.853 Å and therefore only slightly different (0.01 Å) to the pristine derivative **33**. The shortest distance between the carbon allotrope and the buckybowl is 3.315 Å. The distance between the corannulene centroid defined by the five hub atoms and the centroid of the fullerene is 6.864 Å. Which is a significantly shorter distance than that observed for the platinum tweezer (6.92 Å)[37].
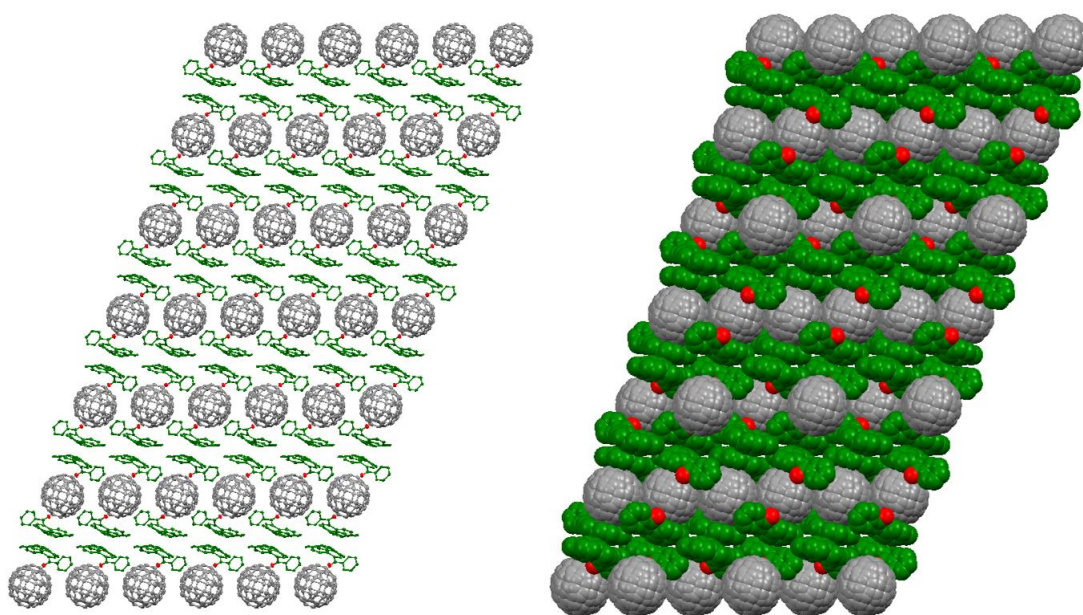
Figure 7.16: Packing diagram of **33** (green, red) and C$_{60}$ (gray) in the solid state ellipsoid (left) and space filling (right); the fullerene is disordered (hydrogen atoms were omitted for clarity).

The packing diagram (figure 7.16) shows that one of the ball shaped fullerenes is surrounded by two corannulene derivatives **33** binding on opposite sides of the disordered fullerene. In contrast to the packing without the guest, the corannulenes now interact with each other over their convex rather than their concaves sides. The fullerenes too, interact with each other forming planar 2D layers. The distance between two neighboring fullerenes is 9.829 Å and thus at the utter limit of the van der Waals radius of roughly 10.0 Å. The distance between each layer, measured between the planes formed by the centroids, is 15.913 Å. These planar layers are quite uncommon for fullerene containing cocrystals[74]. Pristine corannulene **1** crystallizes with C_{60} in a similar arrangement where the fullerenes form corrugated instead of planar sheets[32]. Also, the fullerene in this structure shows a much higher level of disordering than in the one of $(33)_2 \subset C_{60}$. The degree of disordering is related to the strength of the interaction between the receptor and the fullerene guest. If the fullerene is highly disordered it means that there is almost no interaction between the guest and host. In case of derivative **33** even the attachment of only one benzoyl group to the rim of the corannulene bowl improved the interaction with the Buckminsterfullerene drastically.

Since derivative **33** forms a 2:1 complex, the dicarbonyl compounds were expected to behave similar. It was possible to obtain single crystals with a sufficient quality for X-ray analysis of derivative **43**.
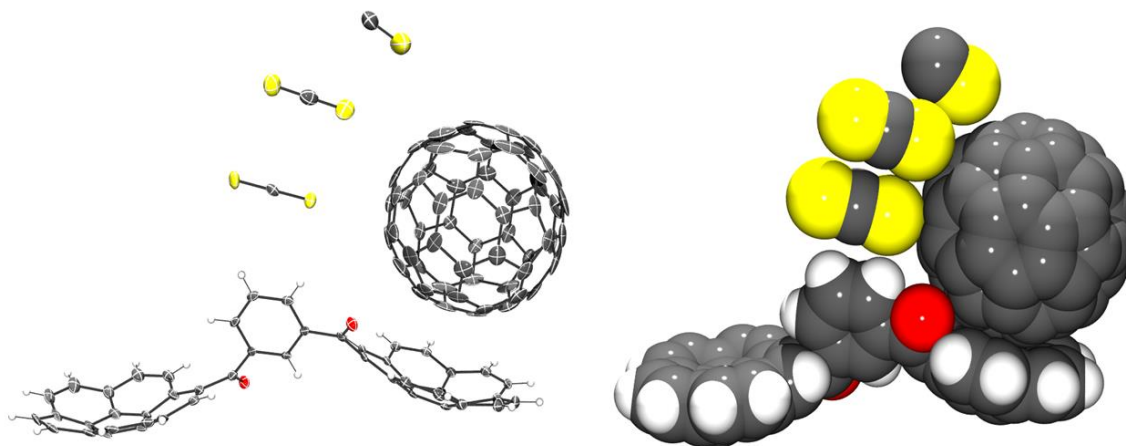
Figure 7.17: Asymmetric unit of **43** and C_{60} in the solid state ellipsoid (left) and space filling (right).

In this case the asymmetric unit (figure 7.17) contains one receptor molecule **43**, one Buckminsterfullerene and two and a half solvent molecules. The guest molecule is positioned above one of the bowls clearly showing the interaction between the ball and bowl.
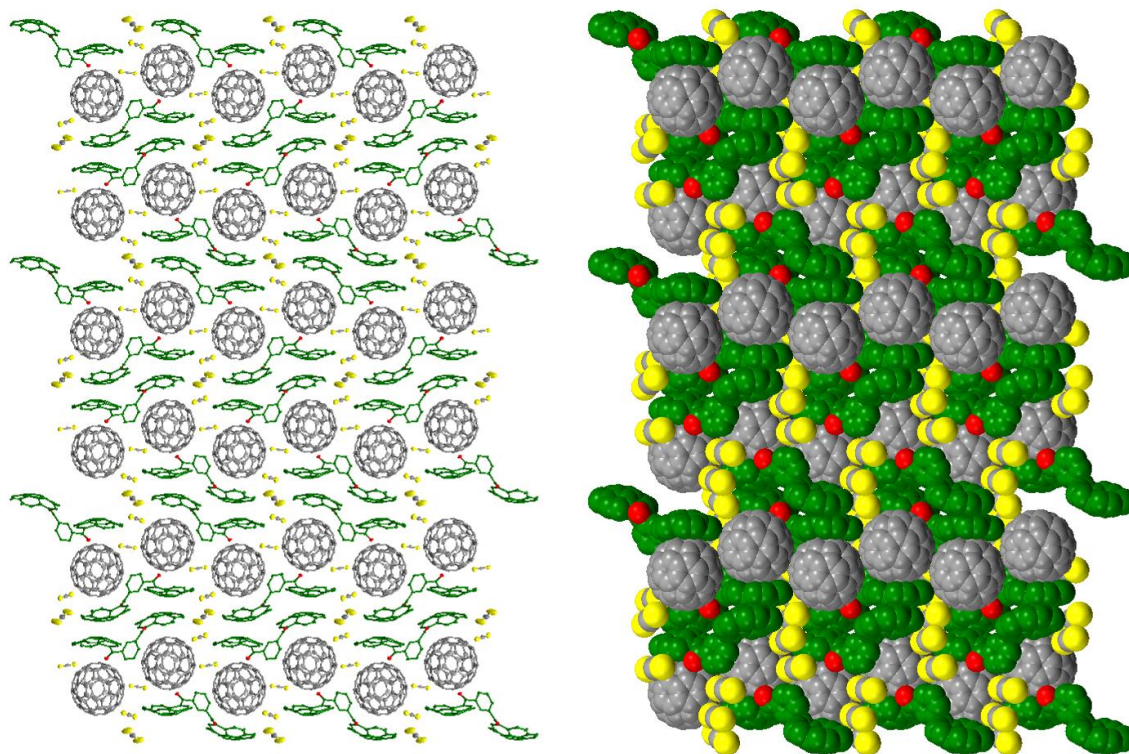
Figure 7.18: Packing of the receptor **43** (green) and the fullerene (gray); left: ellipsoids, right: space fill (hydrogen atoms were omitted for clarity, view along (010)).

However one corannulene bowl per two host molecules always encapsulate one fullerene resulting in a H_nG_n type of stoichiometry (figure 7.18). The receptor changes the previously discussed preferred arrangement and now, like the above discussed cocrystal of **33**, only the convex sides of the bowls are in contact with each other. The fullerenes aggregate in corrugated sheets which appear in a side-on view like zigzag chains. The distance between the centroids of the closest fullerenes is 10.152 Å which is quite close to the van der Waals limit (10.0 Å). The angle between three fullerenes is 141° which is well within the region known for isolated zigzag fullerene chains (118° - 172°). The layers are parallel to each other and have a distance of 16.581 Å which is a little larger than that of the $(\mathbf{33})_2 \subset C_{60}$ complex described prior. The difference results most likely from the corrugation of the layers in contrast to the planar ones. One receptor molecule **43** interacts with two neighboring zigzag chains stabilizing the layers. The distance between the centroid of the hub ring and the centroid of the fullerene has the average length of 6.985 Å which is slightly longer than that of the previously reported receptor **33**. The shortest distance between the bowl and surface of the ball is 3.226 Å which is close to the distance of different layers in multiwalled carbon nanotubes. For the Buckycatcher the shortest distance is 3.128 Å which is quite similar and thus confirms that the fullerenes are indeed located in the cavity of the bowl. In

contrast to the already mentioned crystal structures the fullerene suffers from no disordering indicating a strong host guest interaction.

Since the crystal structure of **43** is not influenced by the intercalated solvent I expected the same behavior for the supramolecular complex. Surprisingly, when the solvent was changed to toluene a completely different packing motif could be observed. The asymmetric unit (figure 7.19) of the toluene solvate contains one receptor molecule **43**, two toluene and one and a half C_{60} molecules.
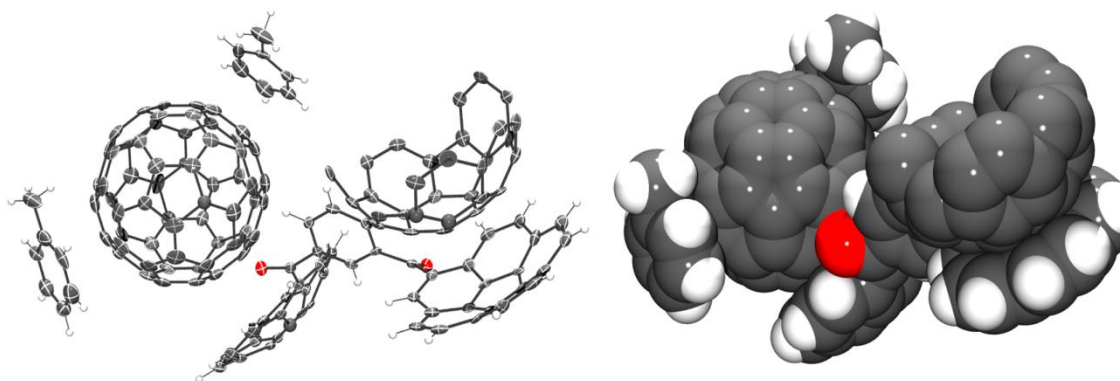
Figure 7.19: Asymmetric unit of the receptor **43** with toluene; left: ellipsoids, right: space fill.

The bowl depth is slightly different than that of pristine receptor **43** (table 7.2), too. The shortest distance between the complete fullerene (black) and the half fullerene (grey) of the asymmetric unit and the closest bowl is 3.192 Å and 3.161 Å, respectively, which is similar to that of the carbon disulfide solvate. The distance between the centroids of the two fullerenes is 15.694 Å which is larger than the van der Waals limit. Thus an interaction between the two Buckyballs can be excluded. Both fullerenes have with 6.816 Å and 6.852 Å a slightly shorter distance, then the carbon disulfide solvate, between the hub and the buckyball centroids.
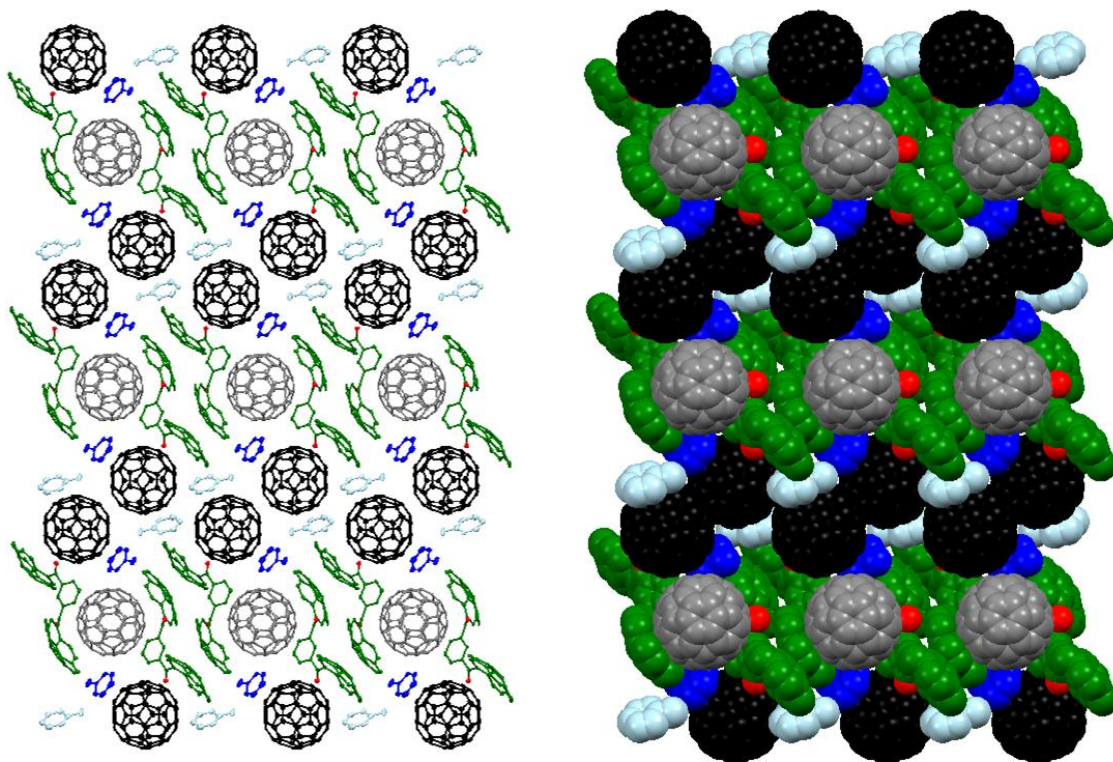
Figure 7.20: Packing diagram of the receptor **43** (green), the fullerenes (gray, black) and the toluenes (light blue, blue); left: ellipsoids, right: space fill (hydrogen atoms were omitted for clarity, view along (100)).

The packing diagram (figure 7.20) of the supramolecular complex is quite complex. The fullerenes form two different motives. One being a corrugated layer consisting of the black fullerenes. These Buckminsterfullerenes have additional π-π contacts to the toluene molecules. As only one corannulene bowl of a receptor molecule coordinates to these buckyballs they can come into close contact (9.804 Å). The angle between three members of the corrugated sheets is 107.6° which is much smaller than that of the carbon disulfide solvate. The distance between the fullerenes in one layer alternates between 9.804 Å and 10.360 Å. The remaining fullerenes (grey) are arranged in linear columns with a distance of 10.149 Å between two fullerenes. They interact with one receptor molecule **43** and one toluene molecule. The different fullerene motives alternate in the packing diagram. As in the two structures prior the corannulene bowls are no longer stacked and the concave sides point towards each other. The overall stoichiometry of the toluene solvate is H_2G_3 and thus different from the carbon disulfide solvate.

In table 7.2 the most important features and values of all the three structures are summarized. The most important realisation is probably the huge influence of the solvent on the packing of the supramolecular complexes. However, while the different chemical shifts in the ^{1}H NMR spectra

indicated that the solvent interacts with the receptors, the molecular structure of the pristine receptor **43** was not influenced at all by the cocrystallized solvent.

Table 7.2: Comparison between the molecular structures of the supramolecular complexes.

	33$\subset C_{60}$	**(43**$\subset C_{60})\cdot CS_2$	**(43**$\subset C_{60})\cdot C_7H_8$
Packing motive	planar layers	corrugated layers	corrugated layers and linear columns
Incorporated solvent in the asymmetric unit	-	2.5 molecules	2 molecules
Bowldepth	0.853 Å	0.855 Å	0.838 Å
Shortest distance Cor-C_{60}	3.315 Å	3.226 Å	3.161 Å
Distance centroids Cor-C_{60}	6.864 Å	6.985 Å	6.816 Å
Disorder of the C_{60}	yes	no	no
Shortest distance C_{60}	9.829 Å	10.152 Å	9.804 Å
Stoichiometry	H_2G	H_nG_n	H_2G_3

Analyzing the packing of the three described molecular structures leads to the assumption that a variety of supramolecular complexes are formed in solution (figure 7.21). Depending on the ratio of receptor to fullerene and on the used solvent, different stoichiometries and arrangements are possible, ranging from a 1:1 complex to oligomeric chains. The motives (7) and (8) could be observed in the studied solid state structures. Considering this, it becomes obvious why it was not possible to define a stoichiometry and thus a binding constant for the titration experiments.
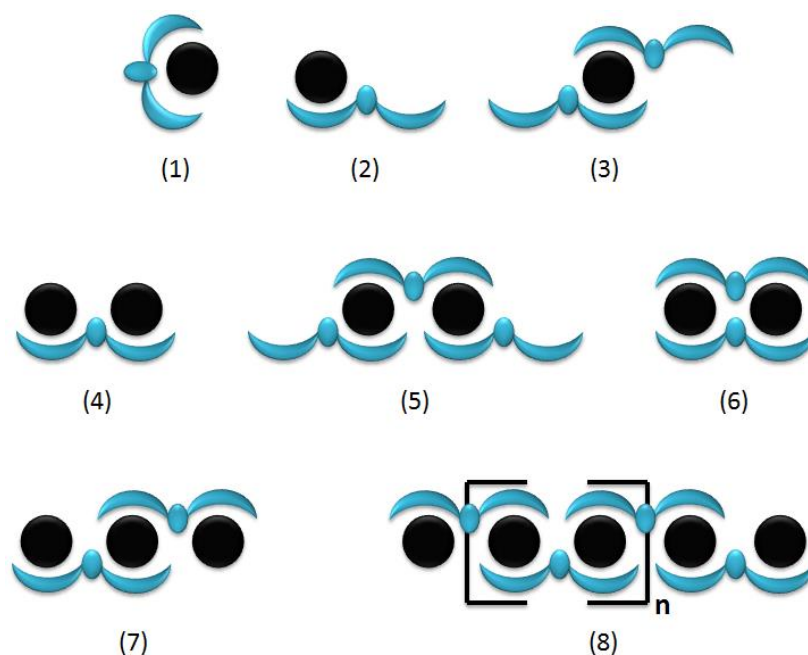
Figure 7.21: A few of the possible aggregates of the fullerenes and the receptors.

8. Summary

This work was dedicated to the investigation of possible methods to connect two corannulene bowls to create non-rigid tweezers. Three different synthetic approaches were investigated. A system based on a trifluorovinyl group **11** could not be purified. The same happened for the higher substituted derivatives **21**, **25** and **26**. Connecting two corannulene bowls with a covalent bond failed, too. No product **32** could be isolated in the last step of the synthesis. While those two projects show great promises but none could provide the desired receptors. A third synthetic route based on Friedel-Crafts acylations finally yielded two corannulene bowls connected by a diketone spacer. These derivatives could be isolated and further studies were attempted.

These dicarbonyl derivatives were screened for their interactions with twelve possible guests in two different solvents. The most promising guests were C_{60} and C_{70} fullerenes. Thus, further studies were deployed with them. However, none of the NMR titrations yielded a significant value for the binding constant. In some cases it was not even possible to fit the data. A crystal structure of the carbon disulfide solvate of **43** and C_{60} helps to shed some light on the problem. The structure shows polymeric chains containing of hosts and guests with a stoichiometry of H_nG_n. One receptor molecule **43** complexes two different fullerenes while a corannulene bowl from a second receptor molecule binds to the opposite side of the Buckminsterfullerene. This alternating fullerene strands interact with each other forming corrugated sheets. The molecular structure of

the supramolecular complex of **43** and C_{60} as a toluene solvate is completely different than the previous one. The fullerenes show alternating layers of corrugated sheets and linear columns with an overall stoichiometry of the supramolecular complex of H_2G_3.

Keeping the behavior of the complexes in the solid state in mind, it seems reasonable to assume that the same polymeric like strands form in the liquid state. Those chains probably depend on the concentrations of both guest and host. However, said concentration changes in the course of a titration. Thus changing the composition of the strands. So far it was impossible to assign a defined stoichiometry because it shifts during the titration. Thus, no values for the binding constants could be obtained because they depend on the stoichiometry of the complex.

9. Zusammenfassung

Die vorliegende Arbeit beschäftigt sich mit Synthesemethoden, die es ermöglichen zwei Corannuleneinheiten zu verbinden, um flexible molekulare Zangen darzustellen. Drei unterschiedliche Corannulen-Linker wurden dafür untersucht. Ein System auf Basis einer Trifluorvinylgruppe **11** war erfolgslos, da sämtliche Isolierungsversuche fehlschlugen. Dieses Problem konnte auch bei den höheren Homologen **21**, **25** und **26** beobachtet werden. Die Corannulenschalen über eine kovalente Bindung zu verbrücken scheiterte ebenfalls, da das gewünschte Produkt **32**, nach dem letzten Syntheseschritt nicht mehr isoliert werden konnte. Beide Projekte haben großes Potential, führten aber nicht zu den gewünschten molekularen Zangen. Es gelang allerdings über eine Friedel-Crafts-Acylierung zwei Corannulene über Carbonylspacer erfolgreich miteinander zu verknüpfen und zu isolieren. Es wurden weitere Untersuchungen mit diesen Verbindungen durchgeführt.

Die Carbonylverbindungen wurden auf ihre Interaktionen mit zwölf unterschiedlichen Gästen in zwei verschiedenen Lösungsmitteln überprüft. Mit den zwei vielversprechendsten, C_{60} und C_{70}, wurden weitere Untersuchungen vorgenommen. Die durchgeführten NMR-Titrationen lieferten keine oder nicht sinnvolle Bindungskonstanten, da die in der Titration ermittelten Daten zum Großteil nicht gefittet werden konnten. Den entscheidenden Hinweis zur Lösung dieses Problems lieferte eine Kristallstruktur des supramolekularen Komplexes von **43** und C_{60}. Die Struktur zeigt, dass der supramolekulare Komplex im Festkörper polymere Ketten mit einer H_nG_n Stöchiometrie ausbildet. Ein Molekül des Rezeptors **43** komplexiert dabei zwei benachbarte Fullerenen. Zwei weitere Moleküle des Rezeptors **43** binden an den gegenüberliegenden Seiten der zwei Buckminsterfullerene. Diese alternierenden Stränge interagieren miteinander und lagern sich zu

gewellten Ebenen an. Das Packungsmuster im Falle eines Toluol Solvats von Derivat **43** und C_{60} unterscheidet sich hiervon gravierend. Die Fullerene bilden erneut gewellte Ebenen, jedoch alternieren diese mit linearen C_{60} Strängen. Die sich ergebene Stöchiometrie ist in diesem Fall H_2G_3.

Es liegt nahe, wenn man das Verhalten im Festkörper betrachtet, dass sich auch in Lösung Ketten unterschiedlichster Länge bilden. Diese Gebilde sind höchst wahrscheinlich abhängig von der Konzentration des Gastes und des Wirtes. Die genaue Zusammensetzung der Ketten ändert sich also im Laufe der Titration, da sich auch die Konzentration des Gastes und Wirtes ändert. Die genaue Stöchiometrie, des supramolekularen Komplexes fluktuiert also in Lösung. Infolgedessen können auch keine Bindungskonstanten ermittelt werden, da diese von der Stoichiometrie abhängen.

10. Experimental Part

10.1. General

10.1.1. Techniques

All experiments dealing with moisture and air sensitive components were conducted using standard Schlenk conditions and argon atmosphere or were handled in an argon-filled *MBraun* glove box (*Labmaster SP/DP*).

10.1.2. Chemicals

Anhydrous THF and diethylether were freshly distilled from potassium/benzophenone ketyl prior to use. Dichloromethane, 1,1,1,3,3-pentafluorobutane and nitromethane were distilled over phosphorous pentoxide. All anhydrous solvents were stored in Young or Normag flasks.

2,4,5,6-Tetrafluoroisophthalic acid, 5-chloroxylene, C_{60}, C_{70}, NIS and gold(III) chloride were purchased from *ABCR*. *n*-Butyllithium was bought from *ACROS ORGANICS* and stored in a Schlenk flask at 4 °C. DDQ, palladium(II) acetate, triptycene, triphenylene and NBS were ordered from *Alfa Aesar*. Common deuterated solvents (toluene-d_8, chloroform-d, THF-d_8, deuterium oxide, DMSO-d_6) were ordered from *eurisotop.* DMF (HPLC grade), 2,3,4,5,6-pentamethylbenzene, 5-bromoisophathalic acid, 2,3,4,5,6-pentafluoro benzoic acid, bromoform-d, aluminum(III) chloride, isophthalic-carboxy-$^{13}C_2$ acid, hexamethylbenzene, perylene, tetracene, AIBN, triethylamine, ammonium formiate, 3-picoline, bromoform-d, C_{70}, carbon disulfide (spectroscopy grade) were

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purchased from *Sigma Aldrich* and THF (HPLC grade), methanol (HPLC grade), dichloromethane (HPLC grade), pentane (HPLC grade), thionyl chloride, chlorobenzene from *VWR*. The used benzoyl chloride, thionyl chloride, formic acid and palladium on carbon were bought from *Merck*. 134a and 1,1,1,3,3-pentafluorobutane were donated by *Solvay*.

Solid anhydrous chemicals were stored in an argon-filled *MBraun* glove box (*Labmaster SP/DP*).

Bought and synthesized acid dichlorides and benzoyl chlorides were sublimated/distillated before use. Solid acid chlorides were stored at -40 °C in the argon-filled *MBraun* glove box (*Labmaster SP/DP*). Liquid acid chlorides were kept at -30 °C under air.

Corannulene **1** [14], 2-methylisophthalic acid[75], 5-fluoroisophthalic acid[10], 5-methylisophthalic acid[10], (1,3-phenylene)bis(corannulene-1-ylmethanone) **43** [10], (5-fluoro-1,3-phenylene)bis-(corannulene-1-ylmethanone) **56** [10], (5-methyl-1,3-phenylene)bis-(corannulene-1-yl-methanone) **54** [10], nitrocorannulene **16** [62], trifluorovinyl zincchloride **17** [63], [Pd(S-Phos)$_2$Cl$_2$][76], 1,6,7,10-tetramethyl-8,9-bis(trifluoromethyl)fluoranthene **18** [25b], 1,6,7,10-tetramethyl-8-(4-(tri-fluoromethyl)phenyl)-9-((4-(trifluoromethyl)phenyl)ethynyl)fluoranthene **30** [77] and monoiodo-corannulene **14** [78] were synthesized according to literature procedures. Nitrocorannulene **16** was additionally precipitated from a dichloromethane and pentane mixture.

10.1.3. Instrumentation

The ^{1}H, ^{19}F and ^{13}C NMR spectra were measured on a *Jeol ECS 400* (400-MHz) and *Bruker AVANCE III 700* (700-MHz) if not stated otherwise at 298 K. The residual solvent peak was used as an internal standard (^{1}H NMR: CDCl$_3$ 7.26 ppm, CDCl$_2$ 5.32 ppm, d^8-toluene 2.09 ppm, d^6-DMSO 2.50 ppm, D$_2$O 4.79 ppm; ^{13}C NMR: CDCl$_3$ 77.16 ppm; always proton decoupled). Chemical shifts are reported in ppm relative to TMS. IR spectra were measured on a *Nicolet iS10* FTIR spectrometer (signals were denoted as followed: s (strong), m (medium) and w (weak)). EI mass spectra were recorded on a *MAT 711 (EI, 80 eV, 3 kV)* the given temperature is noted next to each sample. High resolution spectra were determined by peak match method against perfluorokerosene. ESI mass spectra were measured on an *Agilent 6210* from a dichloromethane methanol mixture. Melting points were measured on a *MPM-H2* and are not corrected. UV-Vis spectra were measured on a *Cary 100 UV-Vis* from *Agilent Technologies*. Single-crystal X-ray crystallographic analysis were performed on a *Bruker Photon CMOS Detector, D8 Venture*. The reduction and empirical absorption correction were performed using the *APEX2*, *SAINT* and *SADABS*[79] programs respectively. The *SHELX* program[80] was used for the structure solution and refinement.

MERCURY[81] and *ORTEP*[82] were used for the visualization of the structures and images were created using *POVray*[83]. Thermal-motion probability ellipsoids were set to 50 % for all structures. Additional supplementary crystallographic data for each of the synthesized compounds is available on the attached DVD in cif-format. TLC, preparative TLC and column chromatography were performed using *Merk Silica gel 60 F$_{254}$*.

10.2. X-ray crystallographic tables:

Table 10.1.: X-ray crystallographic details for the compounds **22**, **30** and **36**.

Compound reference	**22**	**30**	**36**
Chemical formula	$C_{21}H_{17}F_3$	$C_{54}H_{40}F_6$	$C_{22}H_{20}O_2$
Formula Mass	326.36	802.86	316.38
Crystal system	monoclinic	monoclinic	monoclinic
a/Å	21.1643(12)	8.1279(3)	7.1861(7)
b/Å	11.9365(6)	12.3664(5)	21.436(2)
c/Å	12.8317(8)	20.6724(10)	10.6453(11)
α/°	90	90.1657(17)	90
β/°	106.5350(19)	97.9580(16)	93.620(4)
γ/°	90	107.0957(15)	90
Unit cell volume/ Å^3	3107.6(3)	1964.82(14)	1636.5(3)
Temperature/K	100	100(2)	100(2)
Space group	*P2$_1$/c*	*P2$_1$/c*	P2$_1$/n
Z	8	2	4
No. of reflections measured	23923	53806	17821
No. of independent reflections	5485	12013	2886
R$_{int}$	0.0588	0.0573	0.0783
Final *R$_1$* values (I > 2σ(I))	0.0567	0.0547	0.0947
Final *wR(F^2)* values (I > 2σ(I))	0.1301	0.1112	0.2383
Final *R$_1$* values (all data)	0.0929	0.0946	0.1224
Final *wR(F^2)* values (all data)	0.1460	0.1259	0.2591
Goodness of fit on F^2	1.018	1.022	1.059

Table 10.2: X-ray crystallographic details for the compounds **33** and **43**.

Compound reference	**33**	**43**· CDCl$_3$	**43**· toluene-d8
Chemical formula	C$_{27}$H$_{14}$O	C$_{49}$H$_{23}$Cl$_3$O$_2$	C$_{55}$H$_{30}$O$_2$
Formula Mass	354.38	750.02	722.79
Crystal system	monoclinic	orthorhombic	orthorhombic
a/Å	9.3820(11)	19.4531(8)	19.7658(9)
b/Å	9.3002(13)	23.6467(10)	23.8459(9)
c/Å	9.9346(14)	7.1514(3)	7.1894(3)
α/°	90	90	90
β/°	103.227(4)	90	90
γ/°	90	90	90
Unit cell volume/ Å^3	843.84(19)	3289.7(2)	3388.6(2)
Temperature/K	102(2)	100(2)	100(2)
Space group	*P2$_1$*	*Pna2$_1$*	*Pna2$_1$*
Z	2	4	4
No. of reflections measured	14153	27554	28033
No. of independent reflections	2969	5497	6632
R$_{int}$	0.0804	0.0857	0.0441
Final *R$_1$* values (I > 2σ(I))	0.0650	0.0602	0.0424
Final *wR(F^2)* values (I > 2σ(I))	0.1465	0.1404	0.0938
Final *R$_1$* values (all data)	0.0761	0.0818	0.0496
Final *wR(F^2)* values (all data)	0.1525	0.1528	0.0975
Goodness of fit on F^2	0.1525	1.023	1.031

Table 10.3: X-ray crystallographic details for the compounds **74**, **45** and **77**.

Compound reference	75	45	78
Chemical formula	$C_{31}H_{36}O_2$	$C_{30}H_{34}O_2$	$C_{32}H_{38}O_2$
Formula Mass	440.60	426.57	454.62
Crystal system	monoclinic	monoclinic	monoclinic
a/Å	6.0457(2)	15.5579(12)	34.049(3)
b/Å	34.4303(12)	8.3048(6)	8.9991(7)
c/Å	11.7135(5)	18.0133(11)	8.4662(5)
α/°	90	90	90
β/°	95.2270(10)	93.242(3)	96.103(2)
γ/°	90	90	90
Unit cell volume/ Å3	2428.09(16)	2323.7(3)	2579.5(3)
Temperature/K	100(2)	100(2)	100(2)
Space group	$P2_1/n$	$C2/c$	$C2/c$
Z	4	4	4
No. of reflections measured	26162	24887	22764
No. of independent reflections	4986	2687	2984
Rint	0.0366	0.0599	0.0773
Final R1 values (I > 2σ(I))	0.0484	0.0501	0.0504
Final wR(F2) values (I > 2σ(I))	0.1189	0.1332	0.1166
Final R1 values (all data)	0.0591	0.0656	0.0714
Final wR(F2) values (all data)	0.1248	0.1432	0.1281
Goodness of fit on F2	1.079	1.085	1.029

Table 10.4: X-ray crystallographic details for the compounds $33 \cdot C_{60}$, $43 \cdot C_{60}$ (CS_2) and $43 \cdot C_{60}$ (toluene-d8).

Compound reference	$33 \cdot C_{60}$	$43 \cdot C_{60}$ (CS_2)	$43 \cdot C_{60}$ (toluene-d8)
Chemical formula	$C_{114}H_{28}O_2$	$C_{108}H_{22}O_2 \cdot C_2S_5$	$C_{152}H_{38}O_2$
Formula Mass	1429.36	1541.58	1895.82
Crystal system	monoclinic	monoclinic	triclinic
a/Å	32.253(3)	10.1640(5)	10.1565(7)
b/Å	10.2544(10)	32.0614(16)	16.2861(12)
c/Å	19.2526(19)	19.3948(10)	24.8463(18)
α/°	90	90	88.420(3)
β/°	109.936(3)	99.647(2)	84.283(3)
γ/°	90	90	78.256(2)
Unit cell volume/ Å^3	5985.9(10)	6230.8(5)	4003.7(5)
Temperature/K	100(2)	100(2)	100(2)
Space group	*C2/c*	P2$_1$/c	P-1
Z	4	4	2
No. of reflections measured	59069	53616	41800
No. of independent reflections	59069	14274	9077
R_{int}	"Twin-refinement"	0.0484	0.0798
Final R_1 values (I > 2σ(I))	0.0865	0.1101	0.0662
Final $wR(F^2)$ values (I > 2σ(I))	0.1213	0.2743	0.1537
Final R_1 values (all data)	0.1997	0.1350	0.1253
Final $wR(F^2)$ values (all data)	0.2180	0.2915	0.1756
Goodness of fit on F^2	1.037	1.082	1.000

10.3. NMR screening

General procedure

A stock solution (1,3-phenylene)bis(corannulene-1-ylmethanone) in toluene-d_8/CDCl$_3$ with a concentration of 1.3213 mmol/L was prepared. 0.6 mL of this solution was added to a NMR tube and a ^{1}H NMR spectrum (32 scans, 32768 xpoints) and in case of a fluorinated guest a ^{19}F NMR spectrum (with standard) or a ^{13}C labeled host a ^{13}C NMR spectrum was measured. Afterwards 5 eqv. of the guest were added and the sample kept for an hour at room temperature till a second NMR spectrum was measured. The temperature during the measurement of the NMR spectra was set to 25 °C.

Table 10.5: Initial weight and solvent volume of the stocksolutions.

Compound	Solvent	Weight	Volume
(1,3-Phenylene)bis(corannulene-1-ylmethanone) **43**	Toluene	5.0 mg	6.0 mL
	Chloroform	7.7 mg	9.2 mL
(1,3-Phenylene carboxy-^{13}C$_2$)-bis(corannulene-1-ylmethanone) **50**	Toluene	6.3 mg	7.5 mL
	Chloroform	6.0 mg	7.2 mL
(5-Chloro-1,3-phenylene)bis-(corannulene-1-ylmethanone) **57**	Toluene	7.2 mg	8.2 mL
	Chloroform	6.6 mg	7.5 mL
(5-*Tert*-1,3-phenylene)bis-(corannulene-1-ylmethanone) **55**	Toluene	7.9 mg	8.7 mL
	Chloroform	6.5 mg	7.2 mL
(5-Methyl-1,3-phenylene)bis-(corannulene-1-ylmethanone) **54**	Toluene	8.9 mg	10.4 mL
	Chloroform	8.0 mg	9.4 mL
(2-Methyl-1,3-phenylene)bis-(corannulene-1-ylmethanone) **76**	Toluene	9.2 mg	10.8 mL
	Chloroform	6.6 mg	7.8 mL
(5-Fluoro-1,3-phenylene)bis-(corannulene-1-ylmethanone) **56**	Toluene	7.8 mg	9.1 mL
	Chloroform	6.2 mg	7.2 mL
(5-Bromo-1,3-phenylene)bis-(corannulene-1-ylmethanone) **58**	Toluene	7.3 mg	7.8 mL
	Chloroform	12.3 mg	13.1 mL
2,2'-(1,3-Phenylene)bis((corannulene-1-yl)ethanone) **79**	Toluene	6.8 mg	7.8 mL
	Chloroform	5.7 mg	6.5 mL
1,3-Bis(2-corannulene-1-yl)-1,3-dithian-2-yl)benzene **80**	Toluene	8.1 mg	7.6 mL
	Chloroform	7.8 mg	7.3 mL

The following molecules were screened as guests: toluene (0.4 µl), hexamethylbenzene (0.6 mg), naphthalene (0.5 mg), coronene (1.2 mg), corannulene **1** (1.0 mg), tetracene (0.9 mg), perylene (1.0 mg), pyrene (0.8 mg), triphenylene (0.9 mg), triptycene (1.0 mg), C_{60} (2.9 mg) and C_{70} (3.3 mg).

All guests were measured in both solvents as long as they were soluble. ^{19}F NMR standards were prepared using melting point capillary tubes filled with 1,1,1,3,3-pentafluorobutane and flame sealed.

10.4. Jobs Plot

For both C_{60} runs a stock solution of 1 mg (1,3-phenylene)bis(corannulene-1-ylmethanone) **43** in 4 mL toluene-d_8 and a stock solution of 1.1 mg C_{60} in 4 mL toluene-d_8 were prepared and kept in the ultrasonic bath for 10 min. For the C_{70} measurement a stock solution of 1 mg (1,3-phenylene)bis(corannulene-1-ylmethanone) **43** in 4 mL toluene-d_8 and a stock solution of 1.3 mg C_{70} in 4 mL toluene-d_8 was prepared and kept in the ultrasonic bath for 10 min. Afterwards ten NMR tubes were prepared for each run as stated in table 9.6 and kept in the ultrasonic bath for 10 min before measuring a ^1H NMR spectrum (32 scans, 32768 xpoints).

Table 10.6: Volume of the used host and guest solutions and the total volume of both.

V(Host) [ml]	V(Guest) [ml]	V(total) [ml]
0.60	0	0.60
0.54	0.06	0.60
0.48	0.12	0.60
0.42	0.18	0.60
0.36	0.24	0.60
0.30	0.30	0.60
0.24	0.36	0.60
0.18	0.42	0.60
0.12	0.48	0.60
0.06	0.54	0.60
0	0.60	0.60

The complete values and NMR shifts of the signals are available on the attached DVD.

10.5. NMR titration

Standards for the NMR titration were prepared from a Pasteur pipette or a melting point capillary tube. In case of the Pasteur pipette the tip was flame sealed, the deuterated solvent was added and then flame sealed. The capillary tubes were first filled with the standard, then frozen in liquid nitrogen and in the end flame sealed.

Lists of the observed chemical shifts, the concentrations and the superimposed NMR spectra can be found on the attached DVD.

10.5.1. C_{60}

A stock solution of the host molecule in 3 mL of toluene-d_8 was prepared using the amount of host stated below (table 9.7). For the C_{60} solution 15 mg of the fullerene was dissolved in 6.75 mL of toluene-d_8. The host and the fullerene solution were kept for 10 min in an ultrasonic bath before 0.6 mL of the host stock solution was transferred into NMR tubes and a ^{1}H NMR spectrum (32 scans, 32768 xpoints) of each was measured. Afterwards small amounts of the guest solution were added (0.02 mL, 0.02 mL, 0.02 mL, 0.02 mL, 0.02 mL, 0.03 mL, 0.04 mL, 0.05 mL, 0.07 mL, 0.10 mL, 0.10 mL, 0.80 mL or 0.02 mL, 0.02 mL, 0.02 mL, 0.02 mL, 0.02 mL, 0.03 mL, 0.04 mL, 0.05 mL, 0.07 mL, 0.10 mL, 0.10 mL, 0.20 mL, 0.30 mL, 0.40 mL) and a ^{1}H NMR (32 scans, 32768 xpoints) measured after every addition. The temperature for each measurement was set to 25 °C. Every titration was repeated three times.

Table 10.7: Initial weight of the receptors.

Compound	Weight
(5-Methyl-1,3-phenylene)bis-(corannulene-1-ylmethanone) **54**	2.7 mg
(5-*Tert*-1,3-phenylene)bis-(corannulene-1-ylmethanone) **55**	3.5 mg
(1,3-Phenylene)bis(corannulene-1-ylmethanone) **43**	1.2 mg
(1,3-Phenylene)bis(corannulene-1-ylmethanone) **43**	3.0 mg
(2-Methyl-1,3-phenylene)bis-(corannulene-1-ylmethanone) **76**	3.8 mg

In case of carbon disulfide samples containing 2 % of TMS, a stock solution of the solvent and standard was prepared and used to dissolve the C_{60} fullerene (15 mg) and the receptor **43** (2.3 mg). The titration was done according to the protocol described above.

10.5.2. C_{70}

A stock solution of the host molecule in 3 mL of toluene-d_8 was prepared using the amount of host stated below (table 9.8). For the C_{70} solution 8.8 mg of the fullerene was dissolved in 6.75 mL of toluene-d_8. The host and the fullerene solution were kept for 10 min in an ultrasonic bath before 0.6 mL of the host stock solution was transferred into NMR tubes and a ^{1}H NMR spectrum (32 scans, 32768 xpoints) of each was measured. Afterwards small amounts of the guest solution were added (0.02 mL, 0.02 mL, 0.02 mL, 0.02 mL, 0.02 mL, 0.03 mL, 0.04 mL, 0.05 mL, 0.07 mL, 0.10 mL, 0.10 mL, 0.80 mL) and a ^{1}H NMR spectrum measured after every addition. The temperature for each measurement was set to 25 °C. Every titration was repeated three times.

Table 10.8: Initial weight of the receptors.

Compound	Weight
(1,3-Phenylene)bis(corannulene-1-ylmethanone) **43**	2.5 mg
(2-Methyl-1,3-phenylene)bis-(corannulene-1-ylmethanone) **76**	3.8 mg

10.6. Preparation:

10.6.1. Corannulene (1) synthesis

General procedure for the purifying of corannulene 1

The mixture of corannulene **1** and hydrogenated corannulenes was dissolved in dichloromethane and DDQ was added in excess. The dark green suspension was stirred overnight at rt and then quenched with a saturated sodium bicarbonate solution. The organic phase was separated and washed with bicarbonate solution, brine and water. The organic phase was dried over anhydrous sodium sulfate. The suspension was then filtered and the solvent of the filtrate evaporated in vacuum. The solid residue was purified by flash column chromatography on silica gel using *n*-pentane. Pure corannulene **1** could be obtained as pale yellow crystals.

10.6.2. Trifluorovinyl corannulenes

10.6.2.1. 1-(1,2,2-Trifluorovinyl)corannulene (11)
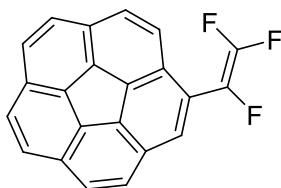
11

A flame-dried Schlenk flask was charged with monoiodocorannulene **14** (76.3 mg, 0.2034 mmol, 1 eqv), triphenylphosphine (21.0 mg, 0.0814 mmol, 40 mol%), palladium acetate (5 mg, 0.0203 mmol, 10 mol%) and trifluorovinylzinc chloride **17** in THF (0.2 M, 4.2 mL, 1.0170 mmol, 5 eqv). The mixture was stirred and heated to 70 °C for 5 h and afterwards diluted with *n*-pentane and filtered over celite. The residue in the flask was dissolved in dichloromethane and also filtered over celite. Both solutions were combined, the solvents evaporated by blowing a stream of Argon over the surface. The residue was purified by column chromatography using silica gel and *n*-pentane.

No product could be isolated.

10.6.2.2. Attempted synthesis of aminocorannulene (15)
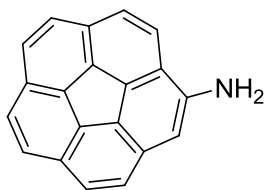
15

 Formic acid procedure:

A flask was charged with nitrocorannulene **16** (56 mg, 0.1693 mmol, 1 eqv), formic acid (78 mg, 0.06 mL, 1.693 mmol, 10 eqv.), triethylamine (171 mg, 0.24 mL, 1.683 mmol, 10 eqv.), 2 mg Pd/C and 0.4 mL 3-piccoline. The mixture was stirred at 135 °C for a day. After cooling to rt the mixture was filtered and the solvent of the filtrate was removed in HV. A ^{1}H NMR spetrum of the remaining solid showed pristine corannulene **1** as the main product.

Ammonium formate procedure:

Nitrocorannulene **16** (50 mg, 0.1693 mmol, 1 eqv.), ammonium formate (160 mg, 2.5399 mmol, 15 eqv), methanol (7 mL) and 3 mg palladium on carbon were placed into a flask and refluxed for 20 h. Afterwards the mixture was filtered and the solvent of the filtrate evaporated in vacuum. A ^{1}H NMR spectrum of the residue showed nitrocorannulene **16** as the main compound.

10.6.2.3. 1,2-Bis(trifluoromethyl)-4,9-bis(1,2,2-trifluorovinyl)-corannulene (21)
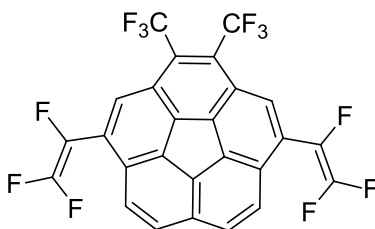
21

NMR reaction:

A flame-dried Young tube was charged with 4,9-dibromo-1,2-(trifluoromethyl)corannulene **20** (5 mg, 0.0092 mmol, 1 eqv), triphenylphosphine (4 mg, 0.0038 mmol, 40 mol%), palladium(II)

acetate (0.2 mg, 0.0009 mmol, 10 mol%), 0.2 M trifluorovinylzinc chloride solution **17** (20 mg, 460 µL, 0.1103 mmol, 12 eqv) and 0.24 mL abs. THF. The black suspension was heated to 70 °C. A ^{19}F NMR spectrum was measured at the start of the reaction and after 25 min, 30 min, 1 h, 90 min, 2 h, 150 min, 3 h, 4 h, 5 h, 6 h and 3 d.

Synthesis:

A flame-dried Young flask was charged with 4,9-dibromo-1,2-(trifluoromethyl)corannulene **20** (30 mg, 0.0551 mmol, 1.0 eqv), triphenylphosphine (6 mg, 0.0216 mmol, 40 mol%), palladium(II) acetate (1 mg, 0.0054 mmol, 10 mol%) and 0.2 M trifluorovinylzinc chloride **17** solution (241 mg, 5.5 mL, 1.3233 mmol, 24 eqv). The mixture was stirred and heated to 70 °C for 5 h and afterwards the suspension diluted with *n*-pentane and filtered over celite. The residue, which remained in the flask, was dissolved in dichloromethane and also filtered over celite. Both solutions were combined and the solvents evaporated by blowing a stream of Argon over the surface.

No product could be isolated.

10.6.2.4. 1,6,7,10-Tetramethyl-8-(trifluoromethyl)fluoranthene (22)
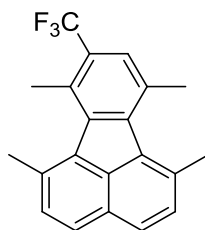
22

A flask was charged with 68 mL methanol and potassium hydroxide (27.5 g, 0.4922 mol, 23 eqv) was added portion wise. The solution was headed to 80 °C for 10 min and afterwards allowed to slowly cool to rt. 3-pentanone (18 mL, 14.5 g, 0.1713 mol, 8 eqv) and 2,7-dimethylnaphthenquinone **4a** (4.5 g, 0.0214 mol, 1 eqv) were added portion wise to the cooled solution. The mixture was allowed to stir at rt for 2 h and then cooled to 0 °C. A cooled solution of conc. hydrochlorid acid (58 g) in water (116.5 g) was added dropwise to the reaction mixture. Once the suspension turned green yellow it was extracted two times with 100 ml of dichloromethane. The combined organic fractions were washed with 100 ml water. Afterwards the organic layer was dried over anhydrous sodium sulfate, filtered and the solvent of the filtrate was evaporated in

vacuum. The residue was dissolved in 52 ml acetic anhydride and degassed trifluoropropyne (9 g, 0.0963 mol, 2 eqv)) was condensed into the flask. The mixture was allowed to slowly warm to rt and was then heated to 80 °C for 7 d. The overpressure was slowly released and the solvent evaporated in high vacuum. The resulting viscose liquid was purified by column chromatography using silica gel and *n*-pentane. The product could be isolated as pale yellow crystals (1.62 g, 0.4977 mmol, 23 %).

^{1}H NMR (700 MHz, CDCl$_3$): δ = 2.78 (s, 3 H, H$_{Me}$), 2.77 (s, 3 H, H$_{Me}$), 2.83 (s, 3 H, H$_{Me}$), 2.84 (s, 3 H, H$_{Me}$), 7.36 (d, ^3J = 8.2 Hz, 1 H, H$_{Ar}$), 7.38 (d, ^3J = 8.2 Hz, 1 H, H$_{Ar}$), 7.71 (d, ^3J = 8.2 Hz, 1 H, H$_{Ar}$), 7.71 (d, ^3J = 8.2 Hz, 1 H, H$_{Ar}$) ppm. **^{19}F NMR** (376 MHz, CDCl$_3$): δ = 59.53 (s, 3 F) ppm. **^{13}C{^{1}H} NMR** (176 MHz, CDCl$_3$): δ = 19.8 (s, C$_{Me}$), 24.1 (s, C$_{Me}$), 24.8 (s, C$_{Me}$), 24.8 (s, C$_{Me}$), 125.4 (q, ^1J = 272.3 Hz, C$_{Ar}$), 126.6 (s, C$_{Ar}$), 126.6 (s, C$_{Ar}$), 127.0 (s, C$_{Ar}$), 127.8 (s, C$_{Ar}$), 128.2 (q, ^1J = 28.6 Hz, C$_{Ar}$), 128.3 (q, ^3J = 5.6 Hz, C$_{Ar}$), 129.0 (s, C$_{Ar}$), 131.6 (s, C$_{Ar}$), 131.8 (s, C$_{Ar}$), 132.7 (s, C$_{Ar}$), 133.1 (s, C$_{Ar}$), 133.2 (s, C$_{Ar}$), 133.9 (s, C$_{Ar}$), 134.0 (s, C$_{Ar}$), 142.0 (s, C$_{Ar}$), 142.6 (s, C$_{Ar}$) ppm. **^{13}C{^{1}H, ^{19}F} NMR** (176 MHz, CDCl$_3$): δ = 19.9 (s, C$_{Me}$), 24.4 (s, C$_{Me}$), 25.0 (s, C$_{Me}$), 25.2 (s, C$_{Me}$), 125.4 (s, C$_{Ar}$), 126.8 (s, C$_{Ar}$), 126.9 (s, C$_{Ar}$), 127.3 (s, C$_{Ar}$), 128.2 (s, C$_{Ar}$), 128.3 (s, C$_{Ar}$), 128.6 (s, C$_{Ar}$), 129.3 (s, C$_{Ar}$), 132.0 (s, C$_{Ar}$), 132.1 (s, C$_{Ar}$), 133.1 (s, C$_{Ar}$), 133.4 (s, C$_{Ar}$), 133.6 (s, C$_{Ar}$), 134.3 (s, C$_{Ar}$), 134.3 (s, C$_{Ar}$), 142.2 (s, C$_{Ar}$), 142.8 (s, C$_{Ar}$) ppm. **MS** (EI, 40 °C): m/z = 326.1 (100 %, [C$_{21}$H$_{17}$F$_3$]$^{\cdot+}$), 311.1 (77 %, [C$_{20}$H$_{14}$F$_3$]$^+$), 257.1 (12 %, [C$_{20}$H$_{17}$]$^+$). **IR**: ν = 3043 (w), 2953 (w), 2921 (w), 2863 (w), 1894 (w), 1613 (w), 1595 (w), 1505 (m), 1463 (m), 1440 (m), 1414 (m), 1397 (w), 1363 (m), 1350 (m), 1307 (m), 1283 (s), 1207 (s), 1190 (m), 1162 (m), 1143 (s), 1103 (s), 1049 (m), 1027 (m), 974 (m), 886 (m), 870 (w), 834 (s), 821 (m), 795 (m), 718 (m), 698 (w), 673 (w), 641 (m), 627 (m), 613 (w), 545 (m) cm^{-1}. **Mp**: 69.9-71.4 °C

10.2.6.5. 1,2,6-Tribromo-4-(trifluoromethyl)corannulene (24)
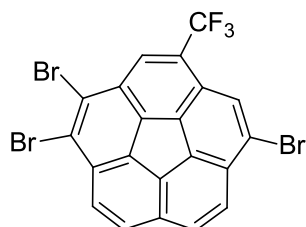
24

A round bottom flask was charged with 1,6,7,10-tetramethyl-8-(trifluoromethyl)fluor-anthene **22** (500 mg, 1.5321 mmol, 1 eqv), NBS (3.3 g, 18.385 mmol, 12 eqv), a spatula tip of AIBN and 8 mL chlorobenzene. The mixture was headed to 90 °C and stirred for 20 h while irradiated with a 150W sunlight lamp. Afterwards the volatile compounds were removed in HV, the residue diluted with

100 mL of dichloromethane and extracted three times with 300 mL of water. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent removed in HV. The reddish brown residue was dissolved in 61 mL 1,4-dioxane and heated to 100 °C and a solution of 0.7 g sodium hydroxide (18.487 mmol, 10 eq.) in 23 mL water was added. The mixture was heated to 110 °C for 30 min, then 23 mL of water was added and the suspension slowly cooled to rt. The product mixture was neutralized with conc. hydrochloric acid and afterwards filtered. The solid was washed with water and dried overnight at rt. The product could be isolated as a brown solid (0.27 g, 0.49 mmol, 26 %).

The solid is not soluble in common organic solvents making it impossible to obtain any NMR data. **IR**: v = 3049 (w), 1900 (w), 1772 (w), 1724 (w), 1613 (m), 1471 (w), 1411 (w), 1394 (m), 1343 (m), 1308 (s), 1277 (s), 1262 (s), 1219 (m), 1200 (m), 1155 (s), 1110 (s), 1078 (m), 1062 (s), 983 (s), 862 (m), 847 (m), 824 (s), 799 (w), 791 (m), 778 (m), 746 (s), 722 (w), 710 (m), 650 (w), 636 (w), 622 (w), 606 (w), 592 (w), 566 (w), 531 (m) cm^{-1}. **Mp**: > 225.0 °C.

10.6.2.6. 4-(Trifluoromethyl)-1,2,6-tris(1,2,2-trifluorovinyl)corannulene (25)
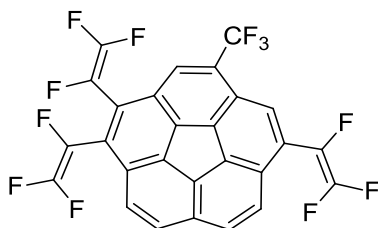
25

A flame-dried Young flask was charged with 1,2,6-tribromo-4-(trifluoromethyl)corannulene **24** (30 mg, 0.0541 mmol, 1.0 eqv), triphenylphosphine (6 mg, 0.0216 mmol, 40 mol%), palladium(II) acetate (1 mg, 0.0054 mmol, 10 mol%) and 0.2 M trifluorovinylzinc chloride **17** solution (230 mg, 5.4 mL, 1.2973 mmol, 24 eqv). The mixture was stirred and heated to 70 °C for 5 h and afterwards the suspension diluted with *n*-pentane and filtered over celite. The residue, which remained in the flask, was dissolved in dichloromethane and also filtered over celite. Both solutions were combined and the solvents were evaporated by blowing a stream of Argon over the surface.

No product could be isolated.

10.6.2.7. 1,2,5,6-Tetrakis(1,2,2-trifluorovinyl)corannulene (26)
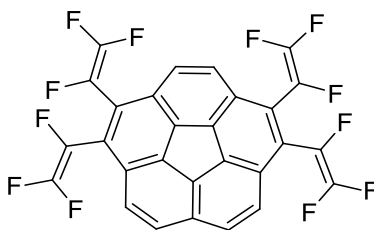
26

A flame-dried Young flask was charged with 1,2,5,6-tetrabromocorannulene **9** (30 mg, 0.0530 mmol, 1 eqv), triphenylphosphine (6 mg, 0.0212 mmol, 40 mol%), palladium(II) acetate (0.5 mg, 0.0021 mmol, 10 mol%) and trifluorovinylzinc chloride **17** (231 mg, 5.3 mL, 1.2724 mmol, 24 eqv). The mixture was stirred and heated to 70 °C for 5 h and afterwards the suspension diluted with *n*-pentane and filtered over celite. The residue, which remained in the flask, was dissolved in dichloromethane and also filtered over celite. Both solutions were combined and the solvents were evaporated by blowing a stream of Argon over the surface.

No product could be isolated.

10.6.3. Biscorannulenyls

10.6.3.1. 1,1',6,6'7,7',10,10'-Octamethyl-9,9'-bis(4-(trifluoromethyl)-phenyl)-8,8'-bifluoroanthene (30)
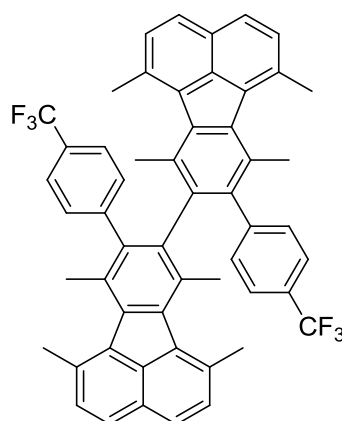
30

A flask was charged with 43 mL methanol and potassium hydroxide (18.60 g, 332 mmol, 23 eqv) was added portion wise. After cooling the solution to rt 3-pentanone (9.67 g, 11.93 mL, 112 mmol,

7.8 eqv) and 3,8-dimethylacenaphthene quinone **4a** (3.02 g, 14.4 mmol, 1.0 eqv) were added. The mixture was stirred at rt for 2 h and then cooled to 0 °C. Cold hydrochloride acid was added to the reaction mixture until the color changed to a green yellow and the pH value was 6. The mixture was warmed to rt and extracted three times with 70 mL of dichloromethane. The organic phases were combined and dried over sodium sulfate. The suspension was filtered and the solvent of the filtrate evaporated in vacuum. A Schlenk tube was charged with the intermediate (834 mg, 2.996 mmol, 5.9 eqv), 1,4-bis[4-(trifluoromethyl)phenyl]buta-1,3-diine **28** (170.0 mg, 0.502 mmol, 1.0 eqv) and 6.0 mL acetic anhydride. The mixture was headed to 140 °C for 6 d and afterwards cooled to rt. Volatile residues were removed in high vacuum. The solid residue was purified using silica gel and *n*-pentane:dichloromethane (2:1). The product could be isolated as a yellow crystalline solid (0.18 g, 0.23 mmol, 8 %).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.24 (s, 6 H, H$_{Me}$), 2.67 (s, 6 H, H$_{Me}$), 2.79 (s, 6 H, H$_{Me}$), 2.82 (s, 6 H, H$_{Me}$), 7.40 (AB, d, ^3J = 8.3 Hz, 2 H, H$_{Ar}$), 7.43 (AB, d, ^3J = 8.2 Hz, 2 H, H$_{Ar}$), 7.73 (AB, d, ^3J = 8.2 Hz, 2 H, H$_{Ar}$), 7.75 (AB, d, ^3J = 8.2 Hz, 2 H, H$_{Ar}$) ppm. **^{19}F NMR** (376 MHz, CDCl$_3$): δ = -62.27 (s, 6 F) ppm. **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 16.1 (s, C$_{Me}$), 16.8 (s, C$_{Me}$), 17.4 (s, C$_{Me}$), 52.4 (s, C$_{CH2}$), 127.6 (s, C$_{Ar}$), 128.7 (s, C$_{Ar}$), 128.8 (s, C$_{Ar}$), 131.6 (s, C$_{Ar}$), 133.2 (s, C$_{Ar}$), 133.2 (s, C$_{Ar}$), 133.7 (s, C$_{Ar}$), 135.7 (s, C$_{Ar}$), 140.3 (s, C$_{Ar}$), 208.8 (s, C=O) ppm. **MS** (EI, 40 °C): *m/z* 802.3065 (found), 802.3034 (calc'd), 802.3 (100 %, [C$_{54}$H$_{40}$F$_6$]$^{.+}$), 787.2 (12 %, [C$_{53}$H$_{37}$F$_6$]$^{.+}$), 772.3 (17 %, [C$_{52}$H$_{34}$F$_6$]$^{.+}$), 757.3 (23 %, [C$_{51}$H$_{31}$F$_6$]$^{.+}$), 401.2 (14 %, [C$_{27}$H$_{20}$F$_3$]$^{.+}$), 393.7 (12 %, [C$_{53}$H$_{37}$F$_6$]$^{-2+}$), 386.4 (12 %, [C$_{26}$H$_{17}$F$_3$]$^{.+}$), 378.6 (13 %, [C$_{51}$H$_{31}$F$_6$]$^{.2+}$), 371.3 (14 %, [C$_{25}$H$_{14}$F$_3$]$^{.+}$). No IR spectra or melting point was determined because of the contamination of the product with 1,6,7,10-tetramethyl-8,9-bis(trifluoro-methyl)fluoranthene **29**.

10.6.3.2. Attempted synthesis of 2,2'-bis(4-(trifluoromethyl)phenyl)-1,1'-bicorannuelene (32)
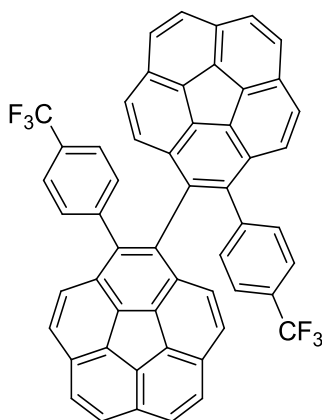
32

A round bottom flask was charged with 1,1',6,6'7,7',10,10'-octamethyl-9,9'-bis(4-(trifluoro-methyl)phenyl)-8,8'-bifluoroanthene **30** (235 mg, 0.2929 mmol, 1 eqv), NBS (1.3 g, 7.0306 mmol, 24 eqv), a spatula tip of AIBN and 15 mL chlorobenzene. The mixture was headed to 90 °C and stirred for 20 h while irradiated with a 150W sunlight lamp. Afterwards the solvent was evaporated in HV, the residue diluted with 50 mL of dichloromethane and then extracted three times with 200 mL of water. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent was removed in HV. The reddish brown residue was dissolved in 13 mL 1,4-dioxane and heated to 100 °C. A solution of 161 mg sodium hydroxide (4.0351 mmol, 20 eq.) in 5 mL water was added. The mixture was heated to 110 °C for 30 min, then 5 mL of water was added and the suspension slowly cooled to rt. The product mixture was neutralized with conc. hydrochloric acid and afterwards filtered. The solid was washed with water and dried overnight at rt. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent was removed in HV. A Young flask was charged with the 4,4',9,9'-tetrabromo-2,2'-bis(4-(trifluoromethyl)phenyl)-1,1'-bicorannulene **31** (370 mg, 0.3356 mmol, 1 eqv.), triethylamine (340 mg, 0.5 mL, 3.3565 mmol, 10 eqv.), formic acid (154 mg, 0.1 mL, 3.3565 mmol), 8 mg Pd/C and 2 mL piccoline. The reaction mixture was headed to 135 °C for 20 h and then cooled to rt. Afterwards the brown solution was filtered and the solvent of the filtrate evaporated in HV. The solid residue was purified by column chromatography using silica gel and a mixture of *n*-pentane and dichloromethane. No product could be isolated.

10.6.4. Corannulene esters

10.6.4.1. Methyl 1,6,7,10-tetramethylfluoranthene-8-carboxylate (36)
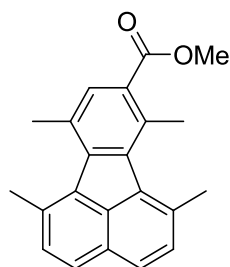
36

A flask was charged with 43 mL methanol and potassium hydroxide (18.6 g, 331.5 mmol, 23 eqv.) was added in portions to the solvent. The mixture was headed to reflux till all of the potassium hydroxide was dissolved. Afterwards the solution was cooled to rt and 3-pentanone (9.7 g, 11.9 mL, 112 mmol, 7.8 eqv.) and 3,8-dimethylacenaphthenequinone **4a** (3.0 g, 14.37 mmol, 1.0 eqv) were added. The brown mixture was stirred at rt for 2 h and afterwards cooled to 0 °C. Cold hydrochloride acid was added to the reaction till the color changed to a green yellow and the pH value was 6. The mixture was warmed to rt and extracted three times with 70 mL dichloromethane. The organic phases were combined and dried over sodium sulfate. The suspension was filtered and the solvent of the filtrate evaporated in vacuum. A schlenk flask was charged with the yellow residue **6** (1.00 g, 3.593 mmol, 1.0 eqv), methyl propiolate (1.8 g, 1.76 mL, 21.56 mmol, 6.0 eqv.) and 7.3 mL acetic anhydride. The mixture was headed to 120 °C for 6 d. Afterwards the reaction was cooled to rt and the solvent was evaporated in HV. The solid residue was purified using silica gel and n-pentane:dichloromethane (2:1). The product mixture after column chromatography was melted in HV at 80 °C till the gas evolution stopped. The product was obtained as a pale yellow solid (0.92 g, 2.91 mmol, 81 %).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.77 (s, 3 H, H$_{Me}$), 2.79 (s, 3 H, H$_{Me}$), 2.84 (s, 3 H, H$_{Me}$), 2.88 (s, 3 H, H$_{Me}$), 3.95 (s, 3 H, H$_{COOMe}$), 7.39 (AB, d, ^3J = 8.2 Hz, 1 H, H$_{Ar}$), 7.40 (AB, d, ^3J = 8.2 Hz, 1 H, H$_{Ar}$), 7.72 (AB, d, ^3J= 7.8 Hz, 1 H, H$_{Ar}$), 7.74 (AB, d, ^3J = 7.8 Hz, 1 H, H$_{Ar}$), 7.77 (s, 1 H, H$_{Ar}$) ppm. **^{13}C NMR** (176 MHz, CDCl$_3$): δ = 22.6 (s, C$_{Me}$), 24.3 (s, C$_{Me}$), 24.8 (s, C$_{Me}$), 25.1 (s, C$_{Me}$), 51.9 (s, C$_{OOMe}$), 126.5 (s, C$_{Ar}$), 126.6 (s, C$_{Ar}$), 127.2 (s, C$_{Ar}$), 129.1 (s, C$_{Ar}$), 129.5 (s, C$_{Ar}$), 131.6 (s, C$_{Ar}$), 131.8 (s, C$_{Ar}$), 131.9 (s, C$_{Ar}$), 132.9 (s, C$_{Ar}$), 133.2 (s, C$_{Ar}$), 133.3 (s, C$_{Ar}$), 133.7 (s, C$_{Ar}$), 134.1 (s, C$_{Ar}$), 134.5 (s, C$_{Ar}$), 141.9 (s, C$_{Ar}$), 143.0 (s, C$_{Ar}$), 168.6 (s, C$_{Carbonyl}$) ppm. **MS** (EI, 50 °C): m/z 316.1486 (found), 316.1463 (calc'd), 316.1 (100 %, [C$_{22}$H$_{20}$O$_2$]$^{\cdot +}$), 285.1 (11 %, [C$_{21}$H$_{17}$O]$^{\cdot +}$), 256.1 (26 %, [C$_{18}$H$_8$O$_2$]$^{\cdot +}$), 227.0 (11 %, [C$_{18}$H$_{11}$]$^{\cdot +}$). **IR**: v = 2996 (w), 2944 (w), 2851 (w), 1925 (w), 1707 (s,CO), 1609 (w), 1586 (w), 1556 (w), 1502 (m),

1461 (m), 1431 (s), 1414 (m), 1375 (m), 1296 (m), 1268 (s), 1243 (w), 1205 (s), 1189 (s), 1163 (m), 1149 (m), 1102 (w), 1063 (s), 1041 (m), 1005 (w), 966 (w), 888 (m), 834 (s), 840 (s), 821 (m), 789 (s), 783 (w), 766 (w), 752 (m), 696 (m), 674 (w), 660 (w), 629 (w), 584 (w), 534 (s) cm^{-1}. **Mp**: 85.5-89.0 °C.

## 10.4.6.2. Ethyl 1,6,7,10-tetramethylfluoranthene-8-carboxylate (37)
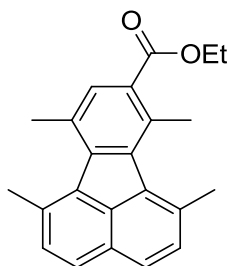
37

A flask was charged with 43 mL methanol and potassium hydroxide (18.6 g, 331.5 mmol, 23 eqv.) was added in portion to the solvent. The mixture was headed to reflux till all of the potassium hydroxide was dissolved. Afterwards the solution was cooled to rt and 3-pentanone (9.7 g, 11.9 mL, 112 mmol, 7.8 eqv.) and 3,8-dimethylacenaphthenequinone **4a** (3.0 g, 14.37 mmol, 1.0 eqv) were added. The brown mixture was stirred at rt for 2 h and afterwards cooled to 0 °C with an ice bad. Cold hydrochloride was added till the color changed to a yellow green and the pH to 6. The mixture was warmed to rt and extracted three times with 70 mL dichloromethane. The organic phases were combined and dried over sodium sulfate. The suspension was filtered and the solvent of the filtrate was evaporated in vacuum. A schlenk flask was charged with the yellow residue (1.00 g, 3.593 mmol, 1.0 eqv), ethyl propiolate (2.11 g, 2.12 mL, 21.56 mmol, 6.0 eqv.) and 7.3 mL acetic anhydride. The mixture was headed to 120 °C for 6 d. Afterwards the reaction was cooled to rt and the solvent evaporated in HV. The solid residue was purified using silica gel and *n*-pentane:dichloromethane (2:1). The product mixture after column chromatography was melted in HV at 80 °C till the gas evolution stopped. The product was obtained as a pale yellow crystalline solid (0.93 g, 2.80 mmol, 78 %).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.45 (t, ^3J = 7.1 Hz, 3 H, H$_{Me}$), 2.77 (s, 3 H, H$_{Me}$), 2.80 (s, 3 H, H$_{Me}$), 2.84 (s, 3 H, H$_{Me}$), 2.88 (s, 3 H, H$_{Me}$), 4.42 (q, ^3J = 7.14 Hz, 1 H, H$_{Ar}$), 7.39 (d, ^3J = 8.2 Hz, 1 H, H$_{Ar}$), 7.41 (d, ^3J= 8.3 Hz, 1 H, H$_{Ar}$), 7.72 (d, ^3J = 7.6 Hz, 1 H, H$_{Ar}$), 7.74 (d, ^3J = 7.8 Hz, 1 H, H$_{Ar}$), 7.76 (s, 1 H, H$_{Ar}$) ppm. **^{13}C NMR** (176 MHz, CDCl$_3$): δ = 14.6 (s, C$_{Me}$), 22.6 (s, C$_{Me}$), 24.3 (s, C$_{Me}$), 24.9 (s, C$_{Me}$), 25.2 (s, C$_{Me}$), 60.9 (s, C$_{Et}$), 126.5 (s, C$_{Ar}$), 126.6 (s, C$_{Ar}$), 127.2 (s, C$_{Ar}$), 129.2 (s, C$_{Ar}$), 130.2 (s, C$_{Ar}$), 131.4 (s,

C$_{Ar}$), 131.9 (s, C$_{Ar}$), 132.0 (s, C$_{Ar}$), 133.0 (s, C$_{Ar}$), 133.1 (s, C$_{Ar}$), 133.3 (s, C$_{Ar}$), 133.9 (s, C$_{Ar}$), 134.2 (s, C$_{Ar}$), 134.7 (s, C$_{Ar}$), 141.9 (s, C$_{Ar}$), 143.0 (s, C$_{Ar}$), 168.4 (s, C$_{Carbonyl}$) ppm. **MS** (EI, 70 °C): *m/z* 330.1608 (found), 330.1620 (calc'd), 330.2 (100 %, [C$_{23}$H$_{22}$O$_2$]$^{\cdot +}$), 301.4 (16 %, [C$_{21}$H$_{17}$O$_2$]$^{\cdot +}$), 256.9 (40 %, [C$_{20}$H$_{17}$O]$^{\cdot +}$), 255.9 (46 %, [C$_{19}$H$_{11}$O]$^{+}$), 241.1 (13 %, [C$_{17}$H$_5$O$_2$]$^{+}$). **IR**: ν = 3049 (w), 2974 (m), 2927 (w), 2863 (w), 1931 (w), 1699 (s,CO), 1609 (w), 1582 (w), 1556 (w), 1502 (m), 1457 (w), 1439 (m), 1427 (w), 1416 (w), 1374 (w), 1365 (m), 1295 (m), 1267 (s), 1243 (w), 1205 (s), 1189 (s), 1164 (m), 1149 (s), 1115 (w), 1062 (s), 1043 (m), 1034 (w), 997 (w), 950 (w), 895 (m), 870 (m), 838 (s), 824 (m), 786 (s), 770 (m), 758 (m), 693 (w), 676 (w), 661 (w), 627 (w), 585 (w), 534 (s) cm^{-1}. **Mp**: 75.6-78.9 °C.

10.6.4.3. Ethyl corannulene-1-carboxylate (39)
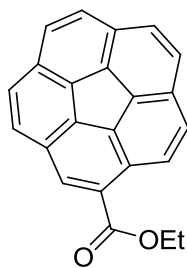
39

A flask was charged with ethyl 1,6,7,10-tetramethylfluoranthene-8-carboxylate **37** (0.66 g, 2.0096 mmol, 1.0 eqv), NBS (4.29 g, 24.115 mmol, 12 eqv), a spatula tip of AIBN and 11 mL chlorobenzene. The mixture was headed to reflux for 24 h while irradiated with a 150W sunlight lamp. Afterwards the solvent was evaporated in HV, the residue diluted with 50 mL of dichloromethane and extracted three times with 200 mL water. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent removed in HV. The dark red residue was dissolved in 79 mL abs. DMF and nickel powder (1.03 g, 17.684 mmol, 8.8 eqv) was added. The mixture was heated to 80 °C overnight and afterwards slowly cooled to rt. The volatile compounds were removed in HV. The solid residue was dissolved in dichloromethane and was washed three times with 30 mL water. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent removed in HV.

Since the product was contaminated with an unknown side product no characterization was attempted.

10.6.4.4. Methyl corannulene-1-carboxylate (41)
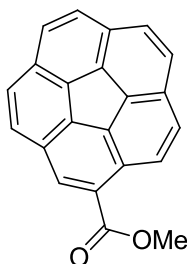
41

The flask was charged with 0.5 g (1.5803 mmol, 1 eq.) 1,6,7,10-tetramethylfluoranthene-8-carboxylate **36** 3.4 g (18.9639 mmol, 12 eq.), 5 mg AIBN and 10 mL chlorobenzene. The mixture was headed to reflux for 24 h while irradiated with a 150W sunlight lamp. Afterwards the mixture was slowly cooled to rt, diluted with 50 mL of dichloromethane and extracted three times with 200 mL of water. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent of the filtrate was evaporated in HV. The reddish brown residue was dissolved in 64 mL 1,4-dioxane and heated to 100 °C. A solution of 0.8 g sodium hydroxide (19.225 mmol, 10 eq.) in 24 mL water was added. The mixture was heated to 110 °C for 30 min, then 24 mL of water was added and the suspension slowly cooled to rt. The product mixture was neutralized with conz. hydrochloric acid and afterwards filtered. The remaining solid was washed with water and dried overnight at rt. More solid formed in the mother liqueur overnight and were filtered of. The residue was again washed with water, dried overnight at rt and combined with the first residue. A Young flask was charged with the 1-(3,4,9-tribromocorannulen-1-yl)ethanone **40** (160 mg, 0.2564 mmol, 1 eqv.), triethylamine (259 mg, 0.4 mL, 2.564 mmol, 10 eqv.), formic acid (118 mg, 0.1 mL, 2.564 mmol), 7 mg Pd/C and 2 mL piccoline. The reaction mixture was headed to 135 °C for 20 h and then cooled to rt. Afterwards the brown solution was filtered and the solvent of the filtrate evaporated in HV. The solid residue was purified by column chromatography using silica gel and a mixture of *n*-pentane and dichloromethane. The product could be isolated as a pale yellow solid (3.8 mg, 0.0123 mmol, 4 %).

1H NMR (400 MHz, CDCl$_3$): δ = 4.09 (s, 3 H, H$_{Me}$), 7.84 (m, 6 H, H$_{Cor}$), 7.88 (d, ^3J = 9.0 Hz, 1 H, H$_{Cor}$), 8.57 (d, ^3J= 9.0 Hz, 1 H, H$_{Cor}$), 8.77 (s, 1 H, H$_{Cor}$) ppm. **13C NMR** (176 MHz, CDCl$_3$): δ = 52.5 (s, C$_{Me}$), 127.3 (s, C$_{rim}$), 127.3 (s, C$_{rim}$), 127.4 (s, C$_{rim}$), 127.6 (s, C$_{rim}$), 127.7 (s, C$_{rim}$), 128.0 (s, C$_{rim}$), 128.1 (s, C$_{spoke}$), 128.3 (s, C$_{rim}$), 128.4 (s, C$_{rim}$), 128.9 (s, C$_{spoke}$), 129.0 (s, C$_{spoke}$), 130.8 (s, C$_{spoke}$), 131.0 (s, C$_{spoke}$), 132.2 (s, C$_{ipso}$), 133.1 (s, C$_{rim}$), 135.1 (s, C$_{hub}$), 135.5 (s, C$_{hub}$), 135.7 (s, C$_{hub}$), 136.5 (s, C$_{hub}$), 137.8 (s, C$_{hub}$), 167.6 (s, C$_{carbonyl}$) ppm. **MS** (EI, 100 °C): *m/z* 308.0846 (found), 308.0837 (calc'd), 308.0 (100 %, [C$_{22}$H$_{12}$O$_2$]$^{\cdot+}$), 277.3 (57 %, [C$_{21}$H$_9$O]$^{\cdot+}$), 249.1 (72 %, [C$_{20}$H$_9$O]$^{\cdot+}$), 154.0 (7 %, [C$_{22}$H$_{12}$O$_2$]$^{\cdot 2+}$), 138.9

(11 %, $[C_{21}H_9O]^{.\ 2+}$), 124.8 (37 %, $[C_{20}H_9O]^{.\ 2+}$). It was not possible to obtain enough material to measure an IR spectra and a melting point.

10.6.5. Diketones

10.6.5.1. Corannulene-1-yl(phenyl)methanone (33)
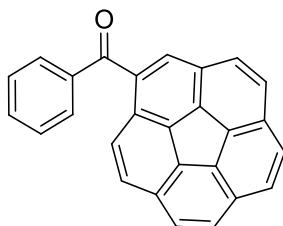
33

A flame-dried Schlenk flask was charged with aluminum(III) chloride (166 mg, 1.249 mmol, 5.0 eqv) and 20 mL abs. dichloromethane. In a second flame-dried Schlenk flask benzoyl chloride (30 mg, 0.247 mmol, 1.0 eqv) and corannulene **1** (75 mg, 0.2997 mmol, 1.2 eqv) were dissolved in 15 mL abs. dichloromethane. After the corannulene **1** was completely dissolved the solution was transferred to the aluminum(III) chloride suspension. The empty flask was rinsed with 5 mL abs. dichloromethane which was then added to the reaction mixture, too. After stirring at rt for 30 min the reaction was quenched with water and the organic layer was separated. The aqueous layer was extracted twice with 50 mL dichloromethane and the combined organic layers dried over anhydrous sodium sulfate. The drying agent filtered off and the solvent of the filtrate removed in vacuum. The residue was purified by preparative TLC using *n*-pentane and dichloromethane (1:1). The product could be isolated as orange crystals (38.4 mg, 0.1084 mmol, 43 %).

^{1}H NMR (700 MHz, CDCl$_3$): δ = 7.74 (t, ^3J = 7.8 Hz, 2 H, H$_{Ph}$), 7.66 (tt, ^3J = 1.2, 7.5 Hz, 1 H, H$_{Ph}$), 7.82 (AB, d, ^3J = 8.9 Hz, 1 H, H$_{Cor}$), 7.82 (AB, d, ^3J = 8.7 Hz, 1 H, H$_{Cor}$), 7.82 (AB, d, ^3J = 8.6 Hz, 1 H, H$_{Cor}$), 7.83 (AB, d, ^3J = 8.7 Hz, 1 H, H$_{Cor}$), 7.84 (AB, s, 1 H, H$_{Cor}$), 7.86 (AB, d, ^3J = 8.6 Hz, 1 H, H$_{Cor}$), 7.86 (AB, d, ^3J = 8.7 Hz, 1 H, H$_{Cor}$), 7.99 (dd, ^3J = 1.2, 8.3 Hz, 2 H, H$_{Ph}$), 8.05 (AB, d, ^3J = 8.8 Hz, 1 H, H$_{Cor}$), 8.20 (s, 1 H, H$_{Cor}$) ppm. **^{13}C NMR** (176 MHz, CDCl$_3$): δ = 127.3 (s, C$_{rim}$), 127.3 (s, C$_{rim}$), 127.4 (s, C$_{rim}$), 127.7 (s, C$_{rim}$), 127.8 (s, C$_{rim}$), 128.1 (s, C$_{rim}$), 128.2 (s, C$_{rim}$), 128.5 (s, C$_{Ph}$), 129.0 (s, C$_{spoke}$), 129.2 (s, C$_{spoke}$), 130.6 (s, C$_{Ph}$), 131.1 (s, C$_{spoke}$), 131.2 (s, C$_{spoke}$), 132.1 (s, C$_{spoke}$), 132.2 (s, C$_{Ph}$), 133.0 (s, C$_{rim}$), 135.4 (s, C$_{hub}$), 135.7 (s, C$_{hub}$), 135.8 (s, C$_{hub}$), 136.6 (s, C$_{hub}$), 136.8 (s, C$_{ipso}$), 137.3 (s, C$_{hub}$), 139.1 (s, C$_{ipso}$), 197.0 (s, C=O) ppm. One rim carbon atom is missing. **MS** (EI, 130 °C): *m/z* 354.1031 (found), 354.1045 (calc'd), 354.1 (100 %, $[C_{27}H_{14}O]^{.+}$), 277.2 (55 %, $[C_{21}H_9O]^{.+}$), 249.0 (68 %, $[C_{20}H_9]^{.+}$), 177.1

(9 %, [C$_{27}$H$_{14}$O]$^{-2+}$), 105.1 (10 %, [C$_7$H$_5$O]$^{\cdot+}$). **IR**: v = 3030 (w), 2959 (w), 2922 (w), 2845 (w), 1724 (m), 1646 (s, CO), 1593 (m), 1576 (m), 1445 (m), 1435 (w), 1372 (w), 1320 (w), 1304 (w), 1257 (s), 1190 (w), 1178 (w), 1165 (w), 1074 (w), 1006 (m), 927 (w), 915 (m), 852 (m), 831 (s), 795 (w), 781 (s), 725 (s), 701 (w), 688 (m), 664 (s), 650 (s), 634 (w), 622 (w), 556 (s), 541 (m), 534 (w) cm^{-1}. **Mp**: 193.1-196.0 °C.

10.6.5.2. 1,3-phenylenebis(corannulene-1-ylmethanone) (43)
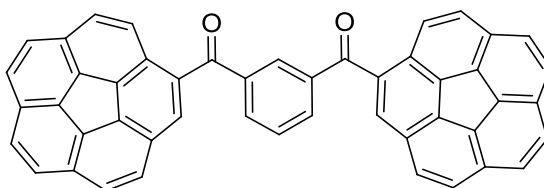
43

For the synthesis using the aluminium(III) chloride Friedel-Crafts acylation conditions see chapter 9.1.2..

Trifluoromethanesulfonic acid:

To a flame-dried Schlenk flask hafnium triflate (6 mg, 0.0080 mmol, 10 mol%), trifluoromethanesulfonic acid (1.2 mg, 0.7 µl, 0.0080 mmol, 10 mol%), isophthalic acid dichloride (16 mg, 0.0799 mmol, 1 eqv), corannulene **1** (50 mg, 0.1998 mmol, 2.5 eqv) and 5 mL nitromethane were added. The mixture was heated to 90 °C for 12 h. Afterwards the reaction was quenched with 50 mL of an aqueous saturated sodium hydrogen carbonate solution. The organic layer was separated and the aqueous layer extracted with 50 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate and filtered. The organic solvents of the filtrate were removed in vacuum.

No product signals could be found in a ^{1}H NMR spectrum.

Lithium perchlorate:

A flame-dried Schlenk flask was charged with hafnium triflate (6 mg, 0.0080 mmol, 10 mol%), lithium perchlorate (102 mg, 0.9588 mmol, 12 eqv), corannulene **1** (50 mg, 0.1998 mmol, 2.5 eqv), isophthalic acid dichloride (16 mg, 0.0799 mmol, 1 eqv) and 5 mL nitromethane. The suspension was headed to 90 °C for 12 h. Afterwards 50 mL of an aqueous saturated sodium hydrogen

carbonate was added. The organic layer was separated and the aqueous layer extracted with 50 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate and filtered. The solvent of the filtrate was removed in vacuum.

No product signals could be found in a ^{1}H NMR spectrum.

10.6.5.3. 1,3-Phenylenebis((2,3,4,5,6-pentamethylphenyl)methanone) (45)
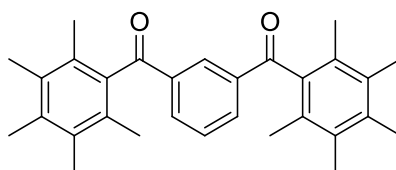
45

A flame-dried Schlenk flask was charged with aluminum(III)-chloride (143 mg, 1.0731 mmol, 3.5 eqv), isophthalic acid dichloride (62 mg, 0.3066 mmol, 1 eqv) and 25 mL dichloromethane. A second Schlenk flask was charged with 1,2,3,4,5-pentamethylbenzene (100 mg, 0.6746 mmol, 2.2 eqv) and 20 mL dichlormethane. After stirring for 30 min at rt the 1,2,3,4,5-pentamethyl solution was transferred to the suspension. The empty flask was rinsed with 5 mL dichloromethane and also added to the reaction mixture. After stirring for 4 h at rt the reaction was quenched with hydrochloride acid and the organic layer was separated. The aqueous layer was extracted twice with 20 mL of dichloromethane and the combined organic layers dried over sodium sulfate. The drying agent was filtered off and the solvent of the filtrate evaporated in vacuum. The residue was purified by flash column chromatography using n-pentane and dichloromethane. The product could be isolated as colorless crystals (102.1 mg, 0.2393 mmol, 78 %).

^{1}**H NMR** (700 MHz, CDCl$_3$): δ = 1.97(s, 12 H, H$_{Me}$), 2.19 (s, 12 H, H$_{Me}$), 2.28 (s, 6 H, H$_{Me}$), 7.53 (t, ^{3}J = 7.7 Hz, 1 H, H$_{Ar}$), 8.03 (d, ^{3}J = 7.7 Hz, 1 H, H$_{Ar}$), 8.15 (s, 1 H, H$_{Ar}$) ppm. ^{13}**C NMR** (101 MHz, CDCl$_3$): δ = 16.0 (s, C$_{Me}$), 16.9 (s, C$_{Me}$), 17.7 (s, C$_{Me}$), 128.9 (s, C$_{Ar}$), 129.4 (s, C$_{Ar}$), 130.8 (s, C$_{Ar}$), 133.1 (s, C$_{Ar}$), 134.0 (s, C$_{Ar}$), 135.9 (s, C$_{Ar}$), 137.1 (s, C$_{Ar}$), 138.4 (s, C$_{Ar}$), 201.3 (s, C=O) ppm. **MS** (ESI-TOF, CH$_2$Cl$_2$/MeOH): m/z = 449.2483 ([M+Na]$^+$), 465.2215 ([M+K]$^+$), 875.5049 ([2M+Na]$^+$). **IR**: v = 2924 (m), 2866 (w), 1922 (w), 1671 (s, CO), 1588 (m), 1442 (m), 1377 (m), 1307 (s), 1266 (s), 1222 (w), 1154 (s), 1073 (m), 1027 (w), 997 (m), 955 (w), 934 (s), 843 (w), 802 (s), 772 (m), 754 (w), 720 (s), 675 (s), 638 (w), 573 (m), 549 (m) cm^{-1}. **Mp**: 205.7-208.6 °C.

10.6.5.4. (1,3-Phenylene carboxy-$^{13}C_2$)bis(corannulene-1-ylmethan-one) (50)
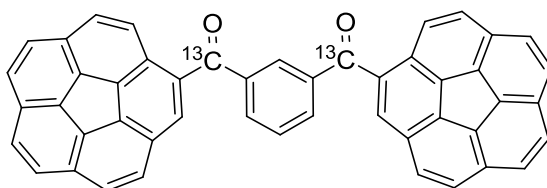
49

In a flame-dried Schlenk flask corannulene **1** (100 mg, 0.3995 mmol, 2.5 eq.) and isophthalic-carboxy-$^{13}C_2$ acid dichloride (33 mg, 0.1598 mmol, 1 eq.) were dissolved in 15 mL abs. dichloromethane. A second Schlenk flask was charged with aluminum(III) chloride (75 mg, 0.5993 mmol, 3.5 eq.) and 20 mL abs. dichloromethane. The corannulene **1** solution was added to the aluminum(III) chloride suspension. And the empty flask was rinsed with 5 mL abs. dichloromethane which was added to the reaction mixture afterwards. The resulting suspension was stirred at rt for 30 min and the reaction was quenched with water. The organic layer was separated and the aqueous phase was extracted once with 50 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate and the solvent evaporated. The residue was purified by preparative TLC using *n*-pentane and dichloromethane (1:3). The product could be isolated as an amorphous orange solid (78.8 mg, 0.1249 mmol, 78 %).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.71 (AB, d, ^3J = 8.8 Hz, 2 H, H$_{Cor}$), 7.73 (AB, d, ^3J = 8.8 Hz, 2 H, H$_{Cor}$), 7.74 (AB, d, ^3J = 8.7 Hz, 2 H, H$_{Cor}$), 7.77 (AB, d, ^3J = 9.0 Hz, 2 H, H$_{Cor}$), 7.79 (AB, d, ^3J = 8.7 Hz, 2 H, H$_{Cor}$), 7.79 (AB, d, ^3J = 8.7 Hz, 2 H, H$_{Cor}$), 7.82 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 8.08 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 8.22 (d, 2 H, ^3J = 5.1 Hz, H$_{Ph}$), 8.29 (m, 2 H, H$_{Ph}$), 8.53 (m, 1 H, H$_{Ph}$) ppm. **^{13}C NMR** (101 MHz, CDCl$_3$): δ = 127.1 (s, C$_{rim}$), 127.3 (s, C$_{rim}$), 127.3 (s, C$_{rim}$), 127.3 (s, C$_{rim}$), 127.7 (s, C$_{rim}$), 127.8 (s, C$_{rim}$), 128.2 (s, C$_{rim}$), 128.3 (s, C$_{rim}$), 128.7 (d, J = 5.0 Hz, C$_{spoke}$), 129.0 (d, J = 2.1 Hz, C$_{spoke}$), 129.1 (t, J = 4.0 Hz, C$_{Ph}$), 131.0 (s, C$_{spoke}$), 131.1 (s, C$_{spoke}$), 132.0 (t, J = 3.2 Hz, C$_{Ph}$), 132.1 (s, C$_{spoke}$), 132.9 (d, J = 3.7 Hz, C$_{rim}$), 134.2 (dd, J = 0.7,2.6 Hz, C$_{Ph}$), 135.2 (s, C$_{hub}$), 135.5 (d, J = 0.4 Hz, C$_{hub}$), 135.8 (d, J = 3.7 Hz, C$_{hub}$), 135.9 (d, J = 54.9 Hz, C$_{ipso}$), 136.4 (s, C$_{hub}$), 137.3 (d, J = 0.8 Hz, C$_{hub}$), 139.4 (dd, J = 3.9, 54.6 Hz, C$_{ipso}$), 196.0 (s, C=O) ppm. **MS** (EI, 230 °C): *m/z* 632.1696 (found), 632.1681 (calc'd), 632.3 (85 %, [$^{12}C_{46}{}^{13}C_2H_{22}O_2$]$^{\cdot +}$), 352.8 (12 %, [$^{12}C_{26}{}^{13}C_1H_{13}O$]$^{\cdot +}$), 278.0 (80 %, [$^{12}C_{20}{}^{13}C_1H_9O$]$^{\cdot +}$), 248.9 (100 %, [C$_{20}H_9$]$^{\cdot +}$). **IR**: v = 3028 (w), 2958 (w), 2921 (w), 2851 (w), 2245 (w), 1894 (w), 1607 (s, CO), 1474 (m), 1451 (w), 1435 (m), 1405 (w), 1372 (m), 1321 (w), 1306 (m), 1265 (m), 1234 (w), 1221 (s), 1187 (m), 1148 (w), 1136 (w), 1045 (w), 1017 (m), 999 (w), 937 (w), 902 (s), 830 (s), 789 (w), 773 (w), 726 (s), 659 (s), 633 (w), 548 (s) cm^{-1}. **Mp**: 177.0-178.1 °C.

10.6.5.5. (5-*Tert*-1,3-phenylene)bis(corannulene-1-ylmethanone) (55)
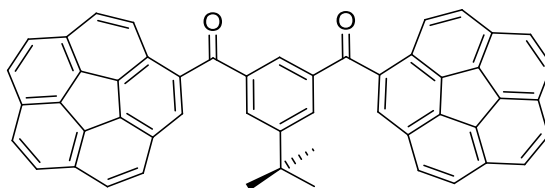
55

A flame-dried Schlenk flask was charged with aluminum(III) chloride (75 mg, 0.5593 mmol, 3.5 eqv) and 20 mL abs. dichloromethane. In a second flame-dried Schlenk flask 5-*tert*-butylisophthaloyl dichloride (41 mg, 0.1598 mmol, 1 eqv) and corannulene **1** (100 mg, 0.3995 mmol, 2.5 eqv) were dissolved in 15 mL abs. dichloromethane. After the corannulene **1** was completely dissolved the solution was transferred to the aluminum(III) chloride suspension. The empty flask was rinsed with 5 mL abs. dichloromethane which was then added to the reaction mixture. After stirring at rt for 30 min the reaction was quenched with water and the organic layer was separated. The aqueous layer was extracted twice with 50 mL dichloromethane and the combined organic layers dried over anhydrous sodium sulfate. The drying agent filtered off and the solvent of the filtrate removed in vacuum. The solid residue was purified by preparative TLC using *n*-pentane and dichloromethane (1:3). The product could be isolated as an amorphous orange solid (90.6 mg, 0.1319 mmol, 83 %).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.46 (s, 9 H, H$_{Me}$), 7.70 (AB, d, ^3J = 8.8 Hz, 2 H, H$_{Cor}$), 7.73 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 7.74 (AB, d, ^3J = 8.8 Hz, 2 H, H$_{Cor}$), 7.78 (AB, d, ^3J = 9.0 Hz, 2 H, H$_{Cor}$), 7.79 (AB, d, ^3J = 8.7 Hz, 2 H, H$_{Cor}$), 7.80 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 7.83 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 8.09 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 8.23 (s, 2 H, H$_{Cor}$), 8.26 (t, ^3J = 1.5 Hz, 1 H, H$_{Ph}$), 8.39 (d, ^3J = 1.5 Hz, 2 H, H$_{Ph}$) ppm. **^{13}C-NMR** (126 MHz, CDCl$_3$): δ = 31.4 (s, C$_{Me}$), 35.4 (s, C$_{tBu}$), 127.2 (s, C$_{rim}$), 127.2 (s, C$_{rim}$), 127.2 (s, C$_{rim}$), 127.2 (s, C$_{rim}$), 127.6 (s, C$_{rim}$), 127.7 (s, C$_{rim}$), 128.2 (s, C$_{rim}$), 128.2 (s, C$_{rim}$), 128.7 (s, C$_{spoke}$), 128.9 (s, C$_{spoke}$), 130.0 (s, C$_{Ph}$), 131.0 (s, C$_{spoke}$), 131.0 (s, C$_{spoke}$), 131.3 (s, C$_{Ph}$), 132.0 (s, C$_{spoke}$), 132.9 (s, C$_{spoke}$), 135.1 (s, C$_{hub}$), 135.5 (s, C$_{hub}$), 135.8 (s, C$_{hub}$), 136.1 (s, C$_{ipso}$), 136.4 (s, C$_{hub}$), 137.3 (s, C$_{hub}$), 139.0 (s, C$_{ipso}$), 196.4 (s, C=O) ppm. **MS** (EI, 270 °C): *m/z* 686.2227 (found), 686.2246 (calc'd), 686.2 (94 %, [C$_{52}$H$_{30}$O$_2$]$^{\cdot+}$), 671.2 (8 %, [C$_{51}$H$_{27}$O$_2$]$^{\cdot+}$), 409.4 (8 %, [C$_{31}$H$_{21}$O]$^+$), 343.4 (9 %, [C$_{52}$H$_{30}$O$_2$]$^{\cdot2+}$), 277.1 (90 %, [C$_{21}$H$_9$O]$^{\cdot+}$), 249.1 (100 %, [C$_{20}$H$_9$]$^{\cdot+}$), 124.3 (8 %, [C$_{20}$H$_9$]$^{\cdot2+}$). **IR**: v = 3022 (w), 2959 (w), 2863 (w), 1648 (s, CO), 1585 (m), 1474 (w), 1435 (m), 1405 (w), 1366 (m), 1325 (m), 1307 (m), 1273 (w), 1239 (s), 1224 (s), 1187 (m), 1152 (m), 1135 (w), 1054 (w), 1019 (m), 941 (w), 899 (m), 828 (s), 791 (m), 724 (s), 693 (m), 663 (s), 576 (w), 548 (s) cm^{-1}. **Mp**: 199.8-202.7 °C.

10.6.5.6. (5-Fluoro-1,3-phenylene)bis(corannulene-1-ylmethanone) (56)

56

For the synthesis using the aluminium(III) chloride Friedel-Crafts acylation see chapter 9.1.2..

A stocksolution of corannulene **1** (16 mg, 0.015 mmol, 3 eqv) in 1.6 mL dichloromethane was prepared in a flame-dried Schlenk flask. Two Schlenk flasks were charged with titanium tetrachloride (15 mg, 0.01 mL, 0.075 mmol, 5 eqv) and boron trifluoride diethyl etherate (12 mg, 0.01 mL, 0.075 mmol, 5 eqv) respectively and diluted with 1.2 mL abs. dichloromethane. The fourth stocksolution contained 5-fluoroisophthaloyl dichloride (5 mg, 0.025 mmol, 1 eqv) that was dissolved in 1.5 mL abs. dichloromethane. A flame-dried Young NMR tube was charged with aluminum(III) chloride (3 mg, 0.025 mmol, 5 eqv) and 0.4 mL abs. dichloromethane. Afterwards 0.3 mL of the acid chloride solution was added. In the same manner the Young tubes were prepared for the other two catalyst (0.3 mL of the stocksolutions). Another flame-dried Young NMR tube was charged with 0.3 mL of the acid chloride solution and 0.7 mL abs. dichloromethane. After 30, 60, 90, 120, 150 and 180 min a ^{19}F NMR was measured from all the NMR tubes. After 5 d ^{19}F NMR spectra were measured and the reaction mixture afterwards quenched with water and another NMR spectrum recorded.

10.6.5.7. (5-Chloro-1,3-phenylene)bis(corannulene-1-ylmethanone) (57)
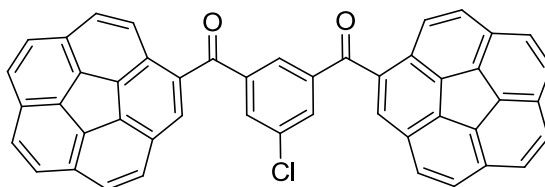
57
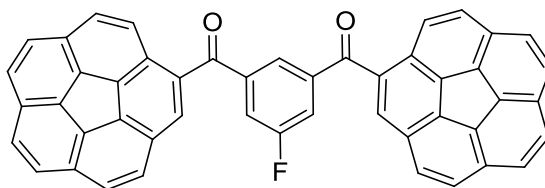
A flame-dried Schlenk flask was charged with aluminum(III) chloride (75 mg, 0.5593 mmol, 3.5 eqv) and 20 mL abs. dichloromethane. In a second flame-dried Schlenk flask corannulene **1** (100 mg, 0.3995 mmol, 2.5 eqv) and 5-chloroisophthalic acid dichloride (38 mg, 0.1598 mmol, 1 eqv) were dissolved in 15 mL abs. dichloromethane. After the corannulene **1** was dissolved the

solution was transferred to the aluminum(III) chloride suspension. The empty flask was rinsed with 5 mL abs. dichloromethane which was added to the reaction mixture. After stirring for 30 min at rt water was added to the suspension and the organic layer was separated. The aqueous layer was extracted twice with 50 mL dichloromethane and the combined organic layers dried over anhydrous sodium sulfate. The drying agent was filtered off and the solvent of the filtrate evaporated in vacuum. The solid residue was purified by preparative TLC using n-pentane and dichloromethane (1:6). The product could be isolated as an amorphous yellow powder (41.8 mg, 0.0628 mmol, 39 %).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.74 (AB, d, ^3J= 8.8 Hz, 2 H, H$_{Cor}$), 7.77 (AB, d, ^3J= 8.8 Hz, 2 H, H$_{Cor}$), 7.78 (AB, d, ^3J= 8.7 Hz, 2 H, H$_{Cor}$), 7.80 (AB, d, ^3J= 8.9 Hz, 2 H, H$_{Cor}$), 7.83 (AB, d, ^3J= 8.8 Hz, 2 H, H$_{Cor}$), 7.83 (AB, d, ^3J= 8.8 Hz, 2 H, H$_{Cor}$), 7.85 (AB, d, ^3J= 8.9 Hz, 2 H, H$_{Cor}$), 8.21 (s, 2 H, H$_{Cor}$), 8.26 (d, ^3J = 1.5 Hz, 2 H, H$_{Ph}$), 8.33 (t, ^3J= 1.5 Hz, 1 H, H$_{Ph}$) ppm. **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 127.0 (s, C$_{rim}$), 127.3 (s, C$_{rim}$), 127.4 (s, C$_{rim}$), 127.4 (s, C$_{rim}$), 127.9 (s, C$_{rim}$), 128.0 (s, C$_{rim}$), 128.5 (s, C$_{rim}$), 128.5 (s, C$_{rim}$), 128.6 (s, C$_{spoke}$), 128.8 (s, C$_{spoke}$), 130.1 (s, C$_{Ph}$), 131.2 (s, C$_{spoke}$), 131.2 (s, C$_{spoke}$), 132.3 (s, C$_{spoke}$), 133.2 (s, C$_{rim}$), 133.8 (s, C$_{Ph}$), 135.2 (s, C$_{ipso}$), 135.3 (s, C$_{Ph}$), 135.6 (s, C$_{hub}$), 135.8 (s, C$_{hub}$), 135.9 (s, C$_{hub}$), 136.5 (s, C$_{hub}$), 137.6 (s, C$_{hub}$), 141.0 (s, C$_{ipso}$), 194.7 (s, C=O) ppm. **MS** (EI, 270 °C): m/z 664.1209 (found), 664.1230 (calc'd), 664.1 (80 %, [C$_{48}$H$_{21}$ClO$_2$]$^{\cdot+}$), 277.2 (79 %, [C$_{21}$H$_9$O]$^{\cdot+}$), 249.2 (100 %, [C$_{20}$H$_9$]$^{\cdot+}$). **IR**: v = 3027 (w), 2955 (w), 1720 (w), 1654 (m, CO), 4642 (m), 1567 (m), 1474 (w), 1454 (w), 1439 (m), 1374 (w), 1325 (m), 1307 (m), 1277 (m), 1237 (s), 1206 (w), 1188 (m), 1151 (m), 1188 (m), 1151 (m), 1134 (w), 1052 (w), 1029 (m), 941 (w), 922 (m), 900 (m), 832 (s), 805 (m), 790 (m), 750 (m), 743 (m), 719 (s), 701 (w), 666 (s), 656 (s), 635 (w), 607 (w), 594 (w), 580 (w), 555 (s), 542 (m) cm^{-1}. **Mp**: > 225 °C.

10.6.5.8. (5-Bromo-1,3-phenylene)bis(corannulene-1-ylmethanone) (58)

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A flame-dried Schlenk flask was charged with aluminum(III) chloride (75 mg, 0.5593 mmol, 3.5 eqv) and 20 mL abs. dichloromethane. A second flame-dried Schlenk flask was prepared with corannulene **1** (100 mg, 0.3995 mmol, 2.5 eqv), 5-bromoisophthaloyl dichloride (45 mg, 118

0.1598 mmol, 1.0 eqv) and 15 mL abs. dichloromethane. After the corannulene **1** was completely dissolved the solution was transferred to the aluminum(III) chloride suspension. The empty Schlenk flask was rinsed with 5 mL abs. dichloromethane which was added to the reaction. The mixture was stirred for 30 min at rt and then quenched with water. The organic layer was separated and the aqueous extracted twice with 50 mL dichloromethane. The combined organic layers were dried over sodium sulfate, filtered and the solvent evaporated in vacuum. The solid residue was purified by preparative TLC using *n*-pentane and dichloromethane (1:3). The product could be isolated as an amorphous yellow solid (13.3 mg, 0.0187 mmol, 5 %).

¹H NMR (400 MHz, CDCl₃): δ = 7.73 (AB, d, ^3J = 8.8 Hz, 2 H, H$_{Cor}$), 7.76 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 7.76 (AB, d, ^3J = 8.7 Hz, 2 H, H$_{Cor}$), 7.79 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 7.82 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 7.82 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 7.83 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 8.09 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 8.20 (s, 2 H, H$_{Cor}$), 8.37 (t, ^3J= 1.4 Hz, 1 H, H$_{Ph}$), 8.40 (d, ^3J = 1.4 Hz, 2 H, H$_{Ph}$) ppm. Due to the poor solubility in common organic solvents no ¹³C NMR could be measured. **MS** (EI, 280 °C): *m/z* 708.0693 (found), 708.0725 (calc'd), 710.1 (47 %, [C₄₈H₂₁BrO₂]· ⁺), 277.1 (81 %, [C₂₁H₉O]· ⁺), 249.2 (100 %, [C₂₀H₉]· ⁺). **IR**: ν = 2958 (w), 2922 (m), 2852 (w), 1717 (w), 1651 (m, CO), 1586 (w), 1564 (w), 1466 (w), 1436 (w), 1375 (m), 1326 (w), 1306 (w), 1259 (s), 1239 (w), 1222 (w), 1187 (m), 1084 (m), 1018 (m), 895 (w), 830 (s), 796 (s), 748 (w), 719 (m), 696 (w), 663 (m), 632 (m), 607 (m), 579 (s), 551 (s) cm⁻¹. **Mp**: > 225 °C.

10.6.5.9. (5-Iodo-1,3-phenylene)bis(corannulene-1-ylmethanone) (59)
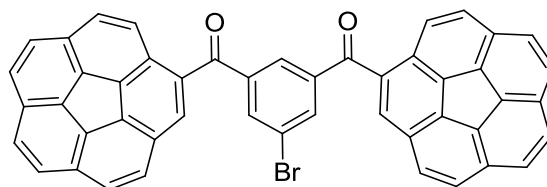

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Classic Friedel-Crafts acylation:

A flame-dried Schlenk flask was charged with aluminum(III) chloride (75 mg, 0.5593 mmol, 3.5 eqv) and 20 mL abs. dichloromethane. A second flame-dried Schlenk flask was prepared with corannulene **1** (100 mg, 0.3995 mmol, 2.5 eqv), 5-iodoisophthaloyl dichloride (53 mg, 0.1598 mmol, 1.0 eqv) and 15 mL abs. dichloromethane. After the corannulene **1** was completely dissolved the solution was transferred to the aluminum(III) chloride suspension. The empty Schlenk flask was rinsed with 5 mL abs. dichloromethane which was also added to the reaction.

The mixture was stirred for 30 min at rt and then quenched with water. The organic layer was separated and the aqueous layer extracted twice with 30 mL dichloromethane. The combined organic layers were dried over sodium sulfate, filtered and the solvent evaporated in vacuum. The solid residue was purified by preparative TLC using *n*-pentane and dichloromethane (1:4). The product could be isolated as an amorphous yellow solid (3.6 mg, 0.0046 mmol, 3 %).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.79 (m, 12 H, H$_{Ar}$), 7.86 (d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 8.09 (d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 8.21 (s, 2 H, H$_{Cor}$), 8.38 (t, ^3J= 1.5 Hz, 1 H, H$_{Ph}$), 8.60 (d, ^3J = 1.5 Hz, 2 H, H$_{Ph}$) ppm. **MS** (EI, 270 °C): *m/z* 756.0557 (found), 756.0587 (calc'd), 756.1 (36 %, [C$_{48}$H$_{21}$IO$_2$]$^{\cdot+}$), 277.1 (71 %, [C$_{21}$H$_9$O]$^{\cdot+}$), 249.3 (100 %, [C$_{20}$H$_9$]$^{\cdot+}$). Due to the poor solubility in common organic solvents no ^{13}C NMR could be measured. It was another not possible to obtain enough material to measure an IR spectra and a melting point.

Triflate catalyzed Friedel-Crafts acylation:

A flame-dried Normag flask was charged with lithium perchlorate (102 mg, 0.9588 mmol, 12 eqv), hafnium triflate (12 mg, 0.0160 mmol, corannulene **1** (50 mg, 0.1998 mmol, 2.5 eqv), 5-iodoisophthalic acid dichloride (26 mg, 0.0799 mmol, 1 eqv) and 5 mL nitromethane. The mixture was headed to 90 °C and stirred at that temperature for 16 h. Afterwards the reaction was quenched with 50 mL of an aqueous saturated sodium hydrogen carbonate solution and 10 mL of dichloromethane was added. The organic layer was separated and the aqueous layer extracted with 50 mL dichlormethane. The combined organic layers were dried over sodium sulfate, filtered and the solvent of the filtrate was removed in vacuum.

No product signals could be found in a ^{1}H NMR spectrum.

10.6.5.10. Attempted synthesis of (5-(trifluoromethyl)-1,3-phenylene)bis(corannulene-1-ylmethanone) (60)
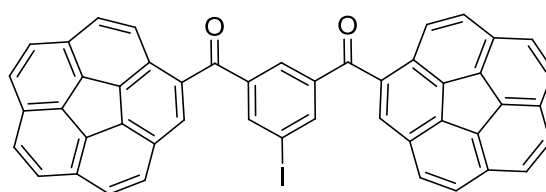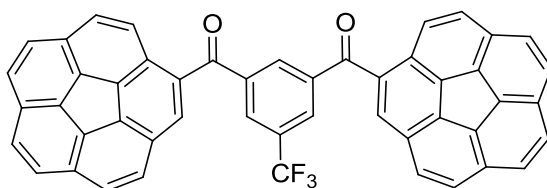

60

A flame-dried Schlenk flask was charged with aluminum(III) chloride (43 mg, 0.3196 mmol, 4.0 eqv) and 7 mL abs. dichloromethane. In an second flame-dried Schlenk flask 5-(trifluoromethyl)isophthaloyl dichloride (22 mg, 0.0799 mmol, 1.0 eqv) and corannulene **1** (50 mg, 0.1998 mmol, 2.5 eqv) were dissolved in 5 mL abs. dichloromethane. The corannulene **1** solution was then transferred to the aluminum(III) chloride suspension and the empty flask was rinsed with 2 mL abs. dichloromethane which was added to the reaction. The mixture was stirred at rt for 30 min and then quenched with hydrochloric acid. The organic layer was separated and the aqueous layer extracted twice with 50 mL dichloromethane. The combined organic layers were dried over sodium sulfate, filtered and the solvent evaporated in vacuum.

No product signals could be found in a ^{1}H or ^{19}F NMR spectrum.

10.6.5.11. Attempted synthesis of (5-Nitro-1,3-phenylene)bis((2,3,4,5,6-pentamethylphenyl) methanone) (62)
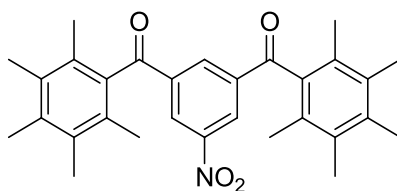
62

A flame-dried Schlenk flask was charged with aluminum(III) chloride (204 mg, 1.5332 mmol, 5 eqv), 5-nitroisophthalic acid dichloride (76 mg, 0.3066 mmol, 1 eqv) and 25 mL dichloromethane. In a second flame-dried Schlenk flask 1,2,3,4,5-pentamethylbenzene was dissolved in 20 mL dichloromethane. After stirring for 15 min at rt the 1,2,3,4,5-pentamethylbenzene solution was transferred to the aluminum(III) chloride suspension. The empty flask was rinsed with 5 mL of dichloromethane which was also added to the reaction mixture. After stirring for 2 h at rt the

reaction was quenched with hydrochloric acid and the organic layer was separated. The aqueous layer was extracted with 100 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered and the solvent of the filtrate evaporated in vacuum. The solid was purified by flash column chromatography using *n*-pentane and dichloromethane.

No product could be isolated.

10.6.5.12. Corannulene-1-yl(3-nitrophenyl)methanone (63)
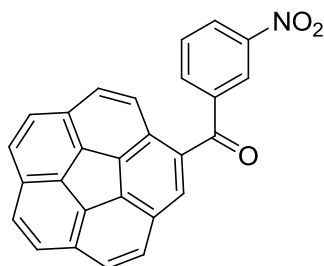
63

A flame-dried Schlenk flask was charged with aluminium(III) chloride (166 mg, 1.2485 mmol, 5.0 eqv) and 20 mL abs. dichloromethane. In a second flame-dried Schlenk flask 3-nitrobenzoyl chloride (46 mg, 0.2497 mmol, 1.0 eqv) and corannulene **1** (75 mg, 0.2997 mmol, 1.2 eqv) were dissolved in 15 mL abs. dichloromethane. The corannulene **1** solution was transferred to the aluminum(III) chloride suspension and the empty flask was rinsed with 5 mL abs. dichloromethane which was as well added to the mixture. After stirring at rt for 30 min the reaction was quenched with water and the organic layer was separated. The aqueous layer was extracted twice with 50 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered and the solvent of the filtrate evaporated in vacuum. The residue was purified by preparative TLC using *n*-pentane and dichloromethane (1:3). The product could be isolated as an amorphous orange solid (50 mg, 0.1242 mmol, 50 %).

^{1}H NMR (700 MHz, CDCl$_3$): δ = 7.75 (m, 1 H, H$_{Ph}$), 7.83 (AB, d, ^3J = 8.6 Hz, 1 H, H$_{Cor}$), 7.84 (AB, d, ^3J = 8.7 Hz, 1 H, H$_{Cor}$), 7.84 (AB, d, ^3J = 8.6 Hz, 1 H, H$_{Cor}$), 7.85 (AB, d, ^3J = 8.8 Hz, 1 H, H$_{Cor}$), 7.87 (AB, d, ^3J = 8.7 Hz, 1 H, H$_{Cor}$), 7.87 (AB, d, ^3J = 8.7 Hz, 1 H, H$_{Cor}$), 7.88 (AB, d, ^3J = 8.7 Hz, 1 H, H$_{Cor}$), 8.07 (AB, d, ^3J = 8.8 Hz, 1 H, H$_{Cor}$), 8.18 (s, 1 H, H$_{Cor}$)), 8.31 (ddd, ^3J = 1.1, 1.6, 7.6 Hz, 1 H, H$_{Ph}$), 8.51 (ddd, ^3J = 1.1, 2.3, 7.7 Hz, 1 H, H$_{Ph}$), 8.8 (t, ^3J = 1.8 Hz, 1 H, H$_{Ph}$) ppm. **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 125.1 (s, C$_{Ph}$), 126.9 (s, C$_{rim}$), 127.1 (s, C$_{rim}$), 127.2 (s, C$_{rim}$), 127.4 (s, C$_{rim}$), 127.4 (s, C$_{rim}$), 127.9 (s, C$_{rim}$), 128.1 (s, C$_{rim}$), 128.5 (s, C$_{rim}$), 128.6 (s, C$_{rim}$), 128.6 (s, C$_{spoke}$), 128.7 (s, C$_{spoke}$), 129.9 (s, C$_{Ph}$), 131.2 (s, C$_{spoke}$),

131.2 (s, C_{spoke}), 132.3 (s, C_{spoke}), 133.1 (s, C_{Ph}), 135.2 (s, C_{hub}), 135.2 (s, C_{hub}), 135.6 (s, C_{hub}), 135.9 (s, C_{ipso}), 135.9 (s, C_{Ph}), 136.5 (s, C_{hub}), 137.6 (s, C_{hub}), 140.6 (s, C_{ipso}), 148.4 (s, C_{Ph}), 194.6 (s, C=O) ppm. **MS** (EI, 170 °C): *m/z* 399.0884 (found), 399.0895 (calc'd), 399.1 (100 %, $[C_{27}H_{13}NO_2]^{+}$), 353.0 (5 %, $[C_{27}H_{13}O]^{+}$), 276.8 (74 %, $[C_{21}H_9O]^{+}$), 248.8 (99 %, $[C_{20}H_9]^{+}$). **IR**: v = 3080 (w), 2961 (w), 2920 (w), 2848 (w), 1720(w), 1654 (s, CO), 1611 (m), 1528 (s), 1474 (m), 1437 (m), 1375 (w), 1347 (s), 1323 (w), 1307 (w), 1288 (w), 1253 (s), 1225 (w), 1191 (w), 1138 (w), 1109 (w), 1077 (m), 1017 (m), 934 (m), 920 (w), 903 (m), 888 (w), 839 (s), 826 (s), 808 (m), 799 (w), 748 (s), 720 (s), 713 (s), 664 (s), 650(s), 634 (m), 553 (s) cm^{-1}. **Mp**: 166.0-167.0 °C.

10.6.5.13. Attempted synthesis of corannulene-1-yl(3-nitrophenyl)-methanone (64)

64

A flame-dried Schlenk flask was charged with 3,5-dinitrobenzoyl chloride (42 mg, 0.1816 mg, 1.0 eqv), aluminum(III) chloride (145 mg, 1.0896 mmol, 6.0 eqv) and 7 mL abs. dichloromethane. In a second flame-dried Schlenk flask corannulene **1** (50 mg, 0.1998 mmol, 1.1 eqv) was dissolved in 5 mL abs. dichloromethane. After the corannulene **1** was dissolved the solution was transferred to the aluminum(III) chloride suspension. The empty flask was rinsed with 3 mL abs. dichloromethane which was then added to the reaction. The mixture was stirred for 2 h at rt and afterwards quenched with hydrochloric acid. The organic layer was separated and the aqueous extracted with 50 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered and the solvent of the filtrate evaporated in vacuum.

No product could be isolated.

10.6.5.14. Attempted synthesis of (3,5-dinitrophenyl)(2,3,4,5,6-penta-methylphenyl)methanone (65)
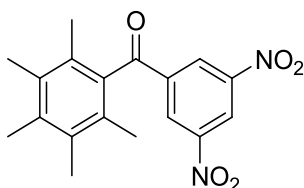
65

A flame-dried Schlenk flask was charged with aluminum(III) chloride (491 mg, 3.6798 mmol, 6 eqv), 3,5-dinitrobenzoyl chloride (141 mg, 0.6133 mmol, 1 eqv) and 20 mL abs. dichloromethane. In a second flame-dried Schlenk flask 1,2,3,4,5-pentamethylbenzene (100 mg, 0.96746 mmol, 1.1 eqv) was dissolved in 20 mL abs. dichloromethane. After stirring for 30 min the 1,2,3,4,5-pentamethylbenzene solution was added to the aluminum(III) chloride suspension. The empty flask was rinsed with 5 mL abs. dichloromethane which was added afterwards to the reaction mixture. After stirring for 2 h at rt the reaction was quenched with hydrochloric acid and the organic layer was separated. The aqueous layer was extracted twice with 100 mL dichloromethane and the combined organic layers dried over sodium sulfate. The drying agent was filtered of and the solvent of the filtrate removed in vacuum.

No product could be isolated.

10.6.5.15. Attempted synthesis of (5-(trifluoromethyl)-1,3-phenylene)bis((2,3,4,5,6-pentamethylphenyl)methanone) (66)
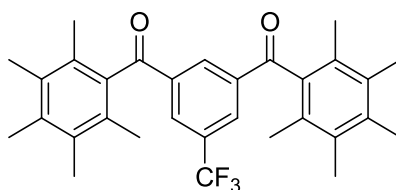
66
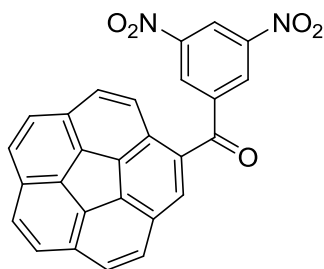
A flame-dried Schlenk flask was charged with aluminum(III) chloride (204 mg, 1.5332 mmol, 5.0 eqv) and 20 mL abs. dichloromethane. 5-Trifluoromethylisophthaloyl chloride (83 mg, 0.3066 mmol, 1.0 eqv) and 1,2,3,4,5-pentamethylbenzene (100 mg, 0.6746 mmol, 2.2 eqv) were dissolved in 15 mL abs. dichloromethane in a second flame-dried Schlenk flask. The 1,2,3,4,5-

pentamethylbenzene solution was transferred to the aluminum(III) chloride suspension and the empty flask was rinsed with 5 mL abs. dichloromethane which was then added to the reaction. The mixture was stirred for 30 min at rt and then quenched with hydrochloric acid. The organic layer was separated and the aqueous layer extracted with 50 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered and the solvent of the filtrate evaporated in vacuum. The residue was purified by flash column chromatography using *n*-pentane and dichloromethane.

No product signals could be found in a ^{1}H or ^{19}F NMR.

10.6.5.16. Attempted synthesis of benzene-1,3,5-triyltris(1-(2,3,4,5,6-pentamethylphenyl)methanone) (67)

67

A flame-dried Schlenk flask was charged with aluminum(III) chloride (218 mg, 1.632 mmol, 5.0 eqv), benzene-1,3,5-tricarbonyl trichloride (87 mg, 0.3264 mmol, 1.0 eqv) and 35 mL dichloromethane. In a second flame-dried Schlenk flask 1,2,3,4,5-pentamethyllbenzene (150 mg, 1.0119 mmol, 3.1 eqv) was dissolved in 35 mL dichloromethane. After stirring for 30 min at rt the 1,2,3,4,5-pentamethylbenzene solution was added to the aluminum(III) chloride suspension and the empty flask was rinsed with 5 mL of dichloromethane which was added to the reaction mixture. After 4 h stirring at rt the reaction mixture was quenched with hydrochloric acid and the organic layer was separated. The aqueous phase was extracted twice with 100 mL dichloromethane and the combined organic layers dried over anhydrous sodium sulfate. The drying agent was filtered of and the solvent of the filtrate evaporated in vacuum.

No product could be isolated.

10.6.5.17. (5-Chloro-1,3-phenylene)bis((2,3,4,5,6-pentamethylphenyl)-methanone) (68)
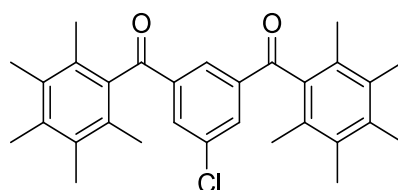
68

A flame-dried Schlenk flask was charged with aluminum(III) chloride (204 mg, 1.5332 mmol, 5.0 eqv) and 20 mL abs. dichloromethane. In a second flamed-dried Schlenk flask 1,2,3,4,5-pentamethylbenzene (100 mg, 0.6746 mmol, 2.2 eqv) and 5-chloroisophthaloyl dichloride (73 mg, 0.3066 mmol, 1.0 eqv) were dissolved in 15 mL abs. dichloromethane. The 1,2,3,4,5-pentamethylbenzene solution was transferred to the aluminum(III) chloride suspension and the empty flask was rinsed with 5 mL abs. dichloromethane which was added to the reaction. The mixture was stirred at rt for 30 min and quenched with water. The organic layer was separated and the aqueous layer extracted two times with 50 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered and the solvent of the filtrate evaporated in vacuum. The residue was purified by flash column chromatography using *n*-pentane and dichloromethane. The product could be isolated as colorless crystals (60.3 mg, 0.1308 mmol, 43 %).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.96 (s, 12 H, H$_{Me}$), 2.19 (s, 12 H, H$_{Me}$), 2.28 (s, 6 H, H$_{Me}$), 7.97 (m, 3 H, H$_{Ar}$) ppm. **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 16.1 (s, C$_{Me}$), 16.9 (s, C$_{Me}$), 17.7 (s, C$_{Me}$), 128.8 (s, C$_{Ar}$), 128.9 (s, C$_{Ar}$), 133.3 (s, C$_{Ar}$), 133.5 (s, C$_{Ar}$), 136.1 (s, C$_{Ar}$), 136.3 (s, C$_{Ar}$), 136.4 (s, C$_{Ar}$), 137.0 (s, C$_{Ar}$), 200.0 (s, C=O) ppm. **MS** (ESI-TOF, CH$_2$Cl$_2$/MeOH): m/z = 461.2256 ([M+H]$^+$), 483.2090 ([M+Na]$^+$), 499.1872 ([M+K]$^+$), 943.4260 ([2M+Na]$^+$). **IR**: v= 2921 (w), 2862 (w), 1803 (w), 1684 (s, CO), 1586 (w), 1575 (m), 1443 (w), 1417 (w), 1381 (w), 1305 (s), 1266 (s), 1229 (m), 1163 (s), 1112 (w), 1066 (m), 1026 (w), 999 (m), 939 (m), 896 (m), 832 (m), 808 (m), 783 (m), 758 (w), 731 (s), 687 (s), 661 (s), 588 (w), 573 (w), 553 (w), 542 (w), 529 (w). **Mp**: > 225.0 °C.

10.6.5.18. (5-Bromo-1,3-phenylene)bis((2,3,4,5,6-pentamethylphenyl)-methanone) (69)
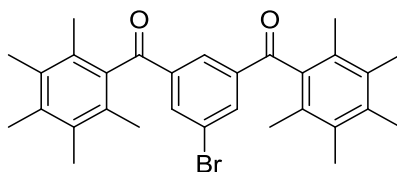
69
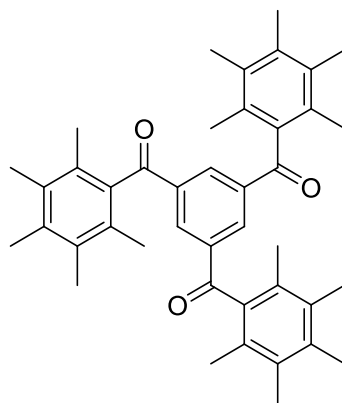
A flame-dried Schlenk flask was charged with aluminum(III) chloride (204 mg, 1.5332 mmol, 5.0 eqv) and 20 mL abs. dichloromethane. In a second flame-dried Schlenk flask 1,2,3,4,5-pentamethylbenzene (100 mg, 0.6746 mmol, 2.2 eqv) and 5-bromoisophthaloyl dichloride (86 mg, 0.3066 mmol, 1.0 eqv) were dissolved in 15 mL abs. dichloromethane. The 1,2,3,4,5-pentamethylbenzene solution was transferred to the aluminum(III) chloride suspension and the empty flask was rinsed with 5 mL abs. dichloromethane which was also added to the reaction. The mixture was stirred for 30 min at rt and then quenched with hydrochloric acid. The organic layer was separated and the aqueous layer extracted with 50 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered and the solvent of the filtrate evaporated in vacuum. The residue was purified by flash column chromatography using *n*-pentane and dichloromethane. The fraction containing the product was further purified by preparative TLC using *n*-pentane and dichloromethane (1:1). The product could be isolated as colorless crystals (18.0 mg, 0.0357 mmol, 12 %).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.95 (s, 12 H, H$_{Me}$), 2.19 (s, 12 H, H$_{Me}$), 2.28 (s, 6 H, H$_{Me}$), 8.08 (d, ^3J = 8.9 Hz, 2 H, H$_{Ar}$), 7.99 (s, 1 H, H$_{Ar}$), 8.14 (d, ^3J = 1.4 Hz, 2 H, H$_{Ar}$) ppm. **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 16.1 (s, C$_{Me}$), 16.9 (s, C$_{Me}$), 17.7 (s, C$_{Me}$), 124.0 (s, C$_{Ar}$), 128.8 (s, C$_{Ar}$), 129.3 (s, C$_{Ar}$), 133.3 (s, C$_{Ar}$), 136.4 (s, C$_{Ar}$), 136.4 (s, C$_{Ar}$), 140.1 (s, C$_{Ar}$), 200.0 (s, C=O) ppm. **MS** (ESI-TOF, CH$_2$Cl$_2$/MeOH): m/z = 527.1579 ([M+Na]$^+$, 8). **IR**: v= 2918 (m), 2843 (w), 1803 (w), 1681 (s, CO), 1585 (w), 1567 (w), 1443 (w), 1411 (w), 1382 (m), 1307 (s), 1268 (s), 1226 (s), 1162 (s), 1109 (w), 1068 (m), 1026 (m), 997 (m), 939 (m), 895 (m), 832 (m), 778 (m), 753 (m), 731 (m), 687 (s), 660 (m), 628 (w), 600 (w), 582 (w), 562 (w), 553 (w), 537 (w), 530 (w). **Mp**: > 225.0 °C.

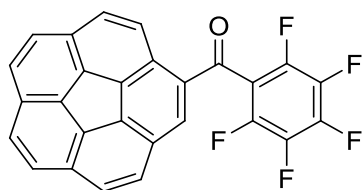## 10.6.5.19. Corannulene-1-yl(2,3,4,5,6-pentafluorophenyl)methanone (70)

70

A flame-dried Schlenk flask was charged with aluminum(III) chloride (82 mg, 0.6148 mmol, 4.0 eqv) and 7 mL abs. dichloromethane. In a second flame-dried Schlenk flask 2,3,4,5,6-pentafluorobenzoyl chloride (35 mg, 0.02 mL, 0.1537 mmol, 1.0 eqv) and corannulene **1** (50 mg, 0.1998 mmol, 1.3 eqv) were dissolved in 5 mL abs. dichloromethane. After the corannulene **1** was completely dissolved, the solution was transferred to the aluminum(III) chloride suspension. The empty flask was rinsed with 2 mL abs. dichloromethane which was then also added to the reaction mixture. After stirring at rt for 30 min the reaction was quenched with hydrochloric acid and the organic layer was separated. The aqueous layer was extracted with 50 mL dichloromethane and the combined organic layers dried over anhydrous sodium sulfate. The drying agent filtered off and the solvent of the filtrate removed in vacuum. The orange residue was purified by column chromatography using *n*-pentane and dichloromethane. The product could be isolated as an amorphous orange solid (28.5 mg, 0.0641 mmol, 42 %).

^{1}H NMR (700 MHz, CDCl$_3$): δ = 7.78 (AB, d, ^3J = 8.5 Hz, 1 H, H$_{Cor}$), 7.80 (AB, d, ^3J = 8.5 Hz, 1 H, H$_{Cor}$), 7.83 (AB, d, ^3J = 8.7 Hz, 1 H, H$_{Cor}$), 7.84 (AB, d, ^3J = 8.7 Hz, 1 H, H$_{Cor}$), 7.85 (AB, d, ^3J = 8.7 Hz, 1 H, H$_{Cor}$), 7.86 (AB, d, ^3J = 8.7 Hz, 1 H, H$_{Cor}$), 7.94 (AB, d, ^3J = 8.9 Hz, 1 H, H$_{Cor}$), 8.17 (s, 1 H, H$_{Cor}$), 8.66 (AB, d, ^3J = 8.9 Hz, 1 H, H$_{Cor}$) ppm. **^{19}F NMR** (376 MHz, CDCl$_3$): δ = -138.78 (m, 2 F, H$_{ortho}$), -150.31 (tt, ^3J = 2.2, 20.7 Hz, 1 H, F$_{para}$), -159.36 (m, 2 F, F$_{meta}$) ppm. **^{13}C{^{1}H} NMR** (176 MHz, CDCl$_3$): δ = 115.4 (t, ^3J = 23 Hz, C$_{PFPh}$), 127.1 (s, C$_{rim}$), 127.4 (s, C$_{rim}$), 127.5 (s, C$_{rim}$), 127.7 (s, C$_{rim}$), 128.0 (s, C$_{rim}$), 128.1 (s, C$_{rim}$), 128.3 (s, C$_{spoke}$), 129.1 (s, C$_{rim}$), 129.4 (s, C$_{rim}$), 131.1 (s, C$_{spoke}$), 131.3 (s, C$_{spoke}$), 132.8 (s, C$_{spoke}$), 134.9 (s, C$_{hub}$), 135.4 (s, C$_{hub}$), 136.0 (s, C$_{hub}$), 136.7 (s, C$_{rim}$), 136.8 (s, C$_{hub}$), 137.8 (m, ^1J = 260 Hz, C$_{PFPh}$), 138.5 (s, C$_{ipso}$), 142.7 (m, ^1J = 257 Hz, C$_{PFPh}$), 144.0 (m, ^1J = 253 Hz, C$_{PFPh}$), 186.1 (s, C$_{carbonyl}$) ppm. One spoke and rim carbon atom could not be observed. **^{13}C{^{1}H, ^{19}F} NMR** (176 MHz, CDCl$_3$): δ = 115.4 (s, C$_{PFPh}$), 127.1 (s, C$_{rim}$), 127.4 (s, C$_{rim}$), 127.5 (s, C$_{rim}$), 127.7 (s, C$_{rim}$), 128.0 (s, C$_{rim}$), 128.1 (s, C$_{rim}$), 128.3 (s, C$_{spoke}$), 129.1 (s, C$_{rim}$), 129.4 (s, C$_{rim}$), 131.1 (s, C$_{spoke}$), 131.3 (s, C$_{spoke}$), 132.8 (s, C$_{spoke}$), 134.9 (s, C$_{hub}$), 135.0 (s, C$_{hub}$), 135.4 (s, C$_{hub}$), 136.0 (s, C$_{hub}$), 136.6 (s, C$_{rim}$), 136.8 (s, C$_{hub}$), 137.9 (s, C$_{PFPh}$), 138.5 (s, C$_{ipso}$), 142.7 (s, C$_{PFPh}$), 144.0 (s, C$_{PFPh}$), 186.1 (s, C$_{carbonyl}$) ppm. One spoke carbon atom could not be observed. **MS** (EI, 100 °C): *m/z* 444.0583 (found), 444.0574 (calc'd),

444.0 (100 %, $[C_{27}H_9F_5O]^{\cdot +}$), 277.1 (46 %, $[C_{21}H_9O]^{\cdot +}$), 249.2 (91 %, $[C_{20}H_9]^{\cdot +}$). **IR**: v = 3028 (w), 2958 (w), 2923 (w), 2854 (w), 1906 (w), 1669 (s, CO), 1649 (m), 1519 (m), 1490 (s), 1453 (w), 1436 (m), 1411 (w), 1374 (w), 1327 (m), 1327 (m), 1311 (m), 1260 (w), 1239 (m), 1224 (s), 1188 (m), 1135 (m), 1101 (s), 1024 (m), 980 (s), 893 (w), 828 (s), 811 (s), 784 (w), 763 (m), 728 (s), 702 (w), 667 (m), 654 (m), 639 (w), 594 (w), 571 (w), 547 (s), 531 (m) cm^{-1}. **Mp**: 167.6-170.2 °C.

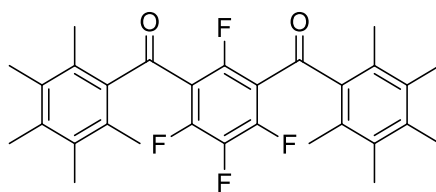## 10.6.5.20. Attempted synthesis of (2,4,5,6-tetrafluoro-1,3-phenylene)bis((2,3,4,5,6-pentamethyl-phenyl)methanone) (71)

71

A flame-dried Schlenk flask was charged with aluminum(III) chloride (204 mg, 1.5332 mmol, 5.0 eqv) and 20 mL abs. dichloromethane. 2,4,5,6-Tetrafluoroisophthaloyl dichloride (84.3 mg, 0.3066 mmol, 1.0 eqv) and 1,2,3,4,5-pentamethylbenzene (100 mg, 0.6746 mmol, 2.2 eqv) were dissolved in 15 mL abs. dichloromethane in a second flame-dried Schlenk flask. The 1,2,3,4,5-pentamethylbenzene solution was transferred to the aluminum(III) chloride suspension and the empty flask was rinsed with 5 mL abs. dichloromethane which was then added to the reaction. The mixture was stirred at rt for 30 min and then quenched with hydrochloric acid. The organic layer was separated and the aqueous layer extracted once with 50 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filterted and the solvent removed in vacuum.

No product could be isolated.

10.6.5.21. (5-Fluoro-1,3-phenylene)bis((2,3,4,5,6-pentamethylphenyl)-methanone) (72)

72

A stocksolution of pentamethylbenzene (8 mg, 0.015 mmol) in 1.6 mL abs. dichloromethane was prepared in a flame-dried Schlenk flask. Two Schlenk flasks were charged with titanium tetrachloride (15 mg, 0.01 mL, 0.075 mmol, 5 eqv) and boron trifluoride diethyl etherate (12 mg, 0.01 mL, 0.075 mmol, 5 eqv) respectively and diluted with 1.2 mL abs. dichloromethane. The fourth stocksolution contained 5-fluoroisophthaloyl dichloride (5 mg, 0.025 mmol) that was dissolved in 1.5 mL abs. dichloromethane. A flame-dried Young NMR tube was charged with aluminum(III) chloride (3 mg, 0.025 mmol, 5 eqv) and 0.3 mL abs. dichloromethane. Afterwards 0.3 mL of the acid chloride solution was added. In the same manner the Young tubes were prepared for the other two catalyst (0.3 mL of the stocksolutions). After 30, 60, 90, 120, 150 and 180 min a ^{19}F NMR was measured from all three NMR tubes. After 5 d a ^{19}F NMR spectra were measured and the reaction mixture afterwards quenched with water and a NMR spectrum recorded.

10.6.5.22. (2,3,4,5,6-Pentamethylphenyl)(o-tolyl)methanone (73)
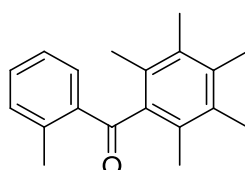
73

A flame-dried Schlenk flask was charged with aluminum(III) chloride (164 mg, 1.2266 mmol, 2 eqv), 2-methylbenzoyl chloride (94.5 mg, 79.7 μL, 0.6133 mmol, 1 eqv) and 25 mL abs. dichloromethane. In a second flame-dried Schlenk flask 1,2,3,4,5-pentamethylbenzene was dissolved in 20 mL abs. dichloromethane. After stirring for 30 min at rt the 1,2,3,4,5-pentamethylbenzene solution was transferred to the aluminum(III) chloride suspension. The empty flask was rinsed with 5 mL abs. dichloromethane which wasso added to the reaction

mixture. The reaction was stirred at rt for 4 h and afterwards quenched with hydrochloric acid. The organic layer was separated and the aqueous layer extracted twice with 50 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered and the solvent of the filtrate was evaporated in vacuum. The product could be isolated as a crystalline colorless solid (109.2 mg, 0.4099 mmol, 67 %).

^{1}H NMR (700 MHz, CDCl$_3$): δ = 2.07 (s, 6 H, H$_{Me}$), 2.24 (s, 6 H, H$_{Me}$), 2.31 (s, 3 H, H$_{Me}$), 2.80 (s, 3 H, H$_{Me}$), 7.16 (t, ^3J = 7.5 Hz, 1 H, H$_{Ar}$), 7.34 (d, ^3J = 7.6 Hz, 1 H, H$_{Ar}$), 7.41 (d, ^3J= 7.6 Hz, 1 H, H$_{Ar}$), 7.43 (d, ^3J = 8.6 Hz, 1 H, H$_{Ar}$) ppm. **^{13}C NMR** (176 MHz, CDCl$_3$): δ = 16.0 (s, C$_{Me}$), 16.8 (s, C$_{Me}$), 17.4 (s, C$_{Me}$), 22.3 (s, C$_{Me}$), 125.9 (s, C$_{Ar}$), 129.1 (s, C$_{Ar}$), 132.3 (s, C$_{Ar}$), 132.4 (s, C$_{Ar}$), 132.8 (s, C$_{Ar}$), 132.9 (s, C$_{Ar}$), 135.4 (s, C$_{Ar}$), 136.8 (s, C$_{Ar}$), 139.6 (s, C$_{Ar}$), 140.3 (s, C$_{Ar}$), 203.0 (s, C=O) ppm. **MS** (EI): *m/z* 266.1677 (found), 266.1671 (calc'd), 266.3 (38 %, [C$_{19}$H$_{22}$O]$^{\cdot+}$), 251.3 (100 %, [C$_{18}$H$_{19}$O]$^{\cdot+}$), 249.3 (10 %, [C$_{19}$H$_{21}$]$^{\cdot+}$), 236.3 (54 %, [C$_{17}$H$_{16}$O]$^{\cdot+}$), 175.0 (21 %, [C$_{12}$H$_{15}$O]$^{\cdot+}$), 147.3 (10 %, [C$_{11}$H$_{15}$]$^{\cdot+}$), 119.3 (13 %, [C$_8$H$_7$O]$^{\cdot+}$), 91.4 (16 %, [C$_7$H$_7$]$^{\cdot+}$). **MS** (ESI-TOF, CH$_2$Cl$_2$/MeOH): m/z = 289.1569 ([M+Na]$^+$, 31), 305.1330 ([M+K]$^+$, 5), 555.3246 ([2M+Na]$^+$, 11). **IR**: v = 3056 (w), 2979 (w), 2923 (w), 2860 (w), 1974 (w), 1943 (w), 1833 (w), 1662 (s,CO), 1599 (w), 1571 (m), 1483 (m), 1453 (m), 1379 (w), 1307 (m), 1284 (w), 1265 (m), 1211 (m), 1166 (w), 1136 (w), 1059 (w), 1203 (w), 981 (w), 892 (s), 845 (w), 780 (m), 766 (m), 737 (s), 722 (m), 659 (s), 633 (m), 564 (w), 554 (w), 531 (w) cm^{-1}. **Mp**: 142.6-148.2 °C.

10.6.5.23. Corannulene-1-yl(o-tolyl)methanone (74)
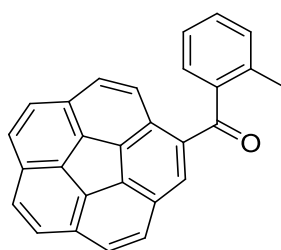
74

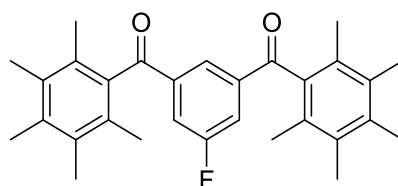In a flame-dried Schlenk flask 2-methylbenzoyl chloride (24 mg, 0.02 mL, 0.1537 mg, 1.0 eqv) and corannulene **1** (50 mg, 0.1998 mmol, 1.3 eqv) were dissolved in 5 mL abs. dichloromethane. A second flame-dried Schlenk flask was charged with aluminum(III) chloride (82 mg, 0.6148 mmol, 4.0 eqv) and 7 mL abs. dichloromethane. After the corannulene **1** was dissolved the solution was transferred to the aluminum(III) chloride suspension. The empty flask was rinsed with 2 mL abs. dichloromethane which was then added to the reaction. The mixture was stirred for 30 min at rt

and afterwards quenched with hydrochloric acid. The organic layer was separated and the aqueous layer extracted with 50 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered and the solvent of the filtrate evaporated in vacuum. The orange residue was purified by column chromatography using *n*-pentane and dichloromethane. The product could be isolated as an amorphous orange solid (22.0 mg, 0.0597 mmol, 39 %).

^{1}H NMR (700 MHz, CDCl$_3$): δ = 2.43 (s, 3 H, H$_{Me}$), 7.28 (t, ^3J = 7.4 Hz, 1 H, H$_{Ph}$), 7.37 (d, ^3J = 7.7 Hz, 1 H, H$_{Ph}$), 7.44 (d, ^3J = 7.6 Hz, 1 H, H$_{Ph}$), 7.46 (td, ^3J = 1.0, 7.6 Hz, 1 H, H$_{Ph}$), 7.75 (AB, d, ^3J = 8.6 Hz, 1 H, H$_{Cor}$), 7.80 (AB, d, ^3J = 8.9 Hz, 1 H, H$_{Cor}$), 7.82 (AB, d, ^3J = 8.8 Hz, 1 H, H$_{Cor}$), 7.83 (AB, d, ^3J = 8.9 Hz, 1 H, H$_{Cor}$), 7.84 (AB, d, ^3J = 8.8 Hz, 1 H, H$_{Cor}$), 7.85 (AB, d, ^3J = 8.6 Hz, 1 H, H$_{Cor}$), 7.87 (AB, d, ^3J = 8.8 Hz, 1 H, H$_{Cor}$), 8.13 (s, 1 H, H$_{Cor}$), 8.41 (AB, d, ^3J = 8.9 Hz, 1 H, H$_{Cor}$) ppm. **^{13}C NMR** (176 MHz, CDCl$_3$): δ = 20.4 (s, C$_{Me}$), 125.5 (s, C$_{Ph}$), 127.3 (s, C$_{rim}$), 127.3 (s, C$_{rim}$), 127.6 (s, C$_{rim}$), 127.7 (s, C$_{rim}$), 127.9 (s, C$_{rim}$), 128.4 (s, C$_{rim}$), 128.5 (s, C$_{rim}$), 128.4 (s, C$_{spoke}$), 128.9 (s, C$_{spoke}$), 129.3 (s, C$_{rim}$), 130.6 (s, C$_{Ph}$), 131.0 (s, C$_{spoke}$), 131.1 (s, C$_{spoke}$), 131.3 (s, C$_{Ph}$), 132.2 (s, C$_{spoke}$), 134.8 (s, C$_{Ph}$), 135.2 (s, C$_{hub}$), 135.5 (s, C$_{hub}$), 136.0 (s, C$_{hub}$), 136.7 (s, C$_{hub}$), 137.1 (s, C$_{ipso}$), 137.3 (s, C$_{hub}$), 137.7 (s, C$_{Ph}$), 140.1 (s, C$_{ipso}$), 199.7 (s, C=O) ppm. **MS** (EI, 130 °C): *m/z* 368.1210 (found), 368.1201 (calc'd), 351.1182 (found), 351.1174 (calc'd), 368.1 (45 %, [C$_{28}$H$_{16}$O]$^{\cdot+}$), 353.3 (13 %, [C$_{27}$H$_{13}$O]$^{\cdot+}$), 351.0 (100 %, [C$_{28}$H$_{15}$]$^{\cdot+}$), 277.2 (5 %, [C$_{21}$H$_9$O]$^{\cdot+}$), 249.1 (31 %, [C$_{20}$H$_9$]$^{\cdot+}$), 351.0 (23 %, [C$_{28}$H$_{15}$]$^{\cdot2+}$). **IR**: v = 3034 (w), 2952 (w), 2922 (m), 2851 (w), 1724 (w), 1648 (s, CO), 1453 (m), 1432 (m), 1372 (w), 1321 (w), 1307 (w), 1285 (w), 1256 (s), 1277 (w), 1181 (w), 1163 (w), 1095 (m), 1024 (m), 1005 (s), 954 (w), 921 (m), 904 (m), 855 (m), 837 (s), 797 (s), 745 (s), 730 (s), 656 (s), 611 (m), 592 (w), 581 (w), 566 (m), 554 (s), 547 (s), 539 (m), 534 (m) cm^{-1}. **Mp**: 158.8-160.6 °C.

10.6.5.24. (2-methyl-1,3-phenylene)bis((2,3,4,5,6-pentamethylphenyl)-methanone) (75)
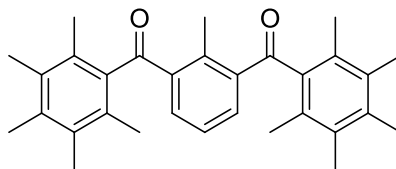
75

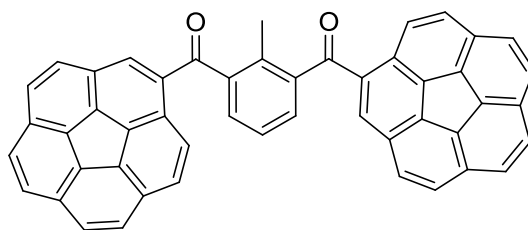A flame-dried Schlenk flask was charged with aluminum(III) chloride (100 mg, 0.6746 mmol, 2.2 eqv) and 20 mL abs. dichloromethane. 2-Methylisophthaloyl dichloride (67 mg, 0.3066 mmol, 1.0 eqv) and 1,2,3,4,5-pentamethylbenzene (100 mg, 0.6746 mmol, 2.2 eqv) were dissolved in

15 mL abs. dichloromethane in a second flame-dried Schlenk flask. The solution was transferred to the aluminum(III) chloride suspension and the empty flask was rinsed with 5 mL abs. dichloromethane which was also added to the mixture. After stirring for 30 min at rt the reaction was quenched with hydrochloric acid and the organic layer was separated. The aqueous layer was extracted with 50 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered and the solvent of the filtrate evaporated in vacuum. The solid was purified by flash column chromatography using *n*-pentane and dichloromethane. The product could be isolated as a colorless crystalline powder (84.9 mg, 0.1927 mmol, 63 %).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.08 (s, 12 H, H$_{Me}$), 2.21 (s, 12 H, H$_{Me}$), 2.28 (s, 6H, H$_{Ar}$), 3.05 (s, 3 H, H$_{Me}$), 7.07 (m, 1H, H$_{Ar}$), 7.46 (d, ^3J= 7.8 Hz, 2 H, H$_{Ar}$) ppm. **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 16.1 (s, C$_{Me}$), 17.0 (s, C$_{Me}$), 17.5 (s, C$_{Me}$), 17.8 (s, C$_{Me}$), 125.4 (s, C$_{Ar}$), 129.3 (s, C$_{Ar}$), 133.2 (s, C$_{Ar}$), 135.1 (s, C$_{Ar}$), 136.0 (s, C$_{Ar}$), 139.5 (s, C$_{Ar}$), 140.2 (s, C$_{Ar}$), 141.2 (s, C$_{Ar}$), 203.9 (s, C=O) ppm. **MS** (ESI-TOF, CH$_2$Cl$_2$/MeOH): m/z = 441.2835 ([M+H]$^+$, 1), 463.2631 ([M+Na]$^+$, 4), 479.2367 ([M+K]$^+$, 1). **IR**: v = 2976 (w), 2927 (w), 2866 (w), 1671 (s,CO), 1571 (w), 1444 (m), 1424 (m), 1385 (m), 1304 (s), 1261 (m), 1229 (m), 1178 (m), 1136 (s), 1067 (m), 1023 (m), 980 (w), 916 (s), 802 (m), 759 (w), 736 (s), 679 (s), 645 (w), 628 (w), 592 (w), 575 (w), 547 (w), 539 (w), 533 (w) cm^{-1}. **Mp**: > 225.0 °C.

10.6.5.25. (2-Methyl-1,3-phenylene)bis(corannulene-1-ylmethanone) (76)

76

In a flame-dried Schlenk flask 2-methylisophthaloyl dichloride (35 mg, 0.1598 mg, 1.0 eqv) and corannulene **1** (100 mg, 0.3995 mmol, 2.5 eqv) were dissolved in 15 mL abs. dichloromethane. A second flame-dried Schlenk flask was charged with aluminum(III) chloride (75 mg, 0.5593 mmol, 3.5 eqv) and 20 mL abs. dichloromethane. After the corannulene **1** was dissolved the solution was transferred to the aluminum(III) chloride suspension. The empty flask was rinsed with 5 mL abs. dichloromethane which was then also added to the reaction. The mixture was stirred for 30 min at rt and afterwards quenched with water. The organic layer was separated and the aqueous extracted twice with 50 mL dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered and the solvent of the filtrate evaporated in vacuum. The red

residue was purified by preparative TLC using *n*-pentane and dichloromethane (1:3). The product could be isolated as an amorphous orange solid (89.2 mg, 0.1384 mmol, 87 %).

¹H NMR (500 MHz, CDCl$_3$): δ = 2.32 (s, 3 H, H$_{Me}$), 7.45 (t, ^3J = 7.6 Hz, 1 H, H$_{Ph}$), 7.61 (d, ^3J = 7.6 Hz, 2 H, H$_{Ph}$), 7.82 (AB, d, ^3J = 8.6 Hz, 2 H, H$_{Cor}$), 7.82 (AB, d, ^3J = 8.6 Hz, 2 H, H$_{Cor}$), 7.84 (AB, d, ^3J = 8.8 Hz, 2 H, H$_{Cor}$), 7.85 (AB, d, ^3J = 8.8 Hz, 2 H, H$_{Cor}$), 7.85 (AB, d, ^3J = 8.7 Hz, 2 H, H$_{Cor}$), 7.86 (AB, d, ^3J = 8.7 Hz, 2 H, H$_{Cor}$), 7.93 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 8.23 (s, 2 H, H$_{Cor}$), 8.58 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$) ppm. **¹³C NMR** (176 MHz, CDCl$_3$): δ = 17.7 (s, C$_{Me}$) 125.6 (s, C$_{rim}$), 127.4 (s, C$_{rim}$), 127.4 (s, C$_{rim}$), 127.4 (s, C$_{rim}$), 127.8 (s, C$_{rim}$), 127.9 (s, C$_{rim}$), 128.0 (s, C$_{rim}$), 128.7 (s, C$_{rim}$), 128.7 (s, C$_{spoke}$), 128.8 (s, C$_{spoke}$), 128.9 (s, C$_{Ph}$), 130.1 (s, C$_{rim}$), 131.1 (s, C$_{spoke}$), 131.2 (s, C$_{spoke}$), 132.5 (s, C$_{spoke}$), 134.6 (s, C$_{Ph}$), 135.1 (s, C$_{hub}$), 135.5 (s, C$_{hub}$), 136.1 (s, C$_{hub}$), 136.1 (s, C$_{Ph}$), 136.3 (s, C$_{hub}$), 136.8 (s, C$_{hub}$), 138.0 (s, C$_{ipso}$), 142.2 (s, C$_{ipso}$), 199.7 (s, C=O) ppm. **MS** (EI, 310 °C): m/z = 644.0 (44 %, [C$_{49}$H$_{24}$O$_2$]$^{\cdot +}$), 627.0 (13 %, [C$_{49}$H$_{23}$O$_1$]$^+$), 367.0 (13 %, [C$_{28}$H$_{12}$O]$^+$), 277.1 (19 %, [C$_{21}$H$_9$O]$^{\cdot +}$), 248.9 (47 %, [C$_{20}$H$_9$]$^{\cdot +}$). **IR**: v = 3028 (w), 2958 (w), 2923 (w), 2852 (w), 2245 (w), 1891 (w), 1651 (s, CO), 1577 (m), 1472 (w), 1433 (m), 1373 (m), 1321 (m), 1306 (m), 1278 (w), 1244 (s), 1217 (w), 1180 (m), 1124 (w), 1070 (w), 997 (w), 929 (w), 903 (s), 873 (m), 832 (s), 800 (w), 727 (s), 669 (w), 655 (m), 633 (w), 600 (w), 582 (w), 552 (m), 526 (m) cm^{-1}. **Mp**: 165.2-166.7 °C.

10.6.5.26. 2,2'-(1,3-Phenylene)bis(1-(2,3,4,5,6-pentamethylphenyl)-ethanone) (78)
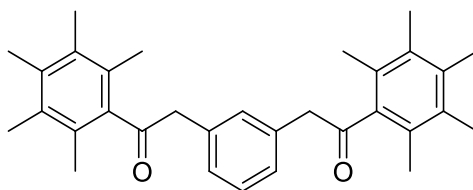
78

A flame-dried Schlenk flask was charged with aluminum(III) chloride (72 mg, 0.5366 mmol, 3.5 eqv) and 10 mL abs. dichloromethane was added. In a second flame-dried Schlenk flask 2,2'-(1,3-phenylene)diacetyl chloride (35 mg, 0.1533 mmol, 1.0 eqv) and 1,2,3,4,5-pentamethylbenzene (50 mg, 0.337 mmol, 2.2 eqv) was dissolved in 10 mL abs. dichloromethane. The solution was transferred to the aluminum(III) chloride suspension and the empty flask was rinsed with 5 mL dichloromethane which was added afterwards to the reaction mixture. The suspension was stirred for 4 h at rt and the quenched with hydrochloric acid. The organic layer was separated and the aqueous layer extracted with two times 100 mL dichloromethane. The combined organic layers

were dried over sodium sulfate, the mixture filtered and the solvent of the filtrate evaporated in vacuum. The residue was purified by column chromatography using *n*-pentane and dichloromethane. The product could be isolated as a colourless crystalline powder (58 mg, 0.1271 mmol, 38 %).

^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.08 (s, 12 H, H$_{Me}$), 2.19 (s, 12 H, H$_{Me}$), 2.25 (s, 6 H, H$_{Me}$), 3.98 (s, 4 H, H$_{CH2}$), 7.09 (s, 1 H, H$_{Ar}$), 7.16 (dd, ^3J = 1.5, 7.6 Hz, 2 H, H$_{Ar}$), 7.31 (t, ^3J= 7.6 Hz, 2 H, H$_{Ar}$) ppm.
^{13}C NMR (126 MHz, CDCl$_3$): δ = 16.1 (s, C$_{Me}$), 16.8 (s, C$_{Me}$), 17.4 (s, C$_{Me}$), 52.4 (s, C$_{CH2}$), 127.6 (s, C$_{Ar}$), 128.7 (s, C$_{Ar}$), 128.8 (s, C$_{Ar}$), 131.6 (s, C$_{Ar}$), 133.2 (s, C$_{Ar}$), 133.2 (s, C$_{Ar}$), 133.7 (s, C$_{Ar}$), 135.7 (s, C$_{Ar}$), 140.3 (s, C$_{Ar}$), 208.8 (s, C=O) ppm. One aromatic carbon atom could not be detected. **MS** (ESI-TOF, CH$_2$Cl$_2$/MeOH): m/z = 477.2769 ([M+Na]$^+$, 26), 931.5634 ([2M+Na]$^+$, 4). **IR**: v = 3006 (w), 2895 (m), 2863 (w), 2729 (w), 1919 (w), 1699 (s,CO), 1611 (m), 1567 (w), 1486 (w), 1448 (m), 1408 (m), 1375 (m), 1315 (s), 1292 (m), 1261 (m), 1158 (w), 1107 (w), 1070 (m), 1021 (w), 995 (m), 961 (w), 927 (s), 904 (w), 886 (m), 807 (w), 767 (m), 714 (s), 700 (w), 684 (w), 633 (m), 610 (m), 572 (w), 557 (w), 538 (s), 528 (w) cm^{-1}. **Mp**: 156.0-160.0 °C.

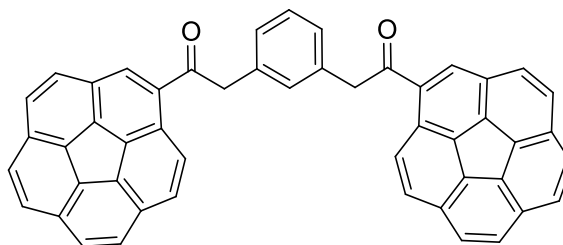## 10.6.5.27. 2,2'-(1,3-Phenylene)bis((corannulene-1-yl)ethanone) (79)

79

A flame-dried Schlenk flask was charged with aluminum(III) chloride (75 mg, 0.5593 mmol, 3.5 eqv) and 20 mL abs. dichloromethane. In an second flame-dried Schlenk flask 2,2'-(1,3-phenylene)diacetyl chloride (37 mg, 0.1598 mmol, 1.0 eqv) and corannulene **1** (100 mg, 0.3995 mmol, 2.5 eqv) were dissolved in 15 mL abs. dichloromethane. The corannulene **1** solution was then transferred to the aluminum(III) chloride suspension and the empty flask was rinsed with 5 mL abs. dichloromethane which was then added to the reaction. The mixture was stirred at rt for 30 min and then quenched with water. The organic layer was separated and the aqueous layer extracted twice with 70 mL dichloromethane. The combined organic layers were dried over sodium sulfate, filtered and the solvent evaporated in vacuum. The solid residue was purified by

preparative TLC using *n*-pentane and dichloromethane (1:4). The product could be isolated as an amorphous off-white solid (40.7 mg, 0.0618 mmol, 39 %).

¹H NMR (700 MHz, CD$_2$Cl$_2$): δ = 2.12 (s, 6 H, H$_{Et}$), 7.24 (dd, J = 1.4, 7.8 Hz, 1 H, H$_{Ar}$), 7.30 (dd, J = 7.1, 8.4 Hz, 2 H, H$_{Ar}$), 7.38 (t, ^{4}J= 1.7 Hz, 1 H, H$_{Ar}$), 7.80 (AB, d, ^{3}J = 8.6 Hz, 2 H, H$_{Cor}$), 7.81 (d, ^{3}J = 8.4 Hz, 2 H, H$_{Cor}$), 7.81 (d, ^{3}J = 8.4 Hz, 2 H, H$_{Cor}$), 7.84 (AB, d, ^{3}J= 8.7 Hz, 2 H, H$_{Cor}$), 7.84 (AB, d, ^{3}J = 8.9 Hz, 2 H, H$_{Cor}$), 7.86 (d, ^{3}J= 8.6 Hz, 2 H, H$_{Cor}$), 8.50 (AB, d, ^{3}J = 8.9 Hz, 2 H, H$_{Cor}$), 8.59 (s, 2 H, H$_{Cor}$) ppm. **¹³C NMR** (176 MHz, CDCl$_3$): δ = 47.3 (s, C$_{CH2}$), 127.2 (s, C$_{rim}$), 127.2 (s, C$_{rim}$), 127.3 (s, C$_{rim}$), 127.6 (s, C$_{rim}$), 127.7 (s, C$_{rim}$), 128.3 (s, C$_{rim}$), 128.4 (s, C$_{rim}$), 128.4 (s, C$_{rim}$), 128.6 (s, C$_{rim}$), 131.1 (s, C$_{spoke}$), 131.3 (s, C$_{spoke}$), 132.8 (s, C$_{spoke}$), 134.9 (s, C$_{hub}$), 135.0 (s, C$_{hub}$), 135.4 (s, C$_{hub}$), 136.0 (s, C$_{hub}$), 136.6 (s, C$_{rim}$), 136.8 (s, C$_{hub}$), 137.9 (s, C$_{PFPh}$), 138.5 (s, C$_{ipso}$), 142.7 (s, C$_{PFPh}$), 144.0 (s, C$_{PFPh}$), 186.1 (s, C$_{carbonyl}$) ppm. One spoke carbon atom could was not observed. **MS** (EI, 300 °C): m/z = 658.2 (13 %, [C$_{50}$H$_{26}$O$_2$]$^{\cdot +}$), 277.1 (100 %, [C$_{21}$H$_9$O]$^{\cdot +}$), 249.4 (46 %, [C$_{20}$H$_9$]$^{\cdot +}$). **IR**: ν = 3056 (w), 3026 (w), 2949 (w), 2917 (w), 2845 (w), 1668 (s, CO), 1472 (w), 1439 (w), 1420 (m), 1373 (m), 1330 (m), 1306 (m), 1261 (m), 1214 (s), 1288 (w), 1138 (w), 1121 (m), 1052 (m), 1029 (m), 935 (m), 875 (s), 832 (s), 823 (s), 795 (m), 750 (w), 737 (s), 694 (s), 661 (s), 638 (w), 627 (w), 613 (w), 588 (w), 543 (s) cm^{-1}. **Mp**: > 225 °C.

10.6.5.28. 1,3-Bis(2-corannulene-1-yl)-1,3-dithian-2-yl)benzene (80)
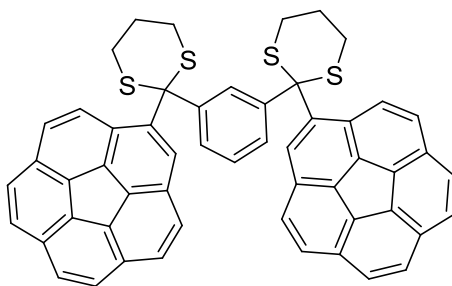
80

In a Young flask diketone **43** (25 mg, 0.0396 mmol, 1.0 eq.) was suspended in 30 mL abs. dichloromethane and 1,3-propanedithiol (82 mg, 0.08 mL, 0.7531 mmol, 18.0 eq.) was added drop wise to the solution. Afterwards trifluouride diethyl etherate (174 mg, 0.15 mL, 1.2276 mmol, 31.0 eq.) was added by syringe. The flask was sealed and stirred overnight at rt. It was quenched with 30 mL of water and the organic layer was separated, then washed once with 50 mL of 10 % sodium hydroxide solution and twice with 50 mL water. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent of the filtrate was evaporated in vacuum. The residue was

purified by preparative TLC (pentane/dichloromethane 1:1). The product was obtained as a yellow solid 76.7 mg (0.0946 mmol, 74 %).

¹H NMR (700 MHz, CDCl$_3$): δ = 1.45 (s, 2 H, H$_{Et}$), 1.82 (s, 2 H, H$_{Et}$), 2.30 (s, 4 H, H$_{SEt}$), 2.63 (s, 4 H, H$_{SEt}$), 7.06 (t, ^3J = 7.8 Hz, 1 H, H$_{Ar}$), 7.33 (d, ^3J = 7.4 Hz, 2 H, H$_{Ar}$), 7.48 (AB, d, ^3J= 9.0 Hz, 2 H, H$_{Cor}$), 7.69 (AB, d, ^3J = 8.7 Hz, 2 H, H$_{Cor}$), 7.71 (AB, d, ^3J = 8.7 Hz, 2 H, H$_{Cor}$), 7.75 (AB, d, ^3J= 8.7 Hz, 2 H, H$_{Cor}$), 7.75 (AB, d, ^3J = 8.7 Hz, 2 H, H$_{Cor}$), 7.77 (AB, d, ^3J= 8.6 Hz, 2 H, H$_{Cor}$), 7.77 (AB, d, ^3J = 8.6 Hz, 2 H, H$_{Cor}$), 7.98 (AB, d, ^3J = 8.9 Hz, 2 H, H$_{Cor}$), 8.07 (s, 1 H, H$_{Ar}$), 8.23 (s, 2 H, H$_{Cor}$) ppm. **¹³C NMR** (176 MHz, CDCl$_3$): δ = 24.1 (s, C$_{Et}$), 29.7 (s, C$_{SEt}$), 61.7 (s, C$_S$), 125.3 (s, C$_{rim}$), 126.9 (s, C$_{rim}$), 127.1 (s, C$_{rim}$), 127.1 (s, C$_{rim}$), 127.3 (s, C$_{rim}$), 127.3 (s, C$_{rim}$), 127.3 (s, C$_{rim}$), 128.5 (s, C$_{Ar}$), 129.0 (s, C$_{Ar}$), 129.3 (s, C$_{spoke}$), 129.4 (s, C$_{rim}$), 129.5 (s, C$_{rim}$), 130.1 (s, C$_{spoke}$), 130.2 (s, C$_{spoke}$), 130.2 (s, C$_{spoke}$), 130.6 (s, C$_{spoke}$), 131.1 (s, C$_{spoke}$), 135.3 (s, C$_{hub}$), 135.4 (s, C$_{hub}$), 135.7 (s, C$_{hub}$), 136.3 (s, C$_{hub}$), 136.7 (s, C$_{hub}$), 141.5 (s, C$_{ipso}$), 143.6 (s, C$_{ipso}$) ppm. **MS** (ESI-TOF, CH$_2$Cl$_2$/MeOH): m/z = 849.1213 ([M+K]$^+$, 94), 1661.2839 ([M+K]$^+$, 6). **IR**: v = 3026 (w), 2902 (m), 1714 (w), 1650 (w), 1592 (w), 1473 (w), 1409 (m), 1307 (m), 1274 (m), 1170 (w), 1134 (m), 1087 (w), 995 (w), 903 (s), 831 (s), 788 (m), 727 (s), 698 (w), 684 (w), 658 (s), 600 (w), 561 (s), 541 (s) cm^{-1}. **Mp**: 177.2-178.4 °C.

11. Abbrevations

AIBN	Azobisisobutyronitrile
cat.	catalytical amount
Cor	Corannulene
d	doublet
DCE	1,2-dichloroethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEPT	Distorsionless Enhancement by Polarization Transfer
	distillated
DMF	N,N-dimathylformamide
eqv	equivalent
EI	Electron impact
ESI	Electrospray ionization
(exTTF)	π-extended tetrathiafulvalene
FVP	Flash vacuum pyrolysis
GRT	Girard's Reagent T
HMBC	Heteronuclear Multiple Bond Coherence
HMQC	Heteronuclear Multiple Quantum Coherence
HPLC	High performance liquid chromatography
HV	High vacuum
IR	Infrared spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
J	coupling constant
m	Medium (IR), multiplett (NMR)
Me	methyl group
mp	Melting point
n/a	Not available
NIS	N-Iodosuccinimide
NMR	Nuclear magnetic resonances
PAH	Polycyclic aromatic hydrocarbons
ppm	Parts per million
q	quartet
rt	Room temperature

s	strong (IR), singlet (NMR)
SWNT	Single-walled carbon nanotubes
*t*Bu	*tert*-butyl group
THF	Tetrahydrofuran
TOF	time-of-flight
w	weak

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